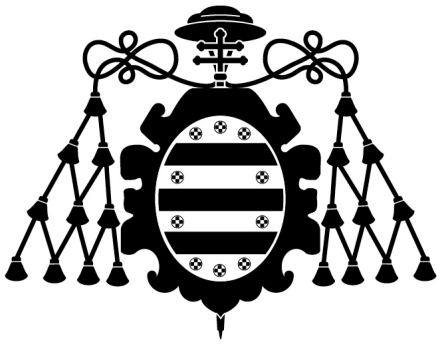

Universidad de Oviedo

Departamento de Química Orgánica e Inorgánica

Nucleophilic additions on 2,2'-bipyridine and 1,10-phenanthroline ligands in rhenium tricarbonyl complexes

Tesis Doctoral

Programa de Doctorado en "Síntesis y Reactividad Química"

Rebeca Arévalo Seco

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RESUMEN DEL CONTENIDO DE TESIS DOCTORAL

1.- Título de la Tesis	
Español: ADICIONES NUCLEOFÍLICAS A LIGANDOS 2,2'-BIPIRIDINA Y 1,10-FENANTROLINA EN COMPLEJOS TRICARBONÍLICOS DE RENIO.	Inglés: NUCLEOPHILIC ADDITIONS ON 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE LIGANDS IN RHENIUM TRICARBONYL COMPLEXES.

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RESUMEN (en español)

Los ligandos 2,2'-bipiridina (bipy) y 1,10-fenantrolina (phen) han sido considerados inertes frente a nucleófilos en complejos de metales de transición. Como consecuencia, las reacciones de formación de enlaces en ligandos bipy o phen son inusuales. En la presente memoria se describen por primera vez adiciones nucleofílicas intramoleculares (iniciadas por la desprotonación de los grupos metilo de un co-ligando) e intermoleculares a ligandos bipy y phen en complejos tricarbonílicos de renio. Se han caracterizado los nuevos compuestos mediante espectroscopia de infrarrojo y de resonancia magnética nuclear 1D y 2D, y análisis estructural por difracción de rayos X, y se han racionalizado los resultados mediante estudios computacionales DFT de los mecanismos de reacción. Algunos de los resultados más novedosos son:

- Síntesis de complejos de renio con ligandos tridentados mediante reacciones de acoplamiento C-C entre grupos metilo desprotonados de ligandos sulfuro, fosfina o α-metilheterociclo y bipy o phen.
- Formación reversible intramolecular de enlaces C-C en la posición 2 del ligando bipy.
- Adición nucleofílica intermolecular del grupo bis(trimetilsilil)amido sobre el ligando phen.
- Adiciones nucleofílicas intermoleculares de grupos alquilo o hidruro sobre bipy o phen.
- Dimerización de grupos piridilo desaromatizados de un ligando bipy iniciados por la adición nucleofílica intermolecular de hidruro.

RESUMEN (en Inglés)

Transition-metal coordinated 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been traditionally considered as inert ligands toward nucleophilic additions. Therefore, examples of bond-forming reactions on bipy and phen are scarce. In this work, novel reactions involving intramolecular (triggered by deprotonation of methyl groups on a co-ligand) or intermolecular nucleophilic additions on bipy and phen ligands in rhenium tricarbonyl complexes are described. The new compounds have been characterized by infrared and 1D and 2D nuclear magnetic resonance spectroscopies, and by X-ray diffraction structural analysis. The results have been rationalized by computational DFT studies on the reaction mechanisms. Some of the new results include:

- Synthesis of rhenium complexes with tridentate ligands by post-coordination C-C coupling between deprotonated methyl groups of sulfides, phosphanes or α-methylheterocycles and bipy or phen.
- Reversible intramolecular C-C bond formation on position 2 of bipy.
- Reversible intermolecular nucleophilic addition of a bis(trimethylsilyl)amide group on phen.
- Nucleophilic intermolecular additions of alkyl and hydride groups on bipy and phen.
- Dimerization of dearomatized pyridyl rings of a bipy ligand promoted by intermolecular hydride addition.

SR. PRESIDENTE DE LA COMISIÓN ACADÉMICA DEL PROGRAMA DE DOCTORADO EN SÍNTESIS Y REACTIVIDAD QUÍMICA

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Gracias

Index

List of abbreviations

Ar	Aryl
Ar^F	3,5-Bis(trifluoromethyl)phenyl
bipy	2,2'-Bipyridine
BIAN	Bisiminoacenaphthene
br	Broad signal
2-(CH=N*p*-tol)py	2-(*para*-Tolyl)iminopyridine
δ	Chemical shift
d	Doublet
dd	Doublet of doublets
ddd	Doublet of doublet of doublets
dmpm	Bis(dimethylphosphino)methane
EA	Elemental Analysis
Et	Ethyl
HDN	Hydrodenitrogenation
*i*Pr	Isopropyl
2,6-*i*Pr_2BIAN	1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene
p-MeBIAN	1,2-Bis[(4-methylphenyl)imino]acenaphthene
IR	Infrared spectroscopy
RIm	Alkylimidazole
Me	Methyl
Me_4phen	3,4,7,8-Tetramethyl-1,10-phenanthroline
1-Me-2-EtIm	1-Methyl-2-ethylimidazole
1,2-Me_2Im	1,2-Dimethylimidazole

2-MeOx	2-Methyloxazoline
2-MePy	2-Methylpyridine
MeIm	1-Methylimidazole
MesIm	1-Mesitylimidazole
m	Multiplet
Mes	Mesityl (2,4,6-trimethylphenyl)
*n*Bu	*n*-Butyl
*n*Hex	*n*-Hexane
NMR	Nuclear Magnetic Resonance
NICS	Nucleus Independent Chemical Shifts
$^{-}$OTf	Triflate ($CF_3SO_3^-$)
Ox	Oxazoline
PDI	Pyridyldiimine
p-tol	*para*-Tolyl (4-methylphenyl)
Ph	Phenyl
phen	1,10-Phenanthroline
py	Pyridine
q	Quadruplet
quint	Quintuplet
QC	Quaternary Carbon
s	Singlet
sept	Septuplet
*t*Bu	*tert*-Butyl
terpy	2,2':6',2''-Terpyridine
TMEDA	Tetramethylethylenediamine
TFA	Trifluoroacetic acid

THF	Tetrahydrofuran
TS	Transition State
td	Triplet of doublets

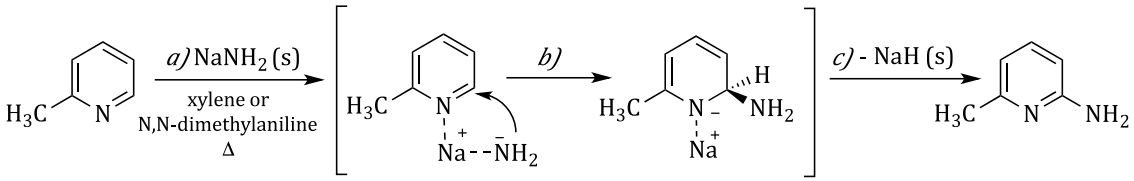
Introduction

Introduction

The work reported in this dissertation is concerned with nucleophilic additions to transition metal-coordinated 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands. One reason why this work is relevant is that pyridines and polypyridines, and chiefly among them, bipy and phen, are ubiquitous ligands in coordination and organometallic chemistry.[1] In the reactions of their transition metal complexes, bipy and phen usually act as spectator ligands, contributing to the stabilization of the complexes, but are not the center of the reactivity. Some of the previous examples of metal-mediated dearomatization and functionalization of pyridines required highly reactive metal centers, which promoted the very unusual κ^2-coordination of the pyridines.[2] In contrast, the majority of the reactions reported here involve the thoroughly studied rhenium(I) tricarbonyl moieties, which form very stable, usually inert complexes. In fact, *fac*-$Re(CO)_3$ complexes containing either bipy or phen have been used in many areas of contemporary research,[3] including CO_2 reduction,[4] luminescent materials[5] and biomedical applications.[6] The reactions reported here could be the basis of future studies aimed at expanding the available typology of rhenium carbonyl complexes, and could help delineate the stability boundaries for these compounds in the presence of strongly basic or nucleophilic reagents.

The reactions of free pyridines toward main group nucleophiles have been known for a long time,[7] and still remain an active field of study. Nucleophilic additions on pyridines usually take place at the most electrophilic positions, *i*. *e*., 2 and 4.[8] The first nucleophilic addition on free pyridines was found by Chichibabin when he serendipitously obtained 2-amino-6-methylpyridine while trying to metalate 2-methylpyridine with sodium amide (Scheme I-1).[9] Since then, the Chichibabin reaction, usually carried out under heterogeneous conditions, is the most widely employed method for the synthesis of 2-aminopyridines. Although mechanistic studies of the reaction are scarce,[10] an addition-elimination ($S_N(AE)$) mechanism has been proposed to operate in this reaction. This mechanism comprises three steps: a) formation of a complex between the pyridine and the sodium cation (Scheme I-1a); b) addition of the amide anion on C2 resulting in the formation of a new C-N bond and pyridine

dearomatization (Scheme I-1b); and c) oxidation with loss of NaH, which re-aromatizes the ring (Scheme I-1c).[9]

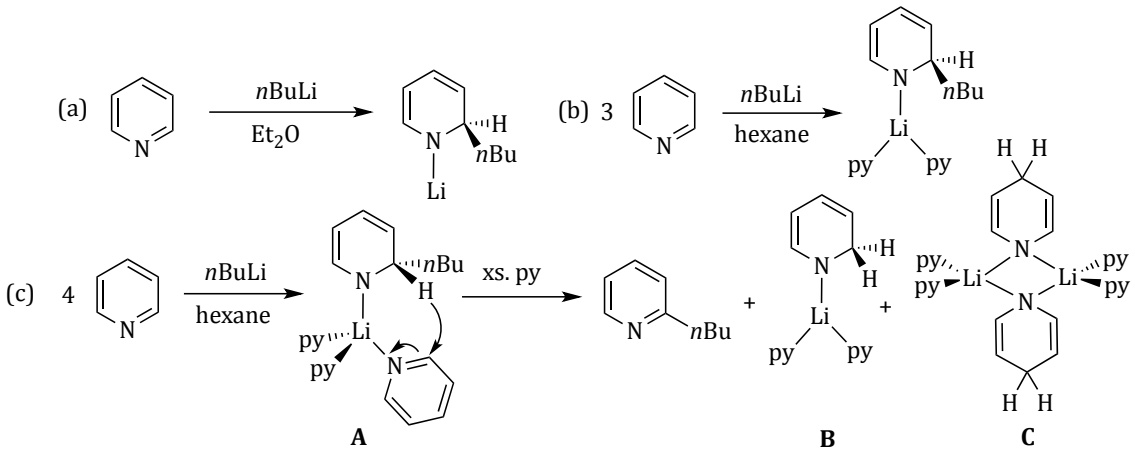


Scheme I-1. Mechanism of the amination of 2-methylpyridine reported by Chichibabin.

Functionalization of pyridines by reaction with alkyllithium reagents (RLi, R = Ph, *n*Bu, *t*Bu, etc.)[6a-c] has been called the "alkyl version of the Chichibabin reaction".[11] These reactions proceed by a similar pathway to that described for the Chichibabin reaction, *i. e*. (a) coordination of pyridine to the lithium cation (thus enhancing pyridine electrophilicity), (b) alkyl group migration and formation of a σ-adduct[12] and (c) rearomatization of the σ-adduct by oxidation.[13]

Due to the high tendency of the σ-adduct to re-aromatize by loss of hydride, these species have been employed in organic synthesis for a long time as *in situ* hydride transfer reagents towards ketones and aldehydes.[14]

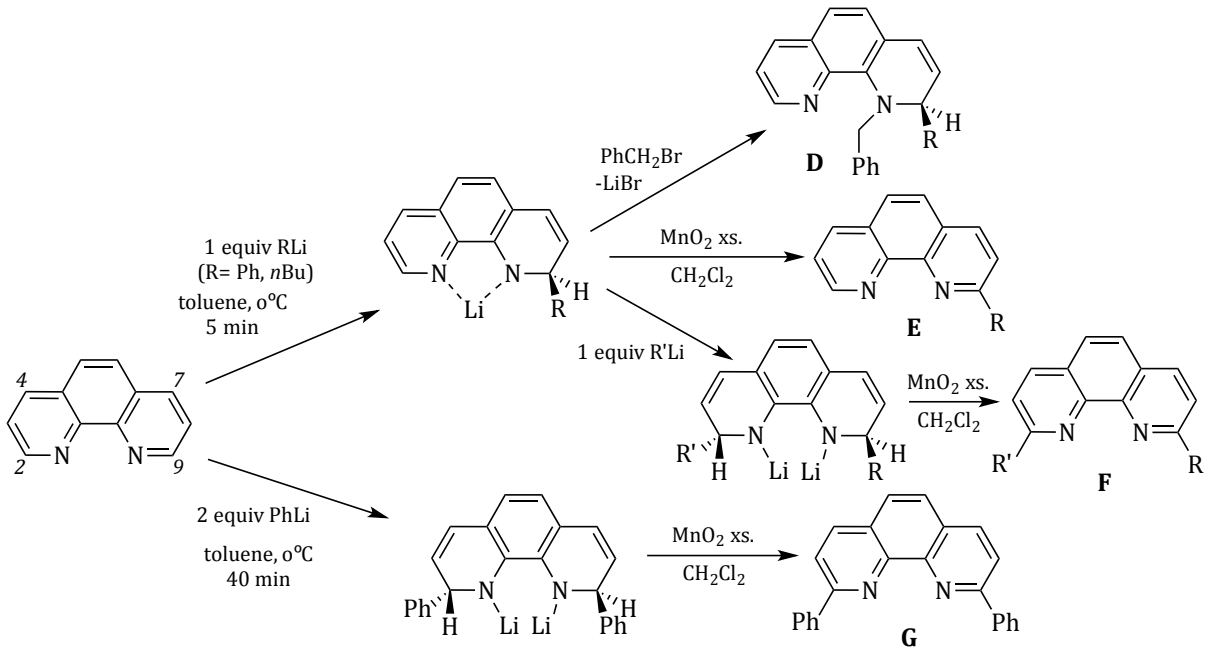
Although addition of RLi reagents to pyridines followed by oxidation is a well-established method for the synthesis of 2-substituted pyridines,[15] full characterization and isolation of the intermediate σ-adducts has remained elusive for a long time. Initial studies aiming to determine the nature of the σ-adduct were carried out in coordinating solvents (such as diethylether or tetramethylethylenediamine (TMEDA)) and species like that shown in Scheme I-2a were proposed to form in solution on the basis of ^{1}H NMR characterization.[16] Mulvey and co-workers reported in 1988 for the first time the isolation and crystallization of the dearomatized species formed in the reaction between butyllithium and a threefold molar amount of pyridine in hexane (Scheme I-2b).[17]



*Scheme I-2. Reaction of pyridine with nBuLi: (a) species proposed to form in the stoichiometric reaction, (b) species formed with a threefold amount of pyridine and (c) species formed with a fourfold excess of pyridine (**A**, **B**, **C**).*

The result of the reaction was found to be crucially ratio-dependent, and when a fourfold excess of pyridine was used, the species depicted in Scheme I-2c were formed.[18] The proposed mechanism comprises three steps: a) coordination of the pyridines to the lithium cation to afford a tetracoordinated lithium complex, b) nucleophilic butyl addition to position 2 of a pyridine to yield the 1,2-dihydropyridine product (**A**) and c) re-aromatization of **A** via intramolecular hydride transfer to a second pyridine (favored by the electron-donating ability of the butyl group) to yield 2-butylpyridine and **B** (Scheme I-2c). Crystallization of the products from this reaction yielded species **C**, which could be formed from a 1,3-hydride shift from **B** followed by dimerization. More recently, insight has been gained on the structures of the σ-adducts from addition of *n*BuLi and *t*BuLi to pyridine in solution, and they have been found to form polymers and trimers respectively.[11]

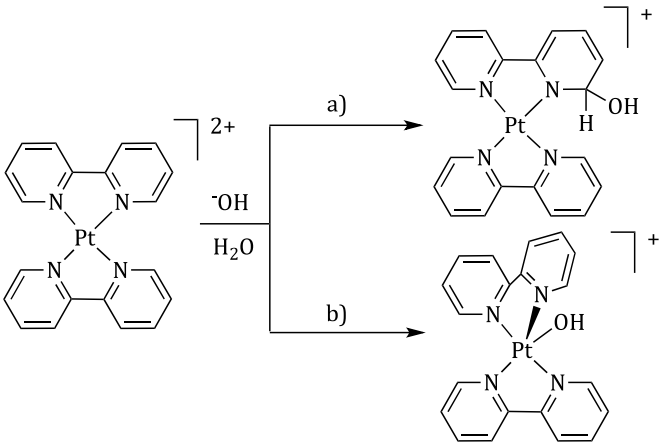
Species from nucleophilic attack on polypyridines,[19] in particular on 2,2'-bipyridine and 1,10-phenanthroline, have been less studied. Reactions with RLi have been employed to synthesize substituted polypyridines by a two-step addition-oxidation reaction which involves dearomatized intermediates.[20] The RLi reagent mainly adds to positions 2/9 and 4/7 of phen and 6/6' of bipy, altough in some cases additions to positions 2/2' of bipy have been found.[21] Monoalkylated (**E**), asymmetric dialkylated (**F**) and symmetric dialkylated (**G**) products can be obtained depending on the polypyridine:RLi ratio employed (Scheme I-3).[20a]



*Scheme I-3. Alkylation of 1,10-phenanthroline with RLi and subsequent oxidation (**E**, **F** and **G**) or electrophilic alkylation (**D**).*

The mechanism of these reactions is presumably similar to that described for simple pyridines (see above) although much less effort has been made to characterize the dearomatized intermediates. Only some dearomatized derivatives from addition of RLi (R = *n*Bu, Ph, *n*Hex) to 1,10-phenanthroline have been isolated by reaction with benzyl bromide (species **D**, Scheme I-3).[22]

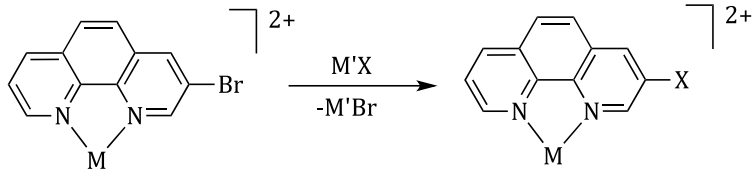
Although coordination to a Lewis-acidic transition metal center has been proposed to enhance the electrophilicity of N-heterocycles[23] nucleophilic additions upon transition metal coordinated bipy or phen are almost unkown. In 1973 Gillard proposed nucleophilic addition of hydroxide anion on Pt-bonded bipy in aqueous medium (Scheme I-4a).[24] However, due to the lack of convincing evidence, Gillard's covalent hydration proposal generated a long-standing controversy.[25] In 2003, Blackman and co-workers demonstrated that the species formed in the basic $[Pt(bipy)_2]^{2+}$ solution was a pentacoordinate platinum (II) complex resulting from nucleophilic attack of the hydroxide ion to the metal (Scheme I-4b).[26]



Scheme I-4. Behavior of $[Pt(bipy)_2]^{2+}$ in basic aqueous media: a) covalent hydrate proposed by Gillard, b) product characterized by Blackman.

Chen and co-workers were able to isolate a product resulting from nucleophilic addition of hydroxide ion on coordinated phen in a copper complex under hydrothermal conditions.[27] However, subsequent studies on this reaction by Latham and co-workers suggested that nucleophilic attack of hydroxide on the metal center could occur first, followed by an intramolecular migration of the hydroxide to C2 of phen.[28]

Nucleophilic addition on substituted 1,10-phenanthroline ligands is proposed as the first step in the mechanism of substitution reactions on the pyridyl ring. In 1997 Tzalis and Tor reported that coordination of 3-bromo-1,10-phenanthroline to Ru(II) or Os(II) fragments enables nucleophilic substitution at the usually deactivated *metha* position (Scheme I-5).[29]

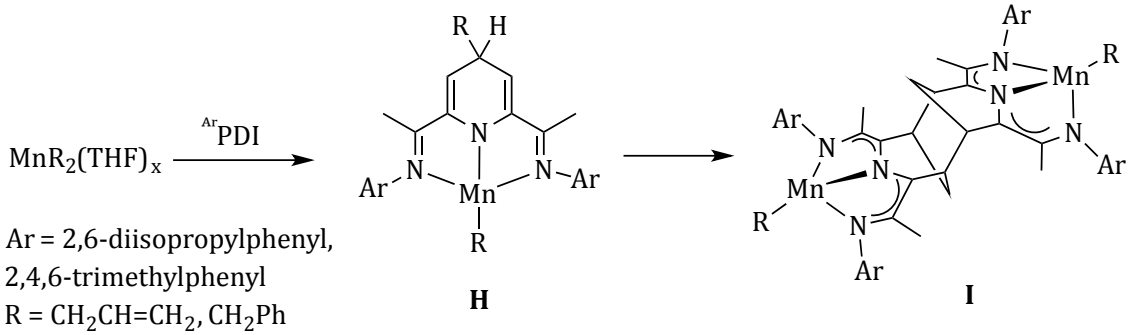


M = $Ru(bipy)_2$, $Os(bipy)_2$ M'X = $NaSCH_3$, $NaOCH_3$, KF; M'Br = NaBr, KBr

Scheme I-5. Substitution of Br in coordinated 3-bromo-1,10-phenanthroline.

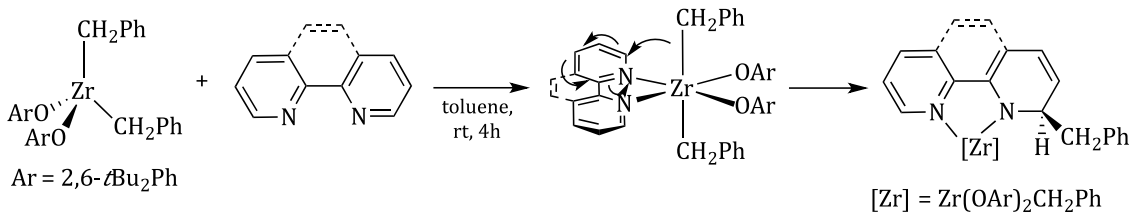
This result is remarkable in that the free ligand is unreactive towards the employed nucleophiles, even under harsh conditions, and thus the authors attribute the enhanced reactivity to coordination to the metal center.

Addition of alkyl nucleophiles to transition metal-coordinated pyridine-containing ligands is rare[30] and some of the few examples have been found to be responsible of the deactivation of polymerization catalysts which contain pyridyldiimine (PDI) ligands.[30d-f] In most cases, the reaction occurs by an intramolecular migration of the alkyl group from the metal to positions 2 or 4 of the pyridine donor. In some instances, addition of alkyl groups to the *para* position of pyridines in PDI ligands led to the dimerization of the pyridyl unit.[30a,e] One recent example of this kind of reactivity has been reported by Cámpora and co-workers in the reaction of $MnR_2(THF)_x$ (R = allyl, benzyl) with ^{Ar}PDI (Ar = 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl), as shown in Scheme I-6.[30a] In this case, coordination of the PDI to the manganese center promotes alkyl migration from manganese to position 4 of the pyridine donor to yield the dihydropyridine species **H** which, in the presence of traces of O_2, dimerizes affording complex, **I**, in which two dearomatized pyridine units of the PDI are bonded through their 3 and 5 positions.



Scheme I-6. Metal-to-PDI alkyl group migration and subsequent dimerization of the product.

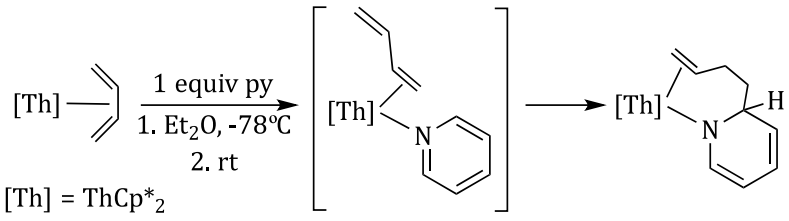
In particular, the additions to polypyridines, such as bipy, phen or 2,2':6',2''-terpyridine (terpy), are scarce. Rothwell reported in 1989 an example of an intramolecular benzyl group migration to bipy and phen in Zr(IV) complexes under mild conditions (Scheme I-7).[31]



Scheme I-7. Benzyl group metal-to-bipy/phen migration in Zr(IV) complexes.

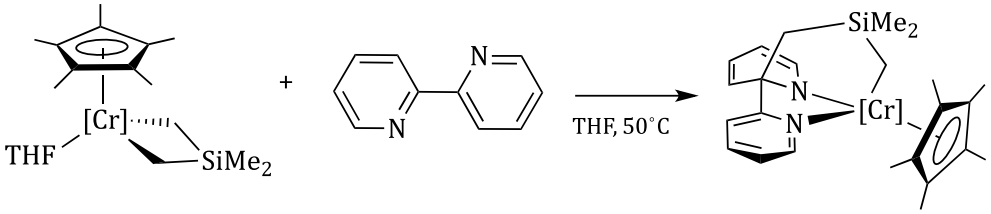
The driving force for this reaction is thought to be a combination of the steric hindrance of the octahedral species and a weak M-benzyl bond, since reaction of the methyl analog (with a stronger M-C bond and less sterically hindered) with bipy or phen does not result in intramolecular methyl migration.

Erker and co-workers reported in 1986 the highly reactive thorium (IV) complex $[Th(Cp^*)_2(\eta^2\text{-}C_4H_6)]$ which was able to activate pyridine toward the nucleophilic addition of the butadiene co-ligand (Scheme I-8).[32]



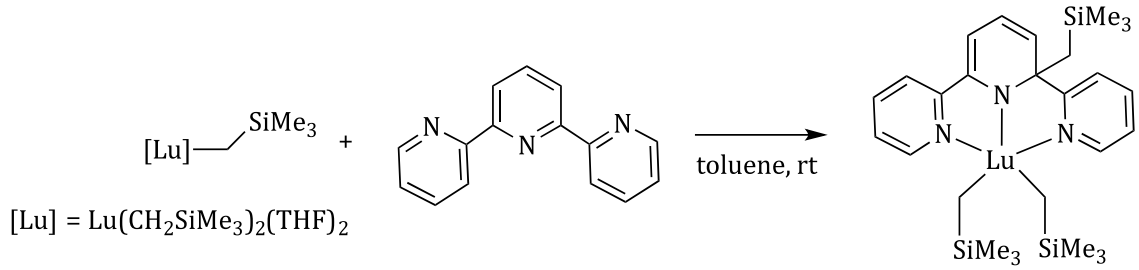
Scheme I-8. Intramolecular alkenyl addition on C2 of pyridine in a thorium (IV) complex.

In 2001 Theopold and co-workers reported an example of an alkyl migration to the position 2 of a bipy ligand, whose product was stable enough to be crystallized, allowing the authors to determine its structure in the solid state by single-crystal X-ray diffraction (Scheme I-9).[33]



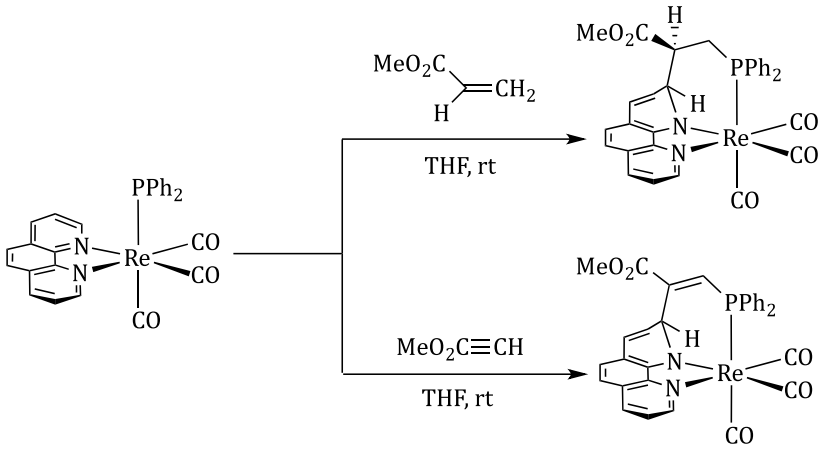
Scheme I-9. Migration of an alkyl group to C2 of bipyridine in a Cr(III) complex.

Some years later Kiplinger reported the addition of a (trimethylsilyl)methyl group to a coordinated terpy ligand in a Lu(III) complex (Scheme I-10).[34]



Scheme I-10. Metal-to-terpy (trimethylsilyl)methyl group migration in a Lu(III) complex.

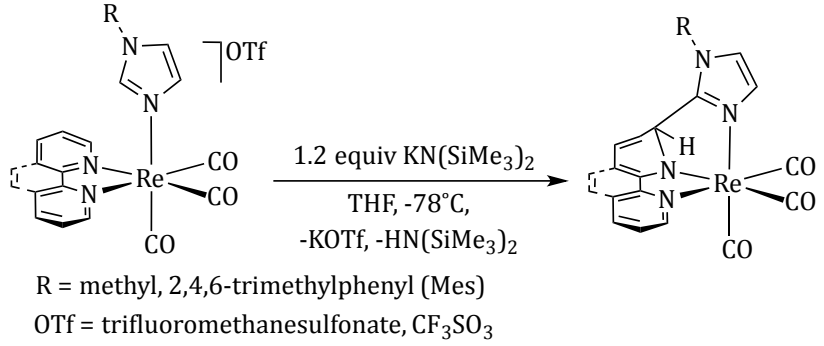
A completely different type of intramolecular additions on coordinated bipy and phen under very mild conditions have been previously reported by our group with the low oxidation state metal fragments *fac*-{$Re(CO)_3$}$^+$ and *cis*-{$Mo(\eta^3\text{-}C_4H_7)(CO)_2$}$^+$.[35] Reaction of a rhenium phosphanido complex with activated alkenes or alkynes resulted in the formation of a phen-dearomatized product (Scheme I-11).[35c,d]



Scheme I-11. Reaction of [Re(phen)(CO)$_3$(PPh$_2$)] with activated alkenes or alkynes.

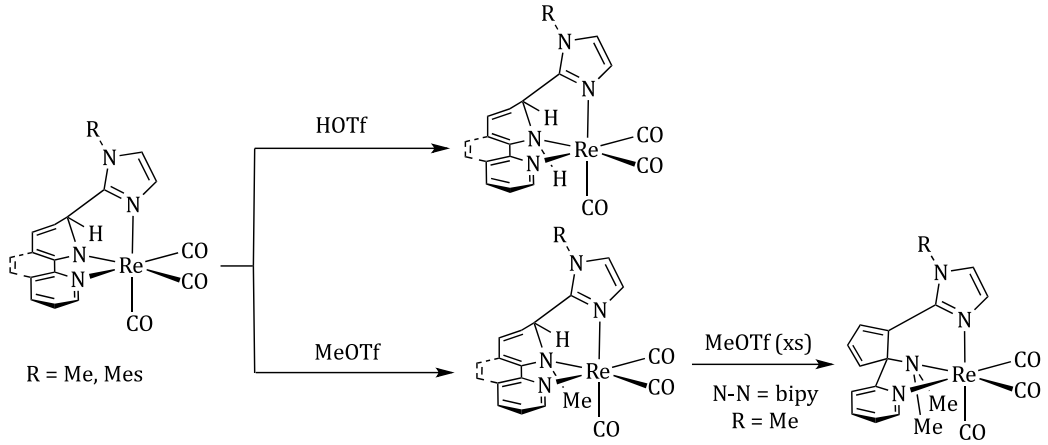
The proposed mechanism involves nucleophilic attack of the phosphanido ligand to the activated alkene or alkyne to generate a zwitterionic intermediate, the negatively charged carbon of which would then add to phen. Remarkably, the reaction, which involves addition to the usually inert phen ligand, takes place under very mild conditions and does not require strongly polar or reducing agents.

Deprotonation of C(2)-H groups of N-alkylimidazole ligands also triggered the intramolecular nucleophilic attack on C6 of bipy or C2 of phen in Re(I) complexes (Scheme I-12).[35b]



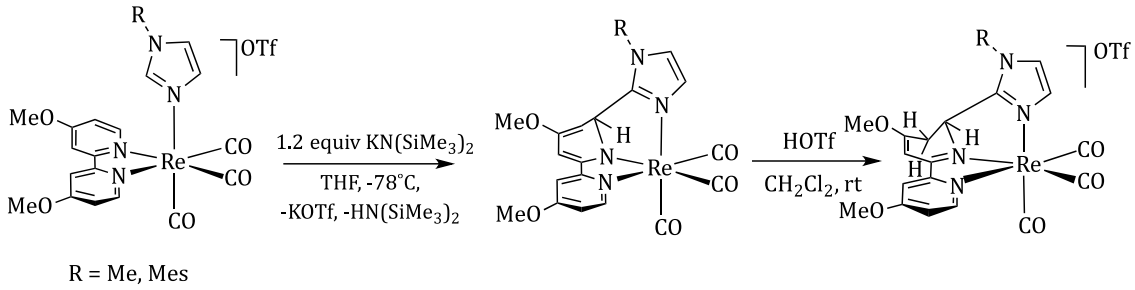
Scheme I-12. Intramolecular nucleophilic addition of a deprotonated N-alkylimidazole on bipy and phen ligands in a Re(CO)$_3$ complex.

The reactions of the neutral pyridyl-dearomatized products with MeOTf and HOTf yielded cationic complexes resulting from methylation and protonation at nitrogen respectively, which retain the dearomatized ring (Scheme I-13). However, for the $[Re(bipy)(CO)_3(MeIm)]OTf$ (OTf = $CF_3SO_3^-$) compound, the presence of excess MeOTf led to the ring opening of the dearomatized pyridyl group, giving rise to a denitrogenated cyclopentadienyl group.



Scheme I-13. Reaction with (a) HOTf and (b) MeOTf of neutral products from intramolecular C-C coupling between bipy and N-alkylimidazole ligands.

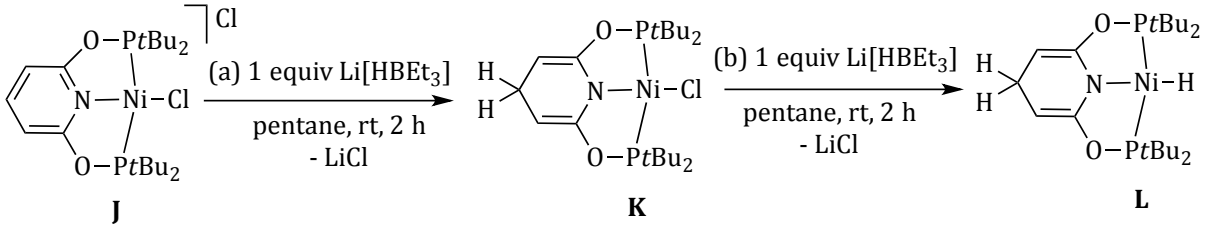
Deprotonation of coordinated N-alkylimidazoles in the same rhenium fragment, but bearing a 4,4'-dimethoxy-2,2'-bipyridine co-ligand instead of the parent bipy, also yielded analogous products of intramolecular nucleophilic attack on position 6 of bipy. However, protonation of the products yielded a cationic complex with a CH_2 group on position 5 of bipy (see Scheme I-14).[35a] Protonation at C5 has been atributted to the presence of the strong electron-donating methoxy groups which enhance its nucleophilic character.



Scheme I-14. Intramolecular nucleophilic addition of a deprotonated N-alkylimidazole on 4,4'-dimethoxy-2,2'-bipyridine in a $Re(CO)_3$ complex and subsequent protonation.

Similar intramolecular additions initiated by deprotonation of C(sp^3)-H groups of ligands, which are the subject of most of the present work, have never been reported.

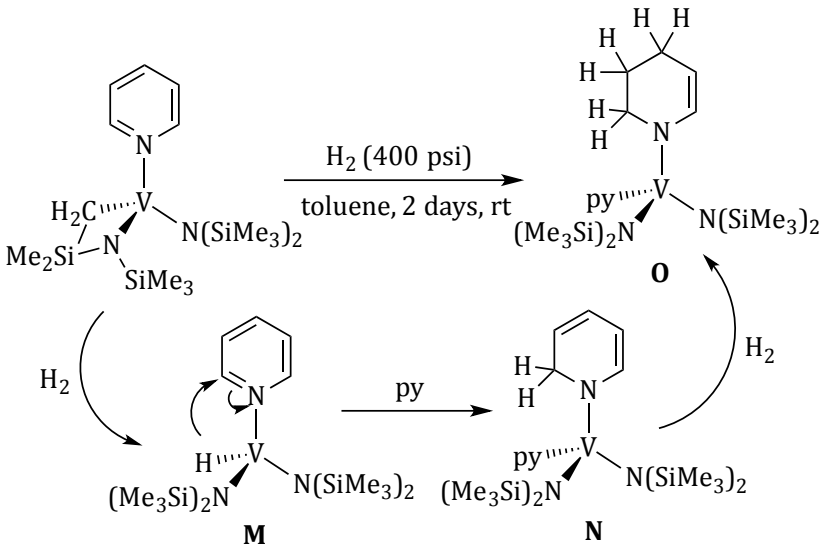
Hydride groups also add to transition metal-coordinated pyridine-containing ligands, disrupting pyridine aromaticity to afford dihydropyridinate derivatives.[30b,36] In the reaction between Li[$HBEt_3$] and [NiCl(PONOP)]Cl (species **J** in Scheme I-15, PONOP = 2,6-bis(di-*tert*-butylphosphinito)-pyridine) reported by Jones,[36a] hydride attack on position 4 of pyridine yields a neutral complex (**K**) containing a dearomatized pyridine ring. Addition of a second equivalent of hydride promotes the substitution of the chloride ligand in **K** to yield a neutral hydride complex (**L**).



J **K** **L**

Scheme I-15. (a) Hydride addition on the pyridine ring of a tridentate PONOP ligand in a Ni(II) complex and (b) attack to the metal by a second equivalent of hydride.

The mechanism of the addition of the first equivalent of hydride to the pyridine ring has been not studied, although it presumably is similar to that found for the reactions with RLi, *i. e.*, coordination of a hydride to the metal center followed by intramolecular metal-to-pyridine migration. This has been found to be the mechanism for the hydride addition, also to the *para* position, on the pyridine ring of an acridine ligand reported by Milstein and co-workers.[36b] However, the second equivalent of hydride remains bonded to the metal and does not migrate to the pyridine ring. Although addition of 2 equivalents of hydride to free pyridines is known[37] reduction of more than one double bond in coordinated pyridyl rings has only been achieved by Gambarotta and co-workers in the reaction of pyridines coordinated to a V(III) center with H_2 (see Scheme I-16).[38]



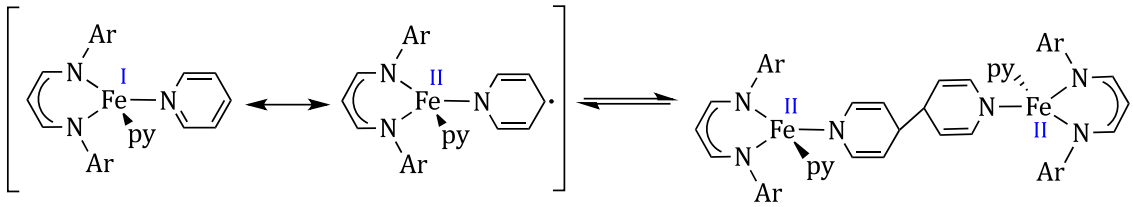
Scheme I-16. Hydrogenation of two double bonds of pyridine in a V(III) complex and its proposed mechanism.

The mechanism of the reaction is unknown, but it is proposed to start with the M-CH_2 bond breaking as a consequence of its reaction with H_2, followed by the formation of a M-H bond (species **M**, see Scheme I-16). A metal-to-pyridine migration would dearomatize the pyridyl ring yielding species **N**, which would further react with a second equivalent of H_2 to yield the product **O**. The authors attribute the lack of reactivity of **O** toward a third equivalent of H_2 to the stability of the enamine in **O** by conjugation of the double bond with the lone electron pair on nitrogen and with the metal *via* the planar trigonal amido nitrogen geometry.

Alkyl or hydride additions to pyridine rings are relevant from the point of view of the hydrodenitrogenation (HDN) processes, since they can lead to pyridine ring opening. The HDN is an industrial process required to remove pyridine and its derivatives from fuels to avoid NO_x emissions. Removal of nitrogen of heterocycles from fuels is normally achieved by extrusion of nitrogen as ammonia promoted by heterogeneous catalysts (mainly CoMo/γ-Al_2O_3 or NiMo/γ-Al_2O_3) under reducing conditions (high pressures of H_2). These conditions promote reduction of aromatic heterocycles followed by disruption of the rings to ultimately yield hydrocarbons and NH_3.[39] Under the same conditions and using the same catalytic system, HDN is carried out simultaneously with hydrodesulfurization (HDS), which removes organic sulfur compounds, such as thiophenes, as hydrocarbons and H_2S. Homogeneous models of HDN can be useful to understand the mechanism of this process. In this context, reactions of pyridine ring

opening promoted by metal complexes have great interest. This kind of reactions are known to be promoted by migration of hydrides or alkyls to activated pyridine ligands, such as pyridines $\kappa^2(C,N)$ coordinated to highly reducing early transition metal fragments.[2,40] A completely different example of pyridine ring opening under mild conditions has also been found in our group (see above).[35b]

Bond-forming reactions on pyridine, bipy or phen ligands can also occur as a result of their redox-active character, usually termed "redox non-innocence", in turn a consequence of the capability of pyridines to accept electron density.[41] This kind of reactivity is well-known, and is promoted by oxidation of the metal center which donates one electron to a pyridine ring that stores that excess electron density on a new C-C bond with an analogous radical. As a result of these intermolecular couplings, dimeric species are usually formed. These couplings could be reversible[42] or irreversible[43] and usually occur in complexes with highly reductive metal fragments. Reversible C-C coupling between two coordinated pyridines has been reported by Holland and co-workers[42c,d] in a low coordinated iron (I) complex (see Scheme I-17). The resulting dimer could be characterized only in the solid state.

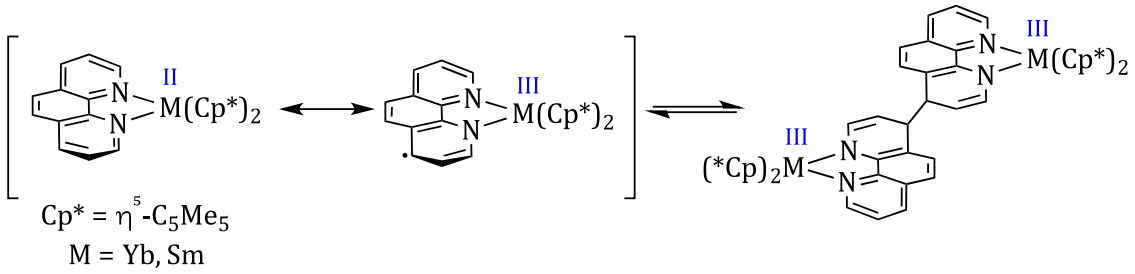


Ar = 2,6-diisopropylphenyl

Scheme I-17. Intermolecular C-C bond formation between the position 4 of two pyridine ligands as a result of one-electron metal-to-ligand transfer.

In the example above, dimerization occurs as a result of a one-electron transfer from the iron center, which is oxidized from iron (I) to iron (II), to the pyridine ligand, which becomes dearomatized and stores that excess of electrons in a new C-C bond.

Characterization in solution of a dimer resulting from a related, reversible C-C coupling, has been recently achieved by Nocton and co-workers in lanthanide (II) complexes. In these instances, new C-C bonds are formed between positions 4 of two phen ligands coordinated to Yb(II) or Sm(II) fragments.[42a,b] Formation of the dimer is promoted by the one-electron reduction of the phen ligand (see Scheme I-18).



Scheme I-18. Dimerization of [M(η⁵-C₅Me₅)₂(phen)] (M = Sm, Yb) complexes by one-electron reduction of phen.

However, the authors report that dimerization does not occur in the analogous bipy complexes, a result attributed to the larger amount of spin density in the 4 positions of phen than in bipy.

In this Ph. D. dissertation the first examples of intramolecular nucleophilic additions on coordinated bipy and phen triggered by deprotonation of CH_3 groups of the co-ligands in $Re(CO)_3^+$ fragments are described. Moreover, intermolecular additions on coordinated bipy and phen have been found for the first time.

Objetivos

Objetivos

1. Los ligandos 2,2'-bipiridina (bipy) y 1,10-fenantrolina (phen) coordinados a fragmentos metálicos son muy inertes y las adiciones nucleofílicas sobre los mismos son inusuales. Estudios previos llevados a cabo por nuestro grupo han demostrado que la desprotonación de grupos C(2)-H de ligandos N-alquilimidazol coordinados al fragmento *fac*-$\{Re(CO)_3(N\text{-}N)\}^+$ (N-N = bipy, phen) puede dar lugar al acoplamiento C-C intramolecular entre el imidazol y el ligando bipy o phen. El primer objetivo de este trabajo ha sido desarrollar una química similar iniciada por la desprotonación de grupos CH alifáticos de ligandos en *cis* a bipy o phen.

2. En la mayoría de los escasos ejemplos conocidos, las adiciones nucleofílicas sobre ligandos bipy o phen son intramoleculares, en concreto, migraciones del metal al ligando de grupos alquilo. El segundo objetivo de este trabajo es el estudio de las adiciones nucleofílicas intermoleculares sobre ligandos bipy y phen.

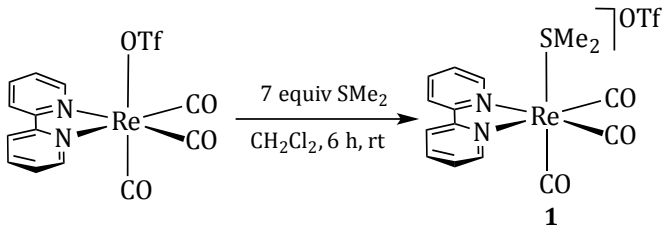
Chapter 1:

Deprotonation of coordinated sulfides.

Part of the results discussed in this Chapter have been included in a *Communication* published in the journal *Inorganic Chemistry.*[44] This Chapter also includes unpublished results which will be discussed in further detail.

1.1 Deprotonation of SMe_2 in $[Re(bipy)(CO)_3(SMe_2)]OTf$

The new compound $[Re(bipy)(CO)_3(SMe_2)]OTf$ (**1**) was obtained from reaction of the precursor $[Re(bipy)(CO)_3(OTf)]$ with excess of SMe_2 in CH_2Cl_2 (see Scheme 1). Compound **1** was isolated by precipitation as an analytically pure yellow solid in a 91 % yield and fully characterized by IR and NMR spectroscopy.



*Scheme 1. Preparation of $[Re(bipy)(CO)_3(SMe_2)]OTf$ (**1**).*

The IR νCO band frequencies of **1** (2039, 1945 and 1931 cm^{-1} in THF) were higher than those of $[Re(bipy)(CO)_3(OTf)]$ (2036, 1935 and 1922 cm^{-1} in THF), in agreement with the presence of a cationic complex. ^1H and ^{13}C NMR spectra of **1** were consistent with a C_s symmetric complex (four signals between 9.03 and 7.79 ppm in the ^1H NMR spectrum for the bipy ligand, see Figure 1) with a coordinated SMe_2 ligand (singlet at 2.28 ppm in contrast with the singlet at 2.17 ppm for free SMe_2).

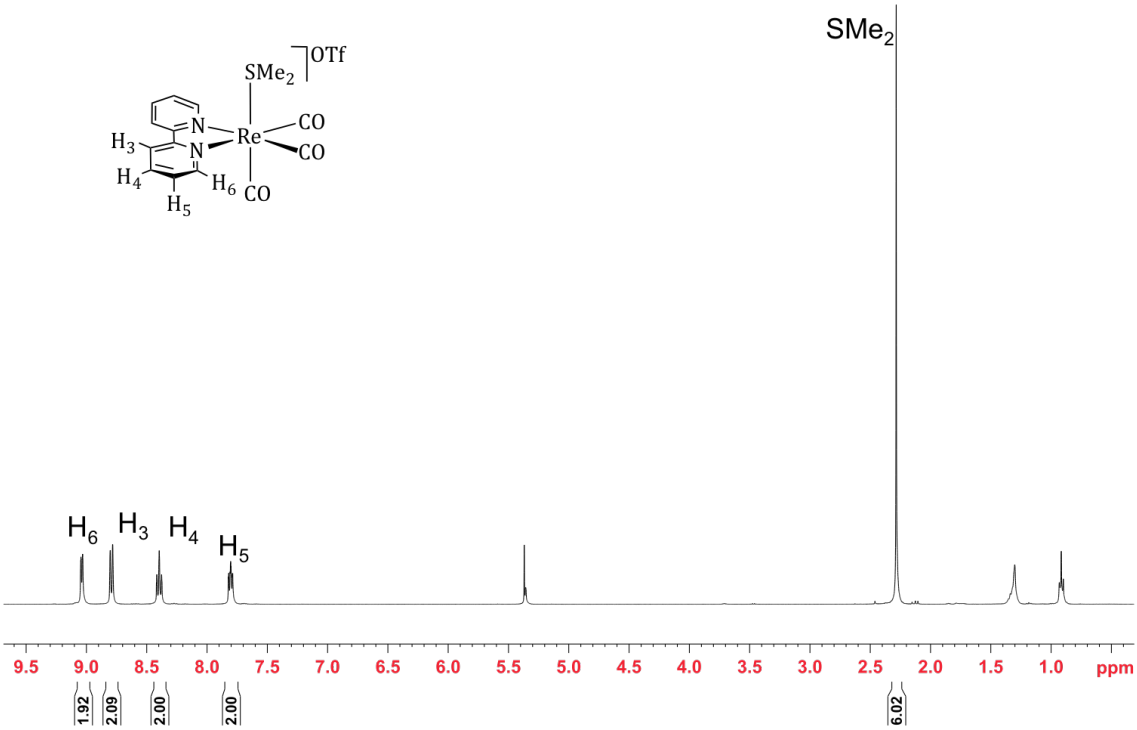


*Figure 1. ^1H NMR spectrum of **1** in CD_2Cl_2*

NMR monitoring of solutions of **1** in CD_2Cl_2 and THF-d_8 showed that **1** is unstable toward the substitution of SMe_2 by the OTf in CD_2Cl_2 and by both the triflate and the solvent in THF-d_8, upon standing in solution for several hours. As a consequence, attempts to crystallize **1** failed due to partial OTf substitution. The analogous compound $[Re(bipy)(CO)_3(SMe_2)]BAr^F_4$ (**1^F**, Ar^F = 3,5-bis(trifluoromethyl)phenyl), with an identical cationic complex and the less coordinating BAr^F_4 counterion instead of OTf, was prepared by methathesis of the triflate in **1** with $NaBAr^F_4$. Slow diffusion of hexane into a concentrated solution of **1^F** in CH_2Cl_2 afforded yellow crystals, one of which was used for X-ray diffraction. The solid-state structure of the cation in **1^F** consisted of a rhenium atom to which bipy, SMe_2 and three carbonyl ligands in *fac* geometry are coordinated in a distorted octahedral geometry (see Figure 2).

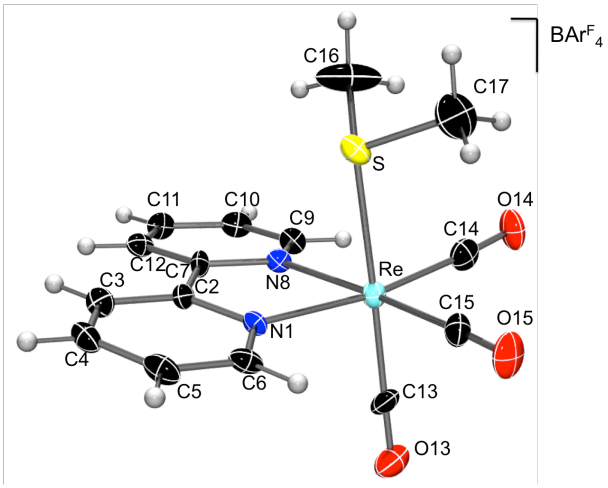
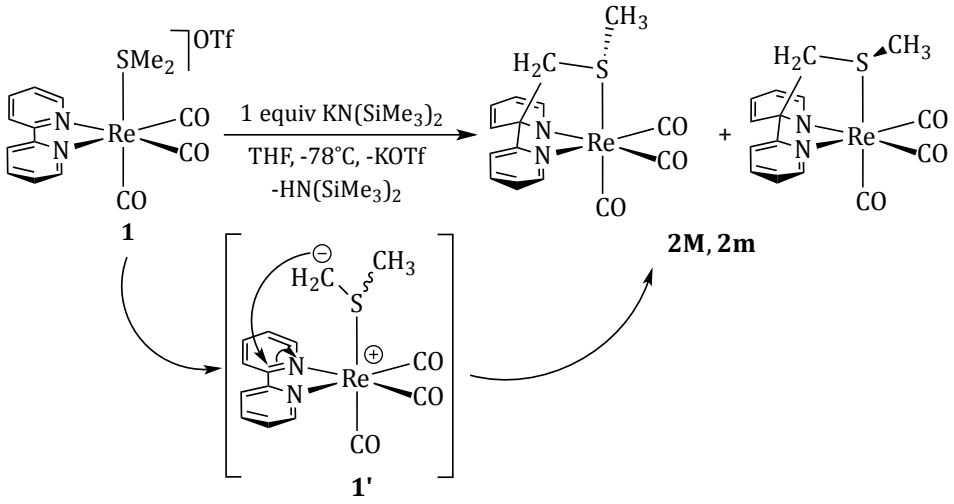


Figure 2. Solid-state structure (thermal ellipsoids at the 30% probability) of the cation in ***1^F****.*

Bond distances and angles in the cation of **1^F** are typical for Re(bipy)(CO)$_3$ complexes, and the Re-S distance (2.501(2) Å) is similar to Re-S distances found for other reported rhenium-sulfide complexes.[45]

Addition of a slight excess of KN(SiMe$_3$)$_2$ to a THF suspension of **1** at -78°C caused the immediate dissolution of the yellow solid and the formation of a red solution with IR νCO bands at lower frequencies (2012, 1910 and 1893 cm^{-1} in THF) than those of **1** (see above), consistent with the formation of a neutral complex. All attempts to isolate the product met with failure due to its instability. Therefore, its NMR characterization was carried out on the reaction crude at low temperature in THF-d$_8$. 1D and 2D spectra showed the product to be formed by two compounds, **2M** and **2m**, in a 2.3:1 ratio (from ^{1}H NMR spectrum integration). The full NMR characterization of these compounds showed them to be diasteromers resulting from sulfide methyl group deprotonation in **1** and subsequent nucleophilic attack by the resulting S-CH$_2^-$ nucleophile on the 2 position of the bipy co-ligand (see Scheme 2).



Scheme 2. Intramolecular nucleophilic addition of a deprotonated methyl group of SMe_2 on position 2 of bipy.

The new S-CH_2 group of each complex, **2M** and **2m**, appears as two doublets (at 2.93 and 1.59 ppm in THF-d_8 for **2M**, see Figure 3) in the ^{1}H NMR spectrum, and as a signal in opposite phase to CH signals (at 32.5 ppm for **2M**) in the ^{13}C DEPT-135 NMR spectrum. As a consequence of the C-C bond formation, the attacked pyridyl ring becomes dearomatized and is asymmetric, its signals becoming upfield shifted (eight signals for the bipy between 8.96 and 4.34 ppm in **2M**) with respect of those of an aromatic ring. Due to pyridyl ring dearomatization, the nitrogen in the attacked ring becomes an amido donor, in contrast to the imino donor in the intact pyridyl ring.

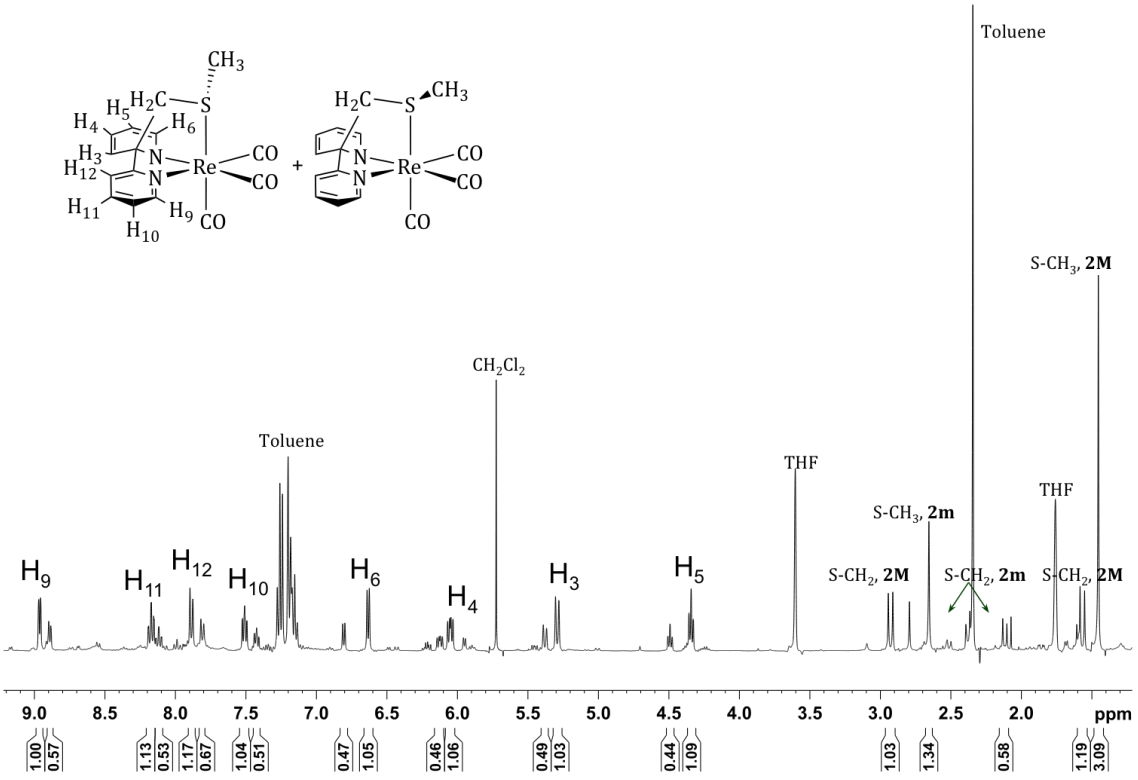


*Figure 3. ^{1}H NMR spectrum of **2M**, **2m** in THF-d_8 at 193 K. Bipy signals of **2M** are assigned.*

The formation of two diasteromers is due to the creation of four stereogenic centers on the deprotonation reaction: the rhenium, the sulfur, the attacked C2, and the nitrogen in the attacked ring (see below), and differ in the relative position of the S-bonded methyl group relative to the attacked pyridyl ring (see Scheme 2). This close similarity between the structure of the two products explains the similarity between their solution IR spectra. Actually, νCO bands of the solution resulting from the reaction of **1** and $KN(SiMe_3)_2$ could lead one to think that a single tricarbonyl complex was formed. Due to the geometric restraints of the reaction the four stereogenic centers only could afford two diasteromers, *SRRR* (and its enantiomer *RSSS* in a 1:1 ratio) and *SRRS* (and its enantiomer *RSSR* in a 1:1 ratio), in agreement with the experimental observation of two products in the reaction crude. Assignment of the configuration of the rhenium has been based on an adaptation of the Cahn, Ingold and Prelog rules to organometallic compounds, considering the three carbonyl groups as a single substituent with the lowest priority. Note that *R* and *S* labels for the rhenium are used instead of the *C* (clockwise) and *A* (anticlockwise) labels recommended by the IUPAC. Stereochemistry labels for the compounds are given in alphabetic order of their stereogenic centers, *i. e.*, C, N, Re and S.[46]

2D NMR experiments support nucleophilic attack of the deprotonated methyl group of the sulfide on position 2 of bipy for both **2M** and **2m**. The ^{1}H, ^{13}C-HMBC spectrum showed crosspeaks between the ^{1}H signals for the CH_2 group (see above) and the ^{13}C signal at 78.0 ppm (for **2M**) or 76.3 (for **2m**), identifying the latter as the attacked carbon atoms. These bipy carbons do not appear in the ^{13}C DEPT-135 NMR spectrum, confirming that nucleophilic attack took place on quaternary carbons.

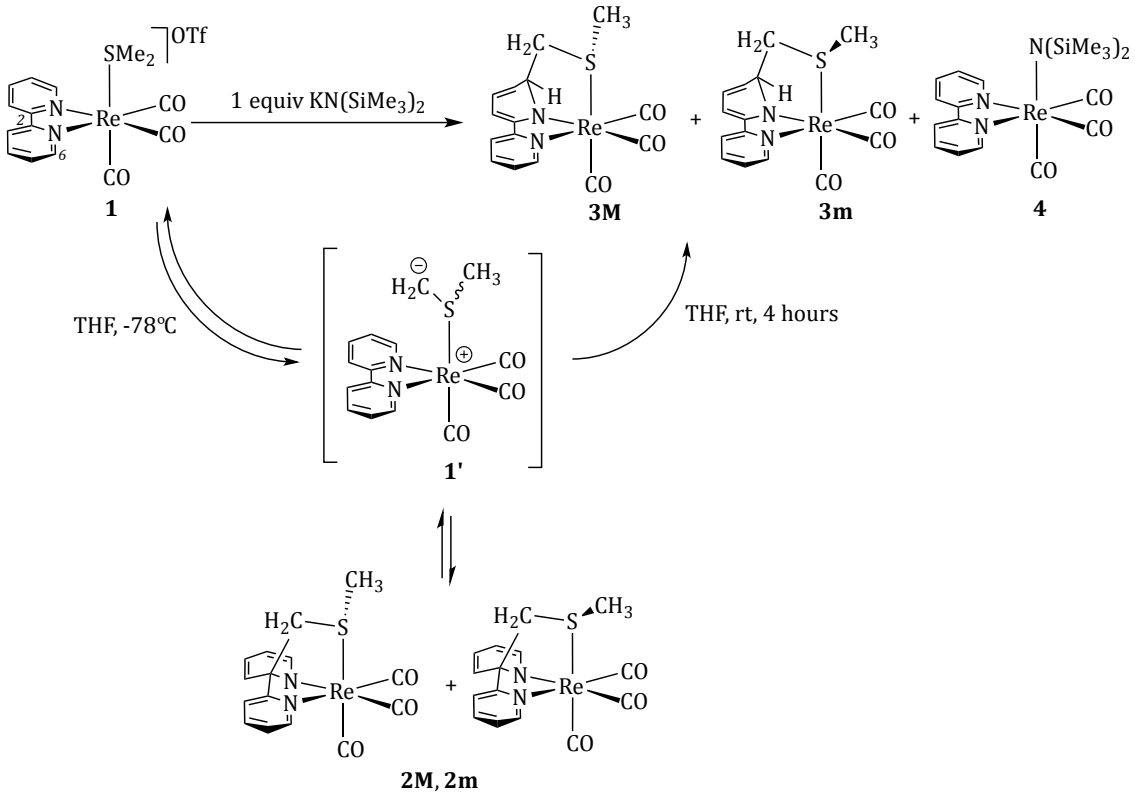
To further confirm the position of the nucleophilic attack of the deprotonated S-CH_3 group, the analogous compound to **1** but with ^{13}C-labeled SMe_2, [Re(bipy)$(CO)_3$S($^{13}CH_3)_2$]OTf (**1***), was synthesized, characterized (analogously to **1**) and deprotonated to yield the diasteromer mixture **2M***, **2m***. The ^{13}C and ^{13}C DEPT-135 NMR spectra of **2M***, **2m*** made possible the unambiguous assignment of the signals at 78.0 (for **2M**) and 76.3 (for **2m**) ppm to the attacked quaternary carbons due to its coupling with the $^{13}CH_2$ group ($^{1}J_{CC}$ = 31.8 Hz for **2M**).

As mentioned above, all attempts to isolate a product from the crude containing the **2M**, **2m** mixture led only to decomposition. However, the ^{1}H, ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC NMR spectra of a THF-d_8 solution of **2M**, **2m** stirred for four hours at room temperature in a J. Young tube showed the presence of at least three organometallic species in solution, **3M**, **3m** and **4** in a 1:0.9:1.5 ratio. Whereas compounds **3M** and **3m**, showed signals consistent with dearomatized bipy ligands, compound **4** displayed signals for a symmetric, aromatic bipy ligand.

Species **3M** and **3m** are proposed to be diasteromers (formed in a 1:0.9 ratio from ^{1}H NMR integration) resulting from nucleophilic attack of the S-CH_2 group on C6 of the bipy ligand (see Scheme 3). The diasteromers (**3M** is *RRRS* and **3m** is *RRRR*) differ in the position of the S-bonded methyl group relative to the attacked pyridyl ring (in *RRRS* the methyl is *syn* and in *RRRR* is *anti*). Signals at 4.47 and 4.32 ppm could be assigned to H6 (of **3M** and **3m** respectively) and showed a cross-peak in the ^{1}H,^{1}H-COSY spectrum with the S-CH_2 group (doublets at 2.83 and 2.58 ppm for **3M** and at 2.67 and 2.38 ppm for **3m** in the ^{1}H NMR spectrum), confirming the proposed connectivity.

The ^{1}H NMR spectrum of the reaction crude from [Re(bipy)$(CO)_3$(OTf)] and KN$(SiMe_3)_2$ in THF-d_8 at room temperature showed signals identical to those found in the sample from evolution of **2M**, **2m** at room temperature, supporting the formulation of **4** as

$[Re(bipy)(CO)_3(N(SiMe_3)_2)]$. Complex **4** would form by the displacement of the labile sulfide ligand in $[Re(bipy)(CO)_3(SMe_2)]^+$ by the bis(trimethylsilyl)amide. In turn, the cationic sulfide complex and the amide, which were the initial reagents, would be produced as the result of the reversibility of the deprotonation and subsequent intramolecular nucleophilic addition discussed above. A singlet attributable to free SMe_2 occurs at 2.07 ppm in the ^1H NMR spectrum supporting ligand dissociation.



*Scheme 3. Reversible intramolecular nucleophilic attack on the C2 position of coordinated bipy in compound **1** by deprotonation of coordinated SMe_2 at low temperature to yield **2M**, **2m**, and evolution to yield **3M, 3m** and **4**. Species **1'** is a proposal and has not been experimentally detected.*

Attempts to investigate the mechanism of formation of $[Re(bipy)(CO)_3(N(SiMe_3)_2)]$ (**4**) have not been made, therefore, the rationale described and depicted in Scheme 3 is a proposal, and assumes reversible deprotonation of SMe_2, *i. e.* C-C bond breaking followed by sulfide displacement, although Re-S bond breaking by $N(SiMe_3)_2$ followed by C-C bond breaking could not be discarded.

DFT calculations on the mechanism of the reaction initiated by deprotonation showed the formation of the C-C bond between the S-CH_2 group and position 2 of bipy to be reversible and to yield species from nucleophilic attack to C6 as the thermodynamic

products (see Figure 4). The displacement of coordinated SMe_2 by $^{-}N(SiMe_3)_2$ to yield $[Re(bipy)(CO)_3(N(SiMe_3)_2)]$ has not been considered on the DFT calculations.

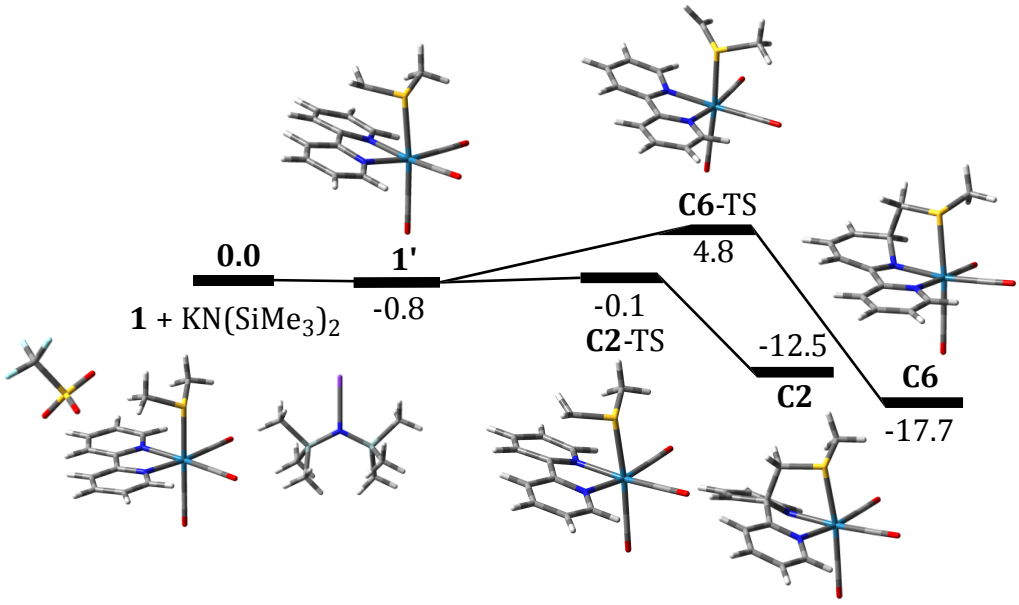


*Figure 4. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol^{-1}) for the reaction of **1** with $KN(SiMe_3)_2$ in THF. Energies are referred to the reactants. Only diasteromers SRRS (**C2**) and RRRS (**C6**) are depicted for products **2M, 2m** and **3M, 3m** respectively.*

Thus, deprotonation of coordinated SMe_2 would occur upon addition of $KN(SiMe_3)_2$ without a barrier to yield the reactive species **1'** (-0.8 kcal·mol^{-1}, not experimentally detected) containing a S-CH_2^- group, which would immediately add to position 2 of bipy (with a barrier of -0.1 kcal·mol^{-1}) to yield **C2** (-12.5 kcal·mol^{-1}). At higher temperatures **1'** would be regenerated by C-C bond breaking and the S-CH_2^- group would attack position 6 of bipy (4.8 kcal·mol^{-1} barrier) to yield product **C6** (-17.7 kcal·mol^{-1}). Thus, product **C2** would be the kinetic product of the reaction and **C6** the thermodynamic one due to its higher stability. This higher stability could be attributed, at least in part, to the conjugation of the double bonds in the attacked pyridyl ring with the intact pyridyl ring (in contrast with **C2** where the double bonds are not conjugated).

The preferential nucleophilic addition to C2 under conditions of kinetic control can be attributed to the electron-withdrawing 2-pyridyl subtituent at this position, which would increase the electrophilic character of position 2. In support of this proposal, NBO charge calculations on the carbon atoms on positions 2 and 6 of the bipyridine ligand in **1** showed a larger positive charge on C2 and C2' (0.198 e·Å^{-3}) than on C6 and C6' (0.070

e·Å^{-3} and 0.063 e·Å^{-3}) supporting charge control on the nucleophilic attack of the S-CH_2 group on bipy and the formation of **C2** as the kinetic product of the reaction (see Figure 5).

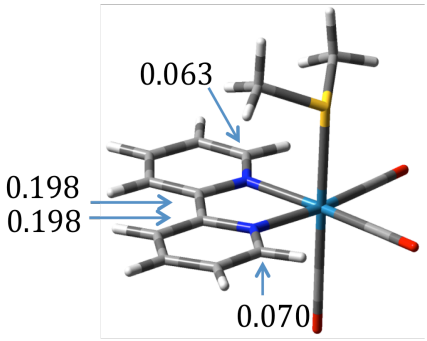


*Figure 5. NBO charges (in e·Å^{-3}) for the 2 and 6 positions of the bipyridine ligand in **1**.*

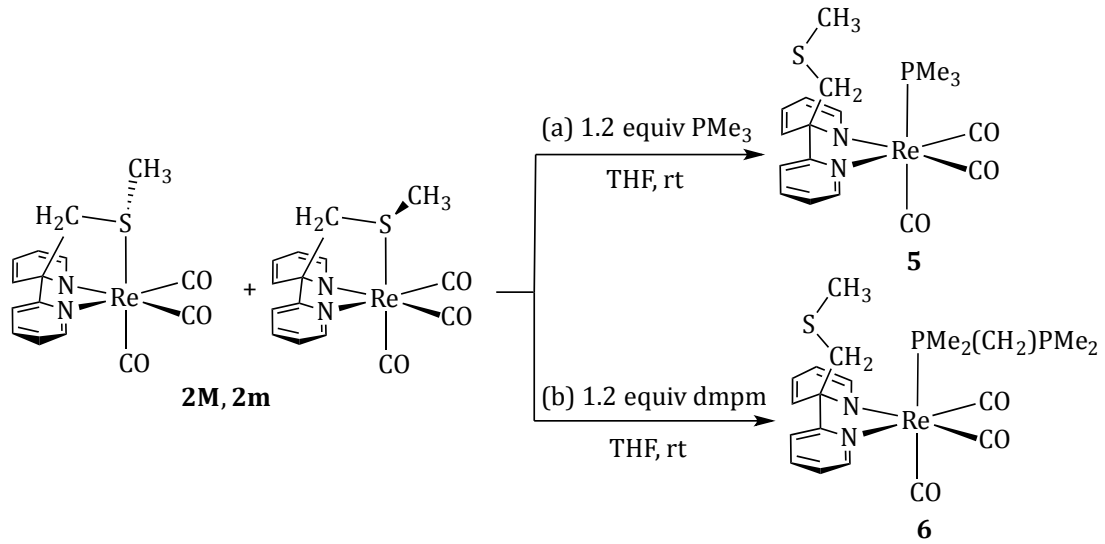
Addition of $KN(SiMe_3)_2$ to free SMe_2[47] and subsequent addition of the resulting mixture to the [Re(bipy)$(CO)_3$(OTf)] precursor failed to yield C-C coupling products (as judged by IR spectroscopy), supporting facilitated deprotonation and C-C coupling of the sulfide upon coordination to the cationic metal center.

The deprotonation of SMe_2 was reported by Peterson in 1967[48] employing *n*BuLi/TMEDA (tetramethylethylenediamine) in hexane at room temperature for 4 hours. However, deprotonation of free SMe_2 by the reported procedure and addition of the resulting solution to [Re(bipy)$(CO)_3$(OTf)] yielded the mixture **2M**, **2m** (as judged by ^{1}H NMR spectroscopy) although with lower purity than the one obtained by the procedure described in this Chapter.

1.2 Reaction of the C-C coupling mixture with PMe_3 and $P(CH_3)_2CH_2P(CH_3)_2$

A slight excess of PMe_3 or $P(CH_3)_2CH_2P(CH_3)_2$ (dmpm) were added to freshly prepared solutions of **2M**, **2m** in THF causing a slight color change from dark red to brown, and an instantaneous shift of the IR νCO bands to slightly lower wavenumbers (2010, 1913 and 1885 cm^{-1} in THF for the reaction with PMe_3) consistent with the formation of a new tricarbonyl species by coordination of PMe_3 or dmpm, which are stronger donors than the sulfide. 1D, and 2D NMR spectroscopy supported the presence of single species, **5**

and **6**, formed as a result of the S donor displacement by PMe_3 or dmpm respectively (see Scheme 4).



*Scheme 4. S-donor displacement in **2M**, **2m** by (a) PMe_3 and (b) dmpm.*

The products, **5** and **6**, were found to be slightly more stable than the precursor mixture **2M**, **2m** and most of their NMR characterization could be carried out at room temperature. ^{1}H, ^{13}C and ^{31}P NMR spectra were consistent with the presence of asymmetric complexes and showed signals for a coordinated PMe_3 (at 1.14 ppm in the ^{1}H NMR spectrum of **5** in CD_2Cl_2, see Figure 6) or monodentate dmpm (two doublets of doublets for the P-bonded CH_3 groups at 1.18 and 1.02 ppm and a mutiplet at 1.54 ppm for the P-CH_2-P unit in the ^{1}H NMR spectrum of **6** in CD_2Cl_2). In addition, their spectra feature signals similar to those of **2M**, **2m** for the CH_3SCH_2-bipy skeleton (*e. g*. doublets assigned to the S-bonded CH_2 at 2.86 and 2.65 ppm in the ^{1}H NMR spectrum of **5** in CD_2Cl_2, which showed a cross-peak in the ^{1}H, ^{13}C-HMBC spectrum with the ^{13}C signal at 72.5 ppm in CD_2Cl_2 assigned to C2 of bipy). The presence of two doublets in the ^{31}P NMR spectrum (at -18.7 and -59.0 ppm) for the dmpm ligand in **6** confirms the coordination of only one of the phosphorous atoms to rhenium (the chemical shift of -59.0 ppm is similar to that for free dmpm, a singlet at -54.8 ppm in CD_2Cl_2). This monodentate coordination of dmpm confirms that the rhenium precursors **2M**, **2m** contain no other labile positions, suggesting that their low thermal stability is not due, for instance, to facile decarbonylation.

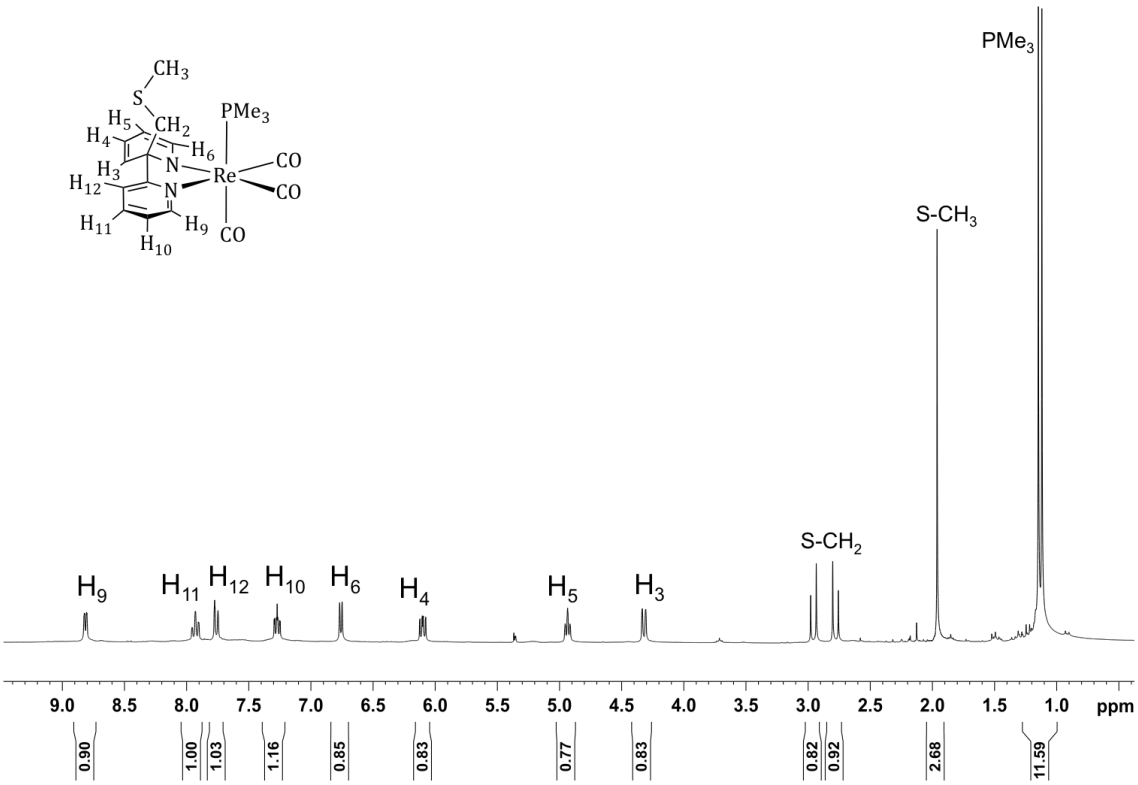


*Figure 6. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at 298 K.*

Complexes **5** and **6** are chiral but were formed as single diasteromers from the mixture **2M**, **2m**, due to the loss of the sulfur atom as an sterogenic center upon its dissociation from the metal center. As a result, **5** and **6** possess three stereogenic centers that yield a single diasteromer (*SRR*)[46] as a racemic mixture.

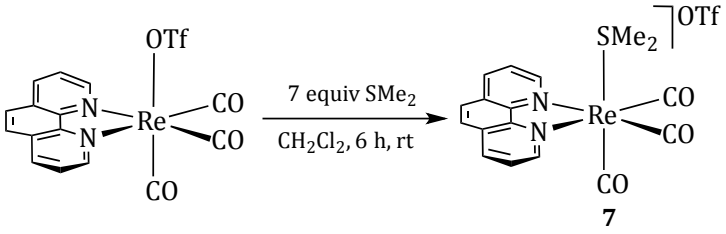
The connectivity of complex **5** was confirmed by reaction of the ^{13}C-labeled mixture, **2M***, **2m*** with PMe_3 to yield complex **5***, an analog of **5** with a $^{13}CH_2S^{13}CH_3$ group (see Experimental Section).

1.3 Deprotonation of SMe_2 in $[Re(phen)(CO)_3(SMe_2)]OTf$

Given the novelty of the results discussed above and the fact that the mixture **2M**, **2m** has been found to be unstable, the deprotonation of coordinated sulfide was extended to the analogous 1,10-phenanthroline compound. Phen has been extensively used, like bipy, in every field of coordination chemistry. Therefore, the study of the fundamental aspects of the chemistry of metal-coordinated phen is of obvious relevance. In addition, in previous studies of our group it has been found that the products of intramolecular

nucleophilic addition to $Re(CO)_3$-coordinated phen are more stable than their bipy analogs.[35c,d] Therefore the exploration of the chemistry similar to that described above, but with phen instead of bipy was carried out partly hoping to obtain similar, yet more stable products.

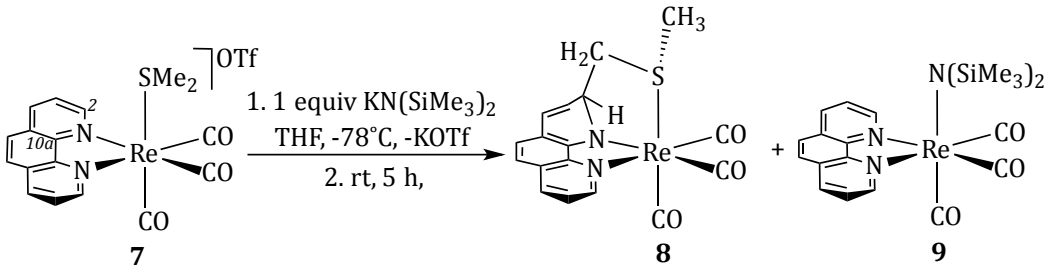
Addition of excess SMe_2 to a CH_2Cl_2 solution of $[Re(phen)(CO)_3(OTf)]$ yielded compound $[Re(phen)(CO)_3(SMe_2)]OTf$ (**7**) upon six hours at room temperature (see Scheme 5).



*Scheme 5. Synthesis of $[Re(phen)(CO)_3(SMe_2)]OTf$ (**7**).*

Compound **7** was isolated as a yellow solid in a 93 % yield and characterized by EA, and IR and NMR spectroscopy. 1D and 2D NMR spectra showed similar features than those of **1** (see above) and were consistent with a C_s symmetric complex with coordinated SMe_2.

Addition of the equimolar amount of $KN(SiMe_3)_2$ to a solution of **7** in THF at -78°C caused an instantaneous color change of the solution from yellow to blue. The solution turned red upon 5 hours stirring at room temperature, and its IR νCO bands were consistent with the presence of neutral tricarbonyl species (2012, 1910 and 1896 cm^{-1} in THF). The ^1H NMR spectrum of the product showed the presence of two rhenium species, **8** and **9**. The ^1H and ^1H, ^1H-COSY NMR spectra indicated that complex **8** was formed as a result of the deprotonation of one of the methyl groups of the dimethylsulfide ligand and subsequent intramolecular nucleophilic attack on position 2 of phen. Note that complex **8** is obtained as a single diasteromer, in contrast to the mixture obtained in the deprotonation of $[Re(bipy)(CO)_3(SMe_2)]OTf$ (**1**). On the other hand, complex **9** formed from the displacement of the SMe_2 ligand by the amide in **7** (see Scheme 6).



*Scheme 6. Reaction of [Re(phen)(CO)$_3$(SMe$_2$)]OTf (**7**) with KN(SiMe$_3$)$_2$.*

DFT calculations on the mechanism of the reaction of **7** with KN(SiMe$_3$)$_2$ revealed that, after deprotonation of the S-bonded methyl group to yield **7'** (0.7 kcal·mol^{-1}, see Figure 7), nucleophilic addition on position 2 of phen occurred with a barrier of 2.7 kcal·mol^{-1} and yielded the most stable product, **8** (-23.5 kcal·mol^{-1}). In contrast, addition of the S-CH$_2^-$ group to C10a of the phen ligand would require a higher energy (3.5 kcal·mol^{-1}) and would yield a product, **C10a** (-11.7 kcal·mol^{-1}), less stable than **8**. These results are in agreement with the experimental formation of complex **8** as the single product of the reaction. Besides, species from nucleophilic addition to C10a of phen were not detected by NMR monitoring of the deprotonation reaction at low temperature.

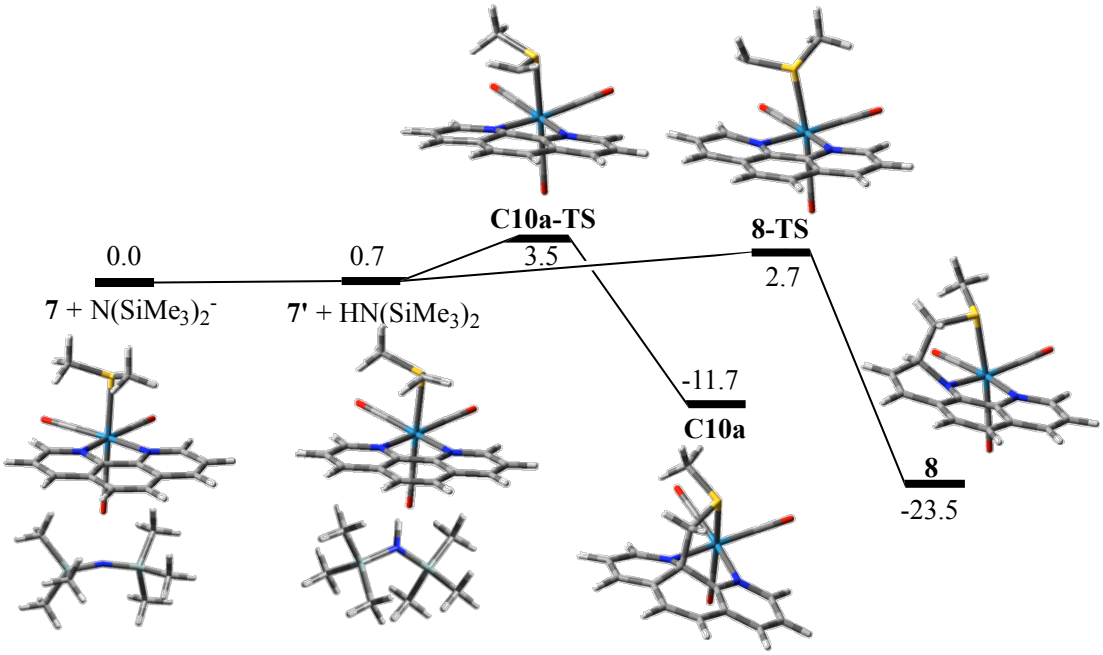


*Figure 7. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol^{-1}) for the reaction of **7** with KN(SiMe$_3$)$_2$ in THF. Energies are referred to the reactants. Only one diasteromer is depicted for products **C10a** and **8** respectively.*

Conducting the addition of $KN(SiMe_3)_2$ to complex **7** in the presence of excess SMe_2 disfavored SMe_2 dissociation and lead to the formation of a larger **8**:**9** ratio (see Figure 8). However, it was not possible to completely suppress the formation of **9** and obtain complex **8** as the single reaction product, even by using SMe_2 as the solvent in the deprotonation (the addition of $KN(SiMe_3)_2$ to a SMe_2 solution of **7** was carried out in the presence of 1 mL of THF to help to dissolve the products).

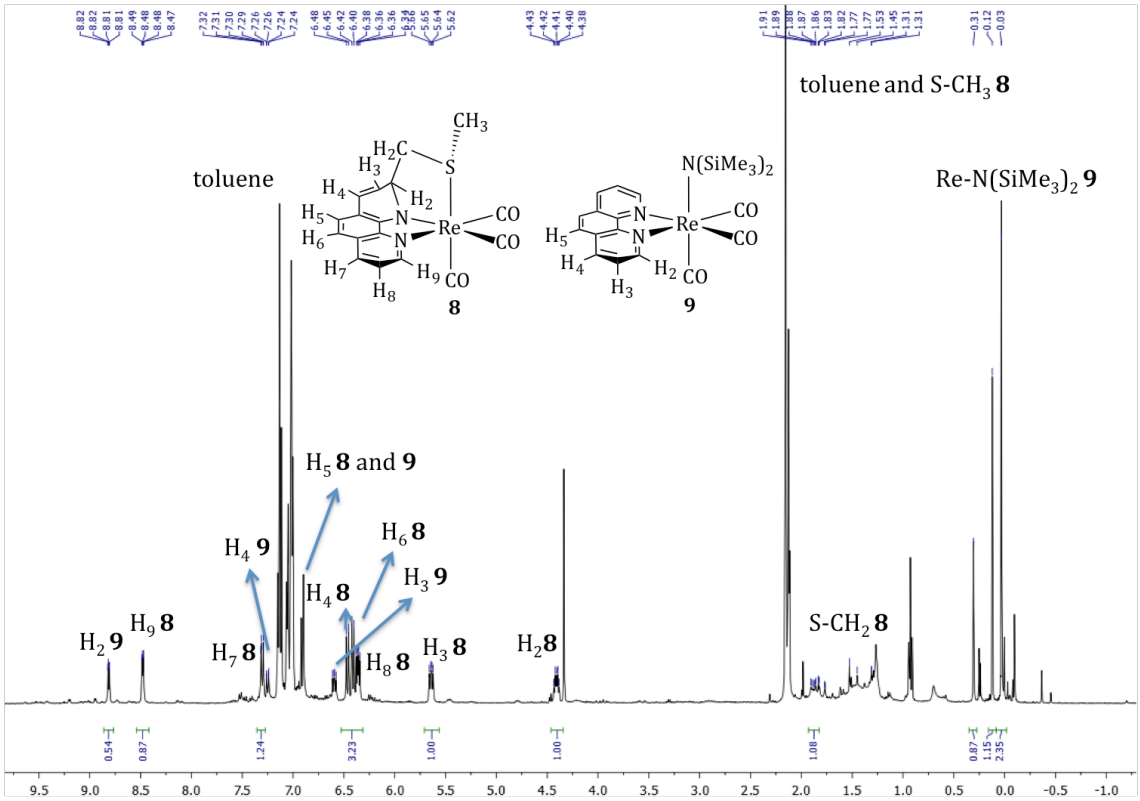
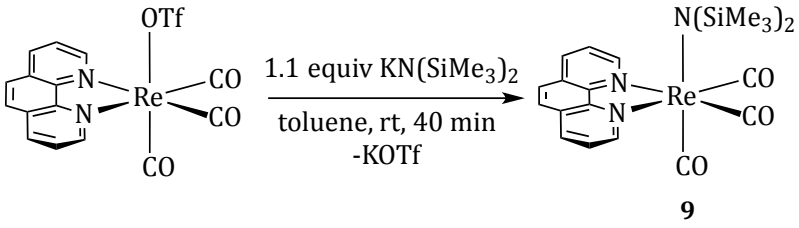


*Figure 8. ^1H NMR spectrum of the mixture of **8** and **9** obtained from reaction of **7** with $KN(SiMe_3)_2$ in the presence of excess SMe_2 in CD_2Cl_2 at 298 K.*

A rational synthesis of complex **9** was carried out by the reaction of $[Re(phen)(CO)_3(OTf)]$ and $KN(SiMe_3)_2$ (see Scheme 7). Complex **9** was isolated by filtration in a moderate yield (46 %) as an oxygen and moisture sensitive red solid which was characterized by IR and NMR spectroscopy in solution.



9

*Scheme 7. Alternative synthesis of [Re(phen)(CO)$_3$(N(SiMe$_3$)$_2$)] (**9**).*

Slow diffusion of hexane into a concentrated solution of **9** in toluene yielded red crystals, one of which was employed for X-ray diffraction. The solid-state structure of **9** showed a typical neutral *fac*-Re(CO)$_3$(phen) complex bonded to a N(SiMe$_3$)$_2$ ligand (see Figure 9).

