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Phosphorus Monoxide, the Analogue of NO: Generation of Coordinated PO via Hydrolysis of an Aminophosphinidene Ligand. X-ray Structure of the Anion $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]^-$

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Although phosphorus monoxide is a spectroscopically well defined molecule[1] and a prime candidate for detection in interstellar space,[2] it remains a scientific curiosity. The lack of a simple synthetic route to PO coupled with its high degree of instability has left the chemistry of this heterodiatomic molecule essentially unexplored. Unlike its analogue NO, for which an extensive coordination chemistry exists,[3] only one report on complexed PO has appeared.[4] In this communication we describe a method for accessing cluster bound phosphorus monoxide ligands, which involves the trapping of a PO fragment from the hydrolytic P–N bond cleavage of an aminophosphinidene group. The *closo* anion $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]^-$, **1**, which has an apical μ_3-PO ligand, has been fully characterized by an X-ray analysis of a salt.

The replacement of μ-PPh_2 groups in the electron rich 64-electron clusters $Ru_4(CO)_{13}(\mu\text{-}PR_2)_2$ by aminophosphido ligands leads to a dramatic increase in reactivity.[5] We have now observed that the rich and diverse chemistry of the mixed main group–transition metal cluster *nido*-$Ru_4(CO)_{13}(\mu_3\text{-}PPh)$, **2**,[6] is significantly expanded by the presence of a π-donor diisopropylamino group on the phosphinidene ligand. Treatment of $K_2[Ru_4(CO)_{13}]$ (1.0 g, 1.2 mmol), generated in situ via the reduction of $Ru_3(CO)_{12}$ by K/Ph_2CO,[7] in THF with $Cl_2PNPr^i_2$ (0.22 mL, 1.2 mmol) at room temperature followed by filtration and chromatography on silica gel (eluant *n*-hexane) afforded $Ru_4(CO)_{13}(\mu_3\text{-}PNPr^i_2)$,[8] **3**, as deep red crystals from CH_2Cl_2/MeOH at -10 °C (18–22% yield). The molecular structure of **3**, not described here, closely resembles that of **2**, with the phosphinidene fragment capping an open Ru_3 face with an overall seven skeletal pair, five-vertex square pyramidal Ru_4P framework. Unlike **2**, however, solutions of **3** (0.100 g in 35 mL of C_6H_{14}, reflux) readily decarbonylate, leading to the high-yield (65%) formation of the cluster $Ru_4(CO)_{12}(\mu_3\text{-}PNPr^i_2)$, **4**, whose spectroscopic features[9] are indicative of a highly symmetrical structure (Scheme 1). X-ray analysis[10] (Figure 1) revealed a *closo* five-vertex polyhedron with the μ_3-$PNPr^i_2$ fragment capping one face of an Ru_4 tetrahedron. The simple conversion of *nido* square pyramidal **3** to *closo* trigonal bipyramidal **4** via loss of a two-electron donor has no precedent in iron group phosphinidene chemistry.[11] Indeed *closo* ruthenium $Ru_4(CO)_{12}(\mu_3\text{-}PR)$ clusters have proven elusive although a single iron analogue $Fe_4(CO)_{12}(\mu_4\text{-}PPr^i)$[12a] has been prepared. It, too, adopts a trigonal bipyramidal structural framework; however, unlike **4**, the μ_4-PPr^i fragment lies in the equatorial plane, symmetrically capping a butterfly array of metal atoms. *closo*-$Os_4(CO)_{12}(\mu_3\text{-}S)$, with a structure related to that of **4**, is also known,[12b] but it is interesting to note that in the related cluster $[FeRu_3(CO)_{12}(NO)]^-$ the nitrosyl ligand adopts a terminal, linear coordination mode to the unique iron atom.[12c]

