The First Metal Cluster Containing a P_2O Ligand: $(CO)_{13}Ru_4(\mu_6,\eta^2\text{-}P_2O)Ru_4(CO)_{13}$
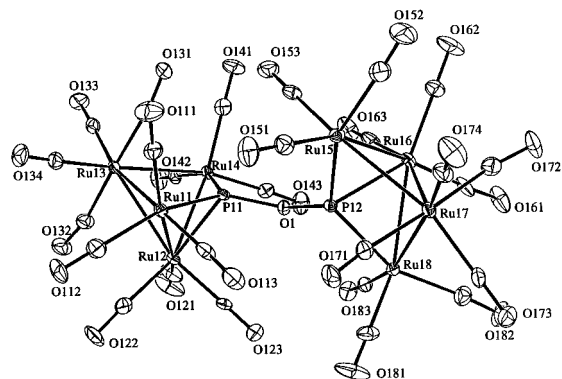
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Phosphorus monoxide (PO) is the simplest binary oxide of phosphorus,[1] but unlike its congener NO for which an extensive coordination chemistry has been developed, complexes of PO have only recently been described.[2−5] We now report the synthesis and characterization of $[\{Ru_4(CO)_{13}\}_2(\mu_6,\eta^2\text{-}P_2O)]$ (**1**), a molecule which can be described as a complex of the lower phosphorus oxide P_2O and the anhydride of the novel organometallic acid $[Ru_4(CO)_{13}(\mu_3\text{-POH})]$.

The phosphorus monoxide cluster anions $[M_4(CO)_{12}(\mu_3\text{-PO})]^-$ (M = Ru, Os) are the ultimate products of acid catalyzed hydrolysis and deprotonation of the aminophosphinidene complexes $Ru_4(CO)_{12}(\mu_3\text{-PNPr}^i_2)$.[3] However, in the reaction of the open faced 62-electron cluster $Ru_4(CO)_{13}(\mu_3\text{-PNPr}^i_2)$ (**2**) with $HBF_4\cdot O(C_2H_5)_2$, the novel fluoro- and hydroxyphosphinidene intermediates $Ru_4(CO)_{13}(\mu_3\text{-PF})$ (**3**) and $Ru_4(CO)_{13}(\mu_3\text{-POH})$ (**4**) can be isolated and characterized.[4,6] Deprotonation and decarbonylation of **4** leads to the conjugate base, the anionic PO cluster $[Ru_4(CO)_{12}(\mu_3\text{-PO})]^-$. We reasoned therefore that as an organometallic acid, the hydroxyphosphinidene complex **4**, like inorganic phosphorus acids, should undergo intermolecular condensation. Indeed small amounts of a side product **1** are always present in the conversion of **2** to **4**.[7] Cluster **1** exhibited no proton resonances in a ${}^1H$ NMR spectrum; however, a ${}^{31}P$-$\{^1H\}$ NMR experiment identified a singlet resonance at 508.97 ppm. This is in a ${}^{31}P$ chemical shift region characteristic of $\mu_3\text{-PO}$ and $\mu_3\text{-POMe}$ ligands.[3,4] A single-crystal X-ray study[8] of **1** revealed details of the molecular structure (Figure 1). There are two independent but virtually identical molecules in the crystallographic asymmetric unit. The structure consists of two

