

COMMUNICATION

One-Step Synthesis and P–H Bond Cleavage Reactions of the Phosphanil Complex *syn*-[MoCp{PH(2,4,6-C₆H₂^tBu₃)}(CO)₂] to Give Heterometallic Phosphinidene-Bridged Derivatives.

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Photolysis of [Mo₂Cp₂(CO)₆] and PH₂R* (R* = 2,4,6-C₆H₂^tBu₃) yielded the title complex, which turned to be a versatile precursor of novel heterometallic phosphinidene-bridged complexes via three different P–H bond activation processes: photolysis, deprotonation and reduction. In this way the new complexes [MoReCp(μ-PR*)(CO)_n] (n = 6,7), [MoFeCp₂(μ-PR*)(CO)_m] (m = 3, 4) and [MoAuCp(μ-PR*)(CO)₂{P(*p*-tol)₃}] were prepared.

Binuclear complexes of the transition metals bearing bridging phosphinidene ligands constitute now a vast family of complexes which span almost all elements from groups 3 to 10, with three different coordination modes clearly identified to date (**A** to **C** in Chart 1). Because of the multiplicity in the corresponding M–P bonds (modes **A** and **B**), or the presence of a lone electron pair at the P atom (mode **C**), these complexes react under mild conditions with a great variety of inorganic and organic compounds, whereby a large diversity of derivatives having novel organophosphorus derivatives or heterometallic architectures can be built,¹ so resembling in many aspects the extensively studied and versatile chemistry of mononuclear phosphinidene complexes.² Previous work on binuclear complexes, however, has been done so far mostly on homometallic species; then, it would be worth exploring the chemical behaviour of related species bearing two distinct metal atoms (heterometallic complexes), since the different electronic and geometric environments of the corresponding metal sites might add cooperative and synergic effects to the reactive M–P–M' core of these molecules.³ Unfortunately, these studies have been hampered so far by the reduced number of heterometallic phosphinidene-bridged species reported to date. The synthesis of the latter relied in most cases on activation processes operating on suitable phosphanil complexes, such as deprotonation of a cationic

PHMes-bridged WFe precursor,⁴ P–C bond cleavage in a P(OR)Cp*-bridged MnFe precursor,⁵ and photolytic P–Cl bond cleavage in a molybdenum PCIR complex, in the presence of [Mn₂(CO)₁₀] or [Co₂(CO)₈].⁶ The group of Malisch still unveiled one other possibility, based on deprotonation of the phosphanil complex *syn*-[WCp(PHR*)(CO)₂] (R* = 2,4,6-C₆H₂^tBu₃), followed by reaction with [FeCpI(CO)₂] to give the phosphinidene derivative [WFeCp(μ-PR*)(CO)₄].^{1,7} More recently, we have reported the preparation of some MoCo and MoMn phosphinidene complexes, starting from suitable thiophosphinidene-bridged precursors, but yields were rather modest.^{8,9} With these precedents at hand, we decided to explore the potential of the molybdenum phosphanil complex *syn*-[MoCp(PHR*)(CO)₂] (**1**) as a precursor of heterometallic phosphinidene-bridged complexes. As it will be shown below, three distinct P–H bond cleavage processes enable compound **1** to build different heterometallic derivatives.

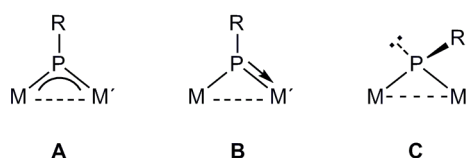
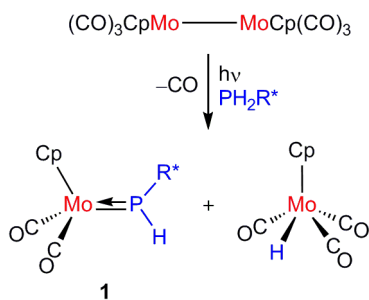


