



Institut de Chimie
Université de Neuchâtel

**Complexes tri- et tétranucléaires de ruthénium
contenant des ligands phosphorés stériquement
encombrants : systèmes saturés et insaturés en
électrons**

Forme réduite de la thèse
présentée à la Faculté des Sciences
de l'Université de Neuchâtel
pour l'obtention du grade de docteur ès sciences

par

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Neuchâtel, décembre 1999

IMPRIMATUR POUR LA THÈSE

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contenant des ligands phosphorés stériquement
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de Mme Isabelle Godefroy

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de
Neuchâtel sur le rapport des membres du jury,

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Neuchâtel, le 17 septembre 1999

Le doyen:



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Liste des Publications

Suss-Fink, Georg; Godefroy, Isabelle; Ferrand, Vincent; Neels, Antonia; Stoeckli-Evans, Helen. **Saturated and unsaturated triruthenium clusters containing three sterically demanding phosphine ligands: synthesis and structure of $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ and $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$.** *J. Chem. Soc., Dalton Trans.* (1998), (4), 515-516.

Suss-Fink, Georg; Godefroy, Isabelle; Beguin, Alain; Rheinwald, Gerd; Neels, Antonia; Stoeckli-Evans, Helen. **Saturated and unsaturated tetraruthenium clusters containing sterically demanding dicyclohexylphosphido ligands: synthesis and structure of $[\text{H}_4\text{Ru}_4(\text{CO})_8(\text{PCy}_2)_4]$ and $[\text{H}_5\text{Ru}_4(\text{CO})_8(\text{PCy}_2)_3]$.** *J. Chem. Soc., Dalton Trans.* (1998), (13), 2211-2214.

Godefroy, Isabelle; Stoeckli-Evans, Helen; Suss-Fink, Georg. **Electron-deficient triruthenium clusters: synthesis and molecular structure of the anion $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^-$, a second example of an Ru_3 cluster presenting an electron count of 44 electrons.** *Inorg. Chem. Commun.* (1999), 2(6), 247-249.

Suss-Fink, Georg; Godefroy, Isabelle; Ferrand, Vincent; Neels, Antonia; Stoeckli-Evans, Helen; Kahlal, Samia; Saillard, Jean-Yves; Garland, Maria Teresa. **Electron-deficient triruthenium and triosmium clusters from the reaction of the cluster anions $[\text{HM}_3(\text{CO})_{11}]^-$ ($\text{M}=\text{Ru}, \text{Os}$) with tricyclohexylphosphine in methanol.** *J. Organomet. Chem.* (1999), 579(1-2), 285-297.

Saturated and unsaturated triruthenium clusters containing three sterically demanding phosphine ligands: synthesis and structure of $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ and $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$

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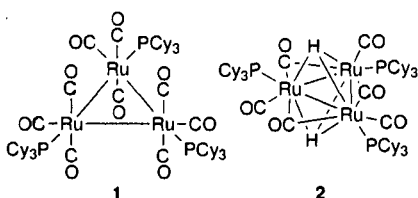
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The reaction of $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ with an excess of tricyclohexylphosphine in methanol afforded, depending on the reaction conditions, the tri-substituted clusters $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ (48e) and $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$ (44e), inaccessible hitherto.

Ligand substitution reactions of dodecacarbonyltriruthenium with tertiary phosphines have been studied in great detail.¹ The thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with PR_3 (R = Ph, Et, Buⁿ, OPh) in general leads to the mono-, di- and tri-substituted derivatives $[\text{Ru}_3(\text{CO})_{11}(\text{PR}_3)]$, $[\text{Ru}_3(\text{CO})_{10}(\text{PR}_3)_2]$ and $[\text{Ru}_3(\text{CO})_9(\text{PR}_3)_3]$.² For the directed synthesis of these substitution products, the trimethylamine oxide-induced carbonyl substitution,³ the radical ion-initiated ligand substitution,⁴ and the bis(triphenylphosphine)iminium salt-catalysed carbonyl substitution⁵ have been developed. However, with sterically demanding phosphine ligands, the synthesis of the tri-substituted derivatives failed. Even a six-fold excess of tricyclohexylphosphine with $[\text{Ru}_3(\text{CO})_{12}]$ in the presence of $\text{Na}[\text{Ph}_2\text{CO}]$ gave only the mono- and the di-substituted complexes, but no $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$.^{4b}

On the other hand, bulky phosphines containing cyclohexyl or *tert*-butyl substituents are known to allow unusual structures and unsaturated configurations for steric reasons.⁶ Thus the electron-deficient triruthenium cluster $[\text{Ru}_3\text{H}_2(\text{CO})_5(\text{PBu}^t)_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ with an electron count of 46 was synthesized by Böttcher *et al.* in 1996.^{6b} Apart from this complex and its adamantyl derivative,^{6b} the only electron-deficient Ru_3 clusters reported so far are $[\text{Ru}_3\text{H}(\text{CO})_9(\text{NSOMePh})]$,⁷ and (very recently) $[\text{Ru}_3\text{H}_2(\text{CO})_{10}]$ as well as its phosphine derivative $[\text{Ru}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)]$,⁸ all of which have an electron count of 46. Interestingly, no unsaturated triruthenium cluster is mentioned in Deeming's review of 1995.¹

In this paper we describe the synthesis and structure of the tris(tricyclohexylphosphine)-substituted derivative $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ **1** and the highly electron-deficient Ru_3 cluster $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$ **2**, both accessible from $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ and PCy_3 .



The reaction of $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$, easily accessible from $[\text{Ru}_3(\text{CO})_{12}]$ and $\text{Na}[\text{BH}_4]$,⁹ with tricyclohexylphosphine (1:5) in methanol leads, upon heating for 1 h at 80 °C in a closed reactor (pressure Schlenk tube), to the tri-substituted derivative $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ **1**, which precipitates from the reaction solution as a purple microcrystalline solid in 55% yield. Cluster **1** can be recrystallised from dichloromethane-methanol to give

dark red, air-stable, cube-like crystals which contain two water molecules of crystallisation (source: methanol).† The single crystal X-ray structure analysis‡ of **1** (Fig. 1) reveals a triruthenium framework with the three phosphine ligands occupying equatorial positions at the three ruthenium atoms. The molecule has a perfect C_3 symmetry. The nine carbonyl ligands are all terminal, six occupying the two axial positions of the Ru atoms, while the other three are alternating with the phosphine ligands in one of the two equatorial positions of each ruthenium atom. The $\text{Ru}-\text{CO}_{(\text{eq})}$ distances of 1.876(7) Å are distinctly shorter than the $\text{Ru}-\text{CO}_{(\text{ax})}$ distances [1.924(7) and 1.931(7) Å]. This is in keeping with the findings in the known cluster $[\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3]$,¹⁰ the Ru-P distances, however, are considerably longer in **1** [2.414(2) Å] than in the methyl derivative [2.330 Å (average)],¹⁰ reflecting the bulkiness of the cyclohexyl substituents. The Ru-Ru bonds in **1** [2.9396(8) Å] are also elongated with respect to those in $[\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3]$ [2.860(1), 2.862(1), 2.854(1) Å]¹⁰ and in $[\text{Ru}_3(\text{CO})_{12}]$ [2.852(1), 2.851(1),

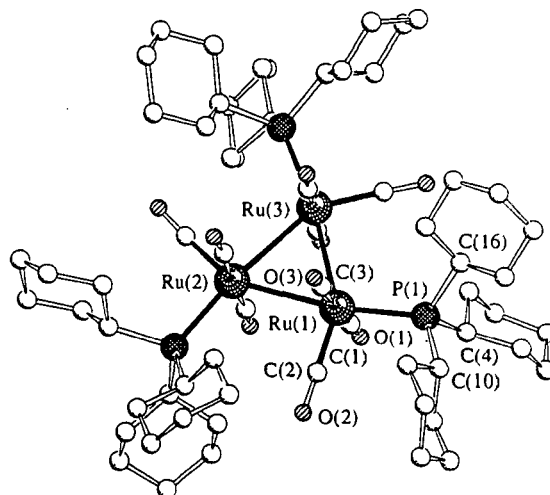


Fig. 1 Molecular structure of $[\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3]$ **1** showing the atom numbering scheme; H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(2) 2.9396(8), Ru(1)-Ru(3) 2.9396(8), Ru(2)-Ru(3) 2.9396(8), Ru(1)-P(1) 2.414(2), Ru(1)-C(2) 1.876(7), Ru(1)-C(1) 1.924(7), Ru(1)-C(3) 1.931(7); Ru(3)-Ru(1)-P(1) 111.21(5), P(1)-Ru(1)-C(2) 98.3(2), P(1)-Ru(1)-C(1) 92.1(2), P(1)-Ru(1)-C(3) 90.3(2), Ru(1)-Ru(2)-Ru(3) 60.0, C(4)-P(1)-C(10) 101.4(3), C(10)-P(1)-C(16) 102.5(3)

† Spectroscopic data for cluster **1**. IR(CH_2Cl_2): $\nu(\text{CO})$ 1959 vs. 1949 vs cm^{-1} ; ^1H NMR (CDCl_3): δ 1.29–2.04 (m, C_6H_{11}); ^{31}P NMR (CDCl_3): δ 47.3 (s, PCy_3); FAB-MS: m/z 1397 (1395 related to ^{101}Ru) (Found: C, 52.64; H, 7.0. Calc. for $\text{C}_{63}\text{H}_{99}\text{O}_9\text{P}_3\text{Ru}_3\cdot 2\text{H}_2\text{O}$: C, 52.82; H, 7.25%).

‡ Crystal data for cluster **1**. $\text{C}_{63}\text{H}_{99}\text{O}_9\text{P}_3\text{Ru}_3\cdot 2\text{H}_2\text{O}$, M 1474.52, cubic space group $Pu\bar{3}$, $a = 24.1347(12)$ Å, $U = 14\,058.1(12)$ Å³, $T = 223(2)$ K, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.802$ mm⁻¹, 4156 Reflections collected. Disordered molecules of dichloromethane and water were found in the crystal structure. Refinement converged at $R1 = 0.0577$ and $wR2 = 0.1346$ for 3224 data with $I > 2\sigma(I)$, and $R1 = 0.0837$ and $wR2 = 0.1536$ for all 4156 unique data.

