

Hydroxyphosphinidene complexes. Novel organometallic cluster acids and precursors of coordinated phosphorus monoxide

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Abstract

The hydroxyphosphinidene cluster $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POH})$ **2**, a member of a new class of organometallic acids has been synthesised and structurally characterised. The $\mu_3\text{-POH}$ ligand which caps an open Ru_3 face of **2** can be deprotonated by base to give a phosphorus monoxide cluster anion $[\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]^-$ **4**. Capping of the Ru_3P face of **2** with $\text{Pt}(\text{CO})(\text{PPh}_3)$ affords the mixed metal cluster acid $\text{Ru}_4\text{Pt}(\text{CO})_{13}(\text{PPh}_3)(\mu_4\text{-POH})$ **5**. © 1997 Elsevier Science S.A.

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The phosphinidene group PR is a highly versatile, strongly coordinating 4-electron ligand for polynuclear chemistry with the capacity to bridge two metals, cap open or closed three or four metal faces [1–9] and provide π -electrons for delocalised metalocycles [10,11]. The seminal contributions of Huttner and his co-workers to this field are well recognised [12]. One interesting class of phosphinidene complexes which has not been explored is that in which the R substituent in $\mu\text{-PR}$ is a hydroxy group [13]. By analogy with their inorganic counterparts the hydroxyphosphines (e.g., $\text{P}(\text{OH})_3$), clusters with $\mu_{2-4}\text{-P}(\text{OH})$ ligands $\text{L}_n\text{M}_m[\mu\text{-P}(\text{OH})]$ might be expected to have acidic properties and hence via deprotonation form conjugate bases $[\text{L}_n\text{M}_m(\mu\text{-PO})]^-$ and salts $[\text{cat}][\text{L}_n\text{M}_m(\mu\text{-PO})]$ containing coordinated phosphorus monoxide PO. In this communication we describe the synthesis and structural characterisation of one such hydroxyphosphinidene complex $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POH})$ **2** and demonstrate its conversion to the phosphorus monoxide cluster anion $[\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]^-$ **4** and to the mixed metal hydroxyphosphinidene cluster $\text{Ru}_4\text{Pt}(\text{CO})_{13}(\text{PPh}_3)(\mu_4\text{-POH})$ **5** via capping of an Ru_3P face in **2** with $\text{Pt}(\text{CO})(\text{PPh}_3)$. An extensive and novel organometallic chemistry for hydroxyphosphinidene complexes can be confidently predicted.

We have previously shown that the P–N bonds in diisopropylaminophosphinidene clusters such as 60-electron $\text{M}_4(\text{CO})_{12}(\mu_3\text{-PNPr}_2^i)$ ($\text{M} = \text{Ru}, \text{Os}$) are susceptible to hydrolytic cleavage on silica gel, thus providing a route to phosphorus monoxide complexes [14,15]. Plausible intermediates in these reactions are hydroxyphosphinidene species. We have now succeeded in synthesising and isolating a representative $\mu_3\text{-POH}$ cluster via the protonation of $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PNPr}_2^i)$ **1** with strong acid in the presence of traces of water. Treatment of a solution of the 62-electron *nido* cluster $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PNPr}_2^i)$ (301 mg, 0.335 mmol) in CH_2Cl_2 (15 ml) dropwise with $\text{HBF}_4 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (0.117 ml of a 85% solution) followed by removal of solvent, extraction and repeated recrystallisation from undried hexane over 2 days afforded $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POH})$ **2** in 53% overall yield¹ based on **1**. Cluster **2** is a covalent molecule, soluble in hexane and sublimable in vacuo. As far as we are aware, **2** along with its osmium analogue [13] are the first examples of hydroxyphosphinidene clusters.