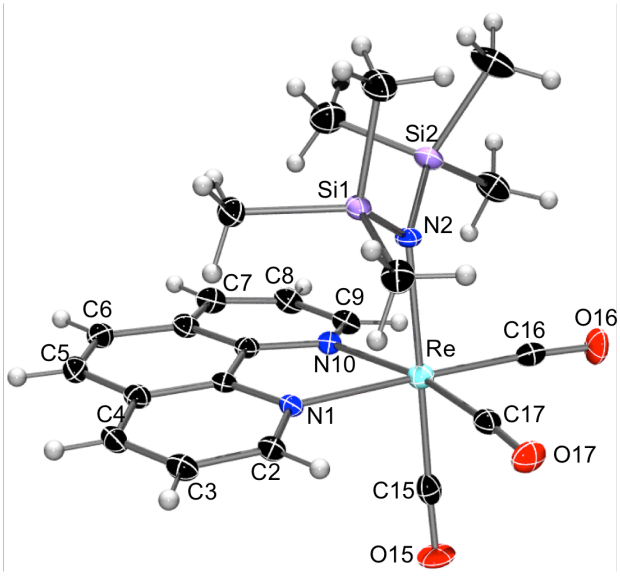


*Figure 9. Solid-state structure (thermal ellipsoids at the 30% probability level) of complex **9**.*

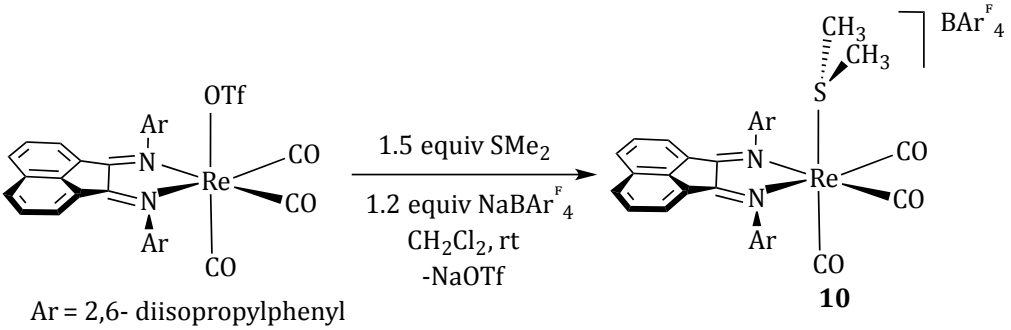
Bond distances and angles in **9** are typical of a neutral *fac*-Re(phen)(CO)$_3$ complex. The Re-N2 distance is 2.247(4) Å and the sum of angles around it is virtually 360° (359.2(2)°) indicating a planar geometry at nitrogen, as found in most N(SiMe$_3$)$_2$ transition metal complexes.[49] Planar amido geometry is due to lone electron pair donation via π interactions.[49] In amido ligands with aryl substituents, this delocalization usually occurs toward the aryl groups. In contrast, amido ligands without aryl substituents in carbonyl complexes have been proposed to delocalize their lone electron pairs toward empty metal d orbitals (via pπ-dπ interaction). In 18 electron carbonyl complexes that donation would yield a 20 electron center, which would be highly unstable. However, the metal donates that excess of electronic density to π* orbitals of the the strong π-acceptor carbonyl ligands.[50] In particular, in N(SiMe$_3$)$_2$

amidos, empty d orbitals of the silicon atoms have been also proposed to play an important role in electron pair delocalization.[51] As a consequence, planarity of the amido in **9** could be due to a combination of both, delocalization of the lone electron pair toward the CO ligands and toward the silicon atoms. Transition metal complexes with monodentate $N(SiMe_3)_2$ ligands are relatively abundant. In fact, the bistrimethylsilylamido ligand has been used to stabilize metal complexes in low coordination numbers.[52] However, a search in the Cambridge Structural Database (CCDC) carried out on 23rd January 2017 revealed that solid-state structures of rhenium complexes with the $N(SiMe_3)_2$ ligand had not been determined.

1.4 Deprotonation of SMe_2 in $[Re(2,6\text{-}iPr_2BIAN)(CO)_3(SMe_2)]BAr^F_4$

Admittedly, the most interesting feature of the reaction of the bipy and phen complexes discussed in the preceding sections is the intramolecular nucleophilic addition on one of the 2-pyridyl rings of the chelate, which results in its dearomatization. Nevertheless, the deprotonation of a dimethylsulfide ligand and the fact that such reaction generates an "internal nucleophile" are also interesting features that lack precedent. Therefore, the deprotonation of coordinated SMe_2 was investigated in a complex analogous to the bipy (**1**) and phen (**7**) species discussed above, but in which the imine functionality is not part of an aromatic ring (in the bis{2,8-(2,6-diisopropylphenylimino)}acenaphthene (2,6-*i*Pr_2BIAN) ligand). The resulting products would be expected to be more stable than those obtained with the bipy chelate.

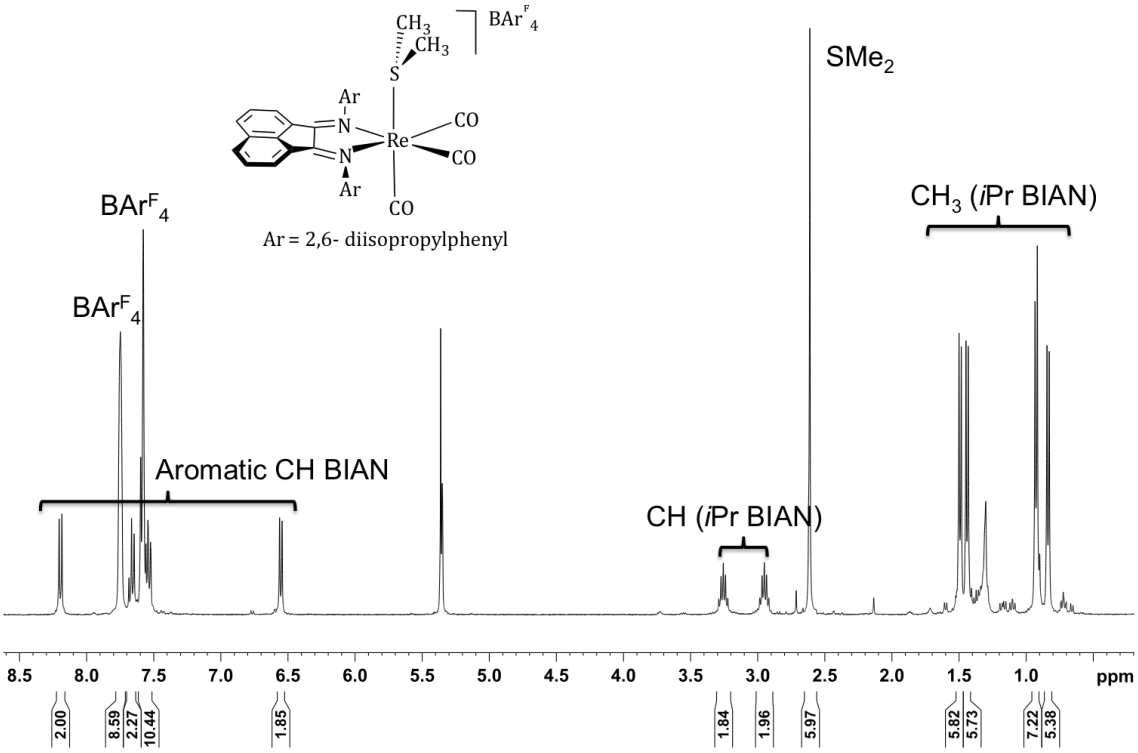
Thus, compound $[Re(2,6\text{-}iPr_2BIAN)(CO)_3(SMe_2)]BAr^F_4$ (**10**) was obtained from reaction of the precursor $[Re(2,6\text{-}iPr_2BIAN)(CO)_3(OTf)]$ with excess SMe_2 and $NaBAr^F_4$ at room temperature in CH_2Cl_2 (see Scheme 8). Reaction of $[Re(2,6\text{-}iPr_2BIAN)(CO)_3(OTf)]$ with a ten molar excess of SMe_2 did not yield product **10**, presumably due to the weak donor ability of the sulfide and the high steric hindrance of the BIAN. Therefore, the salt $NaBAr^F_4$ was required in the synthesis of **10** to aid in triflate abstraction (by precipitation of NaOTf).



Ar = 2,6- diisopropylphenyl

*Scheme 8. Synthesis of [Re(2,6-iPr$_2$BIAN)(CO)$_3$(SMe$_2$)]BAr$^F_4$ (**10**)*

Compound **10** was characterized by IR and NMR spectroscopy. IR νCO bands are consistent with the presence of a cationic species (2041 and 1949 cm^{-1} in CH_2Cl_2) with frequencies slightly higher than those of the precursor [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(OTf)] (2039, 1953 and 1921 cm^{-1} in CH_2Cl_2), as expected for the transformation of a neutral complex into a cationic one. ^{1}H and ^{13}C NMR spectra of **10** were consistent with the presence of a C_s symmetric species (4 signals for the CH_3 and 2 for the CH groups of the *i*Pr substituents of the BIAN ligand, see Figure 10 for the ^{1}H NMR spectrum) with an SMe_2 ligand (singlet at 2.62 ppm).

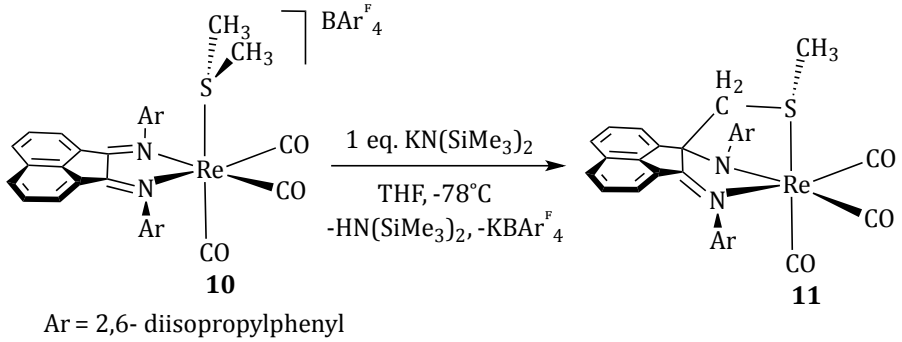


Ar = 2,6- diisopropylphenyl

*Figure 10. ^{1}H NMR spectrum of compound **10** in CD_2Cl_2 at 298 K.*

Slow diffusion of hexane into a concentrated CH_2Cl_2 solution of **10** yielded red crystals, one of which was employed for X-ray diffraction (see section 1.6).

Addition of the equimolar amount of $KN(SiMe_3)_2$ to a solution of **10** in THF at -78°C caused an instantaneous color change from red to purple and a shift to lower wavenumbers of the IR νCO bands (from 2041 and 1949 cm^{-1} to 2007, 1902 and 1885 cm^{-1} in CH_2Cl_2) consistent with the formation of a neutral species. 1D and 2D NMR characterization confirmed the deprotonation of a methyl group of the sulfide and the intramolecular nucleophilic attack by the so generated "internal nucleophile" on the carbon atom of one of diimine groups of the BIAN to yield complex **11** (see Scheme 9).



Ar = 2,6- diisopropylphenyl

*Scheme 9. Intramolecular nucleophilic attack of a deprotonated methyl group of coordinated SMe_2 on the BIAN co-ligand in compound **10**.*

The ^1H and ^{13}C NMR spectra showed **11** to consist of a single diasteromer (see Figure 11 for the ^1H NMR spectrum) in contrast to the mixture of diasteromers found in the deprotonation of complex **1**. The ^1H and ^{13}C NMR spectra of **11** were consistent with a C_1 symmetric species and displayed signals for a new S-bonded CH_2 group from SMe_2 deprotonation (two doublets at 2.76 and 2.55 ppm in the ^1H NMR spectrum, and a singlet at 38.4 ppm in opposite phase to CH signals in the ^{13}C DEPT-135 NMR). The methylene group showed a $^2J_{CH}$ cross-peak with the ^{13}C signal at 91.2 ppm in the ^1H, ^{13}C-HMBC spectrum identifying the latter as the one corresponding to the attacked CN group of the BIAN ligand.

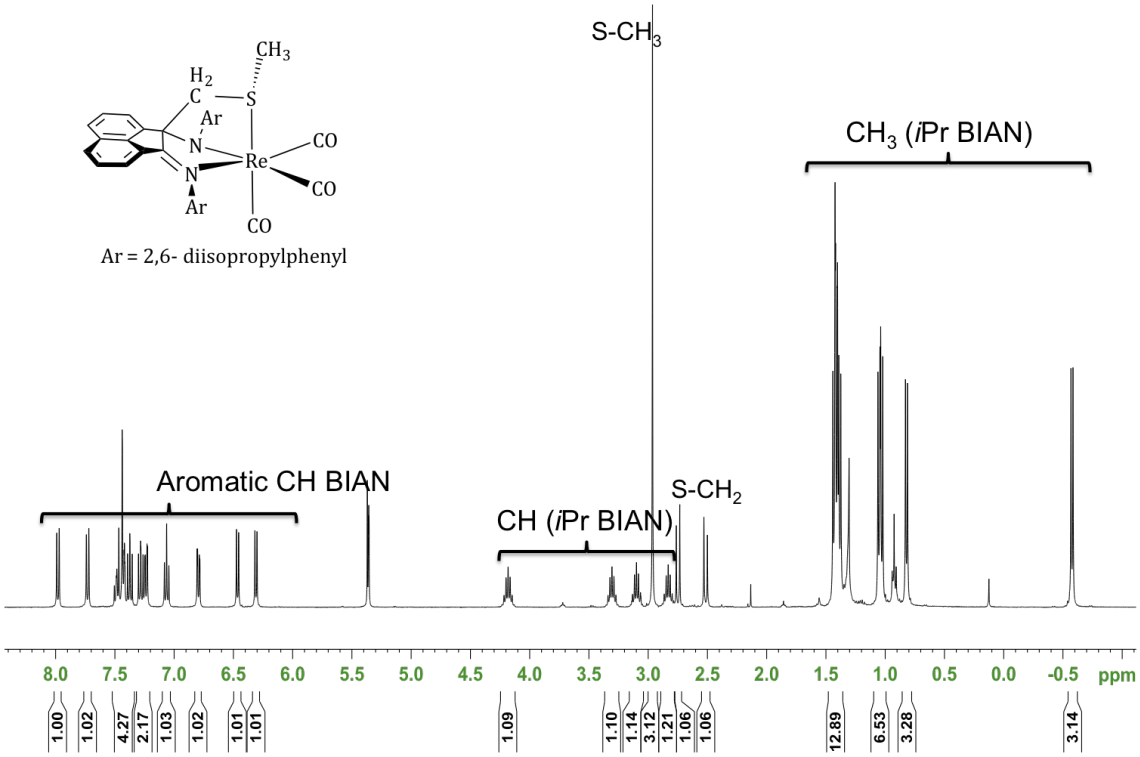


*Figure 11. ^1H NMR spectrum of compound **11** in CD_2Cl_2 at 298 K.*

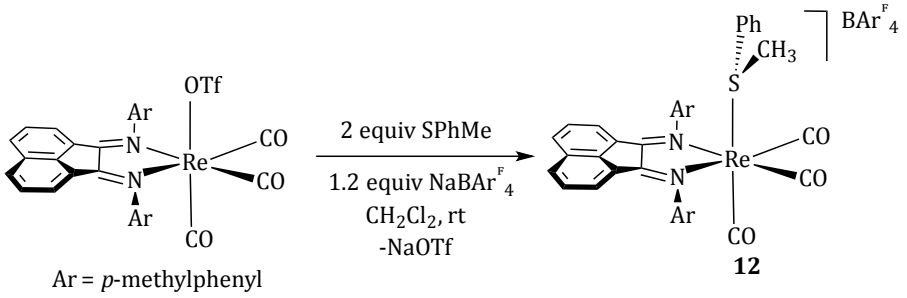
Compound **11** was found to be thermally stable and could be crystallized by slow diffusion of hexane into a concentrated solution of **11** in CH_2Cl_2. X-ray diffraction analysis of the resulting purple crystals confirmed the connectivity proposed for **11** and made possible the assignment of the configuration of the chiral centers, identifying the diasteromer formed in the reaction as the *SRRS* (as a racemic mixture containing the S-bonded methyl group *syn* to the attacked CN group, see section 1.6).[46]

1.5 Deprotonation of SMePh in [Re(*p*-MeBIAN)(CO)$_3$(SMePh)]BAr$^F_4$ (*p*-MeBIAN = bis{2,8-(4-methylphenylimino)}acenaphthene

Since the deprotonation of coordinated sulfides in transition metal complexes lacks precedent, the deprotonation of sulfides other than dimethylsulfide was investigated. In particular, the deprotonation of thioanisole (SMePh) was carried out to determine if it would show a similar reactivity than SMe_2.

Deprotonation of [Re(N-N)(CO)$_3$(SMePh)]BAr$^F_4$ (N-N = bipy, phen) compounds yielded intractable mixtures of thermally unstable species which could not be characterized by NMR even at low temperature. Therefore, given the success in the isolation of stable

BIAN products in the reactions with dimethylsulfide complexes (see above), attempts to deprotonate SMePh were carried out on rhenium complexes containing BIAN diimines. Coordination of SMePh to the $[Re(2,6\text{-}i\text{Pr}_2\text{BIAN})(CO)_3]^+$ fragment was attempted by refluxing a toluene solution of $[Re(2,6\text{-}i\text{Pr}_2\text{BIAN})(CO)_3(OTf)]$ in the presence of 10 equivalents of SMePh and at room temperature in the presence of $NaBAr^F{}_4$ and 2 equivalents of SMePh. Both procedures failed to yield a product with coordinated SMePh. This was attributed to SMePh being bulkier than SMe_2. Thus, compound [Re(*p*-MeBIAN)$(CO)_3$(SMePh)]$BAr^F{}_4$ (**12**), containing the less sterically hindered *p*-MeBIAN, was obtained from [Re(*p*-MeBIAN)$(CO)_3$(OTf)] and a slight excess of SMePh in the presence of $NaBAr^F{}_4$ (see Scheme 10).



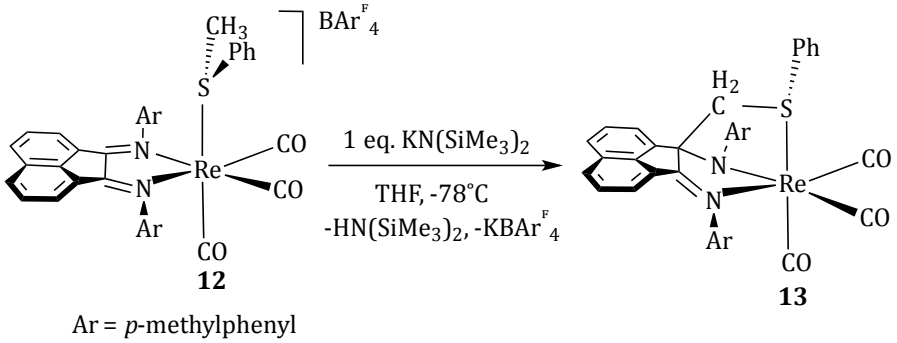
*Scheme 10. Synthesis of [Re(p-MeBIAN)$(CO)_3$(SMePh)]$BAr^F{}_4$ (**12**)*

Compound **12** was isolated as a red solid in good yield (88 %) and fully characterized by IR and NMR spectroscopy. IR monitoring of the coordination of the sulfide showed a shift of the IR νCO bands to higher frequencies (from 2037, 1945 and 1918 cm^{-1} in [Re(*p*-MeBIAN)$(CO)_3$(OTf)] to 2040 and 1946 cm^{-1} in **12** in CH_2Cl_2) as expected for the formation of a cationic species from a neutral complex. The ^1H and ^{13}C NMR spectra displayed similar features than those of **10** and showed signals for a coordinated SMePh (singlet at 3.11 ppm in the ^1H NMR spectrum for the CH_3 group, in contrast to 2.45 ppm for free SMePh in CD_2Cl_2).

Addition of the equimolar amount of $KN(SiMe_3)_2$ to a solution of **12** in THF at -78°C caused an instantaneous color change of the solution from red to brown and a shift to lower wavenumbers of the IR νCO bands consistent with the presence of neutral species. The IR spectrum of the reaction mixture showed the presence of at least two carbonyl species in solution, (a) the major, with broad IR νCO bands at remarkably lower wavenumbers (2000, 1870 and 1854 cm^{-1} in THF) than those of **12** (see above), and (b) the minor, with sharp IR νCO bands at frequencies (2014, 1916 and 1894 cm^{-1} in THF)

lower than those of **12** (see above) but higher than those of the major species. However, the major species decomposed upon removal of the volatiles under vacuum and **13** could be isolated by filtration as a brown solid in low yield (19 %). The major species is proposed to be [Re(*p*-MeBIAN)(CO)$_3$(N(SiMe$_3$)$_2$)] formed as a result of the lability of SMePh in **12** which would be displaced by (SiMe$_3$)$_2$N$^-$. This major species would be thermally unstable due to its steric congestion and high electronic density. To minimize its formation, deprotonation of **12** was carried out in the presence of excess SMePh to yield complex **13** as the major species from the reaction (a similar result was found in the deprotonation of **7**, see above).

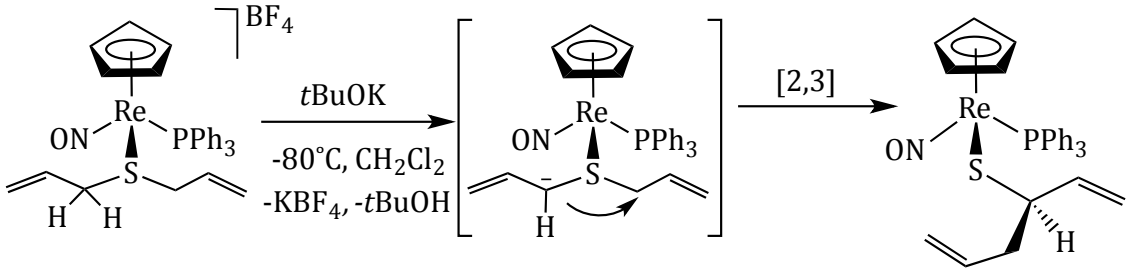
Complex **13** was found to be thermally stable and could be characterized by NMR spectroscopy at room temperature. The ^{1}H and ^{13}C NMR spectra confirmed the selective deprotonation of the methyl group of the sulfide yielding a methylene group which occurs as two doublets at 3.02 and 2.53 ppm in the ^{1}H NMR spectrum in toluene-d$_8$. This nucleophilic methylene would attack the carbon on one of the diimine groups of the BIAN to yield a new C-C bond (see Scheme 11).



*Scheme 11. Intramolecular nucleophilic attack of the deprotonated methyl group of SMePh on the p-MeBIAN in **12**.*

Slow diffusion of hexane into a concentrated solution of **13** in CH_2Cl_2 yielded orange crystals one of which was used for X-ray diffraction. The solid-state structure of **13** confirmed the connectivity proposed and made possible the assignment of the configuration of the chiral centers, identifying the diasteromer formed in the reaction as the *RSSS* (with the S-bonded phenyl group *syn* to the attacked CN group, as found for the SMe_2 analog **11**, see section 1.6).[46]

Reports of deprotonation of coordinated sulfides in the literature are scarce. Attempts to deprotonate SMe_2 coordinated to a transition metal were carried out by Gladysz and co-workers who reported that the deprotonation of the compound [Re(η^5-C_5H_5)(CO)(NO)(SMe_2)]OTf yielded intractable mixtures of unknown species.[53] However, deprotonation of α-CH groups of other alkyl sulfides (such as diallyl sulfide or dibenzyl sulfide) in rhenium,[53] iron or ruthenium[54] complexes yielded thiolate complexes from [2,3]-sigmatropic rearrangements (see Scheme 12 for the deprotonation of rhenium-coordinated diallyl sulfide).



Scheme 12. Deprotonation of $S(C_2H_3)_2$ to yield a thiolate from a [2,3]-sigmatropic rearrangement in a rhenium complex reported by Gladysz and co-workers.

The results obtained by the group of Gladysz and co-workers stand in contrast to those reported in this Chapter, where deprotonation of coordinated SMe_2 and SMePh yielded C-C coupling complexes from intramolecular nucleophilic attack of the S-bonded CH_2 group to the diimine co-ligands (bipy, phen or BIAN). These results are specially remarkable, since, although coordination of SMe_2 to BH_3 has been found to increase the acidity of its methyl groups by 10^{15} times,[55] products from methyl group deprotonation and subsequent reaction with electrophiles or rearrangement were virtually unkown.

1.6 Solid-state structures of BIAN-sulfide complexes

The solid state-structures of compounds **10**, **11** and **13** were determined by X-ray diffraction. The results are displayed using ORTEP diagrams in Figure 12, and selected bond distances and angles have been collected in Table 1.

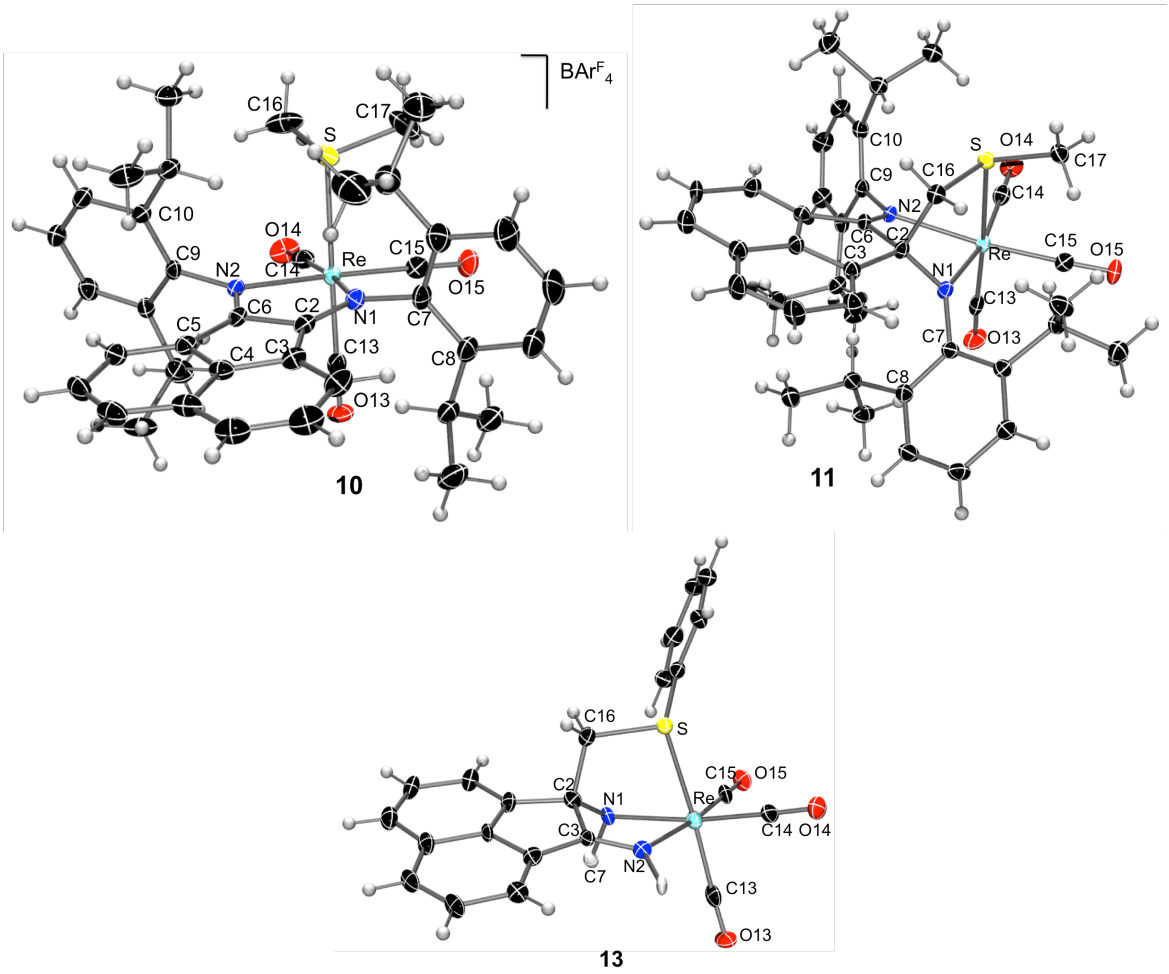


*Figure 12. Solid-state structure (thermal ellipsoids at 30% probability) of the cation in **10**, and complexes **11** and **13**. Aryl subtituents in **13** have been omitted for clarity.*

	10	**11**[56]	**13**[56]
Re-S	2.511(1)	2.526(1)	2.482(2)
Re-N1	2.217(3)	2.149(4)	2.191(7)
Re-N2	2.209(3)	2.247(5)	2.221(7)
Re-C13	1.944(4)	1.922(6)	1.93(1)
Re-C14	1.912(4)	1.928(6)	1.929(9)
Re-C15	1.924(4)	1.912(5)	1.921(9)
C13-O13	1.131(5)	1.147(7)	1.13(1)
C14-O14	1.163(4)	1.151(7)	1.15(1)
C15-O15	1.143(4)	1.159(7)	1.14(1)
N1-C7	1.448(4)	1.424(7)	1.41(1)
N1-C2	1.293(4)	1.446(7)	1.46(1)
C2-C6	1.460(5)	1.517(6)	1.51(1)
C2-C3	1.488(5)	1.541(6)	1.52(1)
C2-C16	-	1.569(6)	1.55(1)
C2-N1-C7	118.0(3)	118.1(4)	119.2(7)
C2-N1-Re	113.5(2)	106.5(3)	104.4(5)
Re-N1-C7	128.5(2)	135.5(3)	117.0(5)
Re-S-C16	107.2(2)	103.3(2)	97.3(3)
C16-C2-N1	-	109.8(4)	107.5(7)
Re-C13-O13	175.1(3)	176.5(4)	177.8(9)
S-Re-C13	175.0(1)	177.2(2)	172.8(3)

*Table 1. Selected bond distances (Å) and angles (°) of the cation in **10** and complexes **11** and **13**.*

The solid state structures of **10**, **11** and **13** showed distorted octahedral *fac*-$Re(CO)_3$ fragments with *i*Pr_2-BIAN and SMe_2 ligands in **10**, and *N*,*N'*,*S* tridentate ligands in **11** and **13** from C-C coupling between the sulfide (SMe_2 in **11** and SMePh in **13**) and an imine carbon atom of the BIAN ligand (*i*Pr_2-BIAN in **11** and *p*-MeBIAN in **13**).

Re-S distances are similar in **10** and **11** (2.511(1) Å and 2.526(1) Å respectively) and slightly longer than that found in the cationic complex $\mathbf{1^F}$ (2.495(2) Å), presumably as a result of the higher steric hindrance of the 2,6-*i*Pr_2BIAN in comparison with bipy. In contrast, the Re-S distance in **13** is similar to that of $\mathbf{1^F}$, due to the lower steric hindrance

of the *p*-MeBIAN ligand in comparison with 2,6-*i*Pr$_2$BIAN. The high steric profile of the 2,6-*i*Pr$_2$BIAN ligand give raise to Re-C13-O13 and S-Re-C13 angles (175.1(3)° and 175.0(1)° respectively in **10**) which deviate from the expected 180° for a regular octahedral geometry (the analogous angles in complex **1^F** with the less sterically hindered bipy ligand are 179.1(8)° and 178.6(2)°).

The attacked carbon atom (C2) in **11** and **13** is sp^3 hybridized (bond distances are typical of single bonds, see Table 1) and, as a consequence, the N-C-C-N unit is no longer planar (in contrast to the planar N-C-C-N group in **10**).

The disposition of the N2-bonded aryl group in **11** is almost perpendicular to the naphthalene plane (the C7-N2-C16-C15 torsion angle is 81.4(6)°), a feature typical of BIAN ligands with bulky aryl substituents.[57] In contrast, the analogous angle for the attacked CN group is smaller (C2-N1-C7-C8 is 74.0(6)°) presumably to alleviate the steric congestion generated upon formation of the new C-C bond and minimize the steric clash with the S-Me group.

The Re-N1 distance in **11** (2.149(3) Å) is shorter than Re-N2 (2.247(3) Å), consistent with N1 being an amido nitrogen. The sum of angles around N1 in **11** close to 360° is diagnostic of a planar amido group. Planar amido nitrogens are usually attributed to lone electron pair delocalization toward co-planar aryl subtituents. However, in this case, the aryl substituent of the amido is far from co-planar (see Figure 12) and, as a consequence, delocalization to the aryl group is not possible. Lone electron pair delocalization toward the metal, which would donate that excess electronic density to the CO groups,[50] is proposed to operate in complex **11**.

We propose that the difference between Re-N1 and Re-N2 distances (Δd) in complexes **11** and **13** can be taken as an indicator of the degree of amido lone electron pair delocalization toward the metal (the larger the Δd value, the stronger the donation of the amido toward the metal which results in a higher tendency to planarity of the nitrogen). Since BIAN and sulfide substituents are not the same on complexes **11** and **13**, a direct comparison of Re-N1 and Re-N2 distances is not fully reliable. Furthermore, Re-N1 and Re-N2 distances are not independent in the same complex: Re-N2 (imino) distance is affected by the degree of lone electron pair donation from N1 (amido), and the stronger the donation toward the metal, the longer the Re-N2 bond. The Δd in **13** is

smaller (Δd(**13**) = 0.027(7) Å) than in **11** (Δd(**11**) = 0.098(3) Å), and the sum of angles around N1 in **13** is 340°, consistent with a pyramidal amido group. Pyramidal amidos are a result of little, if any, lone electron pair delocalization toward the metal center, in agreement with a smaller difference between Re-N1 and Re-N2 distances in comparison with **11**, where the amido is planar. A planar amido group would involve strong π donation to the metal (see above), which would result in a stronger Re-N bond, and, consequently, in a shorter Re-N distance in comparison to the Re-N distance in a pyramidal amido. However, both, pyramidal and planar amidos, are anionic ligands and hence form stronger bonds with the metal (and, consequently, afford shorter Re-N distances) than neutral imino donors.

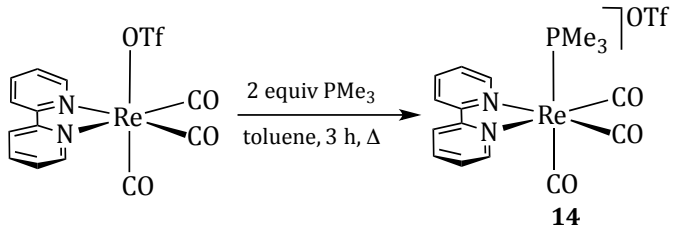
Chapter 2:

Intramolecular and intermolecular additions on a bipy ligand

This Chapter contains material included in a *Communication* published in the journal *Chemistry- A European Jounal*,[58] and also unpublished results which will be discussed in further detail and will be included in a future *Full paper*.

2.1 Synthesis of [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (14)

Compound [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**) was obtained from reaction of [Re(bipy)(CO)$_3$(OTf)] with excess of PMe$_3$ in refluxing toluene (see Scheme 13). Excess PMe$_3$ was required due to its partial loss while refluxing the reaction mixture.



*Scheme 13. Synthesis of **14** by triflate substitution in [Re(bipy)(CO)$_3$(OTf)].*

Due to the low solubility of **14** in toluene most of it precipitated from solution as a yellow solid after cooling down the reaction mixture to room temperature. Further precipitation with hexane allowed isolation of **14** in an 82 % yield, and crystals of **14** could be obtained from slow diffusion of diethyl ether in a concentrated CH_2Cl_2 solution at room temperature.

Characterization of **14** by IR and NMR spectroscopy (^{1}H, ^{13}C and ^{31}P and 2D NMR) showed the presence of a *fac*-Re(CO)$_3$ cationic complex (three IR νCO bands at 2034, 1934, 1913 cm^{-1} in THF) with 2,2'-bipyridine and PMe$_3$ ligands (coordinated PMe$_3$ in **14** appeared as a singlet at -27.8 ppm in the ^{31}P NMR in CD_2Cl_2, in contrast to the singlet at -61.6 ppm for free PMe$_3$). The ^{1}H NMR spectrum displayed four signals for a symmetric bipy ligand (from 9.01 to 7.75 ppm, see Figure 13) and the ^{13}C NMR spectrum showed two signals for the three carbonyl groups (two CO at 194.5 ppm *cis* to PMe$_3$ ($^2J_{CP}$ = 3.8 Hz) and one CO at 187.8 ppm *trans* to PMe$_3$ ($^2J_{CP}$ = 60.9 Hz)), indicating a C_s symmetry of the complex.

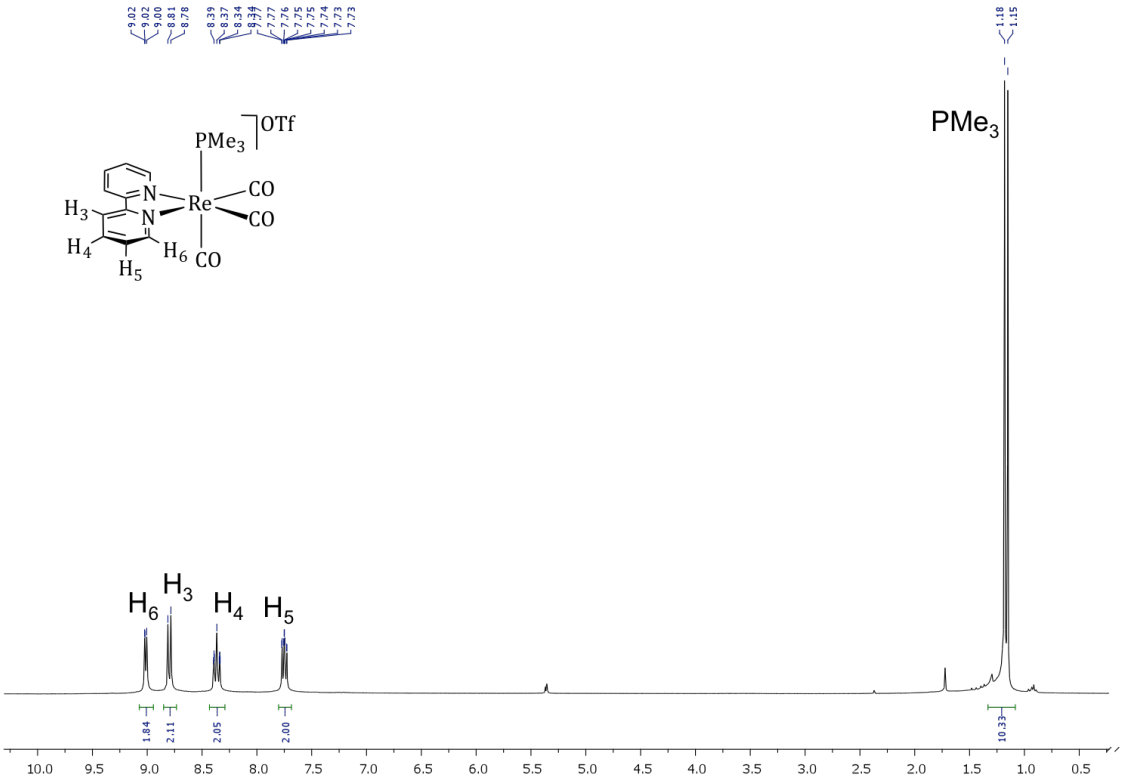
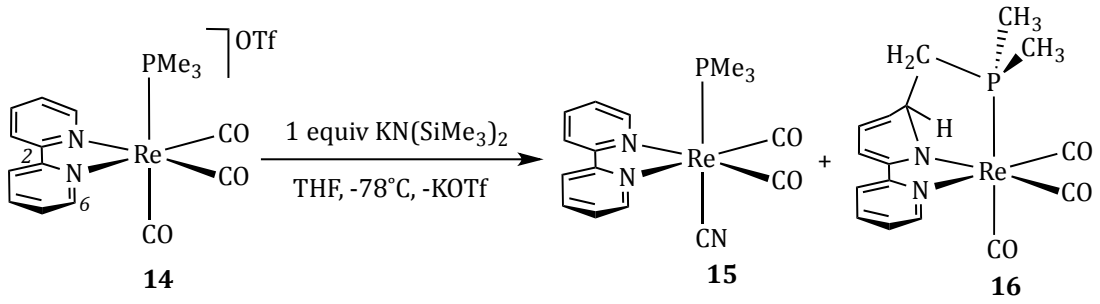


*Figure 13. ^{1}H NMR spectrum of compound **14** in CD_2Cl_2 at 298 K.*

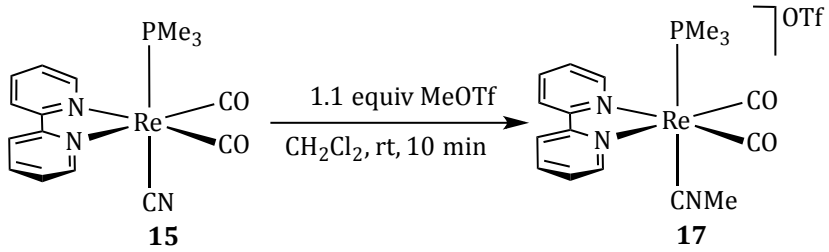
2.2 Reaction of 14 with $KN(SiMe_3)_2$: Intramolecular nucleophilic addition to bipy by a deprotonated P-CH_3 group and intermolecular addition to a CO ligand by $KN(SiMe_3)_2$

Addition of the equimolar amount of $KN(SiMe_3)_2$ to a THF solution of $[Re(bipy)(CO)_3(PMe_3)]OTf$ (**14**) at -78°C yielded a red solution which turned darker upon reaching room temperature. The IR spectrum of this red solution showed the presence of two organometallic species: (a) a neutral *cis*-$Re(CO)_2$ complex, **15** (which showed CO broad bands of similar intensity at 1921 and 1848 cm^{-1} in THF, see Scheme 14), and (b) a neutral *fac*-$Re(CO)_3$ complex, **16**, with three CO bands at lower frequencies (2008 (narrow), 1910 (broad), 1884 (broad) cm^{-1} in THF) than those of **14**. The different solubility of the products in toluene allowed their separation by extracting **16** in toluene as a purple solution.



*Scheme 14. Reaction of **14** with $KN(SiMe_3)_2$: intermolecular nucleophilic attack to a CO ligand to yield **15**, and intramolecular nucleophilic addition of a deprotonated P-CH_3 group on bipy to yield **16**.*

Compound **15** was isolated by filtration as an orange powder in a 48 % yield and fully characterized by IR and NMR spectroscopy. IR spectroscopy proved **15** to be a *cis*-$Re(CO)_2$ neutral complex with a CN ligand (medium intensity νCN band at 2097 cm^{-1} in CH_2Cl_2). The ^{13}C NMR spectrum demonstrated the two equivalent CO groups to be *cis* to the PMe_3 ligand, since their $^2J_{CP}$ was small ($^2J_{CP}$ = 6.0 Hz) and closer to the $^2J_{CP}$ *cis* (3.8 Hz) than to the $^2J_{CP}$ *trans* (60.9 Hz) found in the precursor **14** discussed above. Therefore, although the signal of the CN ligand could not be observed in the ^{13}C NMR spectrum,[59] as is common in cyano complexes, the cyano group must be *trans* to the phosphane. Signals for a symmetric bipy in the ^1H and ^{13}C NMR spectra also indicated that **15** is a C_s symmetric complex. Further proof of the presence of a CN group in **15** was provided by its reaction with MeOTf to yield complex **17**, which featured a methylisocyanide ligand as judged by the IR medium intensity νCN band at 2185 cm^{-1} in CH_2Cl_2. Moreover, the ^1H NMR spectrum featured a doublet ($^5J_{PH}$ = 0.5 Hz) at 3.36 ppm (3H) attributed to the CN-bonded methyl group from CN methylation in **15** (see Scheme 15).[59]



*Scheme 15. Methylation of the isocyanide ligand in **15**.*

Formation of compound *cis*-$[Re(bipy)(CO)_2(CN)(PMe_3)]$ (**15**) in the reaction of **14** with $KN(SiMe_3)_2$ results from intermolecular nucleophilic addition of $^-N(SiMe_3)_2$ to the CO

ligand *trans* to PMe_3 in **14**. The oxophilicity of the silicon atom favors oxygen transfer from the carbonyl group to silicon, leading to the formation of the cyanide ligand, with concomitant elimination of hexamethyldisiloxane. Despite the fact that $KN(SiMe_3)_2$ usually acts as a non-nucleophilic base, additions of this kind are well-known and constitute a method for the preparation of cyanide complexes from sufficiently electrophilic carbonyl precursors.[60]

Product **16** was found to be thermally unstable, decomposing to a significant extent upon standing for several hours in solution at room temperature. Therefore, its 1D and 2D NMR characterization was performed at low temperature. The ^{1}H and ^{13}C NMR spectra of **16** were consistent with a C_1-symmetric complex (*e. g*. eight signals for an asymmetric bipy ligand in the ^{1}H NMR spectrum, see Figure 14) with a new C-C bond between a deprotonated methyl group of the phosphane ligand (two multiplets at 2.12 and 1.37 ppm in the ^{1}H NMR spectrum, and a doublet at 29.5 ppm in opposite phase to CH signals in the ^{13}C DEPT-135 spectrum in THF-d_8) and the carbon in position 6 of bipy (multiplet at 4.36 ppm in the ^{1}H NMR spectrum, and a CH signal at 65.9 ppm in the ^{13}C DEPT-135 spectrum in THF-d_8).

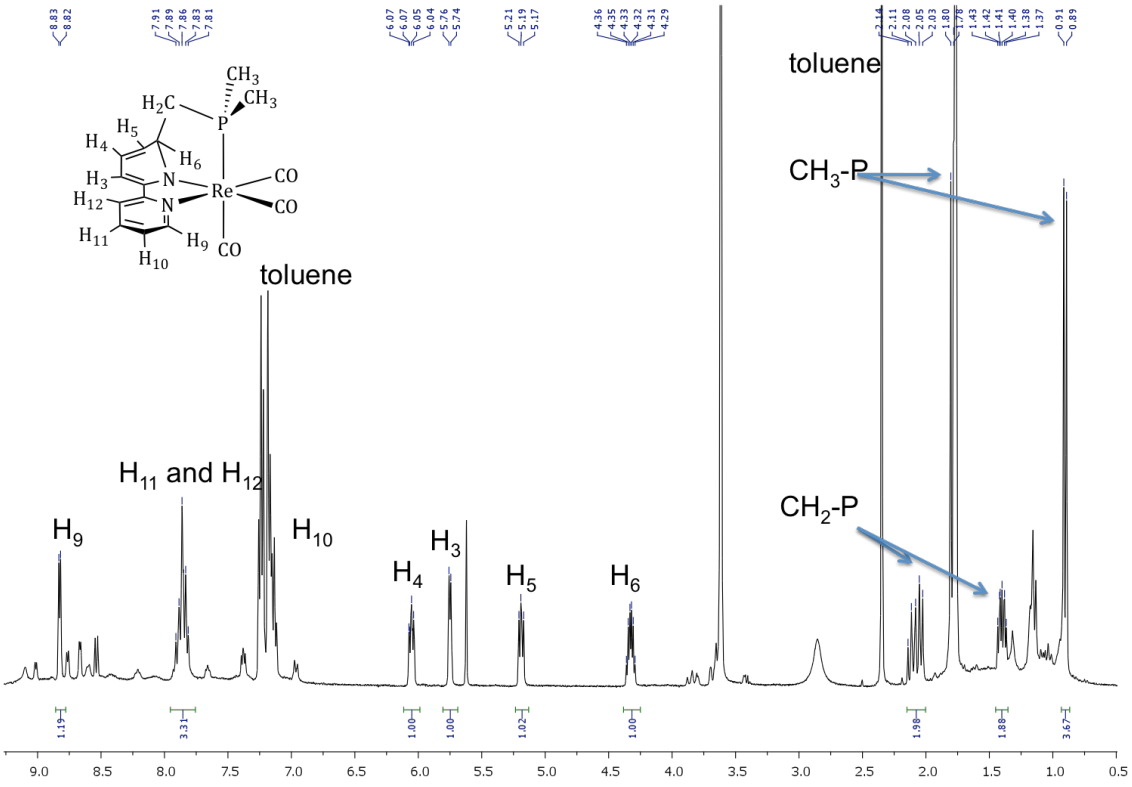


*Figure 14. ^{1}H NMR spectrum of compound **16** in THF-d_8 at 253 K.*

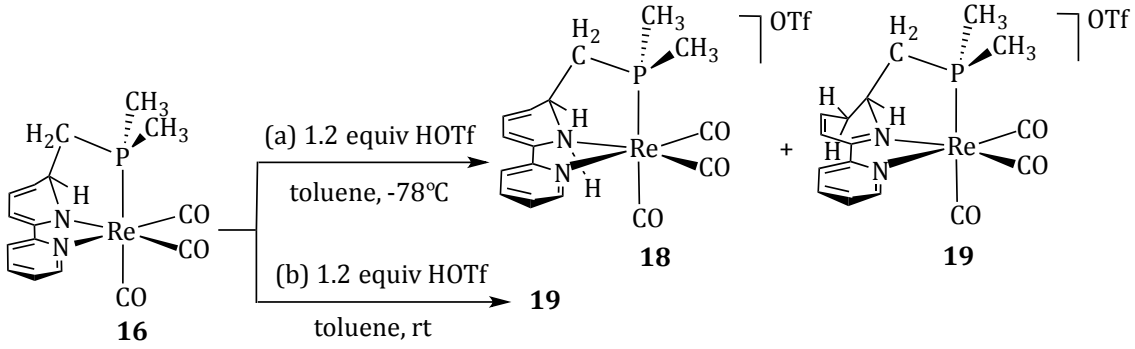
Product **16** is proposed to be formed from P-methyl group deprotonation by $KN(SiMe_3)_2$ followed by intramolecular nucleophilic attack of the generated methylene nucleophile to the 6 position of bipy. As a consequence, the involved pyridyl ring becomes dearomatized, as indicated by the upfield shifted bipy signals (between 6.05 and 4.36 ppm in the ^1H NMR spectrum in THF-d_8) and its nitrogen atom becomes part of an amido donor. Products of intramolecular nucleophilic attack on the 6 position of a bipyridine ligand have been previously obtained in our group in the deprotonation of complexes analogous to **14** but with coordinated alkylimidazoles instead of PMe_3 (see Introduction).[35b]

Attempts to obtain product **16** as the single product from the deprotonation reaction of **14** by the employment of bases different than $KN(SiMe_3)_2$ (such as *n*BuLi, *t*BuLi, lithium diisopropylamide (LDA) and NaO*t*Bu) were unsuccessful (see section 2.7 for the reaction with *n*BuLi and *t*BuLi). The deprotonation of complexes analogous to **14** but containing $PPhMe_2$ or PPh_2Me instead of PMe_3 yielded the C-C coupling products in lower amounts than in the reaction of **14**. In both cases the *cis*-$[Re(bipy)(CO)_2(CN)(PR_3)]$ (PR_3 = $PPhMe_2$ and PPh_2Me) complex was formed as the major product (as judged by IR spectroscopy). The higher amount of cyanide complexes formed in the reaction of the $PPhMe_2$ and PPh_2Me complexes could be attributed to the stronger π-acceptor ability of these phosphanes (in comparison to PMe_3)[61] which renders the CO groups more electrophilic and therefore more prone to undergo nucleophilic attack by the amide.

2.3 Protonation and methylation of complex 16: Isolation of N-H and N-Me products and functionalization of C5 of bipy.

Attempts to crystallize complex **16** were thwarted by its low thermal stability. However, reaction of **16** with acids or methyl triflate yielded thermally stable products, which could be isolated and fully characterized. In particular, treatment of **16** with an acid (HOTf or trifluoroacetic acid (TFA)) yielded a mixture of two compounds, **18** and **19** under all the reaction conditions essayed (Scheme 16), although the ratio of the species varied depending on the particular conditions, as detailed below.

Addition of a slight excess of HOTf to a toluene solution of **16** at -78°C immediately caused the formation of an orange oil. The IR νCO bands of the product were consistent with the presence of cationic *fac*-tricarbonyl species (2037, 1953 and 1924 cm^{-1} in CH_2Cl_2). The ^1H, ^{13}C and ^{31}P NMR characterization demonstrated the product to consist of two major species, **18** and **19**, in a 1.5 to 1.0 ratio (from ^1H NMR integration) both with dearomatized pyridyl rings and CH_3P-CH_2 bipy-bonded groups, but differing in the position of the H atom from the HOTf, as depicted in Scheme 16a. Full NMR characterization of the mixture showed **18** (δ ^{31}P NMR = -1.9 ppm in CD_2Cl_2) to result from protonation at the amido nitrogen in **16**, as the ^1H NMR spectrum showed a broad singlet at 7.81 ppm assigned to the N-H group on the basis of the ^1H,^1H-COSY and ^1H-^{13}C HMBC spectrum. Similar products have been obtained in our group from the reactions with HOTf of the neutral amido complexes resulting from deprotonation of $[Re(bipy)(CO)_3(RIm)]OTf$[35b] (RIm= 1-methylimidazole, 2,4,6-trimethylphenylimidazole).



*Scheme 16. Protonation of complex **16** under different conditions. Major products formed in the reaction are showed.*

On the other hand, the NMR characterization showed **19** (δ ^{31}P NMR = -7.4 ppm in CD_2Cl_2) to be formed as a result of protonation on carbon atom of the dearomatized pyridyl ring, yielding a non-aromatic pyridyl ring with an imino nitrogen and a new CH_2 unit in position 5 (as judged by a ^1H-^1H COSY experiment). This new CH_2 group appeared as two multiplets in the ^1H NMR spectrum (at 3.87 ppm and 3.73 ppm) and a singlet at 28.5 ppm in opposite phase to CH signals in the ^{13}C DEPT-135 NMR and ^1H,^{13}C-HSQC phase-edited spectra. Moreover, the ^{13}C NMR spectrum featured a doublet at 175.0 ppm consistent with the presence of a C=N group in the non-aromatic pyridyl ring

of **19**, in accordance with its nitrogen being sp^2 hybridized and in contrast to the sp^3 hybridization of the corresponding nitrogen in **18**.

To the best of our knowledge, protonation at carbon is an unknown reaction in non-coordinated, dearomatized pyridines. Protonation on the C5 position of pyridyl rings in substituted, coordinated bipyridines has recently been found by our group. Functionalization of the bipy 5 position has been attributed to the electronic influence of strong electron donor groups (such as methoxy groups) which increase the electronic density on pyridyl ring carbon atoms and render them more prone to react with electrophiles.[35a] Although we have not further investigated this aspect, it can be hypothesized that in the present case, the CH_2-$P(CH_3)_2$ substituent could be electron-releasing enough to cause a similar effect.

To determine a possible influence of the reaction temperature on the ratio of the components of the mixture obtained from protonation of **16**, the addition of HOTf was carried out in toluene at room temperature (Scheme 16b). Precipitation of the products as an orange oil occurred instantaneously, and they could be isolated as an orange powder after washings with diethyl ether. The IR νCO bands of the product are consistent with the presence of cationic *fac*-tricarbonyl species (2037, 1953 and 1924 cm^{-1} in CH_2Cl_2), and its NMR characterization shows compound **19** to be the major product of the reaction.

Compound **18** was found to be 7.9 kcal·mol^{-1} thermodynamically less stable than **19** by DFT calculations (see Figure 15 for optimized structures). The results of the calculations are in agreement with the experimentally found formation of **18** upon protonation of **16** at low temperature, while protonation at room temperature yielded the most stable product **19** as a single species.

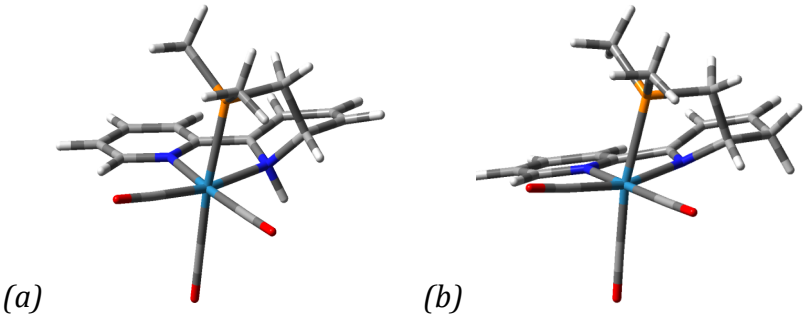
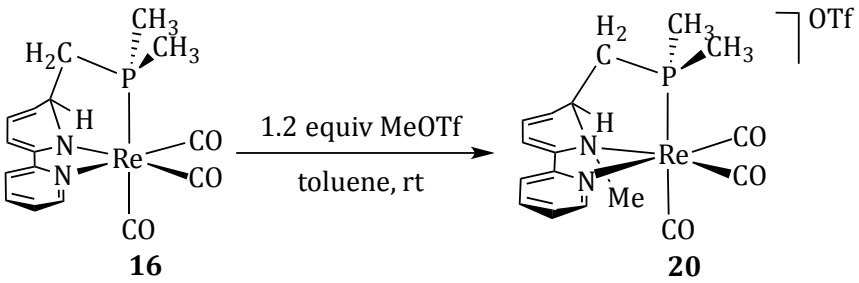


*Figure 15. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) optimized structures of the cations in compounds (a) **18** and (b) **19**, from protonation of **16**.*

In contrast to the protonation reaction, the reaction of **16** with MeOTf yielded a single species as judged by NMR characterization and the variation of the conditions of the methylation reaction (temperature and solvent) did not afford products of methylation on a carbon atom of the pyridyl ring. The product, **20**, was found to be a cationic *fac*-$Re(CO)_3$ compound (as judged by IR νCO bands at 2038, 1950 and 1923 cm^{-1} in CH_2Cl_2). On the basis of the ^1H, ^{13}C-HMBC spectrum of **20**, the methyl group could be proposed to be N-bonded (see Scheme 17), since the ^1H signal of the methyl (at 3.60 ppm) showed a $^3J_{CH}$ crosspeak with the ^{13}C signal of C6 of bipy (at 69.7 ppm).



*Scheme 17. Methylation of the amido nitrogen in **16**.*

Slow diffusion of diethyl ether into concentrated CH_2Cl_2 solutions of (a) a mixture of **18** and **19** and (b) **20**, afforded orange crystals of **18** and **20** respectively, accompanied by an orange oil for (a). Single crystal X-ray diffraction analysis of one of the crystals of each case, confirmed the structures proposed for **18** and **20** on the basis of solution NMR experiments (see Figure 16 and Table 2).

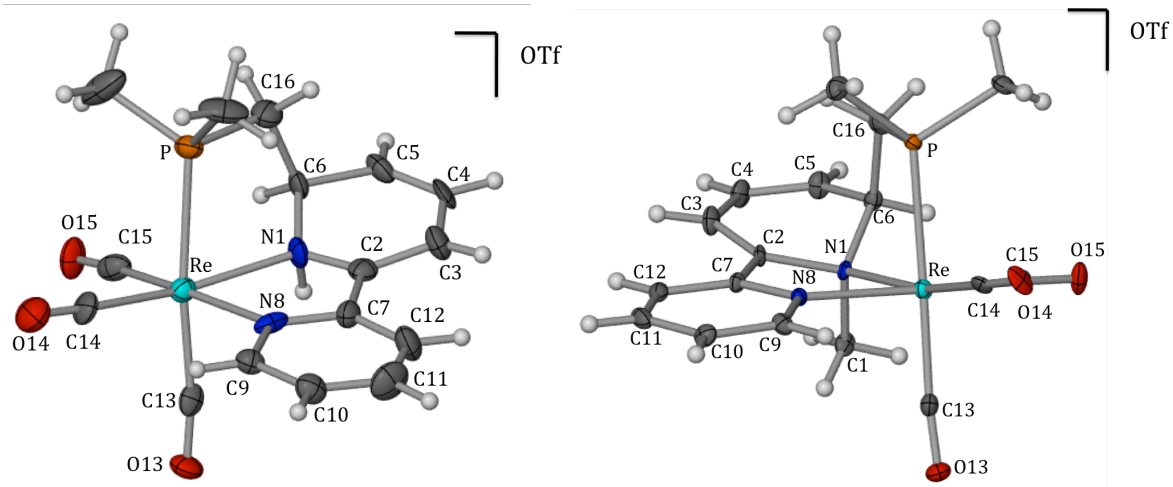


*Figure 16. Solid-state structure (thermal ellipsoids at the 30% probability) of the cationic complexes in **18** (left) and **20** (right).*

	18	**20**
Re-P	2.4223(4)	2.412(2)
Re-N1	2.2006(4)	2.258(5)
Re-N8	2.1852(4)	2.185(6)
Re-C13	1.9492(3)	1.989(9)
Re-C14	1.9784(3)	1.925(9)
Re-C15	1.9445(3)	1.932(8)
C13-O13	1.1760(2)	1.12(1)
C14-O14	1.1271(2)	1.16(1)
C15-O15	1.1311(2)	1.14(1)
N1-C6	1.4548(2)	1.522(9)
N1-C1	-	1.495(9)
N1-C2	1.4548(2)	1.475(9)
C5-C6	1.5080(2)	1.48(1)
C6-C16	1.5487(2)	1.54(1)
C2-N1-Re	116.82(3)	110.3(4)
C2-N1-C1	-	107.4(5)
C6-N1-Re	114.37(3)	110.1(4)
C6-N1-C2	123.77(3)	108.8(5)
C16-C6-N1	106.03(3)	111.5(6)

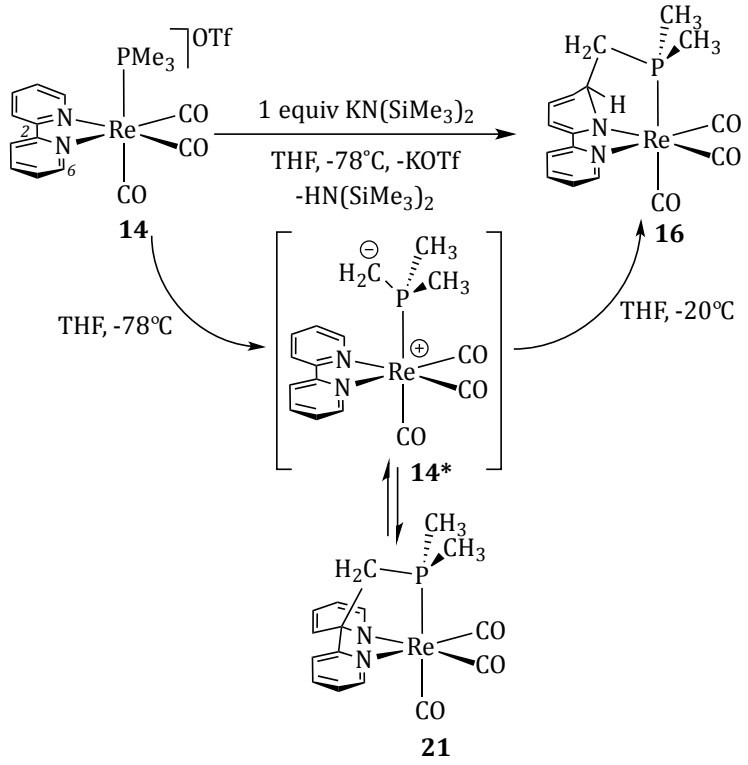
*Table 2. Selected bond distances (Å) and angles (°) of the cations in **18** and **20**.*

The solid-state structures of the cations in **18** and **20** showed a distorted octahedral *fac*-$Re(CO)_3$ complex bonded to a tridentate *N*,*N'*,*P* ligand formed as a result of the nucleophilic addition of the P-CH_2 group (generated in the deprotonation) on bipy and the subsequent protonation (in **18**) or methylation (in **20**) at the amido nitrogen. The attacked pyridyl ring is no planar and the geometry about the attacked carbon atom (C6) reflects sp^3 hybridization (C5-C6 and C6-N1 bond distances are 1.5080(2) and 1.4548(2) Å respectively in **18**, consistent with the presence of single bonds). Re-N1 bond distance (2.258(5) Å) is slightly longer than Re-N8 (2.185(6) Å) in compound **20** supporting the amino character of N1, which forms weaker bonds with the metal than imine donors (N8). The angles around N1 in both, **18** and **20** are close to 109° (*e*. *g*. C2-N1-C6 is 108.8(5)°, C1-N1-C2 is 107.4(5)°, C2-N1-Re is 110.3(4)° and C6-N1-Re is 110.1(4)° in **20**), supporting sp^3 hybridization of N1 as a result of protonation or methylation.

2.4 Reversible C-C bond formation in 14 by PMe_3 deprotonation.

Low temperature NMR monitoring of the deprotonation of **14** by $KN(SiMe_3)_2$ revealed the initial formation of a new species, **21**, which, upon raising the temperature, evolved to **16** (see Scheme 18). ^1H, ^{13}C DEPT-135 and 2D NMR characterization showed **21** to result from phosphane-methyl group deprotonation followed by intramolecular nucleophilic attack on C2 of bipy. The ^1H-^1H COSY NMR spectrum supported this formulation since none of the signals of the dearomatized pyridyl ring showed crosspeaks with the P-CH_2 unit (at 2.25 and 1.06 ppm in the ^1H NMR spectrum in THF-d_8). Furthermore, a $^2J_{CH}$ crosspeak in the ^1H-^{13}C HMBC spectrum between the ^1H signal for the P-CH_2 unit and the ^{13}C signal at 76.7 ppm identified the latter as the attacked bipy carbon atom. This signal could not be seen in the ^{13}C DEPT-135 spectrum, confirming that the P-CH_2 moiety was bonded to one of the quaternary carbons of the bipy ligand (C2). Similar NMR features have been found in the product of intramolecular nucleophilic attack of deprotonated SMe_2 on C2 of bipy in $[Re(CO)_3(bipy)SMe_2]OTf$ (see Chapter 1).

Complex **21** turned out to be unstable at room temperature, and at 253 K yielded complex **16** in 10 minutes (see Scheme 18).



*Scheme 18. Reversible intramolecular nucleophilic attack on the C2 position of coordinated bipy in compound **14** by deprotonation of PMe_3 at low temperature to yield **21**, and evolution to yield **16**. Species **14*** is a proposal and has not been experimentally detected.*

A computational study of the reaction of compound [Re(bipy)$(CO)_3(PMe_3)$]OTf (**14**) with $KN(SiMe_3)_2$ in THF employing DFT methodology afforded the energy profiles displayed in Figure 17. Thus, product **21** was found to possess a lower barrier to form (4.0 kcal·mol^{-1} for **21** in contrast to 9.9 kcal·mol^{-1} for **16**), therefore, formation of **21** is favored at low temperatures. However, complex **21** is less stable than **16** (-7.4 kcal·mol^{-1} for **21** and -10.9 kcal·mol^{-1} for **16**) showing that **16** is the thermodynamic product, which will be formed in higher amount when the temperature is high enough to surmount its kinetic barrier. The transformation of **21** into **16** requires the breaking of the new C-C bond created. Thus, the formation of the C-C bond on C2 of bipy to yield **21** is reversible, and its breaking would regenerate **14*** at higher temperatures. Species **14*** has not been experimentally detected, presumably due to its high reactivity, and it is supposed to immediately yield complex **16** by formation of a C-C bond on position 6 of bipy. Due to the stability of complex **16** (-10.9 kcal·mol^{-1}) and the high barrier to regenerate **14*** (-20.8 kcal·mol^{-1}), the formation of this C-C bond would not be reversible.

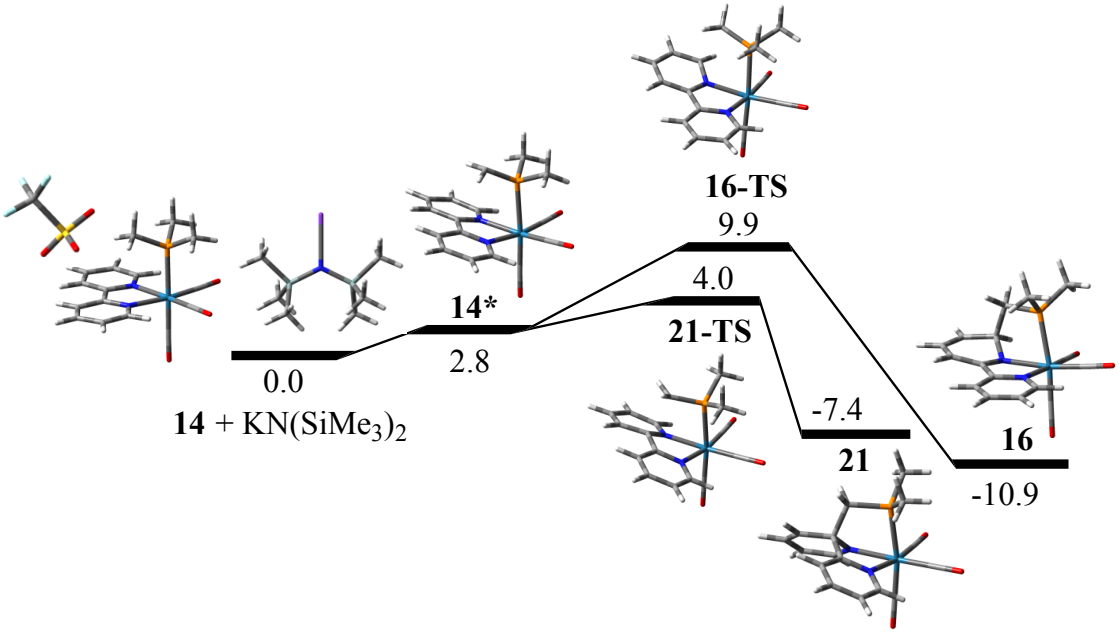


*Figure 17. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol^{-1}) for the reaction of **14** with KN(SiMe$_3$)$_2$ in THF. Energies are referred to the reactants.*

These results provide a satisfactory explanation of our experimental findings. There must be noted, however, that the calculations are only approximate. There are several reasons for this, besides the intrinsic complexity of the system: one of the products of the reaction is potassium triflate, and is likely that most of it precipitates in the reaction conditions. No attempts have been made to estimate the position of such species in the energy diagram of Figure 17, and in the calculation only a KOTf unit has been considered as the product. Obviously, the neglect of the lattice energy of KOTf leads to an underestimation of the driving force of the reaction. Even if under the reaction conditions some KOTf remains in solution, solvation of the potassium cation by molecules of THF would also provide a contribution of the driving force of the reaction. However, the solvent has been incorporated employing a continuum model, and no specific interaction has been taken into account.

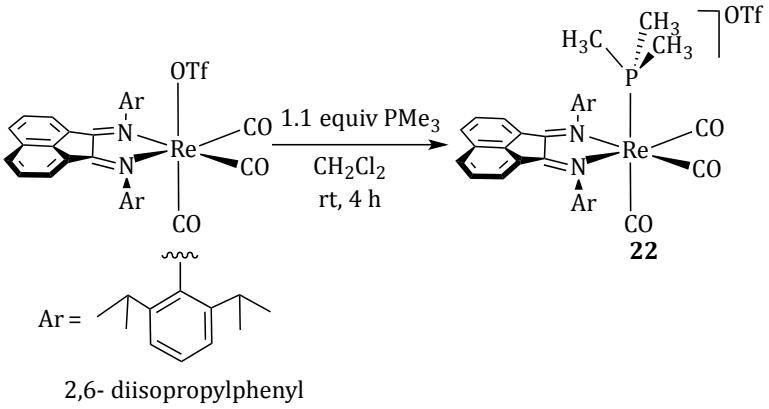
A similar reversible intramolecular C-C bond formation has been found in the deprotonation of compound [Re(bipy)(CO)$_3$(SMe$_2$)]OTf (**1**) (see Section 1.1 of Chapter 1). In contrast to the reaction between **1** and KN(SiMe$_3$)$_2$ described in Chapter 1, signals of [Re(bipy)(CO)$_3$(N(SiMe$_3$)$_2$)] have not been detected in the NMR monitoring of the reaction of **14** with KN(SiMe$_3$)$_2$, presumably as a result of a stronger Re-P bond in **14** in comparison with the Re-S bond in [Re(bipy)(CO)$_3$(SMe$_2$)]$^+$.

Reversible formation of C-C bonds in coordination compounds involving metal-coordinated pyridyl rings is known and has been regarded as a useful electron storage tool,[42a,d] but it usually occurs as a result of the non-innocent character of polypyridine ligands which can accept electrons from the metal center. In the previously known examples the transfers of an electron from a highly reducing metal center of samarium (II), ytterbium (II) or iron (I) generates a pyridyl-based radical, which subsequently dimerizes (see Introduction). In contrast, in the reactions discussed here, in which the C-C coupling takes place between a coordinated pyridyl ring and a nucleophile, one can assume that an important contribution to the reversibility of the nucleophilic additions to pyridine rings results from the recovery of the ring aromaticity.

2.5 Deprotonation of methylphosphanes in $Re(CO)_3$BIAN complexes.

Due to the failure of our repeated attempts to isolate **16,** attributed to its low stability, and even to obtain it as the unique product, the deprotonation of PMe_3 was carried out in $Re(CO)_3$ fragments containing non-aromatic diimines, such as 2,6-*i*Pr_2BIAN. Rhenium tricarbonyl complexes with these ligands have proved to yield stable products in the deprotonation of SMe_2 and SMePh (see Chapter 1), and a similar outcome was hoped for the phosphane complexes.

The new compound [Re(2,6-*i*Pr_2BIAN)$(CO)_3(PMe_3)$]OTf (**22**) was readily obtained in nearly quantitative yield (97%) by triflate substitution in the precursor [$Re(CO)_3$(2,6-*i*Pr-BIAN)(OTf)] with a slight excess of PMe_3 in CH_2Cl_2 (see Scheme 19). Phosphane coordination in [$Re(CO)_3$(2,6-*i*Pr-BIAN)(OTf)] barely changed νCO frequencies (from 2039, 1953 and 1921 cm^{-1} in the triflate precursor to 2039 and 1951 cm^{-1} in **22** in CH_2Cl_2) although the precursor is neutral and the product is cationic. This effect is presumably due to the strong electron-withdrawing ability of the triflate ligand and the strong electron-donating ability of the phosphane, which make both rhenium centers to back-donate a similar amount of electron density to their sets of carbonyl ligands.



*Scheme 19. Synthesis of [Re(2,6-iPr$_2$BIAN)(CO)$_3$(PMe$_3$)]OTf (**22**) by OTf susbtitution*

Compound **22** was isolated as an analytically pure red powder by precipitation, and it was completely characterized in solution by NMR spectroscopy, and in the solid state by X-ray diffraction analysis (see Section 2.6). The NMR spectra showed signals for a C_s symmetric complex (*e. g*. two CH signals and four CH_3 signals for the *i*Pr groups of the BIAN in the ^{1}H and ^{13}C NMR spectra, see Figure 18 for the ^{1}H NMR spectrum) with a coordinated PMe_3 (at -38.4 ppm in the ^{31}P NMR spectrum).

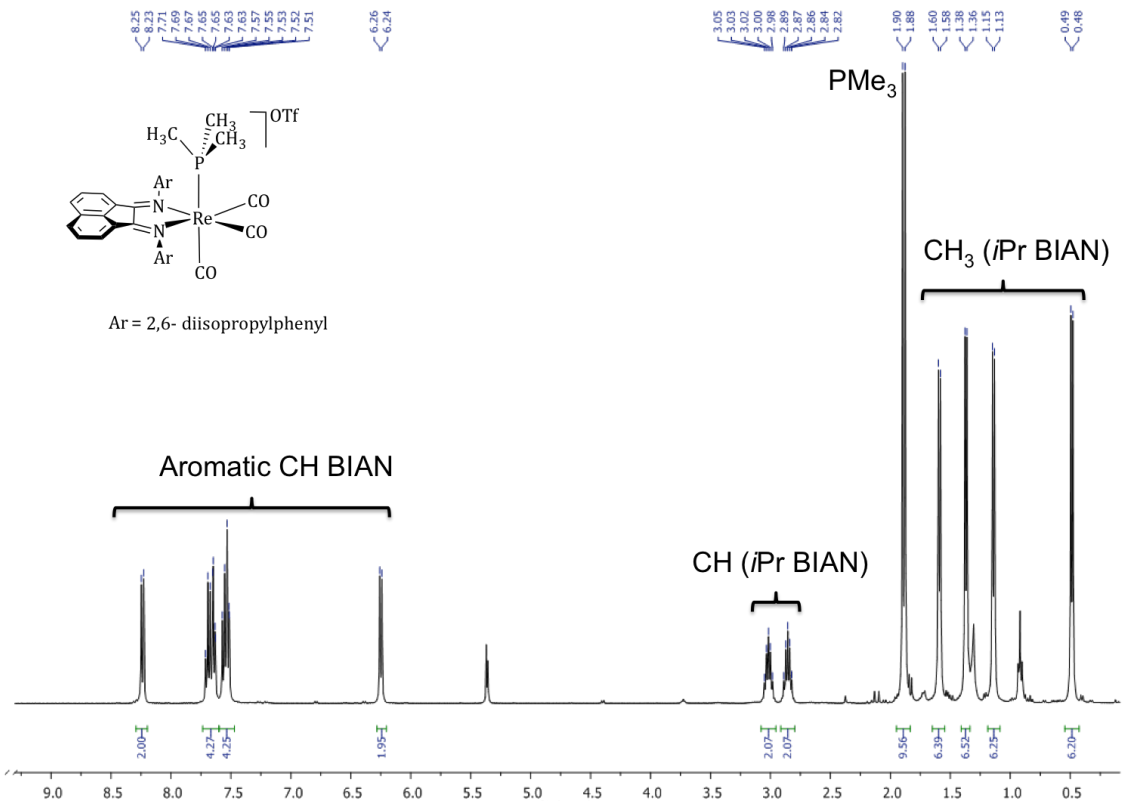
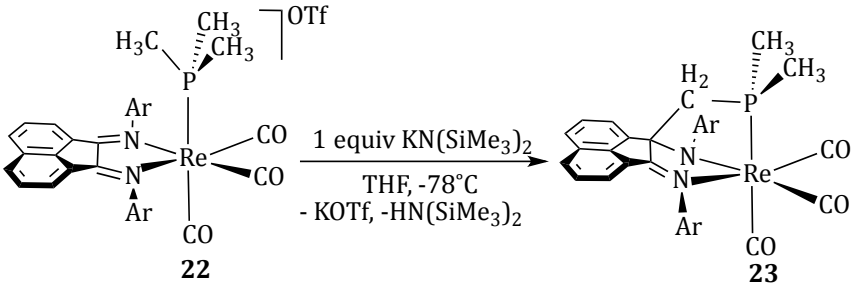


*Figure 18. ^{1}H NMR spectrum of compound **22** in CD_2Cl_2 at 298 K.*

Addition of the equimolar amount of $KN(SiMe_3)_2$ to a THF solution of **22** at -78°C caused an instantaneous color change from red to purple and a shift to lower frequencies of the IR νCO bands (2006, 1908 and 1881 cm^{-1} in THF), consistent with the formation of a neutral species, **23**. Unlike **16**, complex **23** was found to be thermally stable and could be isolated in moderate yield (51 %) and crystallized by slow diffusion of pentane into a concentrated solution of **23** in CH_2Cl_2 (see Section 2.6). Full NMR characterization and X-ray diffraction analysis showed **23** to possess a new C-C bond between a deprotonated group of the PMe_3 and one of the imine carbon atoms of the BIAN co-ligand (see Scheme 20).



Scheme 20. Intramolecular nucleophilic attack of a deprotonated P-CH_3 group of PMe_3 to a BIAN-imine group.

As previously mentioned, addition of $KN(SiMe_3)_2$ to compound **14** yielded a mixture of the C-C coupling product **16** and the cyano complex **15**. Note that nucleophilic attack to produce **15** took place on the carbonyl ligand *trans* to the phosphane, presumably the one most electrophilic. However, IR and NMR characterization of the reaction crude from the addition of $KN(SiMe_3)_2$ to **22** showed **23** to be formed as the single product of the reaction, *i. e.*, no products from nucleophilic attack of the amide on a CO ligand were detected. This could be attributed to the high steric hindrance that the BIAN ligand imposes in the CO group *trans* to the phosphane, which favors the deprotonation of the phosphane over nucleophilic attack on the CO.

^1H and ^{13}C NMR spectra of **23** were consistent with a C_1 symmetric complex due to the loss of the mirror plane in **22** (*e. g*. four multiplets for the CH and eight doublets for the CH_3 of the *i*Pr groups in the BIAN in the ^1H NMR spectrum of **23** in CD_2Cl_2, see Figure 19), and showed signals for a new P-CH_2 group (signal in opposite phase to CH at 34.4 ppm in the ^{13}C DEPT-135 NMR spectrum and two doublets of doublets at 2.31 and 1.66

ppm in the ^{1}H NMR spectrum), and two diasterotopic P-CH_3 units (doublets at 2.16 and 1.84 ppm in the ^{1}H NMR spectrum). A $^{3}J_{CH}$ cross-peak between the P-CH_2 unit and the ^{13}C signal at 92.1 ppm identified the latter as the attacked quaternary (from ^{13}C DEPT-135) carbon, which is upfield shifted as a result of its sp^3 hybridization. In contrast, the intact C=N group in **23** occurs at 192.8 ppm in the ^{13}C NMR spectrum, considerably downfield shifted in comparison to the analogous CN in **22** (which occurs at 177.3 ppm) as a result of the loss of the conjugation.

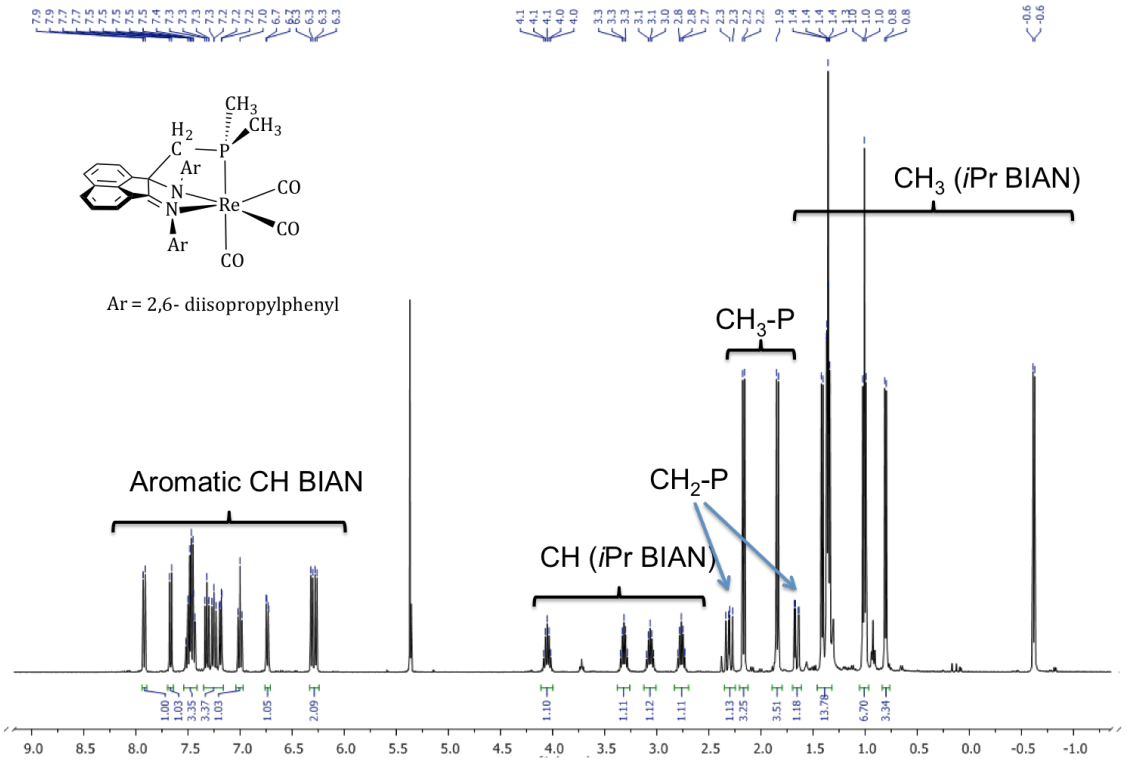
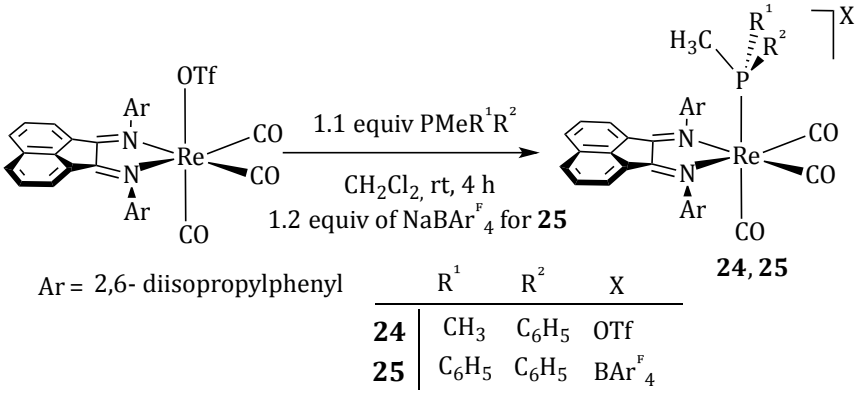


*Figure 19. ^{1}H NMR spectrum of compound **23** in CD_2Cl_2 at 298 K.*

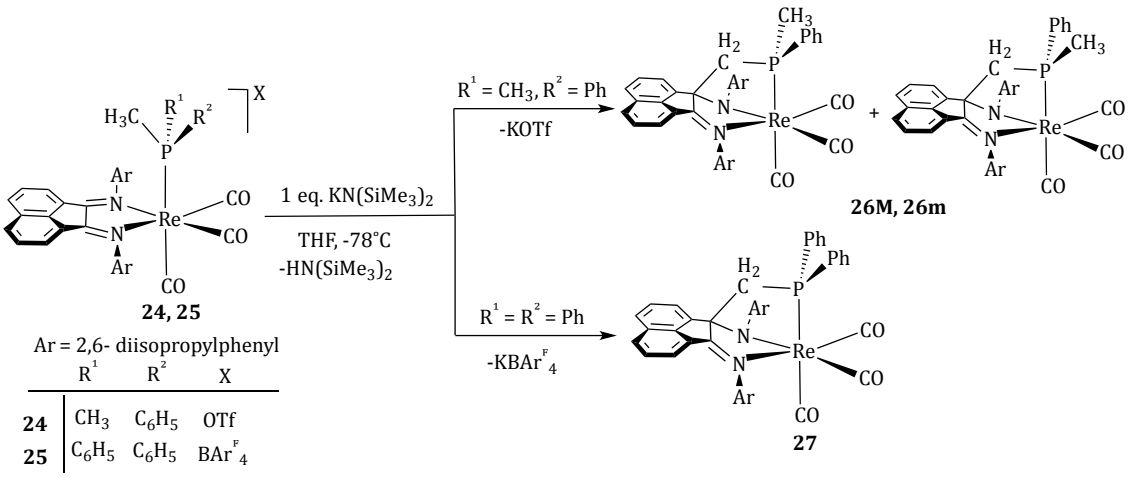
Compound [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PPhMe$_2$)]OTf (**24**) was synthesized in a similar way to that described for **22**. However, due to the increased steric hindrance of PPh$_2$Me (Tolman cone angle is 136° whereas values of 122° for PPhMe$_2$ and 118° for PMe$_3$ have been reported),[61] the phosphane could not displace the triflate in the rhenium precursor and the preparation of complex [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PPh$_2$Me)]$^+$ (**25**) required the presence of the NaBAr$^F_4$ salt which aided the OTf displacement by precipitation of NaOTf in CH_2Cl_2 (see Scheme 21).



*Scheme 21. Synthesis of $PPhMe_2$ (**24**) and PPh_2Me (**25**) $Re(CO)_3$BIAN complexes*

Complete NMR characterization of compounds **24** and **25** confirmed the coordination of the phosphanes and agreed with the proposed structures. However, the ^{1}H NMR spectrum of **25** at room temperature showed line broadening presumably due to the partly hindered rotation of the bulky phosphane as a consequence of the high steric hindrance imposed by the 2,6-*i*$Pr_2C_6H_3$ BIAN substituents. Variable temperature ^{1}H NMR experiments showed signal sharpening on raising the temperature (when rotation around the Re-P bond became rapid in the NMR timescale and the ^{1}H NMR spectrum displayed signals for a symmetric BIAN ligand), and on lowering the temperature (when rotation became frozen and the BIAN ligand appeared as asymmetric in the NMR spectra).

Addition of the equimolar amount of $KN(SiMe_3)_2$ to THF solutions of **24** or **25** yielded purple solutions with lower IR νCO frequencies than their precursors (see Experimental Section) consistent with the formation of neutral products, **26M**, **26m** (from **24**) and **27** (from **25**). Full NMR characterization and X-ray diffraction analysis of the products (see Section 2.6) revealed them to be the products of P-methyl group deprotonation and intramolecular nucleophilic attack of the resulting methylene group on an imine carbon atom of the 2,6-*i*Pr_2BIAN co-ligand (see Scheme 22). These products are formed as single species in the reaction and stand in contrast with the cyano complexes from nucleophilic attack of $KN(SiMe_3)_2$ on a CO ligand of $[Re(bipy)(CO)_3(PPhMe_2)]$OTf and $[Re(bipy)(CO)_3(PPh_2Me)]$OTf complexes (see above).



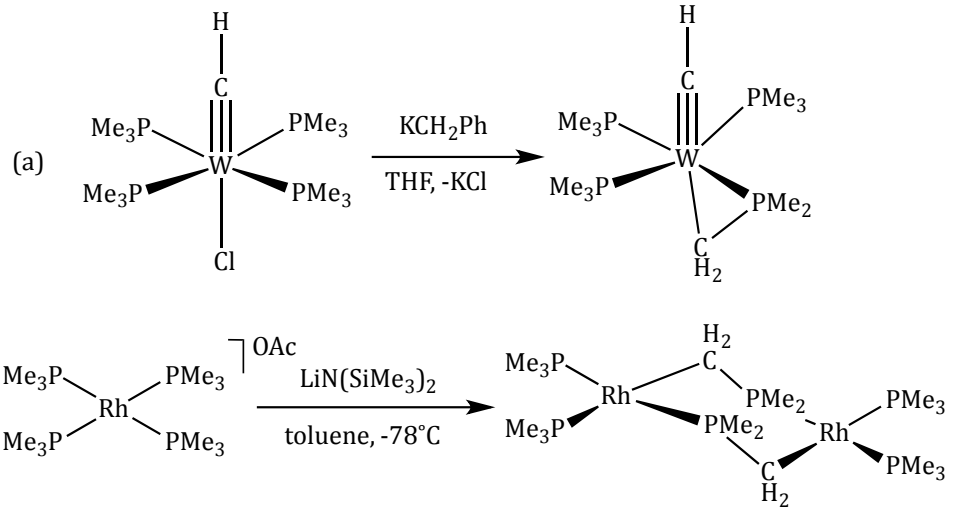
*Scheme 22. Deprotonation of P-CH_3 groups of $PPhMe_2$ (in **24**) and PPh_2Me (in **25**) to yield C-C coupling products **26M**, **26m** and **27** respectively.*

Similar features to those of **23** could be found in the NMR spectra of **26M, 26m** and **27**, which showed the presence of a new P-CH_2 unit and signals for an asymmetric 2,6-*i*Pr_2BIAN ligand consistent with the products being C_1 symmetric. Products **26M**, **26m** were found to be a mixture of two diasteromers (*RSRS* and *RSSS* in the Cahn, Ingold and Prelog nomenclature)[46] in a 5.2:1 ratio which differed in the position of the P-CH_3 group and the attacked imine group of the 2,6-*i*Pr_2BIAN.

Formation of two diasteromers has also been found in the deprotonation of compound [Re(bipy)$(CO)_3(SMe_2)$]OTf (compounds **2M**, **2m** and **3M**, **3m**, see Chapter 1).

Deprotonation of non-coordinated PMe_3 with *t*BuLi[62] was reported in 1977[62a] by Karsch and Schmidbaur. This method is particularly useful to obtain Me_2PCH_2Li which could further react with metal precursors[63] or with organic molecules to yield polydentate ligands.[64] Despite the fact that coordination has been reported to increase the acidity of methyl groups by 10^{15} times in H_3B-PMe_3 adducts,[55] deprotonation of coordinated phosphanes is not common and they usually act as spectators in reactions with strong bases. In the few reported examples,[65] deprotonation of P-bonded methyl groups generates a CH_2 nucleophile which attacks the metal center in an intermolecular or intramolecular fashion. Piers and co-workers reported that the addition of KCH_2Ph to [$(PMe_3)_4ClW{\equiv}C$-H] yielded a bidentate κ^2-$CH_2P(CH_3)_2$ ligand from phosphane methyl group deprotonation and subsequent displacement of the chlorine ligand by the CH_2 nucleophile (see Scheme 23a).[66] Dinuclear complexes with bridging η^2-$CH_2P(CH_3)_2$

ligands have been obtained by intermolecular nucleophilic attack of a deprotonated methyl group of PMe_3 in $[Rh(PMe_3)_4]OAc$ (Scheme 23b).[65b]



Scheme 23. Deprotonation of coordinated PMe_3 and subsequent nucleophilic attack of a the resulting P-CH_2^- group in a (a) intramolecular and (b) intermolecular fashion.