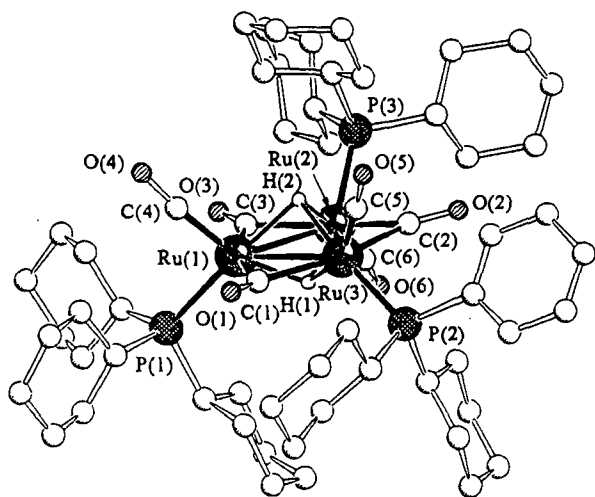


Fig. 2 Molecular structure of $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$ **2** showing the atom numbering scheme: H atoms on carbon have been omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2) 2.6702(6), Ru(1)–Ru(3) 2.7180(7), Ru(2)–Ru(3) 2.6931(7), Ru(1)–P(1) 2.332(2), Ru(2)–P(3) 2.336(2), Ru(3)–P(2) 2.344(2), Ru(1)–H(1) 1.94, Ru(1)–H(2) 1.61, Ru(2)–H(1) 2.04, Ru(2)–H(2) 1.94, Ru(3)–H(1) 1.93, Ru(3)–H(2) 1.85, Ru(1)–C(4) 1.834(7), Ru(2)–C(6) 1.834(7), Ru(3)–C(5) 1.825(8), Ru(1)–C(1) 2.134(7), Ru(1)–C(3) 2.154(6), Ru(2)–C(3) 2.129(6), Ru(2)–C(2) 2.107(7), Ru(3)–C(2) 2.147(5), Ru(3)–C(1) 2.161(6)

2.860(1) Å].¹¹ The molecule **1** has almost D_{3h} symmetry, the three phosphorus atoms being almost in the plane of the three ruthenium atoms (maximum distance between P and the Ru_3 plane 0.20 Å) and the torsion angles C(axial)–Ru–Ru–C(axial) being less than 10°.

If $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ is reacted with PCy_3 (1 : 5) in methanol in an open reactor for 1 h under reflux (80 °C bath temperature), the reaction yields (instead of **1**) the dihydro cluster $[\text{Ru}_3\text{H}_2(\text{CO})_6(\text{PCy}_3)_3]$ **2**. The product precipitates directly from the reaction solution as a purple powder (60% yield). It can be recrystallised from dichloromethane–methanol to give dark red, block-shaped crystals which, in contrast to **1**, are air-sensitive. The ¹H NMR spectrum of **2** shows two signals in the region of μ_3 -hydrides, both showing a homo-spin coupling with the other hydride ligand and two hetero-spin couplings with the two types of phosphorus atoms (two *trans* and one *cis*, or one *trans* and two *cis*).[§]

The single-crystal X-ray structure analysis[¶] of **2** (Fig. 2) shows

§ Spectroscopic data for cluster **2**. IR(CH_2Cl_2): $\nu(\text{CO})$ 2027vw, 1949m, 1917vs, 1871w, 1855w, 1819vs, 1757w cm^{-1} ; ¹H NMR (CDCl_3): δ 1.27–2.30 (99 H, m, C_6H_{11}), –19.46 [1 H, dtd, $J(\text{H}^2\text{–P}^1, \text{P}^2) = 5.3$, $J(\text{H}^1\text{–H}^2) = 2.2$, $\mu_3\text{–H}^2$], –21.02 [1 H, tdd, $J(\text{H}^1\text{–P}^1, \text{P}^2) = 26.4$, $J(\text{H}^1\text{–P}^3) = 5.4$, $J(\text{H}^1\text{–H}^2) = 2.1$ Hz, $\mu_3\text{–H}^1$]; ³¹P-¹H NMR (CDCl_3): δ 74.8 (s, 1 P), 71.3 (s, 2 P), no coupling observed; FAB-MS: m/z 1313 (based on ¹⁰¹Ru) (Found: C, 53.63; H, 7.45. Calc. for $\text{C}_{60}\text{H}_{101}\text{O}_6\text{P}_3\text{Ru}_3 \cdot 2\text{H}_2\text{O}$: C, 53.36; H, 7.84%).

¶ Crystal data for cluster **2**. $\text{C}_{60}\text{H}_{101}\text{O}_6\text{P}_3\text{Ru}_3 \cdot 2\text{H}_2\text{O}$. M 1314.53, monoclinic, space group $P2_1/n$, $a = 10.561(1)$, $b = 36.649(2)$, $c = 15.957(1)$ Å, $\beta = 96.32(1)^\circ$, $U = 6138.4(8)$ Å³, $T = 223(2)$ K, $Z = 4$, $\mu(\text{Mo–K}\alpha) = 0.854$ mm^{-1} , 38 984 Reflections were collected. The cyclohexyl ring C(31)–C(36) was found to be disordered. Two positions for atoms C(33) and C(36) (the head and the foot of the chair conformation) were refined with occupancy 0.5 each. Refinement converged at $R1 = 0.049$ and $wR2 = 0.090$ for 6231 data with $I > 2\sigma(I)$, and $R1 = 0.104$ and $wR2 = 0.103$ for all 11 651 unique data. CCDC reference number 186/846. See <http://www.rsc.org/suppdata/dt/1998/515/> for crystallographic files in .cif format.

a Ru_3 skeleton bearing two μ_3 -hydrido caps, one on either side of the triangle. The three Ru–Ru bonds are bridged by three μ_2 -carbonyl ligands, being almost in the plane of the metal triangle. The three terminal carbonyl ligands as well as the three phosphine ligands are co-ordinated to the three Ru atoms, above and below the metal plane. Complex **2** is, to our knowledge, the only Ru_3 cluster known presenting an electron count of 44. Trinuclear clusters with 44e have been reporting so far only for d^8 metals: $[\text{Pd}_3(\text{SO}_2)_2(\text{Bu}^i\text{NC})_5]$,¹² $[\text{Pt}_3(\text{CO})_3(\text{PCy}_3)_3]$ ¹³ and $[\text{FePt}_3(\text{CO})_5\{\text{P}(\text{O}^i\text{Ph})_3\}_3]$.¹⁴ In accordance with this high electron deficiency, the Ru–Ru bonds in **2** are found to be rather short [2.6702(6), 2.6931(7) and 2.7180(7) Å] with respect to the typical Ru–Ru single bonds [2.9396(8) Å] in **1**. In addition, the Ru–P bonds in **2** [2.332(2), 2.336(2) and 2.344(2) Å] are also shorter than in **1** [2.414(2) Å]. The two capping hydride ligands are slightly unsymmetrically co-ordinated, H(2) is also closer to the Ru_3 triangle than H(1), reflecting the different environments [one PCy_3 and two CO ligands surrounding H(2), two PCy_3 and one CO ligands surrounding H(1)]. Owing to the high degree of unsaturation (4e with respect to the EAN rule) cluster **2** is expected to be a highly reactive species. A study on the reactivity of **2** towards CO and other simple molecules is in progress.

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Received 7th November 1997; Communication 7/08037

Saturated and unsaturated tetraruthenium clusters containing sterically demanding dicyclohexylphosphido ligands: synthesis and structure of $[H_4Ru_4(CO)_8(PCy_2)_4]$ and $[H_5Ru_4(CO)_8(PCy_2)_3]$ †

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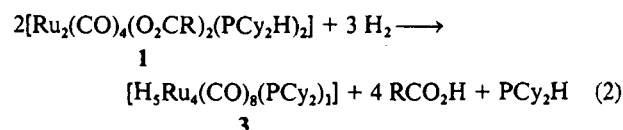
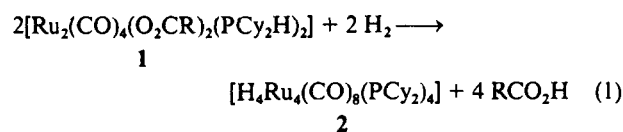
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The thermal reaction of the dinuclear complex $[Ru_2(CO)_4(O_2CH)_2(PCy_2H)_2]$ with molecular hydrogen in cyclohexane afforded the tetranuclear clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ (64e) and $[H_5Ru_4(CO)_8(PCy_2)_3]$ (62e), both of which have a square-planar arrangement of the metal framework.

Tetranuclear ruthenium clusters, mainly accessible by pyrolytic methods, have been obtained from unsystematic synthetic routes.¹ Most of these Ru_4 clusters adopt tetrahedral or butterfly geometries, but there are a small number of compounds which form square-planar clusters.^{2,3} We reported in 1994 the assembly of the square-planar clusters $[Ru_4(CO)_8(PCy_2)_4]$ and $[Ru_4(CO)_8(PCy)_2(PCy_2)_2]$ by condensation of the dinuclear clusters $[Ru_2(CO)_4(O_2CH)_2(PCy_2H)_2]$ or $[Ru_2(CO)_6(PCy_2)_2]$.⁴ In a recent paper, Frediani *et al.* described the thermal behaviour of the dinuclear complex $[Ru_2(CO)_4(O_2CMe)_2(PPh_3)_2]$ towards molecular hydrogen which gives rise to the formation of the tetranuclear clusters $[Ru_4(CO)_8(PPh)_2(PPh_2)_2]$ and $[H_4Ru_4(CO)_7(PPh)(PPh_2)(PPh_3)]$, along with the trinuclear cluster $[H_2Ru_3(CO)_8(PPh)(PPh_3)]$.⁵ This prompted us to report our own findings on the hydrogenation of the dinuclear dicyclohexylphosphine complexes $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ ($R = H$ or Me) to give, with fusion of two Ru_2 units, the tetranuclear square-planar hydrido clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ and $[H_5Ru_4(CO)_8(PCy_2)_3]$.

Results and Discussion

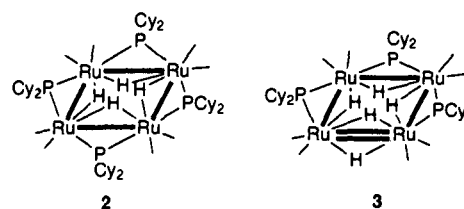
The reaction of the dinuclear ruthenium carboxylato complexes $[Ru_2(CO)_4(O_2CR)_2(PCy_2H)_2]$ ($R = H$ **1a**, $R = Me$ **1b**) in cyclohexane with molecular hydrogen (60 bar) at 160 °C yields the two tetranuclear clusters $[H_4Ru_4(CO)_8(PCy_2)_4]$ **2** and $[H_5Ru_4(CO)_8(PCy_2)_3]$ **3** [equations (1) and (2)], resulting from the



condensation of two Ru_2P_2 units to give a Ru_4P_4 core. If the reaction is performed at 120 °C, only complex **3** is obtained. On the other hand, prolonged reaction (14 h) at 160 °C also gives, along with **2** and **3**, the known violet cluster $[Ru_4(CO)_8(PCy_2)_2(PCy_2)_2]$ as a side-product.¹ Complexes **2** and **3** can be separated

by thin-layer chromatography; they are obtained as yellow crystals from dichloromethane–methanol (**2**) and as red crystals from dichloromethane–hexane (**3**), respectively.