The pattern of the IR [$\nu(\text{CO})$] spectrum of **2** is very similar to that of **1** suggesting that the skeletal geometry

¹ Selected spectroscopic data for **2**: IR: $\nu(\text{OH})$ (KBr) 3583 cm^{-1} ; $\nu(\text{CO})$ (CH_2Cl_2) 2100w, 2062vs, 2055s, 2045m, 2017m, 1988w cm^{-1} . ³¹P NMR (CDCl_3): δ 498.6(s). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{PRu}_4$: C, 19.13; H, 0.12. Found: C, 19.14; H, 0.10.

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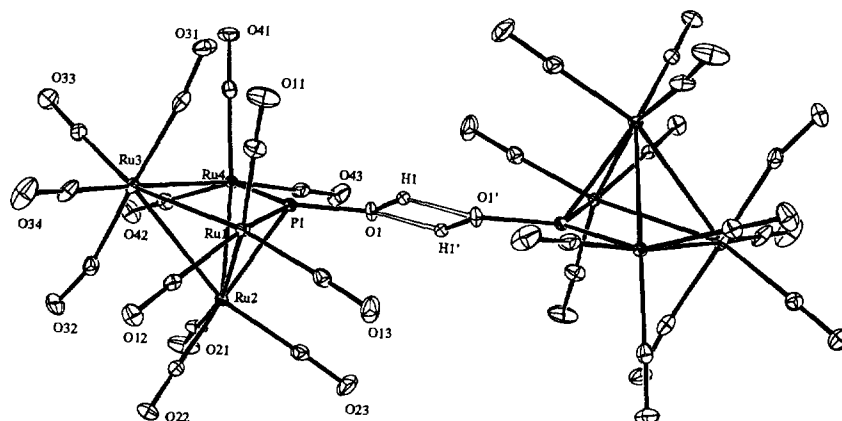


Fig. 1. Molecular structure of $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POH})$ showing the hydrogen bonding between symmetry related molecules. Selected bond lengths: $\text{Ru}(1)\text{-Ru}(2) = 2.802(1)$, $\text{Ru}(1)\text{-Ru}(3) = 2.914(1)$, $\text{Ru}(2)\text{-Ru}(3) = 2.924(1)$, $\text{Ru}(2)\text{-Ru}(4) = 2.830(1)$, $\text{Ru}(3)\text{-Ru}(4) = 2.859(1)$, $\text{Ru}(1)\text{-P}(1) = 2.278(1)$, $\text{Ru}(2)\text{-P}(1) = 2.367(1)$, $\text{Ru}(4)\text{-P}(1) = 2.266(1)$, $\text{P}(1)\text{-O}(1) = 1.627(2)$.

of **2** is essentially the same as that of the precursor **1**. A single crystal X-ray analysis² confirmed this hypothesis. The molecular structure of **2** (Fig. 1) consists of a distorted *nido* square pyramidal Ru_4P framework with the phosphorus atom of the phosphinidene group occupying a basal position and capping an open face of one axial and two basal $\text{Ru}(\text{CO})_3$ units. The remaining vertex of the square pyramid is an $\text{Ru}(\text{CO})_4$ fragment. A major difference is the replacement of the NPr_2^i group in **1**, by a hydroxy group. The P–O bond length (1.627(2) Å) in **2** is significantly longer than in phosphine oxides (e.g. Me_3PO P–O = 1.48 Å) [16] and in phosphorus monoxide clusters (e.g. $[\text{Et}_4\text{N}][\text{Os}_4(\text{CO})_{12}(\mu_3\text{-PO})]$ P–O = 1.48 Å) [15] but similar in magnitude to the P–OMe bond length in $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POMe})$ **3** (P–O = 1.61 Å) [17]³. This

