inorganics

MDPI

Article

Isocyanide Cycloaddition and Coordination Processes at Trigonal Phosphinidene-Bridged MoRe and MoMn Complexes

M. Angeles Alvarez, M. Esther García, Daniel García-Vivó *, Miguel A. Ruiz * and Patricia Vega

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain; maf@uniovi.es (M.A.A.); garciame@uniovi.es (M.E.G.); patriciavegasierra@gmail.com (P.V.)

* Correspondence: garciavdaniel@uniovi.es (D.G.-V.); mara@uniovi.es (M.A.R.); Tel.: +34-985102962 (D.G.-V.); +34-985102978 (M.A.R.)

Abstract: Heterometallic phosphinidene complexes are appealing species for the construction of novel organophosphorus ligands thanks to the high reactivity expected from the combination of M-P multiple bonding and the intrinsically different electronic and coordination preferences of the distinct metals. In a preliminary study, we found that the heterobimetallic complex$MoReCp(\mu\text{-}PMes^*)(CO)_6$ (Mes* = 2,4,6-$C_6H_2{}^tBu_3$) reacted with CN(*p*-C_6H_4OMe) via [2+1]-cycloaddition to form a novel azaphosphallene complex. We have now examined in detail the reactions of the above complex and those of its MoMn analogue with different isocyanides, which turned out to be strongly dependent on experimental conditions and on the size of the substituent at the isocyanide. All the products formed follow from one or several of the following reaction pathways: (i) CO substitution by CNR; (ii) addition of CNR at the group 7 metal centre; and (iii) [2+1] cycloaddition of isocyanide at a Mo=P bond to form azaphosphallene groups, with the former process being dominant in reactions at room temperature and for the Mn system. In contrast, low-temperature reactions of the Re system favoured the addition processes, with the [2+1] cycloaddition at Mo=P bonds only taking place at substrates without metal-metal bonds and when the size of the CNR group does not cause unbearable steric clashes when placed in between the Cp and Mes* groups.

Keywords: heterobimetallic complexes; phosphinidene complexes; binuclear carbonyl complexes; [2+1] cycloaddition reactions; isocyanide complexes

Citation: Alvarez, M.A.; García, M.E.; García-Vivó, D.; Ruiz, M.A.; Vega, P. Isocyanide Cycloaddition and Coordination Processes at Trigonal Phosphinidene-Bridged MoRe and MoMn Complexes. *Inorganics* **2023**, *11*, 364. https://doi.org/10.3390/inorganics11090364

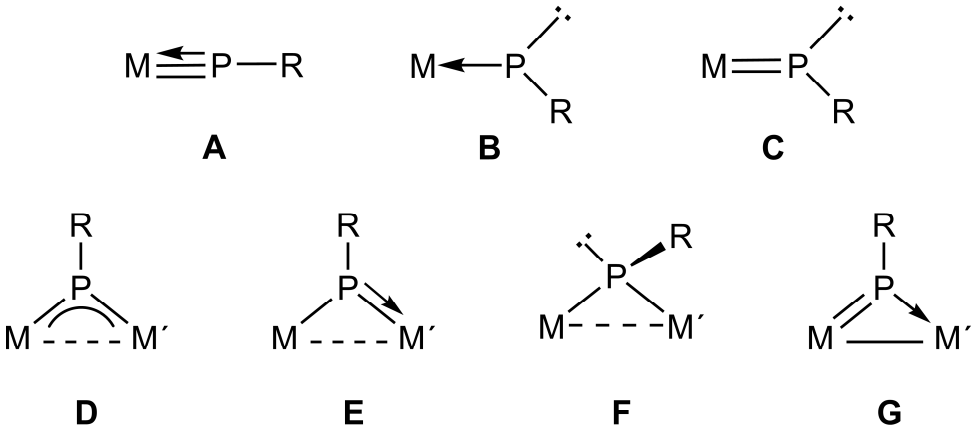
Academic Editor: Philippe Schollhammer

Received: 25 July 2023
Revised: 4 September 2023
Accepted: 5 September 2023
Published: 7 September 2023

1. Introduction

The chemistry of transition metal complexes bearing phosphinidene ligands has emerged as a captivating field of research, driven by their unique reactivity and potential applications in catalytic processes [1–4]. When bound to just one metal atom, up to three extreme coordination modes have been identified for the phosphinidene group (**A**–**C** in Scheme 1), although reactivity studies have been developed so far only for complexes of types **B** and **C**, which in turn are known as electrophilic and nucleophilic complexes, respectively, due to similarities with the related carbene species [5]. Yet, phosphinidenes are not restrained to coordinate to just one metal atom, and, in fact, numerous polynuclear complexes bearing bridging PR groups have been reported in the literature. Amongst them, binuclear complexes (**D**–**G** in Scheme 1) are particularly appealing species for the construction of novel organophosphorus groups through reactions with different small organic and inorganic molecules, since they typically retain a significant multiplicity in their metal-phosphorus bonds (excepting those compounds bearing a lone electron pair at the P atom, type **F**), combined with the potential cooperative effects that the two metal centres can induce [6]. Almost all these studies have been focused so far exclusively on homometallic phosphinidene-bridged complexes, where two identical metals are present. However, in the search for new reactivity patterns for the phosphinidene ligands, an attractive avenue, which has been essentially neglected until recently, is the introduction

of two distinct metals, aka heterometallic complexes. The rationale behind this approach stems from the expected changes that two different metals, each with a set of unique electronic properties and/or coordination preferences, could impart to the coordination and electronic properties of the phosphinidene group itself [7–12]. In this area of work, we recently reported the high-yield synthesis of the heterobimetallic phosphinidene complexes [MoMCp(μ-PMes*)(CO)$_6$] (Mes* = 2,4,6-C$_6$H$_2$^{t}Bu$_3$; M = Re (**1a**), Mn (**1b**)) [13–15]. These complexes displayed unprecedented asymmetric bonding of the PR ligands, whereby the π-bonding interaction was largely located at the Mo–P bonds (**G** in Scheme 1), even when such localisation was not expected in terms of simple electron counting because the PR ligand is bridging over two isoelectronic 15–e$^-$ metal fragments. Obviously, the unprecedented coordination mode of the PR groups in compounds **1a,b** raised the question as to whether this new bonding motif could be translated into new chemical reactivity for the PR group itself, and, hence, we started to study the chemical behaviour of these two compounds. These studies indicated that both complexes display a striking trend to undergo cycloaddition reactions involving their Mo-P double bonds in their reactions with unsaturated organic molecules, sometimes with singular results [13,16,17]. For instance, while the reaction with alkynes and some heterocumulenes (i.e., S=C=NR) proceeds readily via formal [2+2] cycloaddition processes [16], those with molecules having N–N multiple bonds (diazoalkanes and azides) proceed rather via [2+1] cycloadditions [17], yielding in both cases new organophosphorus ligands, hence showcasing the utility of these MoMn and MoRe complexes for synthetic purposes. Our preliminary studies on the chemistry of compound **1a** included the reaction with the isocyanide CN(p-C$_6$H$_4$OMe), which yielded, when performed at low temperature, the novel azaphosphallene complex [MoReCp{μ-$\eta^2$$_{P,C}$:$\kappa^1$$_P$-PMes*CN($p$-C$_6H_4$OMe)}(CO)$_6${2$\kappa$-CN($p$-C$_6H_4$OMe)}], following from an unconventional [2+1] cycloaddition of the isocyanide molecule to the Mo=P bond and additional CO/CNR ligand substitution [13]. Additionally, we noticed that the newly formed azaphosphallene group in this compound displays an unprecedented coordination mode whereby it remains $\kappa^1$$_P$-bound to the Re atom while being $\eta^2$$_{P,C}$-bound to the second metal. This is in contrast with all previously reported coordination modes for these ligands in binuclear complexes, these including μ–$\kappa^1$$_P$:$\kappa^1$$_P$, μ–$\kappa^1$$_P$:$\kappa^1$$_N$ or μ–$\kappa^1$$_P$:$\eta^2$$_{N,C}$ coordination modes in W_2 [18] or Sc_2 [19] dimetallic complexes. Taking into consideration these findings, it was of interest to perform a more detailed study on the reactions of compounds **1a,b** with various isocyanides under different reaction conditions, which is the purpose of the present paper. As will be shown below, our study unveils the existence of three distinct processes occurring in these reactions, namely CNR addition, CO-substitution, and CNR cycloaddition, with the interplay between these processes being highly influenced by the substituent of the incoming isocyanide and/or the reaction temperature and stoichiometry.

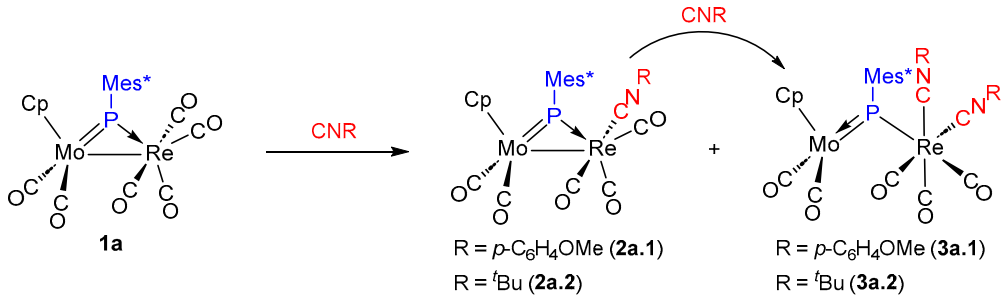


Scheme 1. Coordination modes of PR ligands at mono- and bi-nuclear complexes.

2. Results and Discussion

*2.1. Reactions of Compounds **1a,b** with Isocyanides: Stoichiometric Reactions*

Reactions of compound **1a** with stoichiometric amounts of CN^{t}Bu or CN(*p*-C$_6$H$_4$OMe) take place rapidly at room temperature to mainly produce the corresponding CO-substitution products of formulae [MoReCp(μ-PMes*)(CO)$_5$(2κ-CNR)] [R = *p*-C$_6$H$_4$OMe (**2a.1**), ^{t}Bu (**2a.2**)] (Scheme 2). These compounds are invariably accompanied by smaller amounts of a second type of product now following from CO-substitution and further addition of the reagent, both taking place selectively at the Re centre to form the bis(isocyanide) derivatives [MoReCp(μ-PMes*)(CO)$_5$(2κ-CNR)$_2$] [R = *p*-C$_6$H$_4$OMe (**3a.1**), ^{t}Bu (**3a.2**)]. In the particular case of CN(*p*-C$_6$H$_4$OMe), a third type of product, also derived from the reaction with two equivalents of the reagent, could be identified in the corresponding reaction mixtures, although only in trace amounts, this being the azaphosphallene complex [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**4a.1**). In this product, no displacement of CO has taken place; instead, one of the molecules of the reagent has been added at the Re centre while the second one has been incorporated at the former Mo=P bond via a formal [2+1]–cycloaddition reaction (see below). The formation of products involving the incorporation of two molecules of the reagent raised the question as to whether compounds of type **2** were precursors in their formation. In fact, this is the case for compounds of type **3**, since the addition of a second equivalent of isocyanide to the mixtures obtained after the first addition completed the **2** → **3** transformation. Considering all these observations, it seems clear that these reactions take place initially through the substitution of a carbonyl ligand by the isocyanide, a process then followed mainly by the addition of a second molecule of the reagent selectively at the Re centre, then causing the scission of the intermetallic bond. Unfortunately, reactions of the manganese analogue **1b** with different isocyanides under similar conditions showed very little selectivity, and although complexes of type **2** were identified in the crude reaction mixtures, they could not be separated nor fully characterised.



