

Chemistry of the Phosphinidene Oxide Ligand

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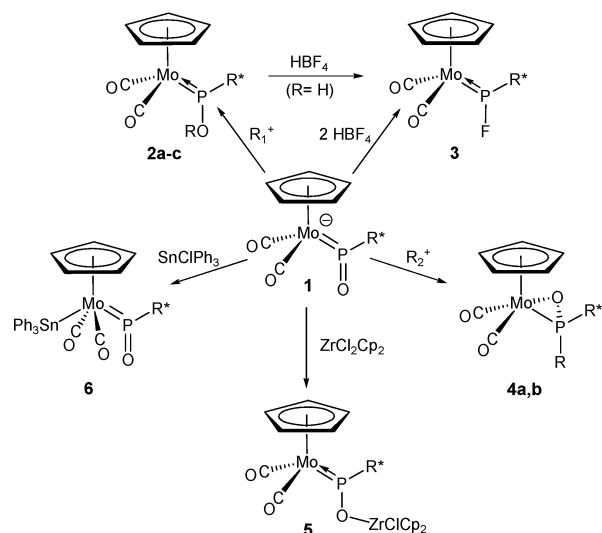
The chemistry of transition metal complexes having the versatile phosphinidene (PR) ligand is an active research area of interest to both organic and inorganic chemists. This is particularly the case for terminal bent complexes, in which the metal-P bond has considerable multiple character and exhibits carbene-like reactivity. As a result, these complexes are useful synthetic reagents in organophosphorus and cluster chemistry.^{1,2} In contrast, the chemical behavior of the phosphinidene oxide (R–P=O) complexes remains virtually unexplored to date.

Uncoordinated phosphinidene oxides are unstable molecules isolobally related to carbenes³ and are thought to be generated in reactions such as the thermal or photochemical decomposition of phospholene, phosphirane or phosphanorbornadiene oxides, and others.⁴ These transient species undergo processes such as addition to dienes and diones or insertion into O–H and S–S bonds and are therefore interesting synthons for new organophosphorus derivatives.^{4a} As for the coordinated R–P=O ligand, we must remark that only a few complexes have been reported. These display terminal (A),^{5a,b} μ_2 -P,O-bridging (B),^{5c} μ_2 -P-bridging (C),^{5d,e} or μ_3 -P,O-bridging (D)^{5f} coordination modes (Chart 1), but their reactivity has not been explored. Interestingly, we note that terminal R–P=O complexes have been proposed as intermediates in the formation of dioxaphospholanes.⁶

Following our studies on the synthesis and reactivity of phosphinidene-bridged complexes,⁷ we accidentally discovered the formation of [MoCp{P(O)R*}(CO)₂][−] (**1**) (R* = 2,4,4,6-C₆H₂’Bu₃; Cp = η^5 -C₅H₅), the first anionic phosphinidene oxide complex reported to date. More importantly, this anion is nucleophilic enough to react with a wide variety of electrophiles at room temperature. Herein we report our initial results on the reactivity of **1**, which is also the first report on the chemistry of a phosphinidene oxide complex. As will be shown, complex **1** exhibits a unique reactivity, with three different nucleophilic sites (at O, P, and Mo), which leads to new compounds that have not yet been prepared otherwise (Scheme 1).

Complex **1** [as the (H-DBU)⁺ salt]⁸ is cleanly formed by the controlled action of air on (H-DBU)[Mo₂Cp₂(μ -PHR*)(CO)₄], a salt prepared in turn from [Mo₂Cp₂(μ -H)(μ -PHR*)(CO)₄]^{7a} and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). No other P- or CO-containing product was formed in significant amounts, and the fate of the lost MoCpH(CO)₂ moiety has not been yet determined. The anion **1** displays a terminally bound phosphinidene oxide ligand lying in the plane bisecting the MoCp(CO)₂ moiety; the terminal oxygen atom is involved in a hydrogen bond with the (H-DBU)⁺ cation and is placed anti with respect to the cyclopentadienyl ligand (Figure 1).⁹ The P–Mo [2.239(1) Å] and P–O [1.514(3) Å] bond lengths are short and comparable to the corresponding values in the two reported neutral compounds with terminal R–P=O ligands.^{5a,b} This supports the formulation of double Mo=PR and

Scheme 1^a



^a HBF₄, [Me₃O]BF₄ or PhC(O)Cl for R₁⁺. MeI or C₃H₅Br for R₂⁺.

