Efficient Synthesis and Multisite Reactivity of a Phosphinidene-Bridged Mo–Re Complex. A Platform Combining Nucleophilic and Electrophilic Features

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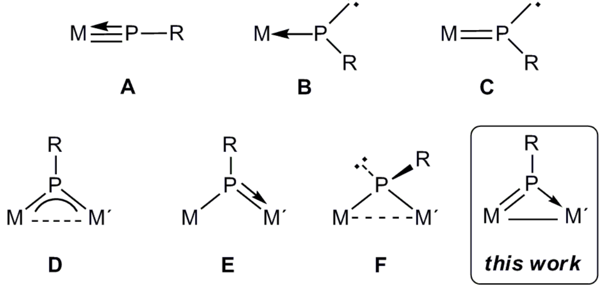
Supporting Information Placeholder

ABSTRACT: The heterometallic complex [MoReCp(μ-PR*)(CO)$_6$] (**3**) was prepared in 60% overall yield from *syn*-[MoCp(PHR*)(CO)$_2$] *via* a 3-step procedure involving complexes *syn*-[MoCp(PClR*)(CO)$_2$] and [MoReCp(μ-PR*)(CO)$_7$] as intermediate species (R* = 2,4,6-$C_6H_2{}^t\mathrm{Bu}_3$). The PR* ligand in **3** displays a novel asymmetric interaction with the dimetal center, involving a double bond with one atom (Mo) and a dative single bond with the other one (Re). Compound **3** underwent thermal isomerization involving a C–H bond cleavage to yield the hydride [MoReCp(μ-H){μ-P(CH$_2$CMe$_2$)C$_6$H$_2{}^t$Bu$_2$}(CO)$_6$], and reacted with I$_2$ to give [MoReCpI$_2$(μ-PR*)(CO)$_6$], which displays a symmetrical phosphinidene bridge. Its reaction with methyl propiolate at 293 K proceeded with [2+2] cycloaddition of the alkyne and decarbonylation, to yield the phosphapropenylidene-bridged complex [MoReCp{μ-$\kappa^2_{\mathrm{P,C}}$:η^3-PR*CHC(CO$_2$Me)}(CO)$_5$] as major product, whereas its reaction with excess CN(4-C$_6$H$_4$OMe) at 273 K proceeded with formal [2+1] cycloaddition of the isocyanide and further isocyanide addition at the Re site to yield complex [MoReCp{μ-$\eta^2_{\mathrm{P,C}}$:κ^1_{P}-PR*CN(4-C$_6$H$_4$OMe)}(CO)$_6${CN(4-C$_6$H$_4$OMe)}], which displays an azaphosphaallene ligand in a novel bridging coordination mode.

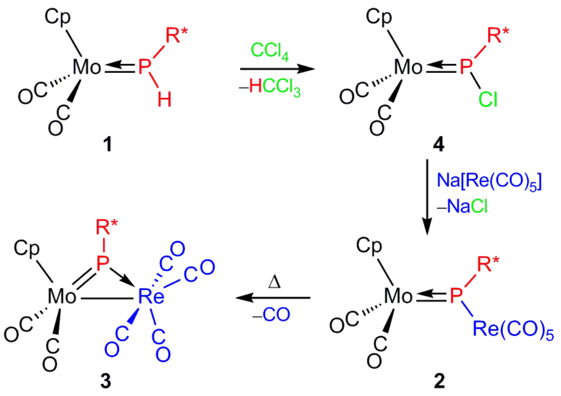
Phosphinidenes (PR) are multifaceted ligands able to bind to transition metal atoms in many different ways.[1] When bound to one or two metal atoms, three extreme coordination modes have been recognized to date in each case, all of them sharing features which provide high reactivity to the corresponding complexes: a low coordination environment around phosphorus, M–P multiple bonding and/or the presence of a lone electron pair at the P site (**A** to **F** in Chart 1). Extensive work on the chemistry of mononuclear complexes, mainly on those of types **B** (so called *electrophilic* ones) and **C** (*nucleophilic* ones), has revealed a high reactivity toward all sorts of organic compounds, whereby many unusual organophosphorus ligands have been built.[2] Although less active than their mononuclear counterparts, PR-bridged binuclear complexes also are able to react with a great variety of organic and inorganic compounds under mild conditions, and in this way a large variety of organophosphorus ligands and heterometallic complexes can be built as well.[1] Most of these studies, however, have been carried out so far on homometallic species (M = M´). Actually, only a few heterometallic PR-bridged complexes are available to date, and their chemical behavior is virtually unexplored.[3-9] Yet, combining different electronic and geometric metal environments, as done in heterometallic complexes,[10] might add cooperative and synergic effects to the reactive M–P–M´ core of these molecules, while enabling modulation of their chemical behavior in new ways. Recently we reported that the photochemical reaction of the phosphanyl complex *syn*-[MoCp(PHR*)(CO)$_2$] (**1**) with [Re$_2$(CO)$_{10}$] yielded the type **E** phosphinidene complex [MoReCp(μ-PR*)(CO)$_7$] (**2**), which could be transformed thermally into the hexacarbonyl [MoReCp(μ-PR*)(CO)$_6$] (**3**), a complex presumably of type **D** and displaying a Mo–Re bond, although the overall yield was rather modest (25%).[9] We viewed this molecule as a good candidate to be used for exploring heterometallic effects in the chemistry of PR-bridged complexes, as it combines two isoelectronic fragments (MoCp(CO)$_2$ and Re(CO)$_4$) having distinct steric and electronic properties. Then we decided to explore its structure and reactivity in detail. This, however, required implementation of a more efficient synthetic procedure for this molecule. As it will be shown below, compound **3** displays structural features and reactivity reminiscent of both nucleophilic and electrophilic mononuclear phosphinidene complexes. These can be in turn related to the asymmetric bonding of the PR ligand in this heterometallic complex, which follows a pattern different from bonding modes previously identified to date (**D** to **F** in Chart 1).

