Communication

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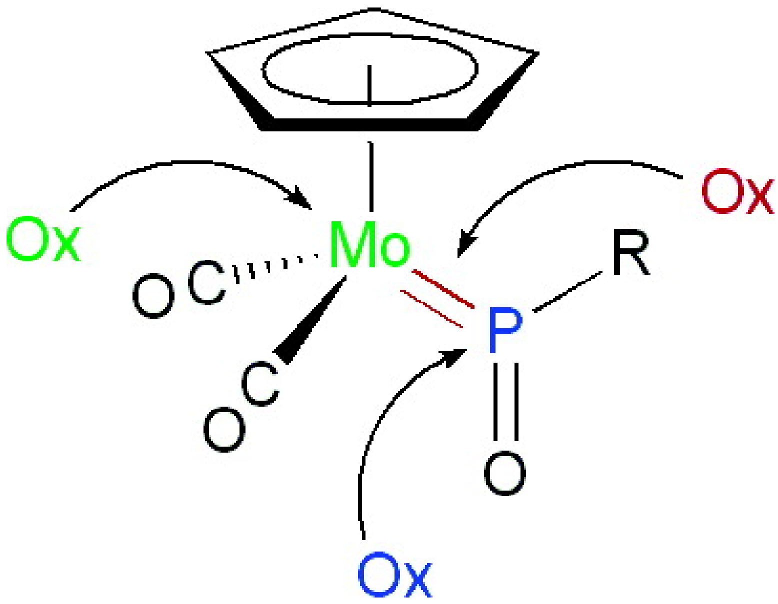

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# Oxidation Reactions of the Phosphinidene Oxide Ligand

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Phosphinidene oxides ($R{-}P{=}O$) are unstable molecules thought to be generated in the thermal or photochemical decomposition of several precursors, such as phospholene, phosphirane, or phosphanorbornadiene oxides, and others. These transient species are very reactive toward different organic molecules and have been thus used as efficient synthons for new organophosphorus derivatives.[1] Stabilization of $R{-}P{=}O$ species can be, in principle, achieved through coordination to metal centers, a strategy that could allow for a more detailed study of the chemical behavior of these unsaturated molecules. However, only a few phosphinidene oxide complexes have been reported so far,[2] and their reactivity has not been explored.

Recently, we reported the preparation of the $(H\text{-}DBU)^+$ salt of the anionic phosphinidene oxide complex $[MoCp(CO)_2\{P(O)R^*\}]^-$ (**1**) ($R^* = 2,4,6\text{-}C_6H_2{}^tBu_3$; $Cp = \eta^5\text{-}C_5H_5$, DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene) and a preliminary study on its reactivity toward different electrophiles.[3] From this, we concluded that anion **1** exhibits unique acid−base properties, with three different nucleophilic sites located at the O, P, and Mo atoms. In this paper, we report a preliminary study on the reactions of anion **1** with different oxidizing reagents, which again reveals a multisite reactivity, now located at the P and Mo atoms or at the $Mo{=}P$ bond. This in turn allows for the synthesis of complexes having novel organophosphorus ligands, displaying new coordination modes or experiencing unexpected bond activation processes under mild conditions (Scheme 1).

Anion **1** reacts with an innocent oxidant such as $[FeCp_2]BF_4$ to cleanly give the binuclear compound $[Mo_2Cp_2(CO)_4\{P(O)R^*\}_2]$ (**2**), which displays two terminally bound phosphinidene oxide ligands.[4] The formation of **2** is interpreted as a result of the dimerization of a metal-centered radical $[MoCp(CO)_2\{P(O)R^*\}]$ arising from the one-electron oxidation of anion **1**. From this, however, it cannot be concluded that other oxidants would preferentially attack the metal position in the anion. In fact, the site of attack turns out to be strongly dependent on the oxidizing agent used.