The tetrahydrido cluster **2**, formed in the reaction of **1** with H_2 , is identical with one of the minor products formed in the pyrolysis of **1** in the absence of molecular hydrogen to give mainly $[Ru_4(CO)_8(PCy_2)_2(PCy_2)_2]$ and $[Ru_4(CO)_8(PCy_2)_4]$. For this product (**2**) we had proposed the formula $[HRu_3(CO)_7(PCy_2)_3]$ on the basis of the spectroscopic and analytical data.⁴ This compound now turns out, by a single-crystal structure analysis (see below), not to be trinuclear but tetranuclear, the microanalytical data being the same within the error limits. The true compound $[HRu_3(CO)_7(PCy_2)_3]$ had been reported in the past by Keister and co-workers⁶ and structurally characterised by Böttcher *et al.*⁷



The $^{31}P\{-^1H\}$ NMR spectrum of **2** shows only one singlet at δ 151, the four phosphorus atoms being equivalent. The IR spectrum shows three absorptions in the area of terminal carbonyls, confirming the high symmetry of this molecule. In the 1H NMR spectrum, **2** gives rise to a doublet of triplets centered at δ -17.70. The four hydrido ligands are equivalent, each hydride being coupled to the μ -phosphorus atom at the same Ru–Ru edge ($^2J_{HP} = 20$ Hz) and to the equivalent vicinal μ -phosphorus atoms ($^2J_{HP} = 10.4$ Hz).

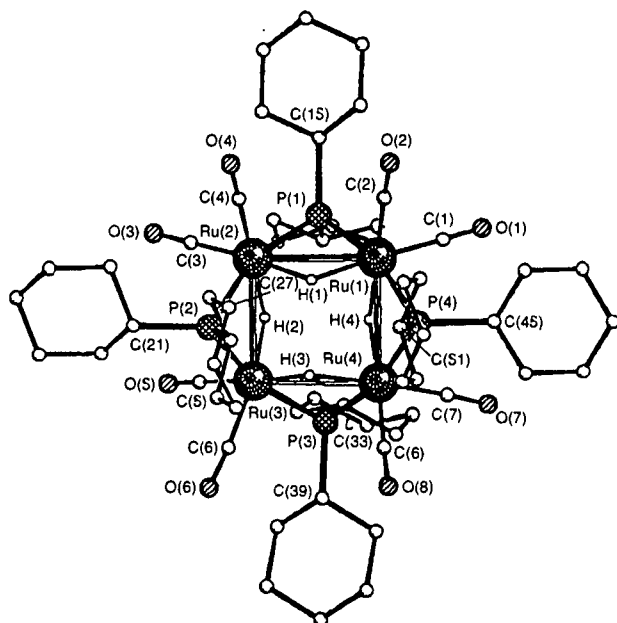
The metal skeleton of complex **2** is saturated with respect to the noble gas rule, the electron count being 64. It consists of a nearly square-planar arrangement of four ruthenium atoms [Ru(2)–Ru(1)–Ru(4) 90.25(4), Ru(1)–Ru(2)–Ru(3) 90.59(4), Ru(2)–Ru(3)–Ru(4) 89.90°, Ru(1)–Ru(4)–Ru(3) 88.88(4)°] (Fig. 1, Table 1). The four edges are bridged by four μ -dicyclohexylphosphido ligands, the Ru–Ru bonds are quite long [Ru(1)–Ru(2) 3.006(1), Ru(1)–Ru(4) 3.047(1), Ru(2)–Ru(3) 3.011(1), Ru(3)–Ru(4) 3.061(1) Å]. These distances are longer than those in the known unsaturated complex $[Ru_4(CO)_8(PCy_2)_4]$ (mean 2.989 Å).⁴ Two opposite edges of the Ru_4 square are bridged by the phosphido ligands [P(2), P(4)] situated above the plane and by the hydrido ligands situated below the plane. The other two Ru–Ru edges have the hydrido bridges above the

† Non-SI unit employed: bar = 10^5 Pa.

Table 1 Selected bond lengths (Å) and angles (°) for complex 2*

Ru(1)–Ru(2)	3.006(1)	Ru(2)–P(2)	2.349(2)
Ru(1)–Ru(4)	3.047(1)	Ru(3)–Ru(4)	3.061(1)
Ru(1)–H(1)	1.81(7)	Ru(3)–H(2)	1.75(5)
Ru(1)–H(4)	1.81(6)	Ru(3)–H(3)	1.81(7)
Ru(1)–P(1)	2.376(2)	Ru(3)–P(2)	2.375(2)
Ru(1)–P(4)	2.365(2)	Ru(3)–P(3)	2.373(2)
Ru(2)–Ru(3)	3.011(1)	Ru(4)–H(3)	1.80(7)
Ru(2)–H(1)	1.86(7)	Ru(4)–H(4)	1.76(6)
Ru(2)–H(2)	1.85(5)	Ru(4)–P(3)	2.364(2)
Ru(2)–P(1)	2.354(2)	Ru(4)–P(4)	2.376(2)
Ru(2)–Ru(1)–Ru(4)	90.25(4)	Ru(2)–Ru(3)–Ru(4)	89.90(4)
H(1)–Ru(1)–P(1)	86(2)	H(2)–Ru(3)–P(2)	83(2)
H(1)–Ru(1)–P(4)	84(2)	H(2)–Ru(3)–P(3)	91(2)
H(4)–Ru(1)–P(1)	86(2)	H(3)–Ru(3)–P(2)	81(2)
H(4)–Ru(1)–P(4)	80(2)	H(3)–Ru(3)–P(3)	80(2)
Ru(1)–Ru(2)–Ru(3)	90.59(4)	Ru(1)–Ru(4)–Ru(3)	88.88(4)
H(1)–Ru(2)–P(1)	85(2)	H(3)–Ru(4)–P(3)	80(2)
H(1)–Ru(2)–P(2)	82(2)	H(3)–Ru(4)–P(4)	92(2)
H(2)–Ru(2)–P(1)	82(2)	H(4)–Ru(4)–P(3)	87(2)
H(2)–Ru(2)–P(2)	82(2)	H(4)–Ru(4)–P(4)	80(2)

* Numbers in parentheses are estimated standard deviations in the least significant digits.

**Fig. 1** Molecular structure of $[H_4Ru_4(CO)_8(PCy_2)_4] 2$

Ru_4 plane and the phosphido bridges [P(1), P(3)] below the plane. The inclination angle of the phosphido bridges with respect to the Ru_4 plane is 123.7° (average). The inclination angle of the hydrido bridges with respect to the Ru_4 plane is found to be 73.26° (average), the four hydrido ligands being closer to the Ru_4 skeleton than the phosphido ligands.

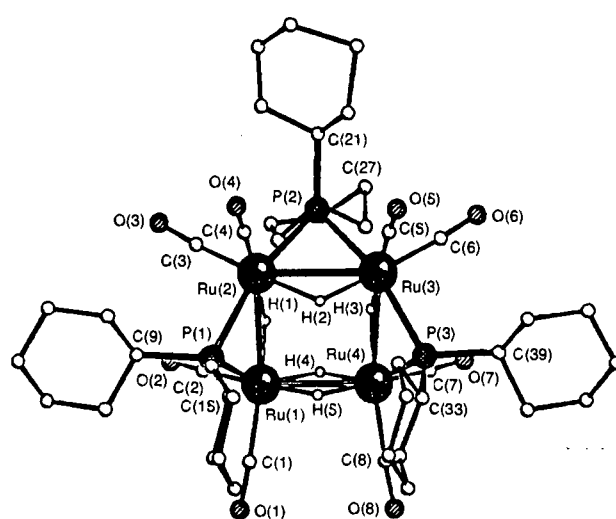
Complex 3 represents, with an electron count of only 62, an electron-deficient species. This electron-deficiency can be expressed either by formulating a Ru_2H_4 four-centre four-electron multicenter interaction or (more conventionally) by formulating a $Ru=Ru$ double bond. We opted for the latter representation in the light of the $Ru-Ru$ distances of 3, as found in the single-crystal X-ray structure analysis.

The Ru_4 metal skeleton of 3 consists of a planar arrangement [torsion angle $Ru(4)-Ru(1)-Ru(2)-Ru(3) = -0.29^\circ$] (Fig. 2, Table 2). Three of the four edges are bridged by both a dicyclohexylphosphido and a hydrido ligand. The fourth edge of the Ru_4 skeleton [$Ru(1)-Ru(4)$] is bridged by two hydrido ligands, thus resulting in a formal double bond between $Ru(1)$ and $Ru(4)$. This distance is indeed shorter [2.798(1) Å] than the other three $Ru-Ru$ bonds (average 2.985 Å) which are similar to

Table 2 Selected bond lengths (Å) and angles (°) for complex 3*

Ru(1)–Ru(2)	2.9699(9)	Ru(2)–P(2)	2.345(2)
Ru(1)–Ru(4)	2.7979(9)	Ru(3)–Ru(4)	2.9777(8)
Ru(1)–H(1)	1.52(5)	Ru(3)–H(2)	1.94(5)
Ru(1)–H(4)	1.92(5)	Ru(3)–H(3)	1.8(1)
Ru(1)–H(5)	1.48(5)	Ru(3)–P(2)	2.345(2)
Ru(1)–P(1)	2.325(3)	Ru(3)–P(3)	2.356(3)
Ru(2)–Ru(3)	3.005(1)	Ru(4)–H(3)	1.76(9)
Ru(2)–H(1)	1.92(6)	Ru(4)–H(4)	1.81(6)
Ru(2)–H(2)	2.02(5)	Ru(4)–H(5)	1.46(6)
Ru(2)–P(1)	2.361(3)	Ru(4)–P(3)	2.325(3)
Ru(4)–Ru(1)–Ru(2)	91.76(4)	Ru(4)–Ru(3)–Ru(2)	87.63(4)
H(1)–Ru(1)–P(1)	82(2)	H(2)–Ru(3)–P(2)	90(2)
H(4)–Ru(1)–P(1)	152(2)	H(2)–Ru(3)–P(3)	87(2)
H(5)–Ru(1)–P(1)	110(2)	H(3)–Ru(3)–P(2)	82(2)
Ru(1)–Ru(2)–Ru(3)	88.37(4)	H(3)–Ru(3)–P(3)	79(2)
P(2)–Ru(2)–P(1)	159.8(1)	P(2)–Ru(3)–P(3)	159.2(1)
H(1)–Ru(2)–P(1)	74(1)	Ru(1)–Ru(4)–Ru(3)	92.23(4)
H(1)–Ru(2)–P(2)	87(1)	H(3)–Ru(4)–P(3)	81(2)
H(2)–Ru(2)–P(1)	87(2)	H(4)–Ru(4)–P(3)	154(2)
H(2)–Ru(2)–P(2)	87(2)	H(5)–Ru(4)–P(3)	111(2)

* Numbers in parentheses are estimated standard deviations in the least significant digits.