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(1) Matthews, H. E.; Feldman, P. A. *Astrophys. J.* **1987,** *312,* 358−362.
(2) Scherer, O. J.; Braun, J.; Walther, P.; Heckmann, G.; Wolmershauser, G. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 852−854.
(3) (a) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *J. Am. Chem. Soc.* **1994,** *116,* 9799−9800. (b) Wang, W.; Corrigan, J. F.; Doherty, S.; Enright, G. D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1996,** *15,* 2770−2776. (c) Wang, W.; Carty, A. J. *New J. Chem.* **1997,** *21,* 773−783.
(4) Foerstner, J.; Olbrich, F.; Butenschön, H. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 1234−1237.
(5) Johnson, M. J. A.; Odom, A. L.; Cummins, C. C. *J. Chem. Soc., Chem. Commun.* **1997,** 1523−1524.
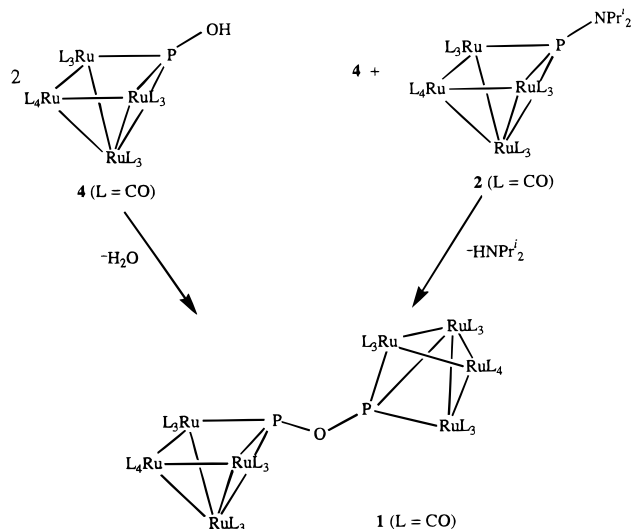(6) Wang, W.; Enright, G. D.; Driediger, J.; Carty, A. J. *J. Organomet. Chem.* **1997,** *541,* 461−464.
(7) Selected spectroscopic data for **1**: IR (CO) (CH₂Cl₂) 2098 w, 2068 vs, 2047 w, 2013 m cm⁻¹. ³¹P NMR (CDCl₃) 508.97 (s) ppm. Anal. Calcd for C₂₆O₂₇P₂Ru₈: C, 19.34; H, 0. Found: C, 19.25; H, 0.
(8) X-ray data were collected up to a 2θ maximum of 50.0° at −100 °C with a Siemens CCD detector, using the ω scan mode. Refinements were carried out with the NRCVAX system of programs. A weight based on statistics was used. Of 45 004 reflections measured 15 060 were unique (10 790 with *I* > 2.5σ(*I*)). All atoms were refined anisotropically. The refinement (based on *F*obs) converged to *R* = 0.039 and *R*w = 0.037. Crystal data for **1**: C₂₆O₂₇P₂Ru₈, *M* = 1614.78 (two molecules in the asymmetric unit cell), monoclinic, space group *P*2₁/*n*, *a* = 18.5210(6) Å, *b* = 16.7922(8) Å, *c* = 28.3183(12) Å, β = 104.653(10)°, *V* = 8520.8(3) Å³, *Z* = 8, μ = 28.7 cm⁻¹, *D*c = 2.52 g cm⁻³.
(9) (a) Andrews, L.; McCluskey, M.; Mielke, Z.; Withnall, R. *J. Mol. Struct.* **1990,** *222,* 95−108. (b) Andrews, L.; Withnall, R. *J. Am. Chem. Soc.* **1988,** *110,* 5605−5611.

Figure 1. Molecular structure of $(OC)_{13}Ru_4(POP)Ru_4(CO)_{13}$ (**1**). Selected bond lengths (Å): Ru(11)−Ru(12) = 2.804(1), Ru(11)−Ru(13) = 2.902(1), Ru(12)−Ru(13) = 2.948(1), Ru(12)−Ru(14) = 2.825(1), Ru(13)−Ru(14) = 2.892(1), Ru(15)−Ru(16) = 2.803(1), Ru(15)−Ru(17) = 2.898(1), Ru(16)−Ru(17) = 2.934(1), Ru(16)−Ru(18) = 2.818(1), Ru(17)−Ru(18) = 2.907(1), Ru(11)−P(11) = 2.279(2), Ru(12)−P(11) = 2.382(2), Ru(14)−P(11) = 2.276(2), Ru(15)−P(12) = 2.270(2), Ru(16)−P(12) = 2.385(2), Ru(18)−P(12) = 2.272(2), P(11)−O(1) = 1.643(5), P(12)−O(1) = 1.658(5).

$[Ru_4(CO)_{13}(\mu_3\text{-P})]$ fragments connected by an oxygen atom such that a nonlinear POP ligand bridges the two Ru_4 butterfly polyhedra. Although several examples of phosphorus monoxide clusters are now known,[2−5] we believe that **1** is the first example of a complex containing the binary oxide P_2O. The transient molecule diphosphorus monoxide P_2O has been characterized spectroscopically in matrices and like its analogue N_2O has a linear structure

$$\bar{P}=\overset{+}{P}=O$$
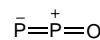
Unlike matrix isolated P_2O, however, the oxide in **1** has an isomeric, nonlinear

$$\underset{P\qquad\qquad P}{\overset{O}{\diagup\;\diagdown}}$$

structure. The ligand in **1** behaves as an 8-electron donor, the equivalent of two 4-electron donor phosphinidene groups. The arrangement of each $Ru_4(CO)_{13}(\mu_3\text{-P})$ fragment is similar to that of $M_4(CO)_{13}(\mu_3\text{-PR})$[3,10] and its phosphorus monoxide and hydroxyphosphinidene analogues,[4,6] i.e., each possesses a distorted *nido* square pyramidal M_4P stereochemistry with the phosphorus atom occupying a vertex of the base of the pyramid. The orientation of the second fragment is such that it appears to have rotated about the P−O−P bridge by approximately 120° (the dihedral angle between the two Ru_3P planes in **1** is 60.84(2)°). The presence of only a single ${}^{31}P$ signal in solution likely indicates rapid rotation of the two Ru_4P fragments relative to each other about the P−O−P bonds.