Chart 1. Coordination Modes of Bridging Phosphinidene Ligands

Compound **1** can be efficiently prepared upon photolysis of an equimolar mixture of the commercially available dimer [Mo₂Cp₂(CO)₆] and PH₂R*, likely a radical process initiated by the homolytic cleavage of the Mo–Mo bond in the parent complex, which eventually renders a mixture of compound **1** and the known hydride [MoCpH(CO)₃]¹⁰ as major products, from which **1** can be isolated in ca. 70% yield (based on phosphane) upon chromatographic workup (Scheme 1). We note that an isomer of **1** with an *anti* conformation of the Cp and R* groups around the multiple Mo–P bond (*anti*-**1**) had been previously prepared by Malisch et al by using several multistep procedures,¹¹ a circumstance which poses notable restrictions on its use for extensive reactivity studies.

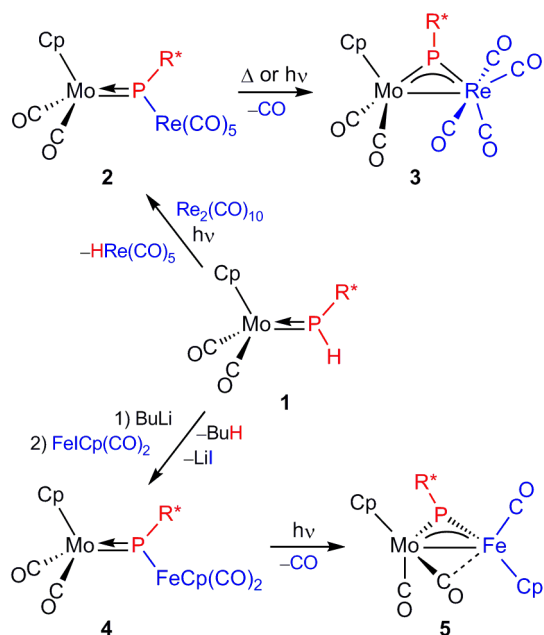
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Scheme 1. One-Step Synthesis of Compound 1

Spectroscopic data for **1** are similar, but not identical to those reported previously for isomer *anti-1*,¹¹ the main differences concerning the NMR parameters for the P-bound H atom (δ 10.20 ppm, $J_{\text{PH}} = 341$ Hz for **1**, to be compared with 9.95 ppm and 408 Hz respectively for *anti-1*, both in C_6D_6 solution). The *syn* conformation of the Cp and R^* groups in **1** was confirmed by the observation of a positive NOE effect of the *ortho*- t -Bu H atoms on the cyclopentadienylic ones. Moreover, B3LYP-DFT calculations revealed that compound **1** has a Gibbs free energy ca. 10 kJ/mol lower than isomer *anti-1* in the gas phase (see the ESI). As expected, the ^{31}P spectrum of **1** displays a significantly deshielded resonance at 272.7 ppm (cf. 266.2 ppm for *anti-1*), which is a characteristic feature of terminally-bound PR_2 ligands with planar environment around the P atom.¹²

Scheme 2. Homolytic and Heterolytic P-H Bond Cleavages of **1**

It was sensible to hypothesize that the photochemically-triggered radical process operating in the synthesis of **1** might be effective also for the activation of the remaining P-H bond of **1**, and indeed we found that photolysis of **1** in the presence of several metal-metal bound carbonyl dimers led to heterometallic phosphinidene derivatives, although the process was of modest selectivity. For instance, photolysis of a mixture of **1** and $[\text{Re}_2(\text{CO})_{10}]$ gave the new phosphinidene

complexes $[\text{MoReCp}(\mu\text{-PR}^*)(\text{CO})_7]$ (**2**) and $[\text{MoReCp}(\mu\text{-PR}^*)(\text{CO})_6]$ (**3**), (Scheme 2), along with the known hydride $[\text{ReH}(\text{CO})_5]$,¹³ and other unidentified species. Similar results were obtained when using $[\text{Mn}_2(\text{CO})_{10}]$ instead. We note that a significant amount of the known Mo_2 complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ ^{14,15} was also formed in these reactions, thus suggesting that P-H and P-Mo bond cleavages somehow compete with each other in these photochemical reactions. We also note that this Mo_2 complex was itself formed in the photochemical preparation of compound **1**, but only in very small amounts in that case (see the ESI).

