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Preliminary Communication

New electron rich Ru_3P_4 and Ru_4P_3 phosphido clusters: synthesis and molecular structures of the expanded triangular and butterfly clusters $(\mu_3\text{-H})Ru_3(CO)_6(\mu\text{-PPh}_2)_3[\mu\text{-P(Ph)}C_6H_4]$ and $(\mu\text{-H})_2Ru_4(CO)_{10}(\mu_3\text{-PPh})(\mu PPh_2)_2$ [*]

John F. Corrigan, Simon Doherty, Nicholas J. Taylor
and Arthur J. Carty

*Guelph-Waterloo Centre for Graduate Work in Chemistry,
Waterloo Campus, Department of Chemistry, University of Waterloo,
Waterloo, Ont. N2L 3G1 (Canada)*

Ermete Boroni and Antonio Tiripicchio

*Istituto di Chimica Generale ed Inorganica, Università di Parma,
Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Viale delle Scienze, I-43100 Parma (Italy)*

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Abstract

Reaction of $Ru_3(CO)_{12}$ with Ph_2PPPh_2 in refluxing n-heptane affords the 50-electron cluster $(\mu_3\text{-H})Ru_3(CO)_6(\mu\text{-PPh}_2)_3[\mu\text{-P(Ph)}C_6H_4]$ **1** containing a μ_3-ligated hydride and an orthometalated phenyl ring. The photolytic reaction of Ph_2PH with electron precise $Ru_4(CO)_{13}(\mu_3\text{-PPh})$ yields the 64-electron butterfly cluster $(\mu\text{-H})_2Ru_4(CO)_{10}(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2$ **2**. Single crystal analyses revealed that both **1** and **2** possess expanded metal atom frameworks, a result of their electronic oversaturation.

Several examples of electron rich M_3, M_4 and M_5 clusters with expanded metal frameworks have recently been described [1]. The unusual patterns of M–M bond elongation in these molecules result from a small HOMO–LUMO gap and the population of molecular orbitals antibonding with respect to the core [2]. Interest in these electron rich clusters stems not only from their novel structural features but from an expectation of enhanced chemical reactivity associated with two electron processes [3]. In this communication we describe two new electron rich phosphido clusters $(\mu_3\text{-H})Ru_3(CO)_6(\mu\text{-PPh}_2)_3[\mu\text{-P(Ph)}C_6H_4]$ **1** and $(\mu\text{-H})_2Ru_4(CO)_{10}(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2$ **2** with distinctive expanded triangular and butterfly frameworks.

Heating a n-heptane solution (220 mL) of $Ru_3(CO)_{12}$ (1.00 g, 1.56 mmol) and Ph_2PPPh_2 (1.80 g, 4.86 mmol) at reflux for 15 min afforded the new cluster **1** [†] in 20% yield after chromatographic workup and fractional crystallisation from n-heptane–CH_2Cl_2 (10:1). This reaction also provides a useful route to the electron-rich system $Ru_4(CO)_{10}(\mu\text{-PPh}_2)_4$ [1d] (17%) and to $Ru_2(CO)_6(\mu\text{-PPh}_2)_2$ [4] (45%). The $^{31}P\{^1H\}$ NMR spectrum of **1** consisted of three resonances all at high field compared to normal μ-PPh_2 chemical shifts in electron precise ruthenium clusters [5]. Although these shifts were indicative of elongated Ru–Ru bonds, an X-ray analysis [††] was necessary to establish the full details of the molecular structure (Fig. 1). The Ru_3 framework is quite unusual in that all three of the metal–metal bonds are exceptionally long, with the average Ru–Ru distance [3.129(1) Å] fully 0.25 Å longer than the standard distance in $Ru_3(CO)_{12}$ (2.85 Å) [6]. Three of the phosphorus atoms [P(1), P(2), P(3)] lie essentially in the Ru_3 plane. The fourth phosphido group is orthometalated on one ring [7] and this μ_3-$P(Ph)C_6H_4$ ligand lies approximately perpendicular to the Ru_3P_3 framework with a pseudo plane of symmetry bisecting the Ru(1)–Ru(2) vector and passing through Ru(3). The 50-electron count associated with **1** presumably accounts for the elongation of the Ru–Ru vectors. Remarkably, there are few other published

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Correspondence to: Prof. A.J. Carty.

[*] Dedicated to Prof. Michael F. Lappert on the occasion of his 65th birthday.

