

Synthesis and characterisation of $[\text{Ru}_4\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ and $[\text{FeRu}_3\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$: cluster expansion by addition of metal carbonyl fragments to *nido*-clusters

Petra Escarpa Gaede,^a Brian F. G. Johnson,^{*a} John F. Nixon,^b Mathias Nowotny^a and Simon Parsons^a

^a Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

^b School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

The two new μ_4 -phosphinidene cluster compounds $[\text{Ru}_4\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ and $[\text{FeRu}_3\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ are prepared by addition of the isolobal 12-valence electron fragments $\text{Ru}(\text{CO})_2$ and $\text{Fe}(\text{CO})_2$ to the *nido*-cluster $[\text{Ru}_3\{\mu_3\text{-PC}(\text{CO})\text{Bu}^t\}_2(\text{CO})_9]$.

For a long time the complex $[\text{Re}_2\text{Pt}(\text{CO})_8(\text{dppe})\{\text{Bu}^t\text{C}(\text{CO})\text{P}\}]^1$ has been the only example of a compound derived from the attack of carbon monoxide on the carbon of a coordinated phosphalkyne resulting in the formation of the ketene substituted μ_n -phosphinidene ligand $\text{RC}(\text{CO})\text{P}$. We have recently reported the formation of the phosphinidene ligand $\text{Bu}^t\text{C}(\text{CO})\text{P}$ from the reaction of $\text{Bu}^t\text{C}\equiv\text{P}$ with $[\text{M}_3(\text{CO})_{12}]$, to yield the *nido*-cluster $[\text{M}_3\{\mu_3\text{-PC}(\text{CO})\text{Bu}^t\}_2(\text{CO})_9]$ ($\text{M} = \text{Ru}$ **1**, Os **2**).² The open framework of these complexes leads us to expect that subsequent addition reactions resulting in a closure of the coordination hole might be possible. Here, we report the formation of the *pseudo*-octahedral *closo*-cluster $[\text{Ru}_4\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ **3** in the reaction of **1** with an excess of $[\text{Ru}_3(\text{CO})_{12}]$ (Scheme 1), formally by an addition of the 12-valence electron (VE) fragment $\text{Ru}(\text{CO})_2$, and the reaction of **1** with $[\text{Fe}_2(\text{CO})_9]$ afforded the analogous mixed-metal cluster $[\text{FeRu}_3\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ **4** in moderate yield.

Complexes **3** and **4** have been fully characterized on the basis of their spectroscopic data (see Table 1) and by single-crystal X-ray analysis.[†]

The overall geometry of **3** and **4** (Fig. 1) is a distorted octahedron with phosphorus atoms in axial positions, while the four metal atoms form an approximately square-planar array with three of the metal–metal distances being essentially equal [**3**, mean $\text{Ru}–\text{Ru}$ 2.8796(12); **4**, mean $(\text{Ru}, \text{Fe})–(\text{Ru}, \text{Fe})$ 2.854(1) Å] and the fourth, which is symmetrically bridged by a carbon monoxide, being significantly shorter [**3**, $\text{Ru}(1)–\text{Ru}(1a)$ 2.7083(13); **4**, $(\text{Ru}, \text{Fe})(1)–(\text{Ru}, \text{Fe})(1a)$ 2.704(2) Å]. The metal square is not perfectly planar but distorted such that the metal atoms below the ketene and the *tert*-butyl group of the phosphinidene ligand are slightly bent away, thereby resulting in a folding of the tetrametal square in **3** and **4** along the $\text{M}(1)–\text{M}(2a)$ vector of 7.8 and 3.7°, respectively. In the structure of **4** the position of the iron atom is disordered over all four

theoretical sites of the tetrametal square with a strong preference for the position $\text{M}(2, 2a)$, which lies apart from the bridging carbonyl group. Contrary to expectation, the single $\mu\text{-CO}$ spans two Ru atoms rather than a Ru–Fe vector.

