

Phosphorus monoxide as a terminal ligand

Marc J. A. Johnson, Aaron L. Odom and Christopher C. Cummins*†

Department of Chemistry, 2-227, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

Dimethyldioxirane oxidation of phosphide $\text{PMo}[\text{N}(\text{R})\text{Ar}]_3$ [$\text{R} = \text{C}(\text{CD}_3)_2\text{Me}$, $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2\text{-3,5}$] efficiently provides $(\text{OP})\text{Mo}[\text{N}(\text{R})\text{Ar}]_3$, a complex shown by X-ray crystallography to contain a terminal phosphorus monoxide ligand, and which reacts with dimethylzirconocene to give addition of a Zr-Me bond across the phosphoryl moiety.

Known phosphorus monoxide complexes^{1–3} are those in which $\text{PO}^{4–10}$ serves as a triply bridging ligand. These have been prepared by oxo transfer to a $\text{P}_2\text{Ni}_2\text{W}$ cluster,¹ and by hydrolysis of a $\mu_3\text{-P}(\text{NPr}_2)$ functional group.³ Recent reports of terminal phosphide (P^{3-}) complexes^{11–15} hint at the possibility of preparing terminal PO complexes by oxygen-atom transfer to the terminal P ligand. Accordingly, dimethyldioxirane oxidation^{16,17} has been found to effect the desired conversion of $\text{PMo}[\text{N}(\text{R})\text{Ar}]_3$ **1** to $(\text{OP})\text{Mo}[\text{N}(\text{R})\text{Ar}]_3$ **2**. Synthetic, structural, and initial reactivity data pertaining to **2** are detailed herein.

Treatment of a -78°C gold-colored solution of **1** (1.0009 g, 1.4853 mmol) in dichloromethane (50 ml) with dimethyldioxirane (20 ml of a 0.075 M solution in acetone¹⁸) elicited a rapid color change to purple, the color of **2**.[‡] Workup consisted of cold-filtration, precipitation of **2** by addition of acetonitrile (75 ml, pre-chilled to just above its melting point), and collection of solid **2** (73.8% yield) by filtration. Once thus obtained in pure form, solid **2** can be manipulated and maintained at 25°C for at least *ca.* 5 days without noticeable decomposition. When dissolved in various solvents (*e.g.* benzene, diethyl ether, heptane and dichloromethane) **2** is more sensitive, undergoing gradual reversion to **1** according to ^1H and ^{31}P NMR spectroscopic monitoring.

Diamagnetic **2** exhibits a single ^{31}P NMR signal at δ 269.8, shifted dramatically upfield relative to **1** but in a range typical of

two-coordinate phosphorus compounds.¹⁹ Proton NMR data for **2** are indicative of a single environment for the $\text{N}(\text{R})\text{Ar}$ ligands, consistent with the threefold (propellor) symmetry typical of complexes containing three $\text{N}(\text{R})\text{Ar}$ ligands.^{20–25}

Single crystals of **2** suitable for an X-ray diffraction study[§] were obtained by slow cooling to -35°C of a diisopropyl ether solution. Molecular **2** evinces pseudo-threefold symmetry about the near-linear $[\text{P-O}]$ moiety, which is flanked by the three *tert*-butyl substituents (Fig. 1). An intriguing feature of the structure is the molybdenum–phosphorus distance $d(\text{MoP}) = 2.079(5) \text{ \AA}$, which is shorter by 0.04 \AA than $d(\text{MoP})$ for terminal phosphide **1**.¹¹ Contraction of the molybdenum–phosphorus distance in this manner is explicable in terms of rehybridization at P upon addition of a terminal substituent.²⁶ The phosphorus–oxygen distance $[1.49(2) \text{ \AA}]$ in **2** is comparable to that measured by IR diode laser spectroscopy for gaseous PO $[1.476370(15) \text{ \AA}]$,^{27,28} and to $d(\text{PO})$ values for $\mu_3\text{-PO}$ complexes: $1.509(3)$,³ $1.462(9)$ and $1.480(10)$.¹ Phosphoryl halide species such as OPCl_3 contrastingly exhibit longer phosphorus–oxygen distances, on the order of $1.54\text{--}1.58 \text{ \AA}$,²⁹ while $d(\text{PO})$ for $\text{OP}(\text{C}_6\text{H}_{11})_3$ is $1.490(2) \text{ \AA}$.³⁰ Other metrical parameters pertaining to the structure of **2** are unexceptional.