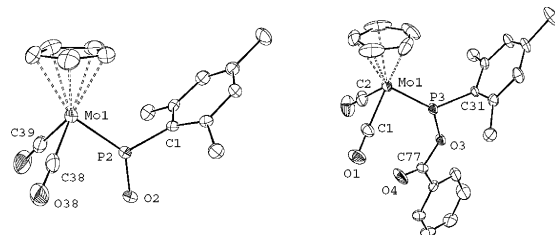
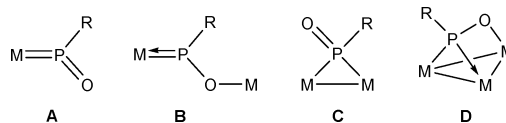


Figure 1. Molecular structure of the anion **1** (left) and compound **2c** (right). Methyl groups are omitted for clarity.

Chart 1



P=O bonds for the P(O)R* ligand in **1**. Besides, the low frequencies of the C–O stretching bands of **1** are indicative of substantial delocalization of the negative charge all over the complex, in agreement with the nucleophilic behavior discussed next.

Anion **1** is protonated by HBF₄·OEt₂ at the oxygen atom, which is consistent with the H···O interaction present in the crystal. The resulting hydroxophosphide complex [MoCp{P(OH)R*}(CO)₂] (**2a**) is easily deprotonated upon manipulation. A similar reaction occurs between **1** and carbon-based electrophiles such as [Me₃O]BF₄ or PhC(O)Cl to give related alkoxyphosphide compounds [MoCp{P(OR)R*}(CO)₂] (R = Me, **2b**; C(O)Ph, **2c**).¹⁰ An X-ray study on **2c** revealed that the phosphide ligand retains the geometry of the parent phosphinidene oxide group (Figure 1).¹¹ The most

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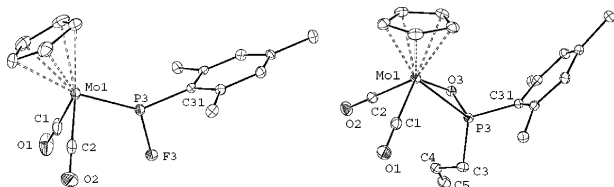


Figure 2. Molecular structure of compounds **3** (left) and **4b** (right). Methyl groups are omitted for clarity.

relevant changes are a substantial increase in the P–O distance [1.671(3) Å, a value typical of single P–O bonds], and a slight decrease in the Mo–P distance [2.196(1) Å]. These structural features are similar to those found for [MoCp{PCH(SiMe₃)₂}(OEt)(CO)₂], a related complex prepared by reaction of EtOH on a phosphavinylidene precursor.¹²

The hydroxoderivative **2a** can be further protonated with HBF₄·OEt₂ to give the fluorophosphide complex [MoCp(PFR*)(CO)₂] (**3**), after elimination of water and fluoride abstraction from the BF₄[−] anion.¹³ The structure of this molecule is similar to that of the alkoxyphosphide **2c**, displaying a quite short Mo–P distance [2.2037(12) Å] (Figure 2).¹⁴ Compound **3** appears to be the first complex reported with a trigonal fluorophosphide (PFR) ligand, although a few related chlorophosphide complexes are known.¹⁵

Carbon-based electrophiles can alternatively attack the P site in **1**. This is the dominant reaction pathway when using milder electrophiles such as MeI or C₃H₅Br, which then give the respective phosphinite derivatives [MoCp(κ²-OPRR*)(CO)₂] (R = Me, **4a**; C₃H₅, **4b**).¹⁶ These are the first complexes reported to have a *P,O*-bound phosphinite ligand. Separate experiments showed that the isomeric methyl derivatives **2b** and **4a** did not interconvert even in refluxing toluene. This proves that compounds **2** and **4** arise from independent reaction pathways. An X-ray study on **4b** revealed an unusual environment in the phosphinite ligand, with the P(3), C(3), and C(31) atoms almost placed in a plane and close to that one bisecting the MoCp(CO)₂ moiety, and the O(3) atom also bonded to molybdenum (Figure 2).¹⁷ This results in a strained MoPO ring with internuclear separations suggesting single (Mo–O) or intermediate (between single and double) bonds (Mo–P and P–O). Similar structural effects have been reported for related thiophosphinite complexes.¹⁸