**Fig. 2** Molecular structure of $[H_5Ru_4(CO)_8(PCy_2)_3] 3$

those observed in complex 2 (average 3.031 Å). The presence of a formal $Ru=Ru$ double bond in the Ru_4 skeleton is responsible for the difference in the angles of the Ru_4 framework: $Ru(4)-Ru(1)-Ru(2)$ [$91.76(4)^\circ$] and $Ru(1)-Ru(4)-Ru(3)$ [$92.23(4)^\circ$] are superior to 90° , while $Ru(1)-Ru(2)-Ru(3)$ [$88.37(4)^\circ$] and $Ru(4)-Ru(3)-Ru(2)$ [$87.63(4)^\circ$] are inferior to 90° . The positions of the phosphido ligands are alternating below and above the Ru_4 plane. The average inclination angle of the phosphido ligands with respect to the Ru_4 skeleton is 123.7° , being similar to that observed in 2. Owing to the different orientation of the cyclohexyl rings C(15) to C(20) and C(33) to C(38), there is no symmetry plane in the molecule.

In accordance with the molecular structure, the $^{31}P\{-^1H\}$ NMR spectrum of 3 shows two signals, a doublet at δ 216.6 ($J_{PP} = 105$ Hz) attributed to the two equivalent phosphorus atoms P(1) and P(3), and a triplet at δ 196.6 ($J_{PP} = 105$ Hz) assigned to the third phosphorus atom P(2). The angles $P(2)-Ru(2)-P(1)$ [$159.8(1)^\circ$] and $P(2)-Ru(3)-P(3)$ [$159.2(1)^\circ$] being different from 90° result in a large coupling (105 Hz) between the two signals. The 1H NMR spectrum of 3 presents a complicated pattern between δ 1.06 and 2.36 corresponding to the cyclohexyl hydrogen atoms. In the hydride area, four signals are observed: the triplet at δ -7.46 (integral ratio 1) ($^2J_{HP} = 20$ Hz) can be assigned to H(4) which is coupled to the two equivalent phosphorus atoms P(1) and P(3). This coupling is large

because of the large angles H(4)–Ru(4)–P(3) [154(2)°] and H(4)–Ru(1)–P(1) [152(2)°]. The pseudo triplet at δ –13.76 (integral ratio 2) ($^2J_{\text{HP}} = 14.3$, $^2J_{\text{HP}} = 15.6$ Hz) can be assigned to H(1) and H(3) which couple to P(1) and P(2) or to P(3) and P(2), respectively. The triplet at δ –17.02 (integral ratio 1) ($^2J_{\text{HP}} = 9.3$ Hz) is attributed to H(5), coupled to P(1) and P(3), the coupling being smaller because of the smaller angles H(5)–Ru(4)–P(3) [111(2)°] and H(5)–Ru(1)–P(1) [110(2)°]. Finally, the multiplet at δ –18.04 (integral ratio 1) must be assigned to H(2), coupled to P(3) and P(1) as well as to P(2); it is the only signal showing in addition a homo-spin coupling [to H(1) and H(3)]. In the signal for H(1) and H(3) this coupling is not seen due to the broadening of the lines.

Conclusion

Tetranuclear ruthenium clusters which are unsaturated with respect to the noble gas configuration are quite rare. The 18-electron rule requires for a tetrahedral Ru₄ cluster 60 electrons, for a butterfly Ru₄ cluster 62 electrons, and for a square-planar Ru₄ cluster 62 electrons. Of the numerous square-planar Ru₄ clusters described hitherto, only a few have less than 64 electrons: the μ_4 -phosphinidyne clusters [Ru₄(CO)₁₁(PPh)₂]⁸ [HRu₄(CO)₁₀(PPh)₂]⁹ and [Ru₄(CO)₈(PPhH)₂(PPh)₂]¹⁰ reported by Haines and co-workers as well as [Ru₄(CO)₈(PCy)₂(PCy₂)₂]⁴ and [Ru₄(CO)₈(PPh)₂(PPh₂)₂]^{4,5} contain only 62 electrons, which can be explained by the fact that they represent a *closo* octahedral Ru₄P₂ framework with seven skeletal electron pairs according to the polyhedral skeleton electron pair theory.¹¹ The cluster [H₄Ru₄(CO)₇(PPh₃)(PPh₂)₂(PPh)], containing only one PPh cap and giving rise to a tetragonal-pyramidal Ru₄P skeleton, also has an electron count of 62 electrons.⁵ The only square-planar Ru₄ cluster with an electron count of 60 is the μ -phosphido bridged cluster [Ru₄(CO)₈(PCy)₄] reported in 1994.⁴ By contrast, the 64e clusters [Ru₄(CO)₁₃(PR₂)₂] (R = Ph, Prⁱ, OEt, NPrⁱ, Cy or Et)^{12,13} and [Ru₄(CO)₁₀(PPh₂)₄]^{13,14} are rhomboidal containing five metal–metal bonds. The two clusters reported in this paper, [H₃Ru₄(CO)₈(PCy)₃] **3** and [H₄Ru₄(CO)₈(PCy)₂] **2** complement the series of square-planar Ru₄ clusters with 60, 62, 64 electrons containing phosphorus ligands with bulky cyclohexyl substituents. Interestingly, the electron-deficiency in cluster **3** can be localised at the two ruthenium atoms carrying the two hydrido bridges by a formal Ru=Ru double bond with respect to the three Ru–Ru single bonds of the Ru₄ square.

Experimental

The organic solvents were refluxed over appropriate desiccants,¹⁵ distilled and saturated with nitrogen prior to use. Thin layer chromatography (TLC) was performed using glass plates (20 × 20 cm) coated with Fluka Silica gel G. The NMR spectra were recorded on a Varian Gemini 200 BB instrument or on a Bruker AMX 400, chemical shifts were measured relative to SiMe₄ (¹H, ¹³C) and to 85% H₃PO₄ (³¹P). The IR spectra were recorded with a Perkin-Elmer FTIR 1720X spectrophotometer (4000–400 cm⁻¹). Microanalytical data were obtained from the Mikroelementaranalytisches Laboratorium der ETH Zürich. Mass spectra were obtained with a LCQ Finnigan instrument using the ESI method. The starting compound [Ru₂(CO)₄(O₂CR)₂(PCy₂H)₂] was synthesised according to the published method.⁴ Dicyclohexylphosphine was purchased from Strem Chemicals Co. and used without further purification.

Reaction of [Ru₂(CO)₄(O₂CR)₂(PCy₂H)₂] with H₂ (R = H or Me)

A solution of [Ru₂(CO)₄(O₂CH)₂(PCy₂H)₂] (200 mg, 0.250 mmol) in 20 ml of cyclohexane was pressurised with 60 bar of H₂ in a stainless-steel autoclave. The yellow solution was stirred at 160 °C for 2 h. After cooling and venting, the autoclave was

opened, the red-brown solution evaporated to dryness, and the residue taken up in a minimum amount of CH₂Cl₂. Thin layer chromatography on silica gel using CH₂Cl₂–pentane (1:8) as eluent afforded a weak yellow and a strong red band. From the yellow band, crystals of [H₄Ru₄(CO)₈(PCy₂)₄] (**2**, 12 mg, 8.45 μ mol, 7%) were obtained by crystallisation from CH₂Cl₂–CH₃OH. IR (pentane): $\nu(\text{CO})$ 2018vs, 1971m, 1963 (sh) cm⁻¹. ¹H NMR (C₆D₆): δ 1.03–2.83 (88 H, m, C₆H₁₁), –17.70 (4 H, dt, μ -H). ³¹P NMR (C₆D₆): δ 151.1 (s); FAB MS: *m/z* 1421 (1420 based on ¹⁰¹Ru) (Found: C, 47.05; H, 6.61. Calc. for C₃₆H₉₂O₈–P₄Ru₄: C, 47.32; H, 6.52%). The red band gives, upon extraction with CH₂Cl₂ and crystallisation from CH₂Cl₂–hexane, red crystals of [H₃Ru₄(CO)₈(PCy₂)₃] (**3**, 85 mg, 70 μ mol, 56%). IR (hexane): $\nu(\text{CO})$ 2046 (sh), 2025vs, 1981m, 1970 (sh) cm⁻¹. ¹H NMR (CDCl₃): δ 1.06–2.36 (66 H, m, C₆H₁₁), –7.46 (1 H, t, 20), –13.76 (2 H, t, 15), –17.02 (1 H, t, 9.3 Hz), –18.04 (1 H, m). ³¹P NMR 216.6 (d, ²J_{PP} = 105), 196.6 (t, ²J_{PP} = 105 Hz) (Found: C, 43.35; H, 5.80. Calc. for C₄₄H₇₁O₈P₃Ru₄: C, 43.13; H, 5.84%).

The analogous reaction of [Ru₂(CO)₄(O₂CMe)₂(PCy₂H)₂] gives the same compounds **2** (yield 5%) and **3** (yield 46%).

Crystal structure of complex 2

A yellow crystal of compound **2** was mounted on a Stoe-Siemens AED2 four-circle diffractometer. Intensity data were measured using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at –50 °C. The ω – 2θ scan technique was used to a maximum 2θ value of 45°. The cell parameters were determined from a least-squares treatment of the setting angles of 24 reflections with $14.0 < \theta < 21.0^\circ$. The intensity of one representative reflection was measured every 60 min. During data collection the intensity of the standards decreased by less than 1%. A semiempirical absorption correction was supplied using ψ scans ($T_{\text{min}} = 0.42$, $T_{\text{max}} = 0.51$).

