

Phosphorus monoxide as a quadruply bridging ligand: syntheses and X-ray crystal structures of $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PF})$ and $[\text{H}_2\text{NCy}_2][\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PO})]$

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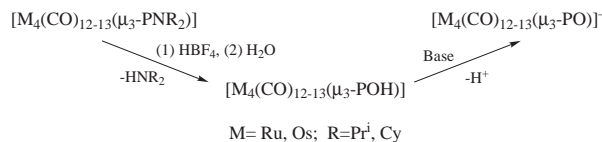
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The reaction of $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PNCy}_2)$ **1** with $\text{Ru}(\text{CO})_5$ in refluxing hexane yields $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PNCy}_2)$ **2** in high yield; treatment of **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ forms $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PF})$ **3** which is the first cluster complex to contain a μ_4 -fluorophosphinidene ligand, while refluxing **2** with $\text{HBF}_4 \cdot \text{H}_2\text{O}$ in CH_2Cl_2 yields **3** and the title compound $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-P=O})][\text{H}_2\text{NCy}_2]$ **4**, an unprecedented example of a cluster complex containing a μ_4 -PO ligand.

Phosphorus monoxide (PO) and diphosphorus monoxide (P_2O) are the simplest binary oxides of phosphorus. They have both been spectroscopically characterized in matrices and in molecular beams,¹ but they are not 'reagents in a bottle' since they are unstable with respect to the normal oxides P_4O_6 and P_4O_{10} .

In contrast to nitric oxide, the coordination and organometallic chemistry of PO and P_2O is poorly developed and only recently have methods of synthesizing complexes of these ligands been described.^{2–6} To date only two types of coordination modes for phosphorus monoxide are known. Triply bridging μ_3 -PO ligands have been trapped or generated in clusters by the direct oxidation of naked phosphide ligands^{2,4,5} or by the hydrolytic cleavage of P–N bonds in aminophosphinidene (μ_3 -PNR₂) clusters.³ Examples of terminal, η^1 -PO coordination, as in $\text{Mo}\{\text{[NC}(\text{CD}_3)_2\text{Me}]\text{(C}_6\text{H}_3\text{Me}_2\text{-3,5)}\}_3(\eta^1\text{-P=O})$,⁵ have also been described. Doubly and quadruply bonded PO ligands are as yet unknown. In this communication we report the synthesis and structural characterization of an anionic cluster $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-P=O})]^-$ containing a quadruply bridging phosphorus monoxide ligand. The designed synthesis of this molecule (Scheme 1) also affords the first example known to us of a μ_4 -fluorophosphinidene ligand in the neutral cluster $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PF})$.

We recently described a rational, versatile route to PO ligands which essentially involves the acid promoted substitution of NR₂ groups in aminophosphinidene (μ -PNR₂) ligands by hydroxyl groups followed by deprotonation of the latter by base, as follows:⁷

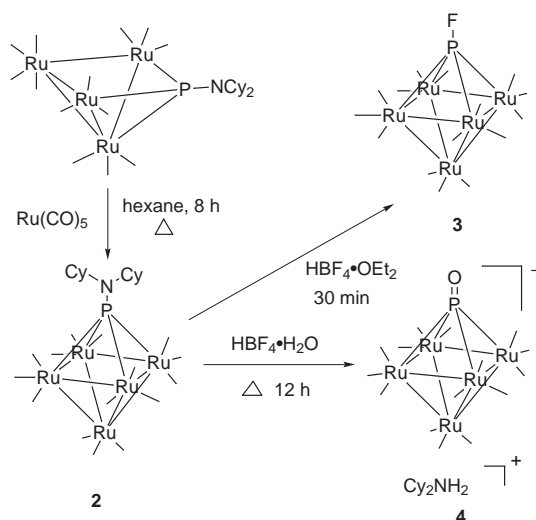


To apply this strategy to the synthesis of a μ_4 -PO ligand, we needed a reliable route to a cluster containing a μ_4 -PNR₂ ligand. Treatment of $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PNCy}_2)$ ⁸ **1** (770 mg, 0.78 mmol) in hexane for 8 h with an excess of $\text{Ru}(\text{CO})_5$ ⁹ forms $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PNCy}_2)$ **2**¹⁰ (867 mg, 0.76 mmol) in greater than 95% yield. The cluster **2** consists of a square based pyramid of five ruthenium tricarbonyl groups, with the square face capped by the μ_4 -aminophosphinidene ligand.