The trigonal phosphinidene ligand in **2** (Figure 1) bridges the metal centres in an asymmetrical way (type **B**), as expected from the different electron counts of the Mo and Re fragments (15 and 17 electrons, respectively), and the relative *syn* conformation that Cp and R^* groups have around the multiple Mo-P bond in **1** is retained here. However, the Mo-P distance of 2.3032(9) Å in **2** is somewhat longer than the value of ca. 2.25 Å found for related double bonds,^{1a} actually comparable to the figure of 2.297(8) Å measured for the symmetrical (type **A**) complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}^*)(\text{CO})_4]$.¹⁴ This suggests that the π bonding interaction of the PR^* ligand in **2** might be delocalized to some extent over the (formally single) P-Re bond, a structural feature previously found for other heterometallic complexes of type **B**,^{8,9} although steric effects surely play a significant role here, since the Re-P length of 2.5733(8) Å in **2** is nearly identical to the single-bond length measured for the pyramidal phosphanyl ligand in $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{N},\text{N}'\text{-phen})]$ (2.571(2) Å).¹⁶ As expected, **2** can be decarbonylated to give **3**, a transformation taking place rapidly in toluene solution at 363 K. The loss of a CO ligand is accompanied by formation of an heterometallic Mo-Re bond, and also involves a substantial change in colour (from green to brown), along with a 235 ppm deshielding of the ^{31}P nucleus (from 437.6 to 673.1 ppm). NMR data for **3** suggest a conformation of C_s symmetry, consistent with the structure found in the solid state for its WRe analogue.¹⁷

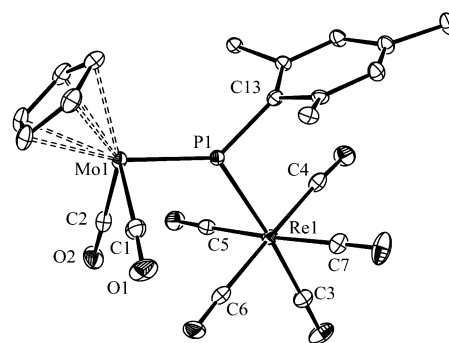
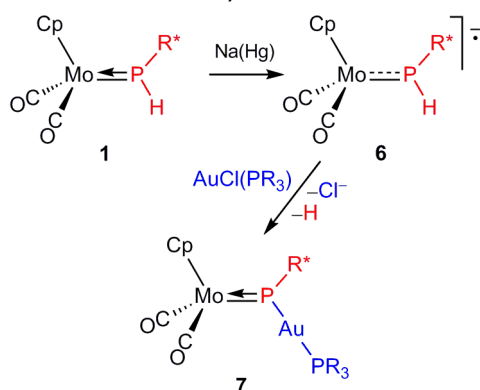


Figure 1. ORTEP diagram of **2**, with H atoms and Me groups omitted. Selected bond lengths (Å) and angles ($^\circ$): Mo-P = 2.3032(9); Re-P = 2.5733(8). C1-Mo-C2 = 82.2(2); Mo-P-Re = 127.01(4); Mo-P-C13 = 130.3(1); Re-P-C13 = 102.7(1).