The mild oxidant *p*-benzoquinone attacks the anion **1** at the phosphorus position to give, after spontaneous $H^+$ transfer from the $(H\text{-}DBU)^+$ counterion, the neutral compound $[MoCp\{\kappa^2\text{-}OP(OC_6H_4OH)R^*\}(CO)_2]$ (**3**), which is the first complex reported to have a *P,O*-bound phosphonite ligand.[5] The binding of the phosphonite ligand in **3** (Figure 1) is similar to that of the phosphinite complex $[MoCp\{\kappa^2\text{-}OP(C_3H_5)R^*\}(CO)_2]$,[3] with the internuclear P−O(3) (1.549(3) Å) and P−Mo (2.354(1) Å) separations being indicative of the retention of significant double bond character in the corresponding bonds.[6]

Bromine attacks the anion **1** at the metal position, but does not give the expected neutral phosphinidene oxide complex. Instead, the phosphinous acid complex *cis*-$[MoBrCp(CO)_2\{P(OH)(CH_2CMe_2C_6H_2{}^tBu_2\}]$ (**4**) is formed (Figure 1).[7,8] Compound **4** is generated in solution as a single diastereoisomer, possibly favored by the presence of substantial O−H···Br hydrogen bonding. This is clear in the solid state, with the value of the relevant normalized length[9] (H(3)···Br = 0.80) pointing to an interaction of medium strength. The formation of **4** requires the intramolecular addition of a C−H bond to the $P{=}O$ bond in the phosphinidene oxide ligand, which is unprecedented and highly remarkable due to the mild reaction conditions used. Only transient dioxophosphoranes ($RPO_2$) have been previously proposed to experience related reactions, this occurring in the gas phase at temperatures in the range of 900−1100 K.[10] Interestingly, the transient $R^*{-}P{=}O$ molecule, generated in the gas phase at 573 K, has been proposed to experience the oxidative addition of a C−H bond to its phosphorus atom to yield the corresponding phosphinic acid.[1b]

Compound **4** experiences hydrolysis readily to give, in the presence of bases, the anionic dioxophosphorane complex [MoCp-

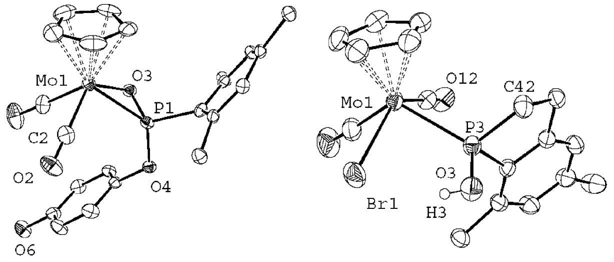
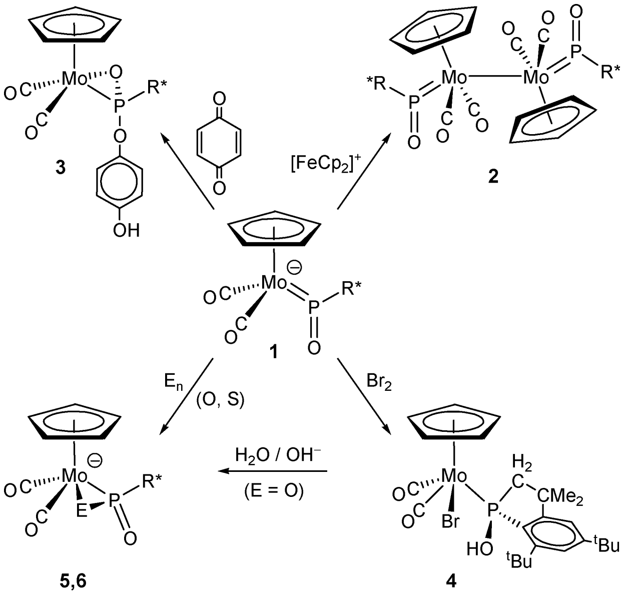


***Figure 1.*** Molecular structure of compounds **3** (left) and **4** (right). Hydrogen atoms and methyl groups are omitted for clarity.