The structure was solved by direct methods using the program SHELXS 86¹⁶ and refined by full-matrix least squares on F^2 with SHELXL 97.¹⁷ The positions of the four hydrides were derived from Fourier-difference maps, while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL 97¹⁷ default parameters. One distorted molecule of dichloromethane (four chlorine positions with an occupancy of 0.5 were derived), 0.5 molecule of water and 0.5 molecule of methanol per asymmetric unit was found in the molecular structure of **2**. The hydrogen atoms of the water molecule were found and fixed in their positions, while the remaining hydrogen atoms of the solvent molecules were included in calculated positions and refined as riding atoms using SHELXL default parameters.

Crystallographic details are given in Table 3 and significant bond lengths and angles are listed in Table 1. The figures were drawn with SCHAKAL.¹⁸

Crystal structure of complex 3

A red crystal of compound **3** was mounted on a Stoe Imaging Plate diffractometer System (Stoe & Cie, 1995) equipped with a one circle ϕ goniometer and a graphite-monochromator. Data collection was performed at –50 °C using Mo-K α radiation ($\lambda = 0.71073$ Å). 120 Exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \phi < 120^\circ$ and with crystal oscillating through 0.5° in ϕ . The resolution was D_{min} – D_{max} 12.45–0.81 Å.

The structure was solved by direct methods using the program SHELXS 86¹⁶ and refined by full-matrix least squares on F^2 with SHELXL 97.¹⁷ The structure is pseudo-centrosymmetric as indicated by the Calc ADDSYM subroutine in PLATON,¹⁹ which indicates the presence of a centre of symmetry at 0.0, 0.5, 0.25. All attempts to solve the structure in the centrosymmetric space group *Pnma* failed. The structure solution and refinement in the non-centrosymmetric space group

Table 3 Crystal data and data collection parameters for complexes **2** and **3**

	2	3
Formula	C ₅₆ H ₉₂ O ₈ P ₄ Ru ₄ ·CH ₂ Cl ₂ ·0.5H ₂ O·0.5CH ₃ OH	C ₄₄ H ₇₁ O ₈ P ₃ Ru ₄ ·CH ₂ Cl ₂
<i>M</i>	1531.41	1310.12
Crystal size/mm	0.53 × 0.46 × 0.19	0.25 × 0.20 × 0.20
<i>T</i> /K	223(2)	223(2)
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁
Colour	Yellow	Red
<i>a</i> /Å	13.505(5)	32.536(1)
<i>b</i> /Å	14.968(6)	14.362(1)
<i>c</i> /Å	16.933(5)	11.495(1)
α°	89.82(3)	
β°	80.21(3)	
γ°	79.73(3)	
<i>U</i> /Å ³	3318(2)	5371.4(6)
<i>Z</i>	2	4
<i>D</i> _c /g cm ⁻³	1.533	1.620
μ /mm ⁻¹	1.119	1.338
<i>F</i> (000)	1568	2648
θ Limits/°	1.56–22.5	2.17–22.5
Reflections measured	8684	12 405
Independent reflections	8684	5530 (<i>R</i> _{int} = 0.027)
Observed reflections	6634	4270
Goodness-of-fit on <i>F</i> ²	1.040	0.857
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)], <i>R</i> 1 (all data)	0.040, 0.060	0.027, 0.040
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)], <i>wR</i> 2 (all data)	0.099, 0.1010	0.046, 0.048
Minimum, maximum residual electron density/e Å ⁻³	–0.986, 1.236	–0.385, 0.433

*Pna*2₁ was successful. The molecule possesses a pseudo-mirror plane which is perpendicular to the crystallographic mirror plane required for the centrosymmetric space group. The positions of the five hydrides were located from Fourier-difference maps and were refined with *U*_{iso} fixed at 0.02 Å². Their final coordinates were displaced from the observed positions by less than 0.05 Å. Two cyclohexyl rings [C(21)–C(26) and C(27)–C(32)] of the P(2) phosphine ligand are highly disordered. Distances and angles for their cyclohexyl rings were constrained to their theoretical values²⁰ with estimated standard deviations of 0.02 for the cycles C(27)–C(32) and C(27A)–C(32A) and 0.05 for the remaining disordered cyclohexyl rings, also the *U*_{eq} values were constrained to be equal in the rings. One molecule of dichloromethane per asymmetric unit was found in the molecular structure of **3**. No absorption correction was applied.

Crystallographic details are given in Table 3 and significant bond lengths and angles are listed in Table 2. The figures were drawn with SCHAKAL.¹⁸

CCDC reference number 186/1008.

See <http://www.rsc.org/suppdata/dt/1998/2211/> for crystallographic files in .cif format.

Acknowledgements

We thank the Fond National Suisse de la recherche scientifique for financial support of this work. A generous loan of ruthenium trichloride hydrate by the Johnson Matthey Technology Centre is gratefully acknowledged.

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Received 27th February 1998; Paper 8/01660G

Electron-deficient triruthenium clusters: synthesis and molecular structure of the anion $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^-$, a second example of an Ru_3 cluster presenting an electron count of 44 electrons

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Received 10 April 1999

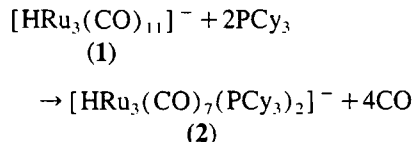
Abstract

The reaction of $[\text{HRu}_3(\text{CO})_{11}]^-$ (**1**) with an excess of PCy_3 in refluxing THF gives the electron-deficient anion $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^-$ (**2**) which has the rare electron count of 44e. As evidenced by the ^1H and ^{31}P NMR spectra, **2** exists in solution in the form of two isomers **2a** and **2b**, one of which crystallises from acetone as the tetraethylammonium salt. The single-crystal X-ray analysis shows a closed Ru_3 framework with the hydride ligand bridging the metal–metal bond between a phosphine-substituted and a phosphine-free ruthenium atom (isomer **2b**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ruthenium complexes; Carbonyl complexes; Cluster complexes

Bulky phosphines containing cyclohexyl or tert-butyl substituents are known to allow unusual structures and unsaturated or oversaturated clusters for steric reasons. Applying this strategy, H.-C. Böttcher et al. obtained the oversaturated clusters $\text{HRu}_3(\text{CO})_9(\text{PCy}_2)_3$ (52e) [1] and $\text{Ru}_3(\text{CO})_6(\mu\text{-Cl})_3(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})$ (50e) [2], and the unsaturated cluster $\text{H}_2\text{Ru}_3(\text{CO})_5(\text{P}^t\text{Bu}_2)_2(\text{dppm})$ and its adamantyl derivative (46e) [3]. Other examples of electron-deficient 46e triruthenium clusters have been reported: $\text{HRu}_3(\text{CO})_9(\text{PPh}_2)$ [4], $\text{Ru}_3(\text{CO})_7(\text{PhCCPh})(\text{dppm})$ [5], $\text{HRu}_3(\text{CO})_7(\text{C}_{12}\text{H}_{10})$ [6], $\text{HRu}_3(\text{CO})_9(\text{NSOMePh})$ [7], $\text{HRu}_3(\text{CO})_{10}$ as well as its phosphine derivative $\text{HRu}_3(\text{CO})_9(\text{PPh}_3)$ [8]. The only triruthenium cluster presenting an electron count of 44e is $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ which we published recently [9,10].

The cluster anion $[\text{HRu}_3(\text{CO})_{11}]^-$ (**1**), employed as the tetraethylammonium or the bis(triphenylphosphine)iminium salt (0.34 mmol), reacts with tricyclohexylphosphine (1.152 mmol) in refluxing THF (40 ml, 75°C, 90 min) to give the highly unsaturated cluster anion $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^-$ (**2**), which can be isolated (62%) by precipitation (THF/pentane 1:10).



Obviously, anion **2** is not a simple phosphine derivative of **1**, since four carbonyl ligands have been replaced by only two phosphine ligands. Hence it follows that **2** is short of 4 electrons with respect to the electron-precise cluster anion **1**. Cluster **2** is only the second example of a 44e triruthenium cluster, and it is the first 44e Ru_3 cluster anion.

The infrared spectrum ¹ of **2** shows four $\nu(\text{CO})$ absorptions, two bands in the area of terminal carbonyls and two (exceptionally strong) bands in the area of bridging carbonyls, indicating a high number of carbonyl bridges. The ^1H NMR spectrum of **2** demonstrates the presence of two isomers in solution, corresponding to the two possibilities of arranging the two phosphine ligands at the Ru_3 core with respect to the bridging hydride ligand (Fig. 1). Apart from the cyclo-

¹ Spectroscopic data for cluster **2**: IR (THF): $\nu(\text{CO})$ 1969m, 1891vs, 1735s, 1713s cm^{-1} ; ^1H NMR (CDCl_3): δ 0.95–1.99 (66H, m, C_6H_{11}), –17.40 (1H, t, $J_{\text{H-P}}=4.7$ Hz), –17.73 (1H, dd, $J_{\text{H-P}}=26.1$ Hz, $J_{\text{H-P}}=5.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 77.8 (s, 1P), 74.3 (s, 1P) 67.6 (s, 1P) no coupling observed. Micro-analytical data for $[\text{N}(\text{PPh}_3)_2]^-[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]$: Found: C, 56.68; H, 6.38. Calc. for $\text{C}_{79}\text{H}_{97}\text{NO}_7\text{P}_2\text{Ru}_3 \cdot 4\text{H}_2\text{O}$: C, 56.76; H, 6.33%.

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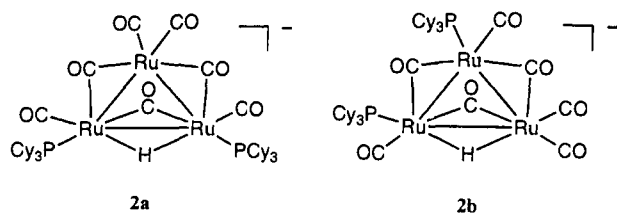


Fig. 1. The two isomers of $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^-$ (**2**).

hexyl multiplet, two hydride resonances which are not coupled to each other are observed: a triplet at $\delta -17.40$ ppm ($J_{\text{H-P}} = 4.7$ Hz), assigned to isomer **2a** with two equivalent phosphorus atoms, and a doublet of doublets at $\delta -17.73$ ppm ($J_{\text{H-P}} = 26.1$ Hz, $J_{\text{H-P}} = 5.5$ Hz), attributed to the isomer **2b** with two non-equivalent phosphorus atoms. Accordingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows 3 signals, the strongest one at $\delta 67.6$ ppm being assigned to isomer **2a**, while the other two signals at $\delta 77.8$ and 74.3 ppm are assigned to isomer **2b**. As no $^{31}\text{P}-^{31}\text{P}$ coupling is observed for the two signals of **2b**, it must be assumed that the two phosphine ligands in **2b** are *cis* with respect to each other. This assumption is confirmed by a single-crystal structure analysis².