Anion **1** also displays dual behavior when reacting with metal-based electrophiles, as illustrated through the reactions with [ZrCl₂-Cp₂] and SnClPh₃. The zirconium fragment binds to the O atom giving the *P,O*-bridged [MoCp{P(OZrClCp₂)R*}(CO)₂] (**5**).¹⁹ The tin fragment, however, binds to the Mo atom to give [MoCp{P(O)-R*}(CO)₂(SnPh₃)] (**6**), which displays a terminal P(O)R* ligand and *trans*-dicarbonyl geometry.²⁰ The formation of **5** provides a new route to heterometallic complexes bridged by the phosphinidene oxide ligand, of which only one compound has been reported so far.^{5c} In addition, the formation of **6** indicates that **1** has a third nucleophilic position located at the metal atom, and this allows the preparation of new neutral complexes with terminal R–P=O groups. Because of the multiple nature of the Mo–P bond in these species, it is expected that they can display some carbene-like reactivity. Currently we are exploring this possibility and extending the electrophiles under study to unravel the factors governing the complex nucleophilicity of anion **1**.

The present work is the first study on the reactivity of a coordinated phosphinidene oxide ligand. The anion **1** has a terminally bound R–P=O ligand and displays unique acid/base properties, with three different nucleophilic sites located at the O, P, and Mo atoms. The binding of different electrophiles to these

sites allows the rational synthesis of novel and unusual derivatives that cannot be prepared otherwise.