The phosphinidene ligands cap the metal atom plane slightly asymmetrically with the distances of the phosphorus to those metal atoms carrying only terminal carbonyls being somewhat shorter [**3**, mean $\text{Ru}–\text{P}$ 2.393(2); **4**, mean $(\text{Ru}, \text{Fe})–\text{P}$ 2.365(2) Å] than the distances to the metal atoms linked by the carbonyl bridge [**3**, mean $\text{Ru}–\text{P}$ 2.494(2); **4**, mean $(\text{Ru}, \text{Fe})–\text{P}$ 2.488(2) Å]. These structural features are analogous to those established for $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(\text{CO})_{10}]$ **5**, $[\text{Fe}_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(\text{CO})_{10}]$ **6** and $[\text{Co}_2\text{Fe}_2(\mu_4\text{-PPh})_2(\mu\text{-CO})(\text{CO})_{10}]$ **7**.^{3–6}

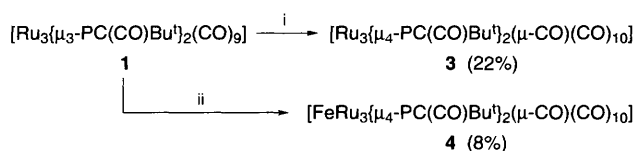
The phosphorus–carbon distances in the phosphinidene ligands [**3**, $\text{P}(1)–\text{C}(1)$ 1.799(6); **4**, $\text{P}(1)–\text{C}(1)$ 1.790(5) Å] are comparable to those previously reported for $\mu_3\text{-PC}(\text{CO})\text{Bu}^t$.^{1,2}

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** and **4** show singlet resonances at δ 146.2 and 168.5, respectively, while the chemical shifts normally associated with a $\text{Ru}_4(\mu_4\text{-P})$ framework are in the range of δ 400–435.⁷ Remarkable in this context is the analogous upfield shift for the resonances of the *tert*-butyl protons in the ^1H NMR spectra of **3** and **4** with respect to the reported value of δ 1.26 for **1**.² A similar upfield shift in the ^1H and ^{31}P NMR spectra of **6** with respect to the resonances of $[\text{Fe}_4(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ **8** has been explained in terms of a weakening of the effective magnetic field by a ring-current effect exerted by a hypothetically unsaturated tetrairon ring in **6**.^{4,8} However, the $\text{M}_4(\mu_4\text{-P})_2$ framework in **3–6** contains seven skeletal electron pairs and must be considered a coordinatively saturated system on the basis of the polyhedral skeleton electron pair theory,⁹ though a molecular-orbital calculation for $[\text{Fe}_4(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ indicated a possible stabilisation of eight skeletal electron pairs.¹⁰

We thank the Deutsche Forschungsgemeinschaft (Bonn, Bad Godesberg) for a postdoctoral fellowship (M. N.) and the EPSRC for support.

Table 1 Spectroscopic data for the new μ_4 -phosphinidene cluster complexes.

Complex	^1H NMR δ (CDCl_3)	^{31}P NMR δ (CDCl_3)	FABMS m/z ($\text{MeCN}/3\text{-noba}$)	IR $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2)
3	0.74	146.2	972 [M] ⁺	2105m, 2095s, 2075w, 2050m, 2038vs, 2020s, 1982m, 1819w
4	0.75	168.5	926 [M] ⁺	2105m, 2095s, 2074w, 2063w, 2038vs, 2032vs, 2021s, 1986m, 1820w



Scheme 1 The synthesis of $[\text{Ru}_4\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ **3** and $[\text{FeRu}_3\{\mu_4\text{-PC}(\text{CO})\text{Bu}^t\}_2(\mu\text{-CO})(\text{CO})_{10}]$ **4** from $[\text{Ru}_3\{\mu_3\text{-PC}(\text{CO})\text{Bu}^t\}_2(\text{CO})_9]$ **1**. *Reagents and conditions*: i, heating under reflux with 2 equiv. of $[\text{Ru}_3(\text{CO})_{12}]$ in thf for 6 h; ii, heating under reflux with 3 equiv. of $[\text{Fe}_2(\text{CO})_9]$ in thf for 2 h. *Isolation and purification*: TLC (CH_2Cl_2 –hexane, 3 : 7 v/v); subsequent crystallization from CH_2Cl_2 .