indicates that the P–O bond in **2** is essentially a single bond. Attempts to detect the hydrogen atom of the hydroxyphosphinidene group by spectroscopic methods were only partially successful. In the IR spectrum only a broad, weak band at 3583 cm^{-1} provided any evidence for $\nu(\text{O-H})$ vibrations and ^1H NMR studies even at low temperatures failed to detect a P–O–H resonance probably due to rapid exchange. The X-ray analysis did however provide strong evidence for the presence of a P–OH group. After anisotropic refinement of all the non-hydrogen atoms, the peak of highest intensity in a Fourier difference map (H(1) in Fig. 1) is 0.96 Å from a P–O oxygen atom (O(1)) and 1.86 Å from a second, symmetry-related P–O oxygen atom. The next 10 peaks are all close to heavy atoms or carbonyl carbon atoms. We conclude that the P–OH hydrogen atom H(1) is hydrogen bonded to O(1') of a second hydroxyphosphinidene cluster as illustrated in Fig. 1. A similar hydrogen bond relationship between O(1')–H(1') and O(1) in the two symmetry related clusters exists. This structural data together with the P–O bond length and the results of HYDEX [18] potential energy calculations which provided no indication of the presence of either terminal or bridging metal hydrides, is strong evidence that the compound **2** is indeed a hydroxyphosphinidene cluster. Further confirmation of the nature of **2** was obtained from its reaction with bases. Treatment of **2** with HNPr_2^i in CH_2Cl_2 afforded $[\text{H}_2\text{NPr}_2^i][\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]$ (**4**) in high yield, identified by comparison with an authentic sample of the known compound synthesized via a different route [14,15]. Thus deprotonation of the acid and loss of a carbonyl converted **2** to a derivative of its base, the phosphorus monoxide cluster anion $[\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]^-$. Treatment of **2** with methanol produced the methoxyphosphinidene cluster $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-POMe})$ **3** via OH for OMe exchange [17]. The structure [17] of **3** is closely related to that of **1** and **2**.

² X-ray data were collected with a Siemens CCD detector using the omega scan mode and refinement was carried out with the NRCVAX system of programs for **2** and **5** and SHELXTL PLUS for **3**. Weights based on statistics were used for all the cases. The data for **2** were collected up to a 2θ maximum of 57.5° at -150° . Of 23858 reflections measured 5388 were unique (4550 with $I > 2.5\sigma(I)$). All nonhydrogen atoms were refined anisotropically. The hydrogen atom was located from the difference map and refined with half occupancy varying only the thermal parameter. The refinement (based on F_{obs}) converged to $R = 0.020$ and $R_w = 0.020$. Crystal data for **2**: $\text{C}_{13}\text{H}_3\text{O}_{14}\text{PRu}_4$, $M = 816.40$, monoclinic, space group $P 2_1/n$, $a = 9.322(1)$, $b = 14.174(1)$, $c = 15.927(1)$, $\beta = 98.71(1)^\circ$, $V = 2080.2(2)\text{ \AA}^3$, $Z = 4$, $\mu = 29.40\text{ cm}^{-1}$, $D_c = 2.61\text{ g cm}^{-3}$.

³ Selected spectroscopic data for **3**: IR: $\nu(\text{CO})$ (CH_2Cl_2) 2099w, 2061vs, 2053s, 2043m, 2014m, 1987w cm^{-1} . ^1H NMR (CDCl_3): δ 3.82(d, $J_{\text{PH}} = 14.9\text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 519.55. ^{31}P NMR (CDCl_3): δ 519.75 (q , $J_{\text{PH}} = 14.7\text{ Hz}$). X-ray data for **3** were collected up to a 2θ maximum of 51.4° at 23° . Of 9966 reflections measured 3841 were unique (3424 with $I > 3.0\sigma(I)$). All nonhydrogen atoms were refined anisotropically. The refinement (based on F_{obs}) converged to $R = 0.023$ and $R_w = 0.023$. Crystal data for **3**: $\text{C}_{14}\text{H}_3\text{O}_{14}\text{PRu}_4$, $M = 830.40$, monoclinic, space group $P 2_1/c$, $a = 15.602(1)$, $b = 9.348(1)$, $c = 15.992(1)$, $\beta = 104.04(1)^\circ$, $V = 2262.7(6)\text{ \AA}^3$, $Z = 4$, $\mu = 27.56\text{ cm}^{-1}$, $D_c = 2.44\text{ g cm}^{-3}$.