Activation of P–N bonds in aminophosphine[13] and aminophosphido[5,14] complexes has been previously observed. Following the conversion of a μ-$P(NPr^i_2)_2$ to a phosphinidene by hydrogenolysis[5a] we reasoned that **4**, with a single P–N bond, might provide access to other μ-PX systems. Absorbing a CH_2Cl_2 solution of **4** onto silica gel and subsequent removal of the solvent led, after extraction with CH_3CN, to the quantitative formation of $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]$**1**$[Pr^i_2NH_2]$.[15] The source of water in the formation of **1** is the column material since rigorously dried silica gel led to only traces of **1**. A rational mechanism for the generation of **1** from **3** via hydrolysis involves the formation of the hydroxyphosphinidene cluster $Ru_4(CO)_{12}(\mu_3\text{-}POH)$ followed by proton transfer to Pr^i_2NH. Solutions of **1**$[Pr^i_2NH_2]$ are pale orange in color. Cluster **1** can also be isolated as its Et_4N^+ (ref 15) salt following metathesis with $Et_4N[Cl]$. The structure[16] of

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[8] Selected data for **3**: Anal. Calcd for $C_{19}H_{14}NO_{13}PRu_4$: C, 25.37; H, 1.57. Found: C, 25.10; H, 1.80. IR (CH_2Cl_2): 2092 w, 2053 vs, 2047 s, 2034 m, 2002 m, 1979 w cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 4.32 (sept, J_{HH} = 6.9 Hz, C*H*), 1.50 (d, J_{HH} = 6.9 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 466.0 (s) ppm.

[9] Selected data for **4**: Anal. Calcd for $C_{18}H_{14}NO_{12}PRu_4$: C, 24.80; H, 1.62. Found: C, 24.56; H, 1.63. IR (C_6H_{14}): ν(CO) 2086 w, 2041 m, 2034 vs, 2008 w, 1994 w, 1986 w cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 4.42 (sept, J_{HH} = 6.8 Hz, C*H*), 1.62 (d, J_{HH} = 6.8 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 467.0 (s) ppm.

[10] Deep red crystals of $Ru_4(CO)_{12}(\mu_3\text{-}PNPr^i_2)$ **4** from C_7H_8 at 263 K are triclinic, space group $P\bar{1}$, with a = 8.656(1) Å, b = 11.509(2), c = 13.760(2) Å, α = 89.84(2)°, β = 89.45(1)°, γ = 68.47(1)° at 200 K, V = 1275.2(4) Å^3, d_{calcd} = 2.270 g cm^{-3}, and Z = 2. Data were collected via ω scans on an LT2-equipped Nicolet-Siemens R3m/V diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the 2θ range 4.0–52°. A total of 5034 reflections were collected of which 4811 were observed [$F > 6.0\sigma(F)$]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to yield R = 0.0200 and R_w = 0.0291.

[11] The molecular and electronic structures of $M_4(CO)_x(\mu_{3/4}\text{-}PR)$ have been the subject of theoretical analyses by Hoffmann and co-workers (see: Halet, J. F.; Hoffmann, R.; Saillard, J.-Y. *Inorg. Chem.* **1985**, *24*, 1695). Thermal conversion of *nido*-$M_4(CO)_{13}(\mu_3\text{-}PR)$ to *closo*-$M_4(CO)_{12}(\mu_3\text{-}PR)$ may violate the noncrossing rule.