Scheme 2. Reactions of compound **1a** with isocyanides under stoichiometric conditions.

Spectroscopic data for compounds **2** (see Section 3 and Table 1) are similar to each other and consistent with the structure shown on Scheme 2, this being reminiscent of that of the parent phosphinidene **1a** after replacing one CO ligand with a CNR group at the Re centre. Accordingly, the IR spectra of these complexes display now weak high energy bands due to the terminally coordinated isocyanide ligands [υ_{CN} = 2149 (**2a.1**) and 2167 (**2a.2**) cm^{-1}], these being accompanied by four C–O stretching bands, with the most energetic ones (*ca.* 2010 cm^{-1}) displaying a high intensity, which denote the presence of pyramidal Re(CO)$_3$ oscillators in these molecules [20], hence a positioning the CNR ligand *cis* to the PMes* ligand. In agreement with this, five carbonyl resonances are clearly identified in the respective ^{13}C NMR spectra at room temperature, with three of them arising from Re-bound carbonyls, of which two display significant two-bond P–couplings, a circumstance also observed for the parent compound **1a**, hence pointing to a similar coordination around the Re atom. Finally, the ^{31}P NMR spectra of these complexes display highly deshielded resonances (*ca.* 700 ppm), as expected from complexes having phosphinidene ligands bridging over M–M bonds, as also found for the parent complexes **1a,b**.

Table 1. Selected IR [1] and $^{31}P\{^{1}H\}$ data [2] for new compounds.

Compound	ν(CO)/ν(CN)	δ(P)
[MoReCp(μ-PMes*)(CO)$_6$] (**1a**) [3]	2077 (m), 1986 (vs), 1951 (s), 1876 (w)	673.1
[MoMnCp(μ-PMes*)(CO)$_6$] (**1b**) [4]	2055 (m), 2039(w), 1974 (vs), 1951 (s), 1888 (w), 1862 (w)	720.9
[MoReCp(μ-PMes*)(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**2a.1**)	2149 (w, C–N), 2011(vs), 1948 (m), 1934 (m), 1911 (m, sh)	697.4
[MoReCp(μ-PMes*)(CO)$_5$(2κ-CN^{t}Bu)] (**2a.2**)	2167 (m, C–N), 2012 (vs), 1944 (s), 1930 (m, sh), 1909 (w, sh)	703.5
[MoReCp(μ-PMes*)(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}$_2$] (**3a.1**)	2184 (w, C–N), 2157 (w, C–N), 2031 (vs), 1980 (m), 1952 (m), 1889 (m), 1803 (m)	522.3
[MoReCp(μ-PMes*)(CO)$_5$(2κ-CN^{t}Bu)$_2$] (**3a.2**)	2198 (w, C–N), 2176 (w, C–N), 2028 (vs), 1969 (m), 1943 (m), 1890 (m), 1803 (m)	535.1
[MoMnCp(μ-PMes*)(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}$_2$] (**3b.1**)	2170 (w, C–N), 2148 (w, C–N), 2027 (vs), 1981 (m), 1961 (m), 1891 (m), 1805 (m)	568.5
[MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**4a.1**) [5]	2180 (w, C–N), 2096 (m), 2024 (s, sh), 2012 (vs), 1976 (m), 1924 (m), 1847 (m)	−268.1
[MoReCp(μ-PMes*)(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**5a.1**)	2183 (w, C–N), 2095 (m), 2020 (s, sh), 2012 (vs), 1977 (m), 1896 (m), 1811 (m)	481.3
[MoReCp(μ-PMes*)(CO)$_6$(2κ-CN^{t}Bu)] (**5a.2**)	2197 (w, C–N), 2096 (m), 2010 (vs), 1972 (m), 1896 (m), 1811 (m)	487.0
[MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(p-C$_6$H$_4$OMe)}(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}$_2$] (**6a.1**)	2181 (w, C–N), 2152 (w, C–N), 2037 (vs), 1989 (m), 1950 (m), 1918 (m), 1840 (m)	−269.1
[MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*o*-C$_6$H$_4$Me)}(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**7a.3**)	2181 (w, C–N), 2097 (m), 2025 (s, sh), 2015 (vs), 1978 (m), 1923 (m), 1847 (m)	−265.4
[MoReCp(μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN^{i}Pr)(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**7a.4**)		−262.6
[MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_6$(2κ-CN^{t}Bu)] (**7a.5**)	2193 (w, C–N), 2097 (m), 2024 (s, sh), 2011 (vs), 1973 (m), 1923 (m), 1847 (m)	−269.5
[MoMnCp(μ-PMes*)(CO)$_4${2κ-CN(*p*-C$_6$H$_4$OMe)}$_3$] (**8b.1**)	2163 (w, C–N), 2128 (w, sh, C–N), 2109 (vs), 1981 (m), 1937 (m), 1883 (m), 1797 (m)	617.9

[1] Recorded in dichloromethane solution, with C–O stretching bands [ν(CO)] in cm^{-1}. [2] Recorded in CD_2Cl_2 solution at 121.54 MHz and 295 K, with chemical shifts (δ) in ppm. [3] Data taken from reference [14]. [4] Data taken from reference [15]. [5] Data taken from reference [13].

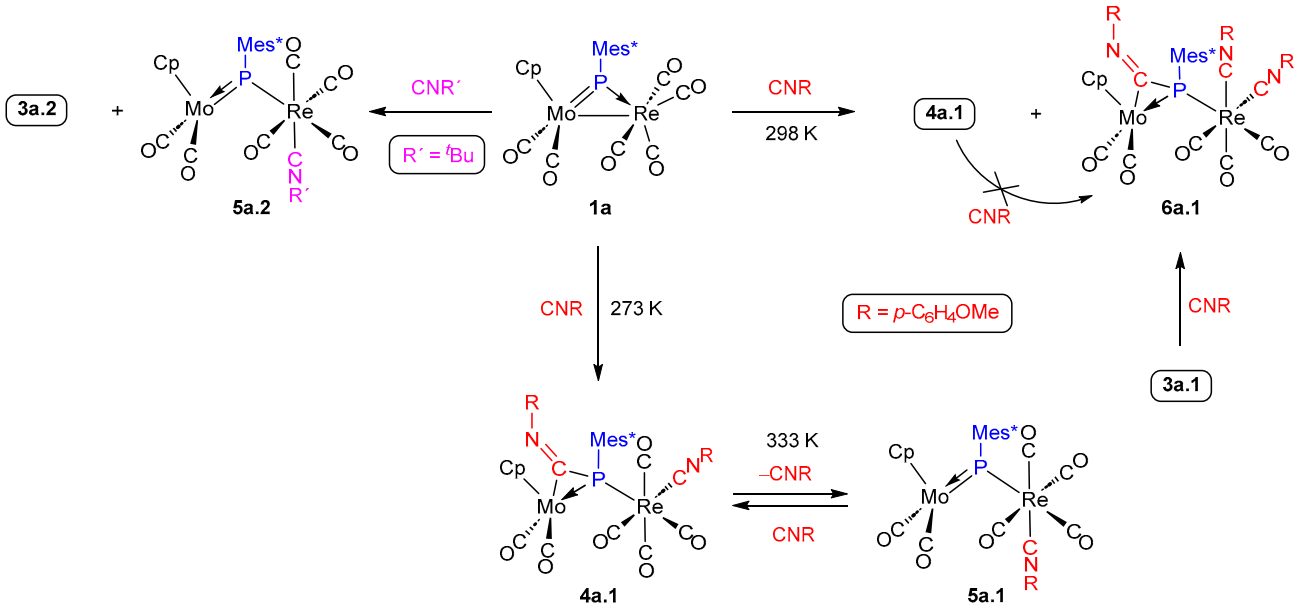
The structure of compounds of type **3a** can be derived from that of corresponding heptacarbonyls [MoMCp(μ-PMes*)(CO)$_7$] [15], after the replacement of two carbonyls at the Re atom with isocyanide ligands. Thus, the IR spectrum of these complexes now displays two high energy C–N bands and five C–O stretches (see Section 3 and Table 1) that are consistent with the presence of essentially independent Mo(CO)$_2$ and Re(CO)$_3$(CNR)$_2$ oscillators, an assumption otherwise consistent with the absence of a Mo–Re bond connecting them, as also observed for the isoelectronic complex [MoReCp{μ-η^3:κ^1_C-PMes*CHC(CO$_2$Me)}(CO)$_5${CN(*p*-C$_6$H$_4$OMe)}$_2$] [16]. As crystallographically confirmed for the latter complex, the two CNR groups display a mutually *cisoid* disposition, which is reflected in the similar intensities of the corresponding C–N stretches observed in the IR spectrum, while the high intensity of the most energetic C–O stretches (*ca.* 2030 cm^{-1}) denotes a facial arrangement of the three Re-bound carbonyls [20]. Another spectroscopic

indication of the lack of metal–metal interaction in compounds **3** arises from the ^{31}P NMR spectra, which for both complexes now display significantly less deshielded resonances (*ca.* 530 ppm) compared to the metal–metal bonded complexes **2**, a circumstance also observed when comparing the related hexa- and hepta-carbonyl complexes [MoMCp(μ-PMes*)(CO)$_n$] (n = 6, 7; M = Mn, Re) [15]. Other spectroscopic data for these complexes are as expected and require no further discussion.

2.2. Reactions of Compounds *1a,b* with Isocyanides: Reactions in the Presence of Excess CNR

Reactions of compounds **1a,b** with excess CNR were found to be particularly complex, with the outcome being highly dependent on the size of the R group in the added reagent as well as on the temperature and the group 7 metal present on the parent phosphinidene.