Previously reported $(\text{SP})\text{Mo}[\text{N}(\text{R})\text{Ar}]_3$ **3**¹¹ was shown recently by X-ray crystallography to resemble **2** in terms of its monomeric nature and gross structural characteristics.³¹ The rough similarity of **2** and **3** was used to advantage to obtain assignment of the ν_{PO} (1232 cm^{-1}) and ν_{PS} (782 cm^{-1}) IR stretching frequencies for the two complexes, by digital subtraction of solution FTIR spectra. The ν_{PO} value for **2** is similar to that reported for gaseous PO (1220.25 cm^{-1}), and also is comparable to values reported for $\mu_3\text{-PO}$ complexes ($1260, 1169 \text{ cm}^{-1}$).

Initial reactivity studies indicate that the phosphoryl phosphorus in **2** is susceptible to nucleophilic attack in a manner reminiscent of the Fischer carbene synthesis.³² Accordingly, treatment of **2** (282.0 mg, 0.4088 mmol) with dimethylzirconocene³³ (103.3 mg , 0.4108 mmol) in benzene (7.5 ml) led to formation of $[(\text{R}^1)(\text{R}^2)\text{O}]\text{P}[\text{Mo}[\text{N}(\text{R})\text{Ar}]_3]$ **4**, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Zr}(\text{Me})(\eta\text{-C}_5\text{H}_5)_2$, which was isolated by crystallization

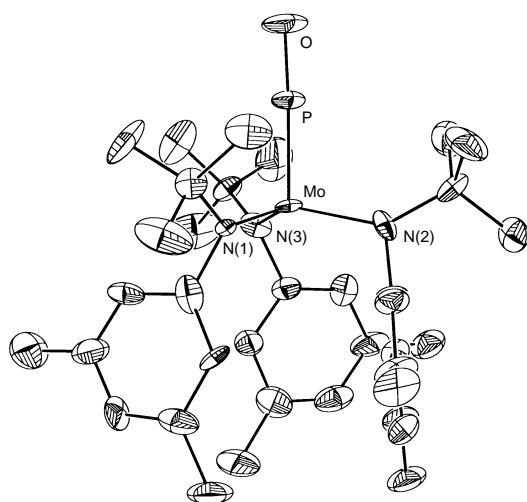
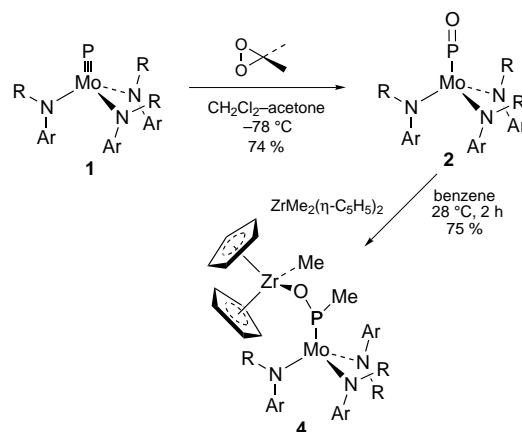


Fig. 1 ORTEP drawing of the molecular structure of **2** with 35% probability ellipsoids. Selected bond lengths (\AA) and angles ($^\circ$): Mo-P $2.079(5)$, $\text{Mo-N}(1)$ $1.95(2)$, $\text{Mo-N}(2)$ $1.94(2)$, $\text{Mo-N}(3)$ $1.994(13)$, P-O $1.49(2)$; Mo-P-O $177.6(8)$, $\text{P-Mo-N}(1)$ $101.7(4)$, $\text{P-Mo-N}(2)$ $101.4(5)$, $\text{P-Mo-N}(3)$ $101.6(5)$, $\text{N}(1)\text{--Mo--N}(2)$ $113.1(6)$, $\text{N}(1)\text{--Mo--N}(3)$ $117.2(6)$, $\text{N}(2)\text{--Mo--N}(3)$ $118.0(6)$.