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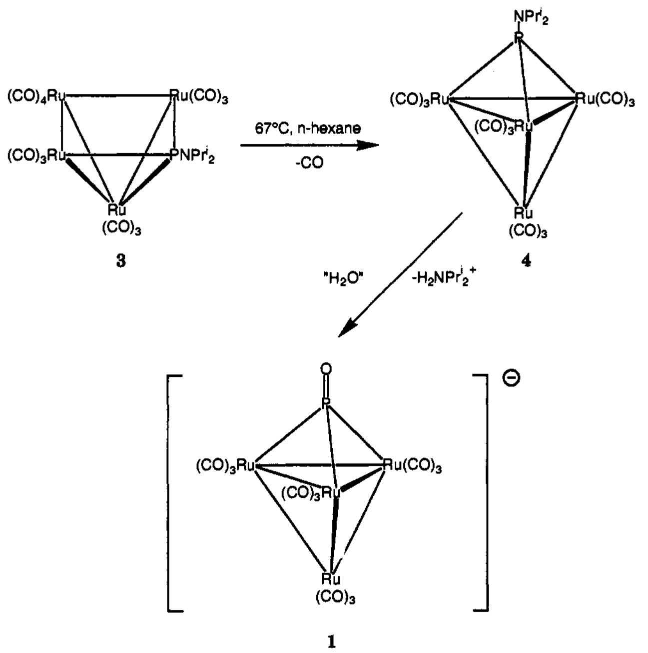
[15] Selected data for **1**$[Pr^i_2NH_2]$: Anal. Calcd for $C_{18}H_{16}NO_{13}PRu_4$: C, 24.30; H, 1.81. Found: C, 24.42; H, 1.53. IR (CH_2Cl_2): ν(CO) 2075 w, 2024 vs, 1978 w; ν(P=O) (KBr) 1075 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.32 (br s, NH_2), 3.48 (sept, J_{HH} = 6.4 Hz, C*H*), 1.41 (d, J_{HH} = 6.2 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 476.2 (s) ppm. Selected data for **1**$[Et_4N]$: Anal. Calcd for $C_{20}H_{20}NO_{13}PRu_4$: C, 26.18; H, 2.20. Found: C, 26.36; H, 2.40. IR (CH_2Cl_2): ν(CO) 2072 w, 2019 vs, 1974 w; ν(P=O) (KBr) 1169 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 3.27 (q, $^3J_{HH}$ = 7.3 Hz, CH_2), 1.35 (tt, $^3J_{HH}$ = 7.3, $^5J_{HH}$ = 1.7 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN, δ): 474.2 (s) ppm.

[16] Red pseudohexagonal plates of $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]$ **1**$[Pr^i_2NH_2]$, from CH_2Cl_2/C_7H_8 at 263 K are triclinic, space group $P\bar{1}$, with a = 8.983(2) Å, b = 11.514(2) Å, c = 14.030(2) Å, α = 80.89(2)°, β = 87.00(2)°, γ = 77.00(2)° at 295 K, V = 1395.8(3) Å^3, d_{calcd} = 2.117 g cm^{-3}, and Z = 2. Data were collected via ω scans as for **4** in the 2θ range 4.0–52°. A total of 5514 reflections were collected, of which 4544 were observed [$F > 6.0\sigma(F)$]. The solution and refinement of the structure gave R = 0.0245 and R_w = 0.0299.

0002-7863/94/1516-9799$04.50/0

Scheme 1



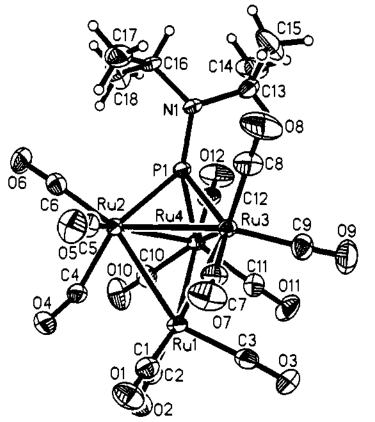


Figure 1. The molecular structure of *closo*-$Ru_4(CO)_{12}(\mu_3\text{-}PNPr^i_2)$, **4**, illustrating the trigonal bipyramidal skeletal framework. Important bond lengths (Å) and angles (deg): Ru(1)–Ru(2) = 2.848(1); Ru(1)–Ru(3) = 2.787(1); Ru(1)–Ru(4) = 2.810(1); Ru(2)–Ru(3) = 2.858(1); Ru(2)–Ru(4) = 2.847(1); Ru(3)–Ru(4) = 2.890(1); Ru(2)–P(1) = 2.270(1); Ru(3)–P(1) = 2.298(1); Ru(4)–P(1) = 2.309(1); P(1)–N(1) = 1.636(3); Ru(1)–Ru(2)–P(1) = 97.4(1); Ru(1)–Ru(3)–P(1) = 98.5(1); Ru(1)–Ru(4)–P(1) = 97.6(1).