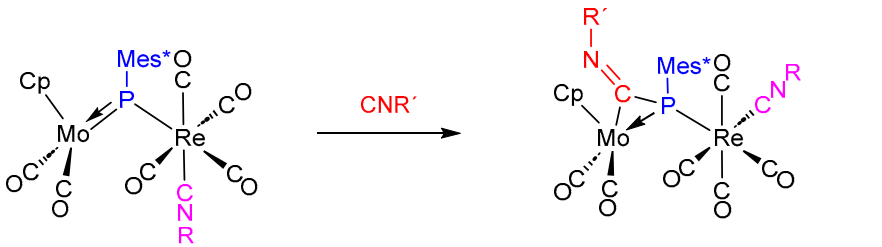
Low-temperature (273 K) reactions of **1a** with three equivalents of CN(*p*-C$_6$H$_4$OMe) led to the slow and progressive formation of the azaphosphallene complex [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**4a.1**) (Scheme 3), following from the addition of two molecules of the reagent without decarbonylation, one of them added at the Re centre and the second one over the former Mo=P bond, to build an azaphosphallene ligand after a formal [2+1]–cycloaddition reaction. Although this compound could be isolated and fully characterized, its solutions evolved slowly at room temperature by elimination of the P–bound isocyanide group to give the phosphinidene complex [MoReCp(μ-PMes*)(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] (**5a.1**) (Scheme 3). This elimination process could be significantly accelerated upon heating (*ca.* 3 h at 333 K) and could be fully reversed upon addition of fresh isocyanide to solutions of **5a.1** to regenerate the azaphosphallene complex **4a.1**. The temperature also has a significant influence on the outcome of these reactions, since the addition of excess CN(*p*-C$_6$H$_4$OMe) to **1a** at room temperature led instead to the formation of a nearly 1:1 mixture of the azaphosphallene complexes **4a.1** and [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}$_2$] (**6a.1**) (Scheme 3). The latter follows, in a formal sense, from an additional CO/CNR ligand substitution at **4a.1**. However, independent experiments proved that such transformation (**4a.1** + CNR → **6a.1**) does not take place under the relevant reaction conditions, hence discarding **4a.1** as the precursor of the azaphosphallene **6a.1** during the course of these reactions. Instead, our experiments proved that the formation of **6a.1** rather follows from the addition of a third molecule of CNR to the phosphinidene **3a.1**, which undergoes cycloaddition with the Mo=P bond of the complex, thus generating the new azaphosphallene ligand (Scheme 3).



Scheme 3. Reactions of compound **1a** with excess CNR.

In contrast with the chemistry just described, the addition of two equivalents of CN^{t}Bu to solutions of **1a** at 273 K did not yield any azaphosphallene product. Instead, a mixture of the addition product [MoReCp(μ-PMes*)(CO)$_6$(2κ-CN^{t}Bu)] (**5a.2**) and the corresponding addition plus substitution product **3a.2** were obtained invariably (Scheme 3). Furthermore, in this case, increasing the temperature did not substantially modify the outcome of the reaction since similar mixtures were then obtained, with the only difference now being the formation of small amounts of the CO–substitution product **2a.2**, as discussed above.

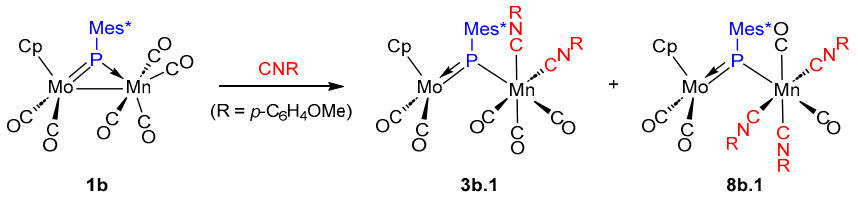
Keeping in mind all these transformations, it seemed likely that compounds of type **5**, formed by the simple addition of an isocyanide molecule to the parent phosphinidene **1a**, could be the actual precursors of the azaphosphallene complexes **4**, much in the same way as the phosphinidene complex **3a.1** is the precursor of the azaphosphallene **6a.1**. To verify this hypothesis, we carried out some cross-experiment reactions between different isocyanides and compounds **5**. Gratifyingly, compound **5a.1** reacted easily with different isocyanides via [2+1] cycloadditions to give the corresponding azaphosphallene complexes of formulae [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CNR}(CO)$_6${2κ-CN(*p*-C$_6$H$_4$OMe)}] [R = *p*-C$_6$H$_4$OMe (**4a.1**), *o*-C$_6$H$_4$Me (**7a.3**), ^{i}Pr (**7a.4**)] (Scheme 4) in a completely selective way. However, this reaction failed for the isocyanide bearing a bulky ^{t}Bu substituent (CN^{t}Bu), and in the case of the ^{i}Pr-substituted product **7a.4**, we found that this complex was only of moderate stability, releasing the added CN^{i}Pr group easily upon solvent removal. Both observations point to an important steric restriction on the nature of the CNR substituent in these cycloaddition reactions so that isocyanides bearing bulky groups such as those found in the alkyl isocyanides mentioned above would likely cause a significant steric clash when placed in between the Cp and Mes* groups as required to form the azaphosphallene groups, this explaining the absence of azaphosphallene products in the reaction of **1a** with excess CN^{t}Bu and the low stability of the ^{i}Pr derivative. Further corroborating the steric restrictions on the added CNR molecule, we found that the CN^{t}Bu derivative **5a.2** reacted smoothly only with CN(*p*-C$_6$H$_4$OMe) to give the corresponding azaphosphallene [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CN(*p*-C$_6$H$_4$OMe)}(CO)$_6${2κ-CN^{t}Bu}] (**7a.5**), but failed to react with sterically more demanding isocyanides such as the alkyl-substituted CN^{t}Bu and CN^{i}Pr, or the aryl-substituted CNXyl (Xyl = 2,6-C$_6$H$_3$Me$_2$).



Scheme 4. Reactions of compounds **5** with CNR.

As for the manganese derivative **1b**, all reactions carried out in the presence of excess isocyanide led to multi-addition products, with no azaphosphallene complexes being observed whatsoever. Thus, reaction with three equivalents of CN(*p*-C$_6$H$_4$OMe) took place easily at 273 K, leading to the formation of mixtures of the phosphinidene complexes [MoMnCp(μ-PMes*)(CO)$_5${2κ-CN(*p*-C$_6$H$_4$OMe)}$_2$] (**3b.1**) and [MoMnCp(μ-PMes*)(CO)$_4${2κ-CN(*p*-C$_6$H$_4$OMe)}$_3$] (**8b.1**) (Scheme 5). As was the case of the reactions of **1a** with stoichiometric amounts of the isocyanide, the reactions of the manganese phosphinidene seem to follow a similar pathway, involving in the first place the substitution of CO by a CNR ligand. In this case, however, the putative intermediate retaining a Mo–Mn bond has not been observed during the reactions, likely due to the fast incorporation of the second CNR molecule to yield complex **3b.1**. Obviously, the formation of the tris(isocyanide) complex

8b.1 would likely follow from an additional CO/CNR ligand substitution taking place at complex **3b.1** in the presence of excess reagent, a type of reaction not observed for the related Re complexes **3**, surely a consequence of the well-known higher reluctance of the $Re(CO)_3$ fragment (compared to the $Mn(CO)_3$ one) to undergo dissociation of CO.



Scheme 5. Reactions of compound **1b** with CN(*p*-C_6H_4OMe).

2.2.1. Characterisation of Azaphosphallene Derivatives **4a.1**, **6a.1** and **7a.3-5**

During our preliminary exploration of the reactivity of **1a**, we determined the solid-state structure of the azaphosphallene complex **4a.1** [13] (Figure 1), which confirmed the incorporation of two molecules of the isocyanide, one of them coordinated to the Re centre and displaying a perpendicular disposition with respect to the MoPRe plane, then rendering a nearly perfect octahedral coordination around the Re atom. The coordination of the second molecule of isocyanide can be visualised as arising from a [2+1] cycloaddition over the Mo=P double bond of the parent complex, which in consequence is significantly elongated to 2.544(1) Å (*cf.* 2.274(1) Å in **1a** [13]), and approaches the reference figures expected for single dative bonds (*c.f.* 2.51 Å in $[Mo(CO)_5(PMe_3)]$ [21]), as well as the figures measured for mononuclear iridium azaphosphallene complexes such as [IrCp*{$\eta^2_{P,C}$-PMes*(CNR)}(CNXyl)}] (*ca.* 2.41 Å [22]), if we allow for the ca. 0.13 Å difference in covalent radii of the metal atoms involved [23]. The newly formed azaphosphallene group then acts as a bridging ligand in an unprecedented $\eta^2_{P,C}$:κ^1_P coordination mode, counterbalancing the quite different electron counts of the Mo and Re fragments (15 and 17 electrons, respectively). Thus, while the Re–P and P–C bonds display lengths close to the reference figures for conventional σ-bonds (*ca.* 2.58 Å for Re–P and 1.80 Å for P–C [23]), the Mo–C separation is slightly shorter than the reference value of 2.27 Å for a Mo–C(sp^2) bond. In all, the azaphosphallene ligand contributes 4 electrons to the dimetal centre, giving a total electron count of 36 valence electrons for the complex. As a result, no metal-metal bond must be proposed according to the 18–electron rule, a circumstance in agreement with the long separation of 4.4675(5) Å between Mo and Re atoms in **4a.1**.

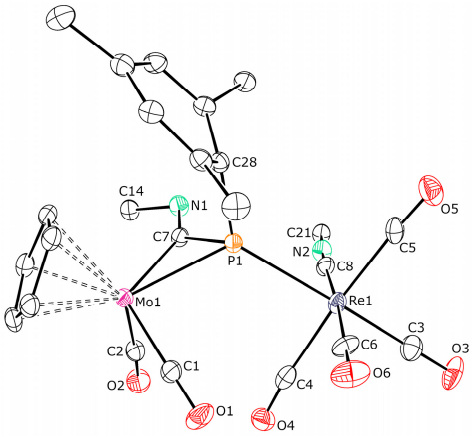


Figure 1. ORTEP drawing (30% probability) of compound **4a.1** with ^{t}Bu and (*p*-C_6H_4OMe) groups (except their C1 atoms) and H atoms omitted. Selected bond distances (Å) and angles (°): Mo1···Re1 = 4.4675(5), Mo1–P1 = 2.544(1). Re1–P1 = 2.585(1), Mo1–C7 = 2.107(5), P1–C7 = 1.796(4), Mo1–P1–Re1 = 121.2(1), Mo1–C7–P1 = 80.9(2), C7–N1-C14 = 120.5(4), P1–Mo1–C1 = 82.2(2), P1–Mo1–C2 = 104.5(2), C1–Mo1–C2 =81.1(2), P1–Re1–C8 = 88.1(2). Data taken from reference [13].