***Scheme 1***



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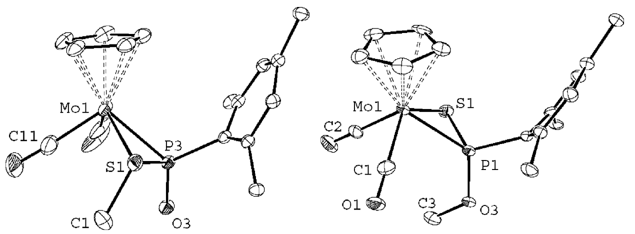
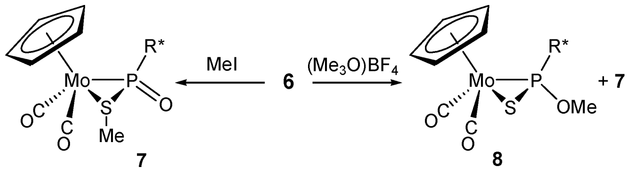


***Figure 2.*** Molecular structure of compounds **7** (left) and **8** (right). Hydrogen atoms and methyl groups are omitted for clarity.

***Scheme 2***



$(CO)_2\{\kappa^2\text{-}OP(O)R^*\}]^-$ (**5**), a transformation implying an easy and unprecedented reversal of the former C−H bond addition to the P═O moiety, which thus appears to be triggered by subtle changes in the coordination sphere around the metal atom. The anion **5** (as its (H-DBU)$^+$ salt)[11] can be more conveniently prepared through direct oxidation of the phosphinidene oxide complex **1** using a mild oxygenating agent such as $Me_2CO_2$. Reaction of **1** with elemental sulfur proceeds analogously by incorporation of a S atom to the Mo═P bond to give the *S*,*P*-bound thiooxophosphorane complex $[MoCp(CO)_2\{\kappa^2\text{-}SP(O)R^*\}]^-$ (**6**).[12]

As it is the case of the phosphinidene oxides, dioxophosphoranes (phosphinidene dioxides, $RPO_2$) and thiooxophosphoranes (RPOS) are unstable molecules thought to be generated in the thermolysis of suitable organophosphorus precursors. These transient species are strongly electrophilic at the phosphorus atom and have thus found use as efficient phosphorylating agents.[13] Surprisingly, the coordination chemistry of these molecules is virtually unknown; no complexes having thiooxophosphorane ligands appear to have been ever prepared, and there is just a single example of a dioxophosphorane complex.[14] The anions **5** and **6** thus provide the opportunity to explore the chemistry of these unsaturated ligands. Initial experiments on **6** reveal that the electrophilic nature of the uncoordinated RPOS ligand is reversed by the negative charge of the complex, which then allows reactions with electrophiles, at either the O or the S positions depending on the reagent used (Scheme 2).

Thus, selective methylation at sulfur is achieved by MeI to yield the *S*,*P*-bound thiolophosphinide complex $[MoCp\{\kappa^2\text{-}(MeS)P(O)\text{-}R^*\}(CO)_2]$ (**7**),[15] whereas reaction with $(Me_3O)BF_4$ gives a mixture of the latter and the isomeric phosphonothiolate complex $[MoCp\text{-}\{\kappa^2\text{-}SP(OMe)R^*\}(CO)_2]$ (**8**),[16] as confirmed crystallographically (Figure 2).[17,18] It should be noted that no complexes containing phosphonothiolate or thiolophosphinide ligands appear to have been previously described, thus further stressing the synthetic potential of anion **1**. In the case of **8**, the coordination geometry is very similar to that of the phosphonite complex **3**, as expected. In contrast, the isomeric complex **7** exhibits internuclear separations within the Mo−P−S ring closer to the values expected for the corresponding single bonds.

In summary, we have shown that anion **1** reacts with innocent and noninnocent oxidizing reagents to give products resulting from reaction at the Mo and P positions, or at the Mo═P bond. New organophosphorus ligands or new coordination modes of the latter can be thus revealed, these including *P*,*O*-bound phosphonite and dioxophosphorane, as well as thiooxophosphorane, phosphonothiolate, and thiolophosphinide ligands. Further work to expand the synthetic potential of anionic phosphinidene oxide or dioxide and thiooxophosphorane complexes is now in progress.