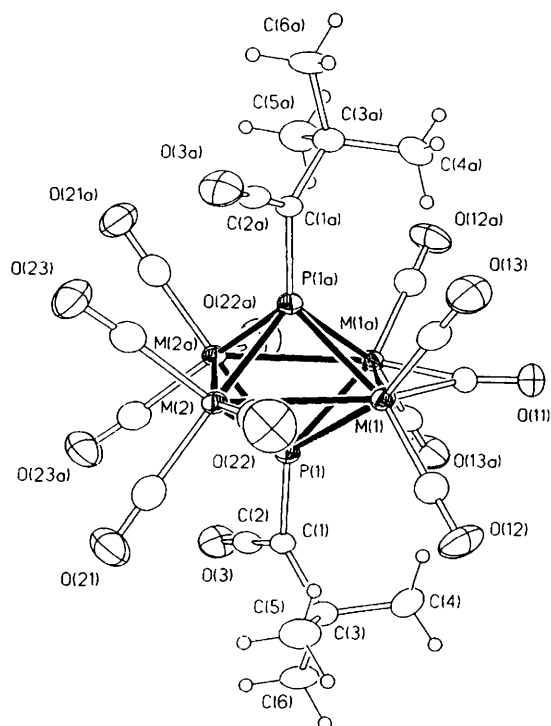


Fig. 1 The molecular structure of $[\text{Ru}_4\{\mu_4\text{-PC}(\text{CO})\text{Bu}\}_2(\mu\text{-CO})(\text{CO})_{10}]_3$ $\{M(1,2) = \text{Ru}\}$ and $[\text{FeRu}_3\{\mu_4\text{-PC}(\text{CO})\text{Bu}\}_2(\mu\text{-CO})(\text{CO})_{10}]_4$ $\{M(1) = 0.9 \text{ Ru} + 0.1 \text{ Fe}, M(2) = 0.6 \text{ Ru} + 0.4 \text{ Fe}\}$ showing the atom labelling. The C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances (Å) and angles ($^\circ$) include: **3**, Ru(1)–Ru(1a) 2.7083(13), Ru(1)–Ru(2) 2.8915(11), Ru(2)–Ru(2a) 2.8558(14), Ru(1)–P(1) 2.556(2), Ru(2)–P(1a) 2.379(2), Ru(1)–P(1a) 2.432(2), Ru(2)–P(1a) 2.407(2), Ru(1)–C(11) 2.036(6), Ru(1)–C(12) 1.901(6), Ru(1)–C(13) 1.875(6), Ru(2)–C(21) 1.919(7), Ru(2)–C(22) 1.926(6), Ru(2)–C(23) 1.938(7), mean C(CO)–O(CO) terminal 1.134(7), C(11)–O(11) 1.174(8), P(1)–C(1) 1.799(6), C(1)–C(2) 1.303(8), C(2)–O(3) 1.157(7), C(1)–C(3) 1.543(8); Ru(1a)–Ru(1)–Ru(2) 91.323(13), Ru(1)–Ru(2)–Ru(2a) 88.408(13), P(1)–Ru(1)–P(1a) 67.87(7), P(1)–Ru(2)–P(1a) 71.21(7), C(2)–C(1)–C(3) 119.6(6), C(2)–C(1)–P(1) 115.2(5), C(3)–C(1)–P(1) 125.2(4), O(3)–C(2)–C(1) 179.0(8); **4**, M(1)–M(2) 2.8770(10), M(1)–M(1a) 2.704(2), M(2)–M(2a) 2.809(2), M(1)–P(1) 2.522(2), M(1)–P(1a) 2.454(2), M(2)–P(1) 2.363(2), M(2)–P(1a) 2.366(2), M(1)–C(11) 2.047(5), M(1)–C(12) 1.902(6), M(1)–C(13) 1.859(6), M(2)–C(21) 1.882(6), M(2)–C(22) 1.867(6), M(2)–C(23) 1.879(6), mean C(CO)–O(CO) terminal 1.141(7), C(11)–O(11) 1.173(8), P–C(1) 1.790(5), C(1)–C(2) 1.317(7), C(2)–O(3) 1.157(6), C(1)–C(3) 1.543(7); M(1)–M(2)–M(2a) 91.019(13), M(1)–M(2)–M(2a) 88.921(13), P(1)–M(1)–P(1a) 67.39(6), P(1)–M(2)–P(1a) 71.45(7), C(2)–C(1)–C(3) 121.0(4), P(1)–C(1)–C(2) 112.6(4), P(1)–C(1)–C(3) 126.2(4), O(3)–C(2)–C(1) 179.7(6).