The results reported in this dissertation constitute the first examples of intramolecular nucleophilic attack of a deprotonated methyl group of PMe_3, $PPhMe_2$ or PPh_2Me ligand on a diimine coligand. Moreover, deprotonation of the phosphane is facilitated by coordination to the $\{Re(CO)_3\}^+$ fragment and deprotonation occurs instantaneously and under milder conditions than the deprotonation of the free ligand.[62]

2.6 Solid-state structures of BIAN-phosphane complexes.

The results of the structural determination of compounds **22**, **23**, **26M** (*RSRS* diasteromer as a racemic mixture) and **27** by X-ray difraction (see Figure 20 and Table 3) are in accordance with the structures in solution as deduced from spectroscopic data. The solid-state structures of **22**, **23**, **26M** and **27** showed distorted octahedral rhenium tricarbonyl fragments bonded to a 2,6-*i*Pr_2BIAN chelate and a PMe_3 ligand in a *fac* disposition in the cation of **22**, and to an *N*,*N'*,*P* tridentate ligand resulting from P-bonded methyl group deprotonation and subsequent attack on one of the C=N groups of the BIAN in complexes **23**, **26M** and **27**.

Similar tendencies in the bond distances and angles can be found in the structures of **23**, **26M** and **27**, therefore, only values of complex **23** will be used in the following discussion (see Table 3 for values in complexes **26M** and **27**).

Due to the severe steric hindrance imposed by the bulky diisopropylphenyl BIAN substituents, the angles Re-C3-O3 and P-Re-C3 in **22** are significantly smaller (169.4(4)° and 164.7(2)° respectively) than the 180° expected for an ideal octahedral geometry.

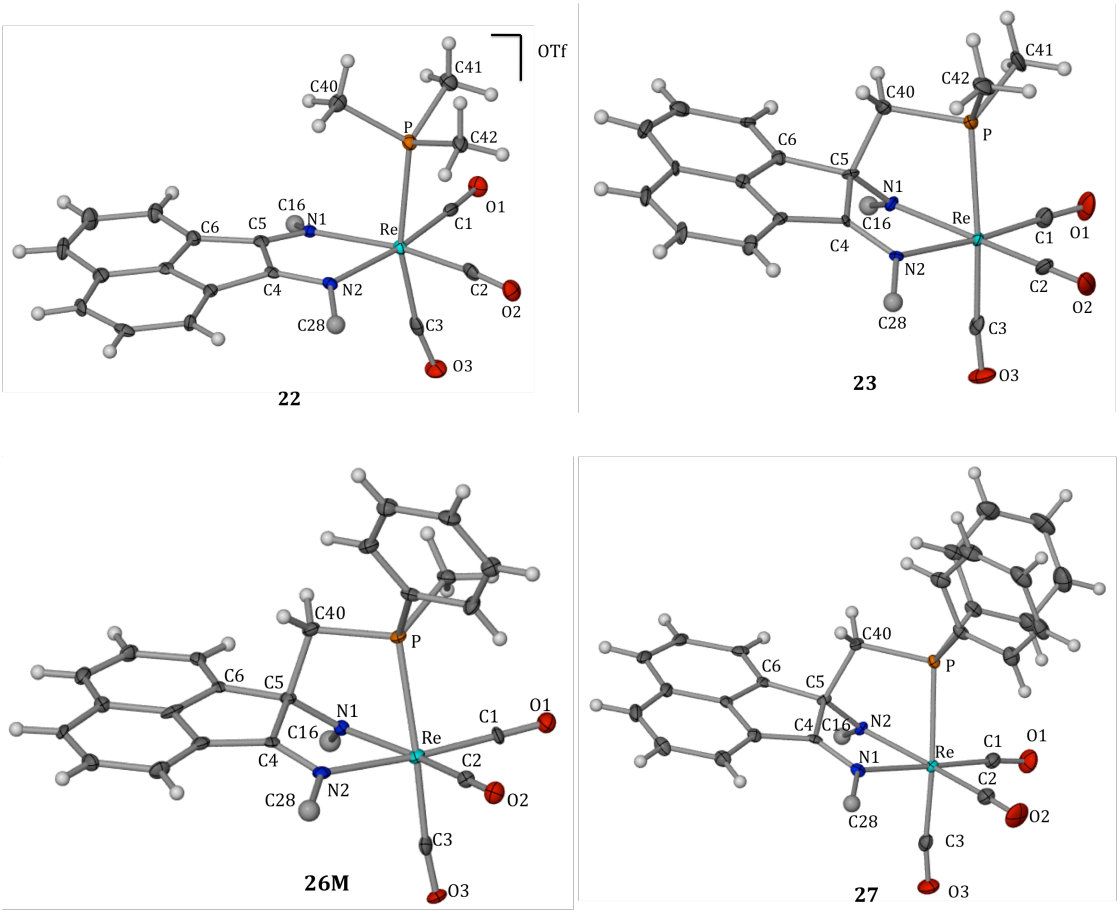


*Figure 20. Solid-state structures (thermal ellipsoids at 30% probability) of the cation in **22** and of complexes **23, 26M** and **27**. 2,6-(iPr$_2$)C$_6$H$_3$ BIAN substituents have been omitted for clarity.*

	22	**23**	**26M**	**27**
Re-N1	2.187(4)	2.179 (6)	2.156 (7)	2.156(3)
Re-N2	2.202(4)	2.246 (7)	2.245 (7)	2.263(3)
Re-P	2.506(2)	2.505(2)	2.478(2)	2.495(2)
N1-C5	1.296(7)	1.454 (8)	2.156 (7)	1.456(4)
N2-C4	1.292(7)	1.284 (9)	2.245 (7)	1.286(5)
N1-C16	1.466(7)	1.414 (9)	1.46 (1)	1.431(5)
N2-C28	1.461(7)	1.452 (9)	1.30 (1)	1.459 (5)
Re-C1	1.935(6)	1.896(9)	1.921(8)	1.908(4)
Re-C2	1.931(6)	1.901(8)	1.89(1)	1.927(4)
Re-C3	1.952(6)	1.923(8)	1.922(9)	1.928(4)
C1-O1	1.141(7)	1.16(1)	1.14(1)	1.156(5)
C2-O2	1.147(7)	1.182(9)	1.18(1)	1.159(5)
C3-O3	1.149(7)	1.168(9)	1.17(1)	1.154(5)
C40-C5	-	1.596(8)	1.57(1)	1.585(5)
C5-N1-C16	114.3(5)	118.8 (6)	118.3 (7)	119.9(3)
C5-N1-Re	114.5(4)	105.2 (4)	105.7 (5)	107.0(2)
C16-N1-Re	129.7(3)	135.9 (5)	134.8 (6)	132.0(2)
C40-P-Re	118.2(2)	99.7 (2)	99.9(3)	100.2(1)
Re-C3-O3	169.4(4)	173.4(7)	173.6(8)	171.3 (4)
Re-C1-O1	176.5(5)	177.6(8)	177.2(8)	175.7(4)
P-Re-C3	164.7(2)	171.7(2)	168.7(3)	170.7(2)
P-Re-N1	97.5(1)	77.2(2)	75.8(2)	74.81(9)
P-Re-N2	94.3(1)	85.0(2)	85.6(2)	84.50(8)
C1-Re-P1	84.8(2)	90.6(3)	90.1(3)	94.4(1)
N1-C5-C6	134.0(5)	122.0(5)	121.7(7)	121.2(3)
N1-C5-C4	117.3(5)	109.1(5)	110.5(7)	109.7(3)
C6-C5-C4	107.9(5)	102.1(5)	101.2(7)	102.2(2)

*Table 3. Selected bond distances (Å) and angles (°) of the cation in **22**, and of complexes **23, 26M** and **27**.*

As a consequence of the C-C bond formation in **23**, **26M** and **27**, the N2=C4-C5-N1 unit is no longer planar (the N2-C4-C5-N1 torsion angle is 33.9(7)° in **23**, in contrast to 4.1(7)° in **22**). Since C5 becomes tetracoordinated, the sum of angles around it (333.2(1)° in **23**, in contrast to 359.2(5)° for the planar C5 in the precursor **22**) indicates pyramidal

geometry. The angle C40-P-Re (*e*. *g*. 99.7(2)° in **23**) is considerably smaller than the same angle for intact P-bonded groups (*e*. *g*. C41-P-Re and C42-P-Re angles are 117.3(3)° and 129.6(2)° respectively in **23**) due to the approach of the phosphane to 2,6-*i*Pr$_2$BIAN to create the C-C bond. Furthermore, the N1-bonded aryl substituents are no longer perpendicular to the C6-C4-C5 BIAN plane (torsion angle is 78.7(1)° in **23**) in contrast to the almost perpendicular disposition of the substituents found in **22**, and in the intact imine group of **23**, **26M** and **27** (torsion angle is 88.3(9)° for the N2-aryl substituent in **23**).[67]

In complexes **23**, **26M** and **27** the Re-N1 distance (*e*. *g*. 2.179(6)Å in **23**) is slightly shorter than Re-N2 (*e*. *g*. 2.246(7)Å in **23**) showing that N1 is an amido donor engaged in stronger bonds with the metal than the imino group. The sum of angles around N1 is virtually 360°, diagnostic of a planar amido. Planar amido ligands have been found in other carbonyl complexes and are attributed to the delocalization of the amido lone electron pair through a coplanar aryl substituent[68] or through the carbonyl ligands via metal dπ orbitals.[50] Since the aryl substituents and the amido groups of **23**, **26M** and **27** are not coplanar (see above), delocalization of the lone electron pair must occur mainly towards the CO groups.

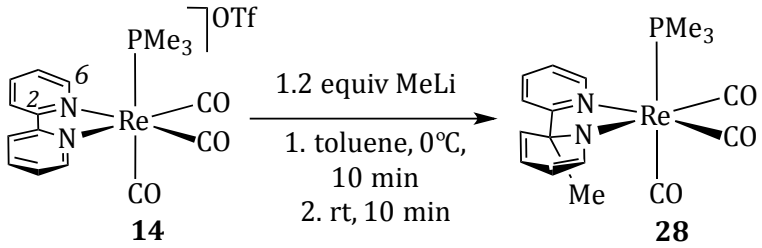
A comparison between the three structures of the neutral complexes reveals that, as the number of phenyl groups on the phosphane increases, so does the difference between the two Re-N distances ($\Delta d_{Re\text{-}N2\text{-}Re\text{-}N1}$ in **27** is 0.107(3), $\Delta d_{Re\text{-}N2\text{-}Re\text{-}N1}$ in **26M** is 0.089(7) and $\Delta d_{Re\text{-}N2\text{-}Re\text{-}N1}$ in **23** is 0.067(7)), suggesting that π-donation from the amido group to the metal is favored by the presence of stronger π-acceptor phosphanes.

2.7 Intermolecular nucleophilic addition of organolithium reagents to bipyridine in 14.

Addition of RLi (R = Me, *n*Bu, *t*Bu) reagents to compound **14** has been demonstrated to afford products resulting from intermolecular nucleophilic addition on the bipy ligand.

Reaction of a toluene suspension of **14** with a slight excess of MeLi (diethyl ether solution) yielded **28**, a neutral *fac*-Re(CO)$_3$ species (as judged by its IR νCO bands at 2012, 1917 and 1884 cm^{-1} in toluene), which was found to be thermally stable and could

be isolated as a red solid in good yield (75%). 1D and 2D NMR characterization showed **28** to bear a methyl group on position 2 of bipy (see Scheme 24) as a result of the intermolecular addition of MeLi on this position. As a consequence, the attacked pyridyl ring became dearomatized (δ ^{15}N from a ^{1}H,^{15}N-HMBC experiment are 82.0 ppm and 233.7 ppm in toluene-d_8, assigned to an amido and imino nitrogens respectively, supporting dearomatization of a pyridyl ring). Further evidence supporting the addition of the methyl group to the 2 position of bipy could be found in (a) the ^{1}H,^{1}H-COSY spectrum which showed no crosspeaks between the CH_3-bipy bonded group (singlet at 1.41 ppm in toluene-d_8) and any hydrogen atoms in the dearomatized pyridyl ring and, (b) the ^{1}H,^{13}C-HMBC spectrum which features a $^{2}J_{CH}$ crosspeak between the CH_3-bipy bonded group and one of the quaternary carbon atoms of bipy (at 70.2 ppm). A ^{1}H,^{1}H-NOESY experiment did not show a crosspeak between the signal of the bipy-bonded methyl group and the methyl groups of the phosphane (doublet at 0.79 ppm). Thus, the stereochemistry of C2 is proposed to be *S*,[46] *i. e.*, the methyl group would be on the opposite face from the phosphane as expected on steric grounds.

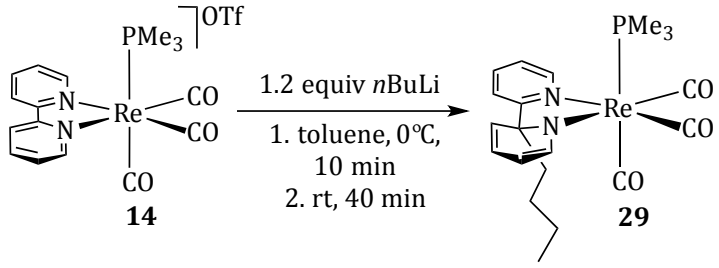


*Scheme 24. Intermolecular nucleophilic attack of MeLi on C2 of bipy in [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**).*

Nucleophilic attack to position 2 of bipy has been previously found in the intramolecular attack of a methylene group from deprotonation of coordinated SMe_2 (see Chapter 1) and PMe_3 (see above), but the reaction of **14** with MeLi constitutes the first example of attack on this position in an intermolecular fashion. Note that the addition is selective toward position 2 of bipy (products of addition to other bipy position have not been detected in the NMR spectra of the reaction crude).

Addition of *n*BuLi (hexane solution) to a suspension of **14** in toluene also yielded a neutral product, **29**, from nucleophilic attack of the *n*BuLi on position 2 of bipy (see

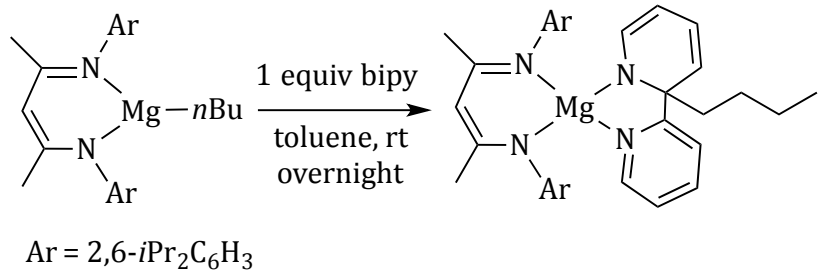
Scheme 25). However, complex **29** was isolated in low yield (21 %) and was found to slowly decompose upon several hours in toluene solution at room temperature.



*Scheme 25. Intermolecular nucleophilic attack of nBuLi on C2 of bipy in [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**).*

1D and 2D NMR characterization of **29** showed similar features than those found in **28**, which allowed to identify the attacked bipy position as C2 and to propose an *S* configuration for the attacked carbon atom (see Experimental Section).

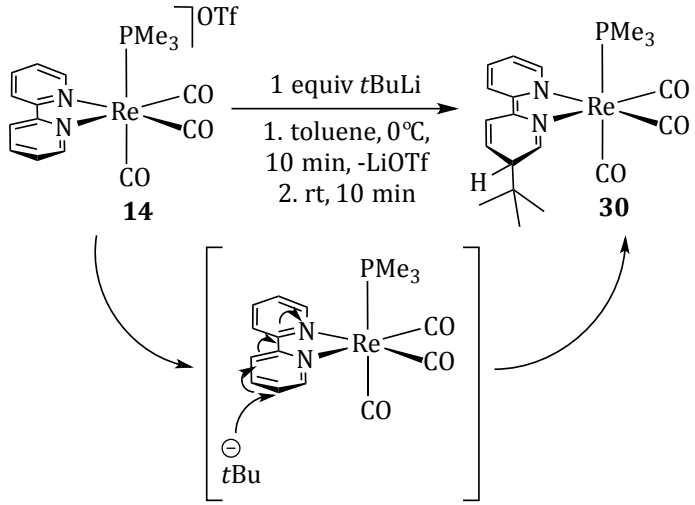
Nucleophilic additions of *n*Bu groups to 2,2'-bipyridine have been reported by Hill and co-workers in the reaction of 2,2'-bipyridine with [Mg(*n*Bu)(N-N)] (N-N = CH{C(CH$_3$)N(Ar)}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$). In this case, the authors were able to characterize a bipy dearomatized product from *n*Bu addition to the position 2/2' of bipy (see Scheme 26).[21]



Scheme 26. Intramolecular magnesium-to-bipy butyl group migration reported by Hill and co-workers.

The reaction depicted in Scheme 26 is mediated by a main group metal and is known to be intramolecular, however, the addition of *n*BuLi to bipy reported in this dissertation is mediated by a transition metal (rhenium) and, since compound [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**) has no labile positions, it is proposed to be intermolecular.

A different regioselectivity was found in the addition of *t*BuLi to bipy in compound **14**. A single neutral species **30** was formed (IR νCO bands at 2019, 1924 and 1894 cm^{-1} in toluene), and, 1D and 2D NMR characterization supported nucleophilic attack of the *t*Bu group on the 5 position of bipyridine. As a result, both pyridyl rings of bipy became dearomatized (see Scheme 27).



*Scheme 27. Intermolecular nucleophilic attack of tBuLi on C5 of bipy in [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**) and its proposed rationale.*

The ^{1}H NMR spectrum of **30** was consistent with the presence of two dearomatized pyridyl rings (signals of the non-substituted pyridyl ring were slightly upfield shifted in comparison to those found for the aromatic ring in complexes **28** and **29**, and occur between 7.82 ppm and 5.61 ppm in C_6D_6), a bipy bonded *t*Bu group and an intact PMe_3 ligand (see Figure 21). Full assignment of the ^{1}H and ^{13}C signals of the attacked pyridyl ring (see Experimental Section) and a cross-peak in the ^{1}H, ^{13}C-HMBC spectrum between H4 and C2 established C5 as the *t*Bu-bonded atom. Moreover, δ ^{15}N chemical shifts (from a ^{1}H, ^{15}N-HMBC experiment) for the nitrogen atoms of the bipyridine-derived ligand were found to substantially differ (174.6 for the non-attacked pyridyl ring, and 232.6 ppm in toluene-d_8 for the *t*Bu-bonded pyridyl ring, chemical shift typical of an imino nitrogen) from those found for the same atoms in **28** (see above), where only one pyridyl ring was dearomatized, supporting dearomatization of both pyridyl rings in **30**. A ^{1}H, ^{1}H-NOESY spectrum showed a NOE between the signal for H5 (at 3.00 ppm) and the signal for the methyl groups of the PMe_3 ligand (at 0.90 ppm), supporting an *S* configuration for C5 (*i. e.* the *t*Bu group would be on the opposite side from the PMe_3).[46]

Low temperature NMR monitoring of the formation of **30** did not reveal the formation of any intermediate prior to **30**.

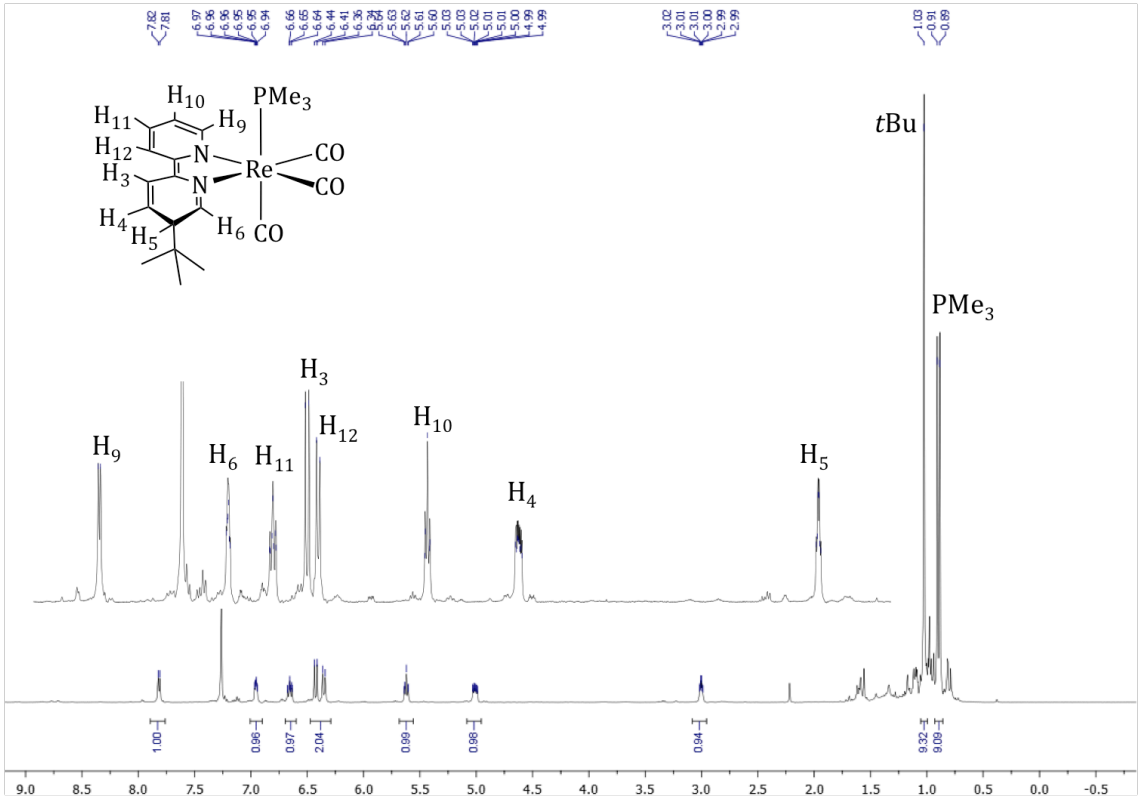


*Figure 21. ^{1}H NMR spectrum of compound **30** in C_6D_6 at 298 K.*

The addition of *t*BuLi to position 5 of bipy in **14** is particularly remarkable since addition of other RLi (R = Me, *n*Bu) reagents to **14** yielded products of nucleophilic attack at position 2 of bipy (products **28** and **29**, see above). *t*BuLi adds to the *ortho* positions of free pyridine[15] and of free bipy,[69] from where 6-*tert*butyl-2,2'-bipyridine is obtained after oxidation. In contrast, the results discussed above show that the presence of the metal center allows the functionalization of the bipyridine ligand on its 2- or 5-positions, which is not accessible by common organic synthetic methods.

Preliminary DFT calculations on the stability of the products from addition of *t*BuLi to **14** (see Figure 22) indicated that complex **30** is more stable (-38.8 kcal·mol^{-1}) than the complexes resulting from nucleophilic addition to positions 2 (**C2**, -18.7 kcal·mol^{-1}), 3 (**C3**, -36.2 kcal·mol^{-1}) and 6 (**C6**, -32.1 kcal·mol^{-1}). Additions to the most electrophilic 2 or 6 positions yielded the less stable species, presumably as a result of the high steric hindrance imposed by the metal fragment. However, addition to position 4 (**C4**, -38.6 kcal·mol^{-1}) afforded a product with similar stability than **30**. Attempts to determine the

energy of the transition state of the products have been unsuccessful, therefore, only thermodynamic stabilities are reported in Figure 22.

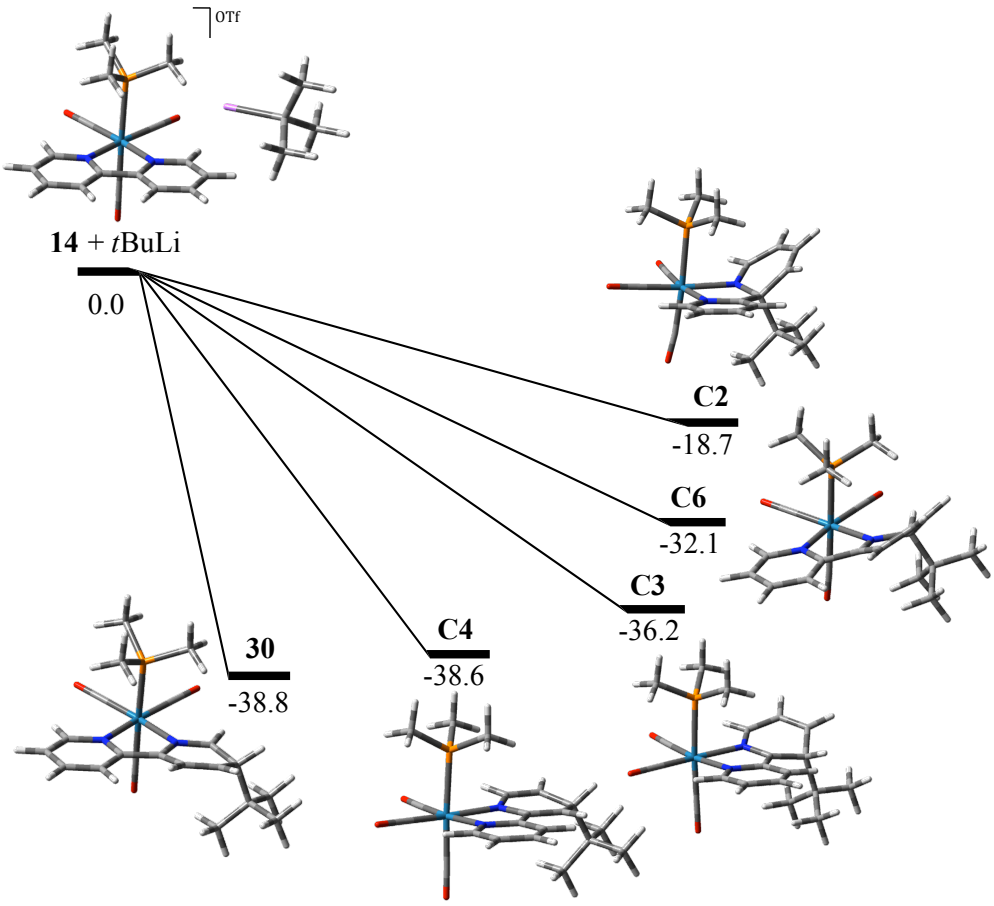


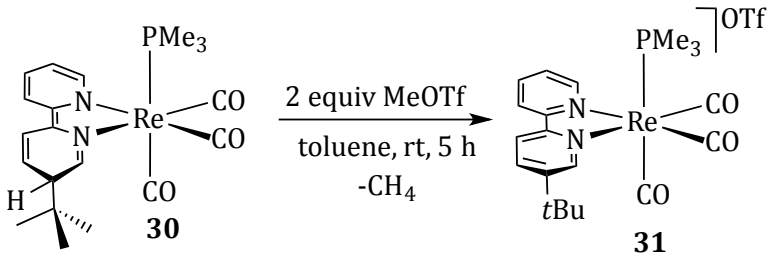
*Figure 22. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) optimized structures from nucleophilic addition of tBuLi to bipy in complex **14** to yield complexes **30**, **C2**, **C3**, **C4**, **C5** or **C6**. Energies are given in kcal·mol^{-1}.*

Dearomatization of both pyridyl rings in **30** as a result of nucleophilic attack on position 5 of bipy is supported by (a) C2-C2' calculated bond distance in the bipy ligand, and (b) calculations of the Nucleus-Independent Chemical Shifts (NICS)[70] on the pyridyl rings. On the one hand, calculated bond distance C2-C2' in **30** is 1.414 Å, shorter than that calculated for the $[Re(bipy)(CO)_3(PMe_3)]^+$ complex (1.477 Å), suggesting some double character of C2-C2'. A conjugated double bond C2-C2' bond distance value (1.420 Å) has been also found for nucleophilic attack on position 3 of bipy. These results support dearomatization of both pyridyl rings upon nucleophilic addition on positions 3 or 5 of bipy. In contrast, single bond C2-C2' distance values have been found for the products of

nucleophilic attack on position 4 (1.478 Å), 6 (1.474 Å) and 2 (1.537 Å), where only one pyridyl ring is dearomatized.

On the other hand, calculations of the NICS on the pyridyl rings of **30** also support dearomatization of both pyridyl rings as a result of the attack on C5. Thus, NICS values are -0.4 for the functionalized pyridyl ring, and 3.8 for the non-substituted ring (average NICS from those calculated at 1 Å above and under the chelate), in sharp contrast with the usual values of NICS found in the aromatic bipy ligand of $[Re(bipy)(CO)_3(PMe_3)]^+$ (-8.9 for both pyridyl rings). These results support a structure of **30** like that depicted in scheme 27 with two dearomatized pyridyl rings. This double dearomatization yields a non-aromatic imino donor in the attacked pyridyl ring and an amido group in the non-substituted ring, both characters supported by calculated Re-N distances of 2.208 Å and 2.192 Å respectively. The character of the N atoms in the pyridyl rings for nucleophilic attacks on positions 3 and 5 is in sharp contrast to that found when the attack occurs on positions 2, 4 or 6, where the amido donor belongs to the attacked pyridyl ring, and the imino donor is part of the aromatic non-substituted ring. Examples of the latter are compounds **16** (the intramolecular attack occurs at position 6) and **28** and **29** (the intermolecular attack occurs at position 2).

Complex **30** readily reacted with electrophiles such as HOTf and MeOTf. Addition of excess MeOTf to a toluene solution of **30** at room temperature caused the partial precipitation of the product, **31**, after 5 hours. Further precipitation afforded compound **31** as an orange powder in a 46% yield. The IR νCO bands of **31** (2037, 1950 and 1922 cm^{-1} in CH_2Cl_2) were consistent with the presence of a *fac*-$Re(CO)_3$ cationic species. 1D and 2D NMR characterization showed that **31** contained a 5-*tert*butyl-2,2'-bipyridine ligand from re-aromatization of the bipy-derived ligand of **30** (see Scheme 28).



*Scheme 28. Rearomatization of the tBu-substituted bipy in **30** by MeOTf.*

The ^{1}H NMR spectrum of **31** (see Figure 23) displayed 7 signals (between 8.94 ppm and 7.69 ppm in CD_2Cl_2) for an asymmetric, aromatic *t*Bu-substituted bipyridine, one signal for a *t*Bu group (singlet at 1.48 ppm) and one signal for an intact PMe_3 ligand (at 1.13 ppm). The most remarkable features are the rearomatization of the ring and the lack of the H5 signal, consistent with the formal abstraction of hydride from that position.

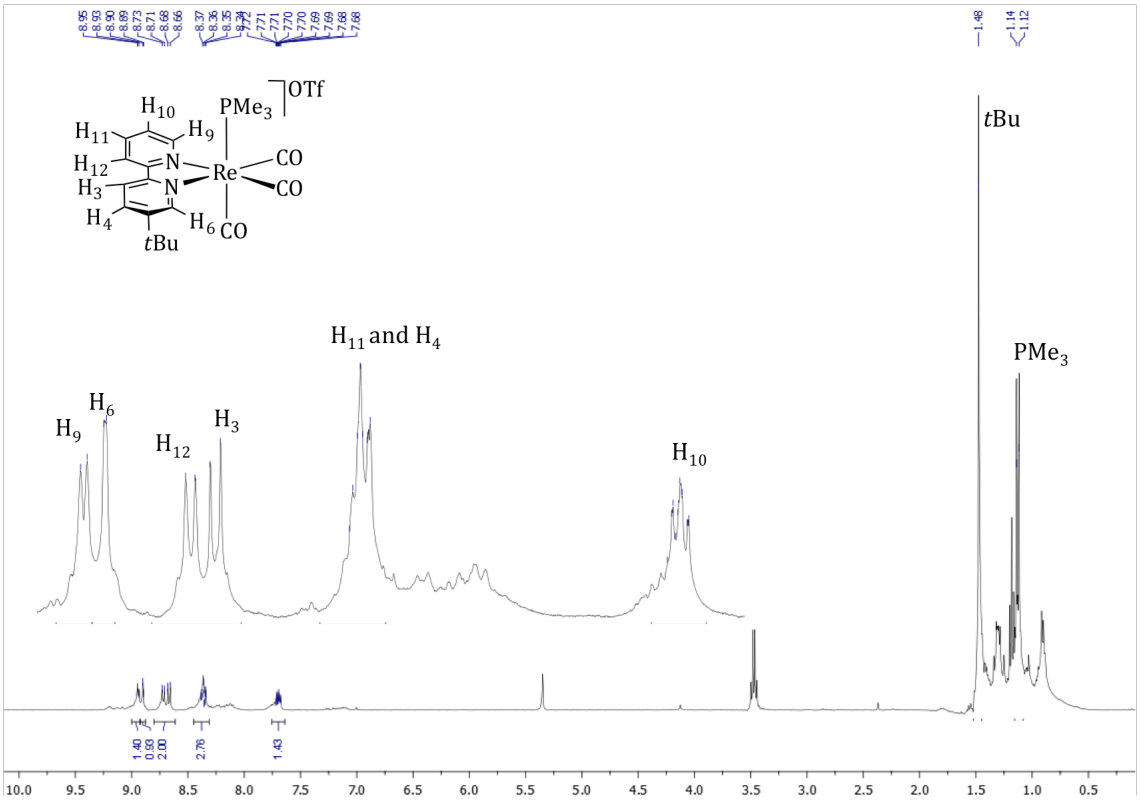
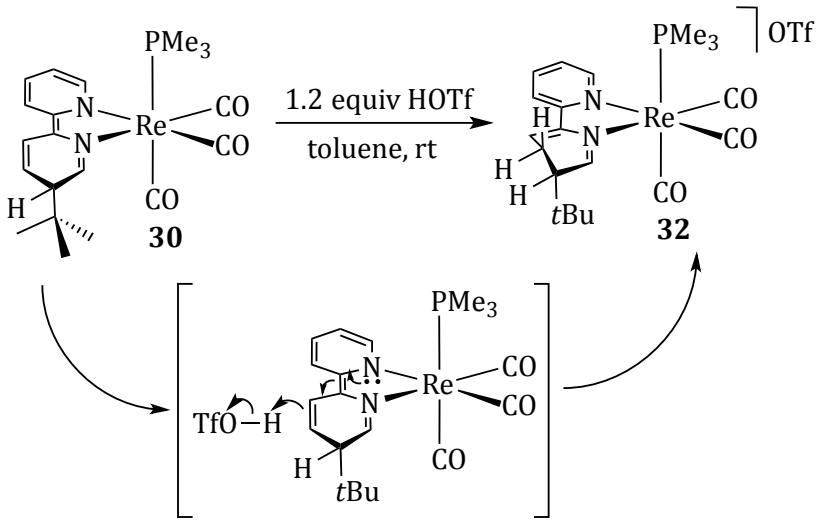


*Figure 23. ^{1}H NMR spectrum of compound **31** in CD_2Cl_2 at 298 K.*

In the formation of **31**, MeOTf, which typically acts as an electrophilic source of the methyl group, has played the role of an oxidant, re-aromatizing the *t*Bu-substituted pyridyl ring in **30** by formal hydride abstraction, with the concomitant formation of methane (which would have been removed from the reaction media by evaporation of volatiles in the work-up of **31**). Product **31** possesses an asymmetric C5-substituted bipyridine ligand which was virtually unknown.

Addition of a slight excess of HOTf to a toluene solution of **30** at room temperature caused the immediate precipitation of the product, **32**, which was isolated as an orange powder in a 38 % yield. IR νCO bands of **32** were consistent with the presence of a cationic *fac*-tricarbonyl species (2039, 1953 and 1925 cm^{-1} in CH_2Cl_2). 1D and 2D NMR

characterization of **32** supported protonation of **30** on C4 of the *t*Bu-substituted pyridyl ring (see Scheme 29).



*Scheme 29. Protonation of complex **30** with HOTf to yield compound **32**, and its proposed rationale.*

^{1}H NMR and ^{13}C NMR spectra showed that **32** contains an aromatic pyridyl ring (signals between 8.69 and 7.45 ppm in the ^{1}H NMR spectrum, see Figure 24) and a non-aromatic *t*Bu-substitued ring. The latter features a *t*Bu substituent on its 5 position (H5 is at 2.66 ppm in the ^{1}H NMR spectrum and C5 is at 45.8 ppm in the ^{13}C NMR spectrum) and a CH_2 group on position 4 (two multiplets at 2.80 and 2.56 ppm in the ^{1}H NMR spectrum and a signal at 19.2 ppm on opposite phase to CH signals in the ^{13}C-DEPT135 spectrum).

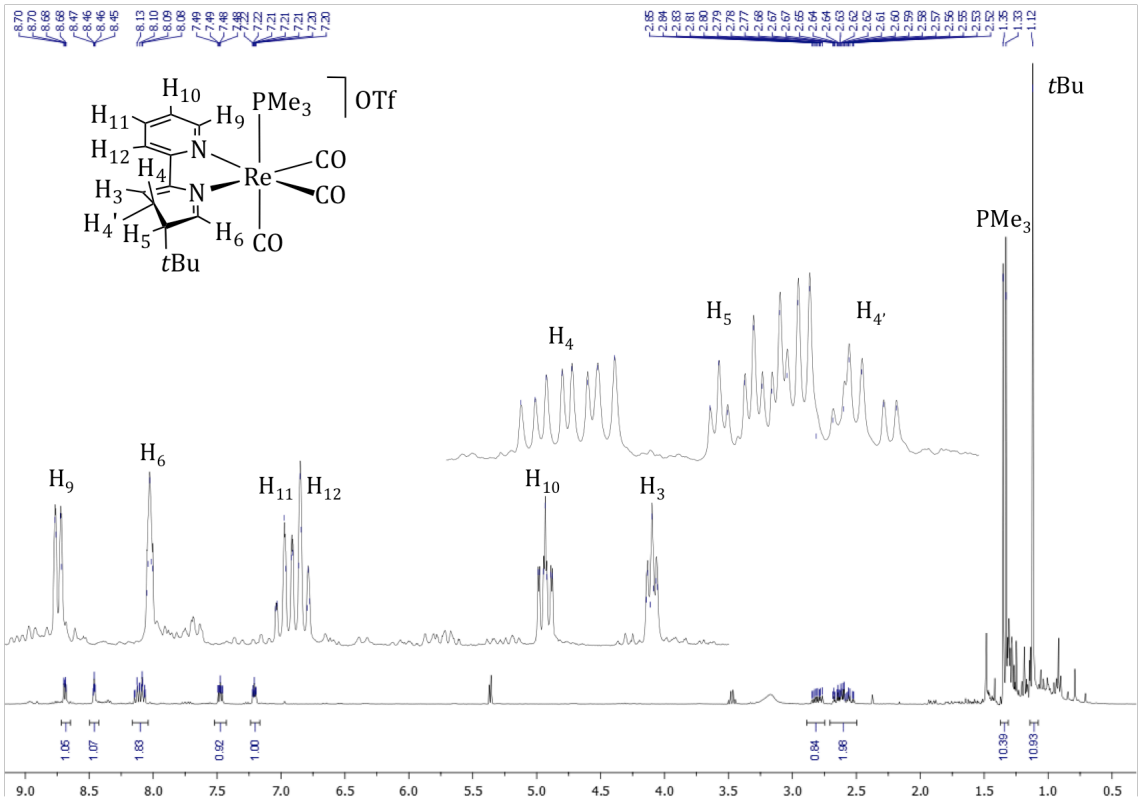


*Figure 24. ^{1}H NMR spectrum of compound **32** in CD_2Cl_2 at 298 K.*

Slow diffusion of hexane into a concentrated CH_2Cl_2 solution of **32** at room temperature yielded yellow crystals, one of which was employed for X-ray diffraction analysis. The results of solid-state structure determination of **32** are depicted in Figure 25 and Table 4.

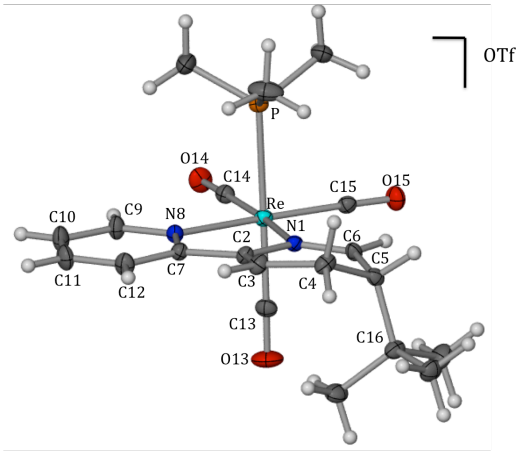


*Figure 25. Solid-state structure (thermal ellipsoids at the 30% probability level) of the cation in **32**.*

Re-P	2.472(1)
Re-N1	2.166(4)
Re-N8	2.179(4)
Re-C13	1.959(5)
Re-C14	1.919(5)
Re-C15	1.939(5)
C13-O13	1.128(6)
C14-O14	1.152(6)
C15-O15	1.134(6)
N1-C6	1.301(6)
C2-C3	1.334(7)
N1-C2	1.431(6)
C4-C3	1.478(7)
C2-C7	1.471(6)
C5-C16	1.566(6)
C6-N1-Re	125.2(3)
C2-N1-Re	116.5(3)
C2-N1-C6	118.2(4)
C3-C4-C5	114.4(4)
C16-C5-C6	109.6(4)

*Table 4. Selected bond distances (Å) and angles (°) of **32**.*

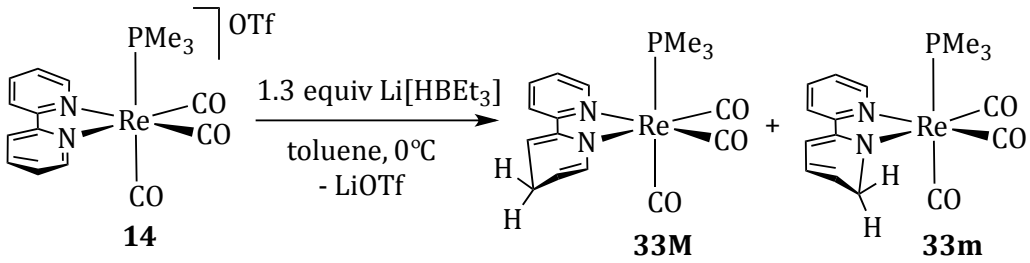
The solid-state structure of **32** showed a *fac*-$Re(CO)_3$ fragment bonded to a PMe_3 and a 4-dihydro-5-*tert*butyl-2,2'-bipyridine.

Re-N1 and Re-N8 distances have similar values (Re-N1 is 2.166(4) Å and Re-N2 is 2.179(4) Å) and are consistent with both, N1 and N8, being imino donors. C2-C7 bond distance is consistent with a single bond (1.471(6) Å), in contrast with the analogous distance in **30** (1.414 Å from DFT calculations, consistent with the presence of a bond with some double character, see above), supporting rearomatization of the non-substituted dearomatized pyridyl ring in **30** upon protonation (see Scheme 29). Bond distances N1-C6 and C2-C3 are in agreement with double bonds at these positions (1.301(6) Å and 1.334(7) Å respectively), in contrast with C3-C4, C4-C5 and C5-C6

(1.478(7) Å, 1.512(7) Å and 1.484(6) Å respectively), which are typical for single bonds. In particular, C3-C4 and C4-C5 single bond distances identifies C4 as an sp^3 hybridized atom, supporting protonation at this position.

2.8 Reaction of 14 with Li[HBEt$_3$]: Intermolecular addition of hydride on bipy and intermolecular C-C coupling between bipy ligands

Reaction of **14** with excess of Li[HBEt$_3$] (1.3 equiv of a 1.0 M solution in THF) in toluene or THF at 0°C yielded a purple solution. The examination of the reaction crude in THF-d_8 by NMR revealed the product to be a mixture of two species, **33M**, **33m**, (in a **33M**:**33m** = 3:1 ratio as judged by ^{1}H NMR integration, see Figure 26) resulting from hydride addition to positions 4 (**33M**) and 6 (**33m**) of the bipy ligand (see Scheme 30).



Scheme 30. Reaction of [Re(bipy)(CO)$_3$(PMe$_3$)]OTf with Li[HBEt$_3$].

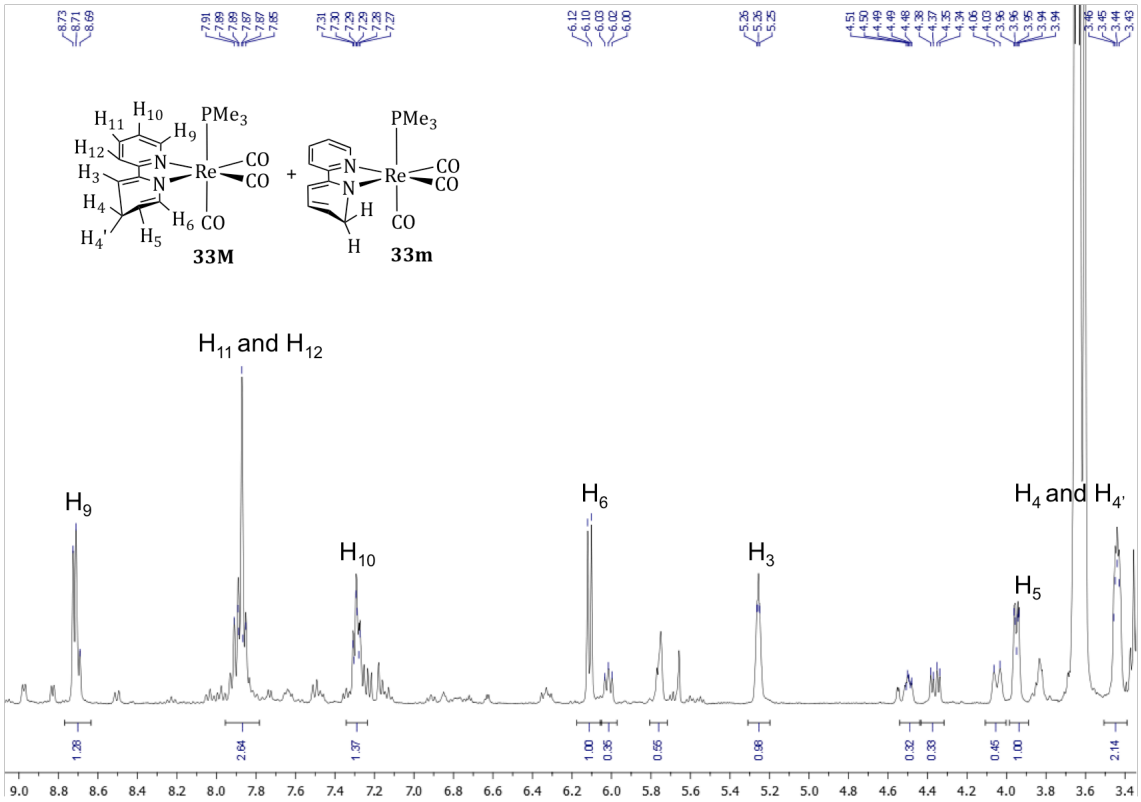
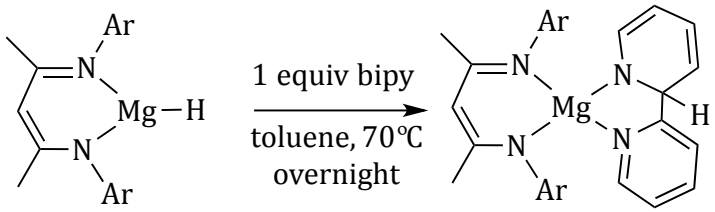


*Figure 26. Bipy signals in the ^{1}H NMR spectrum of mixture **33M**, **33m** in THF-d_8 at 233 K. Signals of **33M** are assigned.*

Hydride addition to bipy has been reported by Hill and co-workers,[21] however, in that case, the reactivity was similar to that found by the same authors for *n*BuLi (see above), and the hydride added to position 2 of magnesium-coordinated bipy (see Scheme 31).



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 31. Intramolecular magnesium-to-bipy hydride migration reported by Hill and co-workers.

As depicted in Scheme 31, reaction of bipy with [MgH(N-N)] (N-N = CH{C(CH$_3$)N(Ar)}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) promoted intramolecular hydride migration to position 2 of bipy. This example stands in contrast with the results reported in this dissertation, since nucleophilic hydride attack on bipy promoted by transition-metal coordination occurs at

positions 6 and 4 and is proposed to be intermolecular, due to the lack of labile positions in compound **14**.

Stirring the mixture **33M**, **33m** at room temperature in toluene or THF caused a color change from purple to red and a slight shift of the IR νCO bands to higher wavenumbers (from 2010, 1913 and 1882 cm^{-1} in **33M**, **33m** to 2014, 1917 and 1890 cm^{-1}), consistent with the presence of a neutral species. The product, **34**, was isolated by filtration as a red powder and characterized by NMR spectroscopy. 1D and 2D NMR characterization showed **34** to be a single species. The chemical shifts and couplings of the signals in the ^{1}H NMR spectrum clearly indicated that **34** contains a CH_2 group in position 4 of bipy but is a different species from **33M**. Moreover, unusually upfield shifted signals in the ^{1}H NMR spectrum for the non-substituted pyridyl ring of bipy and δ ^{15}N chemical shifts (at 247.5 ppm for the attacked ring and at 172.8 ppm for the non-substituted ring in C_6D_6 from a ^{1}H, ^{15}N-HMBC experiment) suggested dearomatization of both pyridyl rings. Similar dearomatization of both pyridyl rings occurred upon nucleophilic attack of *t*BuLi on bipy in **14** (see Section 2.7). ^{1}H and ^{13}C chemical shifts for CH groups (from ^{13}C DEPT-135 and ^{1}H, ^{13}C-HSQC) in position 3 and 5 of bipy (2.63 and 36.7 ppm for C(3)H and 2.26 and 42.42 for C(5)H, from ^{1}H and ^{13}C NMR spectra respectively in C_6D_6) suggested sp^3 hybridization for these carbon atoms.

Red crystals of **34** obtained from slow diffusion of hexane in a toluene solution of **34** were found to be extremely unstable towards atmospheric oxidation, turning yellow upon even minimal exposure to the air. The ^{1}H NMR spectrum of the yellow solid showed the presence of a mixture of unidentified species with aromatic bipyridine ligands.

However, compound **34** readily reacted with the equimolar amount of HOTf in toluene to yield a yellow powder, which instantaneously precipitated from toluene. The product, **35**, was characterized by IR and NMR spectroscopy. Slow diffusion of hexane into a concentrated solution of **35** in CH_2Cl_2 yielded yellow crystals, one of which was used for X-ray diffraction analysis. The results of the structural determination showed that **35** is a dicationic triflate salt formed by a dicationic symmetric binuclear complex produced as the result of the formation of C-C bonds between the 3 and 5 positions of two dearomatized bipy ligands, each coordinated as a chelate to one $\{Re(CO)_3(PMe_3)\}^+$

fragment. As a result of protonation, a new CH_2 group is formed in position 6, so the ring contains two CH_2 groups in positions 4 and 6. The results of the structural determination are given in Figure 27 and in Table 5, which collects selected bond distances and angles.

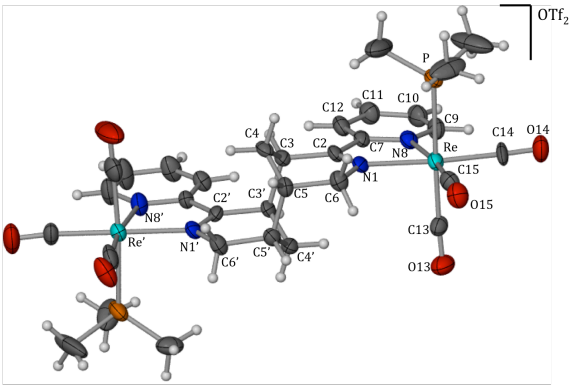


*Figure 27. Solid-state structure (thermal ellipsoids at the 30% probability level) of the cation in **35.***

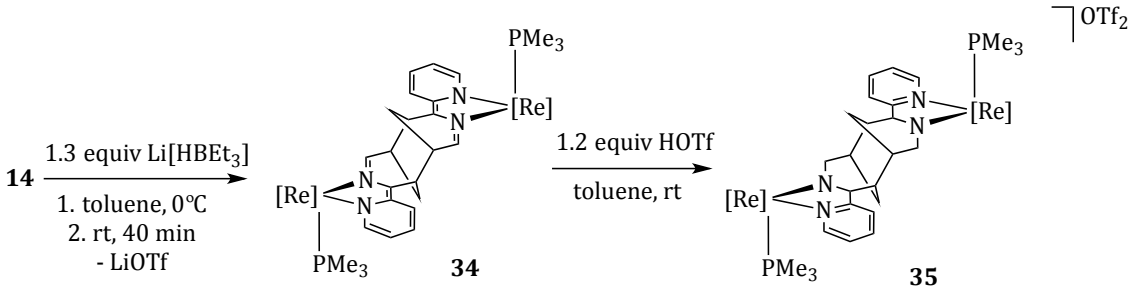
Re-P	2.461(3)
Re-N1	2.143(9)
Re-N8	2.17(1)
N1-C6	1.49(2)
C2-C3	1.52(1)
C3-C4	1.52(2)
C4-C5	1.52(2)
C5-C6	1.54(2)
N8-C7	1.35(2)
N1-C2	1.27(1)
C2-C7	1.48(2)
C5-C5'	1.56(2)
C10-C11	1.38(2)
C11-C12	1.39(2)
C6-N1-Re	118.1(7)
C2-N1-Re	120.7(8)
C2-N1-C6	121.1(9)
C4-C5-C6	108(1)
C3-C4-C5	107.6(9)
C5'-C5-C6	110(1)

*Table 5. Selected bond distances (Å) and angles (°) of **35**.*

Re-N1 and Re-N8 distances in **35** have similar values (2.143(9) Å and 2.17(1) Å respectively) and are consistent with both N1 and N8 being imino nitrogens. Carbon atoms in positions 3, 4, 5 and 6 of the functionalized pyridyl ring are sp^3 hybridized

since they show single bond distances (*e. g*. C2-C3 is 1.52(1) Å and C5-C6 is 1.54(2) Å) and angles close to 109° (*e. g*. C4-C5-C6 is 108(1)° and C3-C4-C5 is 107.6(9)°). In contrast, shorter C-C bond distances could be found in the non-substituted ring (C10-C11 is 1.38(2) Å and C11-C12 is 1.39(2) Å) supporting its aromaticity. The N1-C2 distance of 1.27(1) Å supports the presence of a double bond between N1 and C2.

1D and 2D NMR solution experiments on **35** were in agreement with the structure found in the solid state. The ^{1}H NMR spectrum showed signals consistent with the presence of a C_i compound with two CH_2 groups on positions 4 and 6 of bipy (at 4.58 and 4.30 ppm for position 6 and at 1.85 and 1.06 ppm for position 4) and two C(sp^3)-H groups on positions 3 and 5 (at 4.25 ppm for position 3 and at 2.54 ppm for position 5). Complete NMR characterization of **34** and **35** (see Figure 28 for the ^{1}H NMR spectra) and the solid-state structure of **35** are consistent with the structures depicted in Scheme 32.



*Scheme 32. Reaction of [Re(bipy)(CO)$_3$(PMe$_3$)]OTf with Li[HBEt$_3$] to afford **34** followed by reaction with HOTf to yield **35**. [Re] = Re(CO)$_3$*

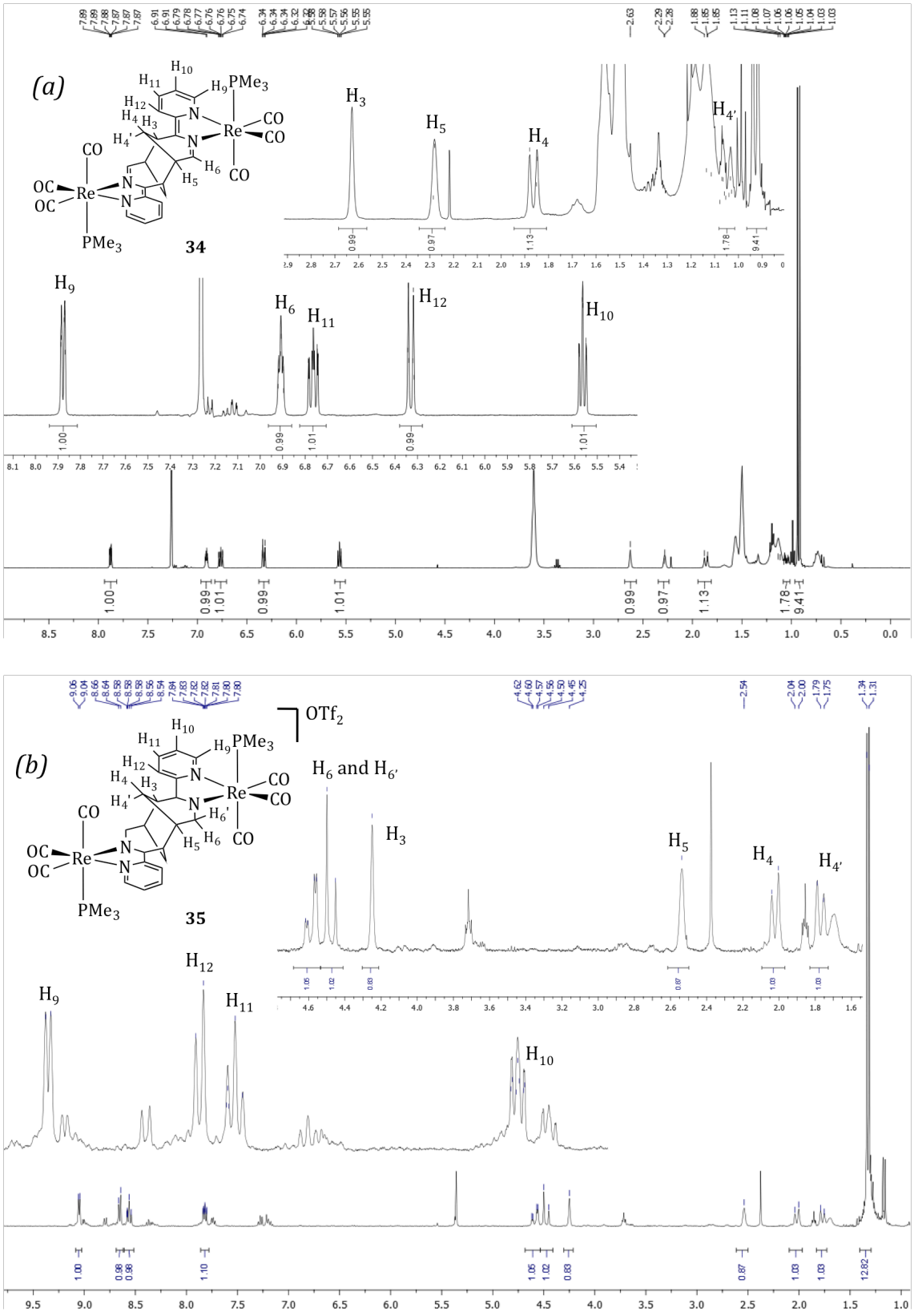
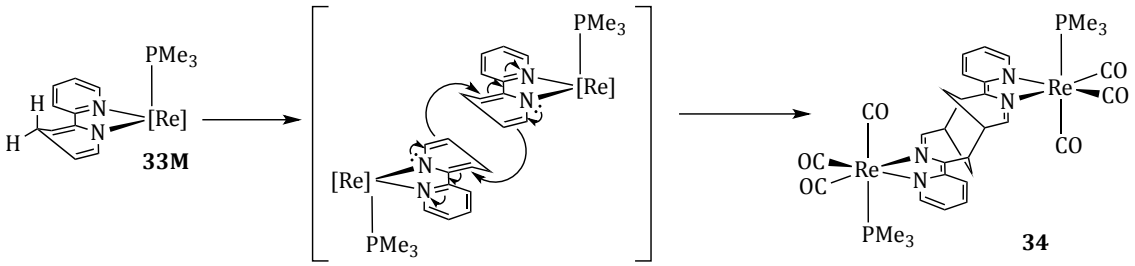


*Figure 28. ^{1}H NMR spectrum of (a) complex **34** in C_6D_6 at 298 K and (b) compound **35** in CD_2Cl_2 at 298 K.*

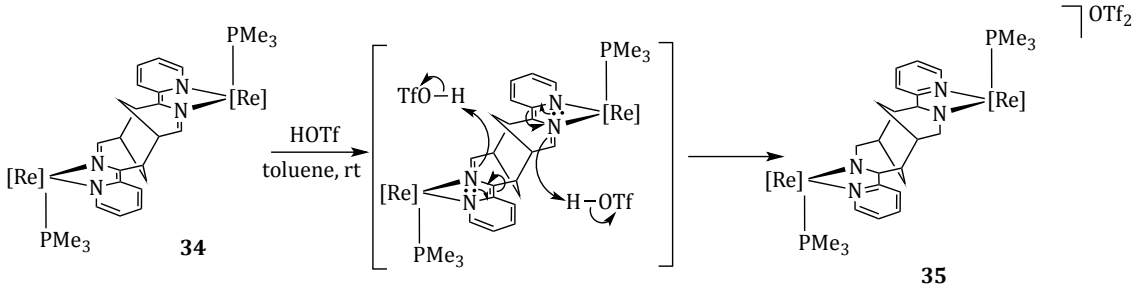
Formation of complex **34** could be conceived only from species **33M** (and not from **33m**) since NMR characterization of **34** clearly showed the presence of a C(sp^2)H group in position 4 of bipy. Products from nucleophilic attack on position 2 of free pyridines (analogous to the position 6 of bipy) are normally formed as the kinetic species which evolve by a 1,3-hydrogen shift to the thermodynamic product containing the C(sp^3)H(R) group on position 4 (analogous to position 4 of bipy).[71] A similar migration of hydride is proposed to occur in the mixture **33M**, **33m** at room temperature, yielding complex **33M** as the sole species in solution. Complex **33M** would dimerize, formally by double intermolecular nucleophilic attack of position 5 of the dearomatized pyridyl ring on position 3 of a dearomatized pyridyl ring of a different molecule yielding two new C-C bonds (see Scheme 33). This dimerization by nucleophilic attack on C3 of bipy results in the dearomatization of the intact pyridyl ring, its nitrogen atom becoming an amido donor. The imino and amido character of the nitrogens in the functionalized and intact pyridyl rings respectively is supported by their ^{15}N chemical shifts (see above).



*Scheme 33. Proposed rationale for the formation of **34.** [Re] = Re(CO)$_3$*

Dimeric structures similar to that of **34** have been found from dimerization of pyridyl groups of PDI ligands coordinated to both transition and main-group[30] metals (see Introduction). However, the formation of **34** reported here constitutes the first example of this kind of dimerization in transition metal coordinated 2,2'-bipyridine. In most of this examples, dimerization has been proposed to follow a radical mechanism. In particular, Cámpora and co-workers proposed that dimerization of the pyridyl ring in PDI ligands upon alkyl transfer from a manganese center (see Scheme I-6 of the Introduction) was promoted by traces of oxygen, evidence that supports a radical mechanism.[30a] However, the rationale proposed for the formation of **34** in Scheme 33 assumes a polar mechanism. At the moment of writing this dissertation, no further experiments have been carried out to elucidate if **34** forms by a polar or by a radical mechanism, and both descriptions could explain the formation of the product.

On the other hand, compound **35** is proposed to form as a result of the 1,4-dihydropyridyl ring protonation on its 6 position, promoted by the rearomatization of the non-substituted pyridyl ring (see Scheme 34). As a result, compound **35** contains two CH_2 groups in the functionalized pyridyl ring at positions 4 and 6 from hydride attack and from reaction with HOTf respectively. CH groups at 3 and 5 positions of the functionalized pyridyl ring of **35** occured at similar chemical shifts in the ^{1}H and ^{13}C NMR spectra than those of **34** supporting sp^3 hybridization of these positions.



*Scheme 34. Proposed rationale for the formation of **35.** [Re] = $Re(CO)_3$*

Formation of compound **35** from protonation at C6 of **34** is particularly remarkable, since protonation at position 6 of dearomatized pyridyl rings has never been previously found. Complex **30**, as **34**, contains two dearomatized pyridyl rings, however, protonation of **30** occurs at C4 and protonation of **34** at C6. This difference in reactivity could be attributed to the presence of sp^3 carbons at positions 3, 4 and 5 of bipy in **34**, which render 2 or 6 as the only positions available for protonation.

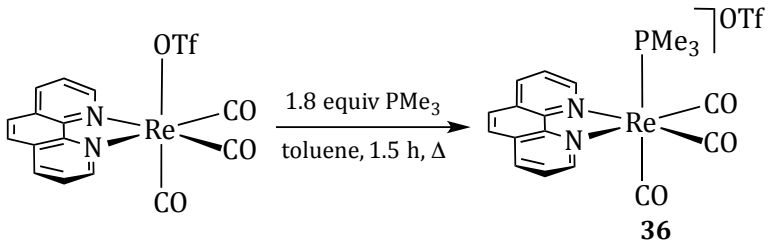
Chapter 3:

Intramolecular and intermolecular additions on a phen ligand

Part of the results discussed in this Chapter have been included in a *Communication* published in the journal *Chemistry- A European Journal.*[72] This Chapter also includes unpublished results which will be included in a future *Full paper*. Since they have not been published, these results will be discussed in further detail.

3.1 Synthesis of [Re(phen)(CO)$_3$(PMe$_3$)]OTf (36)

The new compound [Re(phen)(CO)$_3$(PMe$_3$)]OTf (**36**) was readily synthesized in high yield (89%) from [Re(phen)(CO)$_3$(OTf)], and excess of PMe$_3$ in refluxing toluene (see Scheme 35). The excess PMe$_3$ was required due to the loss of part of it while refluxing the reaction mixture.



*Scheme 35. Synthesis of [Re(phen)(CO)$_3$(PMe$_3$)]OTf (**36**).*

As a consequence of the low solubility of compound **36** in toluene, most of it precipitated from solution as a yellow solid after cooling down the reaction mixture to room temperature. IR, EA and NMR characterization (see ^{1}H NMR spectrum in Figure 29) showed **36** to be analytically and spectroscopically pure. The IR spectrum of **36** in the νCO region featured three bands at 2034, 1945 and 1920 cm^{-1} (in THF) consistent with the presence of a cationic *fac*-tricarbonyl species as the sole product of the reaction. ^{1}H and ^{13}C NMR spectra of **36** were consistent with the proposed formulation and displayed signals that indicated a C_s symmetric complex with a coordinated PMe$_3$. A ^{1}H,^{15}N-HMBC experiment showed one cross-peak for nitrogen nuclei at 226.5 ppm (in THF-d$_8$) assigned to the two equivalent nitrogen atoms of the phen ligand.

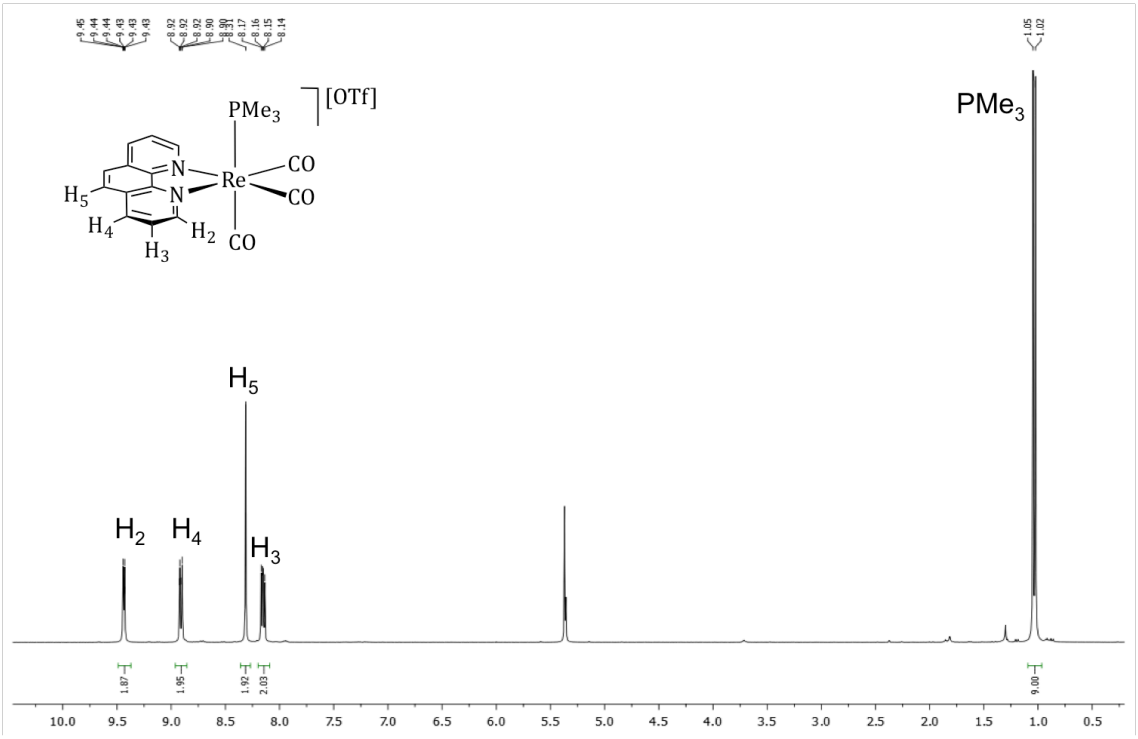


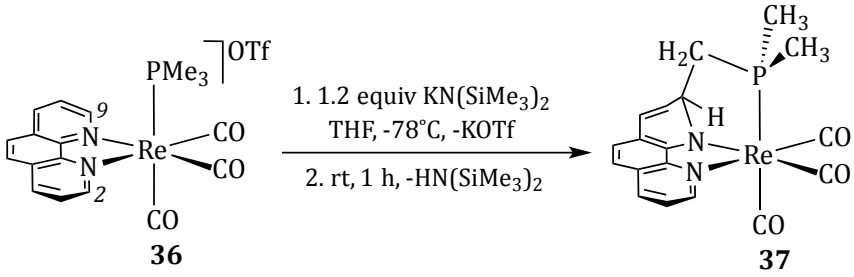
*Figure 29. ^{1}H NMR spectrum of compound **36** in CD_2Cl_2 at 298 K.*

Compound **36** was also obtained from the reaction of [Re(phen)(CO)$_3$(OTf)] with the equimolar amount of PMe_3 in CH_2Cl_2 at room temperature, however, the reaction took longer (4 hours) and the isolated product contained small amounts of unknown impurities (as judged by the ^{1}H NMR spectrum).

3.2 Deprotonation of coordinated PMe_3 in 36: Intramolecular addition of a P-CH_2 group on phen

Addition of a slight excess of KN(SiMe$_3$)$_2$ to a solution of **36** in THF at -78°C caused an instantaneous color change from yellow to purple. The IR spectrum of the resulting solution after 1 hour stirring at room temperature was consistent with the presence of a neutral product (2014, 1918 and 1888 cm^{-1} in THF). Upon reaching room temperature the solution darkened and its IR νCO bands slightly shifted to lower wavenumbers (2010, 1916, 1888 cm^{-1} in THF). The product, **37**, was isolated by filtration as a black microcrystalline solid in a moderate yield (53 %) with good purity, and the slow evaporation of a diethyl ether solution of **37** at room temperature afforded red crystals. Compound **37** was found to be stable, both in the solid state and in THF or toluene

solution, for several days at room temperature. IR, NMR, EA, and X-ray diffraction were found to be consistent with the formulation of **37** displayed in Scheme 36. The molecule of **37** contains a new C-C bond between one deprotonated methyl group of the PMe_3 ligand and the C2/9 carbon of the phenanthroline ligand. Compound **37** is proposed to form as a result of the deprotonation of a PMe_3 methyl group by $KN(SiMe_3)_2$ followed by a nucleophilic attack of the resulting methylene group on C2/9 of the phen co-ligand. As a result of the new C-C bond formation, the attacked pyridyl ring became dearomatized and featured an amido nitrogen (δ^{15}N is 97.7 ppm in contrast to 235.0 ppm for the imino nitrogen in the intact ring, from a ^{1}H,^{15}N-HMBC spectrum).



*Scheme 36. Intramolecular nucleophilic attack on phenanthroline by a deprotonated methyl group of PMe_3 in compound **36**.*

The ^{31}P NMR spectrum of crude **37** displayed one signal at -10.5 ppm (in THF-d_8) in agreement with the formation of **37** as the only organometallic product of the reaction. ^{1}H, ^{13}C and 2D NMR spectra of **37** were consistent with a C_1 symmetric complex as a consequence of the loss of the molecular mirror plane present in **36** and confirmed the connectivity proposed for **37** (see ^{1}H NMR spectrum in Figure 30).

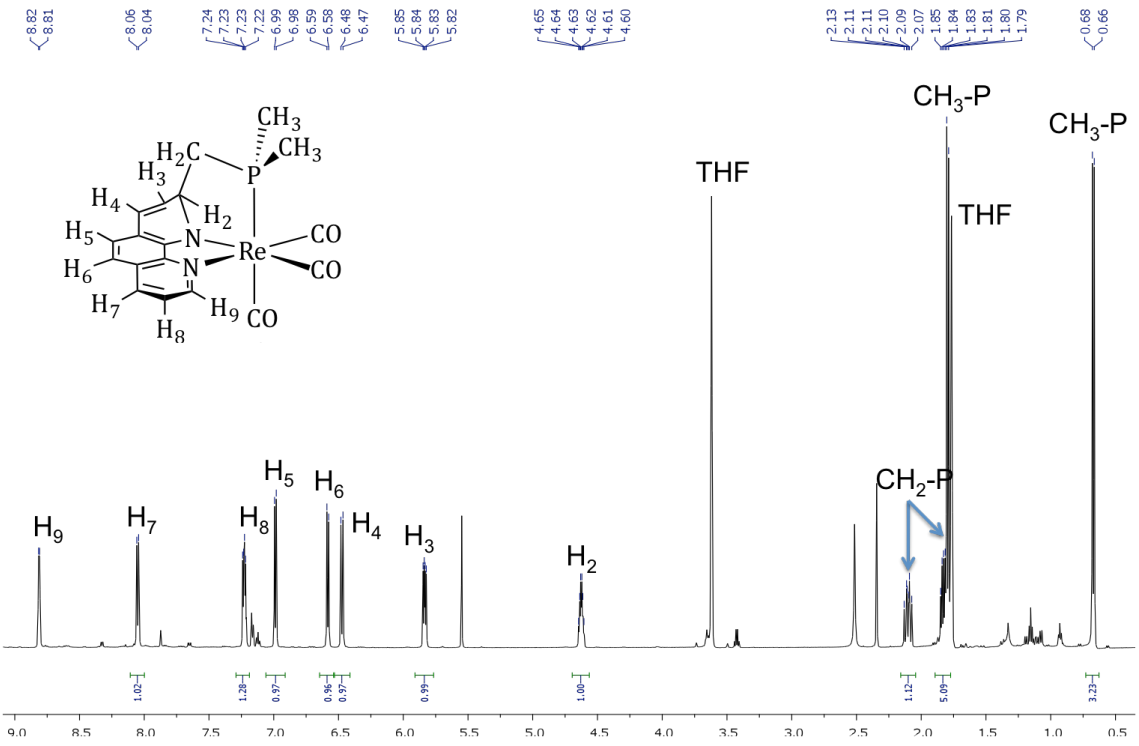


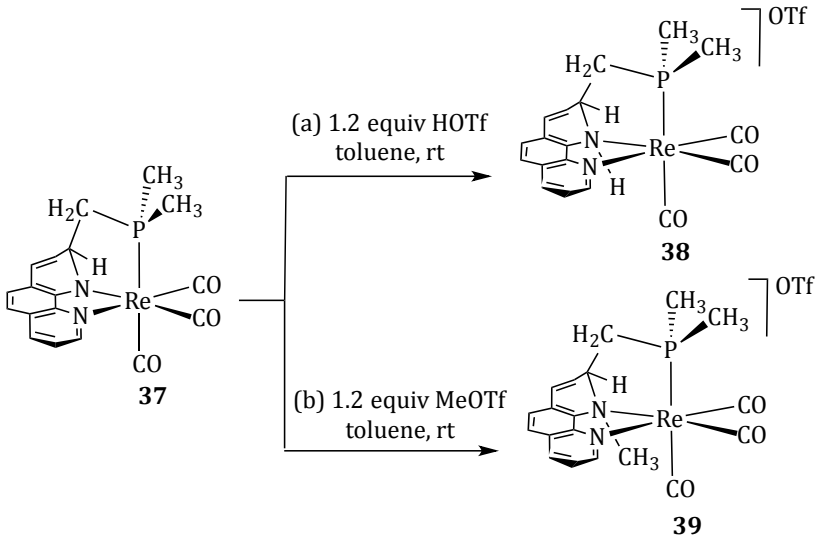
*Figure 30. ^{1}H NMR spectrum of compound **37** in THF-d_8 at 298 K.*

The ^{1}H NMR spectrum of **37** showed signals consistent with a dearomatized bipyridine ligand (between 6.48 and 4.63 ppm in THF-d_8 for the non-aromatic pyridyl ring) and a P-CH_2 from methyl group deprotonation (two multiplets at 2.10 and 1.83 ppm). Moreover, the ^{1}H-^{1}H COSY spectrum supported nucleophilic attack on position 2 of phen since it showed a $^{3}J_{HH}$ crosspeak between the signal assigned to H2 (at 4.63 ppm) and the multiplets for the P-CH_2 groups.

The reaction of **36** with $KN(SiMe_3)_2$ stands in contrast with that of $[Re(bipy)(CO)_3(PMe_3)]OTf$, where nucleophilic attack of the $N(SiMe_3)_2$ on a CO ligand occurred yielding the cyano complex *cis*-$[Re(bipy)(CN)(CO)_2(PMe_3)]$ as the major product. However, formation the analogous *cis*-$[Re(CN)(CO)_2(phen)(PMe_3)]$ complex has not been detected in the reaction of **36** with $KN(SiMe_3)_2$, presumably as a result of the higher electrophilicity of phen in comparison to bipy, which makes intramolecular nucleophilic attack on phen the preferred pathway and disfavors nucleophilic attack on the CO ligands.

3.3 Reaction of 37 with electrophiles (HOTf and MeOTf): Synthesis of N-H and N-Me products

Complex **37** instantaneously reacted with electrophiles such as HOTf or MeOTf to afford compounds **38** and **39** respectively (see Scheme 37). The new compounds were found to be stable in CH_2Cl_2 solution and were characterized by IR, EA, X-ray diffraction and NMR spectroscopy. IR νCO bands at higher wavenumbers than those of their precursor **37** (*e. g*. 2041, 1953, 1923 cm^{-1} in CH_2Cl_2 for **38**) were in agreement with the formulation of **38** and **39** as containing cationic complexes. NMR characterization supported that **38** and **39** form as a result of the protonation or methylation (respectively) of the amido group of **37**. As a consequence, the amido group in **37** (97.7 ppm in the ^{1}H-^{15}N HMBC NMR in THF-d_8, see above) is transformed into an amino group (34.0 ppm in the ^{1}H-^{15}N HMBC NMR spectrum of **38** in CD_2Cl_2).



*Scheme 37. (a) Protonation and (b) methylation of the amido nitrogen in **37**.*

The ^{31}P NMR spectra of crude **38** and **39** compounds showed that both formed as unique species in the reactions (singlets at -0.28 ppm for **38** and at -4.9 ppm for **39** in CD_2Cl_2). ^{1}H and ^{13}C NMR spectra of compounds **38** and **39** displayed signal patterns for asymmetric complexes (see ^{1}H NMR spectrum of **39** in Figure 31). The signal pattern of the phenanthroline-CH_2PMe_2 moiety was similar to that found in complex **37** (see above), indicating that the pyridine ring remained dearomatized and the methylene group was bonded to C2 of phen. Moreover, signals attributed to the new N-H and N-Me groups could be identified in the ^{1}H NMR spectrum (broad signal at 8.74 ppm for the N-

H group of **38**, and a singlet at 3.80 ppm for the N-Me group of **39** in the ^{1}H NMR spectra in CD_2Cl_2). The presence of an N-H group in **38** was further confirmed by a ^{1}H-^{15}N HMQC experiment, which displays a $^{1}J_{NH}$ crosspeak between the ^{1}H signal at 8.74 ppm and the amino nitrogen at 34.0 ppm (CD_2Cl_2).

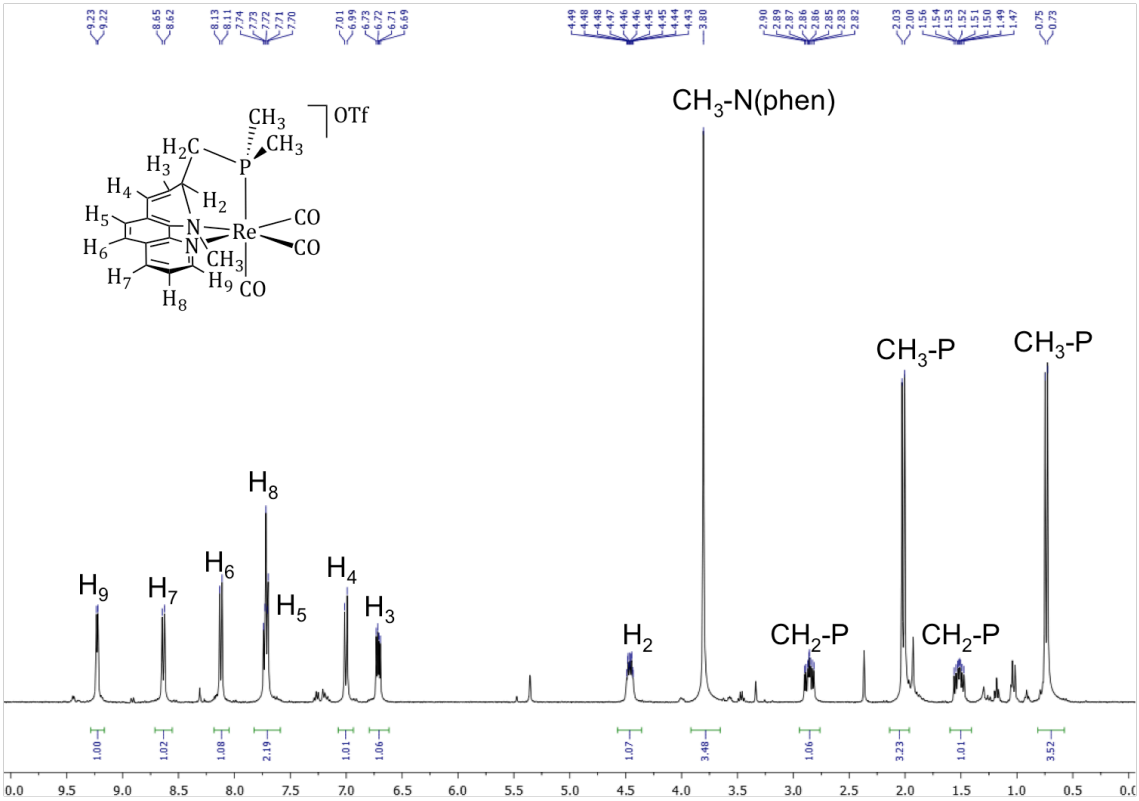


*Figure 31. ^{1}H NMR spectrum of compound **39** in CD_2Cl_2 at 298 K.*

The relatively low solubility of **38** in CD_2Cl_2 precluded its ^{13}C NMR characterization in this solvent. Methathesis of the triflate anion in **38** by $[BAr^{F}_4]^-$ afforded **38^{F}**, with a largely enhanced solubility in CD_2Cl_2 compared to its precursor **38**, which allowed the acquisition of the ^{13}C NMR spectrum.

Protonation of complex **37** exclusively yielded N-H products from amido group protonation, in contrast to protonation of the analogous bipy complex, which yielded a mixture of protonated-at-C5 and protonated-at-N products (see Chapter 2). Protonation-at-C5 has been attributed to the presence of the electron-donating $(CH_3)_2P$-CH_2 unit bonded to bipy. The difference in reactivity between the bipy and the phen complexes could be attributed to the additional aromatic ring of the phen ligand which acts as an electron-withdrawing group, attenuating the electron-donating effect of the $(CH_3)_2P$-CH_2 group, and, favoring formation of N-H products.

3.4 Solid-state structures of phen-phosphane compounds

Crystals of compounds **36**, **37**, **38** and **39** were grown by slow diffusion of appropriate solvents (diethyl ether or hexane) into concentrated solutions of the compounds either in CH_2Cl_2 (for **36**, **38** and **39**) or in toluene (for **37**). The solid-state structures of compounds **36**, **37**, **38** and **39** were determined by X-ray diffraction and showed distorted octahedral *fac*-$Re(CO)_3$ fragments bonded to PMe_3 and phenanthroline ligands (in **36**), and to tridentate *N*,*N'*,*P* ligands from P-bonded methyl group deprotonation and nucleophilic attack on phen (**37**) and subsequent protonation or methylation (**38** and **39** respectively). The results are displayed in Figure 32 (ORTEP diagrams) and Table 6 (selected bond distances in Å and angles in °).

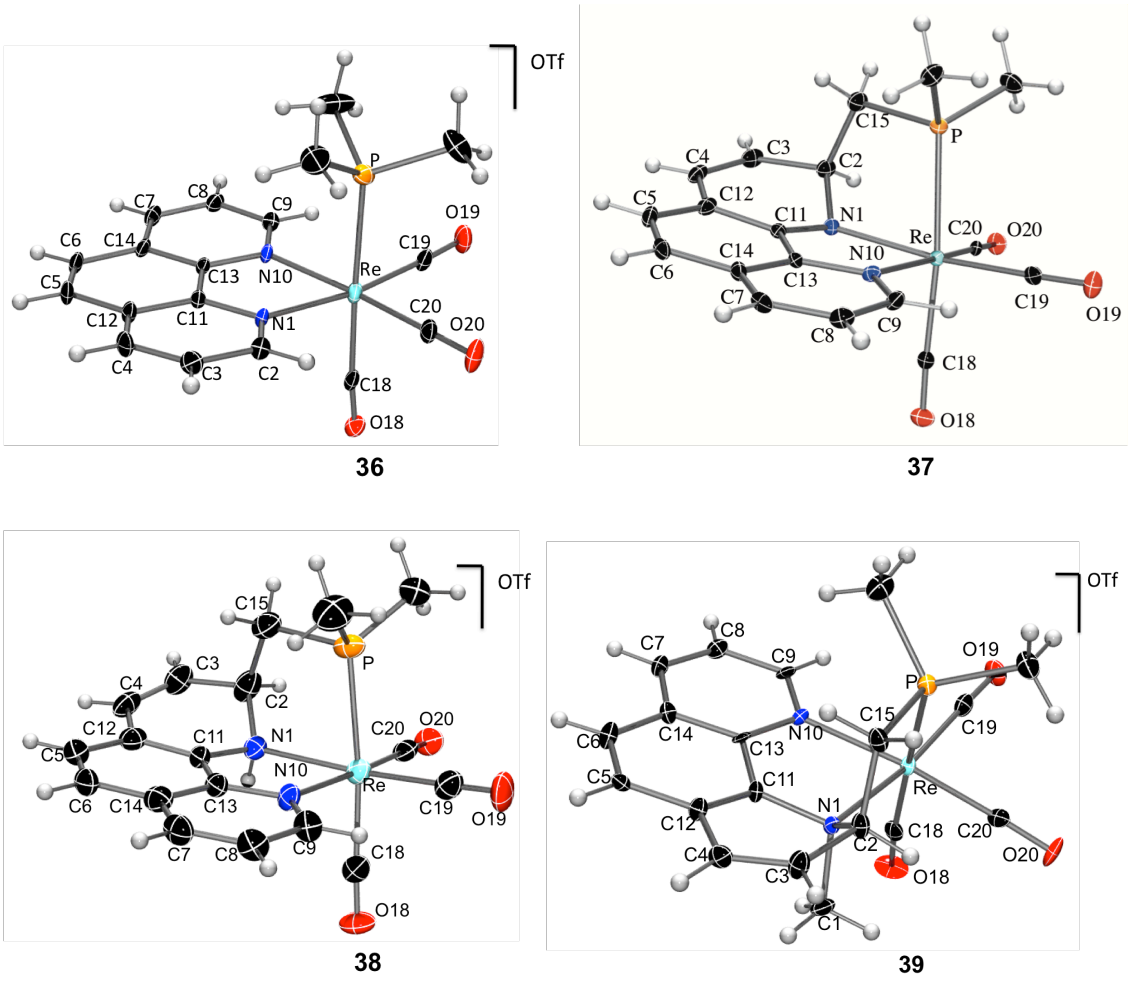


*Figure 32. Solid-state structure (thermal ellipsoids at 30% probability) of the cation in **36**, complex **37**, and the cations in **38** and **39**.*

	36	**37**	**38**	**39**
Re-N1	2.178(3)	2.131(4)	2.200(6)	2.251(7)
Re-N10	2.173(3)	2.202(4)	2.191(6)	2.195(7)
Re-P	2.447(1)	2.447(2)	2.435(2)	2.437(2)
Re-C18	1.988(4)	1.950(5)	2.00(1)	1.95(1)
Re-C19	1.919(4)	1.915(5)	1.94(1)	1.93(1)
Re-C20	1.913(4)	1.928(5)	1.944(9)	1.92(1)
C18-O18	1.115(5)	1.142(6)	1.12(1)	1.15(1)
C19-O19	1.152(5)	1.156(6)	1.11(1)	1.14(1)
C20-O20	1.159(5)	1.156(6)	1.13(1)	1.14(1)
N1-C2	1.340(5)	1.463(6)	1.43(1)	1.50(1)
C4-C3	1.376(7)	1.328(8)	1.33(2)	1.33(2)
C15-C2	-	1.563(7)	1.60(2)	1.52(1)
C12-C4	1.398(7)	1.449(7)	1.46(1)	1.47(1)
C8-C9	1.396(7)	1.398(7)	1.41(1)	1.40(1)
N1-C1	-	-	-	1.53(1)
C2-N1-C11	118.2(3)	115.4(4)	109.9(6)	108.2(7)
C11-N1-Re	114.3(2)	116.3(3)	111.6(5)	110.7(5)
C2-N1-Re	127.5(2)	117.6(3)	117.5(6)	113.6(5)
P-Re-C18	175.7(1)	170.9(1)	173.1(3)	175.9(3)
P-Re-N1	88.37(8)	75.8(1)	78.7(2)	78.7(2)
P-Re-N10	88.4(1)	94.2(1)	90.1(2)	91.5(2)
C2-N1-C1	-	-	-	108.8(7)
C15-C2-C3	-	107.1(4)	113.2(8)	109.2(8)
C1-N1-Re	-	-	-	108.8(6)

*Table 6. Selected bond distances (Å) and angles (°) in compound **36**, complex **37** and the cations in **38** and **39**.*

Complex **37**, and the cations in **38** and **39** show a distorted octahedral geometry around rhenium (*e. g*. P-Re-C18 angle is 170.9(1)° in **37**) and possess new five-member cycles due to the creation of the C15-C2 bond between the deprotonated group of the phosphane and C2 of phen. Due to the formation of the new cycle, the phosphane ligand leans significantly toward N1: the P-Re-N1 angle is 75.8(1)° in **37**, whereas the same

angle in **36** is 88.37(8)°. Dearomatization of the attacked pyridyl ring in **37**, and in the cations in **38** and **39** results in the loss of its planarity as a result of C2-sp^3 hybridization (*e*. *g*. C15-C2-C3 is 109.2(8)°, C15-C2-N1 is 110.5(8)° and C3-C2-N1 is 111.6(7)° for the cation in **39**). Distances in the phenanthroline-CH_2PMe_2 moiety in **38** and **39** are similar for both complexes and to those found in **37** (see Table 6).

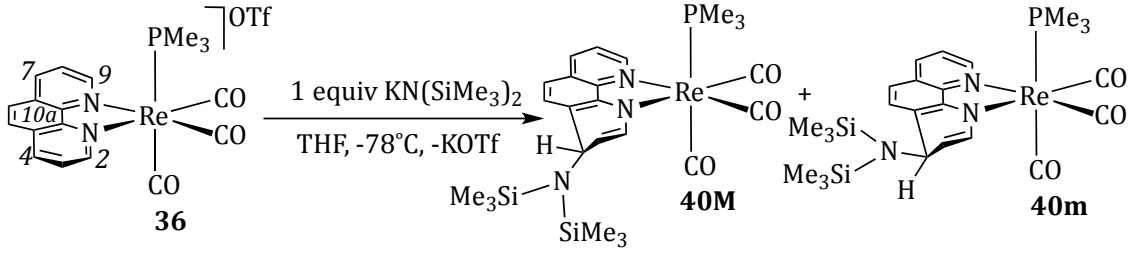
Complex **37** shows a Re-N1 distance (2.131(4) Å) slightly shorter than Re-N10 (2.202(4) Å), in agreement with N1 being an amido-type nitrogen. The sum of angles around N1 is 349.1(4)°, indicating a pyramidal at nitrogen geometry for the amido group.[68] The pyramidal amido in **37** stands in contrast with the planar amido found in the product of deprotonation of [Re(2,6-*i*Pr_2BIAN)$(CO)_3(PMe_3)$]OTf (**22**) (see Chapter 2). This difference could be attributed to the more effective delocalization of the BIAN amido lone electron pair toward the rhenium (via *p*π-*d*π donation) which delocalizes this excess of electronic density toward the carbonyl ligands.[50] The higher ability to delocalize the lone electron pair of the BIAN amido could be a result of its higher flexiblity for being engaged in only one cycle (the metallacycle formed as a result of the C-C coupling), in contrast to the amido in **37**, which is engaged in two cycles (the metallacycle and the pyridyl ring). The more effective electronic donation to the CO ligands in complex **23** is also supported by a larger decrease of the IR νCO band frequencies upon deprotonation (from 2039 and 1951 to 2006, 1908 and 1881 cm^{-1} in THF) in comparison to the shift in the deprotonation of **36** (2034, 1945 and 1920 to 2010, 1916 and 1888 cm^{-1}).