The oxygen atom O(1) lies relatively close to both Ru_3P square faces, being displaced 0.32(1) Å out of the Ru(11)−Ru(13)−Ru(14)−P(11) plane and 0.35(1) Å from the Ru(15)−Ru(17)−Ru(18)−P(12) plane. The M−M bond lengths vary from 2.803(1) to 2.948(1) Å and are within the normal range for Ru−Ru bonds in Ru_4 butterfly phosphinidene clusters.[3,6,10] The P−O distances (P(11)−O(1) = 1.643(5) Å; P(12)−O(1) = 1.658(5) Å) are significantly longer than those in hydroxyphosphinidene (e.g., $[Ru_4(CO)_{13}(\mu_3\text{-POH})]$ P−O = 1.627(2) Å) and methoxyphosphinidene[4] clusters and more than 0.15 Å

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Scheme 1

longer than in PO complexes.[2-5] This suggests that there is little P−O multiple bonding present within the P$_2$O ligand and that the large P(11)−O(1)−P(12) angle (140.8(3)°) reflects steric repulsion between the [Ru$_4$(CO)$_{13}$(μ_3-P)] fragments rather than O$p\pi$−P$d\pi$ interactions. The electronic structure of P$_2$O in **1** is therefore much closer to a P(1) oxide represented by nonlinear

.

One possible mechanism for the formation of cluster **1** is via the condensation of Ru$_4$(CO)$_{13}$(μ_3-POH) (**4**) with the elimination of water (Scheme 1). Efforts to improve the yield of **1** via treatment of **4** with various dehydrating agents met with only

limited success. However, another rational approach, consisting of the elimination of diisopropylamine from a mixture of **2** and **4** (Scheme 1), proved more useful. A 1:1 reaction mixture of complex **4** (32 mg, 0.027 mmol) via the protonation and hydrolysis of **2**, and cluster **2** (35 mg, 0.039 mmol) in CH$_2$Cl$_2$ (0.5 mL) was allowed to stir for 24 h during which time the elimination of HNPr$^i_2$ was monitored by the gradual diminution of the ν(CO) bands of **2**. TLC and recrystallization from CH$_2$Cl$_2$/hexane afforded air stable crystals of **1** in 35% yield.

Although complexes of P$_2$O are limited at present to **1** and its osmium analogue,[11] the synthetic method described herein and the fact that the new class of organocluster acids, the hydroxyphosphinidene (μ_3-POH) clusters, are readily prepared via protonation and hydrolysis of P−N bonds in μ_3-PNPr$^i_2$ compounds suggest that other molecules containing 8-electron donor P$_2$O bridges should be accessible. Clusters such as **1** are, like the inorganic pyrophosphates, the anhydrides of the corresponding phosphorus acids, in this case the hydroxyphosphinidene clusters. We envisage the generation of several new classes of polynuclear anhydrides from clusters with μ_3-POH or μ_2-P(OH)$_2$ groups and are currently exploring this interesting area.

Supporting Information Available: Experimental procedures and characterization data including X-ray structural details for compound **1** (12 pages). See any current masthead page for ordering and Internet access instructions.

(11) Selected spectroscopic data for [{Os$_4$(CO)$_{13}$}$_2$(μ_6,η^2-P$_2$O)]: IR (CO) (CH$_2$Cl$_2$) 2014 w, 2070 vs, 2049 w, 2035 w, 2017 w, 2006 m cm^{-1}. Crystal data for [{Os$_4$(CO)$_{13}$}$_2$(μ_6,η^2-P$_2$O)]: C$_{26}$O$_{27}$P$_2$Os$_8$, M = 2327.8, triclinic, space group $P\bar{1}$, a = 13.4617(6) Å, b = 18.9086(5) Å, c = 19.8632(8) Å, α = 61.836(10)°, β = 76.559(10)°, γ = 79.889(10)°, V = 4322.5(2) Å^3, Z = 4, μ = 244.4 cm^{-1}, D_c = 3.42 g cm^{-3}. There are two molecules in the asymmetric unit cell with a similar structure to that of **1**.