[†] Selected data for **1**: IR: ν(CO)cm^{-1} (CH_2Cl_2) 2048s, 2033s, 2015m, 1975s and 1956m. NMR: $^{31}P\{^1H\}$ 81.0 MHz, $CDCl_3$) δ 45.3 (dt, P_1, P_4, $^2J_{P_1P_4} = 83.8$ Hz, $^2J_{P_{2/3}P_4} = 11.9$ Hz), 26.2 (dd, $P_{2/3}$, $^2J_{P_1P_{2/3}} = 93.4$ Hz, $^2J_{P_{2/3}P_1} = 11.9$ Hz), −89.5 (dt, P_1, $^2J_{P_1P_{2/3}} = 93.5$ Hz, $^2J_{P_1P_4} = 83.9$ Hz) ppm. ^1H (200 MHz, $CDCl_3$) δ 7.9–5.5 ppm (mult., *H* phenyl), −17.9 (mult., μ_3-*H*) ppm. Anal. Calcd. for $C_{54}H_{40}O_6P_4Ru_3$: C, 53.51; H, 3.33. Found: C, 53.18; H, 3.09%.

[††] Crystal data for **1**: red platelets from the slow evaporation of a C_7H_{16}–CH_2Cl_2 solution at 295 K. $C_{54}H_{40}O_6P_4Ru_3$, M = 1212.0, monoclinic, space group $C2/c$, $a = 21.461(3)$, $b = 20.290(2)$, $c = 24.275(3)$ Å, $\beta = 108.79(1)°$, $V = 10007(2)$ Å^3, $Z = 8$, $D_c = 1.609$ g cm^{-3}, $F(000) = 4832$, μ(Mo-Kα) = 10.71 cm^{-1}. The structure was solved (Patterson, Fourier techniques) and refined (full-matrix least-squares, all non-hydrogen atoms anisotropic) on the basis of 7626 observed $[F > 6.0\sigma(F)]$ reflections measured at 200 K on an LT-2 equipped Siemens R3m/V diffractometer ($2\theta_{max} = 50.0°$). The final *R* and *Rw* values were 2.20 and 2.52% respectively.

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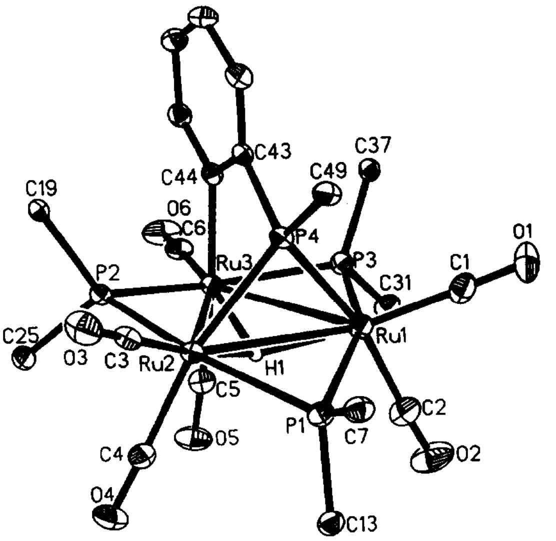
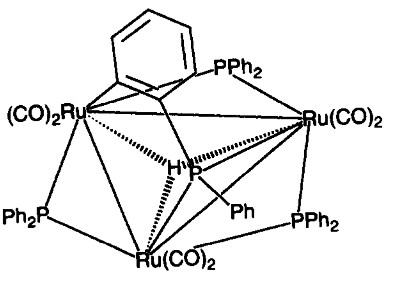


Fig. 1. The molecular structure of $(\mu_3\text{-H})Ru_3(CO)_6(\mu\text{-PPh}_2)_3[\mu\text{-P(Ph)}C_6H_4]$ **1** illustrating the orthometalated phenyl ring and the μ_3-ligated hydride. For clarity, only the *ipso* carbon atoms of the non interacting phenyl rings are shown. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 3.034(1); Ru(1)–Ru(3) 3.207(1); Ru(2)–Ru(3) 3.146(1); Ru(1)–P(1) 2.395(1); Ru(2)–P(1) 2.374(1); Ru(2)–P(2) 2.393(1); Ru(3)–P(2) 2.349(1); Ru(1)–P(3) 2.390(1); Ru(3)–P(3) 2.363(1); Ru(1)–P(4) 2.379(1); Ru(2)–P(4) 2.402(1); Ru(3)–C(44) 2.151(3); Ru(1)–H(1) 1.87; Ru(2)–H(1) 1.84; Ru(3)–H(1) 2.02; Ru(1)–H(1)–Ru(2) 110; Ru(1)–H(1)–Ru(3) 111; Ru(2)–H(1)–Ru(3) 109; P(4)–C(43)–C(44) 115.9(2).