In contrast, **38** and **39** display slightly longer Re-N1 distances (2.200(6) Å in **38** and 2.251(7) Å in **39**) than that found in **37** (2.131(4) Å), as a result of the amino character of the group centered at N1, which forms weaker bonds with the metal than amide donors.

3.5 Intermolecular addition of $KN(SiMe_3)_2$ on phen in compound 36

When the reaction of **36** with $KN(SiMe_3)_2$ was monitored at low temperature in THF-d_8, an intermediate mixture consisting of compounds **40M** and **40m** was revealed. The **40M**:**40m** ratio (17:1) was established by integration of the ^{31}P NMR signals of the two

species. The molecular structures of **40M** and **40m** were determined by NMR, as discussed below. Compounds **40M** and **40m** were found to be neutral complexes formed as a result of the nucleophilic intermolecular attack of $^{-}N(SiMe_3)_2$ on the C4 position of the coordinated phen. As in the intramolecular nucleophilic addition that yields compound **37**, discussed above, the pyridine ring onto which nucleophilic addition took place became dearomatized. The products were found to be diasteromers which differ in the spatial orientation of the amido group (see Scheme 38).



*Scheme 38. Intermolecular reversible nucleophilic attack of $KN(SiMe_3)_2$ on C4(phen) in **36**.*

The **40M**, **40m** mixture was stable for at least 6 hours in THF-d_8 at 233 K and it could be stored overnight in toluene-d_8 at 253 K. At room temperature **37** was formed from **40M**, **40m** in 20 minutes in THF, and in 12 hours in toluene. ^{1}H and ^{31}P NMR monitoring of the transformation of **40M**, **40m** in **37** showed that, after reaching the appropriate temperature, signals of **37** appeared and grew at the expense of the signals of **40M**, **40m**.

The ^{1}H and ^{13}C NMR spectra of **40M**, **40m** (in THF-d_8) displayed signals for two asymmetric complexes, each containing an intact PMe_3 and two diasterotopic trimethylsilyl groups (two broad singlets 9H each at 0.26 and -0.07 ppm for **40M** in the ^{1}H NMR spectrum). The ^{1}H NMR spectrum featured eight signals for the phen ligand of each complex, four of which appear at typical chemical shifts for dearomatized pyridyl rings (between 6.50 and 4.37 ppm). Further confirmation of the presence of a dearomatized pyridyl ring was provided by the ^{13}C NMR spectrum (C4 signal at 50.4 ppm for **40M**) and the $^{1}H,^{15}N$-HMBC (crosspeak for an amido nitrogen at 94.0 ppm for **40M**). A $^{1}H,^{29}Si$-HMBC (see Figure 33) confirmed the position of the $N(SiMe_3)_2$ group at C4 of phen since it displays two crosspeaks between the H4 signal (at 5.80 ppm for **40M**) and the two diasterotopic silicon atoms (at 3.5 and 2.4 ppm for **40M**).

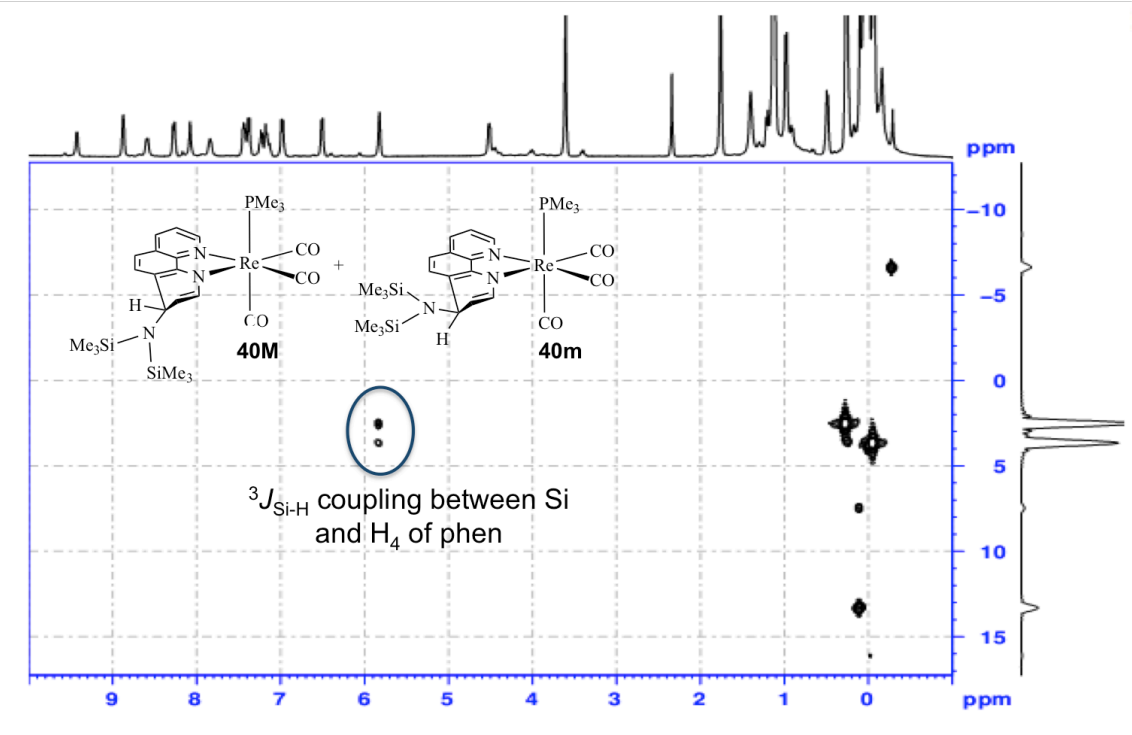


*Figure 33. ^{1}H, ^{29}Si-HMBC of **40M**, **40m** in THF-d_8 at 193 K*

The stereochemistry at the phen C4 atom in **40M** could be elucidated by a ^{1}H-^{1}H NOESY spectrum of the mixture, which showed a crosspeak between the signal of H4 and the methyl groups of PMe_3 (at 1.14 ppm), thus identifying **40M** as the diasteromer with the $N(SiMe_3)_2$ group on the phen face opposite to the phosphane. Due to its much smaller concentration in the mixture, a full assignment of the signals of the minor product, **40m**, could not be made. However, on steric grounds, **40m** is proposed to have the $N(SiMe_3)_2$ group on the phen face closer to the phosphane (see Scheme 38).

Aiming to further support the formulation of **40M**, **40m** as shown in Scheme 38, a ^{1}H DOSY (Diffusion Ordered Spectroscopy)[73] NMR experiment was carried out on a mixture of **40M**, **40m** and **37**. DOSY is a extremely useful NMR technique to estimate the size of a molecule in solution from its diffusion coefficient.[74] The translational diffusion coefficient (D_t) of a molecule can be related to its hydrodynamic radius (r_H) by the Stokes-Einstein equation (*eq. 1*).

$$D_t = \frac{kT}{6\pi\eta r_H} \qquad \text{(eq. 1)}$$

In eq. 1, k is the Boltzman constant, T the temperature (in K) and η the solvent viscosity. Eq. 1 is valid for spherical molecules moving with uniform velocity in the solvent and whose size is at least five times the size of the solvent molecules. According to *eq. 1*, smaller molecules would move faster in solution and, therefore, would have larger D_t values. Furthermore, for two molecules (**A** and **B**) in the same solution, a particularly useful relationship between their diffusion coefficients (*eq. 2*) can be obtained from the Stokes-Einstein equation. [75]

$$\frac{D_{tA}}{D_{tB}} = \frac{r_{HB}}{r_{HA}} \qquad (eq.\ 2)$$

Assuming that the two molecules have a spherical shape, *eq. 2* can be expressed in terms of the molecular weight of each molecule (*eq. 3*). [76]

$$\frac{D_{tA}}{D_{tB}} = \left(\frac{M_B}{M_A}\right)^{1/3} \qquad (eq.\ 3)$$

The ^{1}H DOSY experiment of **40M**, **40m** and **37** in toluene-d_8 (see Figure 34) afforded D_t values of $8.5 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ (for **37**) and $7.7 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$ (for **40M**) calculated from the ^{1}H NMR signals at 4.50 ppm for **40M** and 4.55 ppm for **37**. The $D_{t\mathbf{2}}/D_{t\mathbf{5M}}$ ratio is 1.32, in agreement with **40M** and **37** proposed formulations. Thus, $(M_{\mathbf{5M}}/M_{\mathbf{2}})^{1/3}$ is 1.31, where M has been calculated considering the formulations of **37** and **40M** proposed in Schemes 36 and 38.

Deprotonation of PMe_3 by $KN(SiMe_3)_2$ was accompanied by the formation of $HN(SiMe_3)_2$ which could be identified in both the ^{1}H and the ^{1}H DOSY NMR spectra (see Figure 34).

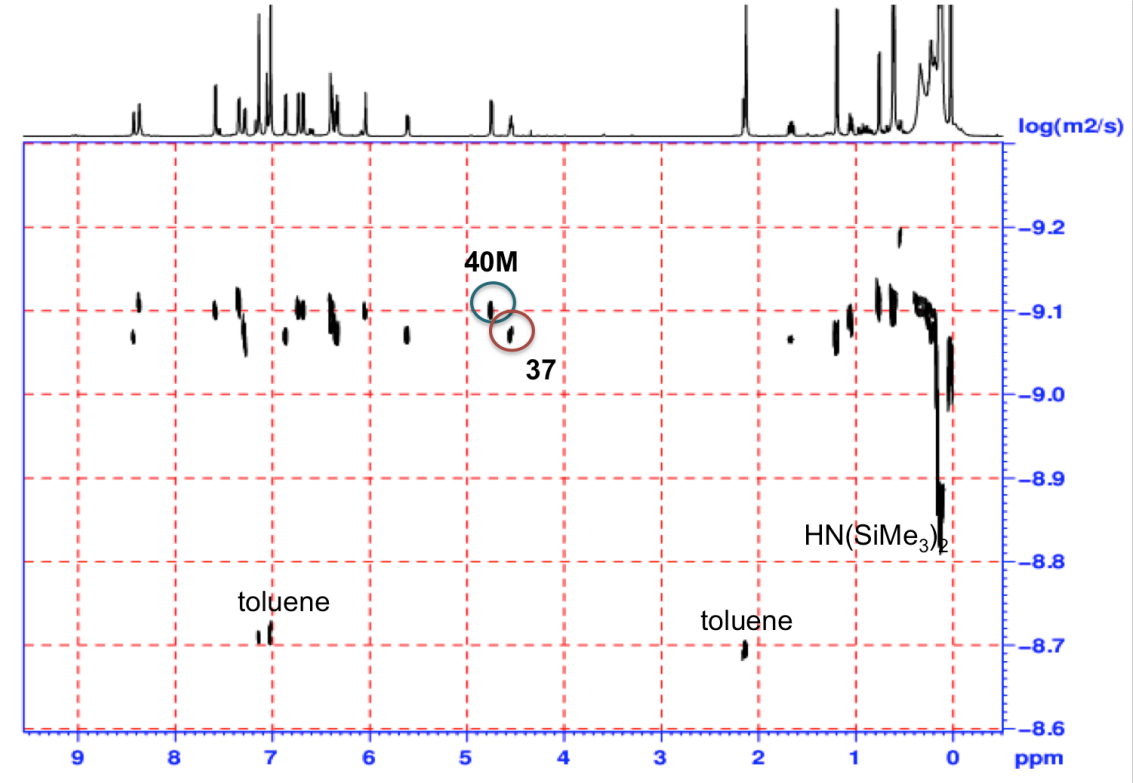


*Figure 34. ^{1}H DOSY NMR spectrum of a mixture of **40M, 40m** and **37** in toluene-d_8 at 298 K.*

The reaction of **36** with $KN(SiMe_3)_2$ has been investigated computationally employing DFT methods. Two different pathways have been considered, (a) intermolecular nucleophilic addition to the phen ligand or (b) deprotonation of PMe_3 by the amide followed by intramolecular addition to phen (see Figure 35). The transition state (*TS*) of the latter pathway was found to be higher in energy, thus at low temperature, intermolecular addition of the $(SiMe_3)_2N^-$ nucleophile on both faces of phen would occur (without a barrier). This addition affords **40m** (0.2 kcal·mol^{-1}) and **40M**, the most stable product (-2.6 kcal·mol^{-1}), and, consequently, the species formed in higher amount. The experimentally observed evolution of **40M**, **40m** toward **37** could be conceived to occur either as a concerted mechanism (for complex **40m**, in which the $N(SiMe_3)_2$ group is spatially closer to the hydrogen atoms of the coordinated phosphane) or by dissociation of the amide (for both, **40M** and **40m**) followed by deprotonation of coordinated PMe_3 by the amide. However, the long distance (5.118 Å) between the nitrogen of the amide and one of the hydrogens in the $P\text{-}CH_3$ group calculated on a computationally generated model, militates against this proposal and supports reversibility of the attack of $(SiMe_3)_2N^-$ on phen and deprotonation of the phosphane by free $(SiMe_3)_2N^-$ at higher

temperatures. Abstraction of a proton of the PMe_3 ligand in **36** yields **36*** (0.2 kcal·mol^{-1}), an experimentally undetected highly reactive species with a CH_2^- group. Two different pathways can be envisaged for the evolution of **36***, corresponding to the nucleophilic intramolecular addition to the two *ortho* positions (the two electrophilic positions geometrically accesible): (a) attack on C10a of phen to afford **37*** (-9.5 kcal·mol^{-1}) or (b) attack to C2 to afford **37** (-22.2 kcal·mol^{-1}). The second pathway was calculated to be slightly more accessible (with a kinetic barrier of 3.9 kcal·mol^{-1}) and to produce a much more stable species, in agreement with the experimental results.

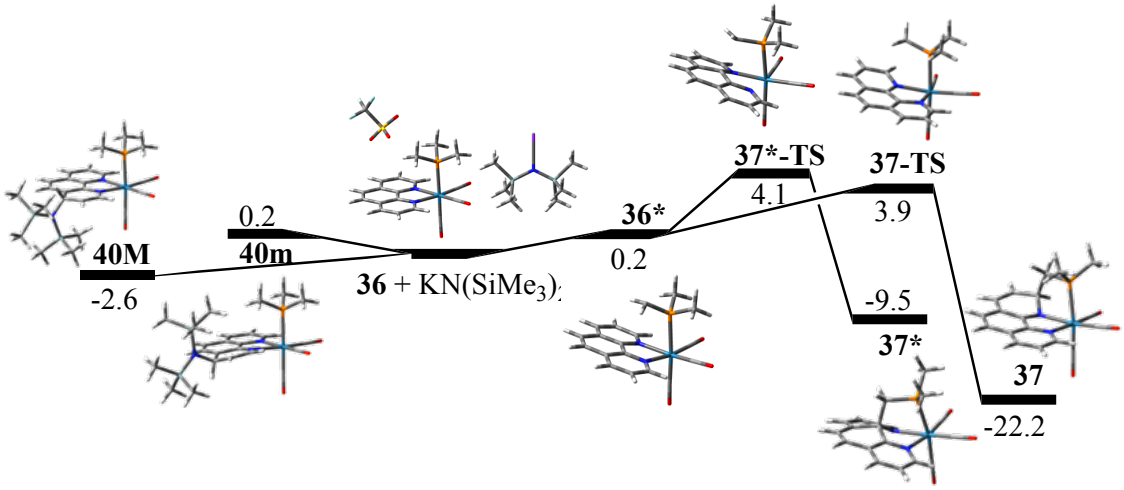
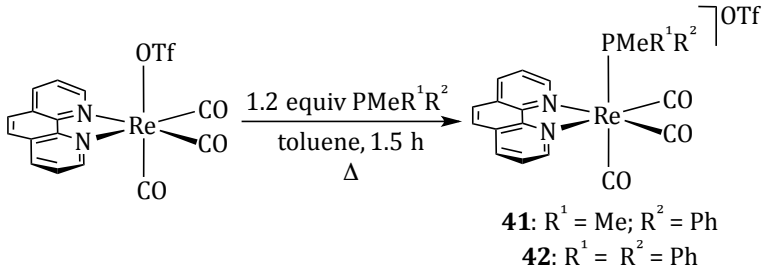


*Figure 35. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol^{-1}) for the reaction of **36** with $KN(SiMe_3)_2$ in THF. Energies are referred to the reactants.*

The results discussed above demonstrate that even the very bulky bis(trimethylsilyl)amide, which is conventionally considered as a non-nucleophilic base, can add to rhenium-coordinated 1,10-phenanthroline. However, low temperature NMR monitoring of the reaction of $[Re(bipy)(CO)_3(PMe_3)]OTf$ with $KN(SiMe_3)_2$ did not reveal the formation of products analogous to **40M**, **40m** with bipy instead of phen. DFT calculations on the addition of $^-N(SiMe_3)_2$ on position 4 of bipy revealed the resulting species to be too energetic to be formed (7.7 kcal·mol^{-1} and 13.0 kcal·mol^{-1} for the products analogous to **40M** and **40m** respectively).

3.6 Intermolecular addition of $KN(SiMe_3)_2$ to the phen ligand in $[Re(phen)(CO)_3(L)]OTf$ (L = $PPhMe_2$, PPh_2Me, PEt_3, SMe_2 and 1-methyl-2-ethylimidazole) complexes

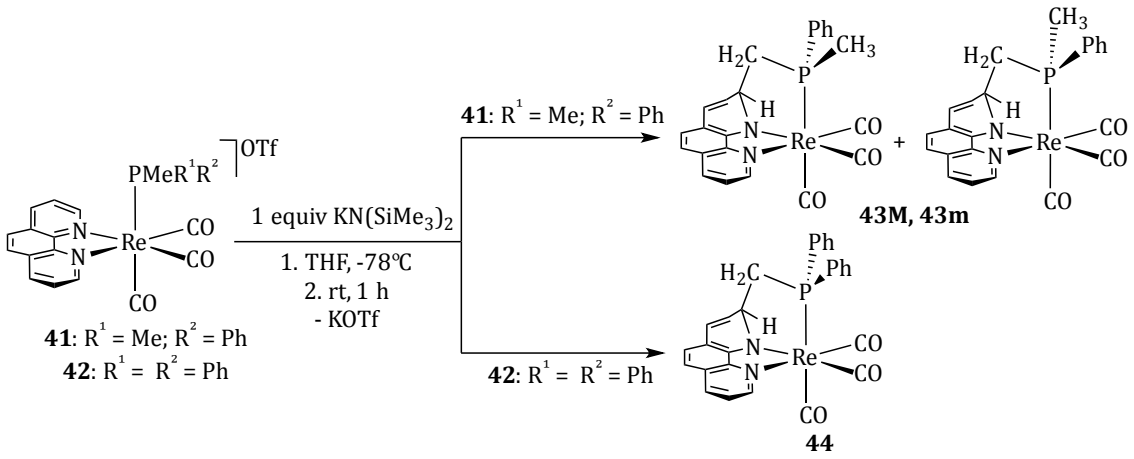
As it will be discussed below, addition of $KN(SiMe_3)_2$ to phen has been found to occur also in complexes analogous to **36** which contain monodentate ligands other than PMe_3, such as $PPhMe_2$, PPh_2Me, PEt_3, SMe_2 and 1-methyl-2-ethylimidazole (1-Me-2-EtIm).
The new compounds $[Re(phen)(CO)_3(PPhMe_2)]OTf$ (**41**) and $[Re(phen)(CO)_3(PPh_2Me)]OTf$ (**42**) were readily obtained in high yields (86% for **41** and 87% for **42**) by reaction of $[Re(phen)(CO)_3(OTf)]$ with a slight excess of the appropriate phosphane in refluxing toluene (Scheme 39).



*Scheme 39. Synthesis of $[Re(phen)(CO)_3(PPhMe_2)]OTf$ (**41**) and $[Re(phen)(CO)_3(PPh_2Me)][OTf]$ (**42**).*

Compounds **41** and **42** were fully characterized by IR, EA and NMR spectroscopy. IR νCO stretching bands of **41** and **42** were slightly higher (2034, 1946 and 1922 cm^{-1} for **41**, and 2037, 1949 and 1924 cm^{-1} for **42** in THF) than those of compound **36**, reflecting both the weaker σ-donor and the stronger π-acceptor character of $PPhMe_2$ and PPh_2Me in comparison to PMe_3.[61]

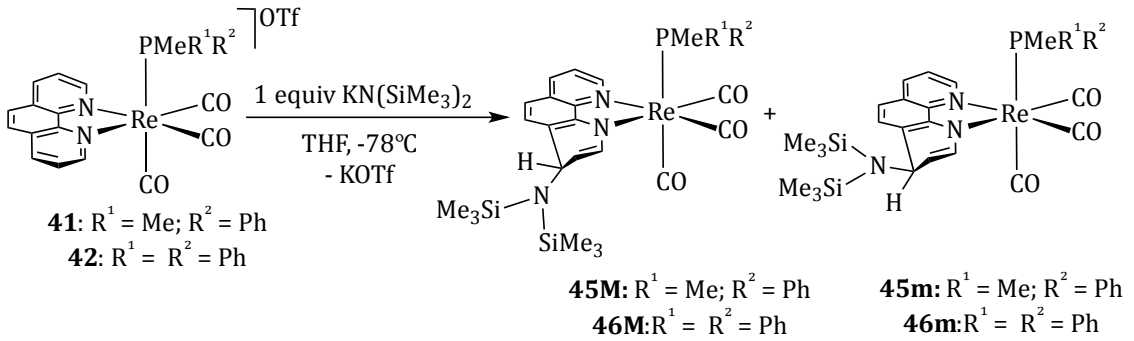
Addition of $KN(SiMe_3)_2$ to THF solutions of **41** or **42** yielded neutral products **43M**, **43m** and **44** respectively, which were characterized by IR, EA and NMR. NMR characterization showed that the new compounds featured a C-C bond between a deprotonated methyl group of the phosphane and C2 of phen (see Scheme 40).



*Scheme 40. Intramolecular nucleophilic additions triggered by deprotonation of methyl groups of $PPhMe_2$ and PPh_2Me in **41** and **42** respectively.*

Deprotonation of **41** yielded two diasteromers, **43M** and **43m** (in a 25:1 ratio as judged by ^{31}P NMR integration) due to the formation of four stereogenic centers in the reaction: Re, P, the amido nitrogen and the C2 atom of phen. Similar formation of two diasteromers has been also found in the deprotonation of $PPhMe_2$ coordinated to the $\{Re(i Pr_2BIAN)(CO)_3\}^+$ fragment (complexes **26M**, **26m** see Chapter 2).

Low temperature NMR monitoring of the formation of **43M**, **43m** and **44** revealed the presence of species resulting from intermolecular nucleophilic attack of $(SiMe_3)_2N^-$ on phen previous to the formation of the C-C coupling products. NMR characterization of the mixtures supported that the amide nucleophile added to both faces of phen in **41** and **42** to yield the diasteromeric mixtures **45M**, **45m** and **46M**, **46m** respectively (see Scheme 41).



*Scheme 41. Intermolecular nucleophilic addition of $(SiMe_3)_2N^-$ on the 4 position of the phen ligand of **41** and **42**.*

The increase in the steric profile of the phosphane (estimated by the Tolman conic angle which is 118° for PMe_3, 122° for $PPhMe_2$ and 136° for PPh_2Me)[61] due to the replacement of Me groups by Ph groups yielded mixtures with a higher relative amount of the less sterically hindered diasteromer (see Figure 36).

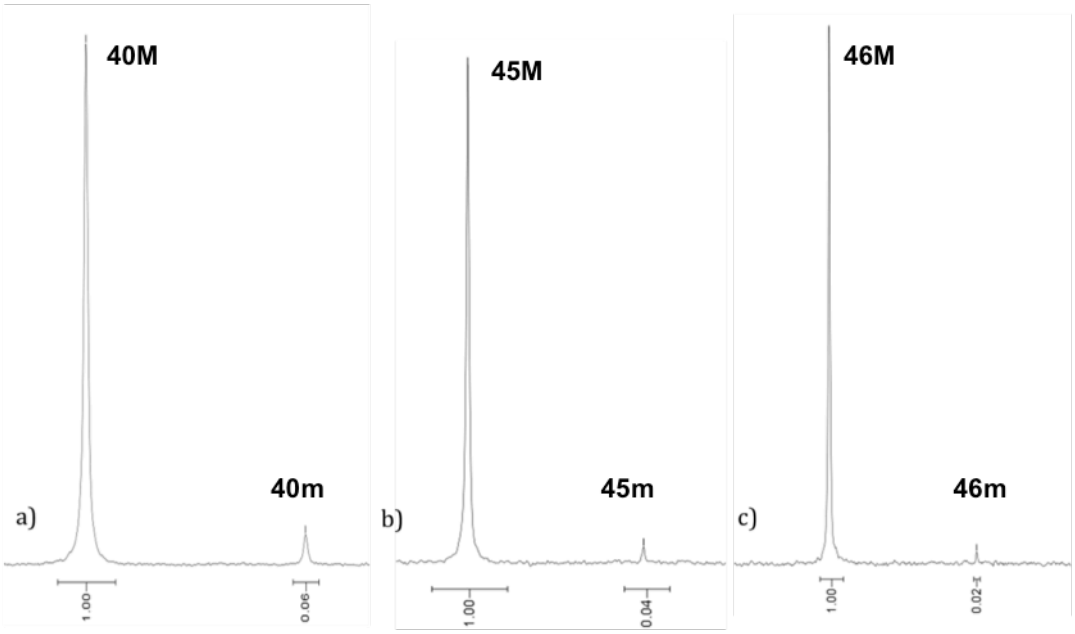
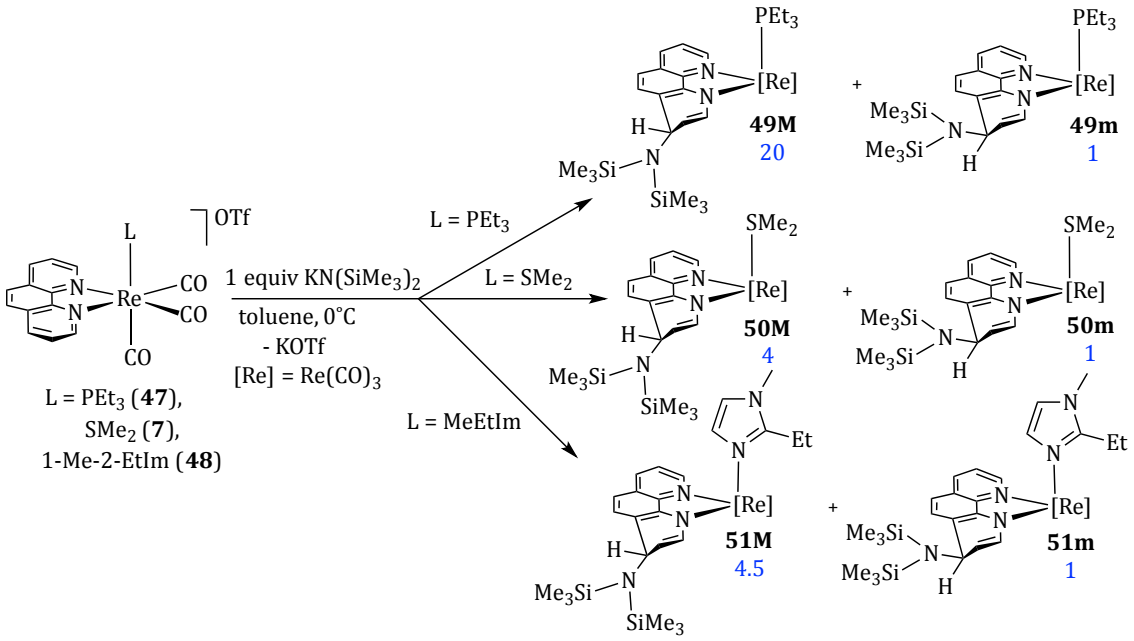


*Figure 36. ^{31}P NMR of mixtures obtained from addition of $KN(SiMe_3)_2$ to coordinated phen in a) $[Re(phen)(CO)_3(PMe_3)]OTf$ (**36**) b) $[Re(phen)(CO)_3(PPhMe_2)]OTf$ (**41**) and c) $[Re(phen)(CO)_3(PPh_2Me)]OTf$ (**42**)*

The mechanism for the formation of **43M**, **43m** and **44** is proposed to be similar to that for **37**: amide addition on phen is favored at low temperatures, and when the temperature is high enough to surmount the barrier for the deprotonation, the C-N bond breaks, and free amide deprotonates the methyl group of the phosphane ligand to yield the C-C coupling products (see above).

Addition of $KN(SiMe_3)_2$ to $[Re(CO)_3(phen)L]OTf$ (L = PEt_3 (**47**), SMe_2 (**7**), 1-methyl-2-ethylimidazole (1-Me-2-EtIm) (**48**), see Experimental Section for detailed synthetic procedures) also afforded diasteromeric mixtures from addition of the amide on C4 of phen (**49M**, **49m**, **50M**, **50m** and **51M**, **51m** respectively, see Scheme 42 and Figure 37).



*Scheme 42. Reaction of $[Re(CO)_3(phen)L]OTf$ (L = PEt_3 (**47**), SMe_2 (**7**), 1-methyl-2-ethylimidazole (1-Me-2-EtIm) (**48**)) with $KN(SiMe_3)_2$. Relative abundances of the products are shown below each product. [Re] = $Re(CO)_3$*

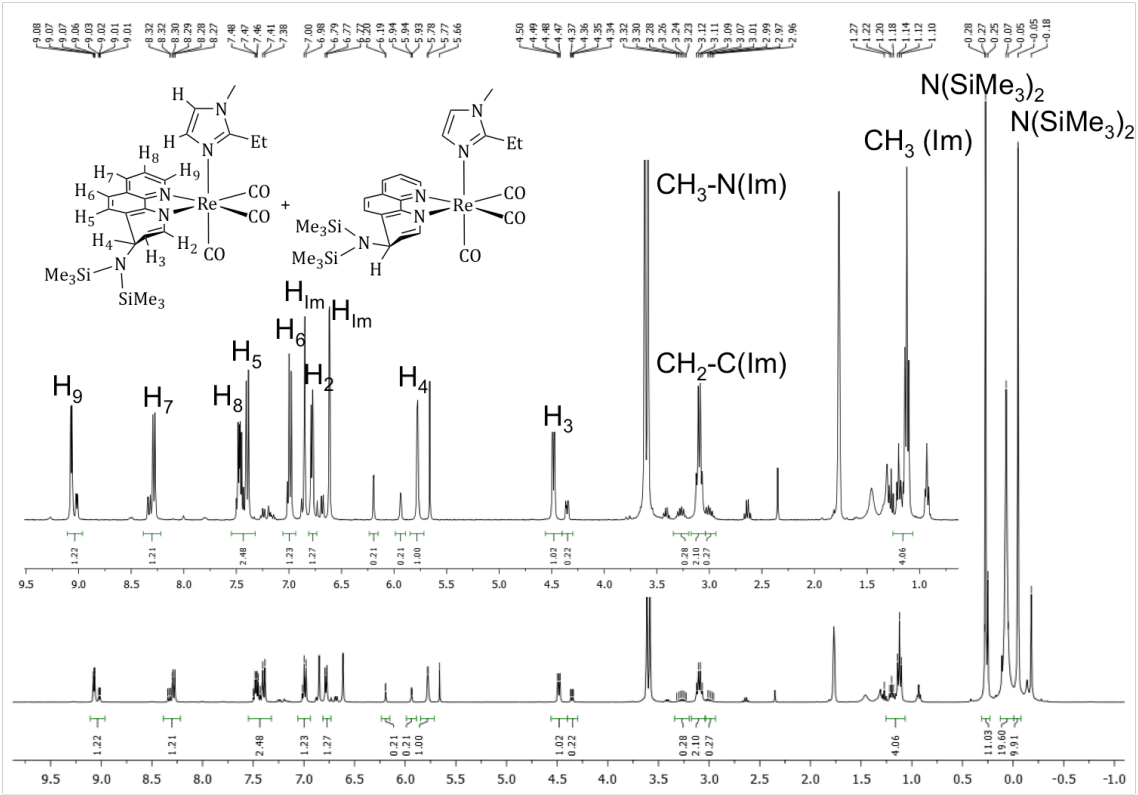


*Figure 37. ^1H NMR spectrum of the **51M**, **51m** mixture in THF-d_8 at 253 K. Signals of the major diasteromer **51M** are assigned.*

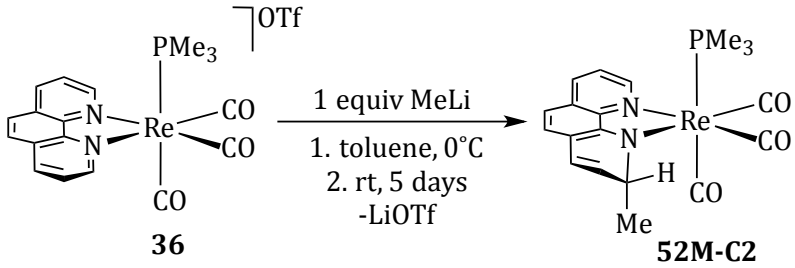
The fact that the **49M**:**49m** ratio (20:1) was found to be the highest is attributed to the higher steric hindrance opposed by the bulkier PEt_3 ligand to the approach of the nucleophile in the formation of **49m** in comparison with the smaller SMe_2 or 1-Me-2-EtIm ligands.

When the temperature was allowed to raise, the **50M**, **50m** mixture was found to transform into a product of C-C coupling as a result of SMe_2 deprotonation and intramolecular nucleophilic addition on C2 of phen (see Section 1.3 of Chapter 1), like in the reactions of $KN(SiMe_3)_2$ with **36**, **41** and **42** discussed above. However, the other mixtures were found to be stable at room temperature for several days in toluene-d_8 or THF-d_8 solution, and formation of C-C coupling products could not be detected. This is attributed to the weaker acidity of the CH bonds of PEt_3 and 1-Me-2-EtIm, which raises the deprotonation barrier, making it insurmountable at room temperature. Heating the mixtures of diasteromers to 50°C only afforded intractable mixtures of unidentified products (as judged by IR and NMR spectroscopy). However, after several days at room temperature, precipitation of a brown solid from the toluene-d_8 solutions of **49M**, **49m** and **51M**, **51m** was observed. ^1H and ^{31}P NMR spectra of CD_2Cl_2 solutions of the brown solids revealed the precipitates to mainly consist of species containing the cationic complexes present in the precursor (compounds **47** and **48**, respectively), impurified with minor amounts of unknown species containing aromatic phen rings. The nature of these reactions is unknown, and the participation of atmospheric oxygen, moisture, or both, seems likely. Moreover, these observations support the idea that the nucleophilic addition of $KN(SiMe_3)_2$ on coordinated phen is reversible.

3.7 Intermolecular additions of organolithium reagents (RLi, R = Me, *n*Bu, *t*Bu) on coordinated phenanthroline

As previously described, the phen ligand of compound **36** undergoes the nucleophilic addition by the bulky, typically non-nucleophilic $KN(SiMe_3)_2$ amide. Aiming to find similar additions to coordinated phen, the reactivity of **36** with organolithium compounds was studied. Thus, MeLi (1.6 M solution in diethyl ether) was added to a toluene suspension of **36** at 0°C and, after stirring the resulting solution at room

temperature for 5 days, a new compound (**52M-C2**) was isolated in moderate yield (38%) and characterized by IR, 1D and 2D NMR, EA and X-ray diffraction. IR νCO bands were consistent with a neutral *fac*-$Re(CO)_3$ complex (2014, 1920 and 1887 cm^{-1} in toluene) and ^1H NMR spectrum of **52M-C2** showed signals for a dearomatized pyridyl ring with a methyl group bonded to C2 (see Scheme 43; signal for the phen-bonded methyl group occurred as a doublet at 1.59 ppm in the ^1H NMR spectrum and showed a cross-peak with the signal at 4.73 ppm (identified as H2) in the ^1H,^1H-COSY spectrum, see Figure 38 for the ^1H NMR spectrum of **52M-C2**).



*Scheme 43. Preparation of **52M-C2** by reaction of **36** with MeLi.*

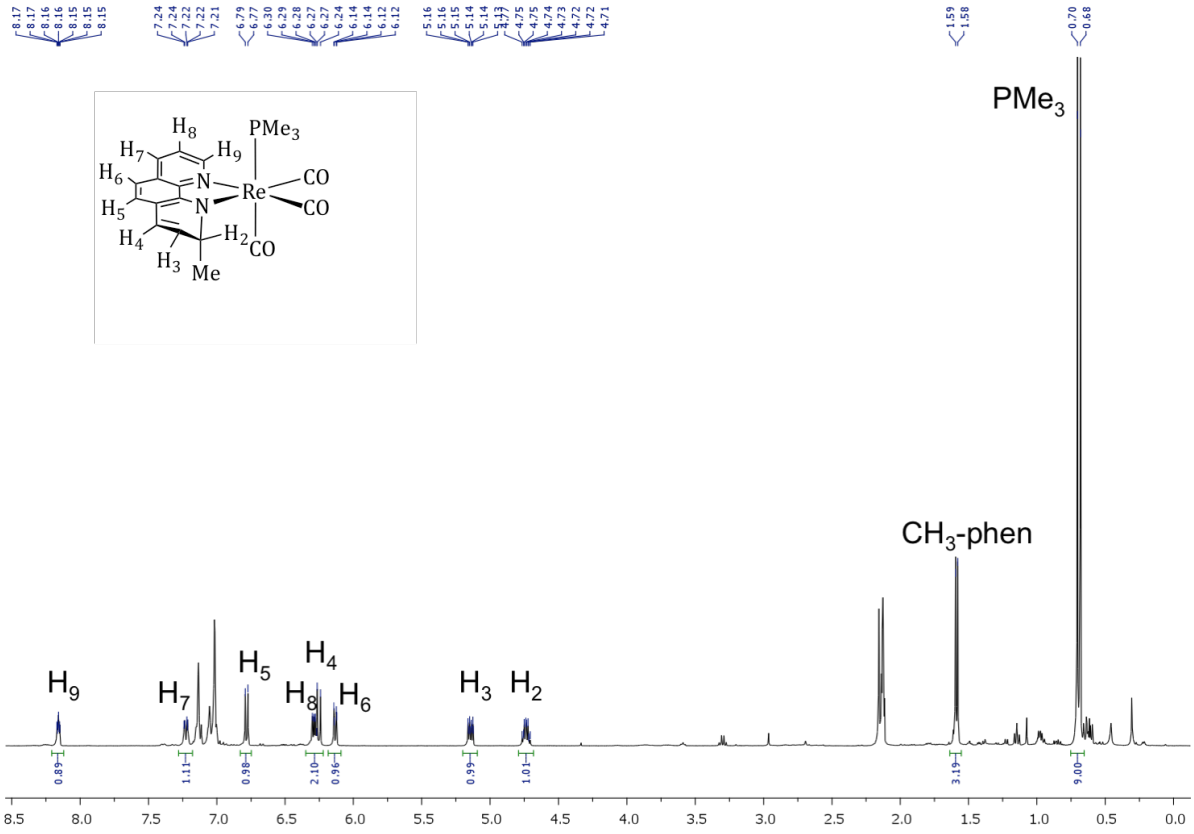


*Figure 38. ^1H NMR spectrum of **52M-C2** in toluene-d_8 at 298 K.*

Like compound **37**, discussed above, **52M-C2** is also a neutral complex containing a dearomatized pyridine ring resulting from the nucleophilic attack –intramolecular in **37**, intermolecular in **52M-C2**- on the C2 atom of the phen ligand (see Figure 39 and Table 7).

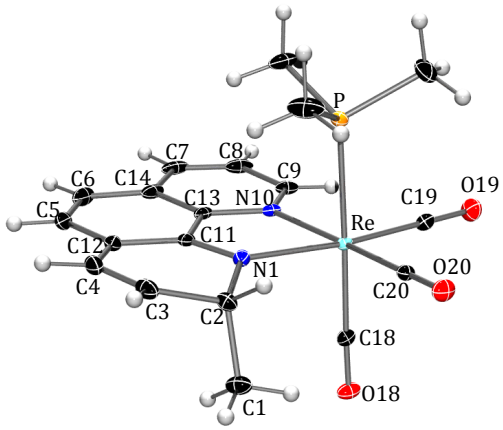


*Figure 39. Solid state structure (thermal ellipsoids at 30% probability) of **52M-C2**.*

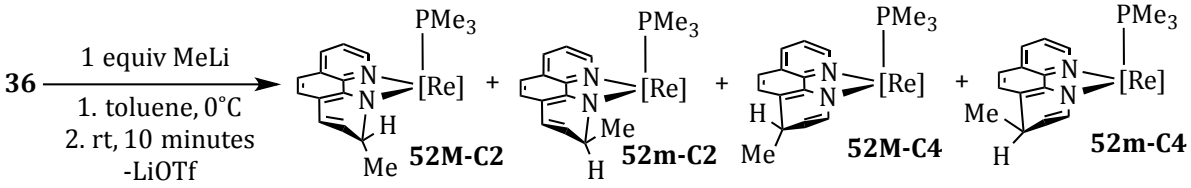
Re-N1	2.151(2)
Re-N10	2.164(2)
Re-P1	2.4631(7)
Re-C18	1.949(3)
Re-C19	1.918(3)
Re-C20	1.922(3)
C18-O18	1.148(3)
C19-O19	1.161(3)
C20-O20	1.148(3)
C1-C2	1.535(4)
N1-C2	1.469(4)
C4-C3	1.327(5)
C12-C4	1.442(5)
C9-C8	1.408(4)
N10-C9	1.331(4)
C2-N1-C11	118.7(2)
C11-N1-Re	115.4(2)
C2-N1-Re	124.7(2)
C1-C2-C3	109.7(2)

*Table 7. Selected bond distances (Å) and angles (°) of compound **52M-C2**.*

The structural differences between **37** and **52M-C2** in the geometry around Re can be mainly attributed to the presence of the new five-member cycle in **37**, responsible of the deviation from the octahedral geometry. Thus, the angles in **52M-C2** are closer to those expected for a regular octahedral geometry (*e. g*. P-Re-C18 is 178.62(8°), P-Re-N1 is 85.50(6)° and P-Re-N10 is 86.88(6)°), and the sum of the angles around N1 is much closer to 360° (358.8(2)°), than in **37** (349.3(4)°, see above), indicating the amido in

52M-C2 to be planar. The presence of a pyramidal amido in **37** could thus be attributed to the strain imposed by the new five-member ring, while the amido in **52M-C2**, which does not belong to a new cycle, is able to delocalize more effectively its lone electron pair and acquire a planar geometry around N.

NMR characterization of the reaction crude showed it to be a mixture of four species, **52M-C4**, **52m-C4**, **52M-C2, 52m-C2** (in a 7:2:10:1 ratio), and a ^{1}H,^{1}H-DOSY experiment revealed similar diffusion coefficients for the four species, supporting their formulation as isomers. 1D and 2D NMR spectra of the products confirmed that they are isomers and showed that they differ on the position of attack by MeLi (C2 or C4 of phen) and on the stereochemistry of the attacked carbon (the Me group can be on the opposite (**M**, major) or on the same phen face (**m**, minor) with respect to the PMe_3 ligand (as shown in Scheme 44).



*Scheme 44. Nucleophilic addition of MeLi to the phen ligand of **36**. [Re] = Re(CO)$_3$*

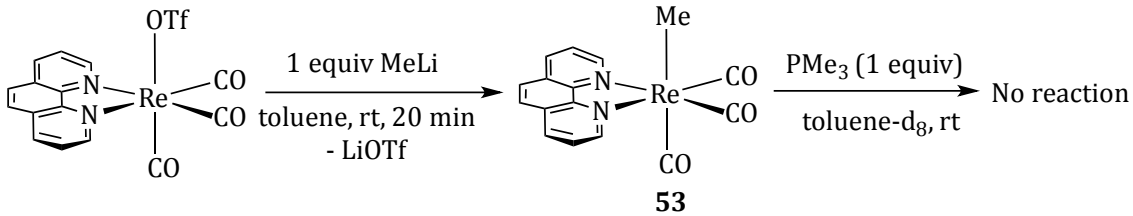
^{1}H NMR signals of H2 and H4 for **52M-C2** and **52M-C4** were unequivocally assigned on the basis of the ^{1}H, ^{13}C-HSQC and ^{1}H, ^{13}C-HMBC spectra. For **52M-C4** the ^{1}H, ^{1}H-COSY spectrum showed a cross-peak between the methyl group signal at 1.33 ppm and H4 signal at 4.03 ppm, supporting the methyl group to be bonded to C4 of phen. Phen signals of **52m-C2** and **52m-C4** were obscured in the ^{1}H NMR spectrum by signals of the major compounds. Therefore, the connectivity **52m-C2** and **52m-C4** was proposed on the basis of the cross-peaks found for their methyl groups in the ^{1}H,^{13}C-HMBC spectrum which were similar to those for **52M-C2** and **52M-C4** respectively, supporting the methyl group to be bonded to C2 in **52m-C2** and to C4 in **52m-C4**.

The stereochemistry of the attacked carbon atoms could be elucidated on the basis of a ^{1}H, ^{1}H-NOESY spectrum which showed cross-peaks between the H2 and H4 signals of **52M-C2** and **52M-C4** respectively, and signals for the methyl groups of the PMe_3, confirming that the methyl group was on the opposite side from the phosphane in the major species. Therefore, on the basis of steric grounds, the minor species, **52m-C2** and

52m-C4, could be proposed to contain the methyl group on the same face than the phosphane.

NMR monitoring of the mixture **52M-C2**, **52m-C2**, **52M-C4**, **52m-C4** in toluene-d_8 at room temperature showed the amount of all the species present in solution to decrease over time at different rates accompanied by the precipitation of a brown solid. Phen-bonded methyl group ^{1}H NMR integration against C_6Me_6 as internal standard afforded $t_{1/2}$ of 1 h, and 10 h and 40 min for **52m-C2** and **52m-C4** respectively. $T_{1/2}$ of **52M-C2** and **52M-C4** were found to be longer than 3 days, with a faster disappearance of the **52M-C4** methyl signal (in comparison with **52M-C2**). A ^{1}H NMR spectrum in CD_2Cl_2 showed the brown solid to consist of several species containing rearomatized rings, and its IR spectrum in CH_2Cl_2 was consistent with a mixture of cationic rhenium tricarbonyl compounds. Rearomatization of the phen ligands in **52M-C2**, **52m-C2**, **52M-C4**, **52m-C4** complexes by formal hydride loss would afford cationic complexes, which would precipitate from toluene-d_8. An obvious possibility is hydride abstraction by traces of dioxygen from the atmosphere. This proposal would explain the different observed decomposition rates: those compounds with the more accessible hydride, *i*. *e*., those whose hydrogen atom points toward the opposite face from the phosphane (**52m-C2** and **52m-C4**) would be less stable towards atmospheric oxygen.

Freshly prepared [Re(phen)$(CO)_3$(Me)] (**53**) did not react with the equimolar amount of PMe_3 upon 1 hour at room temperature (Scheme 45) showing that nucleophilic attack of MeLi on phen in **36** does not proceed by PMe_3 displacement by the methyl to form **53** followed by an intramolecular metal-to-phen migration of the methyl group.



*Scheme 45. Synthesis of [Re(phen)$(CO)_3$(Me)] (**53**) and attempted reaction with PMe_3.*

DFT calculations on the mechanism of the reaction of **36** with MeLi (see Figure 40) showed nucleophilic attack on phen to occur with a lower energy barrier (11.8 and 9.6 kcal·mol^{-1} for **52M-C2** and **52M-C4** respectively) than deprotonation of phosphane

(16.2 kcal·mol^{-1}). The similar kinetic barriers for the formation of the products (11.8 and 9.6 kcal·mol^{-1} for **52M-C2** and **52M-C4** respectively) are in agreement with the experimental formation of both in the reaction.

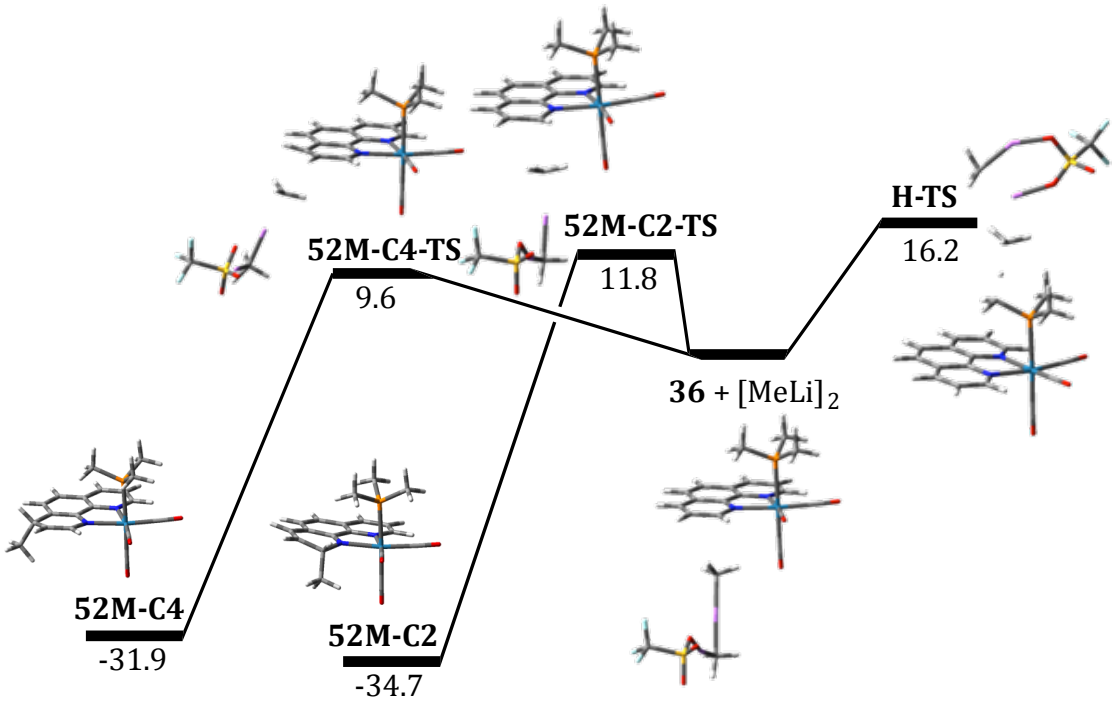
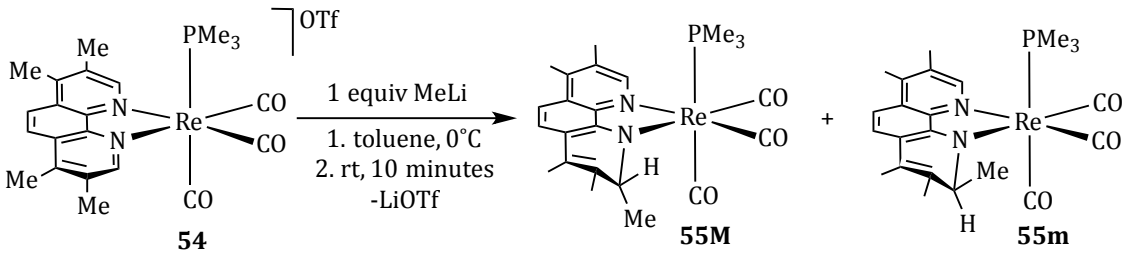


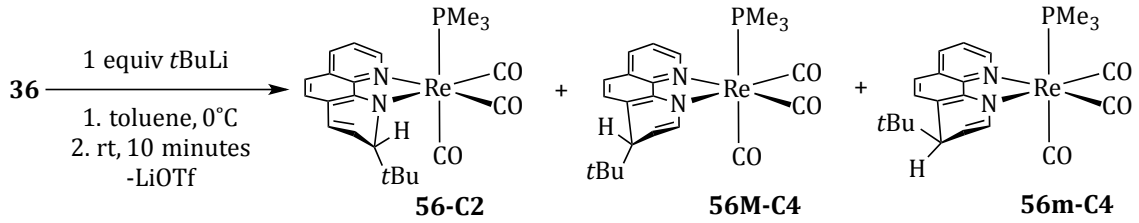
*Figure 40. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol^{-1}) for the reaction of **36** with [MeLi]$_2$[77] in toluene. Energies are referred to the reactants. Only results for the most abundant products, **52M-C2** and **52M-C4** are shown.*

Reaction of [Re(Me$_4$phen)(CO)$_3$(PMe$_3$)]OTf (**54**, Me$_4$phen = 3,4,7,8-tetramethyl-1,10-phenanthroline) with MeLi afforded two products, both containing a new methyl group on position 2 of phen (**55M** and **55m**, see Scheme 46). The increase of steric hindrance due to the presence of methyl substituents at position 4, probably in combination with the increase in electron density due to the electron-releasing effect of the methyl groups, is proposed to disfavor the addition to position 4.



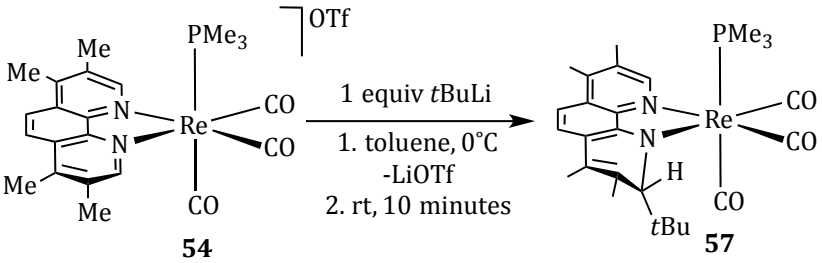
*Scheme 46. Reaction of [Re(Me$_4$phen)(CO)$_3$(PMe$_3$)]OTf (**55**) with MeLi.*

Addition of *t*BuLi to **36** resulted in the formation of three species, **56-C2**, **56M-C4** and **56m-C4** (in a 0.4:1:0.7 ratio based on ^{31}P signal integration, see Scheme 47).



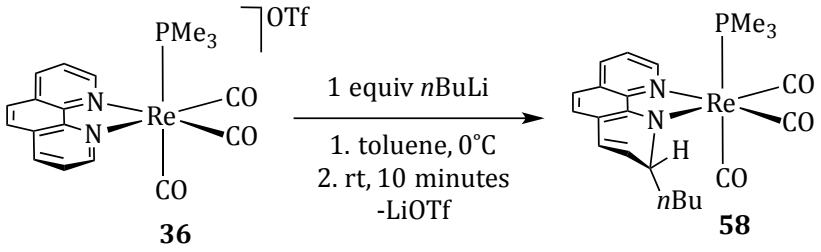
*Scheme 47. Reaction of **36** with tBuLi.*

Obviously, sterics play an important role in the addition of the bulky *tert*-butyl group: only the less abundant product (**56-C2**) beared the *t*Bu group on the C2 atom of phen, and this product was formed only as the diasteromer with the *t*Bu group on the phen side opposite to PMe_3. Presumably, addition to position 2 of phen is sterically more hindered than to position 4, since C2 is closer to the bulky metal fragment. Therefore, attack on position 2 of phen would be disfavored for bulky nucleophiles (such as *t*Bu). Selective addition of *t*BuLi on C2 of phen is obtained in the reaction of [Re(Me_4phen)(CO)$_3$(PMe_3)]OTf (**54**), shown in Scheme 48, where attack to position 4 is disfavored by the presence of the methyl substituent on C4. The product, **57**, featured a *t*Bu group bonded to the C2 position of the Me_4phen ligand on the opposite side of the phosphane (from a ^{1}H-^{1}H NOESY experiment). Note that products from alkyl addition on C2 of pyridines are usually formed as kinetic products which evolve to the C4 thermodynamically stable species by alkyl migration.[71] However, although in this case the low yield of the reaction (14 %) did not allow to rule out the formation of C4 addition products, the characterization of a unique C2 addition species by NMR points to a higher stability of the C2 addition product, probably due to the presence of methyl groups on C4 of the phenanthroline.



Scheme 48. Intermolecular addition of tBuLi on C2 of Me_4phen

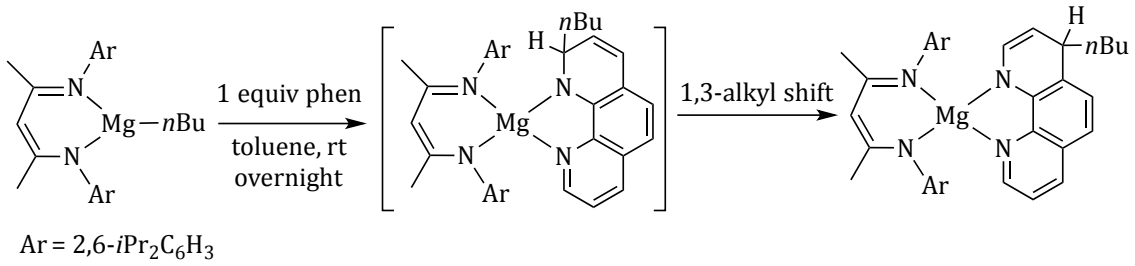
Addition to C2 of phen also occured in the addition of *n*BuLi to **36** yielding complex **58** (see Scheme 49). A NOESY experiment indicated that the butyl group resides on the less sterically hindered face of phen (opposite to PMe_3). The preferential attack to the C2 position could be due to a more electrophilic character of this position, in contrast with the addition of *t*BuLi discussed above; for the less bulky butyl group, this electronic preference would not be overcome by sterics. However, due to the low yield of the reaction (38%), nucleophilic attack on C4 could not be discarded.



*Scheme 49. Reaction of **36** with nBuLi.*

The species resulting from addition of *n*BuLi and *t*BuLi to coordinated phen, like those resulting from addition of MeLi, precipitated as a brown material containing aromatic phen complexes from a toluene-d_8 solution after several hours at room temperature, presumably due to oxidation by traces of atmospheric oxygen.

Nucleophilic attack of *n*BuLi to position 2 of rhenium coordinated phen in **36** stands in contrast to the results of the same addition reported by Hill and co-workers in a magnesium complex. Intramolecular magnesium-to-phen *n*Bu group migration exclusively yielded the product from addition at C4 of phen.[21] The authors hypothesized that nucleophilic attack of the *n*Bu initially occurs at the more electrophilic 2 position to yield a kinetic species which undergoes a 1,3-alkyl shift to yield the more stable C4-substituted product (see Scheme 50). However, the C2-substituted product is a proposal and could not be spectroscopically detected.

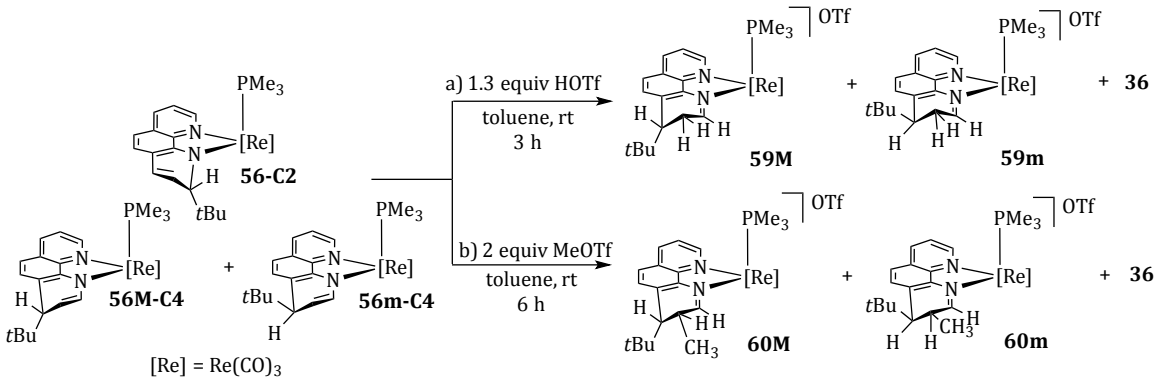


Scheme 50. Intramolecular magnesium-to-phen n-butyl group migration reported by Hill and co-workers.

Formation of species from nucleophilic attack at C4 from 1,3-alkyl shift of the 2-substituted phen in complex **58** has not been detected by NMR monitoring, and a toluene-d_8 solution of **58** did not show products from 1,3-butyl migration in 14 hours at room temperature.

The mixture of products resulting from nucleophilic attack of *t*BuLi to phen (**56-C2**, **56M-C4** and **56m-C4**) reacted with HOTf and with MeOTf. In both cases it took longer than 3 hours for the reactions to reach completion, in contrast with the same reactions in compound **37**, which are instantaneous, as mentioned above.

The 1D and 2D NMR characterization of the products (**59M**, **59m** for the reaction with HOTf and **60M**, **60m** for the reaction with MeOTf) indicated that the protonation and methylation occur at the C3 atom of the pyridyl ring (see Scheme 51 and Figure 41 for the ^{1}H NMR of **59M**, **59m**). In both cases, two diasteromers bearing the *t*Bu group on position 4 of phen were formed in the reaction (in a 1:0.6 ratio for both mixtures, from ^{1}H NMR integration) accompanied by [Re(phen)(CO)$_3$(PMe$_3$)]OTf (**1**). The **59M**:**59m** and **60M**:**60m** ratios were similar to **56M-C4**:**56m-C4** suggesting that **M** products were formed from **56M-C4** and **m** products from **56m-C4.** As a consequence, the products **M** and **m** differ on the stereochemistry of C4 (see Chapter 2).



*Scheme 51. Reaction of **56-C2**, **56M-C4**, **56m-C4** mixture with a) HOTf and b) MeOTf. [Re] = $Re(CO)_3$.*

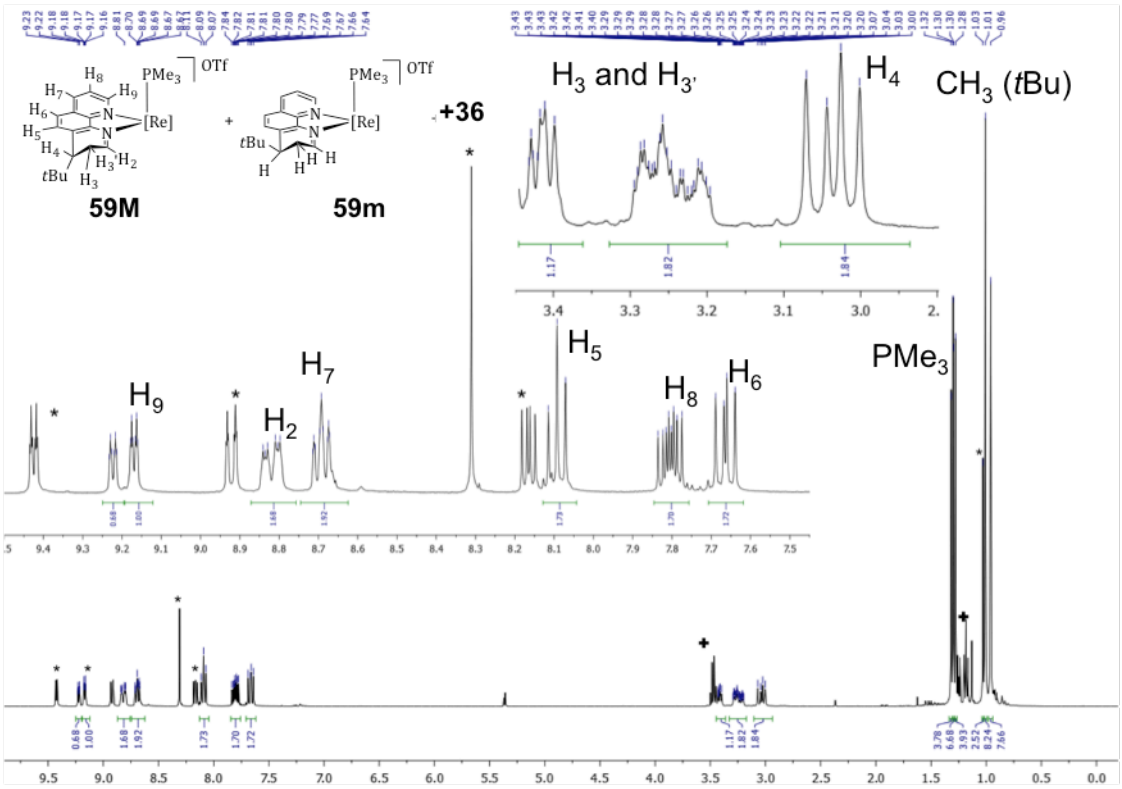
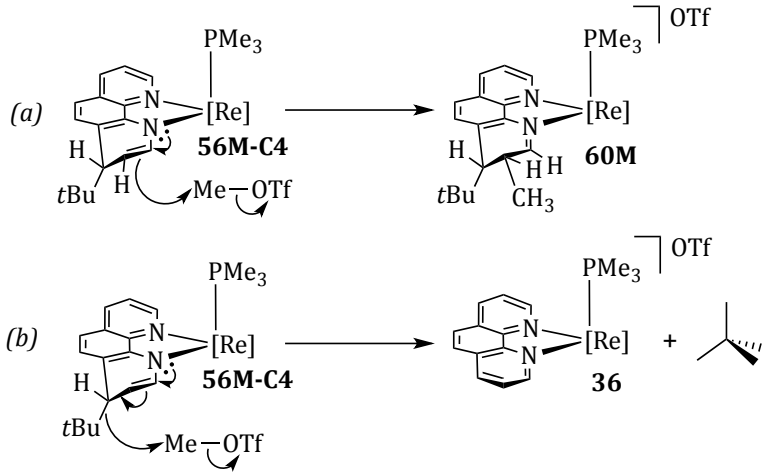


*Figure 41. ^{1}H NMR spectrum of **59M**, **59m** in CD_2Cl_2 at 298 K. * denotes **36** signals and + denotes residual diethylether. Signals of **59M** are assigned.*

The stereochemistry of the carbon atoms in **60M** and **60m** depicted in Scheme 51 is proposed on the basis of the ^{1}H NMR spectrum, which showed a singlet for the hydrogen in position 4 of phen, supporting a *cis* disposition of H_3 and H_4 in both **60M** and **60m**. Therefore, **60M** is the *RRS* diasteromer and **60m** the *SSS* (the stereogenic centers follow the order C-(*t*Bu), C-(Me) and Re).[46]

The formation of **36** in the reactions of **56-C2**, **56M-C4** and **56m-C4** with HOTf or MeOTf could be attributed to the protonation or methylation of the phen-bonded *t*Bu group yielding 2-methylpropane and 2,2-dimethylpropane respectively as byproducts, which are gases at room temperature and, therefore, would be eliminated when the reaction mixture was dried *in vacuo*. In these reactions, the two electrons of the *t*Bu-phen bond would be used to create the new *t*Bu-H or *t*Bu-Me bonds and, concomitantly, the two electrons of the lone pair on the amido group would rearomatize the pyridyl ring, as shown in Scheme 52.



*Scheme 52. Proposed mechanism of the reaction of **56M-C4** with MeOTf to afford (a) **60M** and (b) **36**. [Re] = $Re(CO)_3$.*

In the crude mixtures obtained from the reactions with HOTf or MeOTf (Scheme 51), no products could be detected with the *t*Bu group on the C2 position of phen, *i. e.*, from protonation or methylation of complex **56-C2**. Compound **56-C2** can be expected to be less stable than its isomers **56M-C4** and **56m-C4** due to steric hindrance, since the bulky *tert*-butyl group in **56-C2** is closer to the bulky metal fragment. This lower stability could make **56-C2** more prone to undergo the reaction affording **36** discussed above (Scheme 52b), in which the *tert*-butyl group is eliminated as either 2-methylpropane or neopentane.

Perhaps the most salient feature in the reactions shown in Scheme 51 is that the protonation and methylation do not take place at the amido nitrogen. A possible reason is the increase in the electron density of the phen carbon atom adjacent to the *t*Bu substituent, which is a strongly electron-releasing group. On the other hand, it must be

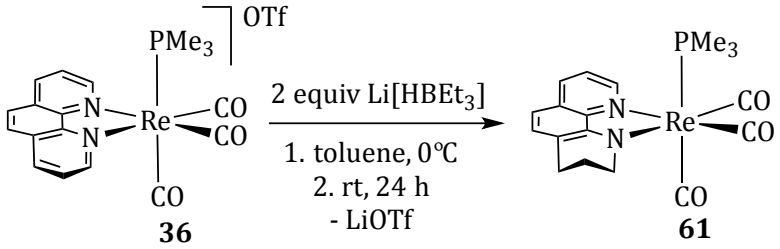
noted that a planar amido is present in **52M-C2** (see above), and similar geometries can be expected for the products of addition of the other RLi reagents (R = Bu, *t*Bu). In contrast, a pyramidal, presumably more nucleophilic amido ligand is present in **37**, therefore, methylation and protonation occurs at the nitrogen. Examples of protonation on a carbon atom of a dearomatized pyridyl ring have been recently found in our group from reaction of products with a dearomatized bipy (compounds **19** and **30** in Chapter 2) or with a dearomatized substituted bipy[35a] with HOTf. However, methylation-at-carbon has never been previously found.

The regioselectivity and number of the products in the additions of RLi to coordinated phen stand in contrast to those found for bipy (see Chapter 2). In general, additions of RLi to coordinated phen in $[Re(CO)_3(phen)(PMe_3)]OTf$ (**36**) yielded products (as mixtures or single species) from addition to positions *ortho* (C2) and/or *para* (C4) resembling the reactivity of free pyridines toward nucleophiles (see Introduction). However, additions of RLi to coordinated bipy in $[Re(bipy)(CO)_3(PMe_3)]OTf$ (**14**) yielded single species from addition to positions 2 (for MeLi and BuLi) and 5 (for *t*BuLi), a reactivity previously unknown (see Chapter 2).

3.8 Intermolecular addition of hydride on coordinated phen in $[Re(phen)(CO)_3(PMe_3)]OTf$ (36)

Addition of excess $Li[HBEt_3]$ to a toluene suspension of **36** yielded a dark green solution which turned dark blue upon stirring at room temperature for 24 hours. The IR of the product (**61**) was consistent with the formation of a single neutral species with three IR νCO bands (2012, 1917, 1884 cm^{-1} in toluene), ruling out addition of hydride on CO ligands or substitution of one of the carbonyl ligands by hydride.

1D, 2D NMR characterization of **61** revealed the presence of a single product where two double bonds of a pyridyl ring of phen have been reduced (see Scheme 53).



*Scheme 53. Reaction of **36** with excess Li[HBEt$_3$].*

The ^{1}H NMR spectrum of **61** showed signals for an aromatic benzo-pyridyl group, three multiplets for three CH_2 groups and a doublet for an intact PMe_3 ligand (see Figure 42). The ^{13}C DEPT-135 NMR spectrum showed three signals in opposite phase to CH signals (at 54.7 ppm for C2, 27.5 ppm for C4 and 22.7 ppm for C3 in toluene-d_8) confirming the presence of three CH_2 groups in **61**. ^{15}N chemical shifts of the nitrogen atoms in **61** (from a ^{1}H,^{15}N-HMBC experiment) were in agreement with the presence of an imino nitrogen (at 230.6 ppm) and of an amido nitrogen (at 80.1 ppm).

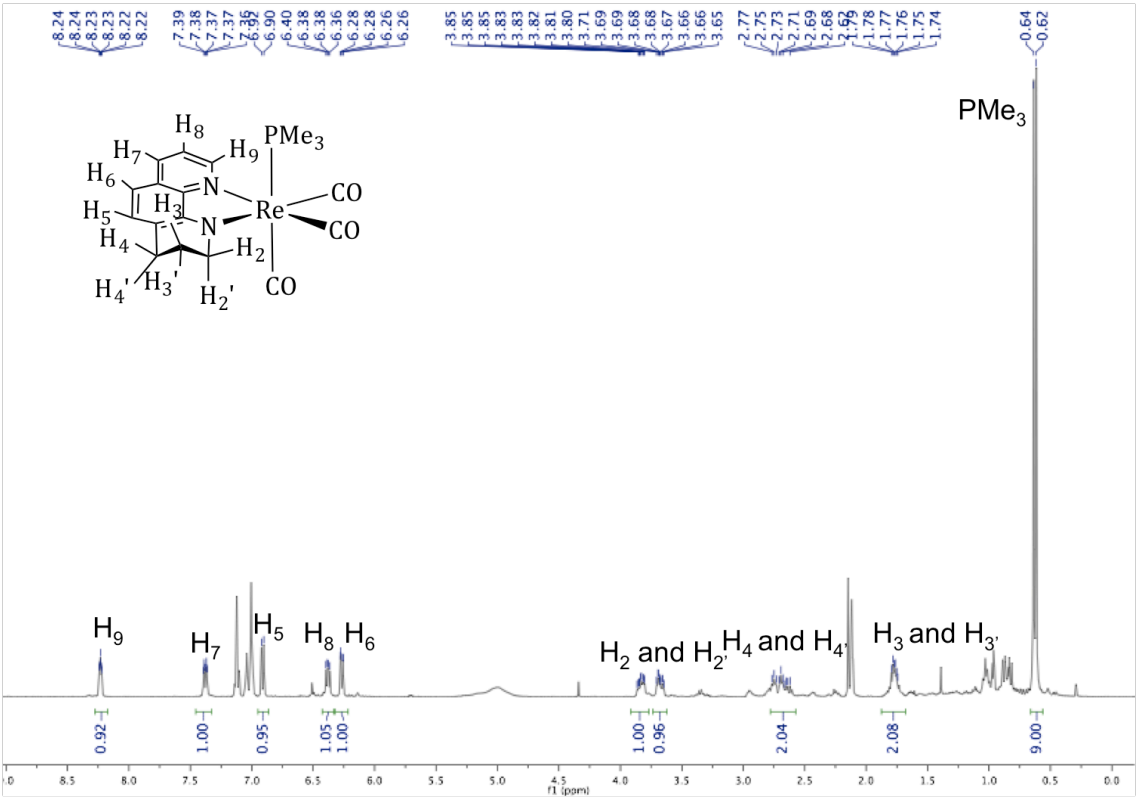


*Figure 42. ^{1}H NMR spectrum of **61** in toluene-d_8 at 298 K.*

Slow diffusion of hexane into a concentrated toluene solution of **61** at -20°C afforded blue crystals one of which was used for X-ray diffraction. The solid-state structure of **61** confirms the proposed connectivity (see Figure 43 and Table 8).

Compound **61** displays a distorted octahedral geometry (P-Re-C18 is 178.1(2)°, P-Re-N1 is 87.1(1)° and P-Re-N10 is 87.1(1)°) and contains a bidentate chelate coordinated to the metal center through its two nitrogen atoms. The *N-N'* chelate is not planar and results from reduction of two double bonds of a pyridyl ring in the phen ligand of the precursor **36**. The partial reduction of the N1 pyridyl ring is supported by the sp^3 hybridation of three of its carbon atoms, C2, C3 and C4, which display bond distances consistent with single bonds (C2-C3 is 1.51(1) Å and C3-C4 is 1.49(1) Å). The geometry in the N1 ring is consistent with the presence of an aromatic double bond between C11 and C12, which show sp^2 hybridization supported by a C11-C12 aromatic bond distance (1.413(8) Å) and their ^{13}C NMR chemical shifts (156.4 ppm for C11 and 118.3 ppm for C12 in the ^{13}C NMR spectrum). The sum of angles around N1 is 359.8(5)° indicating a planar amido, as the N1 in compound **52M-C2** (see above).

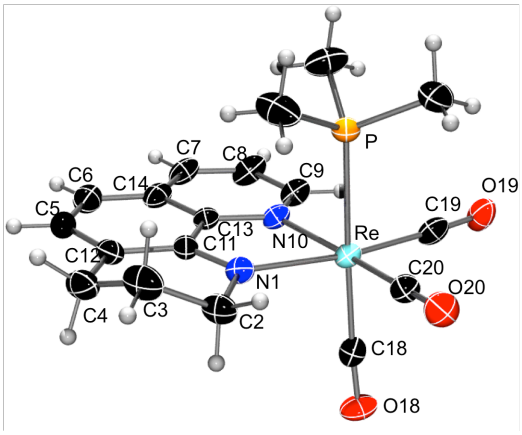
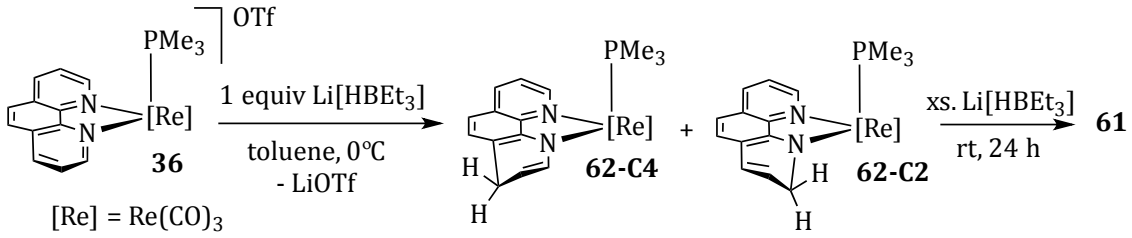


*Figure 43. Solid state structure (thermal ellipsoids at 30% probability) of **61**.*

Re-N1	2.149(4)
Re-N10	2.175(4)
Re-P1	2.459(2)
Re-C18	1.952(7)
Re-C19	1.932(7)
Re-C20	1.917(6)
N1-C2	1.450(7)
C2-C3	1.51(1)
C4-C3	1.49(1)
C12-C4	1.484(9)
C9-C8	1.396(9)
N10-C9	1.349(7)
C11-C12	1.413(8)
C2-N1-C11	117.9(5)
C11-N1-Re	116.2(3)
C2-N1-Re	125.7(4)
C2-C3-C4	113.4(6)
N1-C2-C3	112.6(5)
C3-C4-C12	111.3(6)
N10-C9-C8	121.8(6)

*Table 8. Selected bond distances (Å) and angles (°) of compound **61**.*

Low temperature NMR monitoring of the formation of **61** in toluene-d_8 revealed the presence of two species, **62-C2** and **62-C4** (in a 0.6:1 ratio by ^{1}H NMR spectrum integration), in the green solution initially formed after the addition of Li[HBEt$_3$], both with dearomatized pyridyl rings and intact PMe$_3$ ligands (see Scheme 54). 1D and 2D NMR characterization of **62-C2** and **62-C4** showed the products to be formed as a result of the nucleophilic attack of a hydride on position 2 (**62-C2**) or 4 (**62-C4**) of phen (see the ^{1}H NMR spectrum in Figure 44).



*Scheme 54. Nucleophilic attack of one hydride on phen in **36**. [Re] = $Re(CO)_3$*

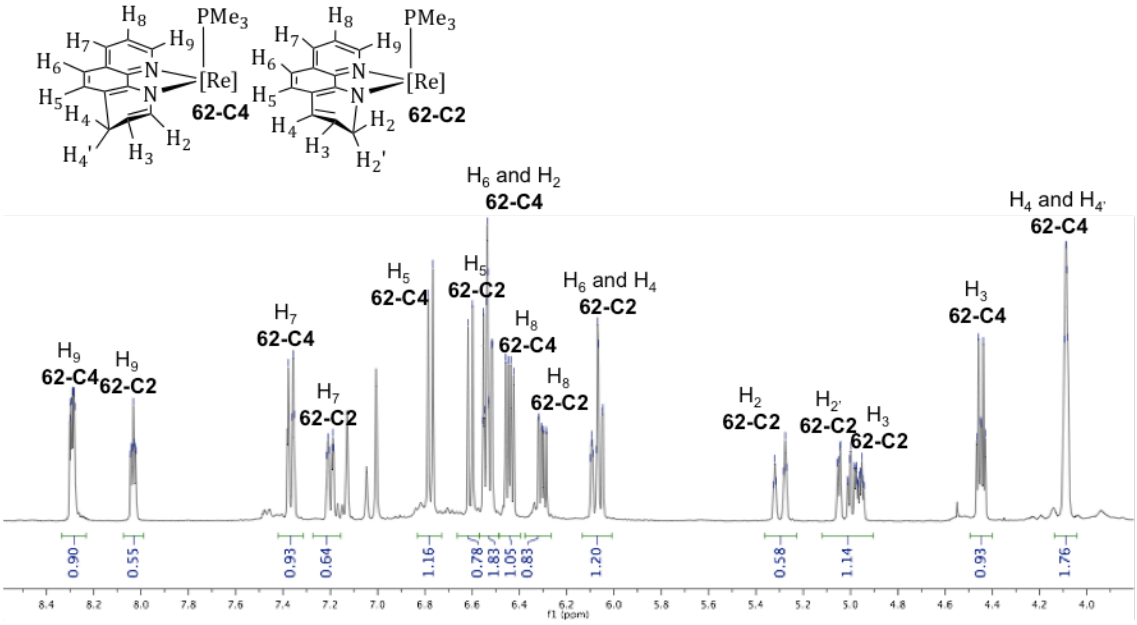
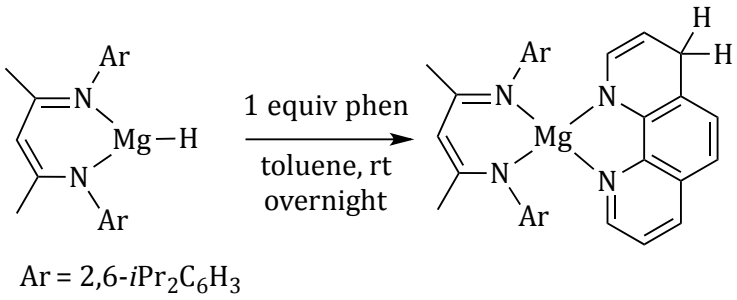


*Figure 44. ^{1}H NMR spectrum of **62-C2** and **62-C4** in toluene-d_8 at 273 K (phen signals).*

The ^{1}H NMR spectrum of the **62-C2** and **62-C4** mixture showed signals for two asymmetric rhenium compounds, both with dearomatized pyridyl rings as a result of nucleophilic hydride addition on the phenanthroline ligand and an intact PMe_3. The ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC spectra made possible the assignment of the signals of both, the major (**62-C4**) and the minor (**62-C2**) species, and showed **62-C2** to contain a CH_2 group in the position 2 of phen (two multiplets at 5.30 and 5.03 ppm, 1H each in the ^{1}H NMR spectrum and a signal in opposite phase to CH signals at 58.5 ppm in the ^{13}C DEPT-135 spectrum, both in toluene-d_8) and **62-C4** a CH_2 group in position 4 of phen (a 2H multiplet at 4.09 ppm in the ^{1}H NMR spectrum and a signal in opposite phase to CH signals at 28.2 ppm in the ^{13}C DEPT-135 spectrum, both in toluene-d_8).

Intramolecular addition of hydride on phen has been previously reported in the [Mg(H)(N-N)] (N-N = $CH\{C(CH_3)N(Ar)\}_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) complex by Hill and co-

workers.[21] However, migration of hydride in the magnesium complex yielded a single species resulting from hydride addition to C4 of phen (see Scheme 55).

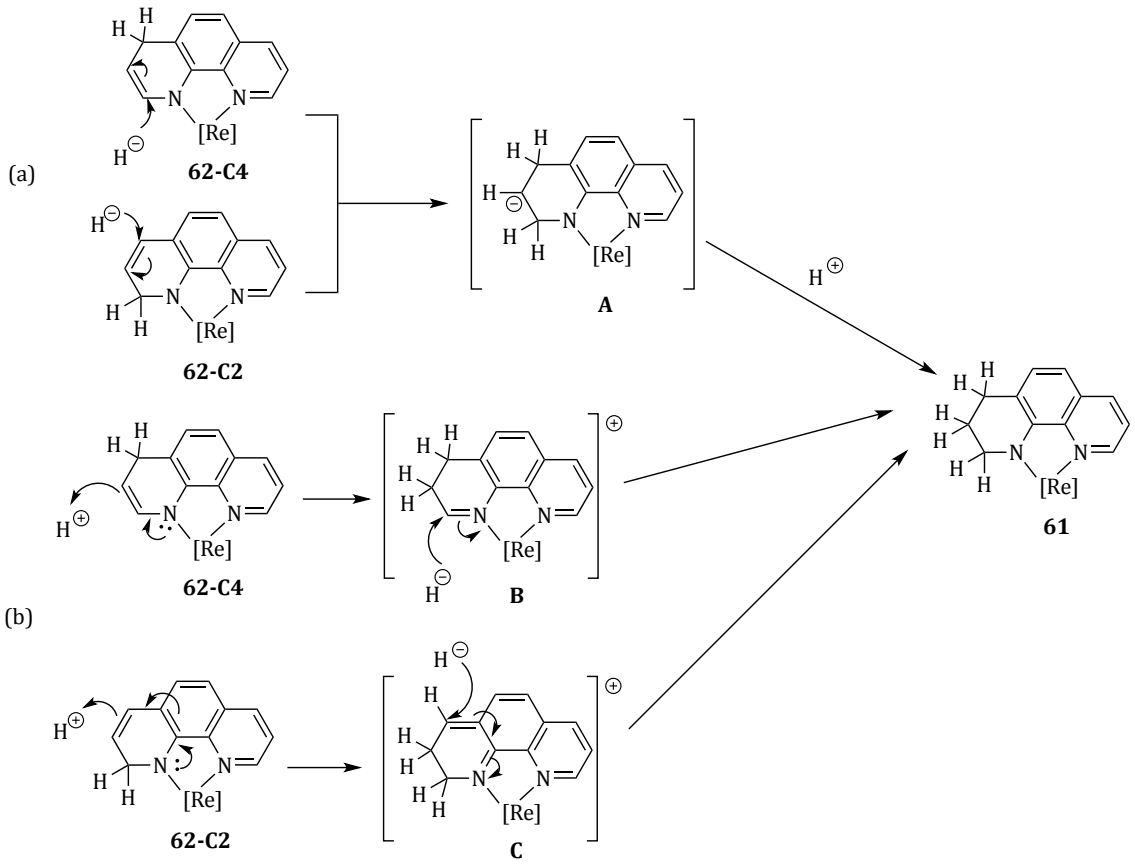


Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 55. Intramolecular hydride migration in a magnesium complex reported by Hill and co-workers.

Although the authors did not hypothesized about the formation of the C4-substituted product, it could be thought that a mechanism similar to that proposed for the addition of *n*BuLi (see above) operates in this case, *i. e.* the hydride initially adds to position 2 of phen and then migrates to C4, which is the thermodinamically preferred position.

At the time of writing this dissertation the mechanism of the formation of complex **61** from the **62-C2**, **62-C4** mixture remained unknown. As a working hypothesis, it is proposed to occur by addition of a second equivalent of hydride and protonation (by traces of acid in the reaction media) to yield the neutral species **61** (see Scheme 56). Compound **61** could be formed as a result of nucleophilic attack of a second equivalent of hydride on C2 of phen in **62-C4** or on C4 of phen in **62-C2** to yield an anionic intermediate **A** which would immediately protonate on its 3 position (Scheme 56a). However, participation of the amido lone electron pair in the reaction cannot be discarded, and protonation at C3 could occur first for both, **62-C4** and **62-C2**, yielding cationic species **B** and **C** respectively, prone to undergo nucleophilic attack of the second equivalent of hydride at C2 (for **62-C4**) or at C4 (for **62-C2**, see Scheme 56b). However, although formation of **61** is possible from both, **62-C2** and **62-C4**, the possibility that **62-C2** evolves to **62-C4** by a 1,3-hydrogen shift[71] yielding **62-C4** as the sole species should not be discarded (as proposed in the case of the reaction of [Re(bipy)(CO)$_3$(PMe$_3$)]OTf with Li[HBEt$_3$], see Section 2.8 of Chapter 2).



*Scheme 56. Possible mechanisms for the formation of **61** from **62-C4** and **62-C2**: (a) nucleophilic attack of the second equivalent of hydride to yield the anionic species **A** followed by protonation and (b) protonation to yield cationic species **B** and **C** followed by nucleophilic attack of a second equivalent of hydride. [Re] = $Re(CO)_3(PMe_3)$*

The reactivity of compound **36** toward $Li[HBEt_3]$ stands in contrast with the reactivity found for compound $[Re(bipy)(CO)_3(PMe_3)]OTf$ (**14**) (see Section 2.8 in Chapter 2). At low temperature, both coordinated bipy and phen add one equivalent of hydride to yield a mixture of complexes from nucleophilic addition of the hydride on their *ortho* and *para* positions (C6 and C4 of bipy and C2 and C4 of phen). However, at room temperature and in the presence of excess $Li[HBEt_3]$, a second equivalent of hydride adds to phen in **36** to yield, after protonation, a product with three CH_2 groups (complex **61**), while bipy in $[Re(bipy)(CO)_3(PMe_3)]OTf$ does not react with a second equivalent of $Li[HBEt_3]$ but dimerizes to yield a product with two new C-C bonds between positions 3 and 5 of bipy ligands from two different molecules (complex **35** in Chapter 2).

Chapter 4:

Deprotonation of α-methyl groups of coordinated heterocycles.

Part of the results discussed in this Chapter have been included in a *Communication* accepted for publication in the journal *Inorganic Chemistry.*[78] This Chapter also includes unpublished results which will be discussed in further detail and will be included in a future *Full paper*.

In order to demonstrate the generality of the C-C coupling reactions, several 2-methylheterocycles (Chart 1a), which differ in ring size and aromaticity degree, have been coupled to different aromatic and non-aromatic diimines (Chart 1b) in $Re(CO)_3^+$ and $Mo(\eta^3\text{-}C_4H_7)(CO)_2^+$ fragments.

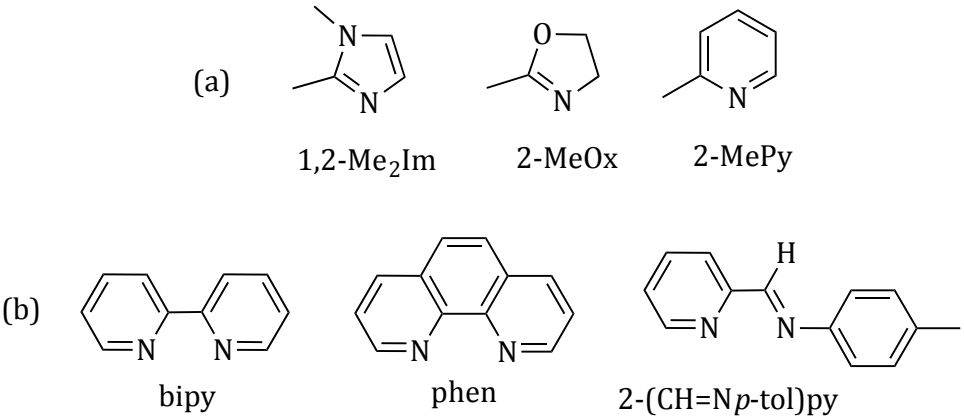
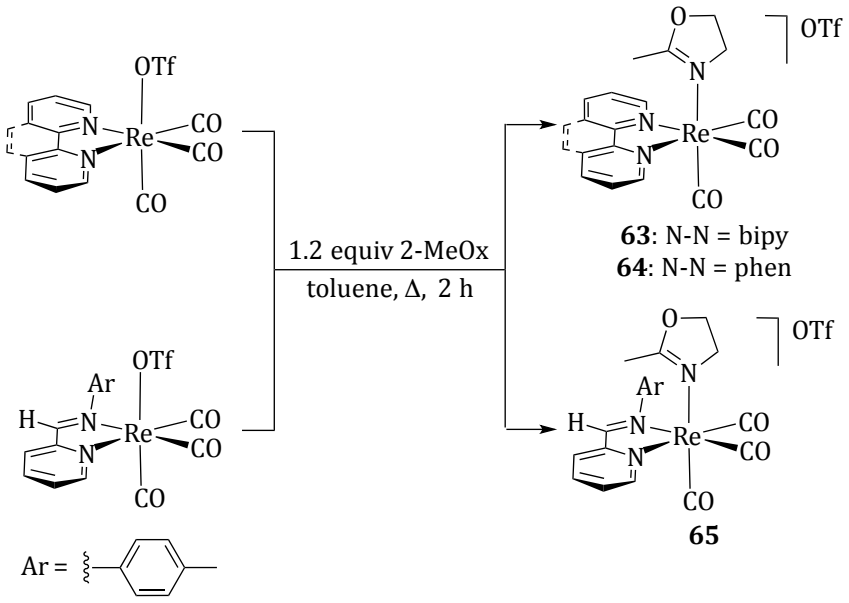


Chart 1. Overview of the 2-methylheterocycles (a) and diimines (b) coupled in this Chapter in rhenium and molybdenum complexes.

4.1 Synthesis and deprotonation of [Re(N-N)(CO)$_3$(2-MeOx)]OTf (N-N = bipy, phen, 2-(CH=N*p*-tol)py) complexes

Reaction of the rhenium precursors [Re(N-N)(CO)$_3$(OTf)] (N-N = bipy, phen, 2-(CH=N*p*-tol)py = 2-(*p*-methylphenylimino)pyridine) with a slight excess of 2-methyloxazoline in CH_2Cl_2 at room temperature yielded mixtures of two rhenium species in each case, which could be attributed to the formation of compounds with *κ*-N (major) and *κ*-O (minor) coordinated oxazoline. Assuming that the *κ*-N isomer is the most stable species (since the softer nitrogen should be a better match for the low-valent rhenium fragment), its formation would be favored employing more forcing conditions. Therefore, the [Re(N-N)(CO)$_3$(*κ*-*N*-2-MeOx)]OTf (N-N = bipy (**63**), phen (**64**), 2-(CH=N*p*-

tol)py (**65**)) compounds were obtained by reaction of the appropriate triflate precursors with a slight excess of 2-methyloxazoline in refluxing toluene (see Scheme 57).