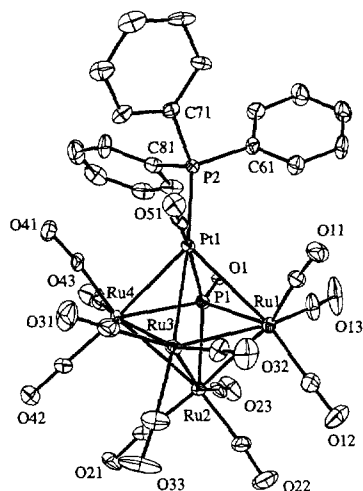


Fig. 2. Molecular structure of $\text{Ru}_4\text{Pt}(\text{PPh}_3)(\text{CO})_{13}(\mu_4\text{-POH})$. Selected bond lengths: $\text{Pt}(1)\text{-Ru}(1) = 2.974(1)$, $\text{Pt}(1)\text{-Ru}(3) = 2.762(1)$, $\text{Pt}(1)\text{-Ru}(4) = 2.967(1)$, $\text{Ru}(1)\text{-Ru}(2) = 2.866(1)$, $\text{Ru}(1)\text{-Ru}(3) = 2.845(1)$, $\text{Ru}(2)\text{-Ru}(3) = 2.881(1)$, $\text{Ru}(2)\text{-Ru}(4) = 2.892(1)$, $\text{Ru}(3)\text{-Ru}(4) = 2.808(1)$, $\text{Pt}(1)\text{-P}(1) = 2.278(3)$, $\text{Ru}(1)\text{-P}(1) = 2.322(3)$, $\text{Ru}(2)\text{-P}(1) = 2.305(3)$, $\text{Ru}(4)\text{-P}(1) = 2.330(3)$, $\text{P}(1)\text{-O}(1) = 1.604(5)$ Å.

The *nido*, 7 skeletal pair, 5 vertex square pyramidal geometry of **2** suggests the possibility of capping the Ru_3P face with a second transition metal fragment to generate new $\mu_3\text{-POH}$ clusters. Reaction of **2** with one equivalent of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ in CH_2Cl_2 gave a green solution. Chromatography on TLC plates, extraction of the green band and recrystallisation via slow evaporation of CH_2Cl_2 afforded $\text{Ru}_4\text{Pt}(\text{CO})_{13}(\text{PPh}_3)(\mu_4\text{-POH})$ **5** in 55% yield⁴. The molecular structure⁵ of the 74-electron cluster **5** (Fig. 2) displays a *closo* octahedral Ru_4PtP skeleton with the $\text{Pt}(\text{CO})(\text{PPh}_3)$ fragment capping the open Ru_3P face of the precursor **2**. The reaction thus involves the loss of ethylene from platinum, exchange of one PPh_3 ligand for CO and coordination of the $\text{d}^{10}\text{-Pt}(\text{CO})(\text{PPh}_3)$ fragment to the ruthenium cluster. Within the Ru_4PtP skeleton the Ru–Ru distances (2.808(1)–2.892(1) Å) lie within the normal