Spectroscopic data for **4a.1** and for the closely related compounds **7a.3-5** are similar and fully consistent with the solid-state structure of compound **4a.1** (see Section 3 and Table 1), with the main differences, obviously, being derived from the particular isocyanide groups present in each case. Thus, all these complexes display an IR spectrum displaying seven C–N and C–O stretching bands, with the most energetic one corresponding to the terminal, linearly coordinated CNR groups, as also found for the isocyanide complexes **2** and **3**. The remaining six bands are indicative of the presence of essentially independent $Mo(CO)_2$ and $Re(CO)_4$ oscillators, with the corresponding intensities being consistent with the presence of a *cisoid* arrangement of carbonyls in the first fragments (81.1° in the solid-state structure of **4a.1**) and of a distorted disphenoidal arrangement in the second ones [20]. The most characteristic spectroscopic feature of all these complexes is the dramatic shielding of the azaphosphallene ^{31}P NMR resonances, which appear around −270 ppm, a decrease of nearly 900 ppm when compared to the parent phosphinidene **1a**. Such strong shielding is, nevertheless, consistent with the presence of a significantly strained three-membered Mo–P–C ring, and the resulting shifts are significantly lower than those measured for Ir [22] and Pt [24] mononuclear azaphosphallene complexes with $\eta^2_{P,C}$–coordinated groups (δ_P in the range −150 to −190 ppm). An opposite effect was observed for the ^{13}C NMR resonances of the MoPC ring carbon atoms in these compounds, which now display quite deshielded resonances (*ca.* 218 ppm) with large one-bond couplings to P (*ca.* 75 Hz), both figures remaining similar to those described for most of the abovementioned mononuclear azaphosphallene complexes. Similar comments can be made for the diagnostic azaphosphallene resonances of the bis(isocyanide) complex **6a.1** (δ_P = −269.2 ppm; δ_C = 225.8 ppm; J_{PC} = 74 Hz). The main difference here is observed in the IR spectrum of this complex, which now displays two bands above 2100 cm^{-1}, instead of one, to be assigned as the corresponding C–N stretches of the two terminally coordinated isocyanide groups placed in a *cisoid* arrangement. The IR spectrum also supports the coordination of these two ligands at the Re atom due to the presence of C–O stretches compatible with essentially independent pyramidal $Re(CO)_3$ and $Mo(CO)_2$ oscillators.

2.2.2. Characterisation of Compounds **5**

The molecule of the phosphinidene complex **5a.1** in the crystal (Figure 2 and Table 2) is comparable to that of the heptacarbonyl complexes [$MoMCp(\mu$-PAr*)$(CO)_7$] (M = Re [14], Mn [15]), if we replace one of the carbonyl ligands of the $M(CO)_5$ fragments in the latter complexes by a CN(*p*-C_6H_4OMe) ligand. Thus, the molecule is built from $MoCp(CO)_2$ and $Re(CO)_4(CNR)$ fragments, expectedly joined by an asymmetrically bridging phosphinidene ligand of type **E**. As also observed for the above-mentioned heptacarbonyls, the Mo–P separation of 2.284(1) Å, is slightly longer than expected for a double bond interaction (*cf.* 2.2212(8) Å in [$MoCp(PClMes^*)(CO)_2$]) [13], while the Re–P distance of 2.581(1) Å remains consistent with the figures expected for an essentially single bond interaction (*cf.* 2.571(2) Å for [$Re(PPh_2)(CO)_3$(N,N′-phen)] [25]). In line with our previous hypotheses, these figures suggest that the π-bonding interaction of the PMes* ligand in **5a.1**, and also in the related heptacarbonyls, is not particularly delocalised over the Mo–P–Re triangle; therefore, the origin of Mo–P elongation must be attributed mainly to the steric pressure created by the $M(CO)_{5-x}(CNR)_x$ (x = 0, 1) fragments in these complexes. As for the CNR group in **5a.1**, we note that the Re–C distance (2.097(5) Å) is almost identical to the corresponding one determined for the azaphosphallene **4a.1**, while the disposition of this ligand nearly perfectly bisects the $Mo(CO)_2$ fragment, surely to minimise the Mes*/CNR repulsions, hence virtually generating a non–crystallographic molecular symmetry plane containing the Mo–P–Re triangle.

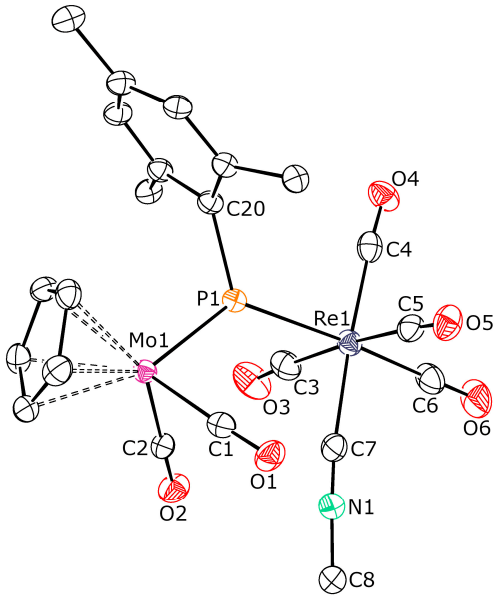


Figure 2. ORTEP drawing (30% probability) of compound **5a.1** with ^{t}Bu and (*p*-C_6H_4OMe) groups (except their C1 atoms) and H atoms omitted.

Table 2. Selected bond distances (Å) and angles (°) for compound **5a.1**.

Parameter	Value	Parameter	Value
Mo1···Re1	4.3573(5)	Mo1–P1–Re1	127.10(5)
Mo1–P1	2.284(1)	P1–Mo1–C1	87.3(1)
Re1–P1	2.581(1)	P1–Mo1–C2	92.4(2)
Mo1–C1	1.945(5)	C1–Mo1–C2	82.4(2)
Mo1–C2	1.957(5)	P1–Re1–C3	84.8(2)
Re1–C3	2.031(7)	P1–Re1–C4	92.3(2)
Re1–C4	2.006(5)	P1–Re1–C5	92.5(2)
Re1–C5	2.005(7)	P1–Re1–C6	176.2(2)
Re1–C6	1.962(7)	P1–Re1–C7	91.4(1)
Re1–C7	2.097(5)	Mo1–P1–C20	109.2(2)
		Re1–P1–C20	123.6(2)

Spectroscopic data for compounds **5** are comparable to each other and totally consistent with the solid-state structure of **5a.1**. The IR pattern of these complexes is almost identical to that of the azaphosphallene complexes **4a.1** and **7a.3-5** due to the presence in all cases of similar and vibrationally isolated $Mo(CO)_2$ and $M(CO)_4(CNR)$ oscillators, although there is a clear difference in the position of the two less energetic bands in the spectrum, which mainly arise from the symmetric and antisymmetric stretches of the dicarbonylic fragment. In fact, these two bands are roughly 30 cm^{-1} lower in energy in compounds **5** when compared to those in **4a.1** or **7a.3-5**, a difference surely caused by the higher electron-releasing properties of the phosphinidene ligand compared to the azaphosphallene one. Indeed, a similar effect can be observed when comparing the IR data for the phosphinidene/azaphosphallene pair **3a.1**/**6a.1**. Finally, we note that the ^{31}P NMR spectra of these complexes are consistent with the presence of asymmetrically coordinated phosphinidene groups of type **E**, displaying moderately deshielded resonances (*ca.* 480 ppm) as expected [6], while the abovementioned non–crystallographic symmetry plane explains the reduced number of signals observed in the ^{1}H and ^{13}C NMR spectra of these complexes.

2.2.3. Characterisation of the Manganese Derivatives **3b.1** and **8b.1**

The spectroscopic data for compound **3b.1** (see Section 3 and Table 1) are indicative of the close structural relationship between this compound and its Re analogues **3a**; hence, a detailed description is not required here. The main spectroscopic difference arises from the change in metal, which is particularly evident in the ^{31}P NMR chemical shift of the phosphinidene group of compound **3b.1**, some 30 ppm higher than that of its Re analogue **3a.1**, a common observation when comparing analogous Re/Mn couples [26]. As for the tris(isocyanide) complex **8b.1**, its IR spectrum displays a set of seven C–N and C–O stretching bands, with those three above 2100 cm^{-1} being assigned to the C–N stretches of linearly coordinated CNR groups, while the relative intensities of these bands are indicative of a meridional disposition of these ligands around the Re atom, and the remaining four bands would arise from essentially uncoupled $Re(CO)_2$ and $Mo(CO)_2$ oscillators. Not unexpectedly, the IR features derived from the $Re(CO)_2(CNR)_3$ fragment in **8b.1** are similar to those observed for the mononuclear complex $[MnBr(CO)_2(CNR)_3]$ [27]. Further support for the proposed arrangement around the Re atom comes from the ^{13}C NMR spectrum, which displays just one resonance for the two Mo–bound carbonyls and another two signals for the Re-bound carbonyls, in agreement with the presence of a symmetry plane containing the metals and the P atom. Finally, the presence of an asymmetrically bridging phosphinidene ligand of type **E** in the molecule is supported by its moderately deshielded ^{31}P–NMR resonance, which is actually not very different from that of the phosphinidene **3b.1**.

3. Materials and Methods

3.1. General Procedures and Starting Materials

All manipulations and reactions were carried out under an argon (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to published procedures and distilled prior to use [28]. Compounds **1a** and **1b** were prepared as described previously [13–15]. All other reagents were obtained from the usual commercial suppliers and used as received unless otherwise stated. Petroleum ether refers to that fraction of distillation in the range 338–343 K. Chromatographic separations were carried out using jacketed columns refrigerated by a cryostat (*ca.* 258 K). Aluminium oxide for chromatography (activity I, 70–290 mesh) was degassed under vacuum prior to use and then mixed under argon with the appropriate amount of water to reach activity IV. IR (Perkin Elmer, Waltham, MA, USA) stretching frequencies of CO and CNR ligands were measured in solution or in Nujol mulls (using CaF_2 windows in both cases) and are referred to as ν(CX)(solvent) or ν(CX)(Nujol), respectively. Nuclear magnetic resonance (NMR) (Bruker, Hamburg, Germany) spectra were routinely recorded at 300.13 (^{1}H), 121.49 (^{31}P{^{1}H}) or 100.63 MHz (^{13}C{^{1}H}) at 295 K, unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hertz. In the description of the NMR resonances, "bs" stands for broad singlet and "fd" for false doublet.

3.2. Preparation of [MoReCp(μ-PMes)(CO)$_5${2κ-CN(p-C$_6$H$_4$OMe)}] (**2a.1**)*

Neat CN(*p*-C_6H_4OMe) (0.006 g, 0.044 mmol) was added to a solution of compound **1a** (0.035 g, 0.044 mmol) in toluene (12 mL) and the mixture was stirred at room temperature for 2 h to give a brown solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:8), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a brown fraction containing small amounts of unreacted **1a**, then a red fraction yielding, after removal of solvents, compound **2a.1** as a red microcrystalline solid (0.018 g, 45%). Elution with dichloromethane/petroleum ether (1:6) gave a green fraction containing small amounts of compound **3a.1**, followed by a yellow fraction containing trace amounts of compound **4a.1**. Anal. Calcd. for $C_{36}H_{41}MoReO_6PN$: C, 48.21; H, 4.61; N, 1.56. Found: C, 48.10; H, 4.53; N, 1.45. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.44 (s, 2 × 1H, C_6H_2), 7.25 [fd, J_{HH} = 9, 2H, H^2(C_6H_4)], 6.89 [fd, J_{HH} = 9, 2H, H^3(C_6H_4)], 5.03 (s, 5H, Cp), 3.82 (s, 3H,

OMe), 1.49, 1.38, 1.33 (3s, 3 × 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 236.0, 233.4 (2s, MoCO), 202.8 (d, J_{CP} = 41, ReCO), 194.5 (s, ReCO), 193.1 (d, J_{CP} = 11, ReCO), 160.5 [s, $C^4(C_6H_4)$], 152.1 [d, J_{CP} = 34, $C^1(C_6H_2)$], 151.5, 151.1, 150.0 [3s, $C^{2,4,6}(C_6H_2)$], 147.7 [bs, $C^1(C_6H_4)$], 147.5 (s, CN), 128.4 [s, $C^2(C_6H_4)$], 122.6 (d, J_{CP} = 5, $C^{3,5}(C_6H_2)$], 122.3 [d, J_{CP} = 3, $C^{5,3}(C_6H_2)$], 115.1 [s, $C^3(C_6H_4)$], 93.8 (s, Cp), 56.1 (s, OMe), 39.0, 38.9, 35.4 [3s, $C^1(^t$Bu)], 33.1, 32.9, 31.2 [3s, $C^2(^t$Bu)].