Scheme 57. Synthesis of compounds with coordinated 2-methyloxazoline.

The products were isolated by precipitation as yellow solids in good yields (*e. g*. 85 % for **64**) and fully characterized by IR, EA, and NMR spectroscopy, which showed them to be analytically and spectroscopically pure and formed as single species in the reaction. The frequencies of the IR νCO bands decreased (from 2037, 1935 and 1915 cm^{-1} in the precursor [Re(phen)$(CO)_3$(OTf)] to 2030 and 1920 cm^{-1} in compound **64**) upon coordination of the oxazoline presumably as a result of its strong donating ability. ^1H and ^{13}C NMR spectra of compounds **63** and **64** were consistent with the products being C_s symmetric complexes (four signals for the phen ligand in the ^1H NMR spectrum of **64** in CD_2Cl_2 between 9.53 and 8.15 ppm) with a coordinated oxazoline (two multiplets at 4.11 and 2.85 ppm for the CH_2-CH_2 unit in CD_2Cl_2, see Figure 45 for the ^1H NMR spectrum of compound **64**). In contrast, NMR spectra of compound **65** were consistent with a C_1 symmetric complex as a result of the asymmetry of the 2-(CH=N*p*-tol)py chelate. As a consequence, all the hydrogens in the CH_2-CH_2 unit of the oxazoline are inequivalent and occur as multiplets in the ^1H NMR spectrum (at 4.33 (2H), 3.49 (1H) and 3.14 (1H) ppm in CD_2Cl_2). Moreover, the three carbonyl ligands occur in the ^{13}C NMR spectrum as three singlets (at 196.3, 194.7 and 189.1 ppm) in contrast to the two signals found in the symmetric compounds **63** and **64** (see Experimental Section).

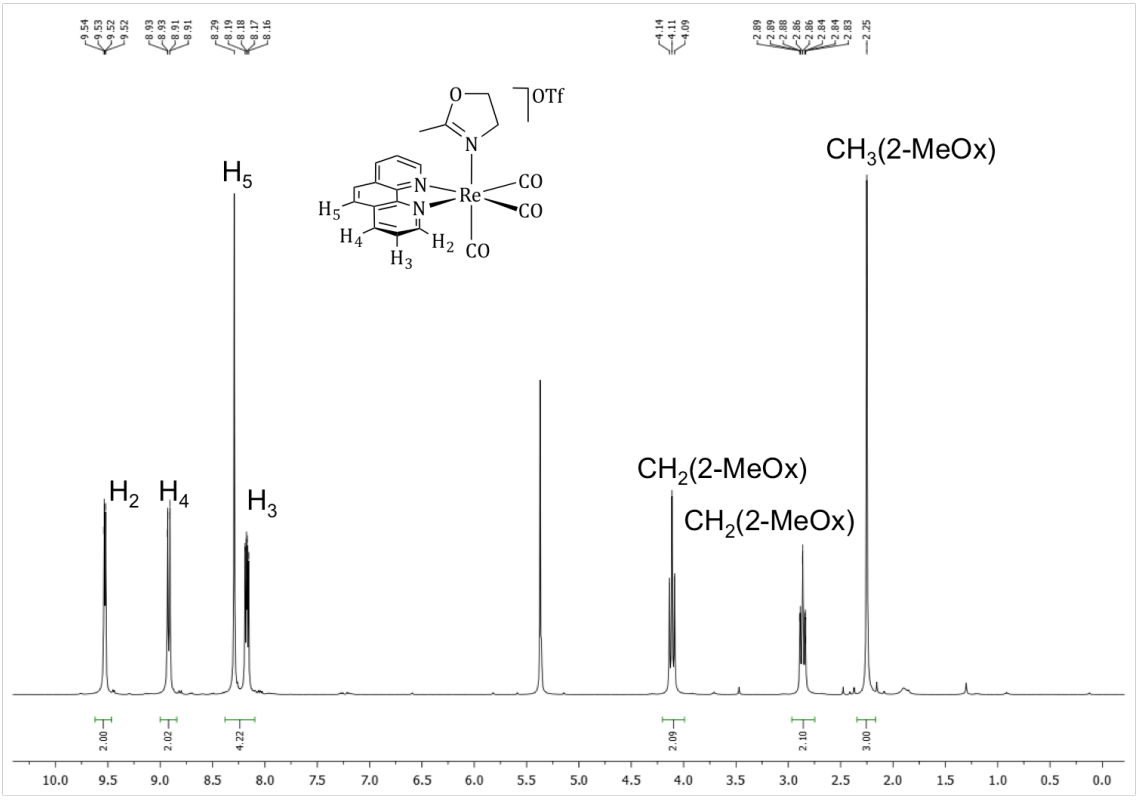
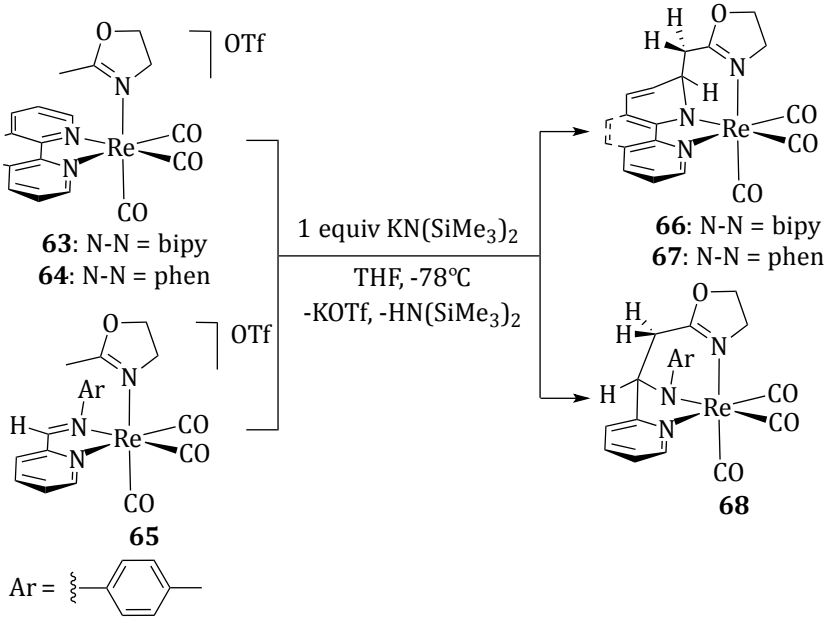


*Figure 45. ^{1}H NMR spectrum of compound **64** in CD_2Cl_2 at 298 K.*

Slow diffusion of diethyl ether into a concentrated solution of compound **64** yielded yellow crystals suitable for X-ray diffraction analysis (see below).

Addition of the equimolar amount of $KN(SiMe_3)_2$ to yellow solutions of **63**, **64** or **65** in THF at -78°C caused a color change to purple (in **63** or **64**) or to dark green (in **65**), and a shift to lower wavenumbers of the IR νCO bands (from 2030 and 1920 to 2007, 1899 and 1885 cm^{-1} for **64**) consistent with the formation of the neutral species, **66**, **67** or **68** respectively. Products **67** and **68** were found to be thermally stable and could be isolated by filtration in moderate yields (68 % for **67**), and characterized by NMR at room temperature. However, as a consequence of the thermal instability of product **66** at room temperature the reaction crude had to be characterized at low temperature (see Experimental Section for further details). 1D and 2D NMR characterization showed the products to be formed as a result of oxazoline 2-methyl group deprotonation and intramolecular nucleophilic attack on a C=N group of the bidentate co-ligand. As a result, the new compounds possess a new C-C bond and, those with bipy and phen (**66** and **67**), a dearomatized pyridyl ring (see Scheme 58).



*Scheme 58. Intramolecular nucleophilic attack of a deprotonated oxazoline 2-methyl group on bipy, phen and 2-(CH=Np-tol)py ligands of compounds **63**, **64** and **65**.*

Full NMR assignment of the ^{1}H and ^{13}C NMR signals of **66** and **67** confirmed that the nucleophilic attack took place on the *ortho* CH groups of the pyridyl rings (position 6 of bipy and 2 of phen). In **66**, **67** and **68**, signals for new diasterotopic CH_2 groups replaced the singlets found in the precursors for the 2-methyl groups of the oxazoline, confirming deprotonation of the methyl group (see Figure 46 for the ^{1}H NMR spectrum of **67**). As a result of the new C-C bond, complexes **66** and **67** lost their mirror plane and were asymmetric (eight signals for the bipy and phen chelates in the ^{1}H NMR spectra). The most remarkable feature in the ^{1}H NMR spectrum of complex **68** is that the signal for the CH group bonded to the currently amido N occurred at 5.58 ppm (in contrast to the signal at 9.25 ppm in CD_2Cl_2 for its precursor **65**) confirming that nucleophilic attack took place on the non-aromatic imine group and the attacked carbon atom is sp^3 hybridized in the product. Moreover, this signal showed a $^{3}J_{HH}$ crosspeak with the two diasterotopic hydrogens in the ^{1}H-^{1}H COSY spectrum supporting the proposed connectivity.

Similar intramolecular nucleophilic additions on the imine group of the 2-(CH=N*p*-tol)py chelate triggered by deprotonation of coordinated N-alkylimidazoles (RIm) in [Mo(2-(CH=N*p*-tol)py)(η^3-C_4H_7)$(CO)_2$(RIm)]OTf (R = methyl, 2,4,6-trimethylphenyl) complexes have been recently reported in our group.[79]

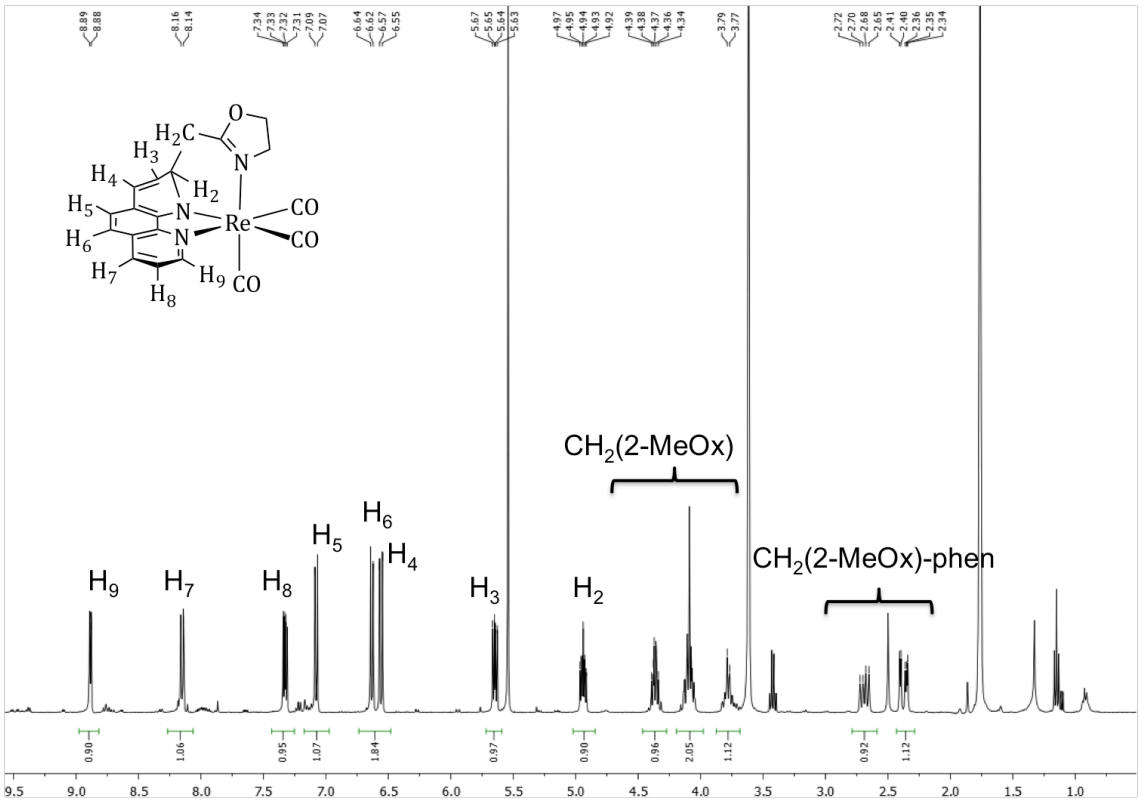
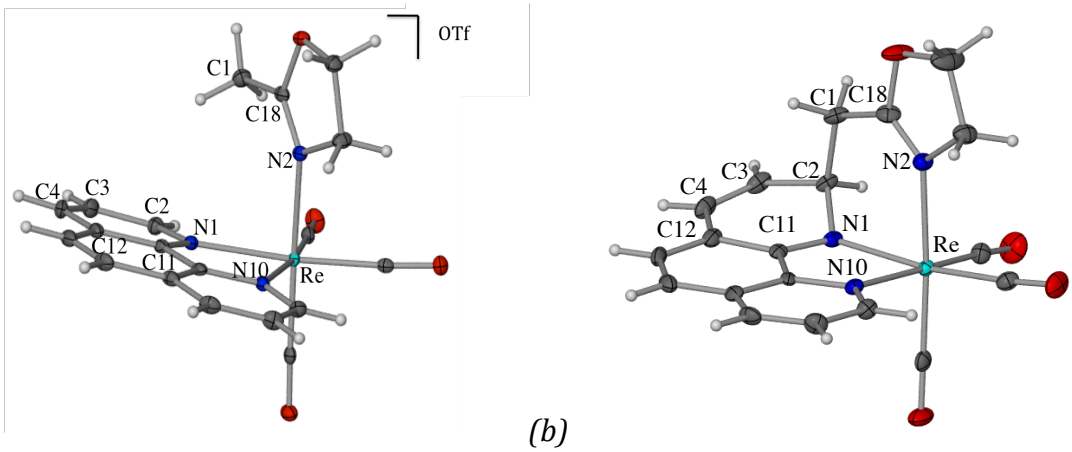


*Figure 46. ^{1}H NMR spectrum of compound **67** in THF-d_8 at 298 K.*

Crystals of complexes **67** and **68** suitable for X-ray diffraction could be obtained by slow evaporation of a diethyl ether solution of **67** and slow diffusion of hexane into a concentrated solution of **6** in CH_2Cl_2 respectively.

The solid-state structures of compounds **64**, **67** and **68** confirmed the connectivity depicted in Schemes 57 and 58 and showed distorted octahedral *fac*-Re(CO)$_3$ fragments bonded to *κ-N* coordinated oxazoline and phenanthroline ligands in the cation of **64**, and to an *N*,*N*',*N*'' tridentate ligand from C-C coupling between the deprotonated methyl group the oxazoline and phen (in **67**) or 2-(CH=N*p*-tol)py (in **68**). The results of the structural determination are depicted in Figures 47 (ORTEP ellipsoid diagrams for **64** and **67**) and 48 (ORTEP ellipsoid diagram for **64**) and Tables 9 (selected bond distances and angles for **64** and **67**) and 10 (selected bond distances and angles for **68**).



(a) (b)

*Figure 47. Solid-state structures (ellipsoids at the 30% probability level) of (a) the cation in **64** and (b) complex **67**.*

	64	**67**
Re-N1	2.168(2)	2.123(3)
Re-N10	2.187(2)	2.189(3)
Re-N2	2.199(2)	2.193(3)
N1-C2	1.336(2)	1.462(4)
C2-C3	1.401(3)	1.518(5)
C3-C4	1.369(3)	1.323(5)
C4-C12	1.406(3)	1.454(5)
C12-C11	1.403(3)	1.405(5)
C11-N1	1.366(2)	1.355(4)
C1-C2	-	1.547(5)
C2-N1-C11	117.8(2)	114.0(3)
C2-N1-Re	127.0(1)	122.2(2)
C11-N1-Re	115.2(1)	116.2(2)
C18-N2-Re	133.7(1)	129.8(2)
C3-C2-N1	122.5(2)	110.6(3)
C1-C2-C3	-	109.4(3)
C1-C2-N1	-	109.9(3)
N2-Re-N1	85.73(6)	79.3(1)

*Table 9. Selected bond distances (Å) and angles (°) of the cation in **64** and complex **67**.*

As a consequence of the C-C bond formation the solid-state structure of **67** showed a non-planar pyridyl ring as a result of C2 sp^3 hybridization (the angles around it are close to 109°, and C2-C3 and C2-N1 bond distances of 1.518(5) Å and 1.462(4) Å, respectively, are consistent with single bonds). Moreover, this ring is dearomatized and the C-C bond distances in the ring alternate values for single and double bonds (see Table 9). Re-N1 bond distance (2.123(3) Å) is consistent with N1 being an amido ligand (in contrast to the Re-N10 distance of 2.189(3) Å, slightly longer) and the sum of angles around N1 (351.4(3)°) indicates a slightly pyramidal geometry.

The solid-state structure of **68** (see Figure 48 and Table 10) confirmed that nucleophilic attack of the CH_2 group occurred on the non-aromatic CN group of the diimine. Re-N1 distance (2.118(8) Å) is also consistent with N1 being an amido nitrogen, however, the sum of angles around it is close to 360°, indicating a planar amido group. The presence of a planar amido nitrogen in **68** stands in contrast to the pyramidal amido in **67** and could be attributed to delocalization through the *p*-tolyl substituent could be also operating in this case, since N1 and the aryl are coplanar.[68] Moreover, the higher flexibility of the amido in **68**, where this group is not part of a cycle, would also result on a higher ability to delocalize the lone electron pair. The planarity of N1 stands in contrast to the pyramidal geometry found in complex **13** (see Chapter 1) where delocalization of the amido lone electron pair through the *p*-tolyl substituent is not possible due to the steric restrictions imposed by the BIAN ligand.

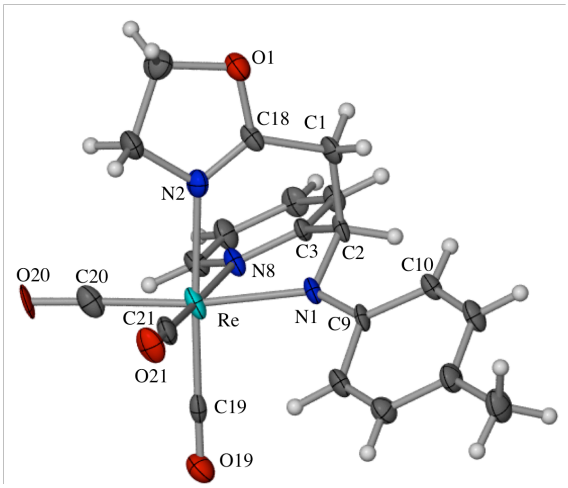


*Figure 48. Solid-state structure (ellipsoids at the 30% probability level) of complex **68**.*

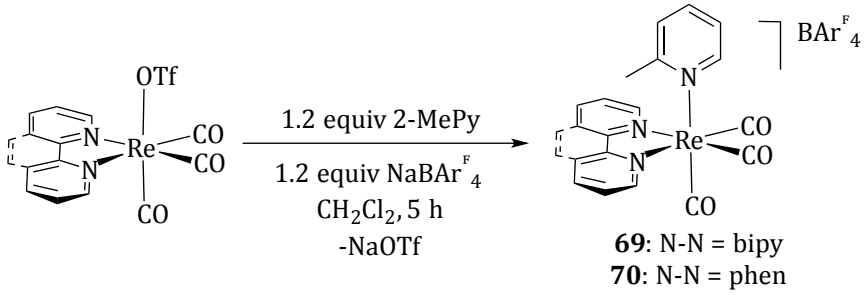
Re-N1	2.118(8)
Re-N8	2.185(9)
Re-N2	2.20(1)
N1-C2	1.45(1)
C2-C3	1.50(1)
C9-N1	1.40(1)
C1-C2	1.56(2)
C18-C1	1.48(2)
C2-N1-C11	115.2(8)
C2-N1-Re	111.3(6)
C11-N1-Re	131.2(7)
C18-N2-Re	129.6(8)
C1-C2-N1	113.6(8)
N2-Re-N1	81.6(3)
N2-Re-N10	82.9(3)

*Table 10. Selected bond distances (Å) and angles (°) of complex **68**.*

4.2 Synthesis and deprotonation of [Re(N-N)(CO)$_3$(2-MePy)]BAr$^F_4$ (N-N = bipy, phen) complexes

Reaction of 2-methylpyridine with precursors [Re(bipy)(CO)$_3$(OTf)], and [Re(phen)(CO)$_3$(OTf)] did not yield products with coordinated 2-MePy even after 8 hours under reflux. Therefore, the preparation of [Re(N-N)(CO)$_3$(2-MePy)]$^+$ (N-N = bipy (**69**), phen (**70**)) complexes was carried out in the presence of the Na[BAr$^F_4$] salt which promoted triflate abstraction by NaOTf precipitation in CH_2Cl_2 (see Scheme 59). The failure to obtain the [Re(N-N)(CO)$_3$(2-MePy)]$^+$ complexes from thermal substitution of the triflate ligand in the precursor stands in contrast to the straightforward synthesis of the [Re(N-N)(CO)$_3$(2-MeOx)]OTf (N-N = bipy, phen, see above) and [Re(N-N)(CO)$_3$(1,2-Me$_2$Im)]OTf (N-N = bipy, phen, see below) complexes by this procedure and could be

attributed to the weaker electron donating ability of the 2-MePy and the higher steric hindrance of its nitrogen atom in comparison to the nitrogen in 2-MeOx and 1,2-Me_2Im, in turn attributed to the different geometry of the rings, that places the methyl group of the 2-picoline ligand pointing towards the metal center, thus making it more capable of steric hindrance than the methyl groups in the other heterocycles.



Scheme 59. Synthesis of complexes with coordinated 2-MePy.

IR νCO bands of products **69** and **70** were considerably higher than those of the triflate precursors, in agreement with the transformation of neutral complexes into cationic species. The higher IR νCO wavenumbers of complexes **69** and **70** stand in contrast to those for complexes [Re(N-N)$(CO)_3$(2-MeOx)]OTf (N-N = bipy, phen, see above) and [Re(N-N)$(CO)_3$(1,2-Me_2Im)]OTf (N-N = bipy, phen, see below) and indicates a weaker electron-donating ability of the 2-MePy ligand in comparison with 2-MeOx and 1,2-Me_2Im.

The new compounds **69** and **70** were isolated by filtration and precipitation as yellow solids in a good yield (79 % for **70**). 1D and 2D spectra of the products were consistent with C_s symmetric complexes with phenanthroline or bipyridine ligands and a coordinated 2-methylpyridine (see Figure 49 for the ^{1}H NMR spectrum of **70**).

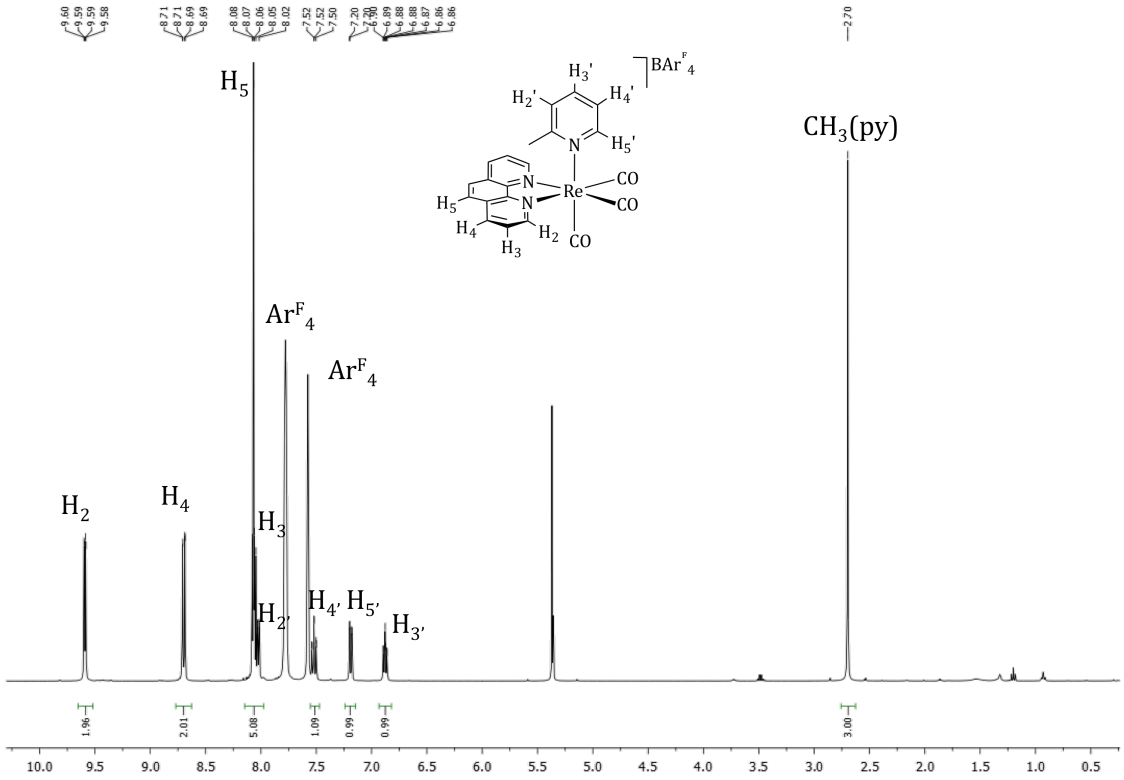
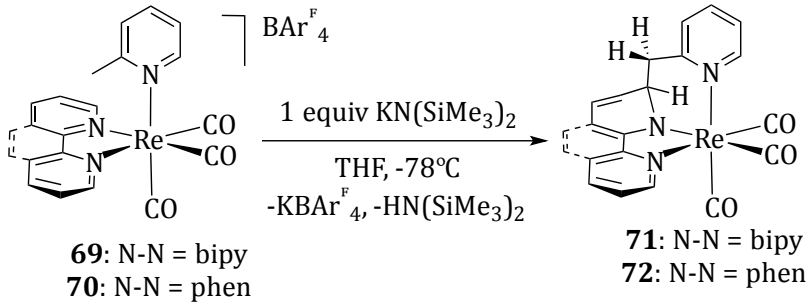


*Figure 49. ^{1}H NMR spectrum of compound [Re(N-N)(CO)$_3$(2-MePy)][BAr$^F_4$] (**70**) in CD_2Cl_2 at 298 K.*

Preparation of compound **69** has been reported from [Re(bipy)(CO)$_3$Cl], $AgClO_4$ and α-picoline.[80] The alternative method given here avoids the use of potentially explosive perchlorate salts.

Addition of the equimolar amount of KN(SiMe$_3$)$_2$ (toluene solution) to THF solutions of **69** or **70** at -78°C caused an instantaneous color change from yellow to purple (in **69**) or dark green (in **70**) and a shift to lower wavenumbers of the IR νCO bands (from 2037 and 1931 to 2008, 1902 and 1885 cm^{-1} for the reaction of **70**), in agreement with the formation of neutral species, **71** and **72** respectively. Product **71** was found to be thermally unstable and was characterized by NMR at low temperature. In constrast, product **72** was thermally stable and could be fully characterized by EA and NMR at room temperature. 1D and 2D NMR spectra showed **71** and **72** to be formed as a result of 2-methyl group deprotonation of the pyridine ligand and its intramolecular nucleophilic attack on position 6 of bipy (to yield **71**) or 2 of phen (to yield **72**, see Scheme 60).



*Scheme 60. C-C coupling between a deprotonated 2-methyl group of α-picoline and bipy or phen to yield complexes **71** and **72**.*

NMR characterization showed **71** and **72** to be formed as single species in the deprotonation of compounds **69** and **70** respectively. The ^{1}H NMR spectrum of both **71** and **72** showed signals for a new CH_2 group (two doublets of doublets at 3.60 and 2.92 ppm for complex **72** in THF-d_8) from the deprotonated methyl group (see Figure 50 for the ^{1}H NMR spectrum of **72**). Signals of the diasterotopic hydrogens of the CH_2 group showed a $^3J_{HH}$ crosspeak with the signal for the H6 (in bipy, at 5.20 ppm) or H2 (in phen, at 5.63 ppm) confirming that nucleophilic attack took place on the *ortho* positions of the pyridyl rings.

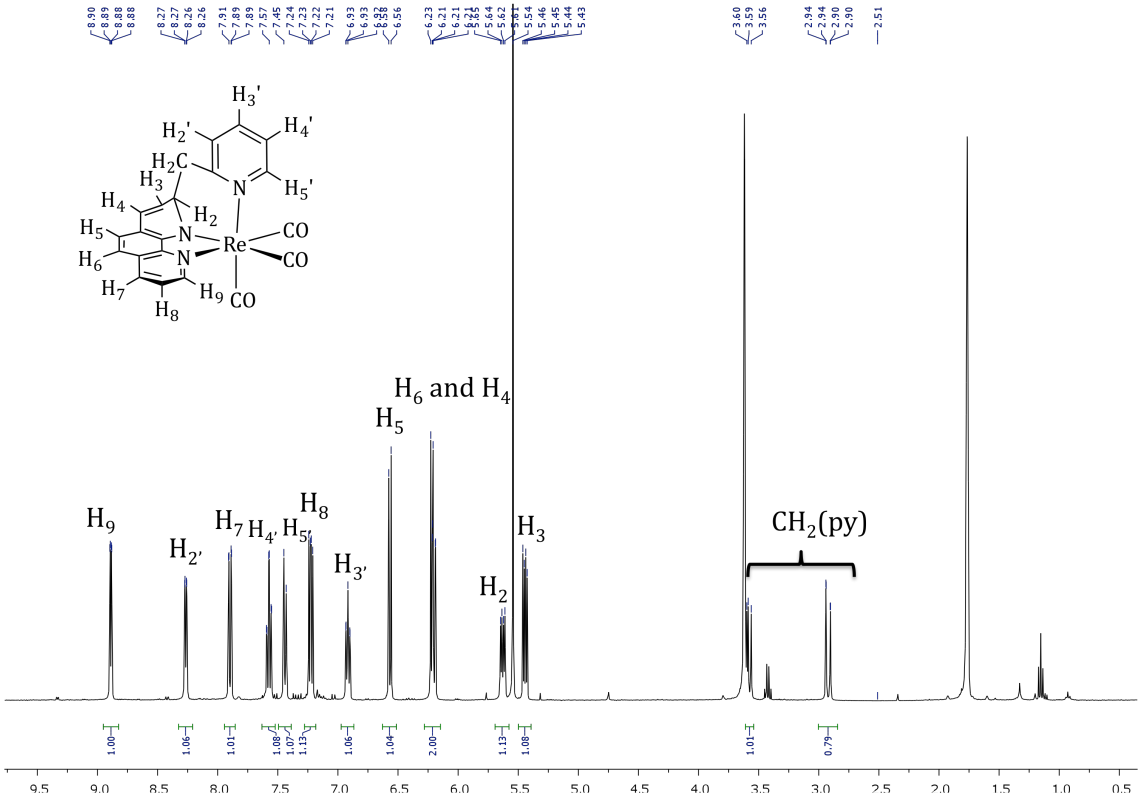


*Figure 50. ^{1}H NMR spectrum of complex **72** in THF-d_8 at 298 K.*

Slow evaporation of a diethyl ether solution of **72** yielded green crystals suitable for X-ray diffraction analysis. The solid-state structure of **72** confirmed the proposed connectivity and showed a distorted octahedral *fac*-$Re(CO)_3$ fragment bonded to a tridentate *N,N',N''* ligand from methyl group deprotonation of the pyridine and coupling to the C2 of phen (see Figure 51 and Table 11).

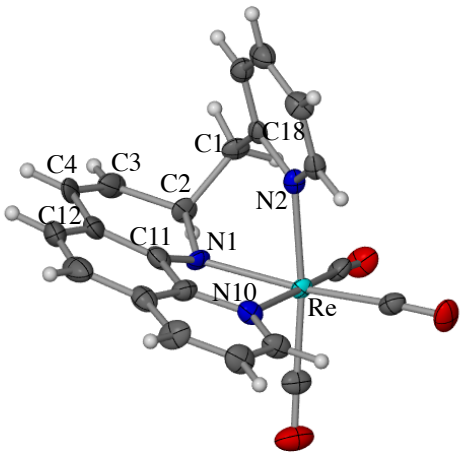


*Figure 51. Solid-state structure (ellipsoids at the 30% probability level) of complex **72**.*

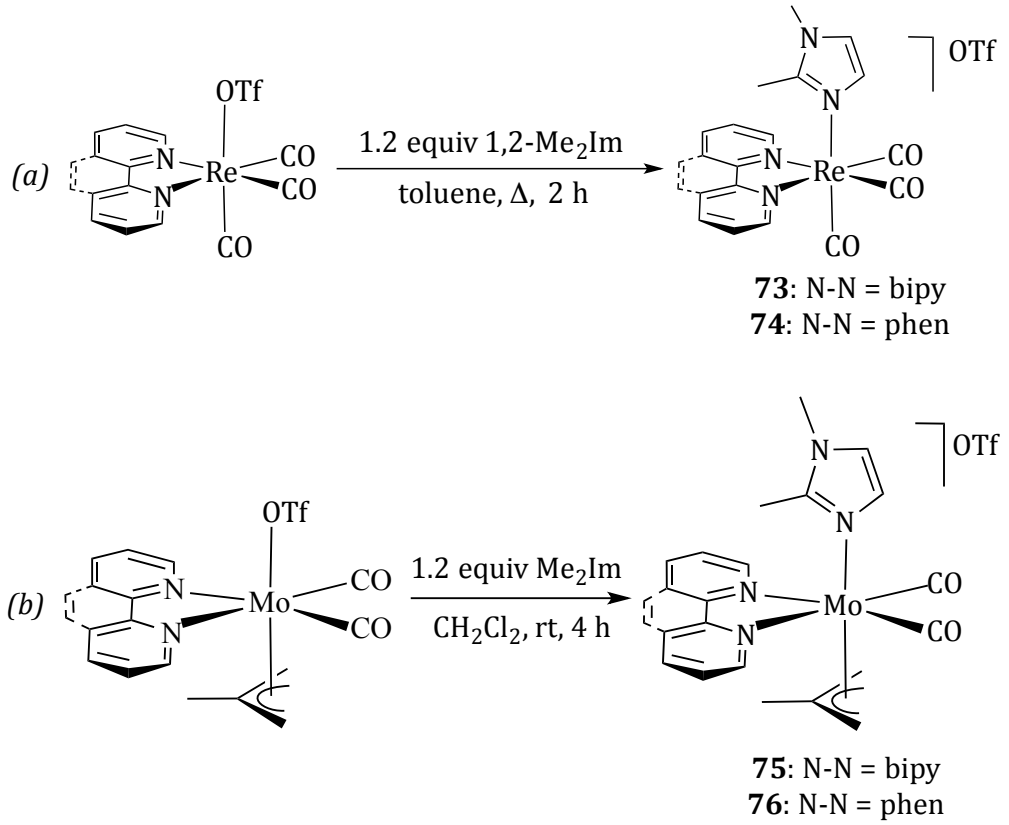
Re-N1	2.135(8)
Re-N10	2.167(9)
Re-N2	2.218(9)
N1-C2	1.46(1)
C2-C3	1.51(2)
C3-C4	1.37(2)
C4-C12	1.44(2)
C12-C11	1.40(2)
C11-N1	1.36(1)
C1-C2	1.57(1)
C18-C1	1.50(1)
C2-N1-C11	118.4(9)
C2-N1-Re	118.4(7)
C11-N1-Re	113.3(7)
C18-N2-Re	122.6(7)
C3-C2-N1	111.1(9)
C3-C2-N1	112.4(9)
C1-C2-N1	110.1(8)
N2-Re-N1	75.7(3)
N2-Re-N10	83.7(3)

*Table 11. Selected bond distances (Å) and angles (°) of complex **72**.*

As a result of the C-C coupling the attacked pyridyl ring became dearomatized and lost its planarity. Moreover, the attacked carbon atom C2 is sp^3 hybridized (angles around it are close to 109°). Although N1 is an amido donor and N10 an imino donor, Re-N1 and Re-N10 bond distances (2.135(8) and 2.167(9) Å respectively) are similar. The geometry around N1 is pyramidal as evidenced by the sum of angles around it (350.1°).

4.3 Synthesis and deprotonation of [Re(N-N)(CO)$_3$(1,2-Me$_2$Im)]OTf and [Mo(N-N)(η^3-C$_4$H$_7$)(CO)$_2$(1,2-Me$_2$Im)]OTf (N-N = bipy, phen) complexes.

New complexes [Re(N-N)(CO)$_3$(1,2-Me$_2$Im)]OTf (N-N = bipy (**73**), phen (**74**)) were obtained from reaction of the appropriate triflate precursor [Re(N-N)(CO)$_3$(OTf)] (N-N = bipy, phen) with a slight excess of 1,2-Me$_2$Im in refluxing toluene (see Scheme 61a). In contrast, coordination of 1,2-Me$_2$Im to the [Mo(N-N)(η^3-C$_4$H$_7$)(CO)$_2$(OTf)] (N-N = bipy, phen) precursors to yield [Mo(N-N)(η^3-C$_4$H$_7$)(CO)$_2$(1,2-Me$_2$Im)]OTf (N-N = bipy (**75**), phen (**76**)) was carried out at room temperature (see Scheme 61b).



Scheme 61. Coordination of 1,2-Me$_2$Im to (a) Re(CO)$_3$ and (b) Mo(η^3-C$_4$H$_7$)(CO)$_2$ fragments.

The products **73**, **74**, **75** and **76** were obtained as yellow (**73** and **74**) or red (**75** and **76**) solids in good yield (*e. g*. 85% for **73**) and were fully characterized by EA and IR and NMR spectroscopy. IR νCO bands were shifted to lower wavenumbers (*e. g*. 2031 and 1924 cm^{-1} for **73**) in comparison to those found for the triflate precursors (*e. g*. 2037, 1935 and 1915 cm^{-1} for [Re(bipy)$(CO)_3$(OTf)]), as a result of the strong electron-donating ability of the 1,2-Me_2Im ligand. Moreover, IR νCO bands of **73** were slightly lower than those of the [Re(bipy)$(CO)_3$(MeIm)]OTf[35b] analog (2033, 1929 and 1918 cm^{-1} in CH_2Cl_2), presumably due to the stronger electron-donating ability of the 1,2-Me_2Im in comparison to MeIm. Analogous shifts could be found in the IR spectra of molybdenum complexes **75** and **76** upon coordination of the 1,2-Me_2Im (*e. g*. from 1963 and 1884 cm^{-1} in the [Mo(bipy)$(\eta^3$-$C_4H_7)(CO)_2$(OTf)] precursor to 1952 and 1869 cm^{-1} in complex **75** both in CH_2Cl_2). NMR characterization was consistent with **73**, **74, 75** and **76** being C_s symmetric complexes (four signals for the bipy or phen in the ^{1}H NMR spectra, see Figure 52 for the ^{1}H NMR spectra of **73** and **76**). Moreover, as a result of the presence of the mirror plane, the CH_2 groups of the 2-methylallyl ligand of **75** and **76** occurred as two singlets (at 1.75 and 0.75 ppm in compound **76**, see Figure 52b). Signals for the methyl groups of the coordinated 1,2-Me_2Im occurred at 3.53 and 2.40 ppm, and at 3.37 and 2.36 ppm in the ^{1}H NMR spectra of **73** and **76** respectively (see Figure 52).

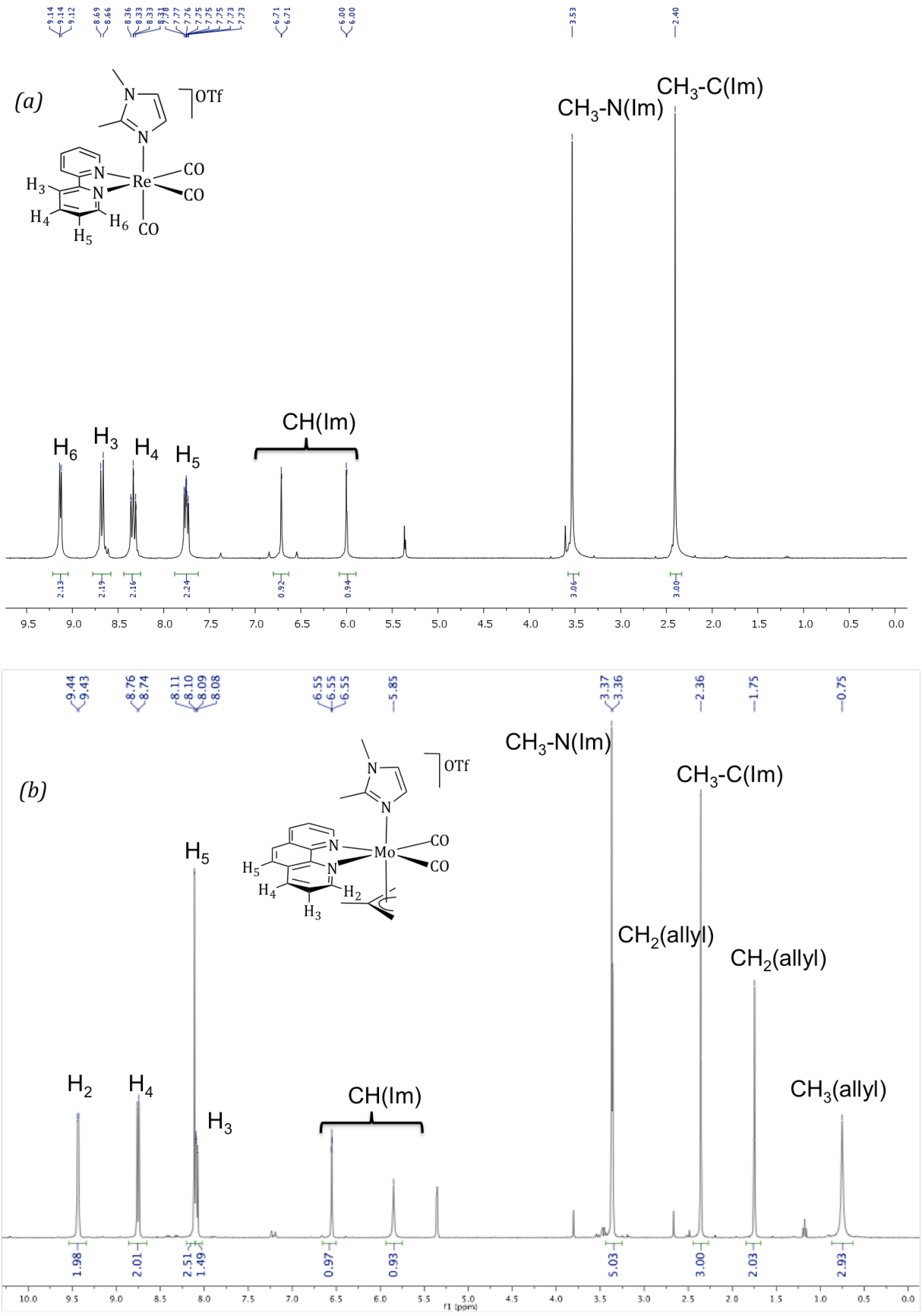
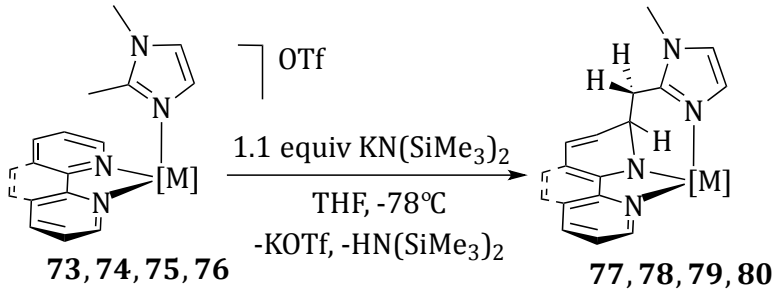


*Figure 52. ^{1}H NMR spectra in CD_2Cl_2 at 298 K of compounds (a) **73** and (b) **76**.*

Addition of a slight excess of $KN(SiMe_3)_2$ to a THF solution of compounds **73**, **74, 75** or **76** caused an instantaneous color change of the solutions from yellow to purple (in **73** and **74**), or from red to fuchsia (in **75**) and to green (in **76**) and a shift to lower wavenumbers of the IR νCO bands (from 2031 and 1924 cm^{-1} to 2003, 1894 and 1876 cm^{-1} for the reaction of **73**, and from 1949 and 1869 cm^{-1} to 1921 and 1835 cm^{-1} for the reaction of **75**, in THF). The products, **77**, **78, 79** and **80** were found to be thermally stable and could be isolated in moderate yields (*e. g*. 60 % for **77**) by filtration. 1D and 2D NMR characterization of the products showed the presence of asymmetric complexes formed as a result of methyl group deprotonation and intramolecular nucleophilic attack on position 6 of bipy and 2 of phen (see Scheme 62).



Compound	[M]	N-N
73, 77	$Re(CO)_3$	bipy
74, 78	$Re(CO)_3$	phen
75, 79	$Mo(\eta^3\text{-}C_4H_7)(CO)_2$	bipy
76, 80	$Mo(\eta^3\text{-}C_4H_7)(CO)_2$	phen

Scheme 62. C-C coupling between a deprotonated 2-methyl group of 1,2-dimethylimidazole and bipy or phen in rhenium and molybdenum complexes.

The ^1H NMR spectra of the products showed two multiplets for new CH_2 groups (at 3.32 and 2.27 ppm for **77**) from 2-methyl group deprotonation of the imidazole and signals for asymmetric bipy and phen ligands (eight signals in the ^1H NMR spectra, see Figure 53 for the ^1H NMR spectra of **77** and **80**). Moreover, due to the asymmetry of the complexes, the three (in **77** and **78**) or two (in **79** and **80**) CO ligands are inequivalent and occurred as three and two signals respectively in the ^{13}C NMR spectrum (at 201.3, 199.4 and 196.7 ppm for **77**). The asymmetry of **79** and **80** was also reflected in the four multiplets in the ^1H NMR spectrum for the CH_2 groups of the $\eta^3\text{-}C_4H_7$ ligand (at 3.20, 3.05, 1.78 and 1.38 ppm for **80**, see Figure 53b).

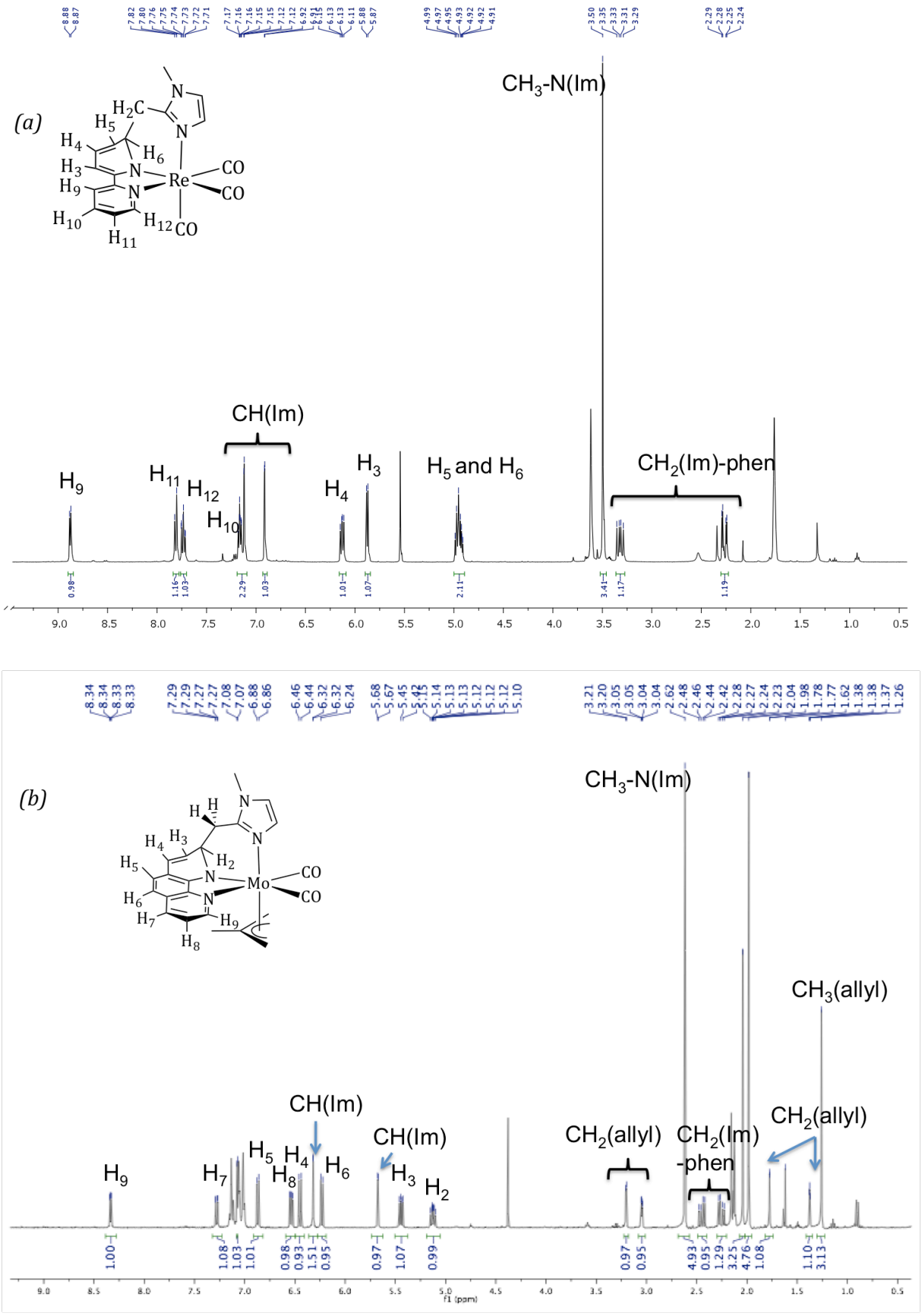


*Figure 53. ^{1}H NMR spectra in THF-d_8 at 298 K complexes (a) **77** and (b) **80**.*

Slow diffusion of pentane into concentrated solutions of **77** and **79** in toluene afforded purple (for **77**) and red (for **79**) crystals that allowed solid-state structure determinations by X-ray diffraction analysis. The solid-state structures of **77** and **79** confirmed the proposed connectivity and showed *fac*-$Re(CO)_3$ (in **77**) or *cis*-$Mo(\eta^3\text{-}C_4H_7)(CO)_2$ (in **79**) fragments bonded to *N,N',N''* ligands resulting from nucleophilic attack of the deprotonated 2-methyl group of the imidazole on position 6 of the bipy ligand (see Figure 54 and Table 12).

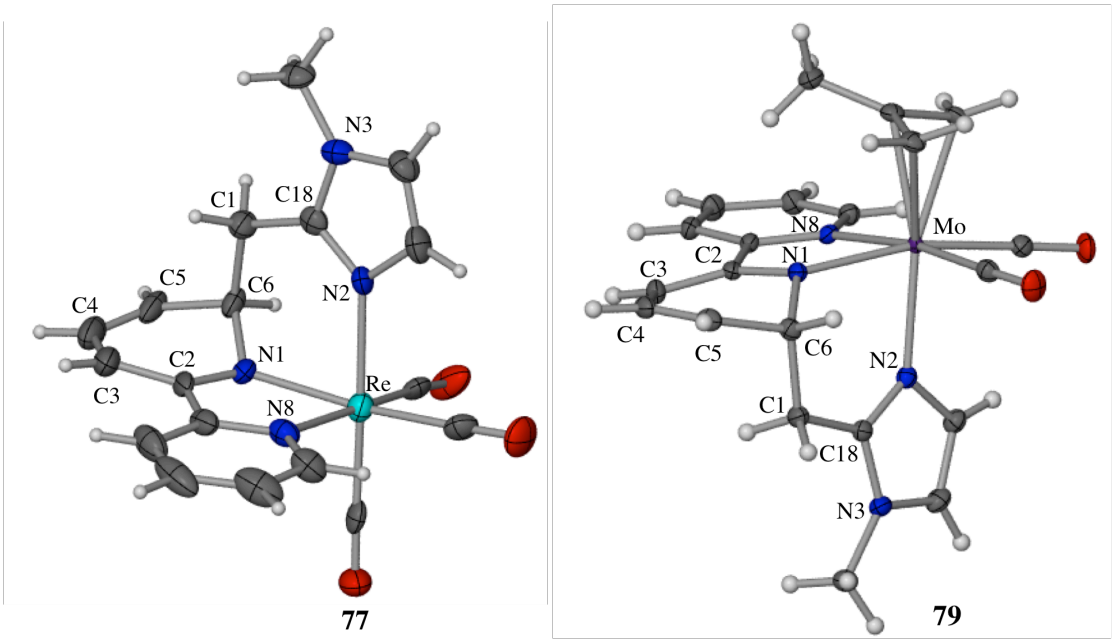


*Figure 54. Solid-state structures (ellipsoids at the 30% probability level) of complexes **77** and **79**.*

	77	**79**
M-N1	2.128(5)	2.160(2)
M-N8	2.183(5)	2.245(3)
M-N2	2.200(5)	2.239(2)
N1-C6	1.467(8)	1.464(4)
C5-C6	1.512(9)	1.512(4)
C4-C5	1.36(1)	1.344(5)
C3-C4	1.42(1)	1.427(5)
C2-C3	1.38(1)	1.377(4)
C1-C6	1.536(9)	1.552(4)
C18-C1	1.493(9)	1.493(4)
C6-N1-C2	115.0(5)	114.1(2)
C6-N1-M	120.2(4)	119.1(2)
C2-N1-M	117.5(4)	120.1(2)
C18-N2-M	128.9(4)	127.8(2)
C1-C6-N1	110.5(5)	109.5(2)
N2-M-N1	79.5(2)	77.52(9)
N2-M-N8	89.5(2)	85.23(9)

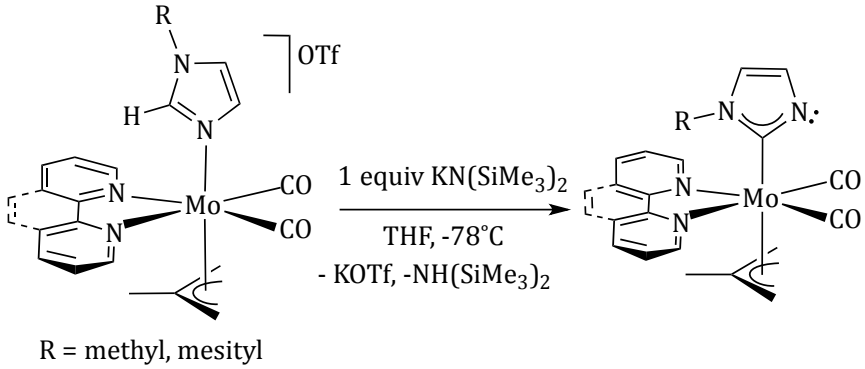
*Table 12. Selected bond distances (Å) and angles (°) of complexes **77** and **79**. "M" label denotes Re in **77** and Mo in **79**.*

M-N1 distances in both **77** and **79** (2.128(5) and 2.160(2) Å respectively) are shorter than M-N8 distances (2.183(5) Å in **77** and 2.245(3) Å in **79**) consistent with N1 being an amido donor as a result of pyridyl ring dearomatization due to nucleophilic attack of the CH_2 group. The sum of angles around N1 is lower than 360° for both complexes (352.7(5)° in **77** and 353.7(2)° in **79**) hinting a pyramidal geometry around N1, as found for complexes **67** and **72** (see sections 4.1 and 4.2). Distances N1-C6 (1.467(8) Å in **77** and 1.464(4) Å in **79**) and C6-C5 (1.512(9) Å in **77** and 1.512(4) Å in **79**) are virtually

identical for both complexes and are consistent with the presence of single bonds, supporting an sp^3 hybridization for C6.

Bond distances and angles in **77** are similar to those found in the product of deprotonation of the MesIm ligand in $[Re(bipy)(CO)_3(MesIm)]OTf$ (see Introduction).[35b] The most remarkable difference is the angle N2-Re-N1 (79.52(18)°) which is larger than the same angle in the product of deprotonation of MesIm (72.4(2)°). This difference could be attributed to the six member ring in **77** in contrast to the five member ring formed in the deprotonation of coordinated MesIm, which forces the imidazole to bend toward the bipyridine co-ligand to be able to accommodate the new C-C bond. Further consequences of this effect could be found in the angle Re-N2-C18 (128.9(4)° for **77**) which is larger than in the MesIm analog (117.5(7)°).

The formation of C-C coupling products in the deprotonation of **75** and **76** stands in contrast to the formation of 2-imidazolyl complexes as a result of the deprotonation of 1-methylimidazole and 1-mesitylimidazole coordinated to the same molybdenum fragments (see Scheme 63).[81]



Scheme 63. Deprotonation of 1-alkylimidazoles (alkyl = methyl, mesityl (2,4,6-trimethylphenyl)) in the Mo(N-N)(η^3-C_4H_7)$(CO)_2^+$ (N-N = bipy, phen) fragment.

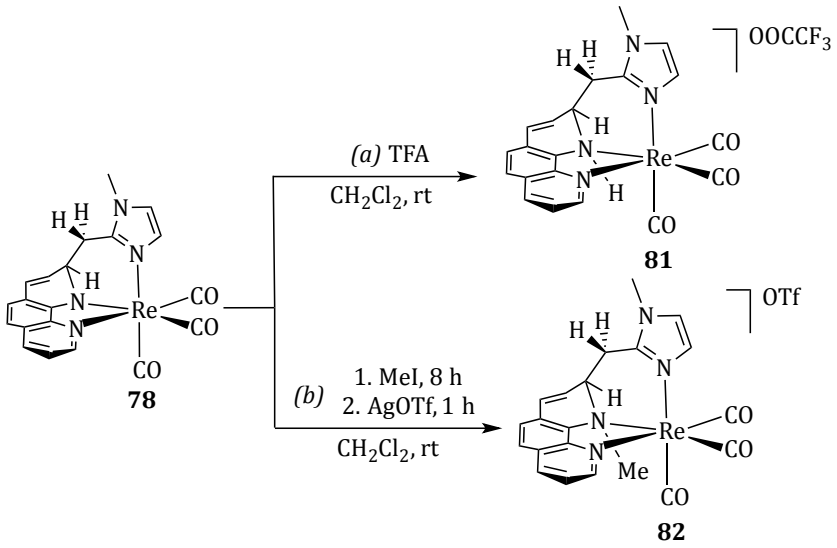
DFT calculations on the formation of imidazolyl complexes on the Mo(bipy)(η^3-C_4H_7)$(CO)_2^+$ fragment showed these species to be slightly more stable (-13.4 kcal·mol^{-1} for the 1-mesitylimidazolyl complex) than those of nucleophilic attack to the bipy chelate (-8.1 kcal·mol^{-1} for the 1-mesitylimidazole C-C coupling product). Therefore, small changes on the system (as the deprotonation of a methyl group in position 2 of the imidazole instead of the imidazole C(2)-H group) could favor the formation of C-C coupling products. This kind of products have been also obtained in the deprotonation

of [Mo(X_2bipy)(η^3-C_4H_7)(CO)$_2$(RIm)]OTf (R = Me, Mes, X_2bipy = 4,4'-chloro-2,2'-bipyridine, 4,4'-bromo-2,2'-bipyridine) complexes where the strong electron-withdrawing chlorine or bromine substituents favor nucleophilic addition on the chelate over the metal.[35a] However, in the reported cases, nucleophilic additions occurred on position 2 of substituted bipyridines, in contrast to the results described in this dissertation, where the additions take place at position 6 of non-substituted bipy.

To our knowledge, deprotonation of transition-metal coordinated 2-methyloxazoline, 2-methylpyridine and 1,2-dimethylimidazole has never been carried out. However, deprotonation of free heterocycles has been used for the synthesis of polydentate ligands with oxazoline,[82] pyridine[83] or imidazole donors.[84] To determine the role of the metal fragment on the C-C coupling reactions, free deprotonated α-methylheterocycles were reacted with bipy or phen. The deprotonation of 2-methyloxazoline, 2-methylpyridine and 1,2-dimethylimidazole ligands described in this Chapter occurred selectively in the methyl groups in alpha positions to the N donors, as reported for the deprotonations of the free molecules. However, attempts to carry out C-C coupling reactions between deprotonated (by reported procedures) α-methylheterocycles and bipy or phen in the absence of the rhenium fragment failed, except in the reaction of deprotonated 2-methylpyridine and phen.

4.4 Reaction of 78 with electrophiles.

Complex **78** readily reacted with electrophiles (CF_3COOH and MeI). Addition of a slight excess of trifluoroacetic acid (TFA) to a CH_2Cl_2 solution of **78** caused an instantaneous color change of the solution from purple to orange. The product, **81**, was isolated by precipitation as an orange solid and characterized by IR and NMR spectroscopy. IR νCO bands at higher frequencies than those of its precursor **78** supported **81** as a cationic compound (2032, 1928 and 1912 cm^{-1} in CH_2Cl_2). 1D and 2D NMR characterization showed that protonation occured at the amido group of complex **78** (see Scheme 64a).



*Scheme 64. (a)Protonation and (b) methylation of the amido nitrogen in **78**.*

^{1}H and ^{13}C NMR spectra of **81** displayed similar features than those found in **78** for the *N*,*N'*,*N''* tridentate ligand. A new broad signal at 7.70 ppm could be attributed to the N-H group which showed a $^{3}J_{HH}$ crosspeak in the ^{1}H,^{1}H-COSY spectrum with H2 of phen that confirmed its connectivity.

Addition of excess of MeI to a CH_2Cl_2 solution of **78** caused a color change from purple to dark orange upon 6 hours stirring at room temperature. The product, **82**, was isolated by filtration and a methathesis reaction with AgOTf was carried out to isolate the product as a triflate salt. IR νCO bands suggested **82** to be a cationic complex (2034 and 1925 cm^{-1} in CH_2Cl_2). 1D and 2D NMR characterization indicated the presence of a new N-Me group from the methylation of the amido nitrogen of **78** (see Scheme 64b). ^{1}H and ^{13}C NMR signals for the phen-CH_2 skeleton were similar to those found for compound **81** except for a new signal (singlet at 3.66 ppm in the ^{1}H NMR spectrum) attributed to the N-bonded methyl group (see Figure 55), which showed a $^{3}J_{CH}$ crosspeak with C2 of phen in the ^{1}H,^{13}C-HMBC spectrum supporting methylation at the nitrogen atom.

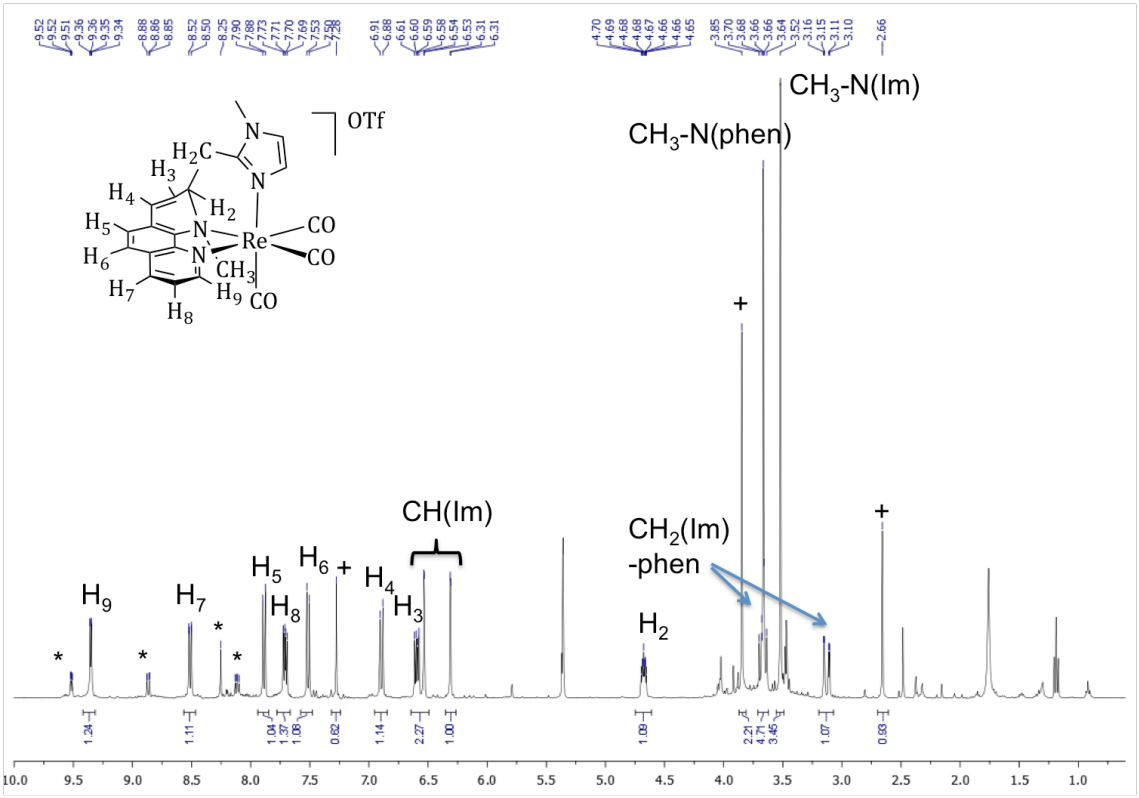
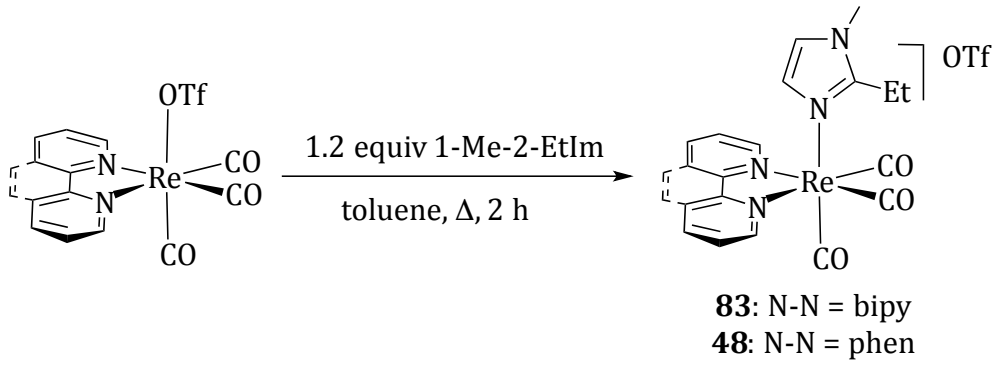


*Figure 55. ^{1}H NMR spectrum of compound **82** in CD_2Cl_2 at 298 K. Signals of [Re(phen)(CO)$_3$(OTf)] are marked * and signals of [1,2,3-Me$_3$Im]OTf are marked +.*

The NMR spectra of **82** showed minor amounts of [Re(phen)(CO)$_3$(OTf)] and an unknown impurity which is proposed to be [1,2,3-Me$_3$Im]OTf[85] (see Figure 55), formed as a result of the C-C bond breaking in **82** (likely promoted by traces of H_2O in the reaction media which would react with MeI to yield the strong acid [MeOH$_2$]OTf) and subsequent methylation (by MeI) and dissociation of the imidazole ligand.

4.5 Synthesis and deprotonation of [Re(N-N)(CO)$_3$(1-Me-2-EtIm)]OTf (N-N = bipy, phen) complexes

Reaction of the appropriate [Re(N-N)(CO)$_3$(OTf)] (N-N = bipy, phen) precursors with a slight excess of 1-Me-2-EtIm in refluxing toluene yielded new [Re(N-N)(CO)$_3$(1-Me-2-EtIm)]OTf (bipy (**83**), phen (**48**)) compounds which were isolated as yellow solids in good yields (*e. g.* 88 % for **48**), and fully characterized by IR (νCO bands at 2029 and 1921 for **83**) and NMR spectroscopy (see Scheme 65).



Scheme 65. Preparation of rhenium complexes with coordinated 1-methyl-2-ethylimidazole.

The ^{1}H and ^{13}C NMR spectra of **83** and **48** were consistent with the presence of C_s symmetric complexes with coordinated 1-Me-2-EtIm (see Figure 56).

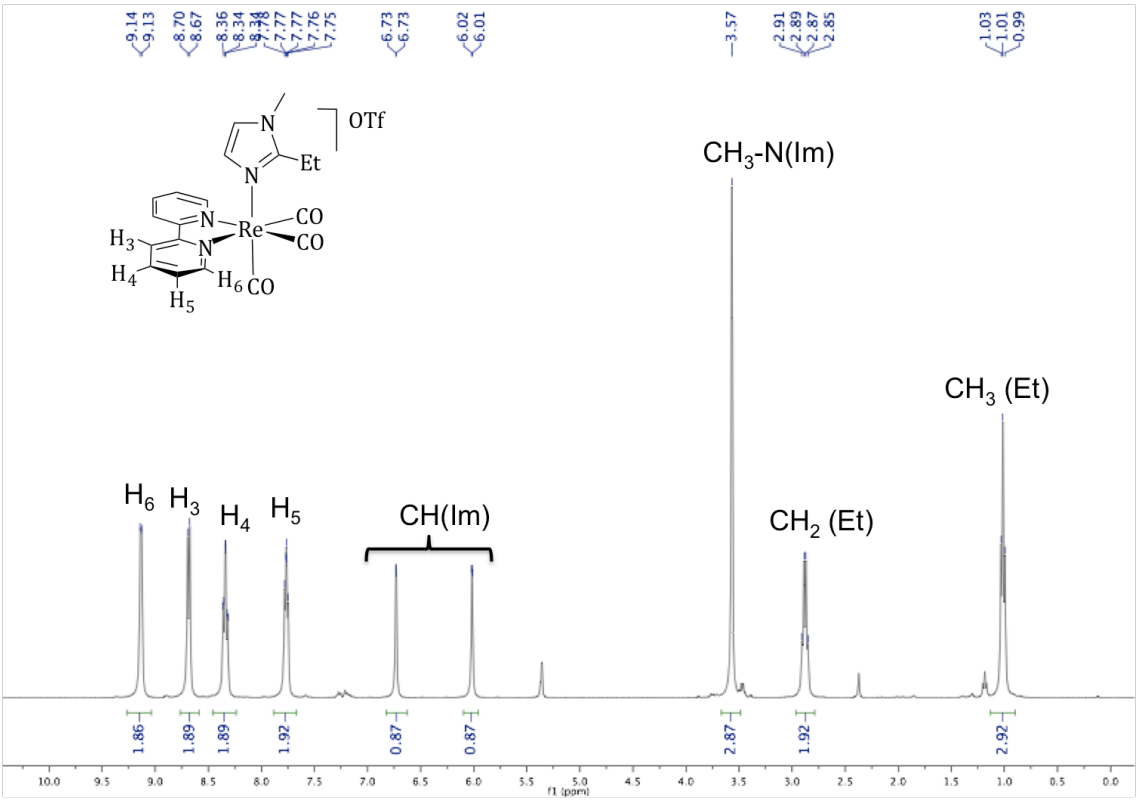
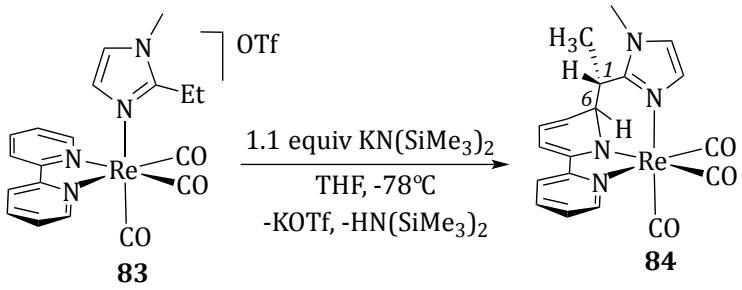


*Figure 56. ^{1}H NMR spectrum of compound **83** in toluene-d_8 at 298 K.*

Addition of a slight excess of $KN(SiMe_3)_2$ to a THF solution of **83** caused an instantaneous color change from yellow to purple and a shift to lower wavenumbers of the IR νCO bands (2007, 1897 and 1882 cm^{-1} in THF) consistent with the formation of a neutral product. After stirring the resulting solution at room temperature for 1 hour, the IR νCO bands slightly increased (2009, 1899 and 1879 cm^{-1} in THF), and the product, **84**,

was isolated as a purple solid in low yield (18 %, see below). 1D and 2D NMR characterization of **84** showed the presence of a single species from deprotonation of the CH_2 group in the 1-Me-2-EtIm ligand and nucleophilic attack on position 6 of the bipy co-ligand (see Scheme 66).



*Scheme 66. Deprotonation of coordinated 1-methyl-2-ethylimidazole in compound **83**.*

The ^{1}H NMR spectrum of **84** showed a quintuplet (1H, $^3J_{HH}$ = 7.2 Hz at 3.30 ppm in THF-d_8) assigned to the CH group of the imidazole bonded ethyl group and a doublet (3H, $^3J_{HH}$ = 7.2 Hz at 1.25 ppm) for the CH_3 of the ethyl group confirming deprotonation of the CH_2 group (see Figure 57).

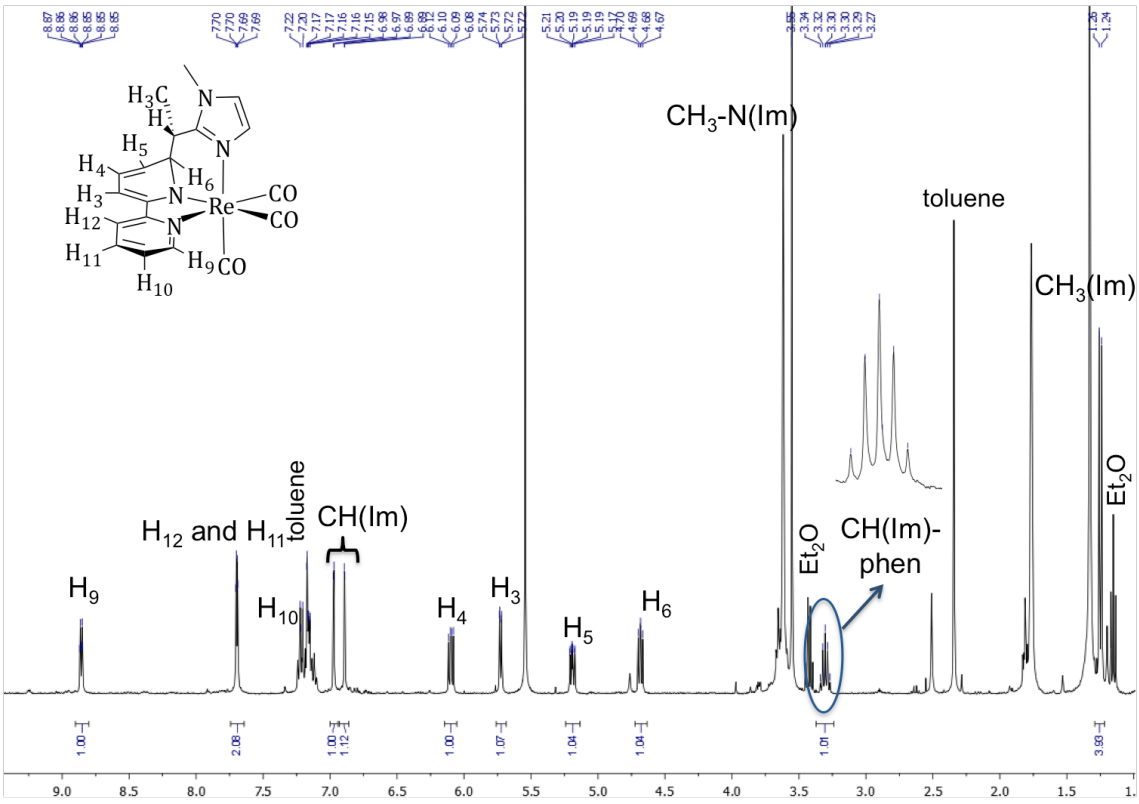


*Figure 57. ^{1}H NMR spectrum of compound **84** in THF-d_8 at 298 K.*

Slow diffusion of hexane into a concentrated solution of **84** in toluene yielded purple crystals suitable for X-ray diffraction. Solid-state structure of **84** confirmed the proposed connectivity and showed a *fac*-$Re(CO)_3$ fragment bonded to a *N,N',N''* ligand from CH_2 group deprotonation of the imidazole and coupling with position 6 of bipyridine (see Figure 58 and Table 13). The product was found to be the *SRRR* diastereomer (racemic mixture).[46,86]

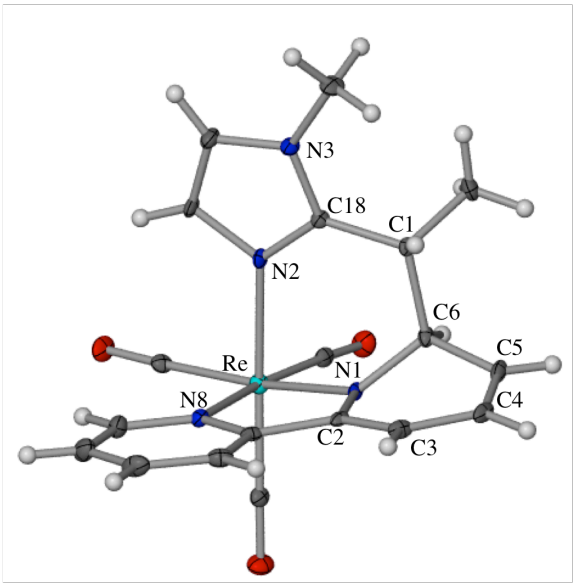


*Figure 58. Solid-state structure (ellipsoids at the 30% probability level) of complex **84**.*

Re-N1	2.106(3)
Re-N8	2.190(3)
Re-N2	2.183(4)
N1-C6	1.452(6)
C5-C6	1.518(6)
C4-C5	1.346(7)
C3-C4	1.425(7)
C2-C3	1.378(6)
C1-C6	1.560(6)
C18-C1	1.501(5)
C6-N1-C2	115.4(3)
C6-N1-Re	119.6(3)
C2-N1-Re	119.4(3)
C18-N2-Re	129.2(3)
C1-C6-N1	112.7(3)
N1-C6-C5	109.9(4)
C1-C6-C5	110.2(3)
N2-Re-N1	78.6(1)
N2-Re-N8	85.4(1)

*Table 13. Selected bond distances (Å) and angles (°) of complex **84**.*

Bond distances and angles in **84** are similar to those found for complex **77** (see above), *i. e.*, Re-N1 distance (2.106(3) Å) is consistent with an amido donor and Re-N8 with an imino group (2.190(3) Å). The geometry around N1 is pyramidal as indicated by the sum of angles around it (354.4(3)°) and the hybridization of the attacked carbon atom C6 is sp^3 (N1-C6 and C5-C6 distances are 1.452(6) Å and 1.518(6) Å respectively).

NMR monitoring of the formation of **84** revealed the presence of an intermediate species, **85**, which could not be isolated due to its evolution to **84**. The IR spectrum of **85** (2007, 1897 and 1882 cm^{-1} in THF) was similar to that found for **84** (see above), indicating that **85** is a neutral complex. ^1H NMR monitoring of the transformation of **85** in **84** at room temperature revealed that 6 hours were required for the reaction to reach completion. Compound **85** partially decomposed during the transformation, which resulted in a low isolated yield of **84** (18 %, see above). Full NMR characterization revealed **85** to have the same connectivity as **84**, from which it only differed in the configuration of the C1 atom (see Scheme 67), *i. e.*, the hydrogen atom in that carbon could be *trans* to the H6 of bipy (in **84**, *SRRR* diasteromer (racemic mixture)) or *cis* (in **85**, *RRRR* diasteromer (racemic mixture)). The ^1H NMR spectrum showed **85** to be the *RRRR* diasteromer (racemic mixture) since the signal at 2.83 ppm assigned to the C1-bonded hydrogen was a quadruplet of doublets ($^3J_{HH}$ = 7.3 Hz (with the CH_3 group) and $^3J_{HH}$ = 3.1 Hz (with bipy H6)) as a consequence of the *cis* disposition of the hydrogen in the imidazole CH group and H6 of bipy (see Figure 59). A similar assignment of the configuration of the imidazole CH group in **84** was made on the basis of its couplings on the ^1H NMR spectrum: the signal was a quintuplet (see above) due to a larger $^3J_{HH}$ with bipy H6 (7.2 Hz), identifying **84** as the *SRRR* diasteromer (racemic mixture) with a *trans* disposition of the C(Im)-H and the H6 of bipy, as confirmed by X-ray diffraction (see above).

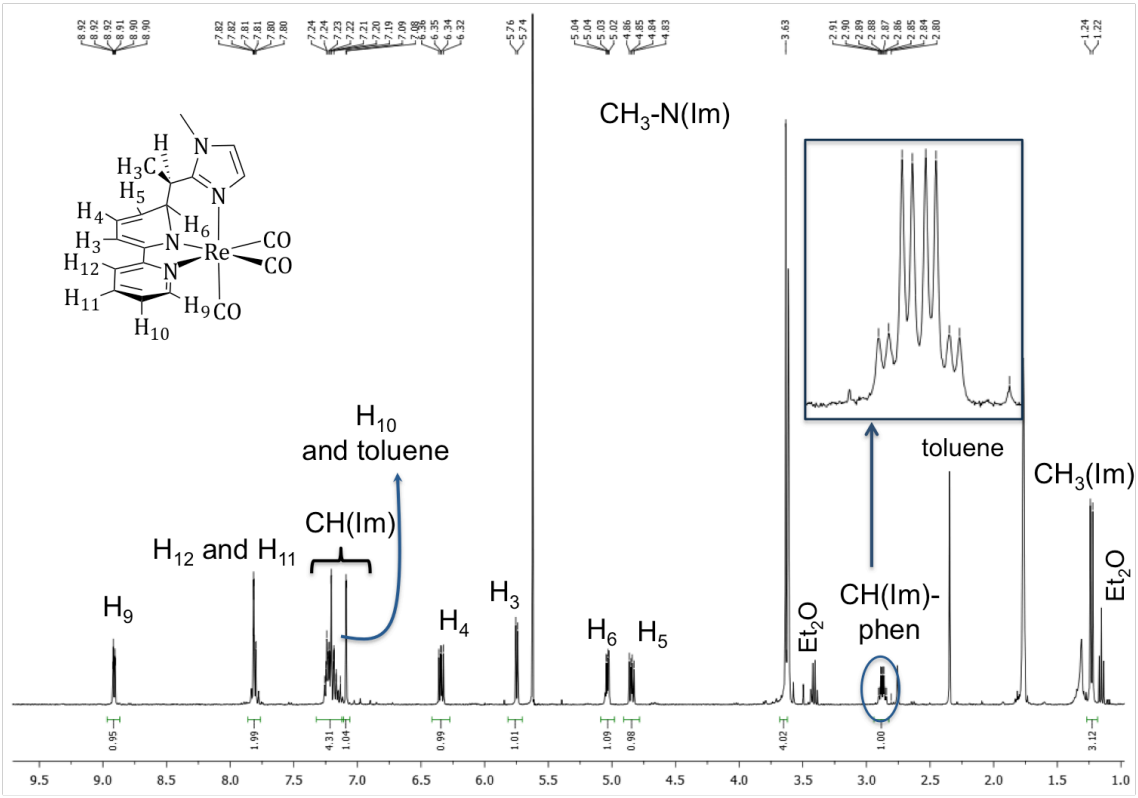
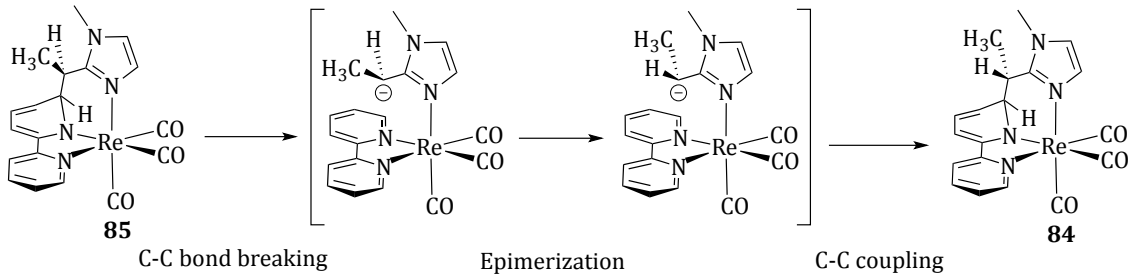


*Figure 59. ^{1}H NMR spectrum of compound **85** in THF-d_8 at 298 K.*

Formation of diasteromers has been found in the deprotonation reactions of compounds [Re(bipy)(CO)$_3$(SMe$_2$)]OTf (**1**) (see Section 1.1 of Chapter 1) and [Re(phen)(CO)$_3$(PPhMe$_2$)]OTf (**41**) (see Section 3.6 of Chapter 3), although in those cases, both diasteromers were formed as a mixture in the reaction. In contrast, in the deprotonation of **83** one diasteromer is formed first as a single species (**85**) and then transforms into the other (**84**). Complex **84** is proposed to be formed as the thermodynamic product of the reaction, suggesting a higher stability of the hydrogen *trans* configuration, in contrast to the *cis* configuration found in complex **85**, which would be the kinetic product. Epimerization of the stereogenic carbon in **85** could occur by C-C bond breaking (rate determining step) promoted by pyridyl ring rearomatization (see Scheme 67). Reversible C-C bond formations have been found to occur in the deprotonation of compounds [Re(bipy)(CO)$_3$(SMe$_2$)]OTf (**1**) (see Section 1.1 of Chapter 1) and [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (**14**) (see Section 2.4 of see Chapter 2).



*Scheme 67. Proposed mechanism for the transformation of complex **85** in **84**.*

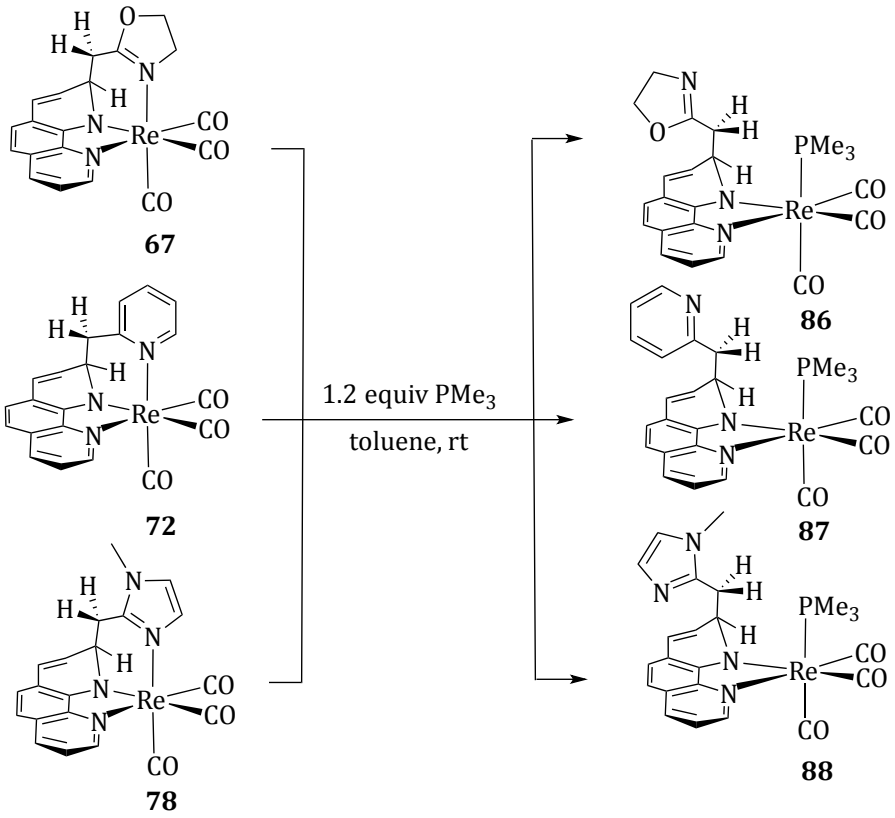
Addition of $KN(SiMe_3)_2$ to compound **48** yielded a neutral complex product of intermolecular nucleophilic attack of $KN(SiMe_3)_2$ on position 4 of phen (see Section 3.5 of Chapter 3). The different reactivity toward $KN(SiMe_3)_2$ of compounds **83** and **48** could be attributed to the weaker acidity of the CH_2(ethyl) group of the 1-Me-2-EtIm in comparison to 1,2-Me_2Im (the 1-Me-2-EtIm possesses an electron-donating CH_3 substituent on the α-CH_2-group), which makes the nucleophilic intermolecular attack of $KN(SiMe_3)_2$ on phen preferred over CH deprotonation. In contrast, the bipy complex (**83**) is not affected by the weak acidity of the CH_2 group as intermolecular attack on coordinated bipy is less favored than on coordinated phen.

Deprotonation of coordinated 1,2-Me_2Im (see section 4.3) and 1-Me-2-EtIm selectively yielded products of deprotonation of the C(sp^3)-H groups in α position to the coordinated nitrogen, *i. e.*, products from deprotonation of the C5-H group (abnormal position) in 1,2-Me_2Im and 1-Me-2-EtIm or of the CH_3 group of the ethyl substituent in 1-Me-2-EtIm have not been detected. This selectivity could be mainly attributed to the lower acidity of the abnormal CH group and of the CH_3 group of the ethyl substituent in comparison to the C(sp^3)-H groups in α position to the N donor.

4.6 Reaction of C-C coupling complexes 67, 72 and 78 with PMe_3

Addition of a slight excess of PMe_3 to THF solutions of **67**, **72** or **78** caused a color change from purple to green and a shift to slightly higher wavenumbers of the IR νCO bands (from 2008, 1902 and 1885 to 2013, 1917 and 1888 cm^{-1} for the reaction of **72**) upon 18 hours, 5 minutes and 3 days respectively at room temperature. 1D and 2D NMR characterization showed the new complexes, **86**, **87** and **88** respectively, to contain a

new PMe_3 ligand, which displaced the oxazoline, imidazole or picoline donor of the *N*,*N'*,*N''* ligands in the precursors (see Scheme 68).



*Scheme 68. Reaction of phen C-C coupling complexes **67**, **72** and **78** with PMe_3.*

^1H, ^{13}C and ^{31}P NMR of the products showed signals for coordinated PMe_3 (*e*. *g*. doublet at 0.68 ppm in the ^1H NMR spectrum of **87**) and for the CH_2-phen skeleton, with CH_2 groups slightly downfield shifted (at 3.77 and 3.58 ppm for **87**, see Figure 60 for the ^1H NMR spectrum) than those of the precursors (see above). ^1H and ^{31}P NMR monitoring of the reaction was consistent with the formation of **86**, **87** and **88** as single species and showed a progressive disappearance of the signals of the precursors and a concomitant growth of those of the products (see Experimental Section).

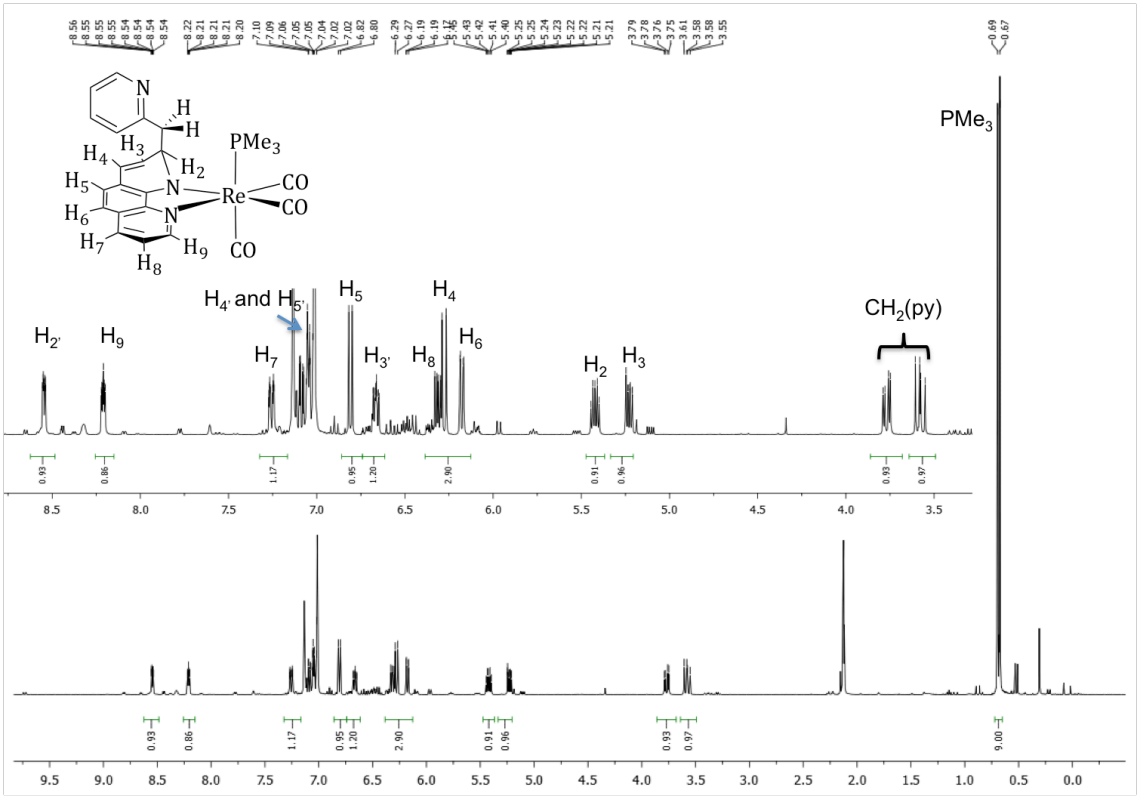


*Figure 60. ^{1}H NMR spectrum of compound **87** in toluene-d_8 at 298 K.*

^{1}H,^{15}N-HMBC experiments of complexes **72** and **87** showed a shift of the picoline donor ^{15}N signal from 252.0 ppm in **72** to 320.0 ppm in **87** (in toluene-d_8) while the chemical shifts for the amido and imino of the phen remained virtually unchanged, supporting picoline donor displacement by PMe_3. Moreover, the chemical shift of the picoline nitrogen in **87** resembled that found for free 2-methylpyridine (319.1 ppm in toluene-d_8).