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Supporting Information Available: Experimental procedures and spectroscopic data for new compounds (PDF); crystallographic data for compounds **1**, **2c**, **3**, and **4b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127–1138. (b) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938–2957. (c) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210*, 181–201. (d) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9–16. (e) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445–451. (f) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743–759.
- (2) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*. Wiley: New York, USA, 1998.
- (3) Schoeller, W. W.; Niecke, E. *Chem. Commun.* **1982**, 569–570.
- (4) (a) Gaspar, P. P.; Qian, H.; Beatty, A. M.; d'Avignon, D. A.; Kao, J. L. F.; Watt, J. C.; Rath, N. P. *Tetrahedron* **2000**, *56*, 105–119 and references therein. (b) Cowley, A. H.; Gabbaï, F. P.; Corbelin, S.; Decken, A. *Inorg. Chem.* **1995**, *34*, 5931–5932. (c) Wang, K.; Emge, T. J.; Goldman, A. S. *Organometallics* **1994**, *13*, 2135–2137. (d) Niecke, E.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 709–710.
- (5) (a) Niecke, E.; Engelmann, M.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 710–712. (b) Hitchcock, P. B.; Johnson, J. A.; Lemos, M. A. N. D. A.; Meidine, M. F.; Nixon, J. F.; Pombeiro, A. J. L. *J. Chem. Soc., Chem. Commun.* **1992**, 645–646. (c) Johnson, M. J. A.; Odum, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1523–1524. (d) Kourkine, V.; Glueck, D. S. *Inorg. Chem.* **1997**, *36*, 5160–5164. (e) Schmitt, G.; Ullrich, D.; Wolmershäuser, G.; Regitz, M.; Scherer, O. J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 702–704. (f) Buchholz, D.; Huttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *388*, 307–320.
- (6) Marinetti, A.; Mathey, F. *Organometallics* **1987**, *6*, 2189–2191.
- (7) (a) García, M. E.; Riera, V.; Ruiz, M. A.; Sáez, D.; Vaisermann, J.; Jeffery, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 14304–14305. (b) García, M. E.; Riera, V.; Ruiz, M. A.; Sáez, D.; Hamidov, H.; Jeffery, J. C.; Riis-Johannessen, T. *J. Am. Chem. Soc.* **2003**, *125*, 13044–13045.
- (8) Selected spectroscopic data for **1**: ν_{CO} (CH₂Cl₂) 1874 (vs), 1790 (s) cm^{−1}. ³¹P{¹H} NMR (CD₂Cl₂) δ 385.0 ppm.
- (9) X-ray data for **1**: Yellow-orange crystals, orthorhombic (P2₁2₁2₁), $a = 9.5709(15)$, $b = 17.391(3)$, $c = 20.501(3)$ Å, $V = 3412.4(9)$ Å³, $T = 173$ K, $Z = 4$, $R = 4.42$, $\text{GOF} = 0.933$.
- (10) Selected spectroscopic data for **2b**: ν_{CO} (CH₂Cl₂) 1935 (vs), 1856 (s) cm^{−1}. ³¹P{¹H} NMR(CD₂Cl₂) δ 350.5 ppm. ¹³C{¹H} NMR(CD₂Cl₂) δ 238.5 (d, $J_{\text{CP}} = 20$, CO), 55.7 (s, OCH₃) ppm.
- (11) X-ray data for **2c**: dark red crystals, orthorhombic (Pbca), $a = 17.1829(15)$, $b = 13.0958(11)$, $c = 27.663(2)$ Å, $V = 6224.8(9)$ Å³, $T = 173$ K, $Z = 8$, $R = 6.51$, $\text{GOF} = 0.944$.
- (12) Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Quashie, S. *Organometallics* **1989**, *8*, 1878–1884.
- (13) Selected spectroscopic data for **3**: ν_{CO} (CH₂Cl₂) 1959 (vs), 1884 (s) cm^{−1}. ³¹P{¹H} NMR δ 323.8 (d, $J_{\text{PF}} = 1132$ Hz) ppm.
- (14) X-ray data for **3**: Red crystals, monoclinic (P2₁/c), $a = 20.947(2)$, $b = 10.4889(10)$, $c = 11.5591(12)$ Å, $\beta = 102.708(2)^\circ$, $V = 2477.4(4)$ Å³, $T = 173$ K, $Z = 4$, $R = 5.67$, $\text{GOF} = 0.969$.
- (15) (a) Cowley, A. H.; Giolando, D. M.; Nunn, C. M.; Pakulski, M.; Westmoreland, D.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2127–2134. (b) Malisch, W.; Hirth, U. A.; Grün, K.; Schmeußer, M. *J. Organomet. Chem.* **1999**, *572*, 207–212.
- (16) Selected spectroscopic data for **4a**: ν_{CO} (CH₂Cl₂) 1940 (vs), 1850 (s) cm^{−1}. ³¹P{¹H} NMR(CD₂Cl₂) δ 28.3 ppm. ¹³C{¹H} NMR(CD₂Cl₂) δ 255.8 (d, $J_{\text{CP}} = 26$, CO), 246.0 (s, CO), 23.8 [d, $J_{\text{CP}} = 27$, PCH₃] ppm.
- (17) X-ray data for **4b**: Red crystals, triclinic P $\bar{1}$, $a = 9.2708(3)$, $b = 12.0224(4)$, $c = 14.3208(5)$ Å, $\alpha = 84.8940(10)$, $\beta = 77.0620(10)$, $\gamma = 75.5350(10)^\circ$, $V = 1505.40(9)$ Å³, $T = 173$ K, $Z = 2$, $R = 2.41$, $\text{GOF} = 0.982$.
- (18) (a) Alper, H.; Einstein, F. W. B.; Hartstock, F. W.; Jones, R. H. *Organometallics* **1987**, *6*, 829–833. (b) Malisch, W.; Grün, K.; Hirth, U. A.; Noltemeyer, M. *J. Organomet. Chem.* **1996**, *513*, 31–36. (c) Reisacher, H. U.; McNamara, W. F.; Duesler, E. N.; Paine, R. T. *Organometallics* **1997**, *16*, 449–455.
- (19) Selected spectroscopic data for **5**: ν_{CO} (CH₂Cl₂) 1921 (vs), 1841 (s) cm^{−1}. ¹H NMR (CD₂Cl₂) δ 6.39 (s, 10H, ZrCp) 5.12 (s, 5H, MoCp) ppm. ³¹P{¹H} NMR (CD₂Cl₂) δ 350.3 ppm.
- (20) Selected spectroscopic data for **6**: ν_{CO} (CH₂Cl₂) 1947 (s), 1889 (vs) cm^{−1}. ³¹P{¹H} NMR (CD₂Cl₂) δ 468.1 ($J_{195\text{SnP}} = J_{177\text{SnP}} = 116$ Hz) ppm.

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