Heterometallic complexes can be also obtained upon deprotonation of **1** followed by addition of a suitable halide complex. Thus, addition of a slight excess BuLi to a tetrahydrofuran solution of **1** rapidly gave a dark green solution thought to contain the Li^+ salt of the anionic

phosphinidene complex $[\text{MoCp}(\text{PR}^*)(\text{CO})_2]^-$, an extremely basic species of which we could not record its IR spectrum (only bands due to the parent **1** were observed). Fortunately, we could record its ^{31}P NMR spectrum by carrying out the reaction within an NMR tube, this showing a very strongly deshielded resonance at 1009.5 ppm (see the ESI), consistent with the formation of a phosphinidene complex.¹ Reaction of this solution with $[\text{FeCp}(\text{CO})_2]$ gave instantaneously the phosphinidene-bridged complex $[\text{MoFeCp}_2(\mu\text{-PR}^*)(\text{CO})_4]$ (**4**) in a very selective way, with no detectable amounts of side-products derived from competing electron-transfer reactions.¹⁸ Compound **4** is isoelectronic with the MoRe complex **2**, and also can be decarbonylated to give a metal-metal bonded derivative. This is now conveniently achieved upon irradiation with visible-UV light at 288 K, to give the tricarbonyl complex $[\text{MoFeCp}_2(\mu\text{-PR}^*)(\text{CO})_3]$ (**5**) in excellent yield. This transformation also is accompanied by the formation of an heterometallic Mo–Fe bond, and a substantial deshielding of the ^{31}P nucleus (from 477.6 to 674.0 ppm). Compound **5** displays ^{13}C NMR resonances indicative of the presence of a terminal Fe-bound carbonyl (δ_{C} 219.9 ppm) and two semibridging carbonyls bound to Mo (δ_{C} 258.0 and 254.2 ppm). This is consistent in part with the results of a diffraction study on the WFe analogue of **5**, which revealed the presence in this case of just one W-bound carbonyl involved in semibridging interaction with the Fe atom.⁷ The IR spectrum of **5** in solution, however, displays four C–O stretches (1945 (m), 1910 (vs), 1770 (m, sh), 1747 (m)), thus suggesting the presence of two rapidly interconverting (on the NMR time scale) conformers in solution. Attempts to obtain crystals of **5** suitable for a diffraction study have been unsuccessful so far.



Scheme 3. Reductive P–H Bond Cleavage of **1**

The third procedure to build heterometallic phosphinidene derivatives of **1** involves its one-electron reduction to give the corresponding anionic radical $[\text{MoCp}(\text{PHR}^*)(\text{CO})_2]^-$ (**6**). This can be easily achieved upon reaction of **1** with Na-amalgam either in tetrahydrofuran or acetonitrile solutions at 243 K, to give in a few minutes a dark-green solution containing the Na⁺ salt of anion **6** as the major product (Scheme 3). This anion however, was extremely air-sensitive (it being rapidly oxidized back to the parent compound **1** upon manipulation, or upon addition of a mild oxidant such as the $[\text{FeCp}_2]^+$ cation), and also decomposed at room temperature to give a mixture of products yet to be characterized. The IR spectra of these dark-

green acetonitrile solutions typically displayed C–O stretching bands corresponding to parent **1** (formed by oxidation of **6** inside the IR cell) and prominent bands at 1858 (vs) and 1760 (s) cm^{-1} which are assigned to the anion **6**, along with weaker bands growing with time inside the cell. The bands assigned to **6** thus are some 100 cm^{-1} less energetic than those of **1**, as expected from the increased negative charge at the metal centre. Addition of $[\text{AuCl}\{\text{P}(p\text{-tol})_3\}]$ to a solution of **6** at 243 K eventually resulted in chloride displacement and loss of hydrogen,¹⁹ to give the green phosphinidene derivative $[\text{MoAuCp}(\mu\text{-PR}^*)(\text{CO})_2\{\text{P}(p\text{-tol})_3\}]$ (**7**) in moderate yield, along with the parent compound **1** (the latter likely derived from competing oxidation by the gold complex). The formation of **7** is accompanied by a strong overall deshielding of the ^{31}P nucleus (δ_{P} increasing from 272.7 (**1**) to 528.4 ppm), as observed in the formation of compounds **2** and **4** (δ_{P} 437.8 and 477.6 ppm respectively). This is a diagnostic signature of formation of trigonal phosphinidene-bridged complexes (types **A** and **B**). The latter typically give rise to strongly deshielded ^{31}P NMR resonances, with chemical shifts (in the range of ca. 450–750 ppm when Mo, Re and Fe atoms are involved) much higher than those of most other P-containing species.¹