The different reaction times of complexes **67**, **72** and **78** could be attributed to the different steric hindrance and electronic donating ability of the oxazoline, imidazole and picoline donors, since the reaction for **72** is remarkable faster than for **67** and **78**. Therefore, the shorter reaction time found for the displacement of the picoline donor in **72** could be attributed to its higher steric hindrance, due to the fact that in the six-member ring the methyl groups are more directed toward the metal fragment, and to the weaker electron-donating ability of the picoline donor in comparison with the 1,2-dimethylimidazole and 2-methyloxazoline.

The formation of the relatively stable complexes **86-88** shows that tridentate coordination is not needed for the stability of the complexes in which one of the pyridyl rings has been dearomatized.

The results described in this Chapter are remarkable in that (a) deprotonation of methyl groups of coordinated ligands occurs when the methyl groups are in position α to the heteroatom, *i. e.*, one position further away from the heteroatom than the C-H groups deprotonated in the alkylimidazole, SMe_2 and methylphosphane ligands previously studied; and (b) new six-member cycles have been formed by C-C coupling between 2-methylheterocycles and bipy, phen or 2-(CH=N*p*-tol)py, in contrast to the five-member cycles formed by deprotonation of alkylimidazole, SMe_2 or methylphosphane ligands.

Conclusiones

Conclusiones:

1. Los ligandos 2,2'-bipiridina y 1,10-fenantrolina coordinados a metales de transición no son inertes y pueden experimentar adiciones nucleofílicas intra- e intermoleculares en condiciones suaves.

2. Se puede desprotonar selectivamente grupos metilo de ligandos metilsulfuro, metilfosfina y α-metilheterociclo con $KN(SiMe_3)_2$ en complejos tricarbonílicos de renio (I).

3. La desprotonación de los grupos metilo de ligandos metilsulfuro, metilfosfina y α-metilheterociclo da lugar a la adición nucleofílica intramolecular sobre bipy o phen. Esta reacción genera productos con ligandos de tipo bipy o phen que contienen un anillo desaromatizado.

4. Los productos de adición nucleofílica sobre bipy o phen pueden ser inestables, presumiblemente debido a la tendencia del anillo atacado a recuperar su aromaticidad. La estabilidad de complejos análogos en los que el ataque nucleofílico se ha producido sobre una diimina no aromática apoya esta hipótesis.

5. La formación de enlaces C-C en la posición 2 de bipy puede ser reversible y dar lugar a productos termodinámicamente más estables en los que el enlace C-C se encuentra en la posición 6.

6. La adición nucleofílica intermolecular de $KN(SiMe_3)_2$ sobre el ligando phen es un proceso que puede competir con la desprotonación de grupos metilo. En algunos

casos esta adición es reversible y se produce la formación del producto de acoplamiento C-C termodinámicamente más estable.

7. Los ligandos bipy y phen pueden experimentar adiciones nucleofílicas intermoleculares de reactivos organolíticos que, normalmente, actúan como bases fuertes (*e*. *g*. *n*BuLi, *t*BuLi o MeLi).

8. La coordinación al metal influye en la posición sobre la que se produce el ataque nucleofílico en bipy y phen. Así, en algunos casos, los ataques nucleofílicos ocurren en posiciones que no son las más electrofílicas en el ligando libre, lo que permite obtener ligandos con nuevos patrones de sustitución no accesibles mediante métodos de síntesis orgánica convencionales. Éste es el caso, por ejemplo, de la preparación de un complejo de renio con el ligando 5-*tert*butil-2,2'-bipiridina mediante adición de *t*BuLi al ligando bipy.

9. La adición intermolecular de un equivalente de hidruro ocurre en los ligandos bipy y phen. Sin embargo, tras la adición, los ligandos se comportan de distinta forma en presencia de exceso de hidruro: mientras que la fenantrolina adiciona un segundo equivalente de hidruro, la bipiridina dimeriza mediante formación de nuevos enlaces C-C generando un complejo dinuclear.

Experimental Section

Experimental Section

General conditions and methods.

All manipulations were performed under a dinitrogen atmosphere using standard Schlenk techniques.

Solvents (Merck, purchased from VWR) were distilled over appropriate drying agents under dinitrogen: CH_2Cl_2 over CaH_2, THF and diethyl ether over Na/benzophenone, and hexane and toluene over freshly wired sodium.

IR solution spectra were obtained in a Perkin-Elmer Spectrum 100 FT-IR spectrometer using 0.2 mm CaF_2 cells. Unless stated otherwise, all IR νCO bands reported have strong intensity.

All chemicals, unless noted otherwise, were purchased from commercial sources and used without further purification.

Unless stated otherwise, all filtrations were carried out via steel cannula with a paper filter on one of the ends, forcing the solution to pass through the cannula by means of dinitrogen pressure.

In the NMR spectra of compounds with the $BAr^F{}_4^-$ anion, only the resonances due to the cation are given. The resonances due to $BAr^F{}_4^-$ anion are: **^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz):** δ 7.77 [s, 8H, H_o], 7.52 [s, 4H, H_p]. **^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz):** δ 161.7 [q (49.1), C_i], 134.8 [C_o], 129.0 [q (31.3), C_m], 125.1 [q (271.2), CF_3], 117.5 [C_p].

The NMR spectra were recorded on Bruker AV 300, Bruker AV 400, and Bruker AV 600. The Bruker AV 400 spectrometer was operating at 400.54 for ^{1}H, 162.14 MHz for ^{31}P, 100.72 MHz for ^{13}C, 79.57 MHz for ^{29}Si and 40.59 MHz for ^{15}N, using a 5 mm PABBI ^{1}H/D-XBB inverse probe with a z-gradient coil. The Bruker AV 600 spectrometer was operating at 600.15 MHz for ^{1}H, using a 5 mm PATXI-^{1}H/D-^{13}C/^{15}N inverse probe with a z-gradient coil. ^{1}H, ^{13}C and ^{29} Si chemical shifts are reported relative to $SiMe_4$, ^{15}N to NH_3 (*l*) and ^{31}P to H_3PO_4 (85% solution in D_2O). Coupling constants (*J*) in parentheses for

NMR spectra are given in hertzs (Hz). The ^{29}Si and ^{15}N spectra were indirectly recorded by ^{15}N HMBC and ^{29}Si HMQC experiments.

All the experiments were acquired with the *TOPSPIN 2.1* Bruker NMR software and processed with the *TOPSPIN 2.1* Bruker NMR or the *MestreNova* software. The COSY, TOCSY, HSQC, HMBC, HMQC and NOESY experiments were recorded on the AV400 spectrometer using the gradient enhanced versions of the pulse sequences. The ^{31}P NMR spectra used for signal integration were registered with inverse gated decoupling, using a 15° pulse and a relaxation delay of 5 seconds. The ^{1}H-^{29}Si correlations were detected through a HMQC experiment optimized for a long-range ^{1}H-^{29}Si coupling constant of 7 Hz. The spectrum was acquired with 1024 × 64 data set, 32 scans and a relaxation delay of 1.5 s. The ^{1}H-^{15}N correlations were detected through a HMBC experiment optimized for a long-range ^{1}H-^{15}N coupling constant of 7 Hz. The spectrum was acquired with 1024 × 64 data set, 32 scans and a relaxation delay of 1.5 s. The FIDs were processed using zero filling to 1024 points in the F1 dimension and no shifted sine bell windows functions in both dimensions. The ^{1}H-DOSY experiments were performed on an AV600 spectrometer equipped with a gradient unit that produces magnetic field pulsed gradients in the z-axis of 53.5 G/cm. For the DOSY experiments the temperature was set to 298 K and maintained with an air flow of 400 l/h. The experiments were acquired with the bipolar longitudinal eddy current delay pulse program (*ledbpgps2s* in Bruker software) with spinning of the sample to avoid convection influence. The diffusion time (D20 = 120 ms) and the gradient duration (P30 = 900 μs) were optimized with the *ledbpgp2s1d* sequence previously for the measurement to get a 1-5% of residual signal with the maximum strength while observing a progressive decay of the signal intensities. The pulse gradients were increased from 5 to 95% of the maximum strength in a linear ramp through 16 steps of 24K data points each. The spectral width was set to AQ = 1.86 s, the number of scans were 16 and a relaxation delay D1 = 1s was used. The direct dimension was zero-filled to 32K, Fourier transformed and phase corrected. The diffusion dimension was zero-filled to 256 and processed with the standard Bruker DOSY algorithm. The diffusion coefficients were measured in a logarithmic scale and the accuracy of the reported values are ±0.01.

For compounds with the $^{-}$OTf anion the signal of the $[CF_3SO_3]^-$ was not seen in the ^{13}C NMR spectrum presumably due to its low intensity for its coupling with fluorine.

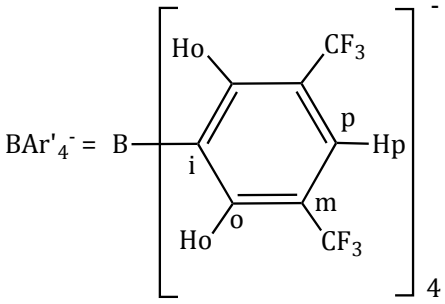
For diastereomeric mixtures, the assignment of the NMR signals to the major (**xM**) and minor (**xm**) components of the mixture is based on relative intensities. The ratio between diasteromers was obtained by integration of the ^{31}P or ^{1}H NMR signals.

The assignment of all the ^{1}H and ^{13}C NMR signals was in part based in 2D NMR and DEPT NMR experiments. QC denotes Quaternary Carbon.

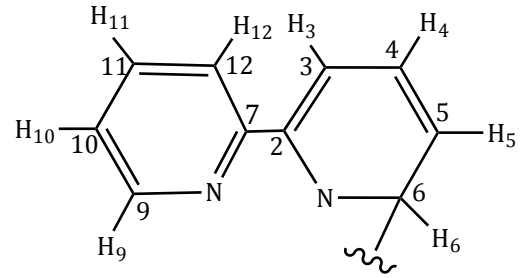
THF-d_8 (Merck) was purchased from VWR, and CD_2Cl_2, benzene-d_6, and toluene-d_8 from Cambridge Isotope Laboratories. Deuterated solvents were degassed by three freeze-pump-thaw cycles, kept in J. Young tubes and stored over oven-activated 4Å molecular sieves. In the case of CD_2Cl_2, potassium carbonate was also added to the J. Young tube, which was stored in a dark place.

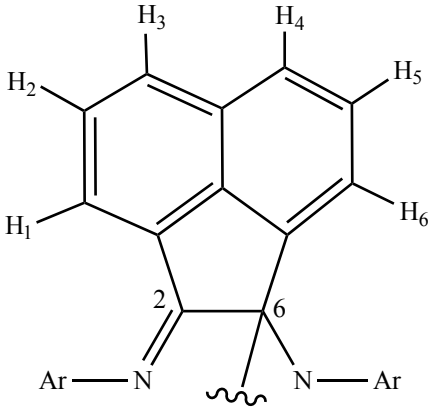
Compounds 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (2,6-*i*Pr_2BIAN),[57] 1,2-bis[(4-methylphenyl)imino]acenaphthene (*p*-MeBIAN),[87] [Re(bipy)$(CO)_3$(OTf)],[88] [Re(phen)$(CO)_3$(OTf)],[88] Na[BAr^F_4] (Ar^F = 3,5-bis(trifluoromethyl)phenyl),[89] [Re(*p*-MeBIAN)$(CO)_3$(OTf)],[44] [Re(*i*Pr_2BIAN)$(CO)_3$(OTf)],[44] K[BAr^F_4],[90] 1-methyl-2-ethylimidazole[91] and [Re{2-(CH=N*p*-tol)py}$(CO)_3$Br][92] were prepared following the reported procedures.

The NMR labelling schemes for the $BAr^F_4^-$ anion, 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2-methylpyridine (2-MePy), 2,6-*i*Pr_2BIAN, *p*-MeBIAN and the ligands resulting from nucleophilic attack to bipy (bipy'), phen (phen') and to 2,6-*i*Pr_2BIAN (2,6-*i*Pr_2BIAN') are depicted below.

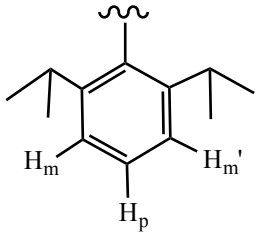


bipy = bipy' =





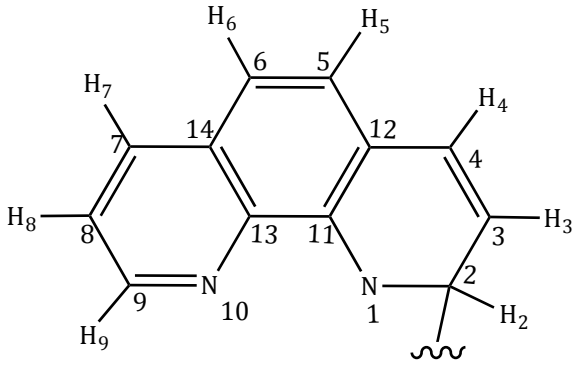
Ar =



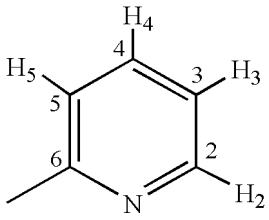
2,6- diisopropylphenyl

2,6-*i*Pr$_2$BIAN, *p*-MeBIAN and 2,6-*i*Pr$_2$BIAN',

phen, phen' =



2-CH$_3$py =



Crystallographic Structure Determination. General Description

Data collection was performed on a Bruker X8 KappaAPEXII or on an Oxford Diffraction Xcalibur Nova single crystal diffractometers, using Mo-Kα radiation (λ = 0.7107 Å) or

Cu-Kα (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program BRUKER APEX2[93] or with CrysAlis$_{Pro}$ CCD.[94] Data reduction and cell refinement was performed with the program BRUKER APEX2[93] or with CrysAlis$_{Pro}$ RED.[94] An empirical absorption correction was applied using the BRUKER SADABS algorithm as implemented in the program BRUKERAPEX2[93] or the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis$_{Pro}$ RED.[94] Crystal structures were solved by direct methods using the program SIR-92.[95] Anisotropic least-squares refinement was carried out with SHELXL-2014.[96] All nonhydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

Computational methods. General description.

Quantum chemical computations have been carried out with the Gaussian 09 series of programs.[97] Full geometry optimizations of stable species and transition states have been performed in THF and toluene solution from the outset with the Polarizable Continuum Model[98] and the Universal Force Field radii[99] in conjunction with the hybrid density functional B3LYP[100] and the 6-31+G(d)[101] basis set for non-metal atoms together with the LANL2DZ[102] for Re and by using the standard Schlegel's algorithm.[103] A relative permittivity of 7.58 and 2.37 has been assumed in the calculations to simulate THF and toluene as the solvents experimentally used, respectively. The nature of the stationary points has been verified by analytical computations of harmonic vibrational frequencies. Thermodynamic magnitudes (ΔH, ΔS, and ΔG) have also been calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations at a pressure of 1 atm and a temperature of 298.15 K.[104] The calculation of thermodynamic magnitudes in solution starting with molecular partition functions developed for computing gas-phase thermodynamics properties is a standard procedure that has proven to be a correct and useful approach.[105]

Preparation and Characterization of Compounds in Chapter 1

Synthesis of [Re(bipy)(CO)$_3$(SMe$_2$)]OTf (1). SMe_2 (0.10 mL, 1.3617 mmol) was added to a solution of [Re(bipy)(CO)$_3$(OTf)] (119 mg, 0.2066 mmol) in CH_2Cl_2 (20 mL). The resulting solution was magnetically stirred at room temperature for 6 hours. Addition of hexane (20 mL) caused the precipitation of **1** as a yellow solid, which was dried under vacuum. Slow diffusion of hexane (20 mL) into a concentrated solution of **1** in CH_2Cl_2 (8 mL) at -20°C afforded yellow crystals. Yield: 120 mg (91 %).

Anal. Calcd. for $C_{16}H_{14}F_3N_2O_6ReS_2$: C 30.15, H 2.21, N 4.39. Found: C 30.08, H 2.39, N 4.63.

IR (CH_2Cl_2, cm^{-1}): 2039, 1945, 1931 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 9.03 [m, 2H, H_6 and H_9 bipy], 8.80 [m, 2H, H_3 and H_{12} bipy], 8.41 [m, 2H, H_4 and H_{11} bipy], 7.79 [m, 2H, H_5 and H_{10} bipy], 2.28 [s, 6H, Re-SMe_2].

^{13}C{^{1}H} NMR (CD_2Cl_2, 300 MHz, 298 K): δ 194.3 [2 CO], 187.5 [CO], 155.8 [C_2 and C_7 bipy], 153.3 [C_6 and C_9 bipy], 141.6 [C_4 and C_{11} bipy], 128.8 [C_5 and C_{10} bipy], 125.6 [C_3 and C_{12} bipy], 22.7 [Re-SMe_2].

Synthesis of [Re(bipy)(CO)$_3$(SMe$_2$)]BAr$^F_4$ (1^F). $NaBAr^F_4$ (193 mg, 0.2183 mmol) was added to a solution of [Re(bipy)(CO)$_3$(OTf)] (119 mg, 0.2066 mmol) and SMe_2 (0.10 mL, 1.3617 mmol) in CH_2Cl_2 (20 mL). The resulting solution was magnetically stirred at room temperature for 6 hours. After filtration via cannula, volatiles were evaporated under vacuum and the resulting residue was washed with hexane (3 × 20 mL). Slow diffusion of hexane (20 mL) into a concentrated solution of **1^F** in CH_2Cl_2 (8 mL) at -20°C afforded yellow crystals, one of which was employed for an X-ray analysis. Yield: 213 mg (87%).

Anal. Calcd. for $C_{47}H_{26}BF_{24}N_2O_3ReS$: C 41.75, H 1.92, N 2.07. Found: C 41.93, H 1.43, N 1.92.

IR (CH_2Cl_2, cm^{-1}): 2042, 1950, 1935 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 9.12 [m, 2H, H_6 and H_9 bipy], 8.66 [m, 2H, H_3 and H_{12} bipy], 8.35 [m, 2H, H_4 and H_{11} bipy], 7.80 [m, 2H, H_5 and H_{10} bipy], 2.27 [s, 6H, Re-SMe_2].

^{13}C{^{1}H} NMR (CD_2Cl_2, 300 MHz, 298 K): δ 194.0 [2 CO], 186.7 [CO], 155.5 [C_2 and C_7 bipy], 153.5 [C_6 and C_9 bipy], 141.0 [C_4 and C_{11} bipy], 128.7 [C_5 and C_{10} bipy], 124.2 [C_3 and C_{12} bipy], 22.9 [Re-SMe_2].

^{1}H NMR monitoring of a solution containing [Re(bipy)$(CO)_3$(OTf)] and a tenfold excess of SMe_2 in CD_2Cl_2 showed complete formation of [Re(bipy)$(CO)_3(SMe_2)$]OTf (**1**) in 4 hours. Compound **1** could be isolated as an ^{1}H NMR and analytically pure compound just by solvent evaporation from its CH_2Cl_2 solution. However, ^{1}H NMR monitoring of its CD_2Cl_2 and thf-d_8 solutions demonstrated its lack of stability, resulting in the growing of the peak corresponding to free SMe_2. Compound [Re(bipy)$(CO)_3(SMe_2)$]$BAr^F{}_4$, which can also be prepared by metathesis from **1** and $NaBAr^F{}_4$ in CH_2Cl_2, was found to be stable in CD_2Cl_2, therefore crystals of this compound were grown for X-ray diffraction.

Synthesis of [Re(bipy)$(CO)_3(S(^{13}CH_3)_2)$]OTf (1*). Compound **1*** was prepared as described for **1** from [Re(bipy)$(CO)_3$(OTf)] (112 mg, 0.1951 mmol), $S(^{13}CH_3)_2$ (0.10 mL, 1.3615 mmol) and CH_2Cl_2 (20 mL). Slow diffusion of hexane (20 mL) into a concentrated solution of **1*** in CH_2Cl_2 (8 mL) at -20°C afforded yellow crystals. Yield: 109 mg (87%).

Anal. Calcd. for $C_{14}{}^{13}C_2H_{14}F_3N_2O_6ReS_2$: C 30.33, H 2.19, N 4.38. Found: C 30.43, H 2.21, N 4.36.

IR (CH_2Cl_2, cm^{-1}): 2041, 1947, 1932 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 9.03 [m, 2H, H_6 and H_9 bipy], 8.81 [m, 2H, H_3 and H_{12} bipy], 8.41 [m, 2H, H_4 and H_{11} bipy], 7.79 [m, 2H, H_5 and H_{10} bipy], 2.28 [dd (142.5, 4.1), 6H, Re-$S(^{13}CH_3)_2$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 300 MHz, 298 K): δ 195.0 [2 CO], 186.9 [CO], 155.5 [C_2 and C_7 bipy], 153.7 [C_6 and C_9 bipy], 141.1 [C_4 and C_{11} bipy], 128.4 [C_5 and C_{10} bipy], 124.1 [C_3 and C_{12} bipy], 23.0 [Re-$S(^{13}CH_3)_2$].

Reaction of 1 with $KN(SiMe_3)_2$. Characterization of 2M, 2m. $KN(SiMe_3)_2$ (0.40 mL of a 0.5 M solution in toluene, 0.2000 mmol) was added to a suspension of **1** (120 mg, 0.1888

mmol) in THF (20 mL) previously cooled to -78°C using an isopropanol/$N_{2(l)}$ bath. A gradual disappearance of the yellow solid afforded a dark red solution. The cooling bath was removed and the solvent was evaporated under vacuum. The resulting residue was extracted with toluene (20 mL) and filtered. Removal of the solvent and washing with hexane (2 × 5 mL) at -78°C yielded the diasteromeric mixture **2M**, **2m** as a microcrystalline solid. Repeated attempts to crystallize **2M**, **2m** were unsuccessful perhaps due to the thermal instability of the mixture.

2M:**2m** ratio = 2:1.

IR (THF, cm^{-1}): 2012, 1910, 1893 (ν_{CO}).

^{1}H NMR (THF-d_8, 400 MHz, 193 K): δ 8.96 [dd (4.9, 0.6), 1H, H_9 bipy', **2M**], 8.89 [dd (5.6, 0.6), 1H, H_9 bipy', **2m**], 8.17 [td (8.1, 0.6), 1H, H_{11} bipy', **2M**], 8.12 [td (8.2, 0.6), 1H, H_{11} bipy', **2m**], 7.89 [dd (8.1, 0.6), 1H, H_{12} bipy', **2M**], 7.81 [dd (8.2, 0.7), 1H, H_{12} bipy', **2m**], 7.51 [ddd (8.1, 4.9, 0.6), 1H, H_{10} bipy', **2M**], 7.42 [ddd (8.2, 5.6, 0.7), 1H, H_{10} bipy', **2m**], 6.80 [dd (6.3, 0.8), 1H, H_6 bipy', **2m**], 6.63 [dd (6.4, 0.6), 1H, H_6 bipy', **2M**], 6.12 [ddd (9.4, 5.9, 0.8), 1H, H_4 bipy', **2m**], 6.05 [ddd (9.4, 5.9, 0.6), 1H, H_4 bipy', **2M**], 5.38 [dd (9.4, 0.5), 1H, H_3 bipy', **2m**], 5.29 [dd (9.4, 0.5), 1H, H_3 bipy', **2M**], 4.49 [ddd (6.3, 5.9, 0.5), 1H, H_5 bipy', **2m**], 4.34 [ddd (6.4, 5.9, 0.5), 1H, H_5 bipy', **2M**], 2.93 [d (12.8), 1H, S-CH_2, **2M**], 2.67 [s, 3H, S-CH_3, **2m**], 2.40 [d (12.1), 1H, S-CH_2, **2m**], 2.15 [d (12.1), 1H, S-CH_2, **2m**], 1.59 [d (12.8), 1H, S-CH_2, **2M**], 1.47 [s, 3H, S-CH_3, **2M**].

^{13}C{^{1}H} NMR (THF-d_8, 400 MHz, 193 K): δ 199.2 [CO, **2m**], 198.2 [CO, **2M**], 197.9 [CO, **2m**], 197.8, 195.6 [CO, **2M**], 195.2 [CO, **2m**], 167.1 [C_7 bipy', **2m**], 165.5 [C_7 bipy', **2M**], 153.7 [C_9 bipy', **2m**], 153.4, 149.8 [C_9 and C_6 bipy', **2M**], 149.4 [C_6 bipy', **2m**], 140.9 [C_{11} bipy', **2M** and **2m**], 127.8 [C_5 bipy', **2M**], 127.4 [C_5 bipy', **2m**], 124.4 [C_{10} bipy', **2M**], 124.2 [C_{10} bipy', **2m**], 121.4 [C_{12} bipy', **2M**], 120.6 [C_{12} bipy', **2m**], 102.1 [C_3 bipy', **2M**], 101.8, 90.0 [C_3 and C_4 bipy', **2m**], 89.6 [C_4 bipy', **2M**], 78.0 [C_2 bipy', **2M**], 76.3 [C_2 bipy', **2m**], 33.8 [S-CH_2, **2m**], 32.5 [S-CH_2, **2M**], 18.4 [S-CH_3, **2M**]. The CH_3 group signal for **2m** is obscured by the signal at 24.5 ppm of the residual protio-THF present in the solvent. Due to its larger intensity, the signal is visible in the spectrum of the analogous ^{13}C-labelled compound resulting from deprotonation of **1*** (see below).

Reaction of 1* with $KN(SiMe_3)_2$. Characterization of 2M*, 2m*. The mixture **2M***, **2m*** was obtained as **2M**, **2m** from $KN(SiMe_3)_2$ (0.35 mL of a 0.5 M solution in toluene,

0.1750 mmol), and a suspension of **1*** (109 mg, 0.1698 mmol) in THF (20 mL). The diasteromeric mixture **2M***, **2m*** was obtained as a dark red microcrystalline solid. Repeated attempts to crystallize **2M***, **2m*** were unsuccessful perhaps due to the thermal instability of the mixture.

Ratio **2M***:**2m*** = 2:1.

IR (THF, cm^{-1}): 2012, 1910, 1893 (ν_{CO}).

^{1}H NMR (THF-d_8, 400 MHz, 193 K): δ 8.95 [d (4.0), 1H, H_9 bipy', **2M***], 8.88 [d (4.2), 1H, H_9 bipy', **2m***], 8.16 [m, 1H, H_{11} bipy', **2M***], 8.12 [m, 1H, H_{11} bipy', **2m***], 7.87 [d (7.1), 1H, H_{12} bipy', **2M***], 7.81 [d (7.6), 1H, H_{12} bipy', **2m***], 7.51 [m, 1H, H_{10} bipy', **2M***], 7.42 [m, 1H, H_{10} bipy', **2m***], 6.80 [d (6.2), 1H, H_6 bipy', **2m***], 6.63 [d (6.2), 1H, H_6 bipy', **2M***], 6.12 [dd (8.7, 6.2), 1H, H_4 bipy', **2m***], 6.05 [dd (8.8, 6.3), 1H, H_4 bipy', **2M***], 5.38 [d (8.7), 1H, H_3 bipy', **2m***], 5.29 [d (8.8), 1H, H_3 bipy', **2M***], 4.49 [m, 1H, H_5 bipy', **2m***], 4.34 [m, 1H, H_5 bipy', **2M***], 2.96 [ddd (149.2, 11.9, 5.1), 1H, S-$^{13}CH_2$, **2M***], 2.67 [d (141.9), 3H, S-$^{13}CH_3$ **2m***], 2.41 [ddd (139.0, 11.1, 6.3), 1H, S-$^{13}CH_2$-bipy', **2m***], 2.15 [ddd (140.0, 11.1, 5.1), 1H, S-$^{13}CH_2$, **2m***], 1.50 [ddd (152.0, 11.9, 4.2), 1H, S-$^{13}CH_2$, **2M***], 1.48 [d (142.3), 3H, S-$^{13}CH_3$, **2M***].

$^{13}C\{^1H\}$ NMR (THF-d_8, 400 MHz, 193 K): (Assignment of C2 and C7 was aided by a DEPT-135 spectrum). δ 199.2 [CO, **2m***], 198.2 [CO, **2M***], 198.0 [CO, **2m***], 197.8, 195.6 [CO, **2M***], 195.2 [CO, **2m***], 167.1 [C_7 bipy', **2m***], 165.4 [C_7 bipy', **2M***], 153.7 [C_9 bipy', **2m***], 153.4, 149.7 [C_9 and C_6 bipy', **2M***], 149.5 [C_6 bipy', **2m***], 141.0 [C_{11} bipy', **2M***], 141.0 [C_{11} bipy', **2m***] 127.8 [C_5 bipy', **2M***], 127.4 [C_5 bipy', **2m***], 124.4 [C_{10} bipy', **2M***], 124.2 [C_{10} bipy', **2m***], 121.4 [C_{12} bipy', **2M***], 120.6 [C_{12} bipy', **2m***], 102.1 [C_3 bipy', **2M***], 101.9, 90.0 [C_3 and C_4 bipy', **2m***], 89.6 [C_4 bipy', **2M***], 78.0 [d (31.8), C_2 bipy', **2M***], 76.1 [d (31.2), C_2 bipy', **2m***], 33.8 [S-$^{13}CH_2$, **2m***], 32.4 [S-$^{13}CH_2$, **2M***], 25.0 [S-$^{13}CH_3$, **2m***], 18.4 [S-$^{13}CH_3$, **2M***].

Reaction of 1 with $KN(SiMe_3)_2$. Characterization of 3M, 3m and 4. Toluene was removed from 0.25 mL of the 0.5 M toluene solution of $KN(SiMe_3)_2$ (0.125 mmol) under vacuum in a J. Young tube at 60°C for two hours. The resulting white solid was dissolved in 0.15 mL of THF-d_8 and added via cannula to a stirred THF-d_8 suspension of **1** (75 mg, 0.1176 mmol) at -78°C. The suspension turned slightly brown. Upon raising the temperature to room temperature, solid **1** dissolved and the solution turned red. The

resulting mixture was let stir for four hours at room temperature after which the solution turned purple. The solution was filtered via cannula to an NMR tube and the ^{1}H and 2D NMR spectra were registered. The NMR spectra showed the presence of at least three rhenium species in solution, **3M**, **3m** and **4,** accompanied by traces of unknown species. Only signals of **3M**, **3m** are listed, see the independent preparation of **4** below for its characterization. Due to the low concentration of the sample, the ^{13}C NMR characterization was not attempted and the ^{13}C NMR signals listed have been obtained from the ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC spectra.

3M:**3m** ratio = 1.1:1.

IR (THF, cm^{-1}): 2009, 1908, 1891 (ν_{CO}).

^{1}H NMR (THF-d$_8$, 400 MHz, 298 K): δ 8.70 [m, 1H, H_9 bipy', **3M**], 8.22 [dd (6.0, 1.7), 1H, H_9 bipy', **3m**], 7.76 [d (8.2), 1H, H_{12} bipy', **3M**], 7.68 [m, 1H, H_{11} bipy', **3M**], 7.13 [m, 1H, H_{10} bipy', **3M**], 6.73 [ddd (8.4, 6.6, 1.7), 1H, H_{11} bipy', **3m**], 6.30 [d (8.4), 1H, H_{12} bipy', **3m**], 6.12 [dd (8.7, 6.1), 1H, H_4 bipy', **3M**], 5.97 [dd (8.6, 5.8), 1H, H_4 bipy', **3m**], 5.81 [m, 1H, H_{10} bipy', **3m**], 5.69 [dd (6.1, 1.1), 1H, H_3 bipy', **3M**], 5.33 [d (5.8), 1H, H_3 bipy', **3m**], 5.14 [m, 1H, H_5 bipy', **3M**], 4.93 [m, 1H, H_5 bipy', **3m**], 4.48 [ddd (10.8, 5.6, 3.1), 1H, H_6 bipy', **3M**], 4.34 [ddd (10.5, 5.5, 3.0), 1H, H_6 bipy', **3m**], 2.85 [dd (12.6, 10.8), 1H, S-CH_2, **3M**], 2.69 [dd (12.8, 10.5), 1H, S-CH_2, **3m**], 2.56 [dd (12.6, 3.1), 1H, S-CH_2, **3M**], 2.36 [d (12.8, 3.0), 1H, S-CH_2, **3m**]. Signals for the S-CH_3 groups could not be seen in the ^{1}H NMR spectrum and could be obscured by residual solvents.

$^{13}C\{^{1}H\}$ NMR (THF-d$_8$, 400 MHz, 298 K): Due to the low concentration of **3M**, **3m**, the ^{13}C NMR signals have been obtained from the ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC spectra, therefore, CO signals have not been seen. δ 160.6 [C_7 bipy', **3M**], 156.0 [C_7 bipy', **3m**], 153.7 [C_2 bipy', **3m**], 151.7 [C_2 bipy', **3M**], 152.9 [C_9 bipy', **3m**], 150.2 [C_9 bipy', **3M**], 130.2 [C_{11} bipy', **3m**], 124.3 [C_4 bipy', **3M** and **3m**], 121.8 [C_{10} bipy', **3M**], 120.4 [C_{11} bipy', **3M**], 120.0 [C_{12} bipy', **3M**], 119.0 [C_{12} bipy', **3m**], 108.0 [C_{10} bipy', **3m**], 106.1 [C_5 bipy', **3M**], 103.3 [C_5 bipy', **3m**], 92.7 [C_3 bipy', **3M**], 89.0 [C_3 bipy', **3m**], 61.6 [C_6 bipy', **3M** and **3m**], 36.6 [S-CH_2, **3M**], 35.9 [S-CH_2, **3m**], 14.8 [S-CH_3, **3M**], 11.7 [S-CH_3, **3m**].

To assign the signals of **4**, it was independently prepared from [Re(bipy)$(CO)_3$(OTf)] (40 mg, 0.070 mmol) and KN$(SiMe_3)_2$ (0.15 mL of a 0.5 M solution in toluene, 0.075 mmol) under the same conditions used for the characterization of **3M**, **3m**, *i. e.*, addition of the

base was carried out in a J. Young tube at -78°C and the resulting mixture was let to stir at room temperature for four hours. The resulting red solution was filtered to an NMR tube and the ^{1}H NMR spectrum was registered. Signals in the ^{1}H NMR spectrum matched those for the species accompanying **3M**, **3m**.

^{1}H NMR (THF-d$_8$, 400 MHz, 298 K): δ 8.63 [m, 2H, H$_6$ and H$_9$ bipy], 8.51 [m, 2H, H$_3$ and H$_{12}$ bipy], 7.83 [m, 2H, H$_4$ and H$_{11}$ bipy], 7.32 [m, 2H, H$_5$ and H$_{10}$ bipy], 0.10 [s, 9H, Re-N(SiMe$_3$)$_2$].

Alternative synthesis of 4. KN(SiMe$_3$)$_2$ (0.25 mL of a 0.5 M solution in toluene, 0.125 mmol) was added to a toluene (10 mL) suspension of [Re(bipy)(CO)$_3$(OTf)] (68 mg, 0.118 mmol) at room temperature. After stirring the resulting mixture for 30 minutes, the dark red solution was filtered. Removal of the volatiles yielded **4** as a red solid in a 86 % yield (60 mg). Due to the high air and moisture sensibility of **4** elemental analysis was not attempted.

IR (toluene, cm^{-1}): 2008, 1907, 1883 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 400 MHz, 298 K): δ 8.62 [m, 2H, H$_6$ and H$_9$ bipy], 6.90 [m, 4H, H$_3$, H$_{12,}$ H$_4$ and H$_{11}$ bipy], 6.38 [m, 2H, H$_5$ and H$_{10}$ bipy], 0.13 [s, 9H, Re-N(SiMe$_3$)$_2$].

^{13}C{^{1}H} NMR (toluene-d$_8$, 400 MHz, 298 K): δ 198.7 [2 CO], 190.5 [CO], 156.2 [C$_2$ and C$_7$ bipy], 154.4 [C$_6$ and C$_9$ bipy], 137.1 [C$_4$ and C$_{11}$ bipy], 124.5 [C$_5$ and C$_{10}$ bipy], 122.2 [C$_3$ and C$_{12}$ bipy], 8.7 [Re-N(SiMe$_3$)$_2$].

Reaction of 1 with KN(SiMe$_3$)$_2$ to yield 2M, 2m and addition of PMe$_3$. Preparation of 5. The addition of PMe$_3$ (20 μL, 0.2234 mmol) to a solution of **2M**, **2m** in THF (20 mL) at -78°C freshly prepared from **1** (120 mg, 0.1888 mmol) and KN(SiMe$_3$)$_2$ (0.40 mL of a 0.5 M solution in toluene, 0.2000 mmol), caused an instantaneous color change from dark red to brown. When the reaction mixture reached room temperature, the solvent and excess PMe$_3$ were eliminated under vacuum and the brown residue was extracted with CH$_2$Cl$_2$ (20 mL) and filtered. Removal of the solvent and washings with hexane (2 × 5 mL) at -78°C yielded **5** as a powdery brown solid. Repeated attempts to crystallize **5** were unsuccessful perhaps due to its thermal instability.

IR (THF, cm^{-1}): 2010, 1913, 1885 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 8.77 [d (5.4), 1H, H_9 bipy'], 7.93 [dd (7.7, 6.6), 1H, H_{11} bipy'], 7.63 [d (7.7), 1H, H_{12} bipy'], 7.27 [dd (6.6, 5.4), 1H, H_{10} bipy'], 6.70 [d (5.9), 1H, H_6 bipy'], 6.07 [dd (8.0, 5.9), 1H, H_4 bipy'], 4.90 [t (5.9), 1H, H_5 bipy'], 4.23 [d (8.0), 1H, H_3 bipy'], 2.86 [d (13.6), 1H, S-CH_2], 2.65 [d (13.6), 1H, S-CH_2], 1.96 [s, 3H, S-CH_3], 1.04 [d (8.5), 9H, PMe_3].

^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 193 K): δ 198.1 [d (7.6), CO], 196.6 [d (7.6), CO], 194.4 [d (79.8), CO], 171.1 [C_7 bipy'], 151.6, 148.5, 138.9, 125.8, 123.8, 123.6, 99.6, 94.8 [bipy'], 72.5 [C_2 bipy'], 36.2 [S-CH_2], 18.0 [S-CH_3], 13.0 [d (28.6), PMe_3].

^{31}P{^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ -25.7.

Reaction of 1* with $KN(SiMe_3)_2$ to yield 2M*, 2m* and addition of PMe_3. Preparation of 5*. Compound **5*** was prepared as described above for **5** starting from **1*** (109 mg, 0.1698 mmol), $KN(SiMe_3)_2$ (0.35 mL of a 0.5 M solution in toluene, 0.1750 mmol) and PMe_3 (18 μL, 0.1746 mmol). Compound **5*** was obtained as a powdery brown solid. Repeated attempts to crystallize **5*** were unsuccessful perhaps due to its thermal instability.

IR (THF, cm^{-1}): 2010, 1913, 1885 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 400 MHz, 193 K): δ 8.77 [d (6.4), 1H, H_9 bipy'], 7.93 [t (7.7), 1H, H_{11} bipy'], 7.61 [d (7.7), 1H, H_{12} bipy'], 7.27 [dd (7.7, 6.4), 1H, H_{10} bipy'], 6.71 [d (5.9), 1H, H_6 bipy'], 6.07 [dd (8.2, 5.9), 1H, H_4 bipy'], 4.90 [t (5.9), 1H, H_5 bipy'], 4.23 [d (8.2), 1H, H_3 bipy'], 2.93 [ddd (80.4, 13.1, 4.3), 1H, S-$^{13}CH_2$], 2.55 [ddd (79.1, 13.1, 4.3), 1H, S-$^{13}CH_2$], 1.95 [dd (138.5, 2.6), 3H, S-$^{13}CH_3$], 1.03 [d (8.5), 9H, PMe_3].

^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 193 K): δ 198.2 [d (7.3), CO], 196.7 [d (6.3), CO], 194.5 [d (80.3), CO], 171.2 [C_7 bipy'], 151.6, 148.6, 139.0, 125.9, 123.9, 123.7, 99.6, 94.9 [bipy'], 72.6 [d (35.0), C_2 bipy'], 36.3 [S-CH_2], 18.1 [S-CH_3], 13.1 [d (28.7), PMe_3].

^{31}P{^{1}H} NMR (CD_2Cl_2, 400 MHz, 193 K): δ -26.0.

Reaction of 1 with $KN(SiMe_3)_2$ and addition of dmpm. Preparation of 6. Compound **6** was prepared as described for **5** from **1** (120 mg, 0.1888 mmol), $KN(SiMe_3)_2$ (0.40 mL of a 0.5 M solution in toluene, 0.2000 mmol) and dmpm (33 μL, 0.2066 mmol). Compound **6** was obtained as a powdery brown solid. Repeated attempts to crystallize **6**

were unsuccessful perhaps due to its thermal instability. It was not possible to remove residual dmpm due to the high solubility of **6** in hexane.

IR (THF, cm^{-1}): 2010, 1913, 1885 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 400 MHz, 193 K): δ 8.85 [m, 1H, H_9 bipy'], 7.93 [m, 1H, H_{11} bipy'], 7.75 [m, 1H, H_{12} bipy'], 7.19 [m, 1H, H_{10} bipy'], 6.77 [d (5.9), 1H, H_6 bipy'], 6.09 [ddd (8.2, 5.8, 0.8), 1H, H_4 bipy'], 4.96 [t (5.9), 1H, H_5 bipy'], 4.32 [m, 1H, H_3 bipy'], 2.94 [d (13.5), 1H, S-CH_2], 2.79 [d (13.5), 1H, S-CH_2], 1.97 [s, 3H, S-CH_3], 1.54 [m, 2H, P-CH_2-P], 1.18 [dd (20.7, 8.1), 6H, P(CH_3)$_2$], 1.02 [dd (22.5, 3.4), 6H, P(CH_3)$_2$]. Resonances due to residual dmpm: 1.45 [m, P-CH_2-P] and 1.12 [m, P(CH_3)$_2$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 193 K): δ 198.3 [d (5.9), CO], 196.8 [d (5.9), CO], 194.4 [d (83.4), CO], 171.3 [C_7 bipy'], 151.9, 148.5, 139.0, 126.2, 123.8, 123.6, 99.8, 95.4 [bipy'], 72.6 [C_2 bipy'], 36.5 [S-CH_2], 28.1 [m, P-CH_2-P], 18.1 [S-CH_3], 11.9 [dd (28.3, 5.3), P(CH_3)$_2$], 10.4 [dd (25.5, 5.6), P(CH_3)$_2$]. Resonances due to residual dmpm: 34.4 [m, P-CH_2-P], 16.1 [m, P(CH_3)$_2$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 400 MHz, 193 K): δ -18.7 [d (32.3), Re-P], -59.0 [d (32.3), P]. Resonances due to residual dmpm: -54.8.

Synthesis of [Re(CO)$_3$(phen)(SMe_2)]OTf (7). SMe_2 (50 μL, 0.6808 mmol) was added to a solution of [Re(phen)(CO)$_3$(OTf)] (110 mg, 0.1835 mmol) in CH_2Cl_2 (15 mL). After stirring the resulting solution for 3 hours, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **7** as a yellow solid which was dried under vacuum (Yield: 115 mg (94.7 %)). Slow diffusion of hexane (10 mL) into a concentrated solution of **7** in CH_2Cl_2 (5 mL) at -20°C afforded yellow crystals of **7**. Yield: 112 mg (92.3 %).

Anal. Calcd. for $C_{18}H_{14}F_3N_2O_6ReS_2$: C 32.68, H 2.13, N 4.23. Found: C 33.01, H 2.10, N 4.18.

IR (THF, cm^{-1}): 2037, 1940, 1929 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.44 [m, 2H, H_2 and H_9 phen], 8.94 [dd (8.3, 1.5), 2H, H_4 and H_7 phen], 8.32 [s, 2H, H_5 and H_6 phen], 8.19 [d (8.3, 5.2), 2H, H_3 and H_8 phen], 2.24 [s, 6 H, SMe_2].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.2 [2 CO], 187.5 [CO], 154.2 [C_2 and C_9 phen], 146.5 [C_{11} and C_{13} phen], 140.5 [C_7 and C_4 phen], 131.5 [C_{12} and C_{14} phen], 128.6 [C_5 and C_6 phen], 126.2 [C_3 and C_8 phen], 22.9 [SMe_2].

Reaction of 7 with $KN(SiMe_3)_2$. Characterization of 8 and $[Re(phen)(CO)_3N(SiMe_3)_2]$ (9). $KN(SiMe_3)_2$ (0.25 mL of a 0.5 M solution in toluene, 0.125 mmol) was added to a THF (10 mL) solution of **7** (78 mg, 0.118 mmol) at -78°C in a J. Young tube. Afterwards, SMe_2 (0.50 mL, 26.095 mmol) was added and the mixture was let to reach room temperature. Stirring the solution at room temperature for 6 hours yielded a red solution. Evaporation of the volatiles to dryness afforded a red residue, which was used for NMR characterization. The NMR spectra showed the presence of two rhenium species, **8** and $[Re(phen)(CO)_3N(SiMe_3)_2]$ (**9**). Only NMR signals of **8** are listed below. For the NMR signals of **9** see section below "Alternative synthesis of **9**".

IR (toluene, cm^{-1}): 2012, 1909, 1896 (ν_{CO}).

^1H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.48 [dd (4.9, 1.4), 1H, H_9 phen'], 7.30 [dd (8.4, 1.4), 1H, H_7 phen'], 6.91 [d (8.0), 1H, H_5 phen'], 6.45 [d (9.4), 1H, H_4 phen'], 6.40 [d (8.0), 1H, H_6 phen'], 6.34 [dd (8.4, 4.9), 1H, H_8 phen'], 5.63 [dd (9.4, 5.6), 1H, H_3 phen'], 4.40 [m, 1H, H_2 phen'], 1.89 [m, 1H, CH_2S], 1.17 [m, 1H, CH_2S]. Signal for the S-bonded methyl group could not have been assigned and is presumably obscured by residual THF or toluene.

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 199.8, 199.6, 194.5 [3 CO (signals of the CO groups of **8** are obscured by CO groups of **9**)], 153.8 [C_{11} phen'], 148.4 [C_9 phen'], 146.8 [C_{13} phen'], 136.5 [C_7 phen'], 130.8 [C_{14} phen'], 126.1 [C_5 phen'], 125.5 [C_4 phen'], 123.6 [C_8 phen'], 120.7 [C_3 phen'], 119.8 [C_{12} phen'], 109.2 [C_6 phen'], 65.4 [C_2 phen'], 38.3 [CH_2S], 21.0 [CH_3S].

Alternative synthesis of 9. Complex **9** was obtained in a similar way to that described for **4,** starting from $KN(SiMe_3)_2$ (0.30 mL of a 0.5 M solution in toluene, 0.150 mmol), toluene (10 mL) and $[Re(CO)_3(phen)(OTf)]$ (85 mg, 0.142 mmol). Yield: 82 % (71 mg). Slow diffusion of hexane (5 mL) into a concentrated solution of **9** in toluene (5 mL) at -20°C yielded red crystals of **9**, one of which was used for X-ray diffraction.

IR (toluene, cm^{-1}): 2008, 1906, 1883 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.80 [m, 2H, H_2 and H_9 phen], 7.26 [m, 2H, H_4 and H_7 phen], 7.06 [s, 2H, H_5 and H_6 phen (obscured by residual toluene)], 6.59 [m, 2H, H_3 and H_8 phen], 0.12 [s, 18H, Re-N($SiMe_3$)$_2$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 199.7 [2 CO], 194.3 [CO], 151.6 [C_2 and C_9 phen], 146.0 [C_{11} and C_{13} phen], 136.5 [C_7 and C_4 phen], 129.8 [C_{12} and C_{14} phen], 125.0 [C_5 and C_6 phen], 124.2 [C_3 and C_8 phen], 2.2 [Re-N($SiMe_3$)$_2$].

Synthesis of [Re(2,6-*i*PrBIAN)(CO)$_3$(SMe_2)]BAr^F_4 (10). [$ReBr(CO)_5$] (42 mg, 0.1033 mmol) and 2,6-*i*PrBIAN (57 mg, 0.1134 mmol) in toluene (20 mL) were refluxed for 3 hours. The IR showed ν_{CO} bands (2027, 1941 and 1905 cm^{-1}) attributed to [Re(2,6-*i*PrBIAN)$(CO)_3$Br]. Toluene was evaporated under reduced pressure and the solid residue was dissolved in CH_2Cl_2 (20 mL). AgOTf (30 mg, 0.1175 mmol) was added and the solution was stirred protected from light for 3 hours. The IR ν_{CO} bands (2039, 1953 and 1921 cm^{-1}) showed the presence of [$Re(CO)_3$(2,6-*i*PrBIAN)(OTf)] as the only metal carbonyl species. After filtration and concentration to 20 mL, SMe_2 (8 μL, 0.1089 mmol) and Na[BAr^F_4] (97 mg, 0.1092 mmol) were added. The reaction mixture was stirred 2 hours and then filtered using a paper plug at the end of a stainless steel cannula. All the volatiles were removed in vacuo. The solid residue was dissolved in CH_2Cl_2 (6 mL) and hexane (10 mL) was added onto the magnetically stirred CH_2Cl_2 solution, giving rise to the formation of a red precipitate. The Schlenk flask was kept in an ice bath 30 minutes and the pale red mother liquors were discarded. Washing with cold hexane (2 × 10 mL) and drying in vacuo afforded **10** as a red powder in a 97 % yield (157 mg). Slow diffusion crystallization from CH_2Cl_2/hexane (8 mL / 20 mL) at -20°C afforded red crystals of **10** suitable for an X-ray analysis. Yield: 150 mg (92 %).

Anal. Calcd. for $C_{73}H_{58}BF_{24}N_2O_3ReS$: C 51.64, H 3.42, N 1.65. Found: C 50.57, H 3.46, N 1.94.

IR (CH_2Cl_2, cm^{-1}): 2041, 1949 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 8.19 [d (8.2), 2H, H_3 and H_4 BIAN], 7.65 [m, 4H, H_m Ar], 7.58 [m, 2H, H_p Ar], 7.54 [m, 2H, H_2 and H_5 BIAN], 6.57 [d (7.4), H_1 and H_6 BIAN], 3.27 [sept (6.8), 2H, CH (*i*Pr)], 2.97 [sept (6.8), 2H, CH (*i*Pr)], 2.62 [s, 6H, Re-SMe_2], 1.50

[d (6.8), 6H, CH_3 (*i*Pr)], 1.45 [d (6.8), 6H, CH_3 (*i*Pr)], 0.94 [d (6.8), 6H, CH_3 (*i*Pr)], 0.85 [d (6.8), 6H, CH_3 (*i*Pr)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz, 298 K): δ 191.7 [2 CO], 184.5 [CO], 177.8 [C=N BIAN], 145.4, 144.0, 139.7, 138.8 [QC BIAN], 133.6, 130.3, 129.2, 127.3, 126.8 [CH BIAN], 125.9 [CH and QC BIAN] 125.5 [QC BIAN], 29.5, 29.2 [CH (*i*Pr)], 25.5 [S-$(CH_3)_2$], 24.8, 24.6, 24.0, 23.9 [CH_3 (*i*Pr)].

Reaction of 10 with $KN(SiMe_3)_2$. Synthesis of 11. $KN(SiMe_3)_2$ (0.20 mL of a 0.5 M solution in toluene, 0.1000 mmol) was added to a solution of **10** (157 mg, 0.0927 mmol) in THF (20 mL) previously cooled to -78°C. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in CH_2Cl_2 and filtered. After solvent evaporation, the residue was extracted in hexane and filtered via cannula. Evaporation to dryness afforded **11** as a purple solid. Slow diffusion of hexane into CH_2Cl_2 at -20°C yielded **11** as a blue crystalline solid suitable for X-ray diffraction. Yield: 45 mg (59 %). Note that the low yield is due to the necessary extraction of **11** in hexane to remove traces of $K[BAr^F{}_4]$.

Anal. Calcd. for $C_{41}H_{45}N_2O_3ReS\cdot\frac{1}{2}CH_2Cl_2$: C 56.94, H 5.15, N 3.20. Found: C 57.08, H 5.25, N 3.04.

IR (CH_2Cl_2, cm^{-1}): 2007, 1902, 1885 (ν_{CO}).

^1H NMR (CD_2Cl_2, 400 MHz, 298 K): (Assignment of the ^1H signals for the 2,6-*i*PrBIAN ligand was aided by a 2D COSY spectrum). δ 7.99 [d (8.0), 1H, H_3 C_6H_{10} BIAN'], 7.74 [d (8.0), 1H, H_4 C_6H_{10} BIAN'], 7.49 [m, 1H, Ar BIAN'], 7.45 [m, 1H, Ar BIAN'], 7.41 [m, 1H, Ar BIAN'], 7.37 [m, 1H, H_2 C_6H_{10} BIAN'], 7.30 [m, 1H, Ar BIAN'], 7.25 [m, 1H, H_5 C_6H_{10} BIAN'], 7.07 [t (8.0), 1H, Ar BIAN'], 6.84 [dd (8.0, 4.0), 1H, Ar BIAN'], 6.47 [d (8.0), 1H, H_1 C_6H_{10} BIAN'], 6.32 [d (8.0), 1H, H_6 C_6H_{10} BIAN'], 4.19 [sept (8.0), 1H, CH (*i*Pr)], 3.31 [sept (8.0), 1H, CH (*i*Pr)], 3.11 [sept (8.0), 1H, CH (*i*Pr)], 2.97 [s, 3H, S-CH_3], 2.84 [sept (8.0), 1H, CH (*i*Pr)], 2.76 [d (12.0), 1H, S-CH_2], 2.55 [d (12.0), 1H, S-CH_2], 1.43 [m, 12H, 4 CH_3 (*i*Pr)], 1.06 [d (8.0), 3H, CH_3 (*i*Pr)], 1.04 [d (8.0), 3H, CH_3 (*i*Pr)], 0.83 [d (8.0), 3H, CH_3 (*i*Pr)], -0.56 [d (8.0), 3H, CH_3 (*i*Pr)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, 298 K): (The distinction between quaternary and CH carbons for the 2,6-*i*PrBIAN ligand was aided by a DEPT-135 spectrum, and between CH

and CH_3 carbons for the *i*Pr groups by a DEPT-90 spectrum. The distinction between sulfide CH_3 and *i*Pr CH_3 was aided by a 2D HMBC spectrum). δ 199.5, 198.6, 195.9 [CO], 192.8 [C2 BIAN'], 152.7, 149.5, 146.9, 143.8, 142.4, 140.6, 140.4, 138.3, 131.7 [QC BIAN'], 131.6, 128.0, 127.8, 127.6, 125.5, 125.3, 125.0, 124.7 [CH BIAN'], 124.2 [QC BIAN'], 123.5, 123.2, 123.0, 122.8 [CH BIAN'], 91.2 [C6 BIAN'], 38.4 [S-CH_2], 28.1, 28.0, 27.9 [CH *i*Pr BIAN'], 26.9 [CH_3 *i*Pr BIAN'], 26.3 [CH *i*Pr BIAN'], 26.0, 25.8, 24.6, 24.5, 24.3, 24.0 [CH_3 *i*Pr BIAN'], 23.2 [S-CH_3], 21.6 [CH_3 Ar BIAN'].

Synthesis of [Re(*p*-MeBIAN)(CO)$_3$(SMePh)]BAr$^F_4$ (12). SMePh (40 μL, 0.340 mmol) was added to a CH_2Cl_2 (10 mL) solution of [Re(*p*-MeBIAN)(CO)$_3$(OTf)] (181 mg, 0.112 mmol) and Na[BAr$^F_4$] (110 mg, 0.127 mmol). After stirring the resulting mixture for four hours at room temperature, the solution was filtered and concentrated to 5 mL. Addition of hexane (20 mL) caused the precipitation of **12** as a red solid, which was washed with hexane (2 × 20 mL) and dried under vacuum. Yield: 88 % (330 mg).

Anal. Calcd. for $C_{68}H_{40}BF_{24}N_2O_3ReS$: C 50.48, H 2.49, N 1.73. Found: C 51.03, H 2.51, N 1.69.

IR (THF, cm^{-1}): 2037, 1939 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 8.19 [d (8.3), 2H, H_3 and H_4 BIAN], 7.58 [m, 2H, H_2 and H_5 BIAN (obscured by Ar^F signal, could be seen in ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-HSQC)], 7.52-7.21 [m, 13H, *p*-tolyl BIAN and S-Ph], 6.88 [br, 2H, H_1 and H_6 BIAN], 3.11 [s, 3H, Re-SMe], 2.54 [s, 6H, CH_3 (Ar)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ 193.2 [2 CO], 184.8 [CO], 174.7 [C=N BIAN], 146.0, 145.1, 140.8 [QC BIAN], 132.9, 131.5, 131.1, 130.6, 130.3, 130.0, 128.9 [CH BIAN and S-Ph], 128.6 [QC S-Ph], 127.7, 126.0 [QC BIAN], 125.8, 121.6, 119.9 [CH BIAN and S-Ph], 26.5 [S-CH_3], 21.3 [CH_3 BIAN].

Reaction of 12 with KN(SiMe$_3$)$_2$. Synthesis of 13. KN(SiMe$_3$)$_2$ (0.40 mL, 0.200 mmol) was added to a THF solution of **12** (330 mg, 0.204 mmol) at -78°C. The cooling bath was removed and the resulting mixture was let to reach room temperature under vacuum. Removal of the volatiles and washings with hexane yielded **13** as a brown solid in a 27 % yield (42 mg). The low yield of **13** could be attributed to the formation of an unknown unstable complex upon deprotonation (see Results and Discussion). Slow diffusion of

hexane (10 mL) into a concentrated solution of **13** in CH_2Cl_2 (5 mL) at room temperature yielded orange crystals of **13**, one of which was used for X-ray diffraction determination.

Anal. Calcd. for $C_{36}H_{27}N_2O_3ReS$: C 57.36, H 3.61, N 3.72. Found: C 58.01, H 3.58, N 3.69.

IR (THF, cm^{-1}): 2014, 1916, 1895 (ν_{CO}).

^{1}H NMR (toluene-d_8, 400 MHz, 298 K): δ 7.47 [d (7.9), 1H, CH BIAN'], 7.39 [d (8.0), 1H, CH BIAN'], 7.10 [m, 7H, CH BIAN' and S-Ph (obscured by residual toluene signals)], 6.88 [m, 5H, CH BIAN' and S-Ph], 6.75 [d (8.0), 3H, CH BIAN'], 6.63 [m, 1H, CH BIAN'], 6.30 [m, 1H, CH BIAN'], 3.02 [d (12.9), 1H, S-CH_2], 2.53 [d (12.9), 1H, S-CH_2], 2.10, 2.02 [s, 3H, CH_3 BIAN' (partially obscured by residual toluene signals)].

^{13}C{^{1}H} NMR (toluene-d_8, 400 MHz, 193 K): δ 199.8, 196.9, 194.0 [CO], 158.1, 147.7, 141.8, 139.6, 138.8, 135.2, 133.0, 132.0, 131.6, 130.8, 130.0, 129.4, 127.1, 126.5, 125.6, 124.2, 123.9, 122.2, 120.4 [QC and CH BIAN' and QC and CH S-Ph], 87.1 [C6 BIAN'], 25.5 [S-CH_2]. CH_3 groups and some aromatic signals of the BIAN' ligand and the S-Ph unit could not be listed since they were obscured by residual toluene.

Preparation and Characterization of Compounds in Chapter 2

For compounds **24**, **24^{F}** and **26M**, **26m**, the ^{13}C NMR spectrum of free $PPhMe_2$ helped in the signal assignment. **$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz):** 143.0 [d (14.5), C_{ipso}], 130.4 [d (17.2), C_{ortho}], 128.2 [d (5.8), C_{meta}], 127.8 [s, C_{para}], 14.2 [d (13.3), CH_3].

Synthesis of [Re(bipy)(CO)$_3$(PMe$_3$)]OTf (14). PMe_3 (20 μL, 0.2294 mmol) was added to a solution of [Re(bipy)(CO)$_3$(OTf)] (98 mg, 0.1702 mmol) in toluene (10 mL). After refluxing the resulting solution for 3 hours, it was concentrated under vacuum to 5 mL. Addition of hexane (15 mL) caused the precipitation of **14** as a yellow solid which was dried under vacuum. Slow diffusion of diethyl ether (15 mL) into a concentrated solution of **14** in CH_2Cl_2 (10 mL) at room temperature afforded yellow crystals. Yield: 91 mg (82 %).

Anal. Calcd. for $C_{17}H_{17}F_3N_2O_6PReS$: C 31.34, H 2.63, N 4.30. Found: C 30.60, H 2.41, N 4.21.

IR (THF, cm^{-1}): 2034, 1934, 1913 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.01 [m, 2H, H_6 and H_9 bipy], 8.79 [m, 2H, H_3 and H_{12} bipy], 8.37 [m, 2H, H_4 and H_{11} bipy], 7.75 [m, 2H, H_5 and H_{10} bipy], 1.16 [d (9.0), 9H, $P(CH_3)_3$].

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ 194.6 [d (3.8), 2 CO], 187.8 [d (60.9), CO], 155.5 [QC bipy], 153.0, 140.9, 128.5, 125.6 [CH bipy], 13.4 [d (31.9), $P(CH_3)_3$].

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ -27.8.

The preparation of the cationic complex in **14** has been reported.[106] The alternative method given here avoids the use of potentially explosive perchlorate salts employed in the previously reported procedure.

Reaction of 1 with KN(SiMe$_3$)$_2$. Synthesis of *cis*, *trans*-[Re(bipy)(CO)$_2$(CN)(PMe$_3$)] (15). $KN(SiMe_3)_2$ (0.20 mL of a 0.7 M solution in toluene, 0.1400 mmol) was added to a

solution of **15** (91 mg, 0.1389 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from yellow to red. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting brown residue was washed with toluene (2 × 10 mL), dissolved in CH_2Cl_2 (10 mL) and filtered. Concentration to 5 mL and addition of diethylether (20 mL) caused the precipitation of an orange solid which was washed with diethylether (2 × 20 mL) and dried under vacuum. Attempts to further purify complex **15** were unsuccessful. Small amounts of non-identified impurities can be seen in the ^{1}H NMR spectrum. Therefore, CHN analysis of **15** was not attempted. Yield: 29 mg (48 %).

IR (CH_2Cl_2, cm^{-1}): 2097 (m, ν_{CN}), 1921 (s, ν_{CO}), 1848 (s, ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.07 [m, 2H, H_6 and H_9 bipy], 8.30 [m, 2H, H_3 and H_{12} bipy], 7.96 [m, 2H, H_4 and H_{11} bipy], 7.46 [m, 2H, H_5 and H_{10} bipy], 1.09 [d (8.1), 9H, $P(CH_3)_3$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 203.8 [d (6.0), 2 CO], 155.3 [QC bipy], 152.2, 137.7, 126.8, 123.3 [CH bipy], 16.1 [d (30.2), $P(CH_3)_3$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ -26.7.

The structure of **15** was further confirmed by its reaction with MeOTf and the identification of key spectroscopic features of the resulting methylisocyanide product *cis*, *trans*-[Re(bipy)$(CO)_2$(CNMe)(PMe_3)]OTf (**17**).

Reaction of 15 with MeOTf. Synthesis of [Re(bipy)$(CO)_2$(CNMe)(PMe_3)]OTf (17). MeOTf (15 μL, 0.1371 mmol) was added to a solution of **15** (46 mg, 0.0919 mmol) in CH_2Cl_2 (10 mL) at room temperature. After stirring for 10 minutes, the solution was concentrated to 5 mL. Addition of hexane (20 mL) caused the precipitation of a brown powder which was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Yield: 54 mg (89 %).

IR (CH_2Cl_2, cm^{-1}): 2185 (m, ν_{CN}), 1950 (s, ν_{CO}), 1880 (s, ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.00 [m, 2H, bipy], 8.68 [m, 2H, bipy], 8.27 [m, 2H, bipy], 7.64 [m, 2H, bipy], 3.36 [d (0.5), 3H, $CNCH_3$], 1.12 [d (8.6), 9H, $P(CH_3)_3$].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 199.0 [d (6.0), 2 CO], 155.6 [QC bipy], 152.4, 139.7, 127.7, 124.8 [CH bipy], 29.7 [d (12.5), CN*C*H_3] 14.8 [d (30.2), P(CH_3)$_3$].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -26.5.

Reaction of 14 with KN($SiMe_3$)$_2$. Characterization of the C6(bipy)-C(P) coupling product (16). KN($SiMe_3$)$_2$ (0.20 mL of a 0.7 M solution in toluene, 0.1400 mmol) was added to a solution of **14** (91 mg, 0.1400 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from yellow to red. The cooling bath was removed and the solvent was evaporated under vacuum. The solid residue was extracted with toluene and filtered. Removal of the solvent and drying under vacuum afforded **16** as a purple microcrystalline solid. **16** could not been washed with hexane due to its high solubility in this solvent. Repeated attempts to crystallize **16** were unsuccessful due to the thermal instability of the product so the NMR spectra were recorded for crude **16**. The ^{13}C, DEPT-135, 2D HSQC and 2D HMBC NMR spectra were recorded at 253 K due to the decomposition of the product in a THF-d_8 solution for several hours.

IR (THF, cm^{-1}): 2008, 1910, 1884 (ν_{CO}).

^1H NMR (THF-d_8, 298 K, 400 MHz): δ 8.81 [m, 1H, H_9 bipy'], 7.80 [m, 2H, H_{11} and H_{12} bipy'], 7.20 [m, 1H, H_{10} bipy'], 6.05 [m, 1H, H_4 bipy'], 5.72 [m, 1H, H_3 bipy'], 5.19 [m, 1H, H_5 bipy'], 4.36 [m, 1H, H_6 bipy'], 2.12 [m, 1H, CH_2-P], 1.37 [m, 1H, CH_2-P], 0.91 [d (8.0), 3H, P-CH_3], 0.12 [d (8.0), 3H, P-CH_3].

$^{13}C\{^1H\}$ NMR (THF-d_8, 253 K, 400 MHz): δ 199.8 [d (7.1), CO], 198.4 [d (8.9), CO], 195.0 [d (71.4), CO], 162.9 [C_7 bipy'], 152.2 [C_9 bipy'], 152.0 [C_2 bipy'], 137.0 [C_{11} bipy'], 123.4 [C_{10} bipy'], 123.2 [C_4 bipy'], 121.4 [C_{12} bipy'], 112.8 [d (10.0), C_5 bipy'], 96.6 [C_3 bipy'], 65.9 [d (8.7), C_6 bipy'], 29.5 [d (44.1), CH_2-P], 12.5 [d (30.5), CH_3-P], 10.9 [d (24.9), CH_3-P].

$^{31}P\{^1H\}$ NMR (THF-d_8, 253 K, 400 MHz): δ -17.3.

Reaction of 16 with HOTf. Characterization of 18 and 19. HOTf (5 μL, 0.0566 mmol) was added to a freshly prepared solution of **16** (27 mg, 0.0540 mmol) in toluene at -78°C. While the temperature was raising to room temperature, the resulting mixture

turned orange and an orange oil was formed. Concentration of the mixture under vacuum and precipitation with diethyl ether (20 mL) yielded an orange oil which was washed with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL). The **18** and **19** mixture was obtained as an orange solid, which was dried under vacuum. Slow diffusion of diethyl ether (1 mL) into a concentrated solution of **18** and **19** in CD_2Cl_2 (0.4 mL) at room temperature yielded orange crystals of **18**, one of which was employed for X-ray diffraction analysis.

When the addition of HOTf to **16** is carried out at room temperature, compound **19** was found to be the major species in the product.

IR (CH_2Cl_2, cm^{-1}): 2036, 1952, 1925 (ν_{CO}).

18:**19** ratio (from ^1H NMR integration) = 1.5:1.0

NMR assignment of 18.

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.75 [m, 1H, H_9 bipy'], 7.98 [td (7.9, 1.6), 1H, H_{11} bipy'], 7.90 [m, 1H, H_{12} bipy'], 7.81 [bs, 1H, H-N(bipy)], 7.35 [m, 1H, H_{10} bipy'], 7.17 [dd (5.6, 2.5), 1H, H_3 bipy'], 6.62 [dd (9.5, 5.1), 2H, H_5 bipy'], 6.47 [dd (9.5, 5.7), 2H, H_4 bipy'], 4.06 [m, 1H, H_6 bipy'], 2.22 [m, 1H, CH_2P], 1.96 [d (9.5), 3H, CH_3P], 1.75 [m, 1H, CH_2P], 1.15 [d (8.8), 3H, CH_3P].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 196.3 [d (6.8), CO], 194.9 [d (6.4), CO], 190.9 [d (63.6), CO], 157.3 [C_7 bipy'], 152.6 [C_9 bipy'], 139.2 [C_{11} bipy'], 135.5 [d (12.3), C_5 bipy'], 134.5 [C_2 bipy'], 125.4 [C_{10} bipy'], 124.9 [C_3 bipy'], 121.8 [C_{12} and C_4 bipy'], 60.9 [d (8.8), C_6 bipy'], 27.7 [d (24.1), CH_2P], 15.5 [d (35.4), CH_3P], 12.2 [m, CH_3P].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -1.8.

NMR assignment of 19.

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.11 [m, 1H, H_9 bipy'], 8.31 [m, 2H, H_{11} and H_{12} bipy'], 7.75 [m, 1H, H_{10} bipy'], 6.14 [m, 2H, H_3 and H_4 bipy'], 5.06 [m, 1H, H_6 bipy'], 3.87 [m, 1H, H_5 (CH_2) bipy'], 3.73 [m, 1H, $H_{5'}$ (CH_2) bipy'], 2.89 [m, 1H, CH_2P], 2.47 [m, 1H, CH_2P], 1.99 [d (9.7), 3H, CH_3P], 1.12 [d (9.1), 3H, CH_3P].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 193.3 [m, 2 CO], 187.9 [d (58.1), CO], 175.0 [d (5.9), C_2 bipy' (C=N)], 155.8 [C_7 bipy'], 153.7 [C_9 bipy'], 140.3 [C_{11} bipy'], 129.4 [C_{10} bipy'], 128.5 [C_{12} bipy'], 124.6 [d (6.9), C_3 bipy'], 118.9 [C_4 bipy'], 65.4 [C_6 bipy'], 41.9 [d (31.4), CH_2P], 28.5 [C_5 bipy'], 14.6 [d (34.6), CH_3P], 12.1 [m, CH_3P].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -7.2.

Reaction of 16 with MeOTf. Synthesis of 20. MeOTf (8 μL, 0.0731 mmol) was added to a freshly prepared solution of **16** (31 mg, 0.0620 mmol) in toluene at room temperature. An orange oil was immediately formed. Concentration of the mixture under vacuum and addition of diethyl ether (20 mL) yielded **20** as an orange oil, which was washed with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL). Compound **20** was obtained as an orange solid, which was dried under vacuum. Slow diffusion of diethyl ether (0.8 mL) into a concentrated solution of **20** in CD_2Cl_2 (0.4 mL) at room temperature yielded orange crystals of **20**, one of which was employed for X-ray diffraction analysis. Yield: 87 % (36 mg)

Anal. Calcd. for $C_{18}H_{19}F_3N_2O_6PReS$: C 32.48, H 2.88, N 4.21. **Found:** C 32.51, H 2.86, N 4.18.

IR (CH_2Cl_2, cm^{-1}): 2038, 1949, 1923 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.78 [m, 1H, H_9 bipy'], 8.10 [m, 2H, H_{11} and H_{12} bipy'], 7.48 [td (6.0, 2.6), 1H, H_{10} bipy'], 7.18 [d (5.4), 1H, H_3 bipy'], 6.52 [m, 2H, H_4 and H_5 bipy'], 4.22 [m, 1H, H_6 bipy'], 3.60 [s, 3H, CH_3-N(bipy')], 2.84 [ddd (15.9, 12.1, 5.7), 1H, CH_2P], 2.02 [d (9.8), 3H, CH_3P], 1.97 [m, 1H, CH_2P (obscured by CH_3P)], 1.19 [d (9.0), 3H, CH_3P].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 193.6 [d (7.6), CO], 193.5 [d (7.8), CO], 192.1 [d (60.9), CO], 156.3 [C_7 bipy'], 152.8 [C_9 bipy'], 141.1 [C_2 bipy'], 140.0 [C_{11} bipy'], 132.8 [d (12.4), C_5 bipy'], 126.4 [C_{10} bipy'], 123.5 [C_{12} and C_3 bipy'], 121.4 [C_4 bipy'], 69.7 [d (6.6), C_6 bipy'], 52.3 [d (2.0), CH_3-N(bipy')], 33.9 [d (23.3), CH_2P], 15.7 [d (36.5), CH_3P], 12.2 [d (29.9), CH_3P].

$^{31}P\{^1H\}$ NMR (THF-d_8, 298 K, 400 MHz): δ -5.6.

Reaction of 14 with $KN(SiMe_3)_2$. Characterization of the C2(bipy)-C(P) coupling product (21). $KN(SiMe_3)_2$ (0.10 mL of a 0.5 M solution in toluene, 0.050 mmol) was evaporated to dryness in a Young Schlenk for 2 hours at 60°C. The white solid obtained was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **14** (30 mg, 0.0460 mmol) in THF-d_8 (0.15 mL) previously cooled to -78°C in a Young Schlenk. There was an instantaneous color change from yellow to red. The resulting solution was kept at -78°C for 5 minutes stirring, and for 5 minutes without stirring and then it was transferred to a NMR tube cooled to -78°C.

^{1}H NMR (THF-d_8, 298 K, 400 MHz): δ 8.81 [m, 1H, H_9 bipy'], 8.02 [m, 1H, H_{11} bipy'], 7.64 [m, 1H, H_{12} bipy'], 7.33 [m, 1H, H_{10} bipy'], 6.63 [m, 1H, H_3 bipy'], 5.97 [m, 1H, H_5 bipy'], 5.18 [m, 1H, H_6 bipy'], 4.22 [m, 1H, H_4 bipy'], 2.25 [dd (13.4, 8.7), 1H, CH_2P], 1.72 [d (9.4), 3H, CH_3P], 1.06 [m, 1H, CH_2P (obscured by unknown impurity)], 0.90 [d (9.0), 3H, CH_3P].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 204.0 [m, 2 CO], 198.7 [m, CO], 169.4 [C_7 bipy'], 153.4 [C_9 bipy'], 150.9 [C_6 bipy'], 140.5 [C_{11} bipy'], 126.4 [C_5 bipy'], 123.8 [C_{10} bipy'], 120.5 [C_{12} bipy'], 103.4 [C_3 bipy'], 87.7 [C_4 bipy'], 76.7 [m, C_2 bipy'], 31.6 [m, CH_2P], 12.9 [d (33.8), CH_3P], 10.1 [d (29.2), CH_3P].

^{31}P{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ -22.9.

Synthesis of [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PMe$_3$)]OTf (22). PMe_3 (11 μL, 0.1260 mmol) was added to a solution of [Re(CO)$_3$(2,6-*i*PrBIAN)(OTf)] (110 mg, 0.1195 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred 4 hours at room temperature. Volatiles were removed in vacuo. The solid residue was dissolved in CH_2Cl_2 (4 mL) and hexane (10 mL) was added onto the magnetically stirred CH_2Cl_2 solution giving rise to the formation of a red precipitate. The Schlenk flask was kept in an ice bath 30 minutes and the pale red mother liquors were discarded. Drying in vacuo afforded **22** as a red powder in a 97 % yield (115 mg). Slow diffusion of hexane (20 mL) into a concentrated solution of **22** in CH_2Cl_2 (8 mL) at -20°C afforded orange crystals of **22** one of which was suitable for an X-ray analysis. Yield: 105 mg (88 %).

Anal. Calcd. for $C_{43}H_{49}F_3N_2O_6PReS$: C 51.84, H 4.92, N 2.81. Found: C 53.11, H 4.63, N 3.07.

IR (CH_2Cl_2, cm^{-1}): 2039, 1951 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.24 [d (8.4), 2H, H_3 and H_4 BIAN], 7.65 [m, 4H, H_m Ar BIAN], 7.56 [m, 2H, H_p Ar BIAN], 7.54 [m, 2H, H_2 and H_5 BIAN], 6.25 [d (7.4), H_1 and H_6 BIAN], 3.02 [m, 2H, CH (*i*Pr)], 2.86 [m, 2H, CH (*i*Pr)], 1.89 [d (8.6), 9H, Re-PMe_3], 1.59 [d (6.7), 6H, CH_3 (*i*Pr)], 1.37 [d (6.7), 6H, CH_3 (*i*Pr)], 1.14 [d (6.7), 6H, CH_3 (*i*Pr)], 0.49 [d (6.7), 6H, CH_3 (*i*Pr)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 191.7 [d (8.7), 2 CO], 184.7 [d (51.5), CO], 177.3 [d (2.8), C_2 BIAN], 145.0, 144.2, 139.6, 139.0 [QC BIAN], 133.2 [CH BIAN], 131.2 [QC BIAN], 130.1, 129.1, 127.6, 127.1 [CH BIAN], 126.0 [QC BIAN], 125.3 [CH BIAN], 29.7 [d (2.4), CH (*i*Pr)], 28.4 [CH (*i*Pr)], 26.2, 25.6, 23.9, 23.8 [CH_3 (*i*Pr)], 16.5 [d (32.1), $P(CH_3)_3$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ -38.4.

Reaction of 22 with $KN(SiMe_3)_2$. Synthesis of 23. $KN(SiMe_3)_2$ (0.20 mL of a 0.5 M solution in toluene, 0.1000 mmol) was added to a solution of **22** (98 mg, 0.0984 mmol) in THF (10 mL) previously cooled to -78°C. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in CH_2Cl_2 (20 mL) and filtered. Evaporation to dryness afforded **23** as a purple solid which was washed with hexane (2 × 10 mL) at 0°C. Slow diffusion of pentane (10 mL) into a concentrated solution of **23** in CH_2Cl_2 (5 mL) at -20°C yielded **23** as a blue crystalline solid. One of the crystals of **23** was used for an X-ray analysis. Yield: 42 mg (51 %).

Anal. Calcd. for $C_{42}H_{48}N_2O_3PRe$: C 59.63, H 5.70, N 3.31. Found: C 59.31, H 5.55, N 3.20.

IR (CH_2Cl_2, cm^{-1}): 2006, 1908, 1881 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 7.92 [d (8.2), 1H, H_3 BIAN'], 7.66 [d (8.2), 1H, H_4 BIAN'], 7.52-7.43 [m, 3H, Ar BIAN'], 7.32 [dd (8.2, 7.3), 1H, H_2 BIAN'], 7.25 [dd (8.2, 7.2), 1H, H_5 BIAN'], 7.20 [dd (7.6, 1.9), 1H, H_m Ar BIAN'], 7.00 [m, 1H, H_p Ar BIAN'], 6.7 [dd (7.6, 1.9), 1H, $H_{m'}$ Ar BIAN'], 6.31 [d (7.3), 1H, H_1 BIAN'], 6.27 [d (7.2), 1H, H_6 BIAN'], 4.05 [m, 1H, CH (*i*Pr)], 3.32 [m, 1H, CH (*i*Pr)], 3.07 [m, 1H, CH (*i*Pr)], 2.76 [m, 1H, CH (*i*Pr)], 2.31 [dd (14.6, 11.5), 1H, P-CH_2], 2.16 [d (7.7), 3H, P-CH_3], 1.84 [d (7.6), 3H, P-CH_3], 1.66

[dd (14.6, 3.7), 1H, P-CH_2], 1.41 [d (6.8), 3H, CH_3 (*i*Pr)], 1.36 [m, 9H, 3 CH_3 (*i*Pr)], 1.02 [d (6.7), 3H, CH_3 (*i*Pr)], 1.00 [d (6.6), 3H, CH_3 (*i*Pr)], 0.80 [d (6.8), 3H, CH_3 (*i*Pr)], -0.61 [d (6.7), 3H, CH_3 (*i*Pr)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 198.6 [d (7.8), CO], 198.0 [d (5.8), CO], 195.4 [d (70.0), CO], 192.8 [d (11.7), C_2 BIAN'], 152.9, 149.7, 147.2, 144.3, 141.7, 141.5 [d (12.3), QC BIAN'], 140.7, 140.1, 131.7 [QC BIAN'], 131.0, 128.0, 127.7, 127.3, 126.5 [CH BIAN'], 125.2 [QC BIAN'], 125.1, 125.0, 123.9, 123.3 [CH BIAN'], 123.0 [2 CH BIAN'], 122.3 [CH BIAN'], 92.1 [d (10.6), C_6 BIAN'], 34.4 [d (35.2), P-CH_2], 28.5, 28.2, 27.8 [CH *i*Pr BIAN'], 26.9, 26.3, 26.1 [CH_3 *i*Pr BIAN'], 26.1 [CH *i*Pr BIAN'], 25.3, 25.2, 24.6, 23.9, 21.4 [CH_3 *i*Pr BIAN'], 19.5 [d (33.5), P-CH_3], 15.9 [d (27.4), P-CH_3].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -19.8.

Synthesis of [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PPhMe$_2$)]OTf (24). Compound **24** was obtained in a similar way to that described for **22**, starting from [$Re(CO)_3$(2,6-*i*Pr-BIAN)(OTf)] (110 mg, 0.1195 mmol) and $PPhMe_2$ (18 μL, 0.1230 mmol). Compound **24** was obtained as a red powder in a 96 % yield (121 mg). Slow diffusion of hexane (20 mL) into a concentrated solution of **24** in CH_2Cl_2 (8 mL) at -20°C afforded red crystals of **24**. Yield: 112 mg (89 %).

Anal. Calcd. for $C_{48}H_{51}F_3N_2O_6PReS$: C 54.48, H 4.86, N 2.65. Found: C 53.81, H 4.12, N 2.21.

IR (CH_2Cl_2, cm^{-1}): 2041, 1952 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.28 [d (7.6), 2H, H_3 and H_4 BIAN], 7.65 [m, 2H, H_m Ar BIAN], 7.52 [m, 8H, H_p Ar BIAN, Ph and H_2 and H_5 BIAN], 7.40 [m, 1H, Ph], 7.24 [m, 2H, Ph], 6.33 [d (7.2), 2H, H_1 and H_6 BIAN], 2.93 [m, 2H, CH (*i*Pr)], 2.86 [m, 2H, CH (*i*Pr)], 2.19 [d (8.1), 6H, P-CH_3], 1.38 [d (6.8), 6H, CH_3 (*i*Pr)], 1.24 [d (6.5), 6H, CH_3 (*i*Pr)], 0.71 [d (6.5), 6H, CH_3 (*i*Pr)], 0.51 [d (6.8), 6H, CH_3 (*i*Pr)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): The CO trans to $PPhMe_2$ was not seen in the ^{13}C NMR spectrum. δ 192.0 [d (8.4), 2 CO], 178.0 [d (1.7), C_2 BIAN], 144.9, 144.1, 139.7, 139.6 [QC BIAN], 133.7 [d (39.9), C_{ipso} Ph], 133.4, 131.8 [CH BIAN], 131.3 [QC BIAN], 130.8 [d (9.7), C_{ortho} Ph], 130.1 [CH BIAN], 130.0 [d (9.7), C_{meta} Ph], 129.1, 127.5, 127.1 [2

CH BIAN and C_{para} Ph], 125.8 [QC BIAN], 125.4 [CH BIAN], 30.0 [d (2.0) CH (*i*Pr)], 28.5 [CH (*i*Pr)], 26.2, 25.7, 23.8, 23.4 [CH_3 (*i*Pr)], 18.5 [d (33.5), $P(CH_3)_2$].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -34.1.

Synthesis of [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PPhMe$_2$)]BAr$^F{}_4$ (24^F). **24^F** was prepared by addition of $NaBAr^F{}_4$ (115 mg, 0.1298 mmol) to a solution of [Re(CO)$_3$(2,6-*i*PrBIAN)(OTf)] (110 mg, 0.1195 mmol) and $PPhMe_2$ (18 μL, 0.1230 mmol) in CH_2Cl_2 (10 mL). The isolation of **24^F** was similar to that described for **24**. Yield: 201 mg (95 %).

Anal. Calcd. for $C_{79}H_{63}BF_{24}N_2O_3PRe$: C 53.54, H 3.58, N 1.58. Found: C 53.02, H 3.35, N 1.40.

IR (CH_2Cl_2, cm^{-1}): 2041, 1953 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.17 [d (8.1), 2H, H_3 and H_4 BIAN], 7.64 [m, 4H, H_m Ar BIAN], 7.56 [m, 2H, H_p Ar BIAN], 7.54 [m, 2H, H_2 and H_5 BIAN], 7.50 [m, 1H, Ph], 7.45 [dd (8.1, 0.9), 1H, Ph], 7.42 [dd (8.1, 0.9), 1H, Ph], 7.36 [td (7.5, 1.8), 1H, Ph], 7.20 [td (7.5, 1.8), 1H, Ph], 6.32 [d (7.3), 2H, H_1 and H_6 BIAN], 2.93 [m, 2H, CH (*i*Pr)], 2.86 [m, 2H, CH (*i*Pr)], 2.18 [d (8.0), 6H, P-CH_3], 1.38 [d (6.7), 6H, CH_3 (*i*Pr)], 1.24 [d (6.6), 6H, CH_3 (*i*Pr)], 0.68 [d (6.6), 6H, CH_3 (*i*Pr)], 0.51 [d (6.7), 6H, CH_3 (*i*Pr)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 191.8 [m, 2 CO], 183.8 [d (53.4), CO], 177.9 [C_2 BIAN], 144.8, 144.1 [QC BIAN], 139.6 [2 QC BIAN], 133.7 [d (39.1), C_{ipso} Ph], 133.1, 131.8 [CH BIAN], 131.2 [QC BIAN], 130.8 [d (10.2), C_{ortho} Ph], 130.1 [CH BIAN], 130.0 [d (9.8), C_{meta} Ph], 129.1, 127.5, 127.1 [2 CH BIAN and C_{para} Ph], 125.8 [QC BIAN], 125.4 [CH BIAN], 30.0, 28.5 [CH (*i*Pr)], 26.1, 25.7, 23.7, 23.3 [CH_3 (*i*Pr)], 18.7 [d (33.3), $P(CH_3)_2$].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -34.7.

Reaction of 24 with KN(SiMe$_3$)$_2$. Synthesis of 26M, 26m. $KN(SiMe_3)_2$ (0.20 mL of a 0.5 M solution in toluene, 0.1000 mmol) was added to a solution of **24** (103 mg, 0.0973 mmol) in THF (10 mL) previously cooled to -78°C. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in CH_2Cl_2 (20 mL) and filtered. Evaporation to dryness afforded **26M**, **26m** as a purple solid. Slow diffusion of pentane (10 mL) into a concentrated

solution of **26M**, **26m** in CH_2Cl_2 (5 mL) at -20°C yielded blue crystals of **26M** one of which was employed for an X-ray diffraction analysis. Yield: 45 mg (51 %).

Anal. Calcd. for $C_{47}H_{50}N_2O_3PRe{\cdot}2CH_2Cl_2$: C 54.60, H 5.05, N 2.60. Found: C 53.22, H 5.15, N 2.35.

26M:**26m** ratio (from ^{1}H NMR spectrum)= 5:1.

IR (CH_2Cl_2, cm^{-1}): 2007, 1909, 1883 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 7.96 [d (8.3), 1 H, H_3 BIAN' **26m**], 7.93 [d (8.2), 1H, H_3 BIAN' **26M**], 7.71 [d (8.2), 1H, H_4 BIAN' **26M**], 7.71 [d (8.2), 1H, H_4 BIAN' **26m**], 7.70-7.35 [m, 12H, 3H Ar (BIAN') and 9H Ph **26M**], 7.70-7.35 [m, 14H, 4 H Ar (BIAN') and 10H Ph **26m**], 7.30 [m, 2H, H_2 and H_5 BIAN' **26M**], 7.30 [m, 2H, H_2 and H_5 BIAN' **26m**], 7.20 [m, 2H, 1H Ar (BIAN') and 1H Ph **26M**], 6.97 [m, 1H, H_p Ar (BIAN') **26M**], 6.97 [m, 1H, H_p Ar (BIAN') **26m**], 6.76 [dd (7.0, 2.5), 1H, H_m Ar (BIAN') **26m**], 6.69 [dd (7.6, 1.9), 1H, H_m Ar (BIAN') **26M**], 6.44 [d (7.0), 1H, H_1 BIAN' **26M**], 6.37 [d (7.0), 1H, H_1 BIAN' **26m**], 6.32 [d (7.2), 1H, H_6 BIAN' **26m**], 6.12 [d (7.3), 1H, H_6 BIAN' **26M**], 4.24 [m, 1H, CH (*i*Pr) **26M**], 3.37 [m, 1H, CH (*i*Pr) **26M**], 3.37 [m, 1H, CH (*i*Pr) **26m**], 3.19 [m, 1H, CH (*i*Pr) **26m**], 3.08 [m, 1H, CH (*i*Pr) **26m**], 2.84 [m, 2H, 1H CH (iPr) **26m** and 1H CH_2-P **26m**], 2.65 [m, 1H, CH (*i*Pr) **26M**], 2.40 [m, 2H, CH_2-P **26M**], 2.25 [m, 1H, CH (*i*Pr) **26M**], 2.13 [d (7.8), 3H, CH_3-P **26M**], 1.94 [dd (14.5, 3.9), 1H, CH_2-P **26m**], 1.88 [d (7.0), 3H, CH_3-P **26m**], 1.43 [d (6.8), 3H, CH_3 (*i*Pr) **26m**], 1.38 [m, 6H, CH_3 (*i*Pr) **26M**], 1.38 [m, 3H, CH_3 (*i*Pr) **26m**], 1.34 [d (6.9), 3H, CH_3 (*i*Pr) **26M**], 1.05 [m, 6H, CH_3 (*i*Pr) **26m**], 1.01 [d (6.5), 3H, CH_3 (*i*Pr) **26M**], 0.94 [d (6.6), 3H, CH_3 (*i*Pr) **26M**], 0.77 [d (6.6), 3H, CH_3 (*i*Pr) **26m**], 0.71 [d (6.6), 3H, CH_3 (*i*Pr) **26m**], 0.56 [d (6.6), 3H, CH_3 (*i*Pr) **26m**], 0.43 [d (6.7), 3H, CH_3 (*i*Pr) **26M**], 0.13 [d (6.7), 3H, CH_3 (*i*Pr) **26M**], -0.52 [d (6.7), 3H, CH_3 (*i*Pr) **26m**], -0.71 [d (6.5), 3H, CH_3 (*i*Pr) **26M**].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): (Note that some of the signals for the phosphine phenyl groups of the minor product, **26m**, cannot be seen). δ 198.5 [d (6.2), CO, **26M**], 198.4 [d (4.4), CO, **26M**], 198.0 [d (5.4), CO, **26m**], 197.7 [d (5.9), CO, **26m**], 195.4 [d (52.1), CO, **26M**], 194.7 [d (6.4), C_2 BIAN', **26M**], 194.5 [d (6.6), C_2 BIAN', **26m**], 194.4 [d (51.2), CO, **26m**], 153.0 [QC BIAN' **26M**], 152.6, 149.6 [QC BIAN' **26m**], 149.1 [QC BIAN' **26M**], 148.0 [QC BIAN' **26m**], 147.1 [QC BIAN' **26M**], 144.7 [QC BIAN' **26m**],

143.8 [QC BIAN' **26M**], 142.0 [QC BIAN' **26M**], 141.3 [d (11.0), QC BIAN' **26m**], 140.8 [d (8.5), QC BIAN' **26M** and C_{ipso} Ph **26M**], 140.3, 139.4, 138.9 [QC BIAN' **26m**], 138.1, 137.8 [QC BIAN' **26M**], 131.8 [QC BIAN' **26M**], 131.7 [QC BIAN' **26m**], 131.6, 131.5, 131.2 [CH BIAN' **26m**], 131.0 [CH BIAN' and CH Ph **26M**], 130.0 [br, CH P-Ph], 129.3, 129.2, 128.1 [CH BIAN' **26m**], 128.0 [CH BIAN' and CH P-Ph **26M**], 127.9 [CH BIAN' **26m**], 127.6, 127.3 [CH BIAN' **26M**], 126.7 [CH BIAN' **26m**], 126.1 [CH BIAN' **26M**], 125.5 [QC BIAN' **26m**], 125.4 [QC BIAN' **26M**], 125.3 [CH BIAN' **26M**], 125.2 [CH BIAN' **26M**], 125.0 [CH BIAN' **26m**], 124.1 [CH BIAN' **26M** and CH BIAN' **26m**], 123.5, 123.3 [CH BIAN' **26m**], 123.2, 122.9, 122.7, 122.3 [CH BIAN' **26M**], 92.2 [d (11.0), C_6 BIAN', **26m**], 91.7 [d (9.1), C_6 BIAN', **26M**], 32.7 [d (37.9), CH_2-P, **26m**], 30.2 [d (35.6), CH_2-P, **26M**], 29.0 [CH (*i*Pr), **26M**], 28.5 [CH (*i*Pr), **26M**], 28.3, 28.2 [CH (*i*Pr), **26m**], 27.8 [CH (*i*Pr), **26M**], 27.2 [CH_3 (iPr) **26m** and CH (*i*Pr), **26m**], 27.0 [CH_3 (iPr) **26M** and CH (*i*Pr), **26m**], 26.7 [CH_3 (*i*Pr) **26m**], 26.3, 26.2 [2 CH_3 (*i*Pr) **26M**, and 1 CH_3 (*i*Pr) **26m**], 26.1 [CH (*i*Pr), **26M**], 26.0, 25.9, 25.5 [CH_3 (*i*Pr) **26m**], 25.3, 24.5, 24.3 [CH_3 (*i*Pr) **26M**], 23.9 [d (34.9), P-CH_3, **26M**], 23.5 [CH_3 (iPr) **26m**], 23.3 [CH_3 (iPr) **26M**], 21.9 [CH_3 (iPr) **26m**], 21.4 [CH_3 (iPr) **26M**], 20.1 [d (25.4), P-CH_3, **26m**].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 1.6 [**26M**], -2.4 [**26m**].