Reaction of a CH_2Cl_2 solution of **2** (503 mg, 0.51 mmol) with dry $\text{HBF}_4 \cdot \text{OEt}_2$ (300 μl) at RT for 3 h afforded $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PF})$ **3**¹¹ (503 mg, 0.51 mmol) as green crystals in 96% yield. The

¹⁹F and ³¹P NMR spectra of **3** consist of doublets [$\delta(^{19}\text{F})$ –20.49; $\delta(^{31}\text{P})$ 548.6] with $J_{\text{P-F}} = 1121$ Hz. Since **3** appears to be the first μ_4 -PF cluster a single crystal X-ray analysis was carried out.¹² Within the Ru_5 square pyramid (Fig. 1) there are two distinctively different sets of Ru–Ru distances with the bond lengths within the base (Ru–Ru av. 2.9196 Å) being distinctly longer than those to the apical atom Ru(5) (Ru–Ru av. 2.8252 Å). The stereochemistry at the phosphorus atom is that of a flattened square pyramid with a P–F distance of 1.595(2) Å which compares well with a value of 1.58 Å¹³ for the axial P–F bonds in PF_5 where the phosphorus atom is also pentacoordinate.

In contrast to the reaction with anhydrous HBF_4 , treatment of **2** (57 mg, 0.05 mmol) with an excess of $\text{HBF}_4 \cdot \text{H}_2\text{O}$ for 6 h gave smaller amounts of **3** (15 mg, 0.01 mmol, 31%) and afforded as the major product $[\text{H}_2\text{NCy}_2][\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PO})]$ **4** (37 mg, 0.03 mmol, 64%). Spectroscopically, **4**¹⁴ is characterized by a medium strong $\nu(\text{P=O})$ band in the infrared spectrum at 1060 cm^{-1} and by a ³¹P resonance at low field (δ 515). The structure¹⁵ of **4** (Fig. 2) consists of tetrahedral dicyclohexylamino cations packed in the crystal lattice with $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PO})]^-$ cluster anions. In contradistinction with $[\text{H}_2\text{N}(\text{iPr}_2)][\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]$ there are no significant hydrogen bond interactions between the PO oxygen atom and the cation ($\text{PO} \cdots \text{HN} = 1.75$ Å). The geometry of the Ru_5P skeleton resembles that in **3** but the substitution of a PO ligand in **4** for μ_4 -PF in **3** causes significant changes in P–X (X = O, F), Ru–P and basal Ru–Ru bond lengths. The P–O distance in **4** [1.516(4) Å] is 0.08 Å shorter than the P–F value [1.595(2) Å] in **3** and is consistent with P=O bond lengths of 1.48–1.52 Å in μ_3 -PO clusters.^{2–5} However the P–Ru bond lengths in **4** (av. 2.374 Å) are significantly elongated compared to **3** (av. 2.308 Å) and the basal Ru–Ru distances in **4** (av. 2.878 Å) are shorter than in **3**