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**Supporting Information Available:** Experimental procedures and spectroscopic data for new compounds (PDF); crystallographic data for compounds **3**, **4**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) The structure of **2** has been confirmed through an X-ray study on its ditungsten analogue (unpublished results from the authors; see also Supporting Information). Selected spectroscopic data for **2**: $\nu_{CO}$ ($CH_2Cl_2$) 1918 (m, sh), 1901 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 463.5 ppm.

(5) Selected spectroscopic data for **3**: $\nu_{CO}$ ($CH_2Cl_2$) 1954 (s), 1865 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 74.5 ppm; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 5.14 (s, 1H, OH), 5.01 (s, 5H, Cp) ppm; $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 252.7 (d, $J_{CP}$ = 30 Hz, CO), 245.6 (s, CO) ppm.

(6) X-ray data for $\mathbf{3}\cdot CH_2Cl_2$: red crystals, monoclinic ($P2_1/c$), $a = 15.229(2)$, $b = 10.935(2)$, $c = 20.058(3)$ Å, $\beta = 103.39(1)°$, $V = 3249.6(8)$ Å$^3$, $T = 293$ K, $Z = 4$, $R_1 = 0.0386$ (observed data with $I > 2\sigma(I)$), GOF = 1.041.

(7) Selected spectroscopic data for **4**: $\nu_{CO}$ ($CH_2Cl_2$) 1972 (vs), 1894 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 132.7 ppm; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 6.86 (s, 1H, OH), 2.66, 2.34 (2 × m, 2 × 1H, $PCH_2$) ppm.

(8) X-ray data for **4**: red crystals, triclinic ($P1$), $a = 10.903(2)$, $b = 11.395(2)$, $c = 12.157(2)$ Å, $\alpha = 104.57(3)$, $\beta = 108.57(3)$, $\gamma = 103.77(3)°$, $V = 1299.8(5)$ Å$^3$, $T = 298$ K, $Z = 2$, $R_1 = 0.0367$ (observed data with $I > 2\sigma(I)$), GOF = 1.031.

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(11) Selected spectroscopic data for **5**: $\nu_{CO}$ ($CH_2Cl_2$) 1904 (vs), 1803 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 39.6 ppm.

(12) Selected spectroscopic data for **6**: $\nu_{CO}$ ($CH_2Cl_2$) 1911 (vs), 1816 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 83.8 ppm; $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 254.6 (d, $J_{CP}$ = 29 Hz, CO), 247.1 (s, CO) ppm.

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(15) Selected spectroscopic data for **7**: $\nu_{CO}$ ($CH_2Cl_2$) 1963 (vs), 1887 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 102.0 ppm; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 2.09 (d, $J_{HP}$ = 3 Hz, 3H, SMe) ppm.

(16) Selected spectroscopic data for **8**: $\nu_{CO}$ ($CH_2Cl_2$) 1947 (vs), 1862 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 122.0 ppm; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 3.18 (d, $J_{HP}$ = 16 Hz, 3H, OMe) ppm.

(17) X-ray data for **7**: yellow crystals, monoclinic ($P2_1/n$), $a = 8.900(2)$, $b = 23.129(5)$, $c = 13.248(3)$ Å, $\beta = 94.72(3)°$, $V = 2717.8(9)$ Å$^3$, $T = 100$ K, $Z = 4$, $R_1 = 0.0214$ (observed data with $I > 2\sigma(I)$), GOF = 1.060.

(18) X-ray data for **8**: orange crystals, monoclinic ($C2/c$), $a = 30.656(10)$, $b = 9.859(3)$, $c = 20.754(7)$ Å, $\beta = 122.01(1)°$, $V = 5319(3)$ Å$^3$, $T = 293$ K, $Z = 8$, $R_1 = 0.0539$ (observed data with $I > 2\sigma(I)$), GOF = 1.018.

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