The existence of two isomers in solution is further evidenced by the variable-temperature ^1H NMR spectra recorded in D_6 -acetone (Fig. 2). While the doublet of doublets signal stays almost unchanged at $\delta -17.73$ ppm over the temperature range from $+45$ to -80°C , the triplet moves from $\delta -17.30$ ($+45^\circ\text{C}$) to $\delta -17.83$ (-80°C). No coalescence is observed, and the intensity of the two signals stays the same, indicating that the two isomers **2a** and **2b** do not interchange in solution over the temperature range from $+45^\circ\text{C}$ to -80°C .

The ^1H NMR spectrum of **2** (precipitated as $[\text{N}(\text{PPh}_3)_2]^+$ salt from THF/pentane) also reveals the presence of water, introduced presumably by the THF despite thorough drying prior to use. The micro-analytical data confirm the composition $[\text{N}(\text{PPh}_3)_2][\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2] \cdot 4\text{H}_2\text{O}$.

² Crystal data for cluster **2**: $\text{C}_{43}\text{H}_{67}\text{O}_7\text{P}_2\text{Ru}_3 \cdot (\text{C}_2\text{H}_5)_4\text{N} \cdot 0.5(\text{CH}_3)_2\text{CO}$, $M = 1220.41$ g mol⁻¹, dark red crystal, crystal dimensions $0.34 \times 0.19 \times 0.11$ mm, monoclinic, space group $P2_1$, $a = 11.783(5)$, $b = 23.478(2)$, $c = 20.519(7)$ Å, $\beta = 93.19(4)^\circ$, $U = 5668(4)$ Å³, $T = 223(2)$ K, $D_c = 1.430$ g cm⁻³, $Z = 4$, $F(000) = 2536$ Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.894$ mm⁻¹, 10850 reflections measured, 7786 observed data [$I > 2\sigma(I)$], $R1 = 0.0791$, $wR2 = 0.1254$ ($R1 = 0.1322$, $wR2 = 0.1430$ for all data). Data collection was performed with a Stoe-Siemens AED2 four-circle diffractometer. Intensity data were measured using a graphite-monochromator, Mo-K α radiation ($\lambda = 0.71073$ Å). The $\omega/2\theta$ scan technique was used to a maximum 2θ values of 50.0 . The cell parameters were determined from the least-squares treatment of the setting angles of 21 reflections with $14.0^\circ < \theta < 19.0^\circ$. The intensities of two representative reflections were measured every 60 min. During data collection the intensity of the standards decreased by less than 2%. The structure was solved by direct methods using the program SHELXS-97 [13] and refined by full matrix least-squares on F^2 with SHELXL-97 [14]. The positions of the two hydrides were located from Fourier difference maps and held fixed while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 [14] default parameters.

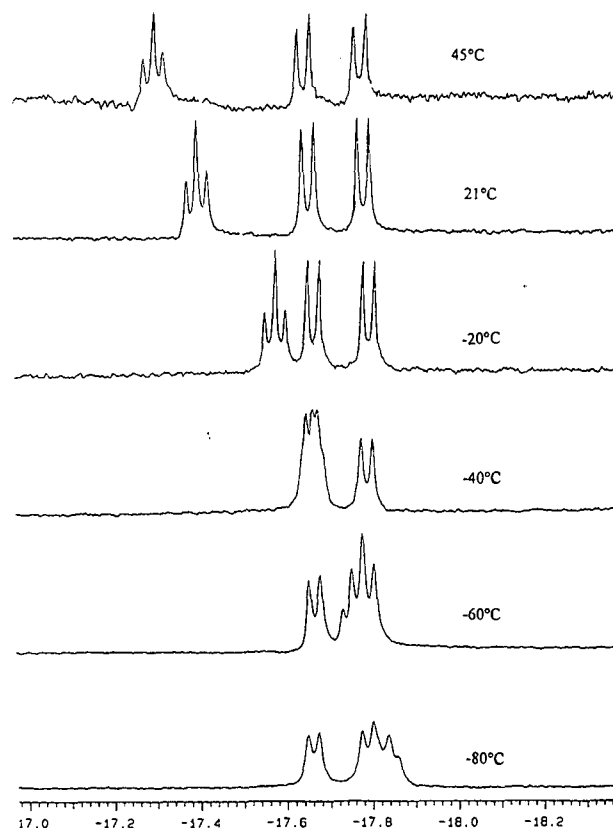


Fig. 2. ^1H NMR spectra of **2** in D_6 -acetone at several temperatures (hydride region).

Recrystallisation of the tetraethylammonium salt of **2**, $[\text{NEt}_4][\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]$, from acetone gave dark red crystals which contain, according to the X-ray structure analysis, only isomer **2b**. Fig. 3 shows one of the two independent anions **2b** which are present in the unit cell together with two tetraethylammonium cations and an acetone molecule. The two independent molecules of **2b** differ only in bond distances and angles, the differences being very small. The three Ru–Ru bonds are bridged by three μ_2 -carbonyl ligands which lie all below the Ru_3 plane. The three Ru–Ru bonds (2.694(2), 2.721(2) and 2.710(3) Å) are shorter than those in $[\text{HRu}_3(\text{CO})_{11}]^-$ (average 2.834 Å) [11], being in line with the high electron-deficiency of **2**. The Ru–CO distances (2.03(2), 2.15(2), 2.04(2), 2.13(2), 2.07(2) and 2.11(2) Å) are shorter than those of the usual carbonyls bridges (2.073–2.219 Å) [12]. The hydride bridge is situated between Ru(1) and Ru(3); it is above the Ru_3 plane. The distances Ru–H (1.9645 and 2.0698 Å) are longer than those in $[\text{HRu}_3(\text{CO})_{11}]^-$ (1.720(9) and 1.655(1) Å) [11]. The tricyclohexylphosphine ligands lie above the Ru_3 plane, the two Ru–P distances (2.324(5) and 2.329(5) Å) being very similar. The two phosphine-substituted ruthenium atoms Ru(1) and Ru(2) carry only one terminal carbonyl, while the phosphine-free ruthenium atom Ru(3), carries two terminal carbonyl ligands.

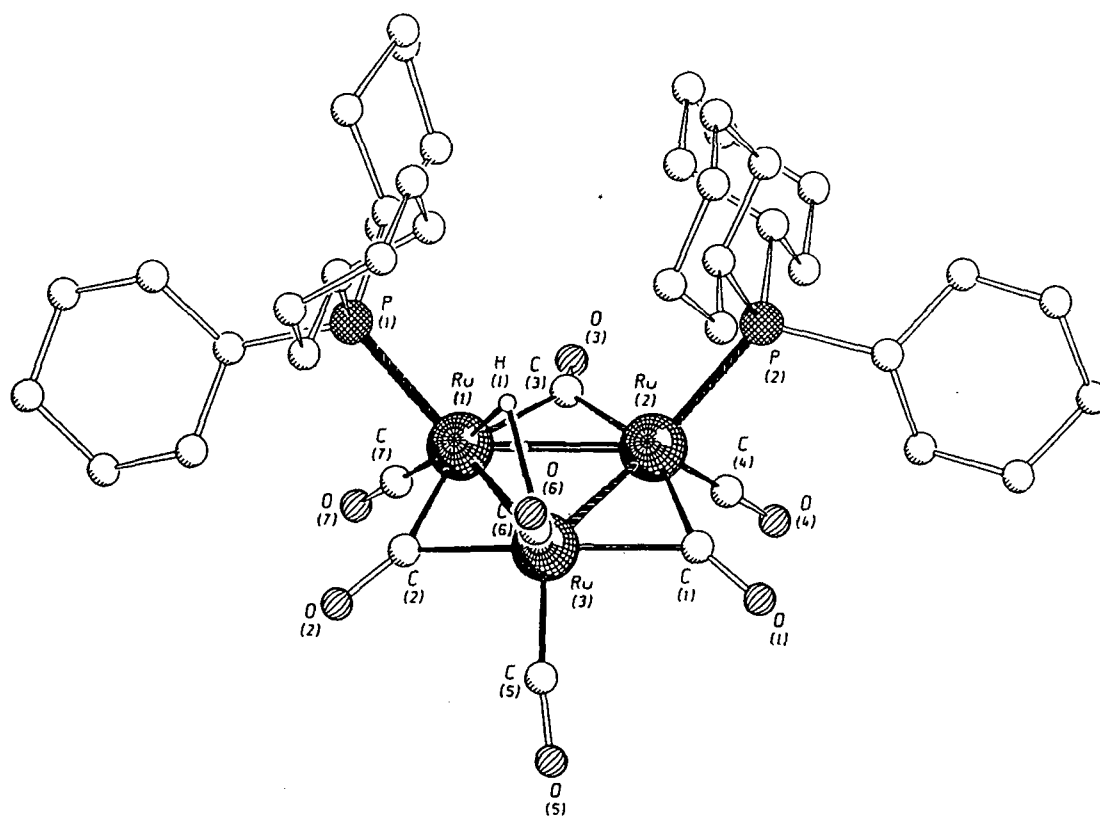


Fig. 3. Molecular structure of $[\text{HRu}_3(\text{CO})_7(\text{PCy}_3)_2]^+$ (**2b**). Selected bond distances (Å) and angles ($^\circ$): Ru(1)–Ru(2) 2.694(2), Ru(1)–Ru(3) 2.721(2), Ru(2)–Ru(3) 2.710(3), Ru(1)–P(1) 2.324(5), Ru(2)–P(2) 2.329(5), H(1)–Ru(1) 1.9645, H(1)–Ru(3) 2.0698, C(1)–Ru(2) 2.03(2), C(1)–Ru(3) 2.15(2), C(2)–Ru(1) 2.04(2), C(2)–Ru(3) 2.13(2), C(3)–Ru(2) 2.07(2), C(3)–Ru(1) 2.11(2), C(4)–Ru(2) 1.81(2), C(5)–Ru(3) 1.83(2), C(6)–Ru(3) 1.87(2), C(7)–Ru(1) 1.81(2); Ru(2)–Ru(1)–Ru(3) 60.07(6), Ru(1)–Ru(2)–Ru(3) 60.45(7), Ru(2)–Ru(3)–Ru(1) 59.48(5), P(1)–Ru(1)–H(1) 84.8, P(1)–Ru(1)–Ru(2) 131.98(2), P(1)–Ru(1)–Ru(3) 126.29(2), P(2)–Ru(2)–Ru(1) 130.47(2), P(2)–Ru(2)–Ru(3) 124.73(2). The second independent molecule of **2b** in the asymmetric unit is almost identical with minor differences in bond lengths and angles.