Chart 1. Coordination Modes of Phosphinidene Ligands at Mono and Binuclear Complexes



Compound **3** can be efficiently prepared (60% overall yield) in a three step procedure starting with chlorination of complex **1** using CCl_4, to give the new chlorophosphanyl derivative *syn*-[MoCp(PClR*)(CO)$_2$] (**4**) almost quantitatively (Scheme 1). In the second step, **4** is reacted with the rhenium carbonylate Na[Re(CO)$_5$] to give the heptacarbonyl complex **2**, which is finally transformed into **3** as previously described by us. To our knowledge, the reaction of a halophosphanyl complex with an anionic complex to give a PR-bridged heterometallic derivative (i.e. the step **4**/**2**) has not been previously reported, and therefore adds to the palette of synthetic methods available to build heterometallic phosphinidene-bridged complexes.[9] We note that this procedure also works efficiently by using manganese instead of rhenium. As for the formation of **4**, the synthetic procedure used here is similar to that reported by Malisch to convert the *anti* isomer of compound **1** into ***anti*-4**.[11] The *syn* conformation of Cp and R* groups in **4** has been verified both in solution and through an X-ray study of the complex (see the SI). As expected, **4** displays a quite short Mo–P length of 2.2212(8) Å, only slightly longer than the one determined for its fluorophosphanyl analogue (2.204(1) Å).[12]

Scheme 1. Synthesis of Compound 3



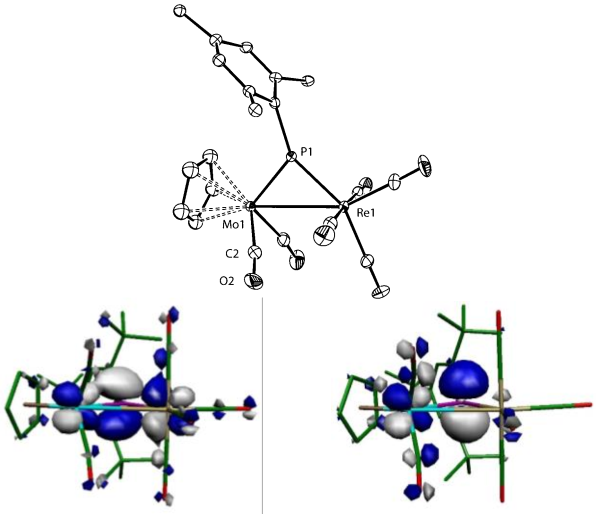
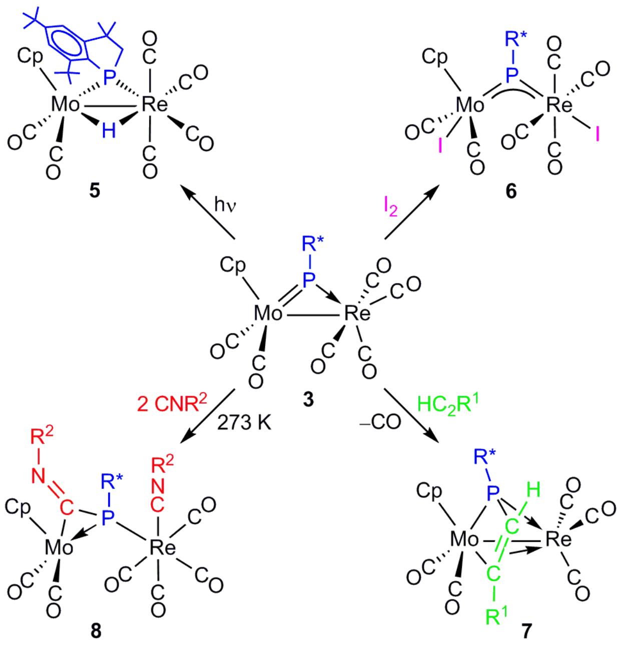


Figure 1. ORTEP diagram (30% probability) of **3**, with H atoms and Me groups omitted. Selected bond lengths (Å): Mo–Re = 3.1745(6); Mo–P = 2.274(1); Re–P = 2.364(1). Below, the ML06-DFT computed HOMO–1 (left, –5.29 eV) and LUMO (right, –3.25 eV) orbitals of **3** are shown.