3.3. Preparation of [MoReCp(μ-PMes)(CO)$_5$(2κ-CN^{t}Bu)] (**2a.2**)*

Neat CN^{t}Bu (4 μL, 0.035 mmol) was added to a solution of compound **1a** (0.025 g, 0.032 mmol) in toluene (8 mL) and the mixture was stirred at room temperature for 1.5 h to produce a red solution. The solvent was then removed under vacuum, the residue extracted with petroleum ether, and the extracts chromatographed on alumina at 258 K. Elution with the same solvent gave a brown fraction containing small amounts of unreacted **1a**. Elution with dichloromethane/petroleum ether (1:20) gave a red fraction yielding, after removal of solvents, compound **2a.2** as a red microcrystalline solid (0.014 g, 52%). Anal. Calcd. for $C_{34}H_{45}Cl_2MoReO_5PN$ (**2a.2**·CH_2Cl_2): C, 43.09; H, 4.93; N, 1.52. Found: C, 42.59; H, 6.52; N, 1.26. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.44 (bs, 2H, C_6H_2), 5.01 (s, 5H, Cp), 1.47, 1.45, 1.40, 1.39 (4s, 4 × 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 236.4 (bs, MoCO), 234.2 (s, MoCO), 203.2 (d, J_{CP} = 32, ReCO), 194.7 (s, ReCO), 193.6 (d, J_{CP} = 12, ReCO), 152.3 [d, J_{CP} = 34, $C^1(C_6H_2)$], 151.4, 151.3 [2s, $C^{2,6}(C_6H_2)$], 150.0 [s, $C^4(C_6H_2)$], 136.6 (bs, CN), 122.6, 122.3 [2bs, $C^{3,5}(C_6H_2)$], 93.7 (s, Cp), 38.9 [s, $3C^1(^t$Bu)], 35.4 [s, $C^1(N^t$Bu)], 33.4, 33.2, 31.3, 30.6 [4s, $C^2(^t$Bu)].

3.4. Preparation of [MoReCp(μ-PMes)(CO)$_5${2κ-CN(p-C$_6$H$_4$OMe)}$_2$] (**3a.1**)*

Neat CN(*p*-C_6H_4OMe) (0.004 g, 0.030 mmol) was added to a solution of compound **1a** (0.029 g, 0.025 mmol) in toluene (5 mL) and the mixture was stirred at room temperature. Other two additions of neat CN(*p*-C_6H_4OMe) (0.004 g, 0.030 mmol) were made to the solution after 3 and 5 h, respectively, obtaining a green solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:4), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a green fraction, yielding, after removal of solvents, compound **3a.1** as a green microcrystalline solid (0.014 g, 54%). Anal. Calcd. for $C_{44.5}H_{49}ClMoReO_7PN_2$ (**3a.1**·0.5CH_2Cl_2): C, 49.84; H, 4.61; N, 2.61. Found: C, 49.38; H, 4.24; N, 2.99. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.42 [fd, J_{HH} = 9, 4H, $H^2(C_6H_4)$], 7.33 (s, 2H, C_6H_2), 6.92 [fd, J_{HH} = 9, 4H, $H^3(C_6H_4)$], 5.04 (s, 5H, Cp), 3.83 (s, 6H, OMe), 1.50 (s, 18H, *o*-^{t}Bu), 1.36 (s, 9H, *p*-^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 251.2 (d, J_{CP} = 13, MoCO), 190.1 (bs, 3ReCO), 166.3 [d, J_{CP} = 59, $C^1(C_6H_2)$], 160.8 [s, $C^1(C_6H_4)$], 148.2 [s, $C^4(C_6H_4)$], 147.6 [s, $C^2(C_6H_2)$], 143.4 (bs, 2CN), 128.9 [s, $C^2(C_6H_4)$], 121.9 [s, $C^3(C_6H_2)$], 115.1 [s, $C^3(C_6H_4)$], 94.6 (s, Cp), 56.1 (s, 2OMe), 39.7 [s, C^1(*o*-^{t}Bu)], 36.0 [s, C^2(*o*-^{t}Bu)], 35.1 [s, C^1(*p*-^{t}Bu)], 31.3 [s, C^2(*p*-^{t}Bu)].

3.5. Preparation of [MoReCp(μ-PMes)(CO)$_5$(2κ-CN^{t}Bu)$_2$] (**3a.2**)*

Neat CN^{t}Bu (12 μL, 0.106 mmol) was added to a solution of compound **1a** (0.030 g, 0.038 mmol) in toluene (8 mL) and the mixture was stirred at room temperature for 1 h to give a green solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:3), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a brown fraction containing small amounts of unreacted **1a**, then a second green fraction yielding, after removal of solvents, compound **3a.2** as a green microcrystalline solid (0.023 g, 66%). Anal. Calcd. for $C_{38}H_{52}MoReO_5PN_2$: C, 49.08; H, 5.64; N, 3.01. Found: C, 48.06; H, 5.41; N, 2.76. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.31 (s, 2H, C_6H_2), 5.02 (s, 5H, Cp), 1.57 (s, 18H, 2CN^{t}Bu), 1.52 (s, 18H, *o*-^{t}Bu), 1.36 (s, 9H, *p*-^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 251.0 (d, J_{CP} = 14, MoCO), 190.9 (s, 2ReCO), 187.7 (d, J_{CP} = 34, ReCO), 166.9 [d, J_{CP} = 59, $C^1(C_6H_2)$], 148.1 [s, $C^2(C_6H_2)$], 147.2 [s, $C^4(C_6H_2)$], 132.8 (bs, 2CN), 121.6 [s, $C^3(C_6H_2)$], 94.4 (s, Cp), 39.7 [s, C^1(*o*-^{t}Bu)], 36.3 [s, C^2(*o*-^{t}Bu)], 35.0 [s, C^1(*p*-^{t}Bu)], 31.3 [s, C^2(*p*-^{t}Bu) + $C^1(N^t$Bu)], 30.6 [s, $C^2(N^t$Bu)].

*3.6. Preparation of [MoReCp{μ-η²$_{P,C}$:κ¹$_P$-PMes*CN(p-C_6H_4OMe)}(CO)$_6${2κ-CN(p-C_6H_4OMe)}] (**4a.1**)*

Neat CN(*p*-C_6H_4OMe) (0.016 g, 0.120 mmol) was added to a solution of compound **1a** (0.030 g, 0.038 mmol) in toluene (8 mL), and the mixture was stirred at 273 K for 3 h to give an orange solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:2), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave first a green fraction containing small amounts of **3a.1**, and then a yellow fraction yielding, after removal of solvents, compound **4a.1** as a yellow microcrystalline solid (0.030 g, 74%). The crystals of **4a.1** used in the X-ray diffraction study were grown by the slow diffusion of layers of petroleum ether and diethyl ether into a concentrated toluene solution of the complex at 253 K. Anal. Calcd. for $C_{45}H_{48}MoReO_8PN_2$: C, 51.09; H, 4.57; N, 2.65. Found: C, 50.85; H, 4.30; N, 2.33. υ(CX)(Nujol): 2194 (w, C–N), 2101 (m), 2025 (s), 2014 (vs), 1968 (s), 1915 (s), 1846 (s). ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 7.37 [fd, J_{HH} = 9, 2H, H^2(C_6H_4)], 7.22 (dd, J_{HP} = 3, J_{HH} = 2, 1H, C_6H_2), 7.19 (d, J_{HH} = 2, 1H, C_6H_2), 6.88 [fd, J_{HH} = 9, 2H, H^3(C_6H_4)], 6.90–6.86 (AA'BB' m, J_{AB} = 9, 4H, C_6H_4), 4.76 (s, 5H, Cp), 3.81, 3.79 (2s, 2 × 3H, OMe), 1.84, 1.61, 1.28 (3s, 3 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.63 MHz): δ 249.0 (d, J_{CP} = 21, MoCO), 239.3 (s, MoCO), 225.0 (d, J_{CP} = 76, PCN), 185.4 (d, J_{CP} = 6, 2ReCO), 184.8 (d, J_{CP} = 8, ReCO), 180.3 (d, J_{CP} = 45, ReCO), 161.3 [s, C^4(C_6H_4)], 160.1 [d, J_{CP} = 13, C^{2,6}(C_6H_2)], 156.4 [s, C^4(C_6H_2)], 156.3 [s, C^4(C_6H_4)], 148.7 [d, J_{CP} = 26, C^1(C_6H_2)], 148.3 (bs, ReCN), 147.5 [d, J_{CP} = 3, C^{6,2}(C_6H_2)], 143.0 [d, J_{CP} = 30, C^1(C_6H_4)], 128.8 [s, C^2(C_6H_4)], 124.0 [d, J_{CP} = 6, C^{3,5}(C_6H_2)], 122.3 [d, J_{CP} = 9, C^{5,3}(C_6H_2)], 122.0 [s, C^2(C_6H_4)], 119.5 [bs, C^1(C_6H_4)], 115.2, 113.7 [2s, C^3(C_6H_4)], 91.8 (s, Cp), 56.1, 55.7 (2s, OMe), 41.2, 40.5 [2s, C^1(^{t}Bu)], 35.5 [d, J_{CP} = 4, C^2(^{t}Bu)], 34.9 [s, C^1(^{t}Bu)], 34.7, 30.9 [2s, C^2(^{t}Bu)].