Supplementary material

The CIF file for structure **2b** has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (deposition no CCDC 116055).

Acknowledgements

We thank the Fonds National Suisse de la Recherche Scientifique for financial support of this work. A generous loan of ruthenium trichloride hydrate by the Johnson Matthey Technology Centre is gratefully acknowledged.

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Electron-deficient triruthenium and triosmium clusters from the reaction of the cluster anions $[\text{HM}_3(\text{CO})_{11}]^-$ ($\text{M} = \text{Ru}, \text{Os}$) with tricyclohexylphosphine in methanol

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Received 10 December 1998

Abstract

The reaction of $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$ with an excess of tricyclohexylphosphine in methanol gives the neutral complex $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ which is the first $44 e^-$ triruthenium cluster reported. This highly electron-deficient species reacts with carbon monoxide to give the saturated $48 e^-$ cluster $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$. The electronic structure of the novel $44 e^-$ cluster was established by EHT and DFT molecular orbital calculations of isoelectronic model compounds. The analogous reaction of $[\text{N}(\text{PPh}_3)_2][\text{HOs}_3(\text{CO})_{11}]$ with PCy_3 in methanol affords the $46 e^-$ cluster $\text{H}_2\text{Os}_3(\text{CO})_7(\text{PCy}_3)_3$, the first trisubstituted derivative of $\text{H}_2\text{Os}_3(\text{CO})_{10}$. In all cases methanol acts as source of protons for the formation of the hydrido clusters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cluster; Trinuclear; Unsaturated; Phosphine; Hydrido

1. Introduction

Ligand substitution reactions of dodecacarbonyl-triruthenium with tertiary phosphines have been studied in great detail [1]: the thermal reaction of $\text{Ru}_3(\text{CO})_{12}$ with PR_3 in general leads to the mono-, di-, and trisubstituted derivatives $\text{Ru}_3(\text{CO})_{11}(\text{PR}_3)$, $\text{Ru}_3(\text{CO})_{10}(\text{PR}_3)_2$, $\text{Ru}_3(\text{CO})_9(\text{PR}_3)_3$ [2]. For the directed synthesis of these substitution products, the radical ion-initiated ligand substitution [3,4], the bis(*t*-riphenylphosphine)iminium salt-catalysed carbonyl substitution [5,6], and the trimethylamine oxide-induced carbonyl substitution [7,8] have been developed. However, with sterically demanding phosphine ligands, the

synthesis of the trisubstituted derivatives failed: even a 6-fold excess of tricyclohexylphosphine with $\text{Ru}_3(\text{CO})_{12}$ in the presence of $[\text{Na}][\text{Ph}_2\text{CO}]$ gave only the mono- and the disubstituted complexes, but no $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$ [4].

On the other hand, bulky phosphines containing cyclohexyl or *tert*-butyl substituents are known to allow unusual structures and unsaturated configurations for steric reasons [9,10]: thus the electron-deficient triruthenium cluster $\text{H}_2\text{Ru}_3(\text{CO})_5(\text{P}^t\text{Bu}_2)_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ with an electron count of $46 e^-$ was synthesised by Böttcher et al. in 1996 [10]. Apart from this complex and its adamantyl derivative [10], the only electron-deficient Ru_3 clusters reported prior to this work are $\text{HRu}_3(\text{CO})_9(\text{PPh}_2)$ [11], $\text{Ru}_3(\text{CO})_7(\text{PhCCPh})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ [12], $\text{HRu}_3(\text{CO})_7(\text{C}_{12}\text{H}_{10})$ [13], $\text{HRu}_3(\text{CO})_9(\text{NSO-MePh})$ [14], and $\text{H}_2\text{Ru}_3(\text{CO})_{10}$ as well as its phosphine derivative $\text{H}_2\text{Ru}_3(\text{CO})_9(\text{PPh}_3)$ [15], all of them with an

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electron count of 46 e^- . Interestingly, no unsaturated triruthenium cluster is mentioned in Deeming's review of 1995 [1].

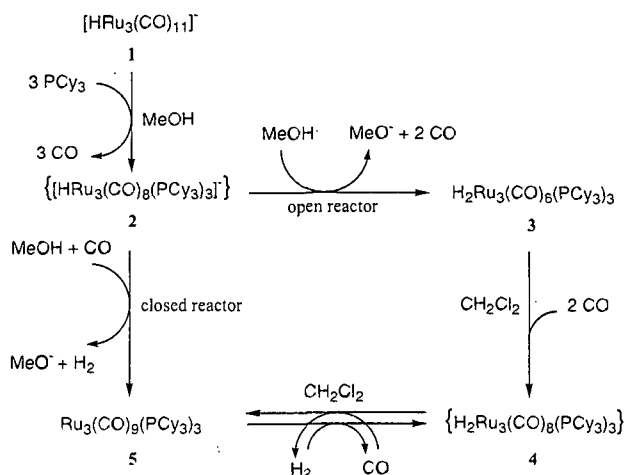
In a preliminary communication [16] we reported the serendipitic isolation and characterisation of the clusters $H_2Ru_3(CO)_6(PCy_3)_3$ and $Ru_3(CO)_9(PCy_3)_3$ from the reaction of $[HRu_3(CO)_{11}]^-$ with tricyclohexylphosphine. We now describe the rational synthesis, the interrelations, and the detailed X-ray structure characterisation of those clusters as well as the analogous reaction of $[HOs_3(CO)_{11}]^-$ leading to $H_2Os_3(CO)_7(PCy_3)_3$.

2. Synthetic and crystallographic results

The thermal reaction of the cluster anion $[HRu_3(CO)_{11}]^-$ (1) with an excess of tricyclohexylphosphine in methanol leads, depending on the reaction conditions, to two different neutral clusters: in an open reaction vessel, the hydrido cluster $H_2Ru_3(CO)_6(PCy_3)_3$ (3) is obtained, while in a closed reactor the cluster $Ru_3(CO)_9(PCy_3)_3$ (5) is formed. Both compounds precipitate directly from the reaction mixture and can be isolated by filtration in high yields.

The neutral clusters 3 and 5 form from the cluster anion $[HRu_3(CO)_{11}]^-$ (1) in thoroughly dried methanol (ultra pure grade) under rigorous exclusion of air and moisture. Addition of water to the reaction mixture causes a decrease in the yields of 3 and 5. We therefore conclude that the methanol not only is the solvent but also acts as a source of protons in the reaction with 1. The strong influence of the reaction condition (closed or open reactor) on the product formation is due to the presence or absence of carbon monoxide resulting from the substitution of carbonyl ligands by the phosphine. Thus, we were able to show that 3 converts into 5 under CO pressure.

On the basis of these findings, we propose the reaction sequence summarised in Scheme 1: in the first step, three carbonyl ligands in 1 are replaced by three phosphine ligands to give the intermediate anion $[HRu_3(CO)_8(PCy_3)_3]^-$ (2) which, however, could not be detected in the reaction mixture. It seems to react immediately with methanol to give, in an open reactor, the unsaturated dihydro cluster $H_2Ru_3(CO)_6(PCy_3)_3$ (3). In a closed reactor, the carbon monoxide pressure inhibits the further elimination of CO and affords, with elimination of H_2 , the saturated cluster $Ru_3(CO)_9(PCy_3)_3$ (5). The isolated unsaturated cluster 3 reacts in dichloromethane with carbon monoxide (1.5 bar) to give an intermediate which could be characterised by NMR spectroscopy to be most likely a saturated dihydro complex $H_2Ru_3(CO)_9(PCy_3)_3$ (4). The red intermediate 4 converts, slowly in CH_2Cl_2 solution but spontaneously on silica gel or alox, into the violet



Scheme 1. Reaction of $[HRu_3(CO)_{11}]^-$ (1) with PCy_3 in methanol. The intermediate {4} is characterised in solution, species {2} is hypothetical.

compound 5. On the other hand, 5 reacts with molecular hydrogen (1.5 bar) in CH_2Cl_2 solution at room temperature to give 4.

The trinuclear clusters 3 and 5, which precipitate in a pure form directly from the corresponding reaction solution, are recrystallised from a mixture of dichloromethane and methanol to give, in all cases, red crystals suitable for X-ray diffraction. Their spectroscopic (IR, MS, 1H - and ^{31}P -NMR) and analytical data, given in Section 4, are in accordance with the structure found by X-ray crystallography (Fig. 1).

The single-crystal X-ray structure analysis of $H_2Ru_3(CO)_6(PCy_3)_3$ (3) shows a Ru_3 skeleton bearing two μ_3 -hydrido caps, on either side of the triangle. The three $Ru-Ru$ bonds are bridged by three μ_2 -carbonyl ligands being almost in the plane of the metal triangle. The three terminal carbonyls as well as the three phosphine ligands are coordinated to the three ruthenium atoms, above and below the metal plane. Important bond lengths and angles are given in Table 1.

The three $Ru-P$ bonds [2.332(2), 2.336(2), 2.344(2) Å] are very similar in length. The three $Ru-C$ bonds of the three terminal carbonyl ligands (1.834(7), 1.834(7), 1.825(8) Å) are shorter than those in $Ru_3(CO)_{12}$ (eq: 1.921(5), ax: 1.942(4) Å) [17]. The bridging carbonyls

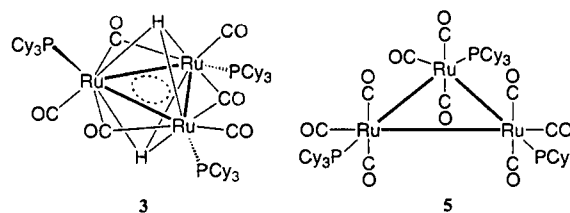


Fig. 1. Structural plots of the 44 e^- $H_2Ru_3((CO)_6(PCy_3)_3)$ (3) and the 48 e^- cluster $Ru_3((CO)_9(PCy_3)_3)$ (5).