Footnote

† *Crystal data for 3*: $\text{C}_{23}\text{H}_{18}\text{O}_{13}\text{P}_2\text{Ru}_4$, $M = 968.60$, monoclinic, space group $I2/a$, $a = 19.693(11)$, $b = 9.108(3)$, $c = 17.612(6)$ Å, $\beta = 101.74(3)^\circ$, $U = 3093$ Å³ [from 2θ values of 28 reflections measured at $\pm\omega$ ($30 \leq 2\theta \leq 32$), $\lambda = 0.71073$ Å], $Z = 4$ (the molecule lies on a crystallographic twofold axis), $D_c = 2.080$ Mg m⁻³, $T = 150 \pm 2$ K, $F(000) = 1864.0$, $\mu(\text{Mo-K}\alpha) = 2.08$ mm⁻¹, black tablet, $0.31 \times 0.31 \times 0.05$ mm.

For 4: $\text{C}_{23}\text{H}_{18}\text{FeO}_{13}\text{P}_2\text{Ru}_3$, $M = 923.37$, monoclinic, space group $C2/c$, $a = 15.236(7)$, $b = 13.991(4)$, $c = 14.556(6)$ Å, $\beta = 90.11(7)^\circ$, $U = 3102.9$ Å³ [from 2θ values of 24 reflections measured at $\pm\omega$ ($30 \leq 2\theta \leq$

31), $\lambda = 0.71073$ Å], $Z = 4$ (the molecule lies on a crystallographic twofold axis), $D_c = 1.977$ Mg m⁻³, $T = 150 \pm 2$ K, $F(000) = 1792$, $\mu(\text{Mo-K}\alpha) = 2.05$ mm⁻¹, red plate developed in $[-111]$, $0.0622 \times 0.272 \times 0.085$ mm.

Data collection and processing: data were collected between $5 \leq 2\theta \leq 50^\circ$ on a Stoe Stadi 4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glaser, *J. Appl. Crystallogr.*, 1986, **19**, 105) using Mo-K α X-radiation. For **3**, ω - 2θ scans with ω width = $(1 + 0.35 \tan \theta)^\circ$; for **4**, ω - θ scans with ω width = $(1.2 + 0.35 \tan \theta)^\circ$. Absorption corrections were applied using ψ -scan data: **3**, $T_{\min} = 0.669$, $T_{\max} = 0.984$; **4**, $T_{\min} = 0.715$, $T_{\max} = 0.943$. Both structures were solved by direct methods (**3**: SHELXS 86, G. M. Sheldrick, University of Göttingen, Germany, 1986; **4**: SIR92, A. Altomare, G. Casciarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343). Hydrogen atoms in both structures were located in difference syntheses calculated over the loci of possible H-positions; methyl groups were treated as rigid bodies with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but the HCCC torsions were allowed to refine. The structure of **3** was refined (SHELXL 93, G. M. Sheldrick, University of Göttingen, Germany, 1993) with anisotropic displacement parameters on all non-hydrogen atoms to $R_1 = 0.032$ [based on F and 2050 data with $F > 4\sigma(F)$] and $wR2 = 0.0746$ (based on F^2 and all 2700 unique data and 135 parameters). The structure of **4** was refined similarly except that spectroscopic evidence suggested that the M_4 framework was Ru_3Fe . The two crystallographically independent metal sites were refined as $\chi \text{ Ru}/(1 - \chi) \text{ Fe}$ with the sum of the Ru occupancies restrained to 1.5. The (Ru/Fe) atoms at each site were constrained to have equal positional and anisotropic displacement parameters. One metal site adopted Ru : Fe = 0.9 : 0.1; the other 0.6 : 0.4. This refinement converged to $R_1 = 0.0344$ [for 1874 data with $F > 4\sigma(F)$] and $wR2 = 0.0816$ (for all 2321 unique data and 196 parameters). The final ΔF synthesis maxima, minima for **3** and **4** were +0.62, -0.88 and +0.79, -0.95 eÅ⁻³, respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/100.

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Received, 7th March 1996; Com. 6/01640E