3.7. Preparation of [MoReCp(μ-PMes)(CO)$_6${2κ-CN(p-C_6H_4OMe)}] (**5a.1**)*

A freshly prepared solution of compound **4a.1** (0.020 g, 0.019 mmol) in toluene (8 mL) was transferred into a Schlenk tube equipped with a Young valve, and the solution was heated at 333 K for 3 h to produce a green solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:4), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a green fraction, yielding, after removal of solvents, compound **5a.1** as a green microcrystalline solid (0.012 g, 71%). The crystals of **5a.1** used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd. for $C_{37}H_{41}MoReO_7PN$: C, 48.05; H, 4.47; N, 1.51. Found: C, 48.87; H, 3.09; N, 1.17. ^{1}H NMR (CD_2Cl_2, 300.09 MHz): δ 7.39 [fd, J_{HH} = 9, 2H, H^2(C_6H_4)], 7.34 (s, 2H, C_6H_2), 6.93 [fd, J_{HH} = 9, 2H, H^3(C_6H_4)], 5.13 (s, 5H, Cp), 3.84 (s, 3H, OMe), 1.53 (s, 18H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.63 MHz): δ 250.5 (d, J_{CP} = 15, MoCO), 186.8 (s, ReCO), 185.5 (d, J_{CP} = 4, 2ReCO), 183.5 (d, J_{CP} = 32, ReCO), 165.5 [d, J_{CP} = 55, C^1(C_6H_2)], 161.3 [s, C^4(C_6H_4)], 148.3 [s, C^{2,4}(C_6H_2)], 148.2 [s, C^1(C_6H_4)], 139.4 (bs, ReCN), 129.0 [s, C^2(C_6H_4)], 122.3 [s, C^3(C_6H_2)], 115.2 [s, C^3(C_6H_4)], 94.9 (s, Cp), 56.2 (s, OMe), 39.8 [s, C^1(*o*-^{t}Bu)], 35.9 [s, C^2(*o*-^{t}Bu)], 35.1 [s, C^1(*p*-^{t}Bu)], 31.3 [s, C^2(*p*-^{t}Bu)].

3.8. Preparation of [MoReCp(μ-PMes)(CO)$_6$(2κ-CN^{t}Bu)] (**5a.2**)*

A solution of compound **1a** (0.040 g, 0.051 mmol) in toluene (8 mL) was cooled down to 273 K, then neat CN^{t}Bu (12 μL, 0.106 mmol) was added, and the mixture was stirred at 273 K for 9 h to give a green solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:8), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a green fraction, yielding, after removal of solvents, compound **5a.2** as a green microcrystalline solid (0.025 g, 53%). Elution with dichloromethane/petroleum ether (1:3) gave a green fraction yielding, after removal of solvents, compound **3a.2** as a green microcrystalline solid (0.010 g, 23%). Satisfactory elemental analysis of compound **5a.2** has not been obtained due

to persistent contamination of the solid material. ^{1}H NMR (CD_2Cl_2, 300.09 MHz): δ 7.32 (s, 2H, C_6H_2), 5.13 (s, 5H, Cp), 1.56 (s, 9H, CN^{t}Bu), 1.55 (s, 18H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 250.4 (d, J_{CP} = 15, MoCO), 187.0 (s, ReCO), 185.8 (s, 2ReCO), 184.4 (d, J_{CP} = 31, ReCO), 165.8 [d, J_{CP} = 55, $C^1(C_6H_2)$], 148.3 [s, $C^2(C_6H_2)$], 148.0 [s, $C^4(C_6H_2)$], 128.2 (bs, ReCN), 122.1 [s, $C^3(C_6H_2)$], 94.8 (s, Cp), 39.7 [s, C^1(*o*-^{t}Bu)], 36.0 [s, C^2(*o*-^{t}Bu) + $C^1(^t$Bu)], 35.1 [s, $C^1(^t$Bu)], 31.3, 30.3 [2s, $C^2(^t$Bu)].

*3.9. Preparation of [MoReCp{μ-η$^2_{P,C}$:κ^1_P-PMes*CN(p-C$_6$H$_4$OMe)}(CO)$_5${2κ-CN(p-C$_6$H$_4$OMe)}$_2$] (**6a.1**)*

Neat CN(*p*-C_6H_4OMe) (0.030 g, 0.225 mmol) was added to a solution of compound **1a** (0.030 g, 0.038 mmol) in toluene (8 mL), and the mixture was stirred at room temperature for 2 h to give an orange solution that contains a mixture of complexes **4a.1** and **6a.1**. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:6), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave first a yellow fraction, yielding, after removal of solvents, compound **4a.1** as a yellow microcrystalline solid (0.020 g, 50%). Then, a second yellow fraction was obtained, yielding, after removal of solvents, compound **6a.1** as a yellow microcrystalline solid (0.020 g, 45%). Anal. Calcd. for $C_{54}H_{59}MoReO_8PN_3$: C, 48.66; H, 4.46; N, 3.15. Found: C, 48.57; H, 2.56; N, 3.08. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ 7.46, 7.39 (2d, J_{HH} = 9, 2 x 2H, C_6H_4), 7.16 (s, 2H, C_6H_2), 6.90–6.87 (m, 4H, C_6H_4), 6.82–6.78 (AA'BB' m, J_{AB} = 10, 4H, C_6H_4), 4.71 (s, 5H, Cp), 3.81 (s, 6H, OMe), 3.77 (s, 3H, OMe), 1.83, 1.63, 1.28 (3s, 3 x 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 248.9 (d, J_{CP} = 20, MoCO), 240.0 (s, MoCO), 225.8 (d, J_{CP} = 74, PCN), 188.7 (d, J_{CP} = 7, ReCO), 188.1 (d, J_{CP} = 5, ReCO), 183.6 (d, J_{CP} = 51, ReCO), 160.9 [s, $2C^4(C_6H_4)$], 160.0 [d, J_{CP} = 12, $C^{2,6}(C_6H_2)$], 156.4 [s, $C^4(C_6H_2)$], 155.8 [s, $C^4(C_6H_4)$], 149.7 [d, J_{CP} = 24, $C^1(C_6H_2)$], 146.8 [s, $C^{6,2}(C_6H_2)$], 144.1, 143.3 (2bs, ReCN), 143.3 [d, J_{CP} = 33, $C^1(C_6H_4)$], 128.7, 128.6 [2s, $C^2(C_6H_4)$], 123.6 [d, J_{CP} = 4, $C^{3,5}(C_6H_2)$], 122.1 [s, $C^2(C_6H_4)$], 121.8 [d, J_{CP} = 9, $C^{5,3}(C_6H_2)$], 120.3 [bs, $2C^1(C_6H_4)$], 115.1, 115.0, 113.5 [3s, $C^3(C_6H_4)$], 91.6 (s, Cp), 56.1 (s, 2OMe), 55.7 (s, OMe), 41.2, 40.4, 34.8 [3s, $C^1(^t$Bu)], 35.3 [d, J_{CP} = 2, $C^2(^t$Bu)], 34.7, 30.9 [2s, $C^2(^t$Bu)].

*3.10. Preparation of [MoReCp{μ-η$^2_{P,C}$:κ^1_P-PMes*CN(o-C$_6$H$_4$Me)}(CO)$_6${2κ-CN(p-C$_6$H$_4$OMe)}] (**7a.3**)*

A solution of compound **5a.1** (0.020 g, 0.022 mmol) in toluene (5 mL) was cooled down to 273 K, then neat CN(*o*-C_6H_4Me) (6 μL, 0.048 mmol) was added, and the mixture was stirred at 273 K for 4 h to give an orange solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:4), and the extracts chromatographed on alumina at 258 K. Elution with dichloromethane/petroleum ether (1:3) gave a yellow fraction yielding, after removal of solvents, compound **7a.3** as a yellow microcrystalline solid (0.012 g, 55%). This solid material was shown (spectroscopically) to contain small amounts of unidentified products. ν(CX)(toluene): 2178 (w, C–N), 2097 (m), 2027 (s, sh), 2011 (vs), 1974 (m), 1931 (m), 1850 (m). ^{1}H NMR (CD_2Cl_2, 300.09 MHz): δ 7.36 [fd, J_{HH} = 9, 2H, $H^2(C_6H_4)$], 7.22–7.09 [m, 5H, C_6H_2 + 3H(C_6H_4)], 6.90 [fd, J_{HH} = 9, 2H, $H^3(C_6H_4)$], 6.48 [d, J_{HH} = 8, 1H, H(C_6H_4)], 4.77 (s, 5H, Cp), 3.81 (s, 3H, OMe), 2.28 (s, 3H, Me), 1.84, 1.62, 1.30 (3s, 3 x 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 248.5 (d, J_{CP} = 21, MoCO), 238.4 (s, MoCO), 224.4 (d, J_{CP} = 77, PCN), 185.5 (s, ReCO), 185.1 (d, J_{CP} = 7, 2ReCO), 180.2 (d, J_{CP} = 45, ReCO), 161.4 [s, $C^4(C_6H_4)$], 160.1 [d, J_{CP} = 13, $C^{2,6}(C_6H_2)$], 156.5 [s, $C^4(C_6H_2)$], 154.4 [d, J_{CP} = 24, $C^1(C_6H_2)$], 148.3 [d, J_{CP} = 8, $C^{6,2}(C_6H_2)$], 147.6 [s, $C^1(C_6H_4)$], 142.4 [d, J_{CP} = 28, C^1(*o*-tol)], 140.0 (bs, ReCN), 130.5 [s, C^2(*o*-tol)], 130.0 [s, C^3(*o*-tol)], 128.8 [s, $C^2(C_6H_4)$], 125.4 [s, C^5(*o*-tol)], 123.9 [d, J_{CP} = 6, $C^{3,5}(C_6H_2)$], 123.0 [s, C^4(*o*-tol)], 122.5 [d, J_{CP} = 10, $C^{5,3}(C_6H_2)$], 119.8 [s, C^6(*o*-tol)], 115.3 [s, $C^3(C_6H_4)$], 92.1 (s, Cp), 56.2 (s, OMe), 41.5, 40.6, 35.9 [3s, $C^1(^t$Bu)], 35.6 [d, J_{CP} = 4, $C^2(^t$Bu)], 35.1, 30.9 [2s, $C^2(^t$Bu)], 19.0 (s, Me).