Synthesis of [Re(2,6-*i*Pr$_2$BIAN)(CO)$_3$(PPh$_2$Me)]BAr$^F_4$ (25). PPh_2Me (19 μL, 0.1021 mmol) was added to a solution of [Re(CO)$_3$(2,6-*i*Pr$_2$BIAN)(OTf)] (90 mg, 0.0980 mmol) and $NaBAr^F_4$ (95 mg, 0.1072 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred 3 hours and filtered. Volatiles were removed in vacuo. Washing with cold hexane (2 × 10 mL) and drying in vacuo afforded **25** as a red powder in a 92 % yield (166 mg). Slow diffusion of pentane (8 mL) into a concentrated solution of **25** in CH_2Cl_2 (4 mL) at -20°C yielded **9** as a red crystalline solid. Yield: 159 mg (89 %).

Anal. Calcd. for $C_{84}H_{65}BF_{24}N_2O_3PRe$: C 55.00, H 3.57, N 1.53. Found: C 54.99, H 3.58, N 1.60.

IR (CH_2Cl_2, cm^{-1}): 2041, 1954 (ν_{CO}).

The presence of very broad signals in the room temperature (298 K) ^1H NMR spectrum of **25** suggests hindered rotation around the rhenium-phosphorous bond, likely a result of steric clash between the bulky phosphane and the bulky diisopropylphenyl groups at the diimine nitrogens. Therefore, ^1H NMR spectrum at variable temperatures from 193

K (CD_2Cl_2) to 368 K (tol-d_8) were recorded. Accordingly, at low temperature, where that rotation is completely frozen, the NMR spectrum indicates the lack of a molecular mirror plane. The signals narrowed and the molecular mirror plane was recovered when the temperature was increased.

^{1}H NMR (CD_2Cl_2, 193 K, 400 MHz): δ 8.09 [d (7.8), 1H, H_3 BIAN], 8.04 [d (7.8), 1H, H_4 BIAN], 7.51-7.33 [m, 14H, Ar BIAN and Ph (partially obscured by aromatic H of [BAr^F_4]). Signals of H_2 BIAN at 7.51 ppm and H_5 BIAN at 7.36 ppm could be seen in the 2D COSY spectrum], 7.06 [m, 3H, Ar BIAN and Ph_2] 6.42 [H_1 BIAN], 6.21 [m, 1H, PPh_2], 6.02 [H_6 BIAN], 2.91 [m, 2H, 2 CH (*i*Pr)], 2.49 [m, 4H, CH_3-P and CH (*i*Pr)], 2.26 [m, 1H, CH (*i*Pr)], 1.32 [d (4.7), 3H, CH_3 (*i*Pr)], 1.28 [br, 3H, CH_3(*i*Pr)], 1.23 [br, 3H, CH_3 (*i*Pr)], 0.96 [br, 3H, CH_3 (*i*Pr)], 0.52 [d (5.6), 3H, CH_3 (*i*Pr)], 0.19 [d (6.0), 3H, CH_3 (*i*Pr)], 0.16 [d (5.7), 3H, CH_3 (*i*Pr)], -0.11 [br, 3H, CH_3 (*i*Pr)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 193 K, 400 MHz): δ 192.5 [m, 2 CO], 183.3 [d (52.2), CO], 179.1, 177.7 [C_2 and C_7 BIAN], 144.7, 144.3, 143.7, 140.9, 139.5, 139.3, 139.1 [QC BIAN and PPh_2Me], 133.2-125.4 [22 CH and 5 QC BIAN and PPh_2Me], 30.8, 30.6, 28.7, 28.4 [CH (*i*Pr)], 26.3, 26.1, 25.6, 24.9, 24.4, 23.8, 23.2, 20.5 [CH_3 (*i*Pr)] 20.0 [d (35.0), CH_3-P].

^{31}P{^{1}H} NMR (CD_2Cl_2, 193 K, 400 MHz): δ -20.4.

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.18 [d (8.3), 2H, H_3 and H_4 BIAN], 7.63-7.29 [m, 22H, 4H BAr^F_4, 10H P-Ph_2 and 8H BIAN (6H Ar and 2H H_2 BIAN (seen at 7.50 ppm in the COSY spectrum)], 6.35 [br, 2H, H_1 and H_6 BIAN], 2.86 [br, 4H, CH (*i*Pr)], 2.52 [d (7.5), 3H, P-CH_3], 1.38 [d (6.5), 6H, 2 CH_3 (*i*Pr)], 0.49 [br, 18H, 6 CH_3 (*i*Pr)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): *d* 191.9 [m, 2 CO], 183.5 [m, CO], 178.5 [C_2 BIAN], 144.7, 143.9 [QC BIAN], 140.4 [br, QC P-Ph_2], 139.7 [2 QC BIAN], 133.1 [CH BIAN], 131.9 [d (7.5), CH Ph], 131.1 [QC BIAN], 130.1 [CH BIAN], 129.8 [d (10.2), 2 CH Ph], 129.1, 127.4 [CH BIAN], 126.9 [br, CH BIAN], 126.1 [QC BIAN], 125.5 [CH BIAN], 30.5, 30.4 [CH (*i*Pr)], 28.5 [2 CH (*i*Pr)], 25.8 [2 CH_3 (*i*Pr)], 25.6, 23.7 [CH_3 (*i*Pr)] 18.9 [br, CH_3-P (only seen in the HSQC spectrum)].

^{31}P{^{1}H} NMR (CD_2Cl_2, 193 K, 400 MHz): δ -20.0.

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 7.33 [d (8.2), 2H, H_3 and H_4 BIAN], 7.22 [m, 2H, H_2 and H_5 BIAN], 7.13-7.01 [m, 6H, Ar (BIAN) and Ph obscured by tol-d_8], 6.84, 6.78 [br, 10H, Ar (BIAN) and Ph], 6.15 [br, 2H, H_1 and H_6 BIAN], 2.73 [br, 4H, CH (*i*Pr)], 1.95 [d (7.5), 3H, P-CH_3], 1.22 [br, 6H, 2 CH_3 (*i*Pr)], 0.31 [br, 18H, 6 CH_3 (*i*Pr)].

^{1}H NMR (toluene-d_8, 368 K, 400 MHz): δ 7.48 [d (8.3), 2H, H_3 and H_4 BIAN], 7.25 [m, 2H, H_2 and H_5 BIAN], 7.12 [m, 2H, Ar (BIAN) and Ph obscured by tol-d_8], 6.97-6.83 [m, 14H, Ar (BIAN) and Ph], 6.18 [d (7.4), 2H, H_1 and H_6 BIAN], 2.78 [m, 2H, CH (*i*Pr)], 2.58 [m, 2H, CH (*i*Pr)], 2.06 [d (7.6), 3H, CH_3-P], 1.24 [d (6.6), 6H, 2 CH_3 (*i*Pr)], 0.65 [d (6.6), 6H, 2 CH_3 (*i*Pr)], 0.45 [d (6.6), 6H, 2 CH_3 (*i*Pr)], 0.35 [d (6.6), 6H, 2 CH_3 (*i*Pr)].

Reaction of 25 with $KN(SiMe_3)_2$. Synthesis of 27. $KN(SiMe_3)_2$ (0.15 mL of a 0.5 M solution in toluene, 0.0750 mmol) was added to a solution of **25** (133 mg, 0.0725 mmol) in THF (10 mL) previously cooled to -78°C. The reaction mixture was allowed to reach room temperature and then evaporated to dryness. The resulting purple residue was extracted in CH_2Cl_2 (20 mL) and filtered. Evaporation to dryness afforded **27** as a purple solid. Slow diffusion of pentane (8 mL) into a concentrated solution of **27** in CH_2Cl_2 (4 mL) at -20°C yielded **27** as a blue crystalline solid. One of the crystals was suitable for an X-ray diffraction analysis. Yield: 38 mg (54 %).

Anal. Calcd. for $C_{52}H_{52}N_2O_3PRe{\cdot}4CH_2Cl_2$: C 51.29, H 4.58, N 2.14. Found: C 50.64, H 5.13, N 2.00.

IR (CH_2Cl_2, cm^{-1}): 2007, 1909, 1887 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 7.97 [d (8.1), 1H, H_3 BIAN'], 7.75 [d (8.3), 1H, H_4 BIAN'], 7.60-7.21 [m, 15H, H_2 and H_5 BIAN', 3H Ar (BIAN') and 10 H Ph], 6.97 [m, 2H, Ar (BIAN')], 6.73 [m, 1H, Ar (BIAN')], 6.49 [d (7.0), 1H, H_1 BIAN'], 6.15 [d (7.3), 1H, H_6 BIAN'], 3.43 [m, 1H, CH (*i*Pr)], 3.22 [m, 1H, CH (*i*Pr)], 2.97 [dd (14.6, 11.5), 1H, CH_2-P], 2.76 [m, 2H, 1 CH (iPr) and 1H CH_2-P], 2.33 [m, 1H, CH (*i*Pr)], 1.41 [d (6.6), 3H, CH_3 (*i*Pr)], 1.06 [d (6.6), 3H, CH_3 (*i*Pr)], 0.85 [d (6.6), 3H, CH_3 (*i*Pr)], 0.64 [d (6.7), 3H, CH_3 (*i*Pr)], 0.61 [d (6.7), 3H, CH_3 (*i*Pr)], 0.46 [d (6.7), 3H, CH_3 (*i*Pr)], 0.21 [d (6.7), 3H, CH_3 (*i*Pr)], -0.61 [d (6.6), 3H, CH_3 (*i*Pr)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 198.3 [d (7.5), CO], 198.1 [d (6.2), CO], 195.0 [d (7.2), C_2 BIAN'], 194.1 [d (70.7), CO], 152.6, 149.2, 148.1, 144.0, 142.1 [QC BIAN'],

141.3 [d (10.4), QC BIAN'], 141.1, 140.7 [QC BIAN'], 140.3 [d (48.1), C_{ipso} Ph], 138.6 [d (36.5) C_{ipso} Ph], 134.8 [CH BIAN'], 133.8 [d (22.0), CH Ph], 131.8 [QC BIAN'], 131.2 [CH BIAN'], 130.1 [d (12.9), CH Ph], 129.4 [d (1.8), 2 CH Ph], 129.3 [d (2.0), 2 CH Ph], 129.2, 129.0 [CH BIAN'], 128.8 [d (22.6), CH Ph], 128.6 [QC BIAN'], 128.1, 127.7, 127.4, 126.3, 125.7, 125.1, 124.3, 123.4, 123.3, 123.1, 122.5 [7 CH BIAN' and 3 CH Ph], 91.7 [d (11.0), C_6 BIAN'], 29.1 [d (1.8) CH (*i*Pr)], 28.4 [d (34.0), CH_2-P], 28.3, 27.9, 27.1 [CH (*i*Pr)], 26.9, 26.6, 26.4, 25.4, 24.8, 23.8, 23.1, 21.9 [CH_3 (*i*Pr)].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ 13.2.

Reaction of 14 with MeLi. Synthesis of 28. MeLi (0.10 mL of a 1.6 M solution in diethyl ether, 0.1600 mmol) was added to a suspension of **14** (100 mg, 0.1535 mmol) in toluene (10 mL) at 0°C. After the addition of MeLi the yellow solid dissolves and a dark red solution is formed. The mixture was stirred at room temperature for 20 minutes and then filtered through diatomaceous earth. Evaporation of volatiles and washing with hexane (2 × 10 mL) afforded **28** as a red microcrystalline powder in a 75 % yield (60 mg).

Anal. Calcd. for $C_{17}H_{20}N_2O_3PRe$: C 39.45, H 3.90, N 5.41. Found: C 39.29, H 3.96, N 5.43.

IR (toluene, cm^{-1}): 2012, 1917, 1884 (ν_{CO}).

^1H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.34 [m, 1H, H_9 bipy'], 6.97 [m, 1H, H_6 bipy'], 6.90 [m, 1H, H_{11} bipy'], 6.78 [m, 1H, H_{12} bipy'], 6.31 [ddd (8.4, 5.8, 1.0), 1H, H_4 bipy'], 6.19 [m, 1H, H_{10} bipy'], 5.18 [m, 1H, H_5 bipy'], 4.20 [m, 1H, H_3 bipy'], 1.41 [s, 3H, CH_3-bipy'], 0.79 [d (8.4), 9H, PMe_3].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 197.6 [d (7.6), CO], 196.5 [d (7.1), CO], 193.7 [d (80.1), CO], 175.0 [C_7 bipy'], 150.5 [C_9 bipy'], 149.0 [C_6 bipy'], 137.8 [C_{11} bipy'], 126.1 [C_4 bipy'], 122.0 [C_{12} bipy'], 121.9 [C_{10} bipy'], 100.8 [C_3 bipy'], 94.4 [C_5 bipy'], 70.2 [C_2 bipy'], 22.6 [d (4.1), CH_3-bipy'], 12.6 [d (27.9), PMe_3].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ -28.2.

$^{15}N\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 233.7 [N_8 bipy'], 82.0 [N_1 bipy'].

Reaction of 14 with *n*BuLi. Characterization of 29. *n*BuLi (0.15 mL of a 1.6 M solution in hexane, 0.2400 mmol) was added to a suspension of **14** (142 mg, 0.1872 mmol) in toluene (10 mL) at 0°C. After the addition of *n*BuLi the yellow solid started to dissolve and a brown solution is formed. After 40 minutes stirring at room temperature all compound **14** was dissolved. The resulting red solution was filtered and volatiles were removed under vacuum. Washing with hexane (1 × 5 mL) afforded **29** as a red microcrystalline powder in a 21 % yield (26 mg).

IR (toluene, cm^{-1}): 2012, 1917, 1886 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.36 [d (5.6), 1H, H_9 bipy'], 7.00 [m, 1H, H_6 bipy' (obscured by residual toluene, could be seen in the ^{1}H,^{1}H-COSY and in the ^{1}H,^{13}C-HSQC spectrum)], 6.89 [m, 1H, H_{11} bipy'], 6.83 [m, 1H, H_{12} bipy'], 6.27 [m, 1H, H_4 bipy'], 6.19 [m, 1H, H_{10} bipy'], 5.13 [m, 1H, H_5 bipy'], 4.12 [d (8.3), 1H, H_3 bipy'], 2.22 [m, 1H, CH_2-bipy'], 1.67 [m, 1H, CH_2-bipy'], 0.78 [d (8.4), 9H, PMe_3]. Signals of two CH_2 groups and the CH_3 group of bipy-bonded *n*BuLi were obscured by unkown impurities and could not be seen in the ^{1}H NMR spectrum.

^{13}C{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ 174.4 [C_7 bipy'], 150.7 [C_9 bipy'], 149.3 [C_6 bipy'], 137.2 [C_{11} bipy'], 126.2 [C_4 bipy'], 122.3 [C_{12} bipy'], 121.8 [C_{10} bipy'], 100.5 [d (2.6), C_3 bipy'], 95.0 [C_5 bipy'], 72.9 [C_2 bipy'], 37.8 [d (4.0), CH_2-bipy'], 26.1, 23.6 [CH_2 *n*Bu], 13.6 [CH_3 *n*Bu], 12.9 [d (27.7), PMe_3]. The ^{13}C NMR signals of **29** were obtained from the ^{13}C-DEPT-135, the ^{1}H,^{13}C-HSQC and the ^{1}H,^{13}C-HMBC spectra, therefore, signals for the CO groups could not be listed.

^{31}P{^{1}H} NMR (benzene-d_6, 298 K, 400 MHz): δ -27.4.

Reaction of 14 with *t*BuLi. Synthesis of 30. *t*BuLi (0.10 mL of a 1.7 M solution in pentane, 0.1700 mmol) was added to a suspension of **14** (108 mg, 0.1658 mmol) in toluene (10 mL) at 0°C. After the addition of *t*BuLi the yellow solid dissolved and a dark red solution was formed. The mixture was stirred at room temperature for 10 minutes and then filtered. Volatiles were evaporated and the red residue was dissolved in hexane and filtered. Removal of hexane under vacuum yielded **30** as a red solid in a 78 % yield (72 mg).

Anal. Calcd. for $C_{20}H_{26}N_2O_3PRe$: C 42.93, H 4.68, N 5.01. **Found:** C 43.02, H 4.60, N 5.10.

IR (toluene, cm^{-1}): 2019, 1924, 1894 (ν_{CO}).

^{1}H NMR (benzene-d$_6$, 298 K, 400 MHz): δ 7.82 [d (6.0), 1H, H$_9$ bipy'], 6.95 [m, 1H, H$_6$ bipy'], 6.65 [m, 1H, H$_{11}$ bipy'], 6.43 [d (9.7), 1H, H$_3$ bipy'], 6.35 [d (8.9), 1H, H$_{12}$ bipy'], 5.63 [m, 1H, H$_{10}$ bipy'], 5.01 [m, 1H, H$_4$ bipy'], 3.00 [m, 1H, H$_5$ bipy'], 1.03 [s, 9H, *t*Bu-bipy'], 0.90 [d (8.8), 9H, PMe$_3$].

^{13}C{^{1}H} NMR (benzene-d$_6$, 298 K, 400 MHz): δ 197.3 [m, 2 CO], 191.9 [d (70.6), CO], 155.8 [C$_7$ bipy'], 150.4 [C$_9$ bipy'], 138.0 [C$_6$ bipy'], 133.4 [C$_{11}$ bipy'], 121.7 [C$_3$ bipy'], 118.3 [C$_2$ bipy'], 112.3 [C$_{12}$ bipy'], 108.1 [C$_{10}$ bipy'], 108.6 [C$_4$ bipy'], 51.2 [C$_5$ bipy'], 39.5 [QC *t*Bu], 25.7 [CH$_3$(*t*Bu)], 12.8 [d (31.7), PMe$_3$].

^{31}P{^{1}H} NMR (benzene-d$_6$, 298 K, 400 MHz): δ -27.3.

^{15}N{^{1}H} NMR (benzene-d$_6$, 298 K, 400 MHz): δ 236.6 [N$_1$ bipy'], 174.6 [N$_8$ bipy'].

Reaction of 30 with MeOTf. Synthesis of 31. MeOTf (20 μL, 0.1828 mmol) was added to a solution of **30** (60 mg, 0.1072 mmol) in toluene (10 mL) at room temperature. The resulting mixture was stirred for 5 hours at room temperature. The solution turned dark orange and an orange oil precipitated. Concentration to 5 mL and addition of hexane (20 mL) caused the precipitation of **31** as an orange solid, which was washed with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL) and dried under vacuum. Yield: 53 % (41 mg).

IR (THF, cm^{-1}): 2037, 1950, 1922 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.96 [d (5.6), 1H, H$_9$ *t*Bu-bipy], 8.90 [br, 1H, H$_6$ *t*Bu-bipy], 8.72 [d (8.3), 1H, H$_{12}$ *t*Bu-bipy], 8.67 [d (8.6), 1H, H$_3$ *t*Bu-bipy], 8.36 [m, 2H, H$_4$ and H$_{11}$ *t*Bu-bipy], 7.69 [m, 1H, H$_{10}$ *t*Bu-bipy], 1.48 [s, 9H, CH$_3$(*t*Bu)], 1.13 [d (9.0), 9H, P(CH$_3$)$_3$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.1 [d (7.2), CO], 194.7 [d (6.1), CO], 188.2 [d (61.0), CO], 155.6 [C$_7$ *t*Bu-bipy], 153.1 [C$_2$ *t*Bu-bipy], 152.7 [C$_9$ *t*Bu-bipy], 152.1 [C$_5$ *t*Bu-bipy], 150.1 [C$_6$ *t*Bu-bipy], 141.1 [C$_{11}$ *t*Bu-bipy], 138.4 [C$_4$ *t*Bu-bipy], 128.1 [C$_{10}$ *t*Bu-bipy], 125.5 [C$_{12}$ *t*Bu-bipy], 125.1 [C$_3$ *t*Bu-bipy], 34.3 [QC *t*Bu], 30.2 [CH$_3$ (*t*Bu)], 13.3 [d (31.8), P(CH$_3$)$_3$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ -27.4.

Reaction of 30 with HOTf. Synthesis of 32. HOTf (13 μL, 0.1472 mmol) was added to a solution of **30** (72 mg, 0.1287 mmol) in toluene (10 mL) at room temperature. The color of the solution immediately changed from red to orange. Concentration to 5 mL and addition of hexane (20 mL) caused the precipitation of the product **32** as an orange solid, which was washed with diethyl ether (1 × 10 mL) and hexane (2 × 10 mL) and dried under vacuum. Yield: 75 % (69 mg). Slow diffusion of hexane (10 mL) into a concentrated solution of **32** in CH_2Cl_2 (5 mL) at room temperature yielded orange crystals of **32** one of which was employed for X-ray analysis.

Anal. Calcd. for $C_{21}H_{27}F_3N_2O_6PReS$: C 35.54, H 3.83, N 3.95. **Found:** C 35.71, H 3.80, N 3.82.

IR (CH_2Cl_2, cm^{-1}): 2035, 1946, 1918 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.69 [d (4.9), 1H, H_9 bipy'], 8.46 [m, 1H, H_6 bipy'], 8.12 [m, 1H, H_{11} bipy'], 8.09 [m, 1H, H_{12} bipy'], 7.48 [m, 1H, H_{10} bipy'], 7.21 [m, 1H, H_3 bipy'], 2.77 [m, 1H, H_4 bipy'], 2.62 [m, 1H, H_5 bipy'], 2.53 [m, 1H, $H_{4'}$ bipy'], 1.34 [d (8.8), 9H, PMe_3], 1.12 [s, 9H, *t*Bu].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.3 [d (7.0), CO], 195.2 [d (6.4), CO], 189.6 [d (65.0), CO], 175.8 [C_6 bipy'], 155.0 [C_7 bipy'], 151.8 [C_9 bipy'], 142.1 [C_2 bipy'], 140.3 [C_{11} bipy'], 127.7 [C_3 bipy'], 125.9 [C_{10} bipy'], 122.1 [C_{12} bipy'], 45.8 [C_5 bipy'], 34.0 [QC *t*Bu], 27.2 [CH_3(*t*Bu)], 19.2 [C_4 bipy'], 13.6 [d (32.0), PMe_3].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ -26.6.

Reaction of 14 with Li[$HBEt_3$]. Characterization of 33M, 33m. Li[$HBEt_3$] (0.10 mL of a 1.0 M solution in THF, 0.100 mmol) was evaporated to dryness in a Young Schlenk for 2 hours at 60°C. The resulting yellow oil was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **14** (62 mg, 0.0952 mmol) in THF-d_8 (0.15 mL) previously cooled to 0°C in a Young Schlenk. There was an instantaneous color change from yellow to purple. The resulting solution was kept at 0°C for 5 minutes stirring, and for 5 minutes without stirring and then it was transferred to a NMR tube cooled to -78°C. It was not possible to completely remove the THF from the Li[$HBEt_3$] solution, therefore, the NMR spectra of **33M**, **33m** showed intense signals of THF.

Ratio **33M:33m** (from ^{1}H NMR spectrum): 3:1.

IR (THF, cm^{-1}): 2010, 1913, 1882 (ν_{CO}).

^{1}H NMR (THF-d$_8$, 233 K, 400 MHz): δ 8.71 [m, 2H, H$_9$ bipy' **33M** and **33m**], 7.89 [m, 4H, H$_{11}$ and H$_{12}$ bipy' **33M** and **33m**], 7.29 [m, 2H, H$_{10}$ bipy' **33M** and **33m**], 6.11 [d (7.5), 1H, H$_6$ bipy' **33M**], 6.06 [m, 1H, H$_4$ bipy' **33m**], 5.75 [m, 1H, H$_3$ bipy' **33m**] 5.26 [m, 1H, H$_3$ bipy' **33M**], 4.49 [m, 1H, H$_5$ bipy' **33m**], 4.35 [m, 1H, H$_6$ bipy' **33m**], 4.03 [d (12.2), 1H, H$_{6'}$ bipy' **33m**], 3.95 [m, 1H, H$_5$ bipy' **33M**], 3.45 [m, 2H, H$_4$ and H$_{4'}$ bipy' **33M**], 1.28 [d (8.7), 9H, PMe$_3$ **33M**], 1.24 [d (8.8), 9H, PMe$_3$ **33m**].

^{13}C{^{1}H} NMR (THF-d$_8$, 233 K, 400 MHz): 198.5 [d (6.9), CO **33m**], 198.3 [d (7.8), CO **33M**], 197.4 [m, 2 CO, 1 CO **33M** and 1 CO **33m**], 192.9 [d (81.1), 2 CO, 1 CO **33M** and 1 CO **33m**], 162.5 [C$_7$ bipy' **33m**], 161.7 [C$_7$ bipy' **33M**], 154.7 [C$_2$ bipy' **33m**], 152.1 [d (27.3), C$_9$ bipy' **33M** and **33m**], 148.5 [C$_2$ bipy' **33M**], 143.2 [d (18.6), C$_6$ bipy' **33M**], 137.4 [C$_{11}$ bipy' **33M**], 137.1 [C$_{11}$ bipy' **33m**], 125.6 [C$_4$ bipy' **33m**], 123.8 [C$_{10}$ bipy' **33M** and **33m**], 119.3 [C$_{12}$ bipy' **33M** and **33m**], 102.2 [C$_5$ bipy' **33m**], 97.9 [C$_3$ bipy' **33M**], 96.4 [C$_3$ bipy' **33m**], 93.3 [C$_5$ bipy' **33M**], 55.6 [m, C$_6$ bipy' **33m**], 25.7 [C$_4$ bipy' **33M** (partially obscured by THF, could be seen in ^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC spectra)], 11.8 [m, PMe$_3$ **33M** and **33m**].

^{31}P{^{1}H} NMR (toluene-d$_8$, 233 K, 400 MHz): δ -23.1 [**33M**], -26.2 [**33m**].

^{15}N{^{1}H} NMR (toluene-d$_8$, 233 K, 400 MHz): δ 226.1 [N$_8$ bipy' **33M**], 77.3 [N$_1$ bipy' **33M**].

Reaction of 14 with Li[HBEt$_3$]. Characterization of 34. Li[HBEt$_3$] (0.30 mL of a 1.0 M solution in THF, 0.3000 mmol) was added to a THF (15 mL) solution of **14** (162 mg, 0.2486 mmol) at 0°C. The solution immediately turned purple. Upon stirring the mixture at room temperature for 1 hour, the solution turned red. Volatiles were evaporated to dryness and the resulting red oil was dissolved in benzene (10 mL) and filtered. Concentration of the solution to 5 mL and addition of hexane (10 mL) caused the precipitation of **34** as a red solid, which was washed with hexane (2 × 10 mL) and dried under vacuum. Complex **34** demonstrated to be highly unstable toward atmospheric air and moisture. Product **34** turned yellow upon exposure to minimal amounts of oxygen

and water (glove-box handling), therefore, it could not be weighted and elemental analysis was not attempted.

IR (THF, cm^{-1}): 2014, 1918, 1891 (ν_{CO}).

^{1}H NMR (benzene-d_6, 298 K, 400 MHz): δ 7.88 [m, 1H, H_9 bipy'], 6.90 [m, 1H, H_6 bipy'], 6.76 [m, 1H, H_{11} bipy'], 6.34 [m, 1H, H_{12} bipy'], 5.57 [m, 1H, H_{10} bipy'], 2.63 [br, 1H, H_3 bipy'], 2.28 [br, 1H, H_5 bipy'], 1.86 [d (12.4), 1H, H_4 bipy'], 1.06 [m, 1H, $H_{4'}$ bipy' (obscured by unkown impurities, could be seen in the 2D spectra)], 0.93 [d (8.8), 9H, $P(CH_3)_3$].

^{13}C{^{1}H} NMR (benzene-d_6, 298 K, 400 MHz): δ 197.7 [d (6.4), CO], 197.6 [d (5.8), CO], 192.2 [d (70.5), CO], 155.2 [C_7 bipy'], 150.9 [C_9 bipy'], 136.5 [d (7.0), C_6 bipy'], 133.1 [C_{11} bipy'], 117.6 [C_2 bipy'], 111.6 [C_{12} bipy'], 105.7 [C_{10} bipy'], 42.3 [C_5 bipy'], 36.7 [C_3 bipy'], 21.9 [C_4 bipy'], 12.5 [d (29.2), $P(CH_3)_3$].

^{31}P{^{1}H} NMR (benzene-d_6, 298 K, 400 MHz): δ -28.9.

^{15}N{^{1}H} NMR (benzene-d_6, 298 K, 400 MHz): δ 247.5 [N_1 bipy'], 172.6 [N_8 bipy'].

Reaction of 34 with HOTf. Synthesis of 35. HOTf (25 μL, 0.2818 mmol) was added to a solution of **34** (obtained from 162 mg, 0.2486 mmol of **14** and 0.30 mL of Li[$HBEt_3$], 1.0 M solution in THF, 0.3000 mmol) in toluene (10 mL) at room temperature. A yellow solid immediately precipitated. The supernatant was removed and the solid was washed with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL). Compound **35** was obtained as a yellow solid, which was dried under vacuum. Slow diffusion of hexane (1 mL) into a concentrated solution of **35** in CD_2Cl_2 (0.3 mL) at -20°C yielded yellow crystals of **35** one of which was employed for X-ray analysis.

IR (CH_2Cl_2, cm^{-1}): 2032, 1944, 1920 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.05 [d (5.5), 1H, H_9 bipy'], 8.65 [d (8.1), 1H, H_{12} bipy'], 8.56 [m, 1H, H_{11} bipy'], 7.82 [m, 1H, H_{10} bipy'], 4.59 [dd (19.4, 5.0), 1H, H_6 bipy'], 4.48 [d (19.4), 1H, $H_{6'}$ bipy'], 4.25 [br, 1H, H_3 bipy'], 2.54 [br, 1H, H_5 bipy'], 2.02 [d (12.6), 1H, H_4 bipy'], 1.06 [d (12.6), 1H, $H_{4'}$ bipy'], 1.32 [d (9.1), 9H, $P(CH_3)_3$].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.9 [d (6.3), CO], 194.3 [d (5.5), CO], 177.4 [C_2 bipy'], 154.1 [C_7 bipy'], 153.2 [C_9 bipy'], 141.3 [C_{11} bipy'], 129.6 [C_{10} bipy'], 129.1 [C_{12} bipy'], 66.0 [C_6 bipy'], 34.9 [C_3 bipy'], 34.7 [C_5 bipy'], 21.8 [C_4 bipy'], 13.6 [d (32.2), $P(CH_3)_3$]. The signal for the CO trans to PMe_3 could not be seen in the ^{13}C NMR spectrum.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -29.7.

Preparation and Characterization of Compounds in Chapter 3

For compounds **41**, **43M**, **43m** and **45M**, **45m**, the ^{13}C NMR spectrum of free $PPhMe_2$ helped in the signal assignment. **$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz):** 143.0 [d (14.5), C_{ipso}], 130.4 [d (17.2), C_{ortho}], 128.2 [d (5.8), C_{meta}], 127.8 [s, C_{para}], 14.2 [d (13.3), CH_3].

Synthesis of [$Re(CO)_3$(phen)(PMe_3)]OTf (36). PMe_3 (20 μL, 0.2294 mmol) was added to a solution of [Re(phen)$(CO)_3$(OTf)] (103 mg, 0.1718 mmol) in toluene (10 mL). After refluxing the resulting solution for 1.5 hours, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **36** as a yellow solid which was dried under vacuum (Yield: 103 mg (89 %)). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **36** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals of **36**. Yield: 97 mg (84 %).

Anal. Calcd. for $C_{19}H_{17}F_3N_2O_6PReS$: C 33.78, H 2.54, N 4.15. Found: C 34.11, H 2.61, N 4.10.

IR (THF, cm^{-1}): 2034, 1945, 1920 (ν_{CO}).

IR (toluene, cm^{-1}): 2036, 1938, 1913 (ν_{CO})

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.44 [m, 2H, H_2 and H_9 phen], 8.91 [m, 2H, H_4 and H_7 phen], 8.31 [s, 2H, H_5 and H_6 phen], 8.15 [m, 2H, H_3 and H_8 phen], 1.04 [d (8.5), 9H, $P(CH_3)_3$].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ 194.4 [d (3.8), 2 CO], 187.9 [d (60.9), CO], 153.9 [C_2 and C_9 phen], 146.3 [C_{11} and C_{13} phen], 139.9 [C_4 and C_7 phen], 131.5 [C_{12} and C_{14} phen], 128.6 [C_5 and C_6 phen], 127.1 [C_3 and C_8 phen], 13.3 [d (30.2), $P(CH_3)_3$].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ -28.5.

$^{15}N\{^1H\}$ NMR (THF-d_8, 298 K, 400 MHz): δ 226.5 [N_{10} and N_1 phen].

Reaction of 36 with $KN(SiMe_3)_2$. Synthesis of 37. $KN(SiMe_3)_2$ (0.25 mL of a 0.7 M solution in toluene, 0.1750 mmol) was added to a solution of **36** (0.097 g, 0.1436 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from yellow to purple. The reaction mixture was allowed to reach room temperature, it was stirred for 30 minutes, and then evaporated to dryness. The solid residue was extracted with toluene (10 mL) and filtered. Removal of the solvent and drying under vacuum afforded **37** as a black microcrystalline solid, which was washed with hexane (2 × 10 mL). Yield: 40 mg (53 %). Slow evaporation of a concentrated solution of **37** in diethyl ether (8 mL) afforded red crystals of **37**, one of which was selected for X-ray diffraction. Yield: 35 mg (47 %).

Anal. Calcd. for $C_{18}H_{16}N_2O_3PRe$: C 41.14, H 3.07, N 5.33. Found: C 42.08, H 3.38, N 4.98.

IR (THF, cm^{-1}): 2010, 1916, 1888 (ν_{CO}).

^{1}H NMR (THF-d_8, 298 K, 600 MHz): δ 8.83 [m, 1H, H_9 phen'], 8.11 [d (8.2), 1H, H_7 phen'], 7.28 [m, 1H, H_8 phen'], 7.00 [d (7.9), 1H, H_5 phen'], 6.61 [d (7.9), 1H, H_6 phen'], 6.48 [d (9.4), 1H, H_4 phen'], 5.85 [dd (9.4, 5.8), 1H, H_3 phen'], 4.55 [m, 1H, H_2 phen'], 2.06 [m, 1H, CH_2P], 1.83 [m, 1H, CH_2P], 1.79 [d (9.0), 3H, CH_3P], 0.66 [d (8.6), 3H, CH_3P].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 600 MHz): δ 199.6 [d (6.1), CO], 197.3 [d (8.6), CO], 194.7 [d (64.8), CO], 154.9 [C_{11} phen'], 148.3 [C_9 phen'], 145.8 [C_{13} phen'], 136.6 [C_7 phen'], 131.2 [C_{14} phen'], 126.7 [C_5 phen'], 124.2 [d (8.5), C_3 phen'], 123.8 [C_4 phen'], 121.5 [C_8 phen'], 119.7 [C_{12} phen'], 107.6 [C_6 phen'], 64.9 [d (7.5), C_2 phen'], 36.1 [d (44.0), CH_2P], 12.8 [d (30.8), CH_3P], 10.8 [d (24.0), CH_3P].

^{31}P{^{1}H} NMR (THF-d_8, 298 K, 300 MHz): δ -10.5.

^{15}N NMR (toluene-d_8, 298 K, 400 MHz): δ 233.2 [N_{10}], 97.7 [N_1].

Reaction of 37 with HOTf. Synthesis of 38. Addition of HOTf (6 μL, 0.0680 mmol) to a solution of **37** (35 mg, 0.0667 mmol) in toluene (10 mL) at room temperature caused the instantaneous precipitation of **38** as an orange solid. Compound **38** was isolated as an orange solid in a 75 % yield (34 mg) after washing with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL) and drying under vacuum. Slow diffusion of diethyl ether (2 mL) into a concentrated solution of **38** in CD_2Cl_2 (0.5 mL) at room temperature afforded

orange crystals of **38**, one of which was employed for X-ray diffraction. Due to the poor CD_2Cl_2 solubility of **38**, a metathesis reaction was carried out. $KBAr^F_4$ (46 mg, 0.0510 mmol) was added to a CH_2Cl_2 (5 mL) solution of **38** (34 mg, 0.0504 mmol). The mixture was stirred at room temperature for 30 minutes, then filtered and volatiles were removed under vacuum to afford **38^F** as an orange solid in a 96 % yield (67 mg) which was used for NMR characterization.

Anal. Calcd. for $C_{19}H_{17}F_3N_2O_6PReS$: C 33.78, H 2.54, N 4.15. Found: C 34.02, H 2.58, N 4.12.

^{1}H and ^{31}P NMR of compound 38:

IR (CH_2Cl_2, cm^{-1}): 2041, 1953, 1918 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.19 [d (4.9), 1H, H_9 phen'], 8.74 [br, 1H, N-H], 8.50 [d (8.4), 1H, H_7 phen'], 7.99 [d (8.4), 1H, H_6 phen'], 7.64 [d (8.4), 1H, H_5 phen'], 7.56 [m, 1H, H_8 phen'], 7.00 [m, 1H, H_4 phen'], 6.81 [m, 1H, H_3 phen'], 4.31 [m, 1H, H_2 phen'], 2.20 [ddd (15.3, 11.6, 5.6), 1H, CH_2P], 1.95 [d (9.4), 3H, CH_3P], 1.32 [m, 1H, CH_2P], 0.77 [d (9.0), 3H, CH_3P].

^{31}P{^{1}H} NMR (THF-d_8, 193 K, 400 MHz): δ -0.3.

Anal. Calcd. for $C_{19}H_{17}F_3N_2O_6PReS$: C 33.78, H 2.54, N 4.15. Found: C 34.10, H 2.62, N 4.16.

Characterization of compound 38^F:

IR (CH_2Cl_2, cm^{-1}): 2040, 1953, 1926 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.19 [d (4.9), 1H, H_9 phen'], 8.47 [d (8.4), 1H, H_7 phen'], 7.97 [d (8.0), 1H, H_6 phen'], 7.60 [d (8.4), 1H, H_5 phen' (obscured by BAr^F_4 signals, can be seen in COSY spectrum)], 7.57 [m, 1H, H_8 phen' (obscured by BAr^F_4 signals, can be seen in COSY spectrum)], 6.94 [d (9.7), 1H, H_4 phen'], 6.76 [dd (9.7, 5.0), 1H, H_3 phen'], 4.21 [m, 1H, H_2 phen'], 2.12 [ddd (15.6, 11.7, 5.4), 1H, CH_2P], 1.95 [d (9.4), 3H, CH_3P], 1.31 [m, 1H, CH_2P], 0.76 [d (8.8), 3H, CH_3P].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 600 MHz): δ 193.9 [d (7.2), CO], 192.9 [d (7.1), CO], 191.0 [d (62.3), CO], 155.3 [C_9 phen'], 145.9 [C_{13} phen'], 139.3 [C_7 phen'], 135.7 [d (11.7), C_3

phen'], 133.4 [C_{12} phen'], 131.4 [C_{11} phen'], 129.5 [C_6 phen'], 129.5 [C_{14} phen' obscured by $BAr^F{}_4$ signal, can be seen in HMBC spectrum], 126.8 [C_5 phen'], 124.7 [C_4 phen'], 123.3 [d (26.0), C_8 phen'], 61.3 [d (8.4), C_2 phen'], 27.0 [d (23.6), CH_2-P], 15.6 [d (34.9), CH_3P], 11.7 [d (28.7), CH_3P].

$^{31}P\{^1H\}$ NMR (THF-d_8, 193 K, 400 MHz): δ -0.04.

Reaction of 37 with MeOTf. Synthesis of 39. Addition of MeOTf (8 μL, 0.0731 mmol) to a solution of **37** (35 mg, 0.0667 mmol) in toluene (10 mL) at room temperature caused the instantaneous precipitation of **39** as an orange oil. Compound **39** was isolated as an orange solid in a 80 % yield (37 mg) after washing with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL) and drying under vacuum. Slow diffusion of diethyl ether (2 mL) into a concentrated solution of **39** in CD_2Cl_2 (0.5 mL) at room temperature afforded orange crystals of **39**, one of which was employed for X-ray diffraction.

Anal. Calcd. for $C_{20}H_{19}F_3N_2O_6PReS$: C 34.83, H 2.78, N 4.06. Found: C 35.01, H 2.80, N 4.09.

IR (CH_2Cl_2, cm^{-1}): 2038, 1950, 1923 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.22 [m, 1H, H_9 phen'], 8.63 [d (8.2), 1H, H_7 phen'], 8.11 [d (8.4), 1H, H_6 phen'], 7.71 [m, 1H, H_8 phen'], 7.70 [d (8.4), 1H, H_5 phen'], 7.00 [m, 1H, H_4 phen'], 6.70 [dd (9.6, 5.0), 1H, H_3 phen'], 4.45 [m, 1H, H_2 phen'], 3.80 [s, 3H, N-Me], 2.84 [ddd (15.9, 12.3, 5.5), 1H, CH_2P], 2.01 [d (9.7), 3H, CH_3P], 1.51 [m, 1H, CH_2P], 0.73 [d (9.1), 3H, CH_3P].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 193.5 [d (4.6), 2 CO], 192.5 [d (62.4), CO], 155.3 [C_9 phen'], 145.1 [C_{13} phen'], 139.7 [C_7 phen'], 137.4 [C_{11} phen'], 133.2 [d (12.6), C_3 phen'], 131.2 [C_{12} phen'], 130.2 [C_6 phen'], 129.9 [C_{14} phen'], 128.0 [C_5 phen'], 124.0 [C_8 phen'], 123.9 [C_4 phen'], 69.8 [d (6.5), C_2 phen'], 54.1 [CH_3-N (obscured by residual CH_2Cl_2 signal, could be seen in HSQC spectrum)], 32.5 [d (23.6), CH_2-P], 15.6 [d (36.5), CH_3P], 11.9 [d (30.1), CH_3P].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ -4.9.

Reaction of 36 with $KN(SiMe_3)_2$. Characterization of 40M, 40m. $KN(SiMe_3)_2$ (0.10 mL of a 0.7 M solution in toluene, 0.0700 mmol) was evaporated to dryness in a PTFE valve

J. Young tube for 2 hours at 60°C. The white solid obtained was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **36** (45 mg, 0.0666 mmol) in THF-d_8 (0.15 mL) previously cooled to -78°C in a J. Young tube. There was an instantaneous color change from yellow to purple. The resulting solution was kept at -78°C for 10 minutes, and then it was transferred to a NMR tube cooled to -78°C. The NMR spectra showed exclusively signals corresponding to **40M**, **40m** (see below) and to a slight excess of $KN(SiMe_3)_2$. The **40M**, **40m** mixture is stable in THF-d_8 for at least 6 hours under 233 K. At 253 K signals for compound **37** appear in the spectra. The transformation of **40M**, **40m** in **37** was complete after 30 minutes at room temperature.

The reaction could be also carried out in toluene-d_8 in an analogous way but working at 0°C which favors the dissolution of **36** and the progress of the reaction. When $KN(SiMe_3)_2$ was added onto a suspension of **36** in tol-d_8 at 0°C, there was a progressive dissolution of **36** to give a dark blue solution of **40M**, **40m**. The solution was stable for at least 48 hours under 253 K. At 273 K signals of compound **37** could be detected. After 5 hours at room temperature the ratio **40M**, **40m**: **37** was appropriate to register the DOSY spectrum. The transformation of **40M**, **40m** in **37** was complete after 24 hours at room temperature.

IR spectra on THF and toluene were obtained right after the addition of $KN(SiMe_3)_2$ at -78°C. **IR (THF, cm^{-1}):** 2014, 1918, 1888 (ν_{CO}). **IR (toluene, cm^{-1}):** 2018, 1924, 1888 (ν_{CO}).

^{1}H NMR (THF-d_8, 193 K, 400 MHz): δ 8.91 [m, 1 H, H_9 phen' **40M**], 8.91 [m, 1 H, H_9 phen' **40m**], 8.35 [d (7.5), 1 H, H_7 phen' **40M**], 8.35 [d (7.5), 1 H, H_7 phen' **40m**], 7.50 [m, 1 H, H_8 phen' **40M**], 7.50 [m, 1 H, H_8 phen' **40m**], 7.37 [d (7.8), 1 H, H_5 phen' **40M**], 7.37 [d (7.8), 1 H, H_5 phen' **40m**], 7.02 [d (7.8), 1 H, H_6 phen' **40M**], 7.02 [d (7.8), 1 H, H_6 phen' **40m**], 6.50 [d (6.9), 1H, H_2 phen' **40M**], 6.40 [d (6.9), 1 H, H_2 phen' **40m**], 5.80 [br, 1H, H_4 phen' **40M**], 5.74 [br, 1 H H_4 phen' **40m**], 4.50 [m, 1H, H_3 phen' **40M**], 4.37 [m, 1 H, H_3 phen' **40m**], 1.21 [d (8.5), 9H, PMe_3 **40m**], 1.14 [d (8.6), 9H, PMe_3 **40M**], 0.26 [br, 9 H, $N(SiMe_3)$ **40M**], 0.26 [br, 9 H, $N(SiMe_3)$ **40m**], -0.02 [br, 9 H, $N(SiMe_3)$ **40m**], -0.07 [br, 9 H, $N(SiMe_3)$ **40M**].

^{13}C{^{1}H} NMR (THF-d_8, 193 K, 400 MHz): (only signals for **40M** are seen) δ 198.0 [d (7.2), CO], 197.2 [d (7.4), CO], 191.9 [d (74.4), CO], 150.1 [C_9 phen'], 149.1 [C_{11} phen'],

144.4 [C_{13} phen'], 139.4 [C_2 phen'], 137.6 [C_7 phen'], 131.0 [C_5 phen'], 129.8 [C_{14} phen'], 125.0 [C_{12} phen'], 122.3 [C_8 phen'], 112.8 [C_6 phen'], 103.4 [C_3 phen'], 50.4 [C_4 phen'], 12.2 [d (28.8), PMe_3], 3.3, 1.7 [$N(Si(CH_3)_3)_2$].

$^{31}P\{^1H\}$ NMR (THF-d_8, 193 K, 400 MHz): δ -23.9 [**40M**], -26.9 [**40m**]. **40M**:**40m** ratio (from ^{31}P NMR spectrum): 17:1.

$^{29}Si\{^1H\}$ NMR (THF-d_8, 193 K, 400 MHz): δ 3.5, 2.4 [$SiMe_3$ **40M**].

$^{15}N\{^1H\}$ NMR (THF-d_8, 193 K, 400 MHz): δ 228.7 [N_{10} phen' **40M**], 94.0 [N_1 phen' **40M**]. The signal of the $N(SiMe_3)_2$ group could not be detected.

^1H NMR (toluene-d_8, 253 K, 400 MHz): δ 8.31 [m, 1 H, H_9 phen' **40M**], 8.31 [m, 1 H, H_9 phen' **40m**], 7.59 [d (8.2), 1 H, H_5 phen' **40M**], 7.54 [d (8.3), 1H, H_5 phen' **40m**], 7.29 [m, 1 H, H_7 phen' **40M**], 7.16 [m, 1 H, H_7 phen' **40m** (obscured by tol-d_8)], 6.74 [m, 1 H, H_2 phen' **40M**], 6.74 [m, 1 H, H_2 phen' **40m**], 6.67 [d (8.2), 1 H, H_6 phen' **40M**], 6.60 [d (8.3), 1 H, H_6 phen' **40m**], 6.33 [m, 1 H, H_8 phen' **40M**], 6.33 [m, 1 H, H_8 phen' **40m**], 6.04 [br, 1 H, H_4 phen' **40M**], 6.04 [br, 1 H, H_4 phen' **40m**], 4.75 [m, 1 H, H_3 phen' **40M**], 4.53 [m, 1H, H_3 phen' **40m**], 0.71 [d (8.5), 9H, PMe_3 **40m**], 0.57 [d (8.5), 9H, PMe_3 **40M**], 0.34 [br, 9H, $N(SiMe_3)$ **40M**], 0.34 [br, 9H, $N(SiMe_3)$ **40m**], 0.19 [br, 9H, $N(SiMe_3)$ **40M**], 0.19 [br, 9H, $N(SiMe_3)$ **40m**].

^{31}P NMR (tol-d_8, 253 K, 400 MHz): δ -26.4 [**40M**], -29.3 [**40m**].

$^{15}N\{^1H\}$ NMR (toluene-d_8, 253 K, 400 MHz): δ 230.4 [N_{10} phen' **40M**], 96.0 [N_1 phen' **40M**]. The signal of the $N(SiMe_3)_2$ group could not be detected.

Synthesis of $[Re(CO)_3(phen)(PPhMe_2)]OTf$ (41). $PPhMe_2$ (50 μL, 0.3503 mmol) was added to a solution of $[Re(phen)(CO)_3(OTf)]$ (156 mg, 0.2602 mmol) in toluene (10 mL). After refluxing the resulting solution for 1.5 hours, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **41** as a yellow solid which was dried under vacuum (Yield: 165 mg (86 %)). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **41** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals of **41**. Yield: 161 mg (84 %).

Anal. Calcd. for $C_{24}H_{19}F_3N_2O_6PReS$: C 39.08, H 2.60, N 3.78. Found: C 38.07, H 2.32, N 3.65.

IR (THF, cm^{-1}): 2034, 1946, 1922 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.24 [d (5.2), 2H, H_2 and H_9 phen], 8.73 [d (8.3), 2H, H_4 and H_7 phen], 8.10 [s, 2H, H_5 and H_6 phen], 8.00 [dd (8.3, 5.2), 2H, H_3 and H_8 phen], 7.03 [m, 1H, H_{para} P-Ph], 6.79 [m, 2H, H_{ortho} P-Ph], 6.18 [m, 2H, H_{meta} P-Ph], 1.76 [d (8.8), 6H, $P(CH_3)_2$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.5 [d (6.0), 2 CO], 187.8 [d (59.7), CO], 153.5 [C_2 and C_9 phen], 146.1 [C_{11} and C_{13} phen], 139.3 [C_4 and C_7 phen], 131.1 [C_{12} and C_{14} phen], 130.0 [CH_{para} P-Ph], 128.4 [d (9.4), CH_{ortho} P-Ph], 128.2 [C_5 and C_6 phen], 127.6 [m, C_{ipso} P-Ph (partially obscured by other Ph signals)], 127.2 [d (8.8), CH_{meta} P-Ph], 126.8 [C_3 and C_8 phen], 12.9 [d (33.5), $P(CH_3)_2$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ -16.7.

Reaction of 41 with $KN(SiMe_3)_2$. Synthesis of 43M, 43m. 43M, **43m** was synthesized in a similar way to that employed for **37**, starting from a solution of **41** (161 mg, 0.2183 mmol) in THF (10 mL) and $KN(SiMe_3)_2$ (0.35 mL of a 0.7 M solution in toluene, 0.2450 mmol). Yield: 61 mg (48 %).

Anal. Calcd. for $C_{23}H_{18}N_2O_3PRe$: C 47.01, H 3.09, N 4.77. Found: C 45.80, H 2.87, N 4.66.

IR (THF, cm^{-1}): 2010, 1915, 1889 (ν_{CO}).

The NMR spectra of **43M, 43m** were registered with a sample obtained from the evolution of a **45M**, **45m** (see below) mixture toluene-d_8 solution in an NMR tube at room temperature for 20 hours. Ratio **43M**:**43m** (from ^{1}H NMR spectrum): 7:1.

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.48 [m, 1H, H_9 phen' **43m**], 8.25 [m, 1H, H_9 phen' **43M**], 7.28 [m, 1H, H_7 phen' **43m**], 7.10 [m, 1H, H_7 phen' **43M** (partially obscured by residual toluene)], 6.89 [d (7.9), 1H, H_5 phen' **43m**], 6.80 [d (8.0), 1H, H_5 phen' **43M**], 6.62 [m, 5H, P-Ph **43m**], 6.56 [m, 5H, P-Ph **43M**], 6.42 [m, 1H, H_4 phen' **43M**], 6.42 [m, 1H, H_4 phen' **43m**], 6.36 [m, 2H, H_8 and H_6 phen' **43m**], 6.21 [d (8.0), 1H, H_6 phen' **43M**], 6.16 [dd (8.3, 5.0), 1H, H_8 phen' **43M**], 5.70 [dd (9.6, 5.5), 1H, H_3 phen' **43M**], 5.60 [dd (9.5, 5.4), 1H, H_3 phen' **43m**], 4.70 [m, 1H, H_2 phen' **43M**], 4.70 [m, 1H, H_2 phen' **43m**], 2.31 [m, 1H, CH_2P **43M**], 1.98 [m, 1H, CH_2P **43m**], 1.64 [m, 1H, CH_2P **43m**], 1.56 [d (8.2),

3H, CH_3P **43M**], 1.29 [m, 1H, CH_2P **43M**], 0.29 [m, 3H, CH_3P **43m** (obscured by impurities, could be seen in the HSQC spectrum)].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): (CO signals and C13 phen' signal of **43m** are not seen) δ 200.0 [d (7.6), CO **43M**], 197.4 [d (7.2), CO **43M**], 194.2 [d (69.9), CO **43M**], 155.2 [C_{11} phen' **43M**], 155.0 [C_{11} phen' **43m**], 147.7 [d (2.5), C_9 phen' **43m**], 147.4 [d (3.4), C_9 phen' **43M**], 146.1 [C_{13} phen' **43M**], 136.0 [C_7 phen' **43m**], 135.5 [C_7 phen' **43M**], 132.8 [d (37.5), C_{ipso} P-Ph **43M**], 132.3 [d (11.3), C_{ipso} P-Ph **43m**], 131.0 [C_{14} phen' **43m**], 131.1 [C_{14} phen' **43M**], 129.4 [d (11.0), P-Ph **43M**], 128.8 [P-Ph **43M** and **43m**, and C_4 phen' **43m** (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectrum)], 127.7 [P-Ph **43M** (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectra)], 127.0 [C_5 phen' **43m**], 126.7 [C_5 phen' **43M** (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectra)], 124.3 [C_4 phen' **43M**], 124.1 [C_3 phen' **43M** and C_3 phen' **43m** (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectra)], 120.9 [C_8 phen' **43m**], 120.6 [C_8 phen' **43M**], 119.7 [C_{12} phen' **43M**], 119.6 [C_{12} phen' **43m**], 108.0 [C_6 phen' **43M**], 107.8 [C_6 phen' **43m**], 65.0 [d (9.2), C_2 phen' **43M**], 64.8 [d (8.9), C_2 phen' **43m**], 38.7 [d (45.1), CH_2-P **43m**], 35.2 [d (43.7), CH_2-P **43M**], 14.1 [d (30.0), CH_3-P **43M**], 11.6 [d (22.8), CH_3-P **43m**].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 300 MHz): δ 4.2 [**43m**], -0.36 [**43M**].

Reaction of 41 with $KN(SiMe_3)_2$. Characterization of 45M, 45m. 45M, **45m** was obtained in a similar way to that described for **40M, 40m** starting from solutions of **41** (49 mg, 0.0664 mmol) in toluene-d_8 (0.15 mL) and of $KN(SiMe_3)_2$ (0.10 mL of a solution 0.7 M in toluene (previously removed), 0.070 mmol) in toluene-d_8 (0.20 mL).

Ratio **45M**:**45m** (from ^{31}P NMR spectrum): 25:1.

IR (THF-d_8, cm^{-1}): 2013, 1917, 1887 (ν_{CO}).

Signals for the minor diasteromer **45m** could be seen only in the ^{31}P NMR spectrum.

^1H NMR (toluene-d_8, 233 K, 400 MHz): δ 7.90 [m, 1H, H_9 phen'], 7.60 [d (8.2), 1H, H_5 phen'], 7.04 [m, 1H, H_7 phen' (obscured by residual toluene, could be seen in COSY spectrum)], 6.81 [d (7.5), 1H, H_2 phen'], 6.75 [m, 1H, P-Ph], 6.61 [m, 3H, H_6 phen' and 2 H P-Ph], 6.37 [m, 2H, P-Ph], 6.12 [br, 1H, H_4 phen'], 6.00 [dd (8.3, 4.9), 1H, H_8 phen'], 4.82

[dd (7.5, 3.2), 1H, H_3 phen'], 1.21 [d (8.2), 3H, $P(CH_3)$], 0.95 [d (8.6), 3H, $P(CH_3)$], 0.42 [bs, 9H, $N(SiMe_3)$], 0.22 [bs, 9H, $N(SiMe_3)$].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 233 K, 400 MHz): δ 197.8 [d (7.2), CO], 197.6 [d (7.4), CO], 191.6 [d (73.4), CO], 149.6 [C_{11} phen'], 148.1 [d (3.7), C_9 phen'], 144.3 [C_{13} phen'], 139.6 [C_2 phen'], 135.8 [d (1.7), C_7 phen'], 132.0 [d (35.3), C_{ipso} P-Ph], 131.2 [C_5 phen'], 129.1 [C_{14} phen' (obscured by residual toluene, could be seen in HMBC spectrum)], 128.9 [CH P-Ph], 128.7 [m, 2 CH P-Ph], 127.6 [m, 2 CH P-Ph], 125.3 [C_{12} phen'], 120.9 [C_8 phen'], 112.3 [C_6 phen'], 104.5 [C_3 phen'], 50.7 [C_4 phen'], 13.8 [d (31.5), $P(CH_3)_2$], 10.3 [d (27.9), $P(CH_3)_2$] 6.9, 2.4 [$N(Si(CH_3)_3)_2$].

^{31}P NMR (toluene-d_8, 253 K, 400 MHz): δ -13.7 [**45M**], -15.8 [**45m**].

Synthesis of $[Re(CO)_3(phen)(PPh_2Me)]OTf$ (42). PPh_2Me (40 μL, 0.2128 mmol) was added to a solution of $[Re(phen)(CO)_3(OTf)]$ (109 mg, 0.1818 mmol) in toluene (10 mL). After refluxing the resulting solution for 1.5 hours, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **42** as a yellow solid which was dried under vacuum (Yield: 126 mg (87 %)). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **42** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals of **42**. Yield: 119 mg (82 %).

Anal. Calcd. for $C_{29}H_{21}F_3N_2O_6PReS$: C 43.55, H 2.65, N 3.50. Found: C 43.64, H 2.41, N 3.53.

IR (THF, cm^{-1}): 2036, 1949, 1923 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.23 [m, 2H, H_2 and H_9 phen], 8.75 [m, 2H, H_4 and H_7 phen], 8.13 [s, 2H, H_5 and H_6 phen], 7.99 [dd (8.3, 5.2), 2H, H_3 and H_8 phen], 7.30 [m, 2H, H_{para} P-Ph_2], 7.16 [m, 4H, H_{ortho} P-Ph_2], 6.90 [m, 4H, H_{meta} P-Ph_2], 1.67 [d (7.9), 3H, P-CH_3].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ 194.7 [d (5.6), 2 CO], 187.2 [d (60.6), CO], 153.7 [C_2 and C_9 phen], 146.2 [C_{11} and C_{13} phen], 139.5 [C_4 and C_7 phen], 131.2 [C_{12} and C_{14} phen], 130.9 [CH_{para}, CH_{ortho} and C_{ipso} P-Ph], 128.8 [CH_{meta} P-Ph], 128.3 [C_5 and C_6 phen], 126.9 [C_3 and C_8 phen], 12.9 [d (31.8), P-CH_3].

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ -0.06.

Reaction of 42 with KN(SiMe$_3$)$_2$. Synthesis of 44. Compound **44** was synthesized in a similar way to that employed for **37**, starting from a solution of **42** (119 mg, 0.1488 mmol) in THF (10 mL) and KN(SiMe$_3$)$_2$ (0.25 mL of a 0.7 M solution in toluene, 0.1750 mmol). Yield: 44 mg (46 %).

Anal. Calcd. for $C_{28}H_{20}N_2O_3PRe$: C 51.77, H 3.10, N 4.31. Found: C 52.02, H 2.95, N 4.40.

IR (THF, cm^{-1}): 2013, 1918, 1888 (ν_{CO}).

The NMR spectra of **44** were registered with a sample obtained from the evolution of a **46M**, **46m** (see below) mixture toluene-d$_8$ solution in an NMR tube at room temperature for 24 hours.

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.23 [m, 1H, H$_9$ phen'], 7.69 [m, 2H, P-Ph], 7.06 [m, 3H, P-Ph (obscured by residual toluene, could be seen in COSY spectrum)], 7.00 [m, 1H, H$_7$ phen' (obscured by residual toluene, could be seen in COSY spectrum)], 6.78 [d (8.0), 1H, H$_5$ phen'], 6.60 [m, 2H, P-Ph], 6.52 [m, 1H, P-Ph], 6.43 [m, 3H, H$_4$ phen' and 2H P-Ph], 6.16 [d (8.0), 1H, H$_6$ phen'], 6.12 [dd (8.3, 4.9), 1H, H$_8$ phen'], 5.65 [dd (9.5, 5.4), 1H, H$_3$ phen'], 4.93 [m, 1H, H$_2$ phen'], 2.74 [m, 1H, CH$_2$P], 1.85 [m, 1H, CH$_2$P].

^{13}C{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): δ 200.2 [d (7.3), CO], 197.0 [d (7.8), CO], 194.2 [d (69.8), CO], 155.4 [C$_{11}$ phen'], 147.4 [d (2.5), C$_9$ phen'], 145.7 [C$_{13}$ phen'], 135.3 [C$_7$ phen'], 134.1 [d (11.9), 2 CH P-Ph], 132.9 [d (43.4), C$_{ipso}$ P-Ph], 130.9 [m, C$_{ipso}$ P-Ph and C$_{14}$ phen' (could be seen in HMBC spectrum)], 130.6 [m, 2 CH P-Ph], 128.7, 128.3 [CH P-Ph (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectrum)], 127.3 [C$_4$ phen' (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectrum)], 126.6 [C$_5$ phen' (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectrum)], 124.3 [2 CH P-Ph (obscured by residual toluene, could be seen in HSQC and DEPT-135 spectrum)], 124.2 [d (6.7), C$_3$ phen'], 120.5 [C$_8$ phen'], 119.4 [C$_{12}$ phen'], 108.0 [C$_6$ phen'], 64.7 [d (8.2), C$_2$ phen'], 38.0 [d (45.0), CH$_2$-P].

^{31}P{^{1}H} NMR (toluene-d$_8$, 298 K, 300 MHz): δ 24.1.

Reaction of 42 with KN(SiMe$_3$)$_2$. Characterization of 46M, 46m. Mixture **46M**, **46m** was obtained in a similar way to that described for **40M**, **40m** and **45M**, **45m** starting from solutions of **42** (53 mg, 0.0663 mmol) in toluene-d$_8$ (0.15 mL) and of KN(SiMe$_3$)$_2$

(0.10 mL of a solution 0.7 M in toluene (previously removed), 0.0700 mmol) in toluene-d_8 (0.20 mL).

IR (THF, cm^{-1}): 2016, 1921, 1889 (ν_{CO}).

Ratio **46M**:**46m** (from ^{31}P NMR spectrum): 50:1. Signals for the minor diasteromer **46m** could be seen only in the ^{31}P NMR spectrum.

^1H NMR (toluene-d_8, 233 K, 400 MHz): δ 7.89 [m, 1H, H_9 phen'], 7.57 [d (8.2), 1H, H_5 phen'], 7.50 [m, 2H, P-Ph], 7.04 [m, 1H, H_7 phen' (obscured by tol-d_8, could be seen in COSY spectrum)], 7.00 [m, 2H, P-Ph (obscured by tol-d_8, could be seen in COSY spectrum)], 6.77 [dd (7.5, 1.2), 1 H, H_2 phen'], 6.67 [m, 1H, P-Ph], 6.57 [d (8.2), 1H, H_6 phen'], 6.50 [m, 5H, P-Ph], 6.10 [br, 1H, H_4 phen'], 5.96 [dd (8.3, 5.0), 1 H, H_8 phen'], 4.78 [dd (7.5, 3.1), 1H, H_3 phen'], 1.43 [d (7.9), 3 H, P-CH_3], 0.45 [bs, 9 H, N($SiMe_3$)], 0.25 [bs, 9 H, N($SiMe_3$)].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 233 K, 400 MHz): δ 198.0 [m, CO], 197.9 [m, CO], 190.9 [d (74.5), CO], 149.5 [C_{11} phen'], 148.3 [C_9 phen'], 144.2 [C_{13} phen'], 139.5 [C_2 phen'], 135.7 [C_7 phen'], 133.9 [CH P-Ph], 133.0 [d (44.7), C_{ipso} P-Ph], 131.1 [d (32.9), C_{ipso} P-Ph], 131.0 [C_5 phen'], 130.5 [CH P-Ph], 130.3 [d (9.8), CH P-Ph], 129.1 [C_{14} phen'], 129.0-128.7 [6 CH P-Ph, obscured by residual toluene, could be seen in HSQC spectrum], 127.4 [d (8.5), CH P-Ph], 125.4 [C_{12} phen'], 121.0 [C_8 phen'], 112.5 [C_6 phen'], 104.7 [C_3 phen'], 50.7 [C_4 phen'], 12.2 [d (28.2), PCH_3], 3.9, 2.3 [$N(Si(CH_3)_3)_2$].

^{31}P NMR (toluene-d_8, 253 K, 400 MHz): δ 5.0 [**46M**], 1.9 [**46m**].

Synthesis of $[Re(CO)_3(phen)(PEt_3)]OTf$ (47). PEt_3 (30 μL, 0.2036 mmol) was added to a solution of $[Re(phen)(CO)_3(OTf)]$ (90 mg, 0.1501 mmol) in toluene (10 mL). After refluxing the resulting solution for 1.5 hours, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **47** as a yellow solid which was dried under vacuum (Yield: 97 mg (91 %)). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **47** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals of **47**. Yield: 94 mg (87 %).

Anal. Calcd. for $C_{22}H_{23}F_3N_2O_6PReS$: C 36.82, H 3.23, N 3.90. Found: C 37.28, H 3.14, N 3.97.

IR (THF, cm^{-1}): 2033, 1945, 1919 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.47 [m, 2H, H_2 and H_9 phen], 8.94 [m, 2H, H_4 and H_7 phen], 8.33 [s, 2H, H_5 and H_6 phen], 8.16 [d (8.3, 5.2), 2H, H_3 and H_8 phen], 1.33 [m, 6 H, $P(CH_2CH_3)_3$], 0.80 [m, 9 H, $P(CH_2CH_3)_3$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 194.7 [d (7.0), 2 CO], 187.0 [d (58.4), CO], 154.1 [C_2 and C_9 phen], 146.5 [C_{11} and C_{13} phen], 140.1 [C_4 and C_7 phen], 131.5 [C_{12} and C_{14} phen], 128.6 [C_5 and C_6 phen], 126.9 [C_3 and C_8 phen], 15.6 [d (27.9), $P(CH_2CH_3)_3$], 7.0 [d (3.6), $P(CH_2CH_3)_3$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ -4.22.

Reaction of 47 with $KN(SiMe_3)_2$. Characterization of 49M, 49m. $KN(SiMe_3)_2$ (0.10 mL of a 0.7 M solution in toluene, 0.0700 mmol) was evaporated to dryness in a polytetrafluoroethylene valve Young tube for 2 hours at 60°C. The white solid obtained was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **47** (47 mg, 0.0655 mmol) in THF-d_8 (0.15 mL) previously cooled to -78°C in a Young tube. There was an instantaneous colour change from yellow to purple. The resulting solution was kept at -78°C for 10 minutes, and then it was transferred to a NMR tube cooled to -78°C. The reaction could also be carried out in toluene-d_8 in an analogous way but working at 0°C which favors the dissolution of **47** and the progress of the reaction.

Ratio **49M**:**49m** (from ^{31}P NMR spectrum): 20:1.

IR (THF, cm^{-1}): 2012, 1915, 1885 (ν_{CO}).

^{1}H NMR (THF-d_8, 233 K, 400 MHz): (only signals for **49M** are seen) δ 8.95 [m, 1 H, H_9 phen'], 8.28 [m, 1 H, H_7 phen'], 7.44 [dd (8.3, 4.9), 1 H, H_8 phen'], 7.39 [d (8.2), 1 H, H_5 phen'], 6.98 [d (8.2), 1 H, H_6 phen'], 6.52 [dd (7.6, 1.2), 1H, H_2 phen'], 5.82 [br, 1H, H_4 phen'], 4.50 [dd (7.6, 3.1), 1H, H_3 phen'], 1.58 [m, 3 H, $P(CH_2CH_3)_3$], 1.43 [m, 3 H, $P(CH_2CH_3)_3$], 0.93 [m, 9 H, $P(CH_2CH_3)_3$], 0.26 [br, 9 H, $N(SiMe_3)$], -0.08 [br, 9 H, $N(SiMe_3)$].

^{13}C{^{1}H} NMR (THF-d_8, 233 K, 400 MHz): (only signals for **49M** are seen) δ 197.8 [d (6.2), CO], 197.1 [d (5.9), CO], 190.5 [d (73.2), CO], 150.1 [C_9 phen'], 149.3 [C_{11} phen'], 144.7 [C_{13} phen'], 139.3 [C_2 phen'], 137.5 [C_7 phen'], 131.1 [C_5 phen'], 129.7 [C_{14} phen'],

125.1 [C_{12} phen'], 121.9 [C_8 phen'], 112.4 [C_6 phen'], 103.5 [C_3 phen'], 50.5 [C_4 phen'], 15.0 [m, P(CH_2CH_3)$_3$], 6.7 [P(CH_2CH_3)$_3$], 3.4, 1.3 [N(Si(CH_3)$_3$)$_2$].

^{31}P{^{1}H} NMR (THF-d$_8$, 233 K, 400 MHz): δ -1.9 [**49M**], -4.4 [**49m**].

^{29}Si{^{1}H} NMR (THF-d$_8$, 193 K, 400 MHz): δ 3.8, 2.5 [SiMe$_3$ **49M**].

Reaction of 7 with KN(SiMe$_3$)$_2$. Characterization of 50M, 50m. KN(SiMe$_3$)$_2$ (0.10 mL of a 0.7 M solution in toluene, 0.0700 mmol) was evaporated to dryness in a polytetrafluoroethylene valve Young tube for 2 hours at 60°C. The white solid obtained was dissolved in toluene-d$_8$ (0.15 mL) and transferred onto a suspension of **7** (42 mg, 0.0635 mmol) in toluene-d$_8$ (0.15 mL) previously cooled to 0°C in a Young tube. The mixture was stirred for 10 minutes at room temperature until all the starting material was dissolved. The resulting blue solution was then transferred to a NMR tube cooled to 0°C.

Ratio **50M**:**50m** (from ^{1}H NMR spectrum): 4:1.

IR (THF, cm^{-1}): 2007, 1893, 1881 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 253 K, 400 MHz): δ 8.35 [dd (5.0, 1.4), 1 H, H_9 phen' **50M**], 8.28 [dd (4.9, 1.4), 1 H, H_9 phen' **50m**], 7.63 [d (8.4), 1 H, H_5 phen' **50M**], 7.56 [d (8.5), 1 H, H_5 phen' **50m**], 7.25 [dd (8.3, 1.4), 1 H, H_7 phen' **50M**], 7.24 [dd (8.3, 1.4), 1 H, H_7 phen' **50m**], 6.85 [dd (7.6, 1.2), 1H, H_2 phen' **50M**], 6.77 [dd (7.6, 1.5), 1 H, H_2 phen' **50m**], 6.72 [d (8.4), 1 H, H_6 phen' **50M**], 6.65 [d (8.5), 1 H, H_6 phen' **50m**], 6.30 [m, 1 H, H_8 phen' **50m**], 6.29 [dd (8.3, 5.0), 1 H, H_8 phen' **50M**], 5.96 [d (3.1), 1H, H_4 phen' **50M**], 5.92 [br, 1 H H_4 phen' **50m**], 4.73 [dd (7.6, 3.1), 1H, H_3 phen' **50M**], 4.56 [dd (7.6, 2.7), 1 H, H_3 phen' **50m**], 1.75 [s, 6 H, SMe$_2$ **50m**], 1.46 [s, 6 H, SMe$_2$ **50M**], 0.35 [br, 9 H, N(SiMe$_3$) **50M**], 0.32 [br, 9 H, N(SiMe$_3$) **50m**], 0.19 [br, 9 H, N(SiMe$_3$) **50M**], 0.19 [br, 9 H, N(SiMe$_3$) **50m**].

^{13}C{^{1}H} NMR (toluene-d$_8$, 233 K, 400 MHz): δ 198.7 [CO **50m**], 198.2 [CO **50M**], 198.0 [CO **50M**], 197.9 [CO **50m**], 192.9 [CO **50m**], 192.5 [CO **50M**], 149.5 [C_{11} phen' **50M** and **50m**], 148.9 [C_9 phen' **50M**], 148.5 [C_9 phen' **50m**], 143.9 [C_{13} phen' **50M** and **50m**], 139.5 [C_2 phen' **50M**], 139.4 [C_2 phen' **50m**], 131.5 [C_7 phen' **50M**], 130.8 [C_7 phen' **50m**], 129.4 [C_{14} phen' **50M** and **50m**], 128.9 [C_5 phen' **50M** (obscured by residual

toluene, can be seen in DEPT-135 spectrum)], 127.9 [C_5 phen' **50m*** (obscured by residual toluene, can be seen in DEPT-135 spectrum)], 126.3 [C_{12} phen' **50M** and **50m**], 121.1 [C_8 phen' **50M**], 120.8 [C_8 phen' **50m**], 113.3 [C_6 phen' **50M**], 113.0 [C_6 phen' **50m**], 104.7 [C_3 phen' **50m**], 104.3 [C_3 phen' **50M**], 51.3 [C_4 phen' **50m**], 50.5 [C_4 phen' **50M**], 21.2 [SMe_2 **50m**], 17.4 [SMe_2 **50M**], 4.3 [$N(Si(CH_3)_3)_2$ **50m**], 3.8, 2.2 [$N(Si(CH_3)_3)_2$ **50M**], 1.9 [$N(Si(CH_3)_3)_2$ **50m**].

$^{29}Si\{^1H\}$ NMR (THF-d_8, 233 K, 400 MHz): δ 3.1, 4.4 [$SiMe_3$ **50M**].

Synthesis of [Re(CO)$_3$(phen)(1-Me-2-EtIm)]OTf (48). 1-Me-2-EtIm (25 μL, 0.2179 mmol) was added to a solution of [Re(phen)(CO)$_3$(OTf)] (105 mg, 0.1751 mmol) in toluene (10 mL). After refluxing the resulting solution for 1 hour, it was concentrated under vacuum to 5 mL. Addition of diethyl ether (20 mL) caused the precipitation of **48** as a yellow solid which was dried under vacuum (Yield: 102 mg (82 %)). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **48** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals of **48**. Yield: 96 mg (77 %).

Anal. Calcd. for $C_{22}H_{18}F_3N_4O_6ReS\cdot 2\ CH_2Cl_2$: C 32.77, H 2.52, N 6.37. Found: C 31.35, H 2.16, N 6.68.

IR (THF, cm^{-1}): 2029, 1920 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.54 [ddd (5.1, 1.3), 2H, H_2 and H_9 phen], 8.89 [ddd (8.3, 1.3), 2H, H_4 and H_7 phen], 8.26 [s, 2H, H_5 and H_6 phen], 8.16 [d (8.3, 5.1), 2H, H_3 and H_8 phen], 6.63 [d (1.8), 1 H, CH Im], 5.90 [d (1.8), 1 H, CH Im], 3.51 [s, 3 H, Me-Im], 2.95 [q (7.6), CH_2 Im], 0.98 [t (7.6), CH_3 Im].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.8 [2 CO], 191.0 [CO], 153.8 [C_2 and C_9 phen], 152.9 [C_{11} and C_{13} phen], 146.8 [C_{12} and C_{14} phen], 140.3 [C_4 and C_7 phen], 131.5 [QC Im], 128.5 [C_5 and C_6 phen], 127.1 [C_3 and C_8 phen], 125.9, 122.7 [CH Im], 34.0 [N-CH_3 Im], 21.0 [CH_2(Et) Im], 12.2 [CH_3(Et) Im].

Reaction of 48 with KN(SiMe$_3$)$_2$. Characterization of 51M, 51m. $KN(SiMe_3)_2$ (0.10 mL of a 0.7 M solution in toluene, 0.0700 mmol) was evaporated to dryness in a polytetrafluoroethylene valve Young tube for 2 hours at 60°C. The white solid obtained was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **48** (44 mg,

0.0620 mmol) in THF-d_8 (0.15 mL) previously cooled to -78°C in a Young tube. There was an instantaneous colour change from yellow to purple. The resulting solution was kept at -78°C for 10 minutes, and then it was transferred to a NMR tube cooled to -78°C. The reaction could also be carried out in toluene-d_8 in an analogous way but working at 0°C which favours the dissolution of **48** and the progress of the reaction.

Ratio **51M:51m** (from ^{1}H NMR spectrum): 5:1.

IR (THF, cm^{-1}): 2009, 1901, 1881 (ν_{CO}).

^{1}H NMR (THF-d_8, 253 K, 400 MHz): δ 9.07 [dd (5.0, 1.5), 1 H, H_9 phen' **51M**], 9.02 [dd (5.0, 1.5), 1 H, H_9 phen' **51m**], 8.33 [dd (8.3, 1.3), 1 H, H_7 phen' **51m**], 8.28 [dd (8.3, 1.3), 1 H, H_7 phen' **51M**], 7.47 [m, 1 H, H_8 phen' **51M**], 7.47 [m, 1 H, H_8 phen' **51m**], 7.40 [d (8.4), 1 H, H_5 phen' **51M**], 7.40 [m, 1 H, H_5 phen' **51m**], 6.99 [d (8.4), 1 H, H_6 phen' **51M**], 6.99 [d (8.4), 1 H, H_6 phen' **51m**], 6.88 [d (1.8), 1H, CH (Im) **51m**], 6.85 [d (1.8), 1H, CH (Im) **51M**], 6.78 [m, 1H, H_2 phen' **51M**], 6.78 [m, 1H, H_2 phen' **51m**], 6.74 [d (1.8), 1H, CH (Im) **51m**], 6.62 [d (1.8), 1H, CH (Im) **51M**], 5.94 [br, 1H, H_4 phen' **51m**], 5.79 [br, 1H, H_4 phen' **51M**], 4.48 [dd (7.6, 3.0), 1H, H_3 phen' **51M**], 4.35 [dd (7.6, 2.8), 1H, H_3 phen' **51m**], 3.59 [s, 3 H, N-Me (Im) **51M**], 3.58 [s, 3 H, N-Me (Im) **51m**], 3.26 [m, 1H, CH_2(Et) **51m**], 3.10 [m, 2H, CH_2(Et) **51M**], 2.98 [m, 1H, CH_2(Et) **51m**], 1.27 [m, 1 H, CH_3(Et) (Im) **51m**], 1.20 [m, 2 H, CH_3(Et) (Im) **51m**], 1.12 [m, 3 H, CH_3(Et) (Im) **51M**], 0.27 [br, 9 H, N($SiMe_3$) **51M**], 0.25 [br, 9 H, N($SiMe_3$) **51m**], -0.05 [br, 9 H, N($SiMe_3$) **51M**], -0.18 [br, 9 H, N($SiMe_3$) **51m**].

^{13}C{^{1}H} NMR (THF-d_8, 253 K, 400 MHz): δ 199.5 [2 CO **51M**], 195.8 [CO **51M**], 151.8 [C_{11} phen' **51M** and **51m**], 149.8 [C_9 phen' **51m**], 149.6 [C_9 phen' **51M**], 143.8 [C_{13} phen' **51M** and **51m**], 139.8 [C_2 phen' **51m**], 139.4 [C_2 phen' **51M**], 138.0 [C_7 phen' **51m**], 137.8 [C_7 phen' **51M**], 130.8 [C_5 phen' **51m**], 130.5 [C_5 phen' **51M**], 129.7 [C_{14} phen' **51M** and **51m**], 126.7 [CH Im **51M** and **51m**], 124.7 [C_{12} phen' **51m**], 124.5 [C_{12} phen' **51M**], 121.8 [C_8 phen' **51M** and **51m**], 121.3 [CH Im **51M**], 120.1 [CH Im **51m**], 112.8 [C_6 phen' **51M**], 112.7 [C_6 phen' **51m**], 102.8 [C_3 phen' **51M**], 102.6 [C_3 phen' **51m**], 51.3 [C_4 phen' **51m**], 50.7 [C_4 phen' **51M**], 32.6 [N-CH_3 Im **51m**], 32.5 [N-CH_3 Im **51M**], 20.7 [CH_2(Et) Im **51m**], 20.3 [CH_2(Et) Im **51M**], 13.8 [CH_3(Et) Im **51m**], 12.0 [CH_3(Et) Im **51M**], 3.5 [N($Si(CH_3)_3$)$_2$ **51m**], 3.3 [N($Si(CH_3)_3$)$_2$ **51M**], 1.9 [N($Si(CH_3)_3$)$_2$ **51m**], 1.6 [N($Si(CH_3)_3$)$_2$ **51M**].

^{29}Si{^{1}H} NMR (THF-d_8, 253 K, 400 MHz): δ 3.7, 2.5 [$SiMe_3$ **51M**].

Reaction of 36 with MeLi. Synthesis of 52M-C2. MeLi (0.10 mL of a 1.6 M solution in diethylether, 0.1600 mmol) was added to a suspension of **36** (101 mg, 0.1495 mmol) in toluene (10 mL) at 0°C. Upon reaching room temperature, there was a progressive dissolution of yellow solid **36** to afford a dark green solution. The mixture was stirred at room temperature for 5 days, solvents were evaporated to dryness and the solid residue was dissolved in hexane and filtered through diatomaceous earth. Evaporation to dryness afforded **52M-C2** as a green powder. Yield: 31 mg (38 %). Dark green crystals of **52M-C2** were obtained from a hexane (10 mL) solution of **52M-C2** at -20°C in a 30 % yield (24 mg).

Anal. Calcd. for $C_{19}H_{20}N_2O_3PRe$: C 42.14, H 3.72, N 5.17. Found: C 41.86, H 3.54, N 5.04.

IR (toluene, cm^{-1}): 2014, 1920, 1887 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.16 [m, 1H, H_9 phen'], 7.23 [m, 1H, H_7 phen'], 6.78 [d (7.8), H_5 phen'], 6.29 [m, 1H, H_8 phen'], 6.25 [d (9.8), 1H, H_4 phen'], 6.13 [d (7.8), 1H, H_6 phen'], 5.14 [dd (9.6, 4.7), 1H, H_3 phen'], 4.73 [m, 1H, H_2 phen'], 1.59 [d (6.3), 3H, phen'-CH_3], 0.69 [d (8.4), 9H, PMe_3].

^{13}C{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ 197.7 [d (5.7), CO], 196.8 [d (5.6), CO], 192.2 [d (79.7), CO], 155.4 [C_{11} phen'], 145.5 [d (5.0), C_9 phen'], 145.4 [C_{13} phen'], 136.0 [d (3.7), C_7 phen'], 131.7 [C_{14} phen'], 128.8 [C_5 phen' (obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 125.3 [C_4 phen' (partially obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 122.2 [C_3 phen'], 120.8 [d (3.5), C_8 phen'], 118.3 [C_{12} phen'], 104.1 [C_6 phen'], 60.0 [C_2 phen'], 26.0 [phen'-CH_3], 12.6 [d (28.1), PMe_3].

^{31}P{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ -28.7.

^{15}N{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ 231.0 [N_{10} phen'], 99.0 [N_1 phen'].

Reaction of 36 with MeLi. Characterization of 52M-C2, 52m-C2, 52M-C4 and 52m-C4. The mixture **52M-C2, 52m-C2, 52M-C4** and **52m-C4** was obtained in a similar way to that used for the synthesis of **52M-C2**, but with stirring of only 5 minutes after reaching room temperature. The reaction was carried out starting from 103 mg of **36**

(0.1525 mmol), 0.10 mL of MeLi (1.6 M solution in diethylether, 0.1600 mmol) and 5 mL of toluene. **52M-C2, 52m-C2, 52M-C4** and **52m-C4** were obtained as a green powder. Yield: 77 mg (93 %).

Ratio **52M-C4**:**52m-C4**:**52M-C2:52m-C2** (from ^{31}P NMR spectrum): 7:2:10:1.

The connectivities of the two major components in the mixture could be fully elucidated by ^{1}H, 2D ^{1}H-^{13}C HSQC, 2D ^{1}H-^{13}C HMBC, DEPT-135 and ^{13}C NMR, and correspond to the products of methyl attack to the positions 2 and 4, respectively, of one of the pyridyl rings of the phen ligand. For the minor compounds, **52m-C2** and **52m-C4**, the doublets corresponding to the phen-bonded methyl groups in the ^{1}H NMR spectrum are the only distinct signals of these minor components that can be clearly seen in the NMR spectra. Therefore, the connectivities of **52m-C2** and **52m-C4** can be proposed on the basis of the similar methyl groups couplings on the ^{1}H-^{13}C HMBC to those found on methyl groups of **52M-C2** and **52M-C4** respectively.

A NOE contact between H_2 and the phosphane methyl groups for compound **52M-C2** was found, and, therefore, a structure in which methyl attack took place to the phen side opposite to PMe_3 was assigned. Compound **52M-C4** is similarly proposed to be the one resulting from attack to the phen C4 position by the opposite face of PMe_3. The two minor components, **52m-C2** and **52m-C4**, are proposed to correspond to the products of methyl attack from the phosphane side.

^{1}H NMR monitoring of the **52M-C2**, **52m-C2**, **52M-C4**, **52m-C4** mixture in the presence of C_6Me_6 as internal standard showed all compounds to decrease its signal intensity with time. This decrease was accompanied by the formation of a brown precipitate. However, the rate of decomposition was different for each species (See Figure S71). $t_{1/2}$ were determined for **52m-C2** and **52m-C4** (1 hour and 10 hours 40 minutes respectively), and were estimated to be longer than 3 days for **52M-C2** and **52M-C4**.

IR (toluene, cm^{-1}): 2014, 1920, 1887 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.31 [m, 1H, H_9 phen' **52M-C4**], 8.16 [m, 1H, H_9 phen' **52M-C2**], 7.32 [m, 1H, H_7 phen' **52M-C4**], 7.23 [m, 1H, H_7 phen' **52M-C2**], 6.94 [d (8.8), H_5 phen' **52M-C4**], 6.78 [d (7.8), H_5 phen' **52M-C2**], 6.71 [d (7.2), 1H, H_2 phen' **52M-C4**], 6.52 [d (7.8), 1H, H_6 phen' **52M-C4**], 6.36 [dd (8.1, 4.8), 1H, H_8 phen' **52M-C4**],

6.29 [m, 1H, H_8 phen' **52M-C2**], 6.25 [d (9.8), 1H, H_4 phen' **52M-C2**], 6.13 [d (7.8), 1H, H_6 phen' **52M-C2**], 5.14 [dd (9.6, 4.7), 1H, H_3 phen' **52M-C2**], 4.73 [m, 1H, H_2 phen' **52M-C2**], 4.58 [dd (7.2, 4.1), 1H, H_3 phen' **52M-C4**], 4.03 [m, 1H, H_4 phen' **52M-C4**], 1.59 [d (6.3), 3H, phen'-CH_3 **52M-C2**], 1.33 [d (6.5), 3H, phen'-CH_3 **52M-C4**], 0.69 [d (8.4), 9H, PMe_3 **52M-C2**], 0.67 [d (8.9), 9H, PMe_3 **52M-C4**].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 197.7 [d (5.7), CO **52M-C2**], 197.5 [m, 2 CO, **52M-C4**], 196.8 [d (5.6), CO, **52M-C2**], 192.2 [d (52.3), CO, **52M-C2**], 191.6 [d (54.2), CO, **52M-C4**], 155.4 [C_{11} phen' **52M-C2**], 150.6 [C_{11} phen' **52M-C4**], 147.8 [d (4.7), C_9 phen' **52M-C4**], 145.5 [d (5.0), C_9 phen' **52M-C2**], 145.4 [C_{13} phen' **52M-C2**], 144.4 [C_{13} phen' **52M-C4**], 139.8 [C_2 phen' **52M-C4**], 136.4 [d (3.0), C_7 phen' **52M-C4**] 136.0 [d (3.7), C_7 phen' **52M-C2**], 131.7 [C_{14} phen' **52M-C2**], 130.4 [C_5 phen' **52M-C4**], 129.3 [C_{14} phen' **52M-C4** (obscured by residual toluene, can be seen in HMBC spectrum)], 128.8 [C_5 phen' **52M-C2** (obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 125.7 [C_{12} phen' **52M-C4**], 125.3 [C_4 phen' **52M-C2** (partially obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 122.2 [C_3 phen' **52M-C2**], 120.8 [d (3.5), C_8 phen' **52M-C2**], 120.5 [d (3.0), C_8 phen' **52M-C4**], 118.3 [C_{12} phen' **52M-C2**], 110.8 [C_6 phen' **52M-C4**], 104.1 [C_6 phen' **52M-C2**], 103.5 [C_3 phen' **52M-C4**], 60.0 [C_2 phen' **52M-C2**], 32.2 [C_4 phen' **52M-C4**], 30.2 [phen'-CH_3, **52M-C4**], 26.0 [phen'-CH_3, **52M-C2**], 13.0 [d (27.4), PMe_3 **52M-C4**], 12.6 [d (28.1), PMe_3 **52M-C2**].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ -25.8 [**52M-C4**], -26.5 [**52m-C4**] -28.7 [**52M-C2**], -33.5 [**52m-C2**].

$^{15}N\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 231.2 [N_{10} phen' **52M-C2**], 230.0 [N_{10} phen' **52M-C4**], 99.1 [N_1 phen' **52M-C2**], 95.0 [N_1 phen' **52M-C4**].

Synthesis of [Re(phen)(CO)$_3$Me] (53). MeLi (0.15 mL of a 1.6 M solution in diethylether, 0.2400 mmol) was added to a suspension of [Re(phen)(CO)$_3$(OTf)] (160 mg, 0.2368 mmol) in toluene (10 mL) at 0°C. After the addition of MeLi the yellow solid begins to dissolve and a dark orange solution is formed. The mixture was stirred at room temperature for 10 minutes and then filtered through diatomaceous earth. Removal of the volatiles under vacuum afforded **53** as a dark orange solid. The analogous bipy compound, [Re(bipy)(CO)$_3$Me], has been previously prepared in our group.[107]

IR (toluene, cm^{-1}): 1993, 1890, 1880 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.96 [dd (5.1, 1.4), 2H, H_2 and H_9 phen], 7.20 [dd (8.1, 1.4), 2H, H_4 and H_7 phen], 6.94 [s, 2H, H_5 and H_6 phen], 6.53 [dd (8.1, 5.1), 2H, H_3 and H_8 phen], -0.47 [s, 3H, Me].

^{13}C{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ 204.0 [2 CO], 192.5 [CO], 151.7 [C_2 and C_9 phen], 145.8 [C_{11} and C_{13} phen], 134.5 [C_4 and C_7 phen], 129.9 [C_{12} and C_{14} phen], 126.3 [C_5 and C_6 phen], 124.1 [C_3 and C_8 phen], 0.0 [Me].