Scheme 1

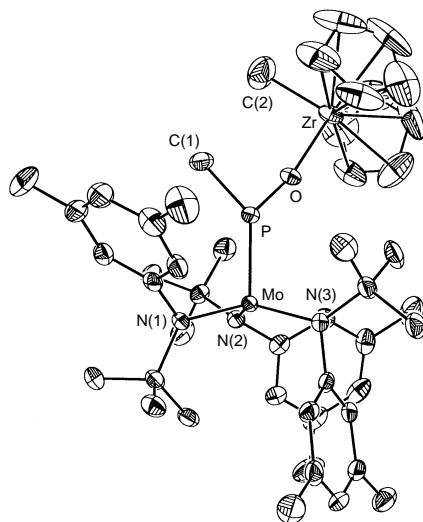


Fig. 2 ORTEP drawing of the molecular structure of **4** with 35% probability ellipsoids. Selected bond lengths (Å) and angles (°): Mo–P 2.169(2), Mo–N(1) 1.995(5), Mo–N(2) 2.011(5), Mo–N(3) 1.993(5), P–O 1.613(5), P–C(1) 1.832(8), Zr–O 2.000(4), Zr–C(2) 2.253(11); Mo–P–O 127.7(2), Mo–P–C(1) 133.9(3), O–P–C(1) 97.6(3), Zr–O–P 163.6(3), O–Zr–C(2) 97.1(4), P–Mo–N(1) 101.6(2), P–Mo–N(2) 103.2(2), P–Mo–N(3) 101.7(2), N(1)–Mo–N(2) 109.1(2), N(1)–Mo–N(3) 112.6(2), N(2)–Mo–N(3) 125.0(2).

from a 1:1 diethyl ether–heptane mixture as orange–brown plates in 75.0% yield (Scheme 1). Diamagnetic **4** exhibits a single ^{31}P NMR signal at δ 284.4 {cf. δ 312 for $\text{Mo}[\text{P}(\text{C}_6\text{H}_{11})_2]_4$ ³⁴}. A reasonable oxidation state assignment for the Mo centre in **4** is +4. Proton NMR data for **4** are indicative of a single N(R)Ar ligand environment on the NMR timescale, although the solid-state structure of **4** reveals a low-symmetry conformation. A doublet ($^2J_{\text{PH}}$ 14 Hz) at δ 1.535 is attributed to the PMe moiety.

The three-coordinate phosphorus in **4** was shown by X-ray diffraction§ to be essentially planar [sum of angles = 359.2(3)°], consistent with Mo–P π bonding in the complex (Fig. 2). The observed $d(\text{MoP})$ of 2.169(2) Å is also consistent with a molybdenum–phosphorus multiple bond {cf. $d(\text{MoP})$ of 2.265(2) Å for $\text{Mo}[\text{P}(\text{C}_6\text{H}_{11})_2]_4$ ³⁴}. The conformation of **4** is noteworthy in that one of the N(R)Ar ligands is oriented with its *tert*-butyl group distal from phosphorus, presenting an Ar π cloud to the methyl substituent on phosphorus. The Zr–O–P(Me)–Mo core in **4** is reminiscent of Zr–O–C(R′)–M cores in zirconoxy carbenes prepared by addition of Zr–R′ (R′ = H, alkyl) bonds across the CO unit in metal carbonyl complexes.³⁵

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Footnotes and References

* E-mail: ccummins@mit.edu

† Alfred P. Sloan Fellow, 1997–2000.

‡ All manipulations were carried out under an atmosphere of dry nitrogen using solvents purified by standard methods. The new compounds **2** and **4** gave satisfactory elemental analyses (C, H and N).

§ Crystallographic data: For **2**: triclinic, space group $P\bar{1}$, a = 10.7615(8), b = 11.4942(9), c = 15.1899(11) Å, α = 89.865(2), β = 80.838(2), γ = 89.4900(10)°, U = 1854.9(2) Å³, Z = 2, 2988 unique reflections, data/

parameter ratio = 7.9, R_1 = 0.1207, wR_2 = 0.2683, GOF 1.050, residuals based on $I > 2\sigma(I)$.

For **4**: orthorhombic, space group $Pbca$, a = 11.3996(2), b = 23.2075(4), c = 39.2443(7) Å, U = 10382.3(3) Å³, Z = 8, 7456 unique reflections, data/parameter ratio 15, R_1 = 0.0669, wR_2 = 0.2023, GOF = 1.269, residuals based on $I > 2\sigma(I)$. CCDC 182/527.

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