$\mathbf{1}[Pr^i_2NH_2]$ (Figure 2) revealed a coordinated μ_3-PO ligand[17] which symmetrically caps a closed triangular Ru_3 face [Ru(2)–P(1) = 2.297(1) Å; Ru(3)–P(1) = 2.282(1) Å; Ru(4)–P(1) = 2.293(1) Å]. The reaction has thus led to the hydrolysis of the P–NPr^i_2 bond in **3** and the elimination of diisopropylamine as the cation $Pr^i_2NH_2^+$. The only other example of a PO complex of which we are aware, $[(\eta^5\text{-}Cp^4)_2Ni_2W(CO)_4(\mu_3\text{-}PO)_2]$, **5** ($Cp^4$ = $Pr^i_4C_5H$), was prepared by Scherer et al.[4] via oxidation of coordinated P_2 by $(Me_3Si)_2O_2$.[18] The P–O bond length of the μ_3-PO ligand in **1** [1.509(3) Å] is short, comparable to values in tertiary phosphine oxides[19] and to that in the PO molecule itself.[1] The ν(P=O) frequency in $\mathbf{1}[Pr^i_2NH_2]$ (1075 cm^{-1}) is at lower energy than that found for $\mathbf{1}[Et_4N]$ (1169 cm^{-1}) and reflects the presence of weak N—H···O=P interactions in the former [O(13)···H(1*x*) = 2.09 Å; O(13*a*)···H(1*y*) = 1.97 Å; ($a = -x, 1 - y, 1 - z$)]. The ν(CO) (CH_2Cl_2) stretches are at slightly higher energy for $\mathbf{1}[Pr^i_2NH_2]$ vs $\mathbf{1}[Et_4N]$, suggesting that weak O···H interactions may also be present in solution.

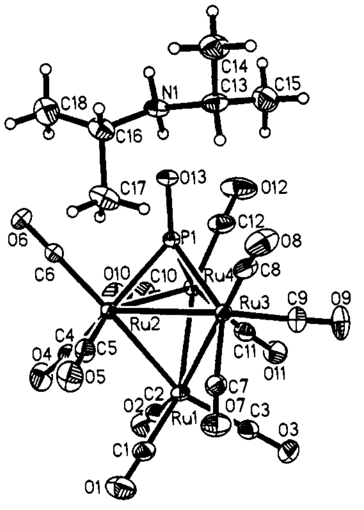


Figure 2. The molecular structure of *closo*-$[Ru_4(CO)_{12}(\mu_3\text{-}P{=}O)]\mathbf{1}[Pr^i_2NH_2]$, illustrating the coordinated P=O ligand. Important bond lengths (Å) and angles (deg): Ru(1)–Ru(2) = 2.799(1); Ru(1)–Ru(3) = 2.788(1); Ru(1)–Ru(4) = 2.818(1); Ru(2)–Ru(3) = 2.865(1); Ru(2)–Ru(4) = 2.856(1); Ru(3)–Ru(4) = 2.855(1); Ru(2)–P(1) = 2.297(1); Ru(3)–P(1) = 2.282(1); Ru(4)–P(1) = 2.293(1); P(1)–O(13) = 1.509(3); Ru(1)–Ru(2)–P(1) = 97.7(1); Ru(1)–Ru(3)–P(1) = 98.4(1); Ru(1)–Ru(4)–P(1) = 97.3(1).

The route described here to coordinated PO ligands should be applicable to other phosphinidene complexes bearing NR_2 substituents. Furthermore, the triply bridging PO ligand provides a basic site for binding clusters to metallic and cationic supports. These results open the door to new developments in PO chemistry.

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Supplementary Material Available: Details of the structure determination of complexes **1** and **4** (Tables S1 and S8) and tables of atomic positional parameters (Tables S2 and S9), bond distances (Tables S3 and S10), bond angles (Tables S4 and S11), anisotropic thermal parameters (Tables S5 and S12), and hydrogen atom positions (Tables S6 and S13) (16 pages); observed and calculated structure factors for **1** and **4** (Tables S7 and S14) (38 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) A referee has pointed out that **1** may also be described as a trimetallophosphine oxide.

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