reports of 50-electron trinuclear ruthenium clusters [1a,1b,1h,8]. Of these $Ru_3(CO)_9[\mu\text{-PPh}(C_5H_4N)]$ [1a], $Ru_3(CO)_9(\mu_3\text{-}C_2R)(\mu\text{-PPh}_2)$ [8a] and $(\mu\text{-H})_2(H)_2Ru_3(CO)_8(\mu\text{-P}^tBu_2)_2$ [8b] have an "open" metal-metal edge whereas only the recently reported $Ru_3(CO)_7(\mu\text{-PPh}_2)_2(\mu\text{-Cl})$ [1b] and $Ru_3(CO)_6(\mu_3\text{-}\eta^2\text{-PhPpy})(\mu\text{-PPh}_2)_3$ [1h] display an elongation of all three Ru–Ru bonds in a similar pattern to that observed in **1**. The bond lengths in $Ru_3(CO)_7(\mu\text{-PPh}_2)_3(\mu\text{-Cl})$ [2.9293(8)–3.2222(7) Å] encompass a wider range than in **1** although the average Ru–Ru distance is quite similar in both molecules.



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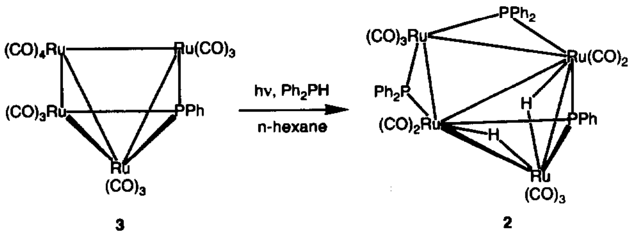

Scheme 1.

The 62-electron butterfly cluster $Ru_4(CO)_{13}(\mu_3\text{-PPh})$ **3** obtained from the thermolysis of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-PPh}_2)$ [9a] has a rich and diverse chemistry [9] which includes the facile activation of dihydrogen [9c] and of reactive X–H bonds and the oligomerisation of alkynes and diynes [9d]. Irradiation of **3** (0.120 g, 0.137 mmol; 450 W Hg lamp) in the presence of diphenylphosphine (50 μl, 0.287 mmol) in n-hexane (120 ml) for 30 min afforded **2** as the major product (35%) after chromatographic workup (Scheme 1). Once again the presence of a high field resonance in the $^{31}P\{^1H\}$ NMR spectrum[†††] was indicative of elongated Ru–Ru interactions and a single crystal X-ray analysis[‡] confirmed the presence of an expanded molecular framework (Fig. 2).

Compound **2** crystallises with two independent but essentially identical molecules in the asymmetric unit. Bond lengths and angles quoted refer to molecule 1. The butterfly cluster **2** contains a μ_3-PPh, two $\mu_2\text{-PPh}_2$ and two μ_2-H ligands which, in addition to the ten carbonyl groups, contribute to the 64-electron count, two in excess of that predicted by the EAN rule. The reaction has thus led to the oxidative addition of two P–H bonds onto the cluster framework. Close examination of the molecular framework reveals three elongated and two "normal" Ru–Ru interactions [Ru(11)–

[†††] Selected data for **2**: ν(CO) cm^{-1} (C_6H_{12}) 2096 w, 2083 m, 2042 vs, 2033 m, 2027 s, 2014 w, 1987 w, 1966 w, 1961 w. NMR: $^{31}P\{^1H\}$ (101.3 MHz, $CDCl_3$) δ 243.0 (t, P_1, $^2J_{PP} = 103.2$ Hz), 71.4 (d, $P_{2/3}$, $^2J_{PP} = 102.2$ Hz) ppm. ^1H (200 MHz. $CDCl_3$) δ 8.4–7.2 (mult., *H* phenyl), −19.18 (dt, μ-*H*, $^2J_{P_1H} = 15.0$ Hz, $^2J_{P_{2/3}H} = 3.0$ Hz). Anal. Calcd. for $C_{40}H_{27}O_{10}P_3Ru_4$: C, 41.25; H, 2.34. Found: C, 41.28; H. 2.26%.