*3.11. Preparation of [MoReCp(μ-η²$_{P,C}$:κ¹$_P$-PMes*CN^{i}Pr)(CO)$_6${2κ-CN(p-C$_6$H$_4$OMe)}] (**7a.4**)*

Compound **7a.4** was prepared in situ for NMR characterisation by mixing compound **5a.1** (0.020 g, 0.022 mmol) and CN^{i}Pr (4 μL, 0.042 mmol) in tol-d_8 at 273 K in an NMR tube equipped with a Young's valve. Removal of solvent under vacuum caused the progressive elimination of CN^{i}Pr, and the concomitant decomposition of **7a.4** to regenerate the parent compound **5a.1**. ^{1}H NMR (tol-d_8, 300.09 MHz): δ 7.27, 7.23 (2s, 2 × 1H, C$_6$H$_2$), 6.94 [fd, J_{HH} = 9, 2H, H^2(C$_6$H$_4$)], 6.26 [fd, J_{HH} = 9, 2H, H^3(C$_6$H$_4$)], 4.70 (s, 5H, Cp), 4.16 (sept, J_{HH} = 6, 1H, CH), 3.02 (s, 3H, OMe), 1.95, 1.89, 1.22 (3s, 3 × 9H, ^{t}Bu), 1.54, 1.53 (2d, J_{HH} = 6, 2 × 3H, Me). ^{13}C{^{1}H} NMR (tol-d_8, 100.63 MHz): δ 249.6 (d, J_{CP} = 21, MoCO), 241.4 (s, MoCO), 211.4 (d, J_{CP} = 78, PCN), 185.4 (d, J_{CP} = 4, ReCO), 185.0 (d, J_{CP} = 8, ReCO), 184.8 (d, J_{CP} = 6, ReCO), 180.1 (s, ReCO), 160.9, 156.9 [2s, C^{2,6}(C$_6$H$_2$)], 148.4 [s, C^1(C$_6$H$_4$)], 147.9 (bs, ReCN), 147.2 [s, C^4(C$_6$H$_4$)], 142.8 [d, J_{CP} = 35, C^1(C$_6$H$_2$)], 123.3 [d, J_{CP} = 6, C^{3,5}(C$_6$H$_2$)], 122.6 [d, J_{CP} = 9, C^{5,3}(C$_6$H$_2$)], 114.8 [s, C^2(C$_6$H$_4$)], 114.7 [s, C^3(C$_6$H$_4$)], 91.2 (s, Cp), 62.1 (d, J_{CP} = 24, CH), 54.9 (s, OMe), 41.6, 40.9, 34.5 [3s, C^1(^{t}Bu)], 36.1, 35.5, 30.9 [3s, C^2(^{t}Bu)], 25.3, 24.9 (2s, Me); the resonance for the C^4(C$_6$H$_2$) carbon could not be unambiguously identified in this spectrum.

*3.12. Preparation of [MoReCp{μ-η²$_{P,C}$:κ¹$_P$-PMes*CN(p-C$_6$H$_4$OMe)}(CO)$_6$(2κ-CN^{t}Bu)] (**7a.5**)*

A solution of compound **5a.2** (0.020 g, 0.023 mmol) in toluene (8 mL) was cooled down to 273 K, then neat CN(*p*-C$_6$H$_4$OMe) (0.009 g, 0.068 mmol) was added, and the mixture was stirred at 273 K for 3 h to give an orange solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:4), and the extracts chromatographed on alumina at 258 K. Elution with the same solvent mixture gave a yellow fraction, yielding, after removal of solvents, compound **7a.5** as a yellow microcrystalline solid (0.015 g, 65%). ^{1}H NMR (CD$_2$Cl$_2$, 400.13 MHz): δ 7.20 (d, J_{HH} = 3, 1H, C$_6$H$_2$), 7.17 (d, J_{HH} = 2, 1H, C$_6$H$_2$), 6.92, 6.85 (AA'BB' m, J_{AB} = 9, 4H, C$_6$H$_4$), 4.74 (s, 5H, Cp), 3.79 (s, 3H, OMe), 1.85, 1.62, 1.48, 1.29 (4s, 4 × 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.63 MHz): δ 248.7 (d, J_{CP} = 23, MoCO), 239.5 (s, MoCO), 225.2 (d, J_{CP} = 73, PCN), 186.0, 184.7, 184.5 (3s, 3ReCO), 180.5 (d, J_{CP} = 48, ReCO), 160.3 [d, J_{CP} = 13, C^{2,6}(C$_6$H$_2$)], 156.4 [s, C^4(C$_6$H$_2$)], 156.2 [s, C^4(C$_6$H$_4$)], 148.9 [d, J_{CP} = 26, C^1(C$_6$H$_2$)], 147.3 [s, C^{6,2}(C$_6$H$_2$)], 142.7 [d, J_{CP} = 29, C^1(C$_6$H$_4$)], 123.8 [d, J_{CP} = 5, C^{3,5}(C$_6$H$_2$)], 122.2 [d, J_{CP} = 10, C^{5,3}(C$_6$H$_2$)], 121.9 [s, C^2(C$_6$H$_4$)], 113.7 [s, C^3(C$_6$H$_4$)], 91.7 (s, Cp), 55.7 (s, OMe), 41.3, 40.5, 36.0, 34.8 [4s, C^1(^{t}Bu)], 35.7, 34.7, 30.9, 30.4 [4s, C^2(^{t}Bu)].

*3.13. Reaction of **1b** with Excess CN(p-C$_6$H$_4$OMe)*

A solution of compound **1b** (0.030 g, 0.045 mmol) in toluene (8 mL) was cooled down to 273 K, then neat CN(*p*-C$_6$H$_4$OMe) (0.018 g, 0.135 mmol) was added, and the mixture was stirred at 273 K for 30 min to produce a brown solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:4), and the extracts chromatographed on alumina at 258 K. Elution with dichloromethane/petroleum ether (1:10) initially and then a 1:6 mixture gave small brown and black fractions, respectively, of unidentified products. Elution with dichloromethane/petroleum ether (1:3) gave a green fraction, yielding, after removal of solvents, compound **3b.1** as a green microcrystalline solid (0.012 g, 30%). Elution with the same solvent mixture gave a second green fraction, yielding, after the removal of solvents, compound **8b.1** as a green microcrystalline solid (0.010 g, 22%). Satisfactory elemental analysis for these compounds was not obtained due to persistent contamination of the solid materials and progressive decomposition of the solid samples. *Spectroscopic data for **3b.1***: ^{1}H NMR (CD$_2$Cl$_2$, 400.13 MHz): δ 7.43 [fd, J_{HH} = 9, 4H, H^2(C$_6$H$_4$)], 7.33 (s, 2H, C$_6$H$_2$), 6.91 [fd, J_{HH} = 9, 4H, H^3(C$_6$H$_4$)], 5.02 (s, 5H, Cp), 3.83 (s, 6H, OMe), 1.52 (s, 18H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.63 MHz): δ 250.7 (d, J_{CP} = 12, 2MoCO), 215.0 (bs, 3MnCO), 168.6 (d, J_{CP} = 66, C^1(C$_6$H$_2$)], 165.9 (bs, 2MnCN), 160.5 [s, C^1(C$_6$H$_4$)], 148.0 [s, C^4(C$_6$H$_4$)], 147.9 [s, C^4(C$_6$H$_2$)], 128.5 [s, C^2(C$_6$H$_4$)], 122.0 [s, C^3(C$_6$H$_2$)], 115.0 [s, C^3(C$_6$H$_4$)], 94.4 (s, Cp), 56.1 (s, OMe), 39.7 [s, C^1(*o*-^{t}Bu)], 35.9 [s, C^2(*o*-^{t}Bu)], 35.1 [s, C^1(*p*-^{t}Bu)], 31.2 [s, C^2(*p*-^{t}Bu)]. *Spectroscopic data for **8b.1***: ^{1}H NMR

(CD_2Cl_2, 300.09 MHz): δ 7.44 [fd, J_{HH} = 9, 2H, $H^2(C_6H_4)$], 7.32 (s, 2H, C_6H_2), 7.31 [fd, J_{HH} = 9, 2H, $H^3(C_6H_4)$], 6.91, 6.87 (2d, J_{HH} = 9, 2 x 4H, $2C_6H_4$), 4.96 (s, 5H, Cp), 3.82 (s, 3H, OMe), 3.81 (s, 6H, 2OMe), 1.48 (bs, 18H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.63 MHz): δ 251.3 (d, J_{CP} = 11, 2MoCO), 172.6, 170.3 (2bs, CN), 160.0 [s, $C^1(C_6H_4)$], 159.7 [s, $2C^1(C_6H_4)$], 147.6 [s, $2C^4(C_6H_4)$], 147.3 [s, $C^4(C_6H_4)$], 128.4 [s, $C^2(C_6H_4)$], 128.2 [s, $2C^2(C_6H_4)$], 121.8 [s, $C^3(C_6H_2)$], 114.9 [s, $C^3(C_6H_4)$], 114.8 [s, $2C^3(C_6H_4)$], 94.3 (s, Cp), 56.1 (s, OMe), 56.0 (s, 2OMe), 39.7 [s, C^1(*o*-^{t}Bu)], 35.9 [s, C^2(*o*-^{t}Bu)], 35.1 [s, C^1(*p*-^{t}Bu)], 31.3 [s, C^2(*p*-^{t}Bu)]. Severe broadness made it impossible to identify the resonances expected for the Mn-bound carbonyls or those of the aromatic $C^{1,2,4}(C_6H_2)$ carbons.

3.14. X-ray Structure Determination of Compound ***5a.1***

Data collection for **5a.1** was performed at 153(4) K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K_α radiation (λ = 1.5418 Å) [29]. Images were collected at a 62 mm fixed crystal-detector distance using the oscillation method with 1.00° oscillation and variable exposure time per image (2.0–5.0 s). The data collection strategy was calculated with the program CrysAlis Pro CCD [30]. Data reduction and cell refinement were performed with the program CrysAlis Pro RED [30]. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED (Oxford Diffraction Ltd., Oxford, UK, 2006). Using the program suite WinGX [31], the structure was solved by Patterson interpretation and phase expansion using SHELXL2018/3 [32,33], and refined with full-matrix least squares on F^2 using the same software. Two ^{t}Bu groups and the methoxyphenyl group were found to be disordered. For the methoxyphenyl group, the best solution was obtained by modelling the disorder over two positions with 0.6/0.4 occupancies. The disorder in two positions present in two of the ^{t}Bu groups was modelled by introducing six instead of three carbon atoms in each case with 0.6/0.4 and 0.5/0.5 occupancies, respectively. All non-hydrogen atoms were refined anisotropically, except for atoms involved in the modelled disorders, which were refined isotropically to prevent their temperature factors from becoming non-positive definite, causing the appearance of an A-level alert in the corresponding checkcif file. All hydrogen atoms were geometrically placed and refined using a riding model. CCDC 2283058 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 4 September 2023) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

The reactions of the heterobimetallic phosphinidene-bridged complexes [MoMCp(μ-PMes*)$(CO)_6$] (Mes* = 2,4,6-$C_6H_2{}^tBu_3$; M = Re, Mn) with isocyanides are intricate, with the result depending critically on the reaction conditions (temperature and stoichiometry) as well as on the nature of the added isocyanide, particularly the steric demands of its substituent. Our experiments indicate that these reactions follow three possible pathways: (i) substitution of CO by CNR at the group 7 metal centre; (ii) addition of CNR at the group 7 metal centre and, iii) [2+1] cycloaddition of CNR at the Mo=P bond to form novel azaphosphallene ligands in the unprecedented μ-$\eta^2_{P,C}$:κ^1_P coordination mode. In particular, room temperature reactions are mainly dominated by CO/CNR ligand substitution yielding, in the case of the Re complex, phosphinidene derivatives of type [MoReCp(μ-PMes*)$(CO)_5$(2κ-CNR)], which retain a Mo–Re bond. However, further addition of the incoming reagent is still a viable option even under stoichiometric conditions, leading to bis(isocyanide) phosphinidene derivatives of type [MoMCp(μ-PMes*)$(CO)_5$(2κ-CNR)$_2$] with no metal–metal bond. In the case of the Mn system, the CO/CNR ligand substitution is even more favourable and the only products obtained are the bis– and tris(isocyanide) complexes [MoMnCp(μ-PMes*)$(CO)_{7-n}$(2κ-CNR)$_n$] (R = *p*-C_6H_4OMe, n = 2, 3). For the Re system, on the other hand, a lowering of the temperature partially suppresses the CO substitution processes, so that single or double addition products are preferentially

obtained, with the second addition step taking place at the Mo=P bond of intermediates of type [MoReCp(μ-PMes*)(CO)$_6$(2κ-CNR)] formed first, to give azaphosphallene complexes of type [MoReCp{μ-$\eta^2_{P,C}$:κ^1_P-PMes*CNR)}(CO)$_6$(2κ-CNR)]. The latter process is largely inhibited when the size of the CNR group would cause unbearable steric clashes if placed in between the Cp and Mes* groups (i.e., CN^{t}Bu). In the same vein, we note that no cycloaddition reactions of the CNR ligands to the Mo=P bonds of the metal-metal-bound complexes **1** or their CNR-substituted derivatives seem to be possible in any case, perhaps due to the higher steric constraints derived from the closer approach of the metal fragments in these molecules.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11090364/s1, Crystal data for compound **5a.1** (CCDC 2283058), and IR and NMR spectra for all new compounds (PDF file).