The crystal structure of **3** confirmed the presence of an intermetallic bonding interaction (Mo–Re = 3.1745(6) Å; cf. 3.172(1) Å in [MoReCp(CO)$_8$]),[13] as predicted on the basis of the 18-electron rule, but revealed a quite asymmetric coordination of the phosphinidene ligand (Figure 1). This was unexpected when considering the isoelectronic nature of the Mo and Re fragments of the complex. Actually, the Mo–P length of 2.274(1) Å is shorter than the one determined in the symmetrical [Mo$_2$Cp$_2$(μ-PR*)(CO)$_4$] (ca. 2.31 Å),[14] while the Re–P length of 2.364(1) Å approaches single-bond values (cf. 2.435(2) Å in [MoReCp(μ-H)(μ-PPh$_2$)(CO)$_6$]).[15] These geometrical features were reproduced in the WRe analogue of **3**,[16] thus pointing to a genuine electronic effect. In agreement with this, a DFT calculation on **3** at the ML06 level (see the SI) revealed that the π-bonding interaction between the P atom and the dimetal center is not delocalized along the Mo–P–Re backbone (type **D** complexes), but essentially localized between the P and Mo atoms, while the LUMO of the molecule can be viewed as the corresponding π-antibonding combination (Figure 1). Thus the best description of the interaction between the phosphinidene ligand and the dimetal center in **3** is one involving a Mo=P double bond, as found in mononuclear nucleophilic complexes (type **C**), and a dative single P→Re bond, as found in mononuclear electrophilic complexes (type **B**), and this can be considered as a new type of interaction in the family of phosphinidene-bridged complexes (Chart 1). In spite of these different M–P interactions, atomic charges at the metal atoms remained comparable to each other (Mulliken charges: +0.27 (Mo), +0.23 (Re), +0.05*e* (P), see the SI).

Scheme 2. Reactivity of Compound 3[a]



[a] R* = 2,4,6-C$_6$H$_2$^{t}Bu$_3$; R^1 = CO$_2$Me; R^2 = 4-C$_6$H$_4$OMe.

Compound **3** reacts with a variety of molecules under mild conditions displaying a remarkable multisite activity, related in part to the ambiphilic nature of the Mo–P–Re interaction discussed above (Scheme 2). First we note that **3** rearranges into its phosphanyl-hydride isomer [MoReCp(μ-H){μ-P(CH$_2$CMe$_2$)C$_6$H$_2$^{t}Bu$_2$}(CO)$_6$] (**5**) (δ_P 84.0, δ_H –12.91

ppm) either photochemically (263 K) or even thermally (385 K), more easily than its Mo_2 analogue $[Mo_2Cp_2(\mu\text{-}PR^*)(CO)_4]$.[17,18] This indicates the operation of some heterometallic effect at facilitating the corresponding C–H bond addition at the P atom,[19] and also resembles the reactivity of mononuclear electrophilic complexes.[2a]

Addition of iodine to compound **3** at 273 K gives the diiodide complex $[MoReCpI_2(\mu\text{-}PR^*)(CO)_6]$ (**6**) in modest yield, this resulting from halogenation of the intermetallic bond and further rearrangement at each metal fragment, to leave each iodine atom *trans* to the bridging phosphinidene ligand (δ_P 757.8 ppm, cf. 673.1 ppm in **3**). An X-ray study of this complex revealed that bonding of the PR* ligand was now much more symmetrical (type **D**), with Mo–P and Re–P distances of 2.384(3) and 2.346(3) Å (see the SI). However, these relatively large values suggest that the π-bonding interaction of the PR* ligand with the dimetal center is largely diminished in this oxidized complex.