Synthesis of [Re(Me$_4$phen)(CO)$_3$(PMe$_3$)]OTf (54). Compound **54** was obtained in a similar way to that for **54** starting from PMe_3 (0.05 mL, 0.5730 mmol) and a suspension of [Re(Me$_4$phen)(CO)$_3$(OTf)] (158 mg, 0.2410 mmol) in toluene (10 mL). Compound [Re(Me$_4$phen)(CO)$_3$(OTf)] was prepared in a similar way to that described for [Re(phen)(CO)$_3$(OTf)] in reference 88. Yield: 167 mg (95 %).

Anal. Calcd. for $C_{23}H_{25}F_3N_2O_6PReS$: C 37.75, H 3.44, N 3.83. Found: C 38.01, H 3.47, N 3.80.

IR (CH_2Cl_2, cm^{-1}): 2036, 1948, 1920 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.07 [s, 2H, H_2 and H_9 phen], 8.39 [s, 2H, H_5 and H_6 phen], 2.93, 2.71 [6H, Me-phen], 1.03 [d (8.5), 9H, P(CH_3)$_3$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.8 [d (3.8), 2 CO], 188.4 [d (60.9), CO], 153.8 [C_2 and C_9 phen], 148.2, 145.2, 135.8, 129.9 [QC phen], 124.3 [C_5 and C_6 phen], 17.7, 15.2 [CH_3-phen], 13.2 [d (30.2), P(CH_3)$_3$].

^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ -28.5.

Reaction of 54 with MeLi. Characterization of 55M, 55m. Mixture **55M**, **55m** was obtained in a way similar to that for **52M-C2**, **52m-C2**, **52M-C4** and **52m-C4** starting from MeLi (0.10 mL of a 1.6 M solution in diethylether, 0.1600 mmol) and a suspension of **54** (101 mg, 0.1495 mmol) in toluene (10 mL).

Ratio **55M**:**55m** (from ^{1}H NMR spectrum): 13:1.

IR (toluene, cm^{-1}): 2011, 1916, 1882 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.33 [d (2.9), 1H, H$_9$ phen' **55M**], 8.19 [d (3.2), 1H, H$_9$ phen' **55m**], 7.23 [d (8.3), H$_5$ phen' **55M**], 7.16 [d (8.3), H$_5$ phen' **55m**], 6.38 [dd (8.3, 1.4), 1H, H$_6$ phen' **55M**], 6.30 [dd (8.3, 1.4), 1H, H$_6$ phen' **55m**], 5.11 [q (6.3), 1H, H$_2$ phen' **55m**], 4.60 [q (6.3), 1H, H$_2$ phen' **55M**], 2.01 [m, 3H, phen'-CH$_3$ **55M**], 1.97 [s, 3H, phen'-CH$_3$ **55M**], 1.79 [s, 3H, phen'-CH$_3$ **55M**], 1.78 [s, 3H, phen'-CH$_3$ **55M**], 1.58 [d (6.3), 3H, phen'-CH$_3$ (from MeLi) **55M**], 1.51 [d (6.3), 3H, phen'-CH$_3$ (from MeLi) **55m**], 0.73 [d (8.2), 9H, PMe$_3$ **55m**], 0.70 [d (8.5), 9H, PMe$_3$ **55M**]. (Signals of the phen-methyl groups could only be assigned for **55M**).

^{13}C{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): (Only signals of **55M** could be seen) δ 198.0 [d (8.0), CO], 197.5 [d (7.8), CO], 192.7 [d (76.0), CO], 154.9 [C$_{11}$ phen'], 146.4 [d (5.1), C$_9$ phen'], 144.0 [C$_{13}$ phen'], 142.0 [d (3.8), C$_7$ phen'], 130.3 [C$_{14}$ phen'], 128.6 [C$_8$ phen' (obscured by residual toluene, could be seen in HMBC spectrum], 124.1 [C$_5$ phen'], 124.0 [C$_4$ phen'], 122.6 [C$_3$ phen'], 119.4 [C$_{12}$ phen'], 100.0 [C$_6$ phen'], 65.6 [C$_2$ phen'], 21.4 [phen'-CH$_3$ (from MeLi)], 17.6, 16.3, 13.7, 13.1 [phen'-CH$_3$], 12.6 [d (27.7), PMe$_3$].

^{31}P{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): δ -28.6 [**21M**], -34.8 [**21m**].

Reaction of 36 with *t*BuLi. Characterization of 56M-C4, 56m-C4 and 56-C2. The mixture **56M-C4**, **56m-C4 and 56-C2** was obtained in a similar way to that employed for the preparation of **52M-C2**, **52m-C2**, **52M-C4** and **52m-C4**, starting from *t*BuLi (0.10 mL of a 1.7 M solution in pentane, 0.1700 mmol) and suspension of **36** (113 mg, 0.1673 mmol) in toluene (10 mL). Slow evaporation of a concentrated diethyl ether solution (10 mL) of **56M-C4, 56m-C4** and **56-C2** at room temperature afforded **56M-C4, 56m-C4** and **56-C2** as a dark blue microcrystalline solid in a 62 % yield (56 mg).

Ratio **56M-C4**:**56m-C4**:**56-C2** (from ^{31}P NMR spectrum): 3:2:1.

IR (toluene, cm^{-1}): 2017, 1922, 1888 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.40 [ddd (4.9, 2.5, 1.5), 1H, H$_9$ phen' **56m-C4**], 8.36 [m, 1H, H$_9$ phen' **56M-C4**], 8.22 [m, 1H, H$_9$ phen' **56-C2**], 7.44 [m, 1H, H$_7$ phen' **56M-C4**], 7.44 [m, 1H, H$_7$ phen' **56m-C4**], 7.28 [m, 1H, H$_7$ phen' **56-C2**], 7.13 [m, 1H, H$_5$ phen' **56M-C4** (obscured by toluene-d$_8$, can be seen in COSY spectrum)], 7.01 [m, 1H, H$_5$ phen' **56m-C4** (obscured by toluene-d$_8$, can be seen in COSY spectrum)], 7.01 [m, 1H, H$_2$ phen' **56m-C4** (obscured by toluene-d$_8$, can be seen in COSY spectrum)], 6.85 [d (7.8),

1H, H_5 phen' **56-C2**], 6.84 [dd (7.2, 0.3), 1H, H_2 phen' **56M-C4**], 6.67 [dd (8.1, 1.0), 1H, H_6 phen' **56M-C4**], 6.62 [dd (8.2, 1.0), 1H, H_6 phen' **56m-C4**], 6.45 [m, 1H, H_8 phen' **56M-C4**], 6.45 [m, 1H, H_8 phen' **56m-C4**], 6.42 [m, 1H, H_4 phen' **56-C2**], 6.36 [ddd (8.3, 4.9, 0.6), 1H, H_8 phen' **56-C2**], 6.18 [dd (7.8, 1.1), 1H, H_6 phen' **56-C2**], 5.05 [ddd (9.4, 5.6, 0.9), 1H, H_3 phen' **56-C2**], 4.74 [dd (7.2, 5.4), 1H, H_3 phen' **56M-C4**], 4.63 [dd (7.4, 5.0), 1H, H_3 phen' **56m-C4**], 4.45 [d (5.5), 1H, H_2 phen' **56-C2**], 3.58 [m, 1H, H_4 phen' **56m-C4**], 3.38 [m, 1H, H_4 phen' **56M-C4**], 1.23 [s, 9H, *t*Bu **56-C2**], 0.94 [s, 9H, *t*Bu **56m-C4**], 0.91 [s, 9H, *t*Bu **56M-C4**], 0.76 [d (8.5), 9H, PMe_3 **56m-C4**], 0.66 [d (8.5), 9H, PMe_3 **56-C2**], 0.53 [d (8.5), 9H, PMe_3 **56M-C4**].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 198.7 [d (8.7), CO **56-C2**], 197.5 [m, 4 CO, 2CO **56M-C4** and 2CO **56m-C4**], 195.9 [d (9.5), CO, **56-C2**], 192.8 [d (73.9), CO, **56-C2**], 191.5 [d (75.7), CO, **56M-C4**], 191.3 [d (75.6), CO, **56m-C4**], 157.0 [C_{11} phen' **56-C2**], 152.2 [C_{11} phen' **56m-C4**], 151.5 [C_{11} phen' **56M-C4**], 147.6 [d (4.1), C_9 phen' **56m-C4**], 147.5 [d (4.0), C_9 phen' **56M-C4**], 145.5 [d (4.5), C_9 phen' **56-C2**], 145.3 [C_{13} phen' **56-C2**], 144.9 [C_{13} phen' **56m-C4**], 144.2 [C_{13} phen' **56M-C4**], 142.2 [C_2 phen' **56m-C4**], 140.8 [C_2 phen' **56M-C4**], 136.5 [d (2.0), C_7 phen' **56m-C4**], 136.5 [d (2.4), C_7 phen' **56M-C4**], 136.1 [d (2.6), C_7 phen' **56-C2**], 133.4 [C_5 phen' **56m-C4**], 133.2 [C_5 phen' **56M-C4**], 131.1 [C_{14} phen' **56-C2**], 129.2 [C_{14} phen' **56M-C4** and **56m-C4**], 127.5 [C_5 phen' **56-C2** (obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 125.5 [C_4 phen' **56-C2** (partially obscured by residual toluene, can be seen in DEPT-135 and HSQC spectrum)], 121.5 [C_{12} phen' **56m-C4**], 120.6 [d (2.3), C_8 phen' **56-C2**], 120.5 [C_{12} phen' **56M-C4** and **56-C2,** obscured by residual toluene, can be seen in HMBC spectrum)], 120.4 [d (1.7), C_8 phen' **56m-C4**], 120.4 [d (1.9), C_8 phen' **56M-C4**], 116.8 [C_3 phen' **56-C2**], 111.2 [C_6 phen' **56m-C4**], 110.8 [C_6 phen' **56M-C4**], 104.5 [C_6 phen' **56-C2**], 98.8 [C_3 phen' **56m-C4**], 98.6 [C_3 phen' **56M-C4**], 71.8 [C_2 phen' **56-C2**], 48.6 [C_4 phen' **56m-C4**], 48.2 [C_4 phen' **56M-C4**], 42.0 [QC *t*Bu, **56-C2**], 38.8 [QC *t*Bu **56M-C4**], 38.3 [QC *t*Bu **56m-C4**], 26.6 [CH_3 *t*Bu **56-C2**], 26.5 [CH_3 *t*Bu **56m-C4**], 25.3 [CH_3 *t*Bu **56M-C4**], 13.2 [m, PMe_3 **56m-C4**], 13.1 [d (27.5), PMe_3 **56-C2**], 12.9 [m, PMe_3 **56M-C4**].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ -27.1 [**56M-C4**], -28.6 [**56-C2**], -29.9 [**56m-C4**].

Reaction of 54 with *t*BuLi. Characterization of 57. Compound **57** was obtained in a way similar to that for **56M-C4, 56m-C4 and 56-C2** starting from *t*BuLi (0.10 mL of a

1.7 M solution in diethylether, 0.1700 mmol) and a suspension of **54** (110 mg, 0.1628 mmol) in toluene (10 mL).

IR (toluene, cm^{-1}): 2014, 1919, 1885 (ν_{CO}).

^{1}H NMR (C_6D_6, 298 K, 400 MHz): δ 8.45 [d (2.7), 1H, H_9 phen'], 7.43 [d (8.2), H_5 phen'], 6.58 [d (8.2), 1H, H_6 phen'], 4.41 [s, 1H, H_2 phen'], 2.13 [s, 3H, phen'-CH_3], 2.11 [s, 3H, phen'-CH_3], 1.97 [s, 3H, phen'-CH_3], 1.81 [s, 3H, phen'-CH_3], 1.33 [s, 9H, *t*Bu], 0.68 [d (8.5), 9H, PMe_3].

^{13}C{^{1}H} NMR (C_6D_6, 298 K, 400 MHz): δ 199.0 [d (3.1), CO], 196.9 [d (5.6), CO], 193.2 [d (80.3), CO], 156.2 [C_{11} phen'], 146.6 [d (4.7), C_9 phen'], 144.0 [C_{13} phen'], 142.2 [d (3.8), C_7 phen'], 137.6 [C_{14} phen'], 129.8 [C_8 phen'], 123.9 [C_5 phen' (obscured by residual benzene, could be seen in HSQC spectrum)], 122.4 [C_4 phen'], 116.6 [C_3 and C_{12} phen'], 100.3 [C_6 phen'], 77.7 [C_2 phen'], 42.6 [QC *t*Bu], 28.3 [CH_3 (*t*Bu)], 22.5, 16.4, 14.0, 13.8 [Me-phen'], 13.3 [d (27.0), PMe_3].

^{31}P{^{1}H} NMR (C_6D_6, 298 K, 400 MHz): δ -28.0.

Reaction of 36 with *n*BuLi. Characterization of 58. Complex **58** was obtained in a similar way to that employed for **56M-C4, 56m-C4** and **56-C2**, starting from *n*BuLi (0.10 mL of a 1.6 M solution in diethylether, 0.1600 mmol) and a suspension of **36** (105 mg, 0.1554 mmol) in toluene (10 mL). Slow evaporation of a concentrated diethylether solution (10 mL) of **58** at room temperature afforded **58** as a dark green microcrystalline solid in a 38 % yield (34 mg).

IR (toluene, cm^{-1}): 2013, 1919, 1888 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298 K, 400 MHz): δ 8.14 [m, 1H, H_9 phen'], 7.19 [m, 1H, H_7 phen'], 6.75 [d (7.7), H_5 phen'], 6.32 [d (9.7), 1H, H_4 phen'], 6.26 [d (8.3, 4.9), 1H, H_8 phen'], 6.09 [dd (7.7, 1.4), 1H, H_6 phen'], 5.14 [ddd (9.7, 4.7, 1.0), 1H, H_3 phen'], 4.83 [m, 1H, H_2 phen'], 2.30 [m, 1H, phen'-CH_2(Bu)], 1.68 [m, 1H, phen'-CH_2(*n*Bu)], 1.63 [m, 2H, CH_2(*n*Bu)], 1.25 [m, 2H, CH_2(*n*Bu)], 0.93 [m, 3H, CH_3(*n*Bu)], 0.71 [d (8.4), 9H, PMe_3].

^{13}C{^{1}H} NMR (toluene-d_8, 298 K, 300 MHz): δ 197.7 [d (5.6), CO], 196.6 [d (7.1), CO], 192.0 [d (75.2), CO], 156.6 [C_{11} phen], 145.3 [d (4.7), C_9 phen], 144.9 [C_{13} phen], 136.0 [d (3.0), C_7 phen], 131.7 [C_{14} phen], 127.5 [C_5 phen (obscured by residual toluene, can be

seen in DEPT-135 and HSQC spectrum)], 125.8 [C_4 phen], 121.0 [C_3 phen], 120.7 [C_8 phen], 118.6 [C_{12} phen], 103.8 [C_6 phen], 64.1 [C_2 phen], 40.5 [phen'-CH_2(*n*Bu)], 25.2 [CH_2(Bu)], 23.0 [CH_2(*n*Bu)], 14.0 [CH_3(*n*Bu)], 12.7 [d (27.9), PMe_3].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 300 MHz): δ -28.5.

Reaction of 56-C2, 56M-C4 and 56m-C4 with HOTf. Characterization of 59M, 59m. HOTf (10 μL, 0.1133 mmol) was added to a solution of **56-C2, 56M-C4** and **56m-C4** (52 mg, 0.0892 mmol) in toluene (10 mL) at room temperature. After stirring the resulting mixture at room temperature for 3 hours, the color of the solution changed from dark blue to orange. Concentration to 5 mL and addition of hexane (20 mL) caused the precipitation of the product as an orange solid, which was washed with diethyl ether (1 × 10 mL) and hexane (2 × 10 mL) and dried under vacuum. The NMR spectra of the product showed the presence of compounds **59M** and **59m** impurified with compound **36**, therefore, elemental analysis was not attempted.

IR (CH_2Cl_2, cm^{-1}): 2038, 1950, 1923 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.22 [m, 1H, H_9 phen' **59m**], 9.17 [m, 1H, H_9 phen' **59M**], 8.84 [m, 1H, H_2 phen' **59m**], 8.80 [m, 1H, H_2 phen' **59M**], 8.70 [m, 1H, H_7 phen' **59m**], 8.68 [m, 1H, H_7 phen' **59M**], 8.10 [d (8.4), 1H, H_6 phen' **59m**], 8.08 [d (8.4), 1H, H_6 phen' **59M**], 7.81 [dd (8.4, 5.1), 1H, H_8 phen' **59m**], 7.79 [dd (8.4, 5.1), 1H, H_8 phen' **59M**], 7.68 [d (8.4), H_5 phen' **59m**], 7.65 [d (8.4), H_5 phen' **59M**], 3.42, 3.26 [m, 2H, H_3 and $H_{3'}$ phen' **59M** and **59m**], 3.05 [d (10.7), 1H, H_4 phen' **59m**], 3.01 [d (9.9), 1H, H_4 phen' **59M**], 1.31 [d (8.5), 9H, PMe_3 **59m**], 1.29 [d (8.5), 9H, PMe_3 **59M**], 1.01 [s, 9H, *t*Bu **59M**], 0.96 [s, 9H, *t*Bu **59m**].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.5 [m, 2 CO, 1 CO **59M** and 1 CO **59m**], 194.0 [m, 2 CO, 1 CO **59M** and 1 CO **59m**], 190.1 [d (62.3), CO, **59M**], 189.3 [d (63.9), CO, **59m**], 177.1 [m, C_2 phen' **59m**], 176.7 [d (3.2), C_2 phen' **59M**], 155.4 [C_9 phen' **59m**], 155.1 [C_9 phen' **59M**], 144.2 [C_{13} phen' **59m**], 143.9 [C_{13} phen' **59M**], 140.1 [C_7 phen' **59M** and **59m**], 139.4 [C_{11} phen' **59m**], 139.3 [C_{11} phen' **59M**], 133.9 [C_{14} phen' **59M**], 133.5 [C_{14} phen' **59m**], 132.4 [C_5 phen' **59m**], 132.2 [C_5 phen' **59M**], 129.2 [C_{12} phen' **59m**], 129.1 [C_{12} phen' **59M**], 128.6 [C_6 phen' **59M** and **59m**], 124.3 [C_8 phen' **59m**], 124.0 [C_8 phen' **59M**], 41.6 [C_4 phen' **59M**], 41.1 [C_4 phen' **59m**], 36.5 [QC *t*Bu **59m**],

36.2 [QC *t*Bu **59M**], 30.4 [C_3 phen' **59m**], 30.2 [C_3 phen' **59M**], 27.1 [CH_3 *t*Bu **59m**], 26.6 [CH_3 *t*Bu **59M**], 14.8 [m, PMe_3 **59M** and **59m**].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ -27.1 [**59M**], -29.1 [**59m**].

Reaction of 56-C2, 56M-C4 and 56m-C4 with MeOTf. Characterization of 60M, 60m. MeOTf (23 μL, 0.2102 mmol) was added to a solution of **56-C2, 56M-C4** and **56m-C4** (60 mg, 0.1030 mmol) in toluene (10 mL) at room temperature. After stirring the resulting mixture at room temperature for 6 hours, the color of the solution changed from dark blue to orange. Concentration to 5 mL and addition of hexane (20 mL) caused the precipitation of the product as an orange solid, which was washed with diethyl ether (1 × 10 mL) and hexane (2 × 10 mL) and dried under vacuum. The NMR spectra of the product showed the presence of compounds **60M** and **60m** impurified with compound **36**, therefore, elemental analysis was not attempted.

IR (CH_2Cl_2, cm^{-1}): 2039, 1951, 1923 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.20 [m, 1H, H_9 phen' **60m**], 9.18 [m, 1H, H_9 phen' **60M**], 8.79 [m, 1H, H_2 phen' **60m**], 8.73 [m, 3H, H_2 phen' **60M** and H_7 phen' **60M** and **60m**], 8.12 [m, 2H, H_6 phen' **60M** and **60m**], 7.82 [m, 1H, H_8 phen' **60M** and **60m**], 7.68 [d (8.4), H_5 phen' **60m**], 7.65 [d (8.4), H_5 phen' **60M**], 3.40 [m, 2H, H_3 phen' **60M** and **60m**], 2.76 [s, 1H, H_4 phen' **60m**], 2.74 [s, 1H, H_4 phen' **60M**], 1.31 [m, 24H, PMe_3 and CH_3-C_3(phen') **60M** and **60m**], 0.99 [s, 9H, *t*Bu **60m**], 0.94 [s, 9H, *t*Bu **60M**].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 194.3 [m, 4 CO, 2 CO **60M** and 2 CO **60m**], 189.7 [d (62.5), CO, **60M**], 189.5 [d (63.6), CO, **60m**], 179.9 [C_2 phen' **60m**], 178.7 [C_2 phen' **60M**], 155.4 [C_9 phen' **60m**], 155.3 [C_9 phen' **60M**], 144.1 [C_{13} phen' **60m**], 143.8 [C_{13} phen' **60M**], 140.1 [C_7 phen' **60M** and **60m**], 138.3 [C_{11} phen' **60m**], 138.1 [C_{11} phen' **60M**], 133.2 [C_{14} phen' **60m**], 133.0 [C_5 phen' **60m**], 132.4 [C_5 phen' **60M**], 132.3 [C_{14} phen' **60M**], 129.3 [C_{12} phen' **60m**], 129.2 [C_6 phen' **60M** and **60m**], 129.1 [C_{12} phen' **60M**], 124.4 [C_8 phen' **60m**], 124.2 [C_8 phen' **60M**], 50.0 [C_4 phen' **60M**], 49.7 [C_4 phen' **60m**], 36.7 [QC *t*Bu **60m**], 36.4 [QC *t*Bu **60M**], 34.1 [C_3 phen' **60m**], 33.9 [C_3 phen' **60M**], 27.3 [CH_3 *t*Bu **60m**], 26.7 [CH_3 *t*Bu **60M**], 15.2 [d (40.7), PMe_3 **60m**], 14.6 [d (31.8), PMe_3 **60M**], 13.3 [CH_3-phen **60M**], 13.0 [CH_3-phen **60m**].

$^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ -28.9 [**60m**], -29.5 [**60M**].

Reaction of 36 with Li[HBEt$_3$]. Synthesis of 61. Li[HBEt$_3$] (0.40 mL of a 1.0 M solution in THF, 0.4000 mmol) was added to a THF (15 mL) solution of **36** (130 mg, 0.1924 mmol) at 0°C. The solution immediately turned green. Upon stirring the mixture at room temperature for 24 hours, the solution turned blue. Volatiles were removed under vacuum and the resulting blue oil was dissolved in toluene (10 mL) and filtered. Concentration of the solution to 5 mL and addition of hexane (10 mL) caused the precipitation of **61** as a blue solid, which was washed with hexane (2 × 10 mL) and dried under vacuum. Yield: 62 % (63 mg). Slow diffusion of hexane (10 mL) into a concentrated solution of **61** in toluene (5 mL) at -20°C yielded blue crystals of **61** one of which was used for X-ray analysis.

Anal. Calcd. for $C_{18}H_{20}N_2O_3PRe$: C 40.83, H 3.81, N 5.29. **Found:** C 41.02, H 3.78, N 5.23.

IR (toluene, cm^{-1}): 2014, 1920, 1887 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.23 [m, 1H, H$_9$ phen'], 7.37 [m, 1H, H$_7$ phen'], 6.91 [d (7.6), 1H, H$_5$ phen'], 6.38 [dd (8.3, 4.8), 1H, H$_8$ phen'], 6.27 [d (7.6), 1H, H$_6$ phen'], 3.81 [m, 1H, H$_2$ phen'], 3.67 [m, 1H, H$_{2'}$ phen'], 2.68 [m, 2H, H$_4$ and H$_{4'}$ phen'], 1.76 [m, 2H, H$_3$ and H$_{3'}$ phen'], 0.63 [d (8.4), 9H, PMe$_3$].

^{13}C{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): δ 198.0 [d (7.2), CO], 197.8 [d (6.7), CO], 192.1 [d (76.1), CO], 156.4 [C$_{11}$ phen'], 145.1 [d (5.6), C$_9$ phen'], 144.3 [C$_{13}$ phen'], 136.0 [d (3.3), C$_7$ phen'], 130.7 [C$_{14}$ phen'], 130.2 [C$_5$ phen'], 120.4 [d (3.6), C$_8$ phen'], 118.3 [C$_{12}$ phen'], 103.3 [d (1.0), C$_6$ phen'], 54.7 [C$_2$ phen' (CH$_2$)], 27.5 [C$_4$ phen' (CH$_2$)], 22.7 [C$_3$ phen' (CH$_2$)], 13.1 [d (27.4), PMe$_3$].

^{31}P{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): δ -27.9.

^{15}N{^{1}H} NMR (toluene-d$_8$, 298 K, 400 MHz): δ 230.6 [N$_{10}$ phen'], 80.1 [N$_1$ phen'].

Reaction of 36 with Li[HBEt$_3$]. Characterization of 62-C2, 62-C4. Li[HBEt$_3$] (0.20 mL of a 1.0 M solution in THF, 0.2000 mmol) was evaporated to dryness in a Young Schlenk for 2 hours at 60°C. The resulting yellow oil was dissolved in THF-d$_8$ (0.15 mL) and transferred onto a suspension of **36** (130 mg, 0.1924 mmol) in THF-d$_8$ (0.15 mL) previously cooled to 0°C in a Young Schlenk. There was an instantaneous color change

from yellow to dark green. The resulting solution was kept at 0°C for 5 minutes stirring, and for 5 minutes without stirring and then it was transferred to a NMR tube cooled to -78°C. It was not possible to completely remove the THF from the Li[HBEt$_3$] solution, therefore, the NMR spectra of **62-C2, 62-C4** showed intense signals of THF.

Ratio **62-C4:62-C2** (from ^{1}H NMR spectrum): 2:1.

IR (toluene, cm^{-1}): 2012, 1917, 1884 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 273 K, 400 MHz): δ 8.29 [ddd (4.9, 2.6, 1.4), 1H, H$_9$ phen' **62-C4**], 8.03 [ddd (4.5, 3.0, 1.4), 1H, H$_9$ phen' **62-C2**], 7.37 [dt (8.4, 1.7), 1H, H$_7$ phen' **62-C4**], 7.20 [dt (8.3, 1.8), 1H, H$_7$ phen' **62-C2**], 6.78 [d (8.0), H$_5$ phen' **62-C4**], 6.61 [d (7.7), H$_5$ phen' **62-C2**], 6.54 [m, 2H, H$_2$ and H$_6$ phen' **62-C4**], 6.44 [dd (8.4, 4.9), 1H, H$_8$ phen' **62-C4**], 6.29 [dd (8.3, 4.5), 1H, H$_8$ phen' **62-C2**], 6.07 [m, 1H, H$_4$ and H$_6$ phen' **62-C2**], 5.30 [dt (17.5, 2.2), 1H, H$_2$ phen' **62-C2**], 5.03 [ddd (17.3, 4.2, 1.3), 1H, H$_{2'}$ phen' **62-C2**], 4.96 [m, 1H, H$_3$ phen' **62-C2**], 4.45 [dt (7.6, 3.1), 1H, H$_3$ phen' **62-C4**], 4.09 [m, 2H, H$_4$ and H$_{4'}$ phen' **62-C4**], 0.75 [d (8.6), 9H, PMe$_3$ **62-C2**], 0.69 [d (8.6), 9H, PMe$_3$ **62-C4**].

^{13}C{^{1}H} NMR (toluene-d$_8$, 273 K, 400 MHz): δ 197.7 [m, CO **62-C2** and **62-C4**], 197.4 [m, CO, **62-C2** and **62-C4**], 192.3 [d (75.5), CO, **62-C2**], 192.0 [d (73.6), CO, **62-C4**], 157.5 [C$_{11}$ phen' **62-C4**], 152.0 [C$_{11}$ phen' **62-C2**], 148.2 [d (4.1), C$_9$ phen' **62-C4**], 145.6 [d (4.1), C$_9$ phen' **62-C2**], 144.2 [C$_{13}$ phen' **62-C2**], 144.0 [C$_{13}$ phen' **62-C4**], 141.5 [C$_2$ phen' **62-C4**], 136.8 [C$_7$ phen' **62-C2**] 136.3 [C$_7$ phen' **62-C4**], 131.9 [C$_{14}$ phen' **62-C2**], 130.8 [C$_5$ phen' **62-C4**], 129.5 [C$_{14}$ phen' **62-C4**], 127.5 [C$_5$ phen' **62-C2** (obscured by residual toluene, can be seen in HSQC spectrum)], 125.7 [C$_{12}$ phen' **62-C4**], 126.2 [C$_4$ phen' **62-C2**], 121.2 [C$_8$ phen' **62-C2**], 120.8 [C$_8$ phen' **62-C4**], 119.8 [C$_3$ phen' **62-C2**], 118.1 [C$_{12}$ phen' **62-C2**], 112.0 [C$_6$ phen' **62-C4**], 104.0 [C$_6$ phen' **62-C2**], 96.6 [C$_3$ phen' **62-C4**], 58.5 [C$_2$ phen' **62-C2**], 28.2 [C$_4$ phen' **62-C4**], 12.9 [d (23.0), PMe$_3$ **62-C4**], 12.6 [d (23.7), PMe$_3$ **62-C2**].

^{31}P{^{1}H} NMR (toluene-d$_8$, 273 K, 400 MHz): δ -26.3 [**62-C4**], -28.4 [**62-C2**].

Preparation and Characterization of Compounds in Chapter 4

Synthesis of [Re(bipy)(CO)$_3$(2-CH$_3$Ox)]OTf (63). 2-CH$_3$Ox (25 μL, 0.2952 mmol) was added to a suspension of [Re(bipy)(CO)$_3$(OTf)] (82 mg, 0.1425 mmol) in toluene (10 mL). After refluxing the resulting mixture for 1.5 hours, a yellow solid precipitated. Toluene was discarded and the yellow residue was washed with diethyl ether (3 × 10 mL). Drying under vacuum afforded **63** as a yellow solid in a 94 % yield (88 mg). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **63** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals. Yield: 87 mg (92 %).

Anal. Calcd. for $C_{18}H_{15}F_3N_3O_7ReS$: C 32.70, H 2.27, N 6.36. Found: C 32.64, H 2.30, N 6.31.

IR (THF, cm^{-1}): 2029, 1918 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.11 [m, 2H, H$_6$ and H$_9$ bipy], 8.72 [m, 2H, H$_3$ and H$_{12}$ bipy], 8.38 [m, 2H, H$_4$ and H$_{11}$ bipy], 7.77 [m, 2H, H$_5$ and H$_{10}$ bipy], 4.24 [m, 2H, CH$_2$-O (Ox)], 3.03 [m, 2H, CH$_2$-N (Ox)], 2.19 [s, 3H, CH$_3$].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 195.6 [2 CO], 190.6 [1 CO], 175.3 [QC Ox], 156.1 [C$_2$ and C$_7$ bipy], 153.2 [C$_6$ and C$_9$ bipy], 141.4 [C$_4$ and C$_{11}$ bipy], 128.3 [C$_5$ and C$_{10}$ bipy], 125.6 [C$_3$ and C$_{12}$ bipy], 68.5 [CH$_2$-O (Ox)], 54.6 [CH$_2$-N (Ox)], 15.6 [CH$_3$].

Synthesis of [Re(bipy)(CO)$_3$(2-CH$_3$Ox)]BAr$^F_4$ (63^F). NaBAr$^F_4$ (115 mg, 0.1275 mmol) was added to a solution of **63^F** (80 mg, 0.1211 mmol) in CH_2Cl_2 (10 mL). After stirring for 2 hours, the solution was filtered and concentrated under vacuum to 5 mL. Adition of hexane (10 mL) caused the precipitation of a yellow solid which was washed with hexane (3 × 10 mL). Drying under vacuum afforded **63^F** as a yellow solid in a 88 % yield (147 mg). Slow diffusion of hexane (10 mL) into a concentrated solution of **63^F** in CH_2Cl_2 (4 mL) at room temperature afforded yellow crystals. Yield: 143 mg (86 %).

Anal. Calcd. for $C_{49}H_{27}BF_{24}N_3O_4Re$: C 42.81, H 1.98, N 3.06. Found: C 41.67, H 2.00, N 3.12.

IR (THF, cm^{-1}): 2031, 1925 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.12 [m, 2H, H_6 and H_9 bipy], 8.41 [m, 2H, H_3 and H_{12} bipy], 8.28 [m, 2H, H_4 and H_{11} bipy], 7.76 [m, 2H, H_5 and H_{10} bipy, obscured by ^{1}H signals of BAr^F_4, could be seen in the HSQC spectrum], 4.19 [m, 2H, CH_2-O (Ox)], 2.99 [m, 2H, CH_2-N (Ox)], 2.18 [s, 3H, CH_3].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 195.2 [2 CO], 190.0 [CO], 175.7 [QC Ox], 155.9 [C_2 and C_7 bipy], 153.6 [C_6 and C_9 bipy], 141.2 [C_4 and C_{11} bipy], 128.6 [C_5 and C_{10} bipy], 124.5 [C_3 and C_{12} bipy], 68.3 [CH_2-O (Ox)], 54.5 [CH_2-N (Ox)], 15.5 [CH_3].

Reaction of 63 with $KN(SiMe_3)_2$. Characterization of 66. $KN(SiMe_3)_2$ (0.25 mL of a 0.5 M solution in toluene, 0.1250 mmol) was added to a solution of **63** (83 mg, 0.1234 mmol) in THF (10 mL) previously cooled to -78°C. The reaction mixture was evaporated to dryness from -78°C to room temperature. The resulting purple residue was extracted in toluene and filtered. Evaporation to dryness afforded **66** as a purple solid. Due to the partial decomposition of the compound while the evaporation of the toluene (an insoluble black residue on the Schlenk walls could be seen), it was no possible to obtain NMR spectra of the product. An alternative working way was used to obtain the NMR spectra of the crude product: $KN(SiMe_3)_2$ (0.10 mL of a 0.5 M solution in toluene, 0.050 mmol) was evaporated to dryness in a Young Schlenk for 2 hours at 60°C. The white solid obtained was dissolved in THF-d_8 (0.15 mL) and transferred onto a suspension of **63^F** (34 mg, 0.0496 mmol) in THF-d_8 (0.15 mL) previously cooled to -78°C in a Young Schlenk. There was an instantaneous color change from yellow to purple. The resulting solution was kept at -78°C for 5 minutes stirring, and for 5 minutes without stirring and then it was transferred to a NMR tube cooled to -78°C. Compound **63^F** was used as starting material instead of **63** in order to increase its solubility in THF at low temperature which favors the reaction even at -78°C. As a consequence, signals of $BAr^F_4$$^-$ are present in the spectra.

IR (THF, cm^{-1}): 2006, 1898, 1881 (ν_{CO}).

^{1}H NMR (THF-d_8, 233K, 400 MHz): δ 8.90 [d (5.3), 1H, H_9 bipy'], 7.97 [d (8.0), 1H, H_{12} bipy'], 7.90 [m, 1H, H_{11} bipy', (signal obscured by BAr_4^F, could be seen in the HSQC spectrum)], 7.29 [m, 1H, H_{10} bipy'], 6.13 [m, 1H, H_4 bipy'], 5.97 [d (5.8), 1H, H_3 bipy'],

4.99 [m, 1H, H_5 bipy'], 4.74 [m, 1H, H_6 bipy'], 4.43 [m, 1H, CH_2-O (Ox)], 4.18 [m, 2H, 1H CH_2-O and 1H CH_2-N (Ox)], 3.94 [m, 1H, CH_2-N (Ox)], 3.03 [dd (17.7, 10.1), 1H, bipy'-CH_2(Ox)], 1.94 [d (17.7), 1H, bipy'-CH_2(Ox)].

$^{13}C\{^1H\}$ NMR (THF-d_8, 233 K, 400 MHz): δ 200.3, 198.5, 197.2 [CO], 173.6 [QC (Ox)], 162.7 [C_7 bipy'], 151.8 [C_9 bipy'], 151.5 [C_2 bipy'], 137.2 [C_{11} bipy'], 124.4 [C_4 bipy'], 123.1 [C_{10} bipy'], 121.3 [C_{12} bipy'], 108.6 [C_5 bipy'], 97.1 [C_3 bipy'], 67.9 [CH_2-O (Ox)], 58.9 [CH_2-N (Ox)], 57.5 [C_6 bipy'], 27.5 [bipy'-CH_2 (Ox)].

Synthesis of [Re(phen)(CO)$_3$(2-CH$_3$Ox)]OTf (64). 2-CH_3Ox (40 μL, 0.4724 mmol) was added to a solution of [Re(phen)(CO)$_3$(OTf)] (149 mg, 0.2483 mmol) in toluene (10 mL). After refluxing the resulting solution for 1.5 hours, **64** precipitated as a yellow solid. Removal of toluene and washing with diethyl ether (2 × 10 mL) afforded **64** as a yellow microcrystalline solid, which was dried under vaccum (146 mg, yield: 86 %). Slow diffusion of diethyl ether (15 mL) into a solution of **64** in CH_2Cl_2 (10 mL) at room temperature afforded yellow crystals of **64**. Yield: 144 mg (85 %).

Anal. Calcd. for $C_{20}H_{15}F_3N_3O_7ReS$: C 35.09, H 2.21, N 6.14. Found: C 35.17, H 2.25, N 6.18.

IR (THF, cm^{-1}): 2030, 1920 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.53 [dd (5.1, 1.5), 2H, H_2 and H_9 phen], 8.90 [dd (8.3, 1.5), 2H, H_4 and H_7 phen], 8.28 [s, 2H, H_5 and H_6 phen], 8.15 [dd (8.3, 5.1), 2H, H_3 and H_8 phen], 4.11 [m, 2H, CH_2-O (Ox)], 2.85 [m, 2H, CH_2-N (Ox)], 2.25 [s, 3H, CH_3 (Ox)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.3 [2 CO], 190.5 [CO], 175.3 [QC (Ox)], 154.2 [C_2 and C_9 phen], 146.7 [C_{11} and C_{13} phen], 140.5 [C_4 and C_7 phen], 131.4 [C_{12} and C_{14} phen], 128.5 [C_5 and C_6 phen], 127.0 [C_3 and C_8 phen], 68.5 [CH_2-O (Ox)], 54.5 [CH_2-N (Ox)], 15.7 [CH_3].

Reaction of 64 with KN(SiMe$_3$)$_2$. Synthesis of 67. KN($SiMe_3$)$_2$ (0.30 mL of a 0.7 M solution in toluene, 0.2102 mmol) was added to a suspension of **64** (144 mg, 0.2102 mmol) in THF (10 mL) previously cooled to -78°C. The yellow solid was dissolved and the color of the solution changed from yellow to purple. The reaction mixture was

evaporated to dryness from -78°C to room temperature. The resulting residue was extracted in CH_2Cl_2 (10 mL), filtered, washed with hexane (2 × 10 mL) and dried under vacuum. Compound **67** was obtained as a black microcrystalline powder in a 76 % yield (85 mg). Slow evaporation of a solution of **67** in diethyl ether (8 mL) at room temperature afforded red crystals suitable for X-ray diffraction. Yield: 73 mg (68 %).

Anal. Calcd. for $C_{19}H_{14}N_3O_4Re$: C 42.69, H 2.64, N 7.86. Found: C 42.81, H 2.56, N 7.45.

IR (THF, cm^{-1}): 2007, 1899, 1885 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298K, 300 MHz): δ 8.87 [d (4.8), 1H, H_9 phen'], 8.11 [d (7.9), 1H, H_7 phen'], 7.29 [dd (7.9, 4.8), 1H, H_8 phen'], 7.14 [d (8.0), 1H, H_5 phen'], 6.70 [d (8.0), 1H, H_6 phen'], 6.63 [d (9.2), 1H, H_4 phen'], 5.71 [dd (9.2, 5.8), 1H, H_3 phen'], 4.96 [m, 1H, H_2 phen'], 4.35 [m, 1H, CH_2 (Ox)], 4.08 [m, 2H, CH_2 (Ox)], 3.79 [m, 1H, CH_2 (Ox)], 2.73 [dd (17.9, 10.1), 1H, phen'-CH_2(Ox)], 2.35 [dd (17.9, 4.5), 1H, phen'-CH_2(Ox)].

Compound **67** decompossed upon standing in CD_2Cl_2 for several hours at room temperature. All the spectra were recorded in THF-d_8 at room temperature.

^{1}H NMR (THF-d_8, 298K, 400 MHz): δ 8.89 [d (4.8), 1H, H_9 phen'], 8.15 [d (8.2), 1H, H_7 phen'], 7.33 [dd (8.2, 4.8), 1H, H_8 phen'], 7.08 [d (8.0), 1H, H_5 phen'], 6.63 [d (8.0), 1H, H_6 phen'], 6.56 [d (9.2), 1H, H_4 phen'], 5.65 [dd (9.2, 5.8), 1H, H_3 phen'], 4.94 [m, 1H, H_2 phen'], 4.37 [m, 1H, CH_2 (Ox)], 4.10 [m, 2H, CH_2 (Ox)], 3.78 [m, 1H, CH_2 (Ox)], 2.73 [dd (17.9, 10.1), 1H, phen'-CH_2(Ox)], 2.35 [dd (17.9, 4.5), 1H, phen'-CH_2(Ox)].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 201.0, 197.7, 196.4 [CO], 172.3 [QC Ox], 154.6 [C_{11} phen'], 148.0 [C_9 phen'], 146.1 [C_{13} phen'], 137.1 [C_7 phen'], 131.2 [C_{14} phen'], 127.4 [C_5 phen'], 124.7 [C_4 phen'], 121.3 [C_8 phen'], 121.1 [C_3 phen'], 120.3 [C_{12} phen'], 107.2 [C_6 phen'], 67.8 [CH_2-O (Ox)], 58.2 [CH_2-N (Ox)], 56.5 [C_2 phen'], 32.8 [phen'-CH_2(Ox)].

Synthesis of [Re{2-(CH=N*p*-tol)py}(CO)$_3$(2-CH_3Ox)]OTf (65). AgOTf (60 mg, 0.2335 mmol) was added to a solution of [Re{2-(CH=N*p*-tol)py)}(CO)$_3$Br] (100 mg, 0.1829 mmol) in CH_2Cl_2 (10 mL). After stirring the solution protected from light for 3 hours, a white precipitated of AgBr formed and the only carbonyl species in solution was [Re{2-(CH=N*p*-tol)py)}(CO)$_3$(OTf)] (IR: 2039, 1941, 1918 ν_{CO} in CH_2Cl_2). The solution was

filtered and the solvent was removed under vacuum. 2-Methyloxazoline (13 μL, 0.1476 mmol) was added to a solution of [Re{2-(CH=N*p*-tol)py)}$(CO)_3$(OTf)] (88 mg, 0.1427 mmol) in toluene (10 mL). After refluxing the resulting solution for 2 hours, it was concentrated under vacuum to 5 mL. Addition of hexane (20 mL) caused the precipitation of **65** as an orange microcrystalline solid, which was washed with hexane (3 × 10 mL) and dried under vacuum. Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **65** in CH_2Cl_2 (6 mL) at room temperature afforded orange crystals of **65**. Yield: 55 mg (55 %).

IR (toluene, cm^{-1}): 2030, 1923 (ν_{CO}). **IR (THF, cm^{-1}):** 2030, 1923 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.26 [s, 1H, CN(H)], 9.12 [m, 1H, py], 8.50 [m, 1H, py], 8.32 [m, 1H, py], 7.79 [m, 1H, py], 7.73 [d (8.4), 2H, H(*p*-tol)], 7.42 [d (8.4), 2H, H(*p*-tol)], 4.33 [m, 2H, CH_2 (Ox)], 3.49 [m, 1H, CH_2 (Ox)], 3.14 [m, 1H, CH_2 Ox], 2.49 [s, 3H, CH_3 *p*-tol], 1.89 [s, 3H, CH_3 (Ox)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 196.3, 194.7, 189.1 [CO], 175.5 [QC oxazoline], 170.1 [CN(H)], 156.2 [QC py], 152.9 [CH py], 147.5 [QC *p*-tol] 141.2, [CH py], 141.1 [QC *p*-tol], 131.7 [CH py], 130.6 [2 CH *p*-tol], 129.6 [CH py], 122.7 [2 CH *p*-tol], 68.8, 55.9 [CH_2 (Ox)], 20.9 [CH_3 *p*-tol], 15.4 [CH_3 (Ox)].

Reaction of 65 with $KN(SiMe_3)_2$. Synthesis of 68. $KN(SiMe_3)_2$ (0.15 mL of a 0.7 M solution in toluene, 0.1050 mmol) was added to a solution of **65** (74 mg, 0.1054 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from orange to dark green. The reaction mixture was evaporated to dryness from -78°C to room temperature. The resulting green residue was extracted in toluene and filtered. Evaporation to dryness afforded **68** as a green solid, which was washed with hexane (2 × 10 mL) and diethyl ether (1 × 10 mL) and dried under vacuum. Slow diffusion of hexane (15 mL) into a concentrated solution of **68** in CH_2Cl_2 (5 mL) at -20°C afforded yellow crystals suitable for X-ray diffraction.

IR (THF, cm^{-1}): 2005, 1899, 1875 (ν_{CO}). **IR (CH_2Cl_2, cm^{-1}):** 2007, 1898, 1878 (ν_{CO}). **IR (toluene, cm^{-1}):** 2007, 1905, 1875 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 8.87, 7.89, 7.61, 7.28 [m, 1H, py], 6.93 [d (8.5), 2H, *p*-tol], 6.81 [d (8.5), 2H, *p*-tol], 5.58 [dd (4.9, 1.9), 1H, CN(H)], 4.28, 4.26, 4.02, 3.92 [m,

4H, CH_2 (Ox)], 3.46 [dd (18.3, 4.9), 1H, CH_2(Ox)-CN], 2.59 [dd (18.3, 1.9), 1H, CH_2(Ox)-CN], 2.20 [s, 3H, CH_3(*p*-tol)].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 400 MHz): δ 200.3 [CO], 199.4 [2 CO], 169.5 [QC (Ox)], 167.8 [QC *p*-tol], 155.2 [QC py], 152.5, 139.2 [CH py], 129.6 [2 CH *p*-tol], 123.4, 121.2 [CH py], 120.6 [QC *p*-tol], 114.3 [2 CH *p*-tol], 68.9 [CH_2 (Ox)], 64.4 [C(H)=N], 59.8 [CH_2 (Ox)], 30.5 [CH_2-CN], 19.7 [CH_3 *p*-tol].

Synthesis of [Re(bipy)(CO)$_3$(2-CH$_3$py)]BAr$^F_4$ (69). 2-CH_3py (15 μL, 0.1519 mmol) was added to a solution of [Re(bipy)(CO)$_3$(OTf)] (72 mg, 0.1251 mmol) and NaBAr$^F_4$ (122 mg, 0.1377 mmol) in CH_2Cl_2 (20 mL). After stirring the resulting solution at room temperature for 3 hours a white precipitate of NaBAr$^F_4$ appeared. The solution was filtered and concentrated under vacuum to 5 mL. Addition of hexane (20 mL) caused the precipitation of **69** as a yellow solid which was washed with hexane (3 × 10 mL). Drying under vacuum afforded **69** in a 89 % yield (154 mg). Slow diffusion of hexane (8 mL) into a concentrated solution of **69** in CH_2Cl_2 (4 mL) at -20°C afforded yellow crystals. Yield: 152 mg (88 %).

Anal. Calcd. for $C_{51}H_{27}BF_{24}N_3O_3Re$: C 44.26, H 1.95, N 3.04. Found: C 44.19, H 1.90, N 2.95.

IR (THF, cm^{-1}): 2034, 1926 (ν_{CO}).

^1H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.25 [d (5.5), 2H, H_6 and H_9 bipy], 8.19 [m, 4H, H_3 and H_{12} and H_4 and H_{11} bipy], 8.01 [d (5.9), 1H, H_2 py], 7.73 [m, 2H, H_5 and H_{10} bipy (signal obscured by aromatic H of BAr$^F_4$)], 7.62 [m, 1H, H_4 py (signal obscured by aromatic H of BAr$^F_4$)], 7.25 [d (7.6), 1H, H_5 py], 6.98 [m, 1H, H_3 py], 2.59 [s, 3H, CH_3 py].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, 300 MHz): δ 195.2 [2 CO], 189.2 [CO], 162.6 [C_6 py], 155.7 [C_2 and C_7 bipy], 153.9 [C_6 and C_9 bipy], 150.9 [C_2 py], 141.1 [C_4 and C_{11} bipy], 139.4 [C_4 py], 128.4 [C_5 and C_{10} bipy], 128.0 [C_5 py], 124.1 [C_3 and C_{12} bipy], 123.3 [C_3 py], 27.1 [CH_3].

Reaction of 69 with KN(SiMe$_3$)$_2$. Preparation of 71. KN($SiMe_3$)$_2$ (0.30 mL of a 0.5 M solution in toluene, 0.1500 mmol) was added to a solution of **69** (185 mg, 0.1334 mmol)

in THF (20 mL) previously cooled to -78°C. After the addition the solution changed its color from yellow to purple. The reaction mixture was evaporated to dryness upon reaching room temperature. The majority of the product decomposed during the THF evaporation, so the working conditions described for the acquisition of the crude NMR spectra of **66** were used. Consequently, signals for $BAr^F{}_4^-$ are present in the spectra.

IR (THF, cm^{-1}): 2006, 1897, 1883 (ν_{CO}).

^{1}H NMR (THF-d_8, 193 K, 400 MHz): δ 9.03 [d (4.6), 1H, H_9 bipy'], 8.48 [m, 1H, H_2 py], 7.80 [m, 1H, H_{12} bipy' (signal obscured by the Ar^F, could be seen in the COSY spectrum)], 7.78 [m, 1H, H_4 py (signal obscured by the Ar^F, could be seen in the COSY spectrum)], 7.66 [m, 1H, H_{11} bipy'], 7.57 [m, 1H, H_5 py], 7.40 [m, 1H, H_{10} bipy'], 7.12 [m, 1H, H_3 py], 5.85 [m, 1H, H_4 bipy'], 5.20 [m, 1H, H_6 bipy'], 5.10 [m, 1H, H_3 bipy'], 5.00 [m, 1H, H_5 bipy'], 3.30 [dd (17.7, 10.1), 1H, CH_2], 2.79 [m, 1H, CH_2].

^{13}C{^{1}H} NMR (THF-d_8, 193 K, 400 MHz): δ 205.0, 203.0, 197.6 [CO], 161.6 [C_7 bipy'], 159.3 [C_6 py], 152.8 [C_2 bipy'], 152.2 [C_2 py], 152.0 [C_9 bipy'], 138.5 [C_4 py], 137.4 [C_{11} bipy'], 127.7 [C_5 py], 127.0 [C_4 bipy'], 126.2 [C_3 py], 122.6 [C_{10} bipy'], 121.8 [C_{12} bipy'], 119.3 [C_5 bipy'], 95.3 [C_3 bipy'], 59.9 [C_6 bipy'], 51.0 [CH_2].

Synthesis of [Re(phen)(CO)$_3$(2-CH$_3$py)]BAr$^F{}_4$ (70). 2-CH_3py (14 μL, 0.1418 mmol) was added to a solution of [Re(phen)(CO)$_3$(OTf)] (79 mg, 0.1312 mmol) and $NaBAr^F{}_4$ (125 mg, 0.1386 mmol) in CH_2Cl_2 (10 mL). After 3 hours stirring at room temperature, a white precipitate of NaOTf appeared. The solution was filtered and concentrated to 5 mL. Addition of hexane (20 mL) caused the precipitation of a yellow solid which was washed with hexane (3 × 20 mL). Compound **70** was obtained as a yellow solid in a 78 % yield (145 mg). Yellow crystals of **70** could be obtained from slow diffusion of hexane (10 mL) into a concentrated solution of **70** in diethyl ether (5 mL) at room temperature. Yield: 145 mg (78 %).

Anal. Calcd. for $C_{53}H_{27}BF_{24}N_3O_3Re$: C 45.25, H 1.93, N 2.99. Found: C 45.02, H 1.87, N 2.86.

IR (THF, cm^{-1}): 2037, 1931 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.59 [dd (5.1, 1.2), 2H, H_2 and H_9 phen], 8.72 [dd (8.2, 1.2), 2H, H_4 and H_7 phen], 8.10 [m, 4H, H_3 and H_8 and H_5 and H_6 phen], 8.02 [m, 1H, H_2 py], 7.53 [m, 1H, H_4 py], 7.21 [d (7.7), 1H, H_5 py], 6.89 [m, 1H, H_3 py], 2.70 [s, 3H, CH_3].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 196.2 [2 CO], 189.1 [CO], 162.6 [C_6 py, obscured by CF_3 ($BAr^F{}_4$) signal], 154.1 [C_2 and C_9 phen], 150.7 [C_2 py], 146.7 [C_{11} and C_{13} phen], 140.3 [C_4 and C_7 phen], 139.2 [C_4 py], 131.4 [C_{12} and C_{14} phen], 128.3 [C_5 and C_6 phen], 127.8 [C_5 py], 126.7 [C_3 and C_8 phen], 123.2 [C_3 py], 27.2 [CH_3].

^{15}N NMR (CD_2Cl_2, 298 K, 400 MHz): 241.2 [N_1 and N_{10} phen], 235.4 [2-Mepy].

Reaction of 70 with $KN(SiMe_3)_2$. Synthesis of 72. $KN(SiMe_3)_2$ (0.15 mL of a 0.7 M solution in toluene, 0.1050 mmol) was added to a solution of **70** (145 mg, 0.1030 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from yellow to dark green. The reaction mixture was evaporated upon reaching room temperature. The resulting residue was extracted in toluene and filtered. Evaporation to dryness and drying under vacuum afforded **72** as a green solid in a 52 % yield (30 mg). Slow evaporation of a solution of **72** in diethyl ether (8 mL) at room temperature afforded green crystals suitable for X-ray diffraction. Yield: 24 mg (43 %).

Anal. Calcd. for $C_{21}H_{14}N_3O_3Re$: C 46.40, H 2.78, N 7.73. Found: C 46.29, H 2.67, N 7.54.

IR (THF, cm^{-1}): 2008, 1902, 1885 (ν_{CO}).

^{1}H NMR (THF-d_8, 298K, 400 MHz): δ 8.89 [dd (4.9, 1.3), 1H, H_9 phen'], 8.27 [dd (5.6, 1.0), 1H, H_2 py], 7.90 [dd (8.4, 1.3), 1H, H_7 phen'], 7.57 [ddd (7.7, 7.6, 1.0), 1H, H_4 py], 7.44 [m, 1H, H_5 py], 7.23 [dd (8.4, 4.9), 1H, H_8 phen'], 6.92 [m, 1H, H_3 py] 6.57 [d (7.9), 1H, H_5 phen'], 6.22 [d (7.9), 1H, H_6 phen'], 6.20 [dd (9.7, 1.0), 1H, H_4 phen'], 5.63 [m, 1H, H_2 phen'], 4.94 [dd (9.7, 4.7), 1H, H_3 phen'], 3.60 [dd (15.5, 10.1), 1H, CH_2], 2.92 [dd (15.5, 0.8), 1H, CH_2].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 200.0, 198.9, 196.4 [CO], 159.8 [C_6 py], 155.4 [C_{11} phen'], 153.5 [C_2 py], 146.6 [C_9 phen'], 142.9 [C_{13} phen'], 137.7 [C_4 py], 137.3 [C_7 phen'], 131.6 [C_{14} phen'], 128.0 [C_5 py], 126.8 [C_5 phen'], 124.7 [C_4 phen'], 123.3 [C_3 phen'], 122.2 [C_3 py], 121.4 [C_8 phen'], 117.8 [C_{12} phen'], 106.0 [C_6 phen'], 59.1 [C_2 phen'], 50.7 [CH_2].

^{15}N NMR (CD_2Cl_2, 298 K, 400 MHz): 252.0 [2-Mepy], 245.3 [N_{10} phen'], 106.1 [N_1 phen'].

Synthesis of [Re(bipy)(CO)$_3$(1,2-Me$_2$Im)]OTf (73). 1,2-Me_2Im (15 μL, 0.1691 mmol) was added to a suspension of [Re(bipy)(CO)$_3$(OTf)] (84 mg, 0.1460 mmol) in toluene (10 mL). After refluxing the resulting mixture for 1.5 hours, a yellow solid precipitated. Toluene was discarded and the yellow residue was washed with diethyl ether (3 × 10 mL). Drying under vacuum afforded **73** as a yellow solid in a 87 % yield (85 mg). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **73** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals. Yield: 83 g (85%).

Anal. Calcd. for $C_{19}H_{16}F_3N_4O_6ReS$: C 33.98, H 2.40, N 8.34. Found: C 34.05, H 2.51, N 8.45.

IR (THF, cm^{-1}): 2031, 1924 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): δ 9.13 [m, 2H, H_6 and H_9 bipy], 8.66 [m, 2H, H_3 and H_{12} bipy], 8.33 [m, 2H, H_4 and H_{11} bipy] 7.75 [m, 2H, H_5 and H_{10} bipy], 6.70 [d (1.7), 1H, CH-NRe (Im)], 6.00 [d (1.7), 1H, CH-NMe (Im)], 3.53 [s, 3H, CH_3-N(Im)], 2.40 [s, 3H, CH_3-C(Im)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 300 MHz): δ 196.1 [2 CO], 191.2 [CO], 156.0 [C_2 and C_7 bipy], 153.2 [C_6 and C_9 bipy], 148.6 [QC Im], 141.3 [C_4 and C_{11} bipy], 129.1 [C_5 and C_{10} bipy], 125.8 [CH-NMe (Im)], 125.2 [C_3 and C_{12} bipy], 122.3 [CH-NRe (Im)], 34.3 [CH_3-N(Im)], 13.6 [*C*H_3-C(Im)].

Reaction of 73 with KN(SiMe$_3$)$_2$. Synthesis of 77. KN($SiMe_3$)$_2$ (0.25 mL of a 0.5 M solution in toluene, 0.1250 mmol) was added to a solution of **73** (83 mg, 0.1234 mmol) in THF (20 mL) previously cooled to -78°C. The solution color changed from yellow to purple. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in toluene until the toluene was colorless (3 × 10 mL) and filtered. Evaporation to dryness afforded **77** as a purple solid in a 78 % yield (50 mg). Slow diffusion of pentane (6 mL) into a concentrated solution of **77** in toluene (2 mL) at -20°C yielded purple crystals of **77** one of which was employed for X-ray diffraction. Yield: 38 mg (59 %).

Anal. Calcd. for $C_{18}H_{15}N_4O_3Re$: C 41.45, H 2.90, N 10.74. Found: C 41.83, H 2.78, N 10.68.

IR (THF, cm^{-1}): 2003, 1894, 1876 (ν_{CO}).

^{1}H NMR (THF-d_8, 298 K, 400 MHz): δ 8.88 [d (5.6), 1H, H_9 bipy'], 7.81 [d (8.2), 1H, H_{12} bipy'], 7.73 [m, 1H, H_{11} bipy'] 7.16 [ddd (7.1, 5.6, 1.3), 1H, H_{10} bipy'], 7.12 [d (1.6), 1H, CH-NRe (Im)], 6.91 [d (1.6), 1H, CH-NMe (Im)], 6.13 [dd (8.4, 5.8), 1H, H_4 bipy'], 5.88 [d (5.8), 1H, H_3 bipy'], 4.96 [m, 2H, H_6 and H_5 bipy'], 3.50 [s, 3H, CH_3], 3.32 [dd (16.6, 9.9), 1H, CH_2], 2.27 [dd (16.6, 3.7), 1H, CH_2].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 201.3, 199.4, 196.7 [CO], 162.9 [C_7 bipy'], 151.5 [C_2 bipy'], 151.3 [C_9 bipy'], 149.5 [QC Im], 136.5 [C_{11} bipy'], 129.4 [CH-NRe (Im)], 124.3 [C_4 bipy'], 122.5 [C_{10} bipy'], 120.8 [C_{12} bipy'], 120.7 [CH-NMe (Im)], 107.7 [C_5 bipy'], 96.8 [C_3 bipy'], 57.1 [C_6 bipy'], 31.4 [CH_3], 26.1 [CH_2].

Synthesis of [Re(phen)(CO)$_3$(1,2-Me$_2$Im)]OTf (74). 1,2-Me_2Im (15 μL, 0.1691 mmol) was added to a suspension of [Re(phen)(CO)$_3$(OTf)] (77 mg, 0.1290 mmol) in toluene (10 mL). After refluxing the resulting mixture for 1.5 hours, a yellow solid precipitated. Toluene was discarded and the yellow residue was washed with diethyl ether (3 × 10 mL). Compound **74** was obtained as a yellow solid in a 86 % yield (78 mg). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **74** in CH_2Cl_2 (5 mL) at room temperature afforded yellow crystals. Yield: 76 mg (85 %).

Anal. Calcd. for $C_{21}H_{16}F_3N_4O_6ReS$: C 36.26, H 2.32, N 8.05. Found: C 36.58, H 2.48, N 7.93.

IR (THF, cm^{-1}): 2031, 1925 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.52 [dd (5.1, 1.3), 2H, H_2 and H_9 phen], 8.87 [dd (8.3, 1.3), 2H, H_4 and H_7 phen], 8.26 [s, 2H, H_5 and H_6 phen], 8.12 [dd (8.3, 5.1), 2H, H_3 and H_8 phen], 6.58 [d (1.8), 1H, CH-NRe (Im)], 5.79 [d (1.8), 1H, CH-NMe (Im)], 3.47 [s, 3H, CH_3-N(Im)], 2.49 [s, 3H, CH_3-C(Im)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.9 [2 CO], 191.1 [CO], 153.8 [C_2 and C_9 phen], 148.7 [QC Im], 146.7 [C_{11} and C_{13} phen], 140.2 [C_4 and C_7 phen], 131.4 [C_{12} and C_{14}

phen], 128.4 [C_5 and C_6 phen], 126.7 [C_3 and C_8 phen], 125.6 [CH-NMe (Im)], 122.1 [CH-NRe (Im)], 34.2 [CH_3-N(Im)], 13.7 [CH_3-C(Im)].

Reaction of 74 with $KN(SiMe_3)_2$. Synthesis of 78. $KN(SiMe_3)_2$ (0.20 mL of a 0.7 M solution in toluene, 0.1400 mmol) was added to a solution of **74** (86 mg, 0.1238 mmol) in THF (10 mL) previously cooled to -78°C. The solution color changed from yellow to purple. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in CH_2Cl_2 (10 mL) and filtered. Evaporation to dryness and washing with hexane (2 × 10 mL) afforded **78** as a black microcrystalline powder in a 71 % yield (48 mg). Slow evaporation of a diethyl ether solution (10 mL) of **78** at room temperature afforded purple crystals. Yield: 47 mg (69 %).

Anal. Calcd. for $C_{20}H_{15}N_4O_3Re$: C 44.03, H 2.77, N 10.27. Found: C 44.27, H 2.74, N 10.14.

IR (THF, cm^{-1}): 2005, 1896, 1881 (ν_{CO}).

^{1}H NMR (THF-d_8, 298 K, 400 MHz): δ 8.87 [dd (4.9, 1.4), 1H, H_9 phen'], 8.05 [dd (8.3, 1.4), 1H, H_7 phen'], 7.26 [dd (8.3, 4.9), 1H, H_8 phen'], 7.04 [d (1.7), 1H, CH-NRe (Im)], 7.01 [d (8.0), 1H, H_5 phen'], 6.86 [d (1.7), 1H, CH-NMe (Im)], 6.53 [m, 2H, H_4 (6.54) and H_6 (6.52) phen'], 5.66 [dd (9.3, 5.6), 1H, H_3 phen'], 5.12 [m, 1H, H_2 phen'], 3.45 [s, 3H, CH_3], 3.00 [dd (16.7, 9.7), 1H, CH_2], 2.75 [dd (16.7, 4.9), 1H, CH_2].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 201.0, 198.9, 196.5 [CO], 155.0 [C_{11} phen'], 148.0 [QC Im], 147.4 [C_9 phen'], 146.1 [C_{13} phen'], 136.8 [C_7 phen'], 131.2 [C_{14} phen'], 129.3 [CH-NRe (Im)], 127.2 [C_6 phen'], 124.7 [C_4 phen'], 121.2 [C_8 phen'], 120.8 [C_3 phen'], 120.7 [CH-NMe (Im)], 120.2 [C_{12} phen'], 106.5 [C_5 phen'], 56.4 [C_2 phen'], 31.7 [CH_3], 31.5 [CH_2].

Synthesis of [Mo(bipy)$(CO)_2(\eta^3$-$C_4H_7)$(1,2-Me_2Im)]OTf (75). 1,2-Me_2Im (25 μL, 0.2820 mmol) was added to a suspension of [Mo(bipy)$(CO)_2(\eta^3$-$C_4H_7)$(OTf)] (134 mg, 0.2596 mmol) in CH_2Cl_2 (20 mL). After stirring at room temperature for 3 hours the solution was concentrated to 5 mL and diethyl ether (15 mL) was added. The red precipitate was washed with diethyl ether (3 × 10 mL). Compound **75** was obtained as a

red solid in a 92 % yield (145 mg). Slow diffusion of diethyl ether (10 mL) into a concentrated solution of **75** in CH_2Cl_2 (5 mL) at -20°C afforded red crystals of **75**.

IR (THF, cm^{-1}): 1952, 1869 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.02 [m, 2H, H_6 and H_9 bipy], 8.48 [m, 2H, H_3 and H_{12} bipy], 8.22 [m, 2H, H_4 and H_{11} bipy] 7.71 [m, 2H, H_5 and H_{10} bipy], 6.68 [d(1.9), 1H, CH-NMe (Im)], 5.89 [d(1.9), 1H, CH-NMo (Im)], 3.47 [s, 3H, CH_3-N(Im)], 3.21 [s, 2H, CH_2 η^3-C_4H_7], 2.38 [s, 3H, CH_3-C(Im)], 1.67 [s, 2H, CH_2 η^3-C_4H_7], 1.07 [br, 3H, CH_3 η^3-C_4H_7].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 224.7 [2 CO], 154.0 [C_2 and C_7 bipy], 152.0 [C_6 and C_9 bipy], 147.7 [QC Im], 140.6 [C_4 and C_{11} bipy], 126.9 [C_5 and C_{10} bipy], 125.0 [CH-NMo (Im)], 124.3 [C_3 and C_{12} bipy], 121.8 [CH-NMe (Im)], 83.6 [QC η^3-C_4H_7], 57.0 [CH_2 η^3-C_4H_7], 34.1 [CH_3-N(Im)], 18.3 [CH_3 η^3-C_4H_7], 13.8 [CH_3-C(Im)].

Reaction of 75 with $KN(SiMe_3)_2$. Synthesis of 79. $KN(SiMe_3)_2$ (0.35 mL of a 0.7 M solution in toluene, 0.245 mmol) was added to a solution of **75** (145 mg, 0.2378 mmol) in THF (10 mL) previously cooled to -78°C. The solution color changed from red to fuchsia. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting residue was extracted in toluene (10 mL) and filtered. Evaporation to dryness and washing with hexane (2 × 10 mL) afforded **79** as a fuchsia microcrystalline powder in a 62 % yield (68 mg). Slow diffusion of hexane (10 mL) into a concentrated solution of **79** in toluene (5 mL) at -20°C yielded fuchsia crystals of **79** one of which was used for X-ray diffraction analysis.

IR (THF, cm^{-1}): 1921, 1835 (ν_{CO}).

^{1}H NMR (THF-d_8, 273 K, 400 MHz): δ 8.65 [d (5.4), 1H, H_9 bipy'], 7.66 [m, 2H, H_{12} and H_{11} bipy'], 7.35 [d (1.7), 1H, CH-NMo (Im)], 7.14 [m, 1H, H_{10} bipy'], 7.01 [d (1.7), 1H, CH-NMe (Im)], 6.04 [dd (8.2, 5.4), 1H, H_4 bipy'], 5.78 [d (5.4), 1H, H_3 bipy'], 4.77 [m, 2H, H_6 and H_5 bipy'], 3.48 [s, 3H, CH_3-N(Im)], 3.15 [dd (16.5, 7.5), 1H, CH_2-N(Im)], 2.79 [d (3.7), 1H, CH_2 η^3-C_4H_7], 2.68 [d (2.5), 1H, CH_2 η^3-C_4H_7], 2.21 [dd (16.5, 3.6), 1H, CH_2-N(Im)], 1.26 [br, 1H, CH_2 η^3-C_4H_7], 1.20 [s, 3H, CH_3 η^3-C_4H_7], 1.01 [br, 1H, CH_2 η^3-C_4H_7].

^{13}C{^{1}H} NMR (THF-d_8, 263 K, 400 MHz): δ 229.4, 226.8 [CO], 160.6 [C_7 bipy'], 150.1 [C_9 and C_2 bipy' (HMBC spectrum)], 148.2 [QC Im], 136.4 [C_{11} bipy'], 128.5 [CH-NMo (Im)],

124.0 [C_4 bipy'], 121.6 [C_{10} bipy'], 120.4 [CH-NMe (Im)], 119.9 [C_{12} bipy'], 104.0 [C_5 bipy'], 95.5 [C_3 bipy'], 80.3 [QC η^3-C_4H_7], 56.6 [C_6 bipy'], 54.6, 53.5 [CH_2 η^3-C_4H_7], 31.7 [CH_3 (Im)], 26.0 [CH_2 (Im)], 18.1 [CH_3 η^3-C_4H_7].

Synthesis of [Mo(phen)(CO)$_2$(η^3-C$_4$H$_7$)(1,2-Me$_2$Im)]OTf (76). 1,2-Me_2Im (25 μL, 0.2820 mmol) was added to a suspension of [Mo(phen)(CO)$_2$(η^3-C_4H_7)(OTf)] (122 mg, 0.2258 mmol) in CH_2Cl_2 (20 mL). After stirring at room temperature for 3 hours the solution was concentrated to 5 mL and diethylether (15 mL) was added. The red precipitate was washed with diethyl ether (3 × 10 mL). Compound **76** was obtained as a red solid in a 89 % yield (128 mg). Slow diffusion of hexane (10 mL) into a concentrated solution of **76** in CH_2Cl_2 (5 mL) at -20°C afforded red crystals of **76**.

IR (CH_2Cl_2, cm^{-1}): 1953, 1870 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.43 [d (5.0), 2H, H_2 and H_9 phen], 8.75 [d (8.2, 1.3), 2H, H_4 and H_7 phen], 8.11 [s, 2H, H_5 and H_6 phen (overlap with H_3 and H_8 phen)], 8.09 [m, 2H, H_3 and H_8 phen (overlap with H_5 and H_6 phen)], 6.55 [s, 1H, CH-NMe (Im)], 5.85 [s, 1H, CH-NMo (Im)], 3.37 [s, 3H, CH_3-N(Im)], 3.36 [s, 2H, CH_2 η^3-C_4H_7], 2.36 [s, 3H, CH_3-C(Im)], 1.75 [s, 2H, CH_2 η^3-C_4H_7], 0.75 [br, 3H, CH_3 η^3-C_4H_7].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 224.3 [2 CO], 152.5 [C_2 and C_9 phen], 147.6 [QC Im], 144.6 [C_{11} and C_{13} phen], 139.7 [C_4 and C_7 phen], 130.6 [C_{12} and C_{14} phen], 128.1 [C_5 and C_6 phen], 125.7 [C_3 and C_8 phen], 125.1 [CH-NMo (Im)], 121.7 [CH-NMe (Im)], 83.1 [QC η^3-C_4H_7], 56.7 [CH_2 η^3-C_4H_7], 33.9 [CH_3-N(Im)], 18.2 [CH_3 η^3-C_4H_7], 13.8 [CH_3-C(Im)].

Reaction of 76 with KN(SiMe$_3$)$_2$. Synthesis of 80. KN($SiMe_3$)$_2$ (0.30 mL of a 0.7 M solution in toluene, 0.2100 mmol) was added to a solution of **76** (128 mg, 0.2012 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from red to green. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting purple residue was extracted in toluene (10 mL) and filtered. Evaporation to dryness and washing with hexane (2 × 10 mL) afforded **80** as a green microcrystalline powder in a 68 % yield (66 mg).

IR (THF, cm^{-1}): 1923, 1837 (ν_{CO}).

^{1}H NMR (toluene-d$_8$, 298 K, 400 MHz): δ 8.34 [dd (4.8, 1.5), 1H, H_9 phen'], 7.28 [dd (8.5, 1.3), 1H, H_7 phen'], 6.87 [d (8.0), 1H, H_5 phen'], 6.54 [dd (8.3, 4.8), 1H, H_8 phen'], 6.45 [d (9.1), 1H, H_4 phen'], 6.32 [d (1.3), 1H, CH-NMo (Im)], 6.23 [d (8.0), 1H, H_6 phen'], 5.67 [d (1.3), 1H, CH-NMe (Im)], 5.44 [dd (9.1, 5.6), 1H, H_3 phen'], 5.13 [ddd (7.6, 6.4, 5.6), 1H, H_2 phen'], 3.20 [d (3.7), 1H, CH_2 η^3-C_4H_7], 3.05 [dd (3.7, 1.5), 1H, CH_2 η^3-C_4H_7], 2.62 [s, 3H, CH_3-N(Im)], 2.45 [dd (16.3, 7.6), 1H, CH_2-N(Im)], 2.25 [dd (16.3, 6.4), 1H, CH_2-N(Im)], 1.78 [m, 1H, CH_2 η^3-C_4H_7], 1.38 [m, 1H, CH_2 η^3-C_4H_7], 1.26 [br, 3H, CH_3 η^3-C_4H_7].

^{13}C{^{1}H} NMR (THF-d$_8$, 298 K, 400 MHz): δ 229.2, 227.1 [CO], 153.4 [C_{11} phen'], 146.2 [QC Im], 144.9 [C_{13} phen'], 144.5 [C_9 phen'], 135.6 [C_7 phen'], 130.8 [C_{14} phen'], 127.2 [C_5 phen'], 124.8 [C_4 phen' (obscured by residual toluene signal, can be seen in HSQC, HMBC and DEPT-135 spectra], 120.3 [C_8 phen'], 119.8 [CH-NMe (Im)], 119.3 [C_3 phen', CH-NMo (Im) and C_{12} phen'], 105.8 [C_6 phen'], 81.4 [QC η^3-C_4H_7], 56.2 [C_2 phen'], 55.7 [CH_2 η^3-C_4H_7], 51.8 [CH_2 η^3-C_4H_7], 33.1 [CH_2 (Im)], 31.1 [CH_3 (Im)], 18.6 [CH_3 η^3-C_4H_7].

Reaction of 78 with CF_3COOH. Synthesis of 81. Addition of CF_3COOH (6 μL, 0.0784 mmol) to a solution of **78** (35 mg, 0.0643 mmol) in toluene (10 mL) at room temperature caused the instantaneous precipitation of **81** as an orange solid. Compound **81** was isolated in a 78 % yield (35 mg) after washing with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL) and drying under vacuum.

IR (CH_2Cl_2, cm^{-1}): 2032, 1928, 1911 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.30 [m, 1H, H_9 phen'], 8.52 [m, 1H, H_7 phen'], 8.04 [d (8.3), 1H, H_5 phen'], 7.58 [d (8.3), 1H, H_6 phen'], 7.62 [dd (8.4, 4.9), 1H, H_8 phen'], 7.18 [1H, d (1.7), CH-NRe (Im)], 7.10 [br, 1H, N-H], 7.07 [d (9.8), 1H, H_4 phen'], 6.84 [d (1.7), 1H, CH-NMe (Im)], 6.77 [dd (9.6, 5.1), 1H, H_3 phen'], 4.65 [m, 1H, H_2 phen'], 3.42 [s, 3H, N-Me(Im)], 3.13 [dd (17.9, 4.2), 1H, CH_2], 2.34 [m, 1H, CH_2].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.4, 194.5, 193.4 [CO], 154.5 [C_9 phen'], 153.8 [C_{11} phen'], 146.1 [C_{13} phen'], 144.0 [QC Im], 139.3 [C_7 phen'], 139.2 [C_{14} phen'], 135.2 [C_3 phen'], 132.3 [C_{12} phen'], 130.2 [CH-NRe (Im)], 129.0 [C_5 phen'], 126.4 [C_6

phen'], 125.4 [C_4 phen'], 122.8 [C_8 phen'], 122.4 [CH-NMe (Im)], 51.6 [C_2 phen'], 33.3 [CH_3], 24.9 [CH_2].

Reaction of 78 with MeI and subsequent addition of AgOTf. Synthesis of 82. Addition of MeI (1 mL, 16.0631 mmol) to a solution of **78** (35 mg, 0.0643 mmol) in toluene (10 mL) at room temperature caused the precipitation of an orange solid after 18 hours stirring at room temperature. The supernatant was removed and the orange residue was washed with diethyl ether (2 × 20 mL) and hexane (2 × 20 mL) and dried under vacuum. The orange residue was dissolved in CH_2Cl_2 and AgOTf (25 mg, 0.0973 mmol) was added. After stirring the resulting solution in the dark for three hours, it was filtered and concentrated to 5 mL. Addition of hexane caused the precipitation of **82** as an orange solid, which was washed with hexane (2 × 20 mL) and dried under vacuum. NMR spectra of **82** showed that it was accompanied by small amounts of 1,2,3-[Me_3Im]OTf and **74**, therefore, elemental analysis was not attempted.

IR (CH_2Cl_2, cm^{-1}): 2033, 1925 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.35 [m, 1H, H_9 phen'], 8.51 [m, 1H, H_7 phen'], 7.89 [d (8.4), 1H, H_6 phen'], 7.71 [dd (8.4, 5.1), 1H, H_8 phen'], 7.51 [d (8.4), 1H, H_5 phen'], 6.89 [d (9.7), 1H, H_4 phen'], 6.60 [dd (9.7, 5.2), 1H, H_3 phen'], 6.53 [d (1.7), 1H, CH-NRe (Im)], 6.31 [d (1.7), 1H, CH-NMe (Im)], 4.67 [m, 1H, H_2 phen'], 3.66 [m, 4H, N(phen)-CH_3 and CH_2(Im)], 3.52 [s, 3H, N-Me(Im)], 3.13 [dd (16.7, 3.6), 1H, CH_2].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 195.7, 195.0, 193.7 [CO], 154.5 [C_9 phen'], 146.1 [QC Im], 143.5 [C_{13} phen'], 140.1 [C_7 phen'], 139.1 [C_{11} phen'], 131.2 [C_3 phen'], 130.3 [C_{14} phen'], 129.2 [C_6 phen'], 127.5 [CH-NRe (Im)], 127.4 [C_5 phen'], 123.5 [C_8 phen'], 122.7 [CH-NMe (Im)], 122.4 [C_4 phen'], 122.2 [C_{12} phen'], 62.5 [C_2 phen'], 55.7 [CH_3-phen'], 35.2 [CH_3], 29.3 [CH_2].

Synthesis of [Re(bipy)(CO)$_3$(1-Me-2-EtIm)]OTf (83). Compound **83** was obtained in an analogous way to that employed for compound **73** starting from [Re(bipy)(CO)$_3$(OTf)] (156 mg, 0.2711 mmol), 1-Me-2-EtIm (35 μL, 0.3050 mmol) and toluene (20 mL). Yield: 172 mg (93 %).

IR (CH_2Cl_2, cm^{-1}): 2032, 1926 (ν_{CO}).

^{1}H NMR (CD_2Cl_2, 298 K, 400 MHz): δ 9.13 [m, 2H, H_6 and H_9 bipy], 8.69 [m, 2H, H_3 and H_{12} bipy], 8.34 [t (7.4), 2H, H_4 and H_{11} bipy], 7.75 [t (7.4), 2H, H_5 and H_{10} bipy], 6.73 [s, 1H, CH-NMe (Im)], 6.00 [s, 1H, CH-NRe (Im)], 3.57 [s, 3H, CH_3-N(Im)], 2.88 [q (7.6), 2H, CH_3CH_2-C(Im)], 1.01 [t (7.6), 3H, CH_3CH_2-C(Im)].

^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K, 400 MHz): δ 195.9 [2 CO], 191.0 [CO], 155.9 [C_2 and C_7 bipy], 153.1 [C_6 and C_9 bipy], 152.9 [QC Im], 141.2 [C_4 and C_{11} bipy], 128.3 [C_5 and C_{10} bipy], 125.9 [CH-NRe (Im)], 125.2 [C_3 and C_{12} bipy], 122.7 [CH-NMe (Im)], 34.0 [CH_3-N(Im)], 20.9 [CH_3CH_2-C(Im)], 12.0 [CH_3CH_2-C(Im)].

Reaction of 83 with $KN(SiMe_3)_2$. Synthesis of 84. $KN(SiMe_3)_2$ (0.55 mL of a 0.5 M solution in toluene, 0.2750 mmol) was added to a solution of **83** (172 mg, 0.2509 mmol) in THF (20 mL) previously cooled to -78°C. The solution color changed from yellow to purple. The reaction mixture was allowed to stir at room temperature for 6 hours and then was evaporated to dryness. The resulting purple residue was extracted in toluene and filtered. Evaporation to dryness afforded **84** as a purple solid in a 78 % yield (50 mg). Slow diffusion of hexane (8 mL) into a concentrated solution of **84** in toluene (6 mL) at -20°C yielded purple crystals of **84** one of which was employed for X-ray diffraction analysis. Yield: 18 % (24 mg).

IR (THF, cm^{-1}): 2004, 1893, 1875 (ν_{CO}).

^{1}H NMR (THF-d_8, 298 K, 400 MHz): δ 8.86 [dt (5.6, 1.3), 1H, H_9 bipy'], 7.70 [m, 2H, H_{12} and H_{11} bipy'], 7.17 [m, 1H, H_{10} bipy' (obscured by residual toluene, can be seen in COSY, HSQC and HMBC spectra)], 6.97 [d (1.7), 1H, CH-NMe (Im)], 6.89 [d (1.7), 1H, CH-NRe (Im)], 6.10 [dd (7.7, 6.0), 1H, H_4 bipy'], 5.73 [dd (6.0, 1.0), 1H, H_3 bipy'], 5.19 [ddd (7.2, 6.0, 0.9), 1H, H_5 bipy'], 4.58 [dd (7.2, 6.0), 1H, H_6 bipy'], 3.55 [s, 3H, N-CH_3 (Im)], 3.30 [q (7.2), 1H, CH_3CH (Im)], 1.25 [d (7.2), 3H, CH_3CH (Im)].

^{13}C{^{1}H} NMR (THF-d_8, 298 K, 400 MHz): δ 201.1, 199.9, 196.6 [CO], 162.0 [C_7 bipy'], 151.8 [C_2 bipy'], 151.2 [QC Im and C_9 bipy'], 136.4 [C_{11} bipy'], 128.0 [CH-NRe (Im)], 123.8 [C_4 bipy'], 122.5 [C_{10} bipy'], 121.3 [CH-NMe (Im)], 120.8 [C_{12} bipy'], 107.8 [C_5 bipy'], 96.5 [C_3 bipy'], 64.9 [C_6 bipy'], 36.8 [CH_3-CH(Im)-bipy], 32.6 [CH_3-N(Im)], 16.6 [CH_3-CH(Im)-bipy].

Reaction of 83 with $KN(SiMe_3)_2$. Characterization of 85. $KN(SiMe_3)_2$ (0.55 mL of a 0.5 M solution in toluene, 0.2750 mmol) was added to a solution of **83** (172 mg, 0.2509 mmol) in THF (10 mL) previously cooled to -78°C. The color of the solution changed from yellow to purple. The reaction mixture was allowed to reach room temperature and volatiles were removed under vacuum. The resulting purple residue was extracted in toluene and filtered. Volatiles were removed under vacuum and **85** was obtained as a purple oil, which was dissolved in THF-d_8 for NMR characterization.

^{1}H NMR (THF-d_8, 253 K, 400 MHz): δ 8.90 [d (5.5), 1H, H_9 bipy'], 7.75 [m, 1H, H_{12} and H_{11} bipy'], 7.22 [m, 2H, H_{10} bipy' and CH-NMe (Im)], 7.01 [d (1.6), 1H, CH-NRe (Im)], 6.34 [dd (8.8, 5.8), 1H, H_4 bipy'], 5.72 [d (5.8), 1H, H_3 bipy'], 5.05 [dd (6.0, 3.1), 1H, H_6 bipy'], 4.84 [dd (8.8, 5.8), 1H, H_5 bipy'], 3.63 [s, 3H, N-CH_3 (Im)], 2.83 [qd (7.3, 3.1), 1H, CH_3CH (Im)], 1.24 [d (7.3), 3H, CH_3CH (Im)].

^{13}C{^{1}H} NMR (THF-d_8, 253 K, 400 MHz): δ 201.6, 199.6, 196.7 [CO], 162.4 [C_7 bipy'], 154.8 [C_2 bipy'], 154.3 [QC Im], 151.2 [C_9 bipy'], 136.4 [C_{11} bipy'], 130.2 [CH-NRe (Im)], 127.3 [C_4 bipy'], 122.5 [C_{10} bipy'], 121.3 [CH-NMe (Im)], 120.6 [C_{12} bipy'], 107.0 [C_5 bipy'], 97.7 [C_3 bipy'], 62.0 [C_6 bipy'], 40.8 [CH_3-*C*H(Im)-bipy], 31.6 [CH_3-N(Im)], 14.0 [*C*H_3-CH(Im)-bipy].

Reaction of 67 with PMe_3. Synthesis of 86. PMe_3 (15 μL, 0.1719 mmol) was added to a freshly prepared solution of **67** (73 mg, 0.1366 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 18 hours and then evaporated to dryness. The resulting green residue was extracted in toluene (15 mL), filtered and evaporated to dryness. Compound **86** was obtained as a green microcrystalline powder in a 50 % yield (41 mg).

IR (THF, cm^{-1}): 2012, 1916, 1888 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298K, 400 MHz): δ 8.17 [m, 1H, H_9 phen'], 7.24 [m, 1H, H_7 phen'], 6.80 [d (7.9), 1H, H_5 phen'], 6.36 [d (9.6), 1H, H_4 phen'], 6.29 [dd (8.3, 4.9), 1H, H_8 phen'], 6.17 [dd (7.9, 1.3), 1H, H_6 phen'], 5.71 [ddd (9.6, 4.9, 0.8), 1H, H_3 phen'], 5.33 [m, 1H, H_2 phen'], 3.64 [m, 2H, CH_2 (Ox)], 3.53 [m, 2H, CH_2 (Ox)], 3.12 [m, 2H, phen'-CH_2(Ox)], 0.66 [d (8.5), 9H, PMe_3].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 196.9 [d (5.7), CO], 196.5 [d (6.8), CO], 192.2 [d (74.0), CO], 164.3 [QC Ox], 155.5 [C_{11} phen'], 145.8 [C_9 phen'], 145.2 [C_{13} phen'], 136.1 [C_7 phen'], 131.5 [C_{14} phen'], 127.8 [C_5 phen', not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 125.4 [C_4 phen'], 120.8 [C_8 phen'], 120.0 [C_3 phen'], 118.6 [C_{12} phen'], 104.8 [C_6 phen'], 66.2 [CH_2-O (Ox)], 62.0 [C_2 phen'], 54.7 [CH_2-N (Ox)], 37.9 [phen'-CH_2(Ox)], 12.5 [d (28.1), PMe_3].

^{31}P NMR (toluene-d_8, 298K, 400 MHz): δ -28.8.

Reaction of 72 with PMe_3. Synthesis of 87. PMe_3 (15 μL, 0.1459 mmol) was added to a freshly prepared solution of **72** (obtained starting from 140 mg of **70** and 0.15 mL of 0.7 M solution of $KN(SiMe_3)_2$ in toluene) in THF (10 mL) at -78°C. The mixture was allowed to reach room temperature and then was evaporated to dryness. The resulting green residue was extracted in toluene (15 mL), filtered and evaporated to dryness. Compound **87** was obtained as a green microcrystalline powder in a 45 % yield (28 mg).

Anal. Calcd. for $C_{24}H_{23}N_3O_3PRe$: C 46.60, H 3.75, N 6.79. Found: C 46.92, H 3.70, N 6.71.

IR (THF, cm^{-1}): 2013, 1917, 1888 (ν_{CO}).

^1H NMR (toluene-d_8, 298K, 400 MHz): δ 8.55 [ddd (4.8, 1.9, 1.0), 1H, H_2 py], 8.21 [m, 1H, H_9 phen'], 7.25 [m, 1H, H_7 phen'], 7.09 [m, 1H, H_4 py], 7.04 [m, 1H, H_5 py], 6.81 [d (7.8), 1H, H_5 phen'], 6.66 [m, 1H, H_3 py], 6.31 [m, 1H, H_8 phen'], 6.28 [d (9.6), 1H, H_4 phen'], 6.18 [dd (7.8, 1.4), 1H, H_6 phen'], 5.42 [m, 1H, H_2 phen'], 5.23 [dd (9.6, 4.8, 1.0), 1H, H_3 phen'], 3.77 [dd (12.4, 4.2), 1H, CH_2], 3.58 [dd (12.4, 9.8), 1H, CH_2], 0.68 [d (8.5), 9H, PMe_3].

$^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K, 400 MHz): δ 197.1 [d (4.0), CO], 196.7 [d (5.8), CO], 192.4 [d (74.1), CO], 158.7 [C_6 py], 155.7 [C_{11} phen'], 149.2 [C_2 py], 145.7 [d (5.1), C_9 phen'], 145.3 [C_{13} phen'], 136.1 [d (3.7), C_7 phen'], 134.9 [C_4 py], 131.6 [C_{14} phen'], 127.7 [C_5 phen', not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 125.0 [C_4 phen', not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 124.2 [C_5 py], 120.8 [C_8 phen'], 120.6 [C_3 phen'], 120.3 [C_3 py], 118.9 [C_{12} phen'], 104.5 [C_6 phen'], 65.0 [C_2 phen'], 48.5 [CH_2], 12.6 [d (28.0), PMe_3].

^{31}P NMR (toluene-d_8, 298K, 400 MHz): δ -28.8.

^{15}N NMR (CD_2Cl_2, 298 K, 400 MHz): δ 320.0 [2-Mepy], 231.4 [N_{10} phen], 97.8 [N_1 phen].

Reaction of 78 with PMe_3. Synthesis of 88. PMe_3 (10 μL, 0.1146 mmol) was added to a freshly prepared solution of **78** (48 mg, 0.0880 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature in a Young sealed flask for 48 hours and then evaporated to dryness. The resulting green residue was extracted in toluene (15 mL), filtered and evaporated to dryness. Washing with hexane (2 × 10 mL) and drying under vacuum afforded **88** as a green microcrystalline powder in a 50 % yield (27 mg).

Anal. Calcd. for $C_{23}H_{24}N_4O_3PRe$: C 44.44, H 3.89, N 9.01. Found: C 44.86, H 3.81, N 8.97.

IR (THF, cm^{-1}): 2011, 1915, 1889 (ν_{CO}).

^{1}H NMR (toluene-d_8, 298K, 400 MHz): δ 8.21 [m, 1H, H_9 phen'], 7.26 [m, 1H, H_7 phen'], 7.17 [d (1.7), 1H, CH-N (Im)], 6.84 [d (7.8), 1H, H_5 phen'], 6.37 [d (1.3), 1H, CH-NMe (Im)], 6.32 [dd (8.3, 4.8), 1H, H_8 phen'], 6.29 [d (9.6), 1H, H_4 phen'], 6.20 [dd (7.8, 1.4), 1H, H_6 phen'], 5.70 [ddd (9.6, 5.0, 1.1), 1H, H_3 phen'], 5.42 [m, 1H, H_2 phen'], 3.42 [dd (14.2, 4.1), 1H, CH_2], 3.31 [dd (14.2, 10.2), 1H, CH_2], 2.90 [s, 3H, CH_3], 0.66 [d (8.5), 9H, PMe_3].

^{13}C{^{1}H} NMR (toluene-d_8, 298 K, 400 MHz): δ 196.8 [d (7.6), CO], 196.6 [d (7.5), CO], 192.8 [d (73.8), CO], 155.4 [C_{11} phen'], 145.8 [d (5.1), C_9 phen'], 145.3 [QC Im], 144.4 [C_{13} phen'], 136.1 [d (2.2), C_7 phen'], 131.5 [C_{14} phen'], 127.8 [C_6 phen', not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 127.6 [CH-N (Im), not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 124.7 [C_4 phen', not seen in ^{13}C NMR spectrum due to toluene signals, could be seen in DEPT-135, HSQC and HMBC spectra], 121.6 [C_3 phen'], 120.8 [d (3.5), C_8 phen'], 119.6 [CH-NMe (Im)], 118.9 [C_{12} phen'], 104.7 [C_5 phen'], 63.3 [C_2 phen'], 36.2 [CH_2], 31.4 [CH_3], 12.5 [d (28.3), PMe_3].

^{31}P NMR (toluene-d_8, 298K, 400 MHz): δ -28.9.

Notes and References

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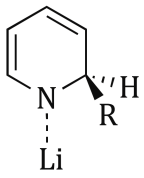

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