Examples of homolytic P–H bond cleavages leading to phosphinidene complexes from paramagnetic phosphanyl precursors are rare, and only a few precedents involving *neutral* Ni²⁰ and Os²¹ complexes seem to have been reported so far, these requiring the action of H-atom acceptors such as the radical OR*. DFT calculations on anion **6** indicate that the unpaired electron expectedly occupies a molecular orbital with $\pi^*(\text{Mo–P})$ character, so the Mo–P bond is considerably weakened upon reduction of **1**. This is reflected in a substantial increase in the Mo–P length (from 2.271 Å in **1** to 2.417 Å in **6**; see the ESI), and in significant pyramidalization at the P atom (the sum of angles around P decreasing from 360.0 to 342.9°). The spin density in **6** is mainly located around the Mo (55%) and P (29%) atoms (Figure 2), this leaving the P atom as the most reactive site because of its higher accessibility to external reagents. Indeed, we have found that many other electrophilic reagents readily add at the P site of **6** with concomitant loss of hydrogen, and further studies on the synthetic potential of this elusive paramagnetic anion in the formation of novel organophosphorus ligands are now in progress.

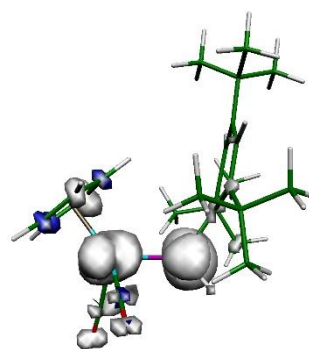


Figure 2. B3LYP-DFT-computed spin density for anion **6**

Conclusions

We have implemented a one-pot, high yield synthesis for the new phosphanyl complex *syn*-[MoCp(PHR*)(CO)₂] (**1**), which in turn is a very versatile precursor of a variety of heterometallic phosphinidene-bridged derivatives. The latter is possible due to the easy cleavage of the P–H bond in **1**, a process which in turn can be accomplished in three different ways: (a) photochemical activation, (b) deprotonation, and (c) one-electron reduction. The resulting phosphinidene-bridged complexes here described are the first reported examples combining Mo with Re, Fe or Au atoms, and the synthesis of several more heterometallic combinations can be anticipated by using similar reactions. Eventually this will allow for a very fine tuning of the chemical behaviour of the central M–P–M' skeleton of these reactive molecules, which is now under further investigation.

Conflicts of interest

There are no conflicts to declare.

Notes and references

§ We thank the MINECO of Spain and FEDER for financial support (Project CTQ2015-63726-P), the SCI of the Universidad de Málaga, Spain, for access to computing facilities, and the X-Ray unit of the Universidad de Oviedo for acquisition of diffraction data.

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- Reactions of anionic carbonyl complexes (A⁻) with halide complexes (MX) often result in electron-transfer processes (A⁻ + MX \rightarrow A⁺ + M + X⁻), rather than nucleophilic displacement of the halide ligand (A⁻ + MX \rightarrow A–M + X⁻), and this usually represents an undesired side-process in these reactions. In our reaction with [FeCp(CO)₂], such a side process would likely yield [Fe₂Cp₂(CO)₄] as a Fe-containing byproduct (from dimerization of radical FeCp(CO)₂ originated in the electron-transfer step), which actually is not observed, while no other P-containing complexes –different from **4**– are detected either.
- We trust that **6** first displaces the chloride ligand from the gold reagent to give a paramagnetic Mo(μ -PR*H)Au neutral intermediate which then undergoes spontaneous dehydrogenation or H transfer (perhaps to the solvent) to yield the diamagnetic phosphinidene complex **7**.
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