Compound **3** reacts readily with different terminal and internal alkynes to give products following from [2+2] cycloaddition steps at the Mo═P bond, thus resembling the chemical behavior of mononuclear nucleophilic complexes (type **C**).[2] This is exemplified by the reaction with methyl propiolate, which proceeds readily at room temperature to give a mixture of the phosphapropenylidene-bridged isomers $[MoReCp\{\mu\text{-}\kappa^2{}_{P,C}{:}\eta^3\text{-}PR^*CHC(CO_2Me)\}(CO)_5]$ (**7**) and $[MoReCp\{\mu\text{-}\kappa^2{}_{P,C}{:}\eta^3\text{-}PR^*C(CO_2Me)CH\}(CO)_5]$ (**7´**) in a ratio of ca. 5:1. The crystal structure of the major isomer (see the SI) confirmed that the resulting P–C coupling involved the less hindered terminal carbon of the alkyne to give an almost flat metallaphosphacyclobutene MoPCC ring, which is further bound to a $Re(CO)_3$ fragment through the remaining C–C double bond (C–C = 1.399(4) Å). This coordination mode of a phosphapropenylidene ligand has been only observed previously in diiron complexes of type $[Fe_2\{\mu\text{-}\kappa^2{}_{P,C}{:}\eta^3\text{-}P^tBuCRCR'\}(CO)_6]$.[20] In the case of **7**, the distinct electronic needs of the Mo and Re fragments require a stronger binding of the P atom to rhenium in order to fulfill the 18-electron rule, which is in agreement with the shorter Re–P length of 2.4538(6) Å (cf. Mo–P = 2.5671(7) Å).

Reactions of compound **3** with isocyanides at room temperature give CO-substitution products of no particular interest. However, [2+1] cycloaddition products are formed when working at lower temperatures to prevent displacement of CO. For instance, reaction of **3** with excess $CN(4\text{-}C_6H_4OMe)$ at 273 K gives the azaphosphaallene derivative $[MoReCp\{\mu\text{-}\eta^2{}_{P,C}{:}\kappa^1{}_P\text{-}PR^*CN(4\text{-}C_6H_4OMe)\}(CO)_6\{CN(4\text{-}C_6H_4OMe)\}]$ (**8**) as major product. Compound **8** is a rare example of an azaphosphaallene-bridged complex and displays a novel bridging coordination mode which involves $\kappa^1{}_P$ coordination to one metal and $\eta^2{}_{P,C}$ coordination to the other one. Previous examples of related binuclear species are restricted to a few ditungsten[21] and discandium complexes,[22] which displayed $\mu\text{-}\kappa^1{}_P{:}\kappa^1{}_P$-, $\mu\text{-}\kappa^1{}_P{:}\kappa^1{}_N$- or $\mu\text{-}\kappa^1{}_P{:}\eta^2{}_{N,C}$- coordination of their RP═C═NR´ ligands. Compound **8** gives rise to a strongly shielded ^{31}P NMR resonance at –268.1 ppm, which is a diagnostic signature for the retention in solution of the 3-membered PCMo ring ($\eta^2{}_{P,C}$ coordination) found in the crystal (Mo–P = 2.544(1); Mo–C = 2.107(4); P–C = 1.796 (4) Å; see the SI). This chemical shift still is some 50-80 ppm lower than those of mononuclear complexes of type $[IrCp^*(CNR)(\eta^2{}_{P,C}\text{-}PR'CNR)]$.[23] At the same time, the ^{13}C NMR resonance of the ring carbon in **8** appears strongly deshielded and coupled to the P atom (δ_C 225.0 ppm; J_{CP} = 76 Hz). The scope and sequence of the elemental steps leading to compound **8** are now under current study.

In summary, we have implemented an efficient synthesis for the heterometallic complex **3**, and unveiled a new type of interaction of a phosphinidene ligand with two metal atoms, it involving a M═P double bond with one of them, as found in mononuclear nucleophilic complexes, and a dative single P→M´ bond with the other one, as found in mononuclear electrophilic complexes. Nucleophilic-like behavior is found in reactions with alkynes and isocyanides, which formally involve [2+2] and [2+1] cycloadditions, with the latter yielding bridging azaphosphaallene ligands in a novel coordination mode. Electrophilic-like behavior can be traced in the thermal or photochemical rearrangement of **3** into its hydride isomer **5**, since this likely involves a C–H bond cleavage step at the P site. Yet, the intermetallic bond itself is another reaction site of **3**. Interestingly, addition of iodine to this heterometallic bond changes the π bonding interaction of the PR ligand into one of the delocalized type **D**, thus proving the subtle role of the metal environment on the M–P interactions in these heterometallic complexes.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

Preparative procedures, spectroscopic and microanalytical data for new compounds, crystallographic data and results of DFT calculations (PDF)

Cartesian coordinates for all computed species (XYZ)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interests.

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Table of Contents Graphic and Synopsis

The title complex displays a novel coordination mode of the phosphinidene ligand involving a Mo═P double bond, as found in mononuclear nucleophilic complexes, and a dative single P→Re bond, as found in mononuclear electrophilic complexes. Nucleophilic behavior is observed in reactions with alkynes and isocyanides, which render [2+2] and [2+1] cycloaddition products, respectively.