Scheme 1

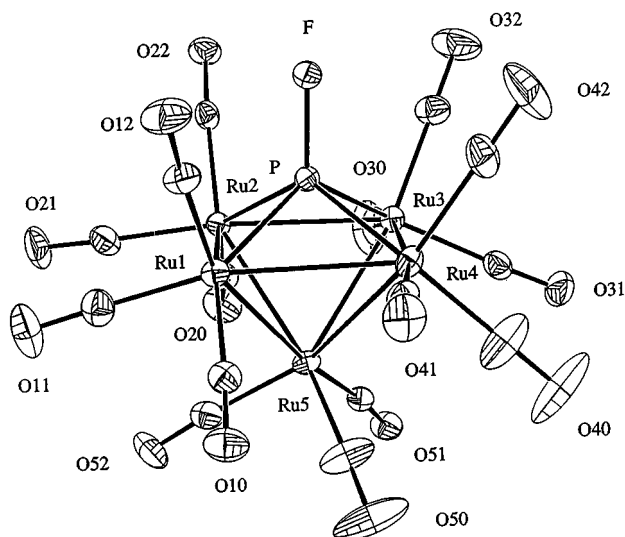


Fig. 1 An ORTEP diagram of $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PF})$ **3** showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths not mentioned in the text (\AA): Ru(1)–Ru(2) = 2.9558(4), Ru(1)–Ru(4) = 2.9310(4), Ru(2)–Ru(3) = 2.8983(4), Ru(3)–Ru(4) = 2.8932(4), Ru(5)–Ru(3) = 2.8535(4), Ru(1)–Ru(5) = 2.7771(4), Ru(4)–Ru(5) = 2.8432(4), Ru(5)–Ru(2) = 2.8271(4).

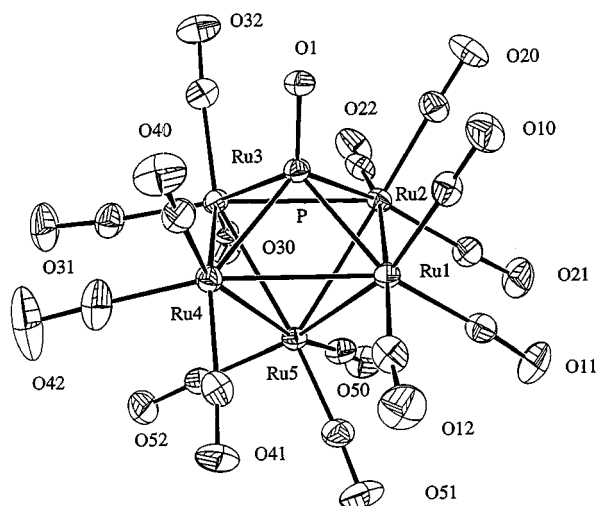


Fig. 2 An ORTEP diagram of $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PO})][\text{H}_2\text{NCy}_2]$ **4** showing 30% probability thermal ellipsoids. Hydrogen atoms and the cation $[\text{H}_2\text{N}(\text{Cy})_2]$ are omitted for clarity. Selected bond lengths not mentioned in the text (\AA): Ru(1)–Ru(2) = 2.850(1), Ru(1)–Ru(4) = 2.876(1), Ru(2)–Ru(3) = 2.893(1), Ru(3)–Ru(4) = 2.908(1), Ru(5)–Ru(3) = 2.908(1), Ru(1)–Ru(5) = 2.836(1), Ru(4)–Ru(5) = 2.803(1), Ru(5)–Ru(2) = 2.843(1).

(av. 2.9196 \AA). A simplistic explanation of these facts is that stronger phosphorus bonding to the *exo*-cage oxygen atom weakens cluster phosphorus bonding and strengthens metal–metal bonding.

Although **3** and **4** are obtained in the same reaction of **2** with $\text{HBF}_4 \cdot \text{H}_2\text{O}$, attempts to directly convert **3** to **4** in the presence of H_2O and HO^- have not been successful.

The synthesis and characterization of a quadruply bridging P=O ligand in **4** adds to the terminal and triply bridging modes now known for this transient ligand. We are currently

attempting to expand the range of $\mu_4\text{-PO}$ complexes and compare the chemistry of these coordinated ligands.