range but the Pt–Ru(3) bond length of 2.762(1) Å is more than 0.2 Å shorter than the average of the Pt–Ru(1) and Pt–Ru(4) distances (av. 2.971 Å). This reflects the fact that the $\text{Ru}(1)\text{-Ru}(3)\text{-Ru}(4)\text{-P}(1)$ rhombus is compressed along the $\text{Ru}(3)\dots\text{P}(1)$ diagonal to accommodate a strong Pt–P(1) interaction, and short $\text{Ru}(1)\text{-P}(1)$ (2.322(3) Å) and $\text{Ru}(4)\text{-P}(1)$ (2.330(3) Å) bonds such that the angles $\text{Ru}(1)\text{-Ru}(3)\text{-Ru}(4)$ (94.79°) and $\text{Ru}(1)\text{-P}(1)\text{-Ru}(4)$ (126.83°) are consistently larger than $\text{P}(1)\text{-Ru}(1)\text{-Ru}(3)$ (68.68°) and $\text{P}(1)\text{-Ru}(4)\text{-Ru}(3)$ (69.26°). The PPh_3 ligand occupies a *cis* position with respect to the OH group of the phosphinidene. The ^{31}P NMR spectrum of **5** shows two doublets in both the phosphinidene and phosphine regions indicating the presence of two isomers in solution. The similarity of J_{PP} and J_{PtP} coupling constants and ^{31}P chemical shifts in these isomers suggests that they differ only in the location of the phosphine in the P(2) or C(51) sites shown in Fig. 2. The P–O distance (1.604(5) Å) indicates a predominantly single bond and is consistent with the presence of an-OH moiety. The hydroxyphosphinidene group behaves as a μ_4 -ligand in this case, capping three Ru atoms and the Pt atom in the octahedral Ru_4PtP core. Although **5** is structurally analogous to homopentanuclear clusters such as $\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PPh})$ [1b, [19]], mixed metal pentametallic phosphinidene clusters are rare and there are no examples of such molecules with $\mu_4\text{-POH}$ ligands.

As the first μ_3 - and μ_4 -hydroxyphosphinidene clusters of ruthenium **2** and **5** represent members of a new class of organometallic acids. Furthermore, the conversion of **2** to the phosphorus monoxide cluster anion **4** via deprotonation indicates the potential for a novel acid–base and coordination chemistry. Application of the synthetic strategies described herein to the generation of a broader range of hydroxyphosphinidene and phosphorus monoxide clusters as well as coordination complexes of anionic “metallated phosphine oxides” such as $[\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PO})]^-$ is underway.

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⁴ Selected spectroscopic data for **5**: IR: $\nu(\text{OH})$ (KBr) 3065 cm^{-1} ; $\nu(\text{CO})$ (CH_2Cl_2) 2086w, 2053vs, 2048s,sh, 2032vw, 2020m, 1979w cm^{-1} . ^1H NMR (CDCl_3): δ 7.46–7.54(m). ^{31}P NMR (CDCl_3): δ 488.52(d, $J_{\text{PP}} = 10.2$ Hz, $J_{\text{PtP}} = 635.6$ Hz), 483.10(d, $J_{\text{PP}} = 11.0$ Hz, $J_{\text{PtP}} = 644.7$ Hz), 33.51(d, $J_{\text{PP}} = 11.1$ Hz, $J_{\text{PtP}} = 1603.1$ Hz), 33.42(d, $J_{\text{PP}} = 10.5$ Hz, $J_{\text{PtP}} = 1613.2$ Hz). Anal. Calcd for $\text{C}_{33}\text{H}_{16}\text{O}_{14}\text{P}_2\text{Ru}_4\text{Pt}$: C, 29.23; H, 1.27. Found: C, 29.18; H, 1.22.

X-ray data for **5** were collected up to a 2θ maximum of 50.0° at -100° using the omega scan mode. Of 7428 reflections measured 5184 were unique (4103 with $I > 2.5\sigma(I)$). 125 reflections with $2\theta < 50.0^\circ$ were missed. All nonhydrogen atoms were refined anisotropically. The refinement (based on F_{obs}) converged to $R = 0.034$ and $R_w = 0.040$. Crystal data for **3**: $\text{C}_{31}\text{H}_{16}\text{O}_{14}\text{P}_2\text{Ru}_4\text{Pt}$, $M = 1233.77$, triclinic, space group $\text{P}\bar{1}$, $a = 10.176(1)$, $b = 13.204(1)$, $c = 14.395(1)$, $\alpha = 72.86(1)^\circ$, $\beta = 88.13(1)^\circ$, $\gamma = 85.23(1)^\circ$, $V = 1841.8(5)$ Å³, $Z = 2$, $\mu = 55.50$ cm^{-1} , $D_c = 2.30$ g cm^{-3} .

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