Author Contributions: All authors designed the experiments; M.A.R. and D.G.-V. wrote the paper; P.V. performed the experimental work; and M.A.A. carried out the crystal structure determinations. All authors have read and agreed to the published version of the manuscript.

Funding: We thank the MICIU and AEI of Spain and FEDER for financial support (Project PID2021–123964NB-I00), the Universidad de Oviedo, and Gobierno del Principado de Asturias for a grant (to P.V.).

Data Availability Statement: The data presented in this study are available in the Supplementary Materials.

Acknowledgments: We also thank the X-ray unit of the Universidad de Oviedo for the acquisition of diffraction data.

Conflicts of Interest: The authors declare no conflict of interest.

References and Note

1. Mathey, F.; Duan, Z. Activation of AH bonds (A = B, C, N, O, Si) by using monovalent phosphorus complexes [RP→M]. *Dalton Trans.* **2016**, *45*, 1804–1809. [CrossRef]
2. Aktas, H.; Slootweg, J.C.; Lammertsma, K. Nucleophilic phosphinidene complexes: Access and applicability. *Angew. Chem. Int. Ed.* **2010**, *49*, 2102–2113. [CrossRef]
3. Waterman, R. Metal-phosphido and -phosphinidene complexes in P-E bond-forming reactions. *Dalton Trans.* **2009**, *1*, 18–26. [CrossRef]
4. Mathey, F. Developing the chemistry of monovalent phosphorus. *Dalton Trans.* **2007**, 1861–1868. Available online: https://pubs.rsc.org/en/content/articlelanding/2007/dt/b702063p (accessed on 4 September 2023). [CrossRef]
5. Dillon, K.B.; Mathey, F.; Nixon, J.F. *Phosphorus: The Carbon-Copy*; Wiley: Chichester, UK, 1998.
6. García, M.E.; García-Vivó, D.; Ramos, A.; Ruiz, M.A. Phosphinidene-bridged binuclear complexes. *Coord. Chem. Rev.* **2017**, *330*, 1–36. [CrossRef]
7. Navarro, M.; Moreno, J.J.; Pérez-Jiménez, M.; Campos, J. Small molecule activation with bimetallic systems: A landscape of cooperative reactivity. *Chem. Commun.* **2022**, *58*, 11220–11235. [CrossRef]
8. Sinhababu, S.; Lakliang, Y.; Mankad, N.P. Recent advances in cooperative activation of CO_2 and N_2O by bimetallic coordination complexes or binuclear reaction pathways. *Dalton Trans.* **2022**, *51*, 6129–6147. [CrossRef] [PubMed]
9. Knorr, M.; Jourdain, I. Activation of alkynes by diphosphine- and μ-phosphido spanned heterobimetallic complexes. *Coord. Chem. Rev.* **2017**, *350*, 217–247. [CrossRef]
10. Mankad, N.P. Selectivity effects in bimetallic catalysis. *Chem. Eur. J.* **2016**, *22*, 5822–5829. [CrossRef]
11. Buchwalter, P.; Rosé, J.; Braunstein, P. Multimetallic catalysis based on heterometallic complexes and clusters. *Chem. Rev.* **2015**, *115*, 28–126. [CrossRef]
12. Eisenhart, R.J.; Clouston, L.J.; Lu, C.C. Configuring Bonds between First-Row Transition Metals. *Acc. Chem. Res.* **2015**, *48*, 2885–2894. [CrossRef]
13. Alvarez, M.A.; García, M.E.; García-Vivó, D.; Ruiz, M.A.; Vega, P. Efficient Synthesis and Multisite Reactivity of a Phosphinidene-Bridged Mo−Re Complex. A Platform Combining Nucleophilic and Electrophilic Features. *Inorg. Chem.* **2020**, *59*, 9481–9485. [CrossRef] [PubMed]
14. Alvarez, M.A.; Burgos, M.; García, M.E.; García-Vivó, D.; Ruiz, M.A.; Vega, P. One-Step Synthesis and P−H Bond Cleavage Reactions of the Phosphanyl Complex *syn*-[MoCp{PH-(2,4,6-$C_6H_2{}^tBu_3$)}(CO)$_2$] to Give Heterometallic Phosphinidene-Bridged Derivatives. *Dalton Trans.* **2019**, *48*, 14585–14589. [CrossRef] [PubMed]
15. Alvarez, M.A.; García, M.E.; García-Vivó, D.; Ruiz, M.A.; Vega, P. Heterometallic Phosphinidene-Bridged Complexes Derived from the Phosphanyl Complexes *syn*-[MCp(PHR*)(CO)$_2$] (M = Mo, W; R* = 2,4,6-$C_6H_2{}^tBu_3$). *J. Organomet. Chem.* **2022**, *977*, 122460. [CrossRef]

16. Alvarez, M.A.; García, M.E.; García-Vivó, D.; Ruiz, M.A.; Vega, P. Cycloaddition and C-S Bond Cleavage Processes in Reactions of Heterometallic Phosphinidene-Bridged MoRe and MoMn Complexes with Alkynes and Phenyl Isothiocyanate. *Organometallics* 2023, *in press*. [CrossRef]
17. Alvarez, M.A.; Cuervo, P.M.; García, M.E.; Ruiz, M.A.; Vega, P. P–C, P–N, and M–N Bond Formation Processes in Reactions of Heterometallic Phosphinidene-Bridged MoMn and MoRe Complexes with Diazoalkanes and Organic Azides to Build Three- to Five-Membered Phosphametallacycles. *Inorg. Chem.* **2022**, *61*, 18486–18495. [CrossRef]
18. Seidl, M.; Schiffer, M.; Bodensteiner, M.; Timoshkin, A.Y.; Scheer, M. Reactivity of Bridged Pentelidene Complexes with Isonitriles: A New Way to Pentel-Containing Heterocycles. *Chem. Eur. J.* **2013**, *19*, 13783–13791. [CrossRef]
19. Lv, Y.; Kefalidis, C.E.; Zhou, J.; Maron, L.; Leng, X.; Chen, Y. Versatile Reactivity of a Four-Coordinate Scandium Phosphinidene Complexes: Reduction, Addition, and CO Activation Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 14784–14796. [CrossRef] [PubMed]
20. Braterman, P.S. *Metal Carbonyl Spectra*; Academic Press: London, UK, 1975.
21. Davies, M.S.; Aroney, M.J.; Buys, I.E.; Hambley, T.W.; Calvert, J.L. X-ray Crystallographic Study of the Complexes $Cr(PCl_3)(CO)_5$, $W(PCl_3)(CO)_5$, $Cr(PBr_3)(CO)_5$, $W(PBr_3)(CO)_5$ and $Mo(PMe_3)(CO)_5$: Insight into π-Acceptance by Phosphorus. *Inorg. Chem.* **1995**, *34*, 330–336. [CrossRef]
22. Aktas, H.; Mulder, J.; de Kanter, F.J.J.; Slootweg, J.C.; Schakel, M.; Ehlers, A.W.; Lutz, M.; Spek, A.L.; Lammertsma, K. Iridium Phosphinidene Complexes: A Comparison with Iridium Imido Complexes in Their Reaction with Isocyanides. *J. Am. Chem. Soc.* **2009**, *131*, 13531–13537. [CrossRef] [PubMed]
23. Cordero, B.; Gómez, V.; Platero-Prats, A.E.; Revés, M.; Echevarría, J.; Cremades, E.; Barragán, F.; Alvarez, S. Covalent Radii Revisited. *Dalton Trans.* **2008**, *21*, 2832–2838. [CrossRef]
24. David, M.-A.; Alexander, J.B.; Glueck, D.S.; Yap, G.P.A.; Liable-Sands, L.M.; Rheingold, A.L. Phosphaazaallene Dimerization and Phosphaallene Isomerization: Catalysis by Zerovalent Palladium and Platinum Complexes. *Organometallics* **1997**, *16*, 378–383. [CrossRef]
25. Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. New Octahedral Rhenium(I) Tricarbonyl Amido Complexes. *Organometallics* **2002**, *21*, 1966–1974. [CrossRef]
26. Carty, A.J.; McLaughlin, S.A.; Nucciarone, D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J.G., Quin, L.D., Eds.; VCH: Deerfield Beach, FL, USA, 1987; Chapter 16.
27. Treichel, P.M.; Dirreen, G.E.; Mueh, H.J. Manganese(I) isocyanide complexes. *J. Organomet. Chem.* **1972**, *44*, 339–352. [CrossRef]
28. Armarego, W.L.F.; Chai, C. *Purification of Laboratory Chemicals*, 7th ed.; Butterworth-Heinemann: Oxford, UK, 2012.
29. Crystal Data for $C_{37}H_{41}MoNO_7PRe$ (**5a.1**) (M = 924.82 g/mol): Triclinic, space group P$-$1 (no. 2), a = 8.9166(2) Å, b = 12.7525(4) Å, c = 17.1297(5) Å, α = 75.851(3)°, β = 82.477(2)°, γ = 87.540(2)°, V = 1872.33(9) Å^3, Z = 2, T = 153(4) K, $\mu(CuK_\alpha)$ = 9.756 mm^{-1}, D_{calc} = 1.640 g/cm^3, 18192 reflections measured (3.57° $\leq \Theta \leq$ 69.473°), 6940 unique (R_{int} = 0.0548) which were used in all calculations. The final R_1 was 0.0428 ($I > 2\sigma(I)$) and wR_2 was 0.1173 (all data).
30. *CrysAlis Pro*; Oxford Diffraction Ltd.: Oxford, UK, 2006.
31. Farrugia, L.J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838. [CrossRef]
32. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. [CrossRef]
33. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, *71*, 5–8. [CrossRef]