[‡] Crystal data for **2**: deep orange prisms from C_7H_{16}–C_7H_8 at 263 K. $C_{40}H_{27}O_{10}P_3Ru_4 \cdot 0.75C_7H_8$, $M = 1233.9$, triclinic, space group $P\bar{1}$, $a = 12.642(2)$, $b = 15.255(2)$, $c = 24.692(3)$ Å, $\alpha = 89.62(2)$, $\beta = 84.26(2)$, $\gamma = 84.46(2)$°, $V = 4715.9(10)$ Å^3, $Z = 4$, $D_c = 1.738$ g cm^{-3}, $F(000) = 2422$, μ(Mo-Kα) = 14.13 cm^{-1}. The structure was solved (Patterson and Fourier) and refined (blocked-matrix least-squares, all non-hydrogen atoms anisotropic) on the basis of 10961 observed [$F > 6.0\sigma(F)$] reflections measured at 200 K on an LT-2 equipped Siemens R3m/V diffractometer ($2\theta_{max} = 46.0$°). The hydride ligands were fixed in their found positions with refined isotropic U. The final *R* and *Rw* values were 2.28 and 2.68% respectively.

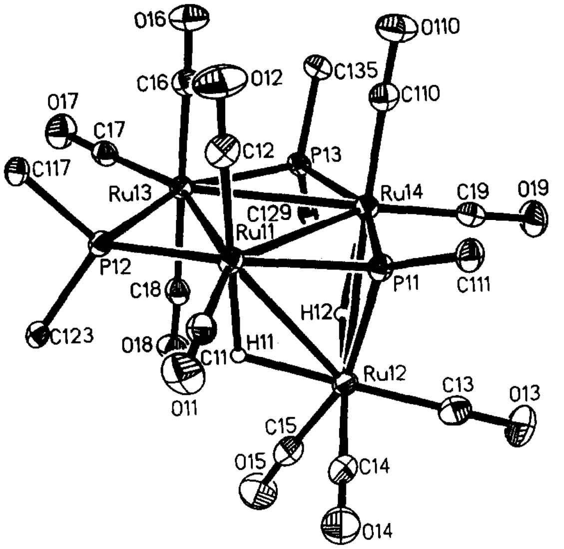

Fig. 2. A perspective view of one of the independent molecules of $(\mu\text{-H})_2Ru_4(CO)_{10}(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2$ 2 (molecule 1). Only the *ipso* carbon atoms of the phenyl rings are illustrated. Selected bond lengths (Å) and angles (°): Ru(11)–Ru(12) 2.977(1); Ru(11)–Ru(13) 3.232(1); Ru(11)–Ru(14) 3.159(1); Ru(12)–Ru(14) 3.012(1); Ru(13)–Ru(14) 3.177(1); Ru(11)–P(11) 2.293(1); Ru(12)–P(11) 2.317(1); Ru(14)–P(11) 2.291(1); Ru(11)–H(11) 1.83; Ru(12)–H(11) 1.79; Ru(12)–H(12) 1.72; Ru(14)–H(12) 1.88; Ru(11)–H(11)–Ru(12) 111; Ru(12)–H(12)–Ru(14) 114.

Ru(13) = 3.232(1), Ru(11)–Ru(14) = 3.159(1), Ru(13)–Ru(14) = 3.177(1), Ru(11)–Ru(12) = 2.977(1) and Ru(12)–Ru(14) = 3.012(1) Å]. This pattern of three long/two normal bonds has only been previously observed for the flat butterfly or rhomboidal clusters $Ru_4(CO)_{13}(\mu\text{-PR}_2)_2$ [1d] and for $(\mu\text{-H})_2Ru_4(CO)_8\text{-}[CH_3C{=}C(H)C(H){=}N^iPr]_2$ [1e] which have essentially planar molecular frameworks. In 2 the dihedral angle between the Ru(11)–Ru(12)–Ru(14) and Ru(11)–Ru(13)–(Ru14) planes is 113.9°. The phosphinidene fragment, which was bonded to one hinge and two wingtip metal atoms in 3, now caps a closed triangular face in 2. Although a butterfly arrangement of ruthenium atoms is retained in the transformation of 3 to 2, substantial rearrangement of the metal–metal interactions has taken place since the μ_3-PPh ligand is no longer bound within the butterfly cavity.

The structural characterisation of 1 and 2 together with other recent observations [1] establishes that polyphosphido carbonyl clusters in general exhibit unusual electronic and structural features. Furthermore, recent evidence that the related class of 64-electron phosphido clusters $Ru_4(CO)_{13}(\mu\text{-PR}_2)_2$ undergo facile CO loss and intramolecular ligand activation chemistry [10] suggests that framework-electronic structure-reactivity relationships of M_3 and M_4 clusters bearing π-donor ligands deserves further attention.

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