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Notes and References

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- 10 Spectral data for $\text{Ru}_5(\text{CO})_{13}\text{PN}(\text{Cy})_2$ **2**: IR (ν in hexane), 2091 w, 2050 vs, 2031 m, 2000 w, 1989 cm^{-1} . ^1H NMR (δ in CDCl_3), 3.52 (m, 2H), 1.78 (m, 9H), 1.62 (m, 9H), 1.24 (m, 2H). ^{31}P NMR (δ in CDCl_3), 490 (s). Anal. Calc. for **2**: C, 28.53, H, 1.95, N, 1.23. Found: C, 28.05, H, 1.85, N, 1.19%.
- 11 Spectral data for $\text{Ru}_5(\text{CO})_{15}\text{PF}$ **3**: IR (ν in hexane), 2068 vs, 2039 s, 2024 w, 2004 cm^{-1} . ^{31}P NMR (δ in CDCl_3), 548.6 (d, $J_{\text{P-F}} = 1121$). ^{19}F NMR (δ in CDCl_3 vs. CF_3COOH), -20.49 (d, $J_{\text{P-F}} = 1121$). Anal. Calc. for **3**: C, 18.47, H, 0.00, N, 0.00. Found: C, 19.20, H, 0.00, N, 0.00%.
- 12 Crystal data for **3**: green crystals, $\text{Ru}_5\text{PO}_{15}\text{C}_{15}\text{F}$, monoclinic, space group $P2_1/n$, $a = 9.6072(4)$, $b = 16.7952(7)$, $c = 15.4589(7)$ \AA , $\beta = 100.65(1)^\circ$, $V = 2451.4(2)$ \AA^3 , $Z = 4$, $M = 975.5$ $D_{\text{calc}} = 2.64$ mg m^{-3} , $\mu = 3.15$ mm^{-1} , Mo-K α , $\lambda = 0.70930$ \AA , $T = 123$ K, Siemens SMART CCD, crystal size $0.27 \times 0.22 \times 0.09$ mm, $2\theta_{\text{max}} = 57.5^\circ$, 28166 reflections measured, 6349 unique reflections, 5396 observed reflections [$I > 2.5\sigma(I)$], semi-empirical absorption correction. Structure solution by direct methods, refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Final R and R_w 0.033, 0.031. NRCVAX computer programs. CCDC 182/1001.
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- 14 Spectral data for $[\text{Ru}_5(\text{CO})_{15}\text{PO}][\text{H}_2\text{N}(\text{Cy})_2]$ **4**: IR (ν in CH_2Cl_2 for CO), 2061 (m), 2044(vs), 2031(m), 2013(s) cm^{-1} . IR (ν in CH_2Cl_2 for PO), 1060 (m) cm^{-1} . ^1H NMR (δ in CDCl_3), 6.72 (br s, 2H), 3.06 (m, 2H), 2.00 (d, 4H, $J_{\text{H-H}} = 11.30$), 1.90 (d, 4H, $J_{\text{H-H}} = 11.61$), 1.70 (d, 2H, $J_{\text{H-H}} = 10.63$), 1.45–1.18 (m, 10H). ^{31}P NMR (δ in CDCl_3), 515. Anal. Calc. for **4**: C, 28.08, H, 2.09, N, 1.21. Found: C, 27.50, H, 1.62, N, 1.52%.
- 15 Crystal data for **4**: green crystals, $\text{Ru}_5\text{PO}_{16}\text{C}_{15}\text{NC}_{12}\text{H}_{24}$, triclinic, space group $P\bar{1}$, $a = 10.241(2)$, $b = 12.914(3)$, $c = 30.897(6)$ \AA , $\alpha = 91.52(3)^\circ$, $\beta = 99.07(3)^\circ$, $\gamma = 108.18(3)^\circ$, $V = 3821.4(1)$ \AA^3 , $Z = 4$, $M = 1548$, $D_{\text{calc}} = 2.08$ mg m^{-3} , $\mu = 2.04$ mm^{-1} , Mo-K α , $\lambda = 0.70930$ \AA , $F(000) = 2324$, $T = 123$ K, Siemens SMART CCD, crystal size $0.04 \times 0.02 \times 0.15$ mm, $2\theta_{\text{max}} = 57.5^\circ$, 34779 reflections measured, 19259 unique reflections, 19259 observed reflections [$I > 2.5\sigma(I)$], semi-empirical absorption correction. Structure solution by direct methods, refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Final R and R_w 0.059, 0.093. ShelXNT computer programs. CCDC 182/1001.

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