Table 1
Selected bond lengths (Å) and angles (°) for $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ (**3**)

Bond lengths ^a		Angles ^a	
Ru(1)–Ru(2)	2.6702(6)	Ru(2)–Ru(1)–Ru(3)	59.97(2)
Ru(1)–Ru(3)	2.7180(7)	Ru(1)–Ru(2)–Ru(3)	60.90(2)
Ru(2)–Ru(3)	2.6931(7)	Ru(2)–Ru(3)–Ru(1)	59.14(2)
Ru(1)–P(1)	2.332(2)	H(1)–Ru(1)–P(1)	101.0
Ru(2)–P(3)	2.336(2)	H(1)–Ru(2)–P(3)	168.3
Ru(3)–P(2)	2.344(2)	H(1)–Ru(3)–P(2)	104.4
Ru(1)–H(1)	1.94	H(2)–Ru(1)–P(1)	172.6
Ru(1)–H(2)	1.61	H(2)–Ru(2)–P(3)	104.7
Ru(2)–H(1)	2.04	H(2)–Ru(3)–P(2)	171.8
Ru(2)–H(2)	1.94	C(4)–Ru(1)–P(1)	91.1(2)
Ru(3)–H(1)	1.93	C(6)–Ru(2)–P(3)	92.3(2)
Ru(3)–H(2)	1.85	C(5)–Ru(3)–P(2)	88.2(2)
Ru(1)–C(4)	1.834(7)		
Ru(2)–C(6)	1.834(7)		
Ru(3)–C(5)	1.825(8)		
Ru(1)–C(1)	2.134(7)		
Ru(3)–C(1)	2.161(6)		
Ru(2)–C(2)	2.107(7)		
Ru(3)–C(2)	2.147(5)		
Ru(1)–C(3)	2.154(6)		
Ru(2)–C(3)	2.129(6)		

^a Estimated standard deviations in parantheses.

are coordinated unsymmetrically, the Ru–C distances (2.134(7), 2.161(6), 2.107(7), 2.147(5), 2.154(6), 2.129(6) Å) being in the usual range of ruthenium carbonyl bridges (2.073–2.219 Å) [18] (Fig. 2).

The two capping hydrido ligands are unsymmetrically coordinated, H(2) being closer to the Ru_3 triangle than H(1). The different environment (one PCy_3 and two CO ligands surrounding H(2), two PCy_3 and one CO ligands surrounding H(1)) is also reflected in $^1\text{H-NMR}$ spectrum of **3**, where two different hydride resonances are observed, both showing a homo-spin coupling to the other one and two hetero-spin cou-

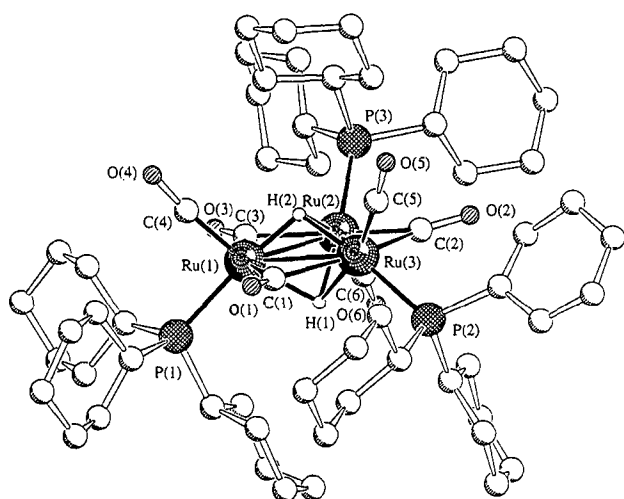


Fig. 2. Molecular structure of $\text{H}_2\text{Ru}_3((\text{CO})_6(\text{PCy}_3)_3)$ (**3**). The hydrogen atoms of the cyclohexyl groups have been omitted for clarity.

plings to the three phosphorus atoms. The signal at $\delta - 19.46$ ppm (doublet of triplets of doublets), assigned to H(1), shows a large coupling (28.3 Hz) to P(3) and a smaller coupling (5.3 Hz) to P(1) and P(2), apart from H(1)–H(2) coupling of 2.2 Hz. The larger coupling to P(3) is presumably due to the large H(1)–Ru(2)–P(3) angle (168.3°) with respect to the smaller angles H(1)–Ru(1)–P(1) and H(1)–Ru(3)–P(2) which measure 101.0° and 104.4° , respectively. The second signal, attributed to H(2), appears as a triplet of doublets of doublets at $\delta - 21.02$ ppm. It shows a large coupling (26.4 Hz) to the two phosphorus atoms P(1) and P(2), the angle H(2)–Ru(1)–P(1) and H(2)–Ru(3)–P(2) being 172.6° and 171.8° , respectively. The smaller hetero-spin coupling (5.4 Hz) is with P(3) because of the smaller H(2)–Ru(2)–P(3) angle 104.7° .

Complex **3** is, to our knowledge, the only Ru_3 cluster known presenting an electron count of $44 e^-$. Trinuclear clusters with $44 e^-$ have been reporting so far only for d^{10} and d^6 metals: $[\text{Pd}_3(\text{SO}_2)_2(t\text{-BuNC})_5]$ [19], $[\text{Pt}_3(\text{CO})_3(\text{P}(\text{C}_6\text{H}_{11})_3)_4]$ [20], $\text{Pd}_3(\text{P}^i\text{Bu}_2)_3(\text{CO})_2\text{Cl}$ [21], $\text{Pt}_3(\text{PPh}_2)_3(\text{PPh}_2)_2\text{Ph}$ [22], $\text{Pt}_3(\text{SO}_2)_3(\text{dppp})(\text{PCy}_3)_2$ [23], $[\text{Pt}_3(\text{SO}_2)_2(\text{PCy}_3)_3\text{Br}]^-$ [24], $[\text{Pd}_3(\text{PPh}_2)_2(\text{PEt}_3)_3\text{Cl}]^+$ [25], $[\text{Pd}_3(\text{PPh}_2)_2(\text{PPh}_3)_3\text{Cl}]^+$ and $[\text{Pd}_2\text{Pt}(\text{PPh}_2)_2(\text{PPh}_3)_3\text{Cl}]^+$ [26], $[\text{H}_3\text{Pt}_3(\text{dppm})_3\{\text{P}(\text{OMe})_3\}_3]^+$ [27], $[\text{FePt}_2(\text{CO})_5(\text{P}(\text{O}^i\text{Ph})_3)_3]$ [28], $\text{Cr}_3(\text{dppe})_3\text{S}_5$ [29], $\text{Mo}_3(\text{PMe}_3)_6\text{S}_5$ [30], $[\text{Mo}_3\text{Cl}_9\text{S}_5]^{3-}$ [31], $[\text{W}_3(\text{OOCCH}_3)_6(\text{H}_2\text{O})_3\text{O}]^{2+}$ [32]. In accordance with the high electron-deficiency, the Ru–Ru bonds in **3** are found to be rather short (2.6702(6), 2.6931(7) and 2.7180(7) Å) with respect to the typical Ru–Ru single bonds of (2.9396(8) Å) in **5** (see below). In addition, the Ru–P bonds in **3** (2.332(2), 2.336(2) and 2.344(2) Å) are also shorter than in **5** (2.414(2) Å). The electron deficiency of **3** (four electrons missing with respect to the noble gas rule) is expressed by a dotted circle within the Ru_3 triangle (Figs. 1 and 3).

The single-crystal X-ray structure analysis of $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$ (**5**) reveals a triruthenium framework with the three phosphine ligands occupying equatorial positions at the three ruthenium atoms. The nine carbonyl ligands are all terminal, six occupying the two axial positions of the Ru atoms, while the other three are alternating with the phosphine ligands in one of the two equatorial positions of each ruthenium atom. The Ru– CO_{eq} distances being 1.876(7) Å are distinctly shorter than the Ru– CO_{ax} distances (1.924(7) and 1.931(7) Å). This is in line with the findings in the known cluster $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$ [16], the Ru–P distances, however, are considerably longer in **5** (2.414(2) Å) than in the methyl derivative (2.330 Å (average)) [33], reflecting the bulkiness of the cyclohexyl substituents. The Ru–Ru bonds in **5** (2.9396(8) Å) are also elongated with respect to those in $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$ (2.860(1), 2.862(1), 2.854(1) Å) [33] and in $\text{Ru}_3(\text{CO})_{12}$

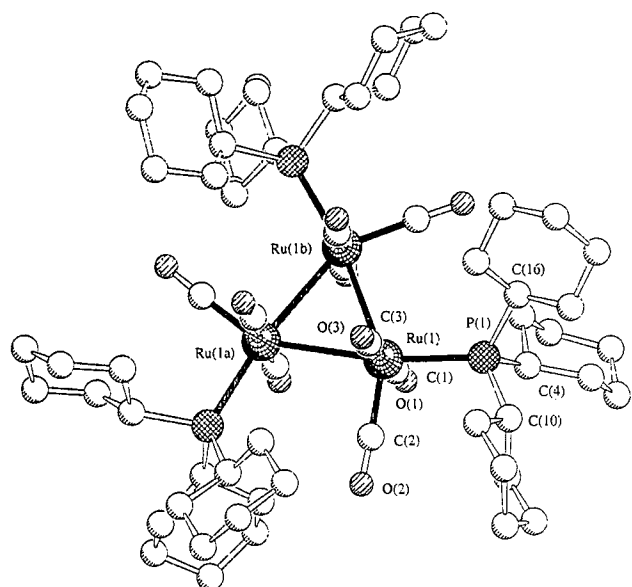


Fig. 3. Molecular structure of $\text{Ru}_3((\text{CO})_9(\text{PCy}_3)_3)$ (**5**). The hydrogen atoms of the cyclohexyl groups have been omitted for clarity.

(2.852(1), 2.851(1), 2.860(1) Å) [17]. The molecule **5** has almost D_{3h} symmetry, the three phosphorus atoms being almost in the plane of the three ruthenium atoms (maximum distance between P and the Ru_3 plane 0.20 Å) and the torsion angles C(axial)–Ru–Ru–C(axial) being less than 10° (Table 2).

The intermediary cluster **4** is observed in the reaction of the $44 e^-$ cluster $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ (**3**) with carbon monoxide (1.5 bar) in dichloromethane to give the $48 e^-$ cluster $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$ (**5**). It is also obtained from the reaction of **5** with molecular hydrogen (1.5 bar) in dichloromethane. Because of its rapid decomposition to **5**, it was not possible to isolate **4**; it could only be characterised by mass spectroscopy and its IR and NMR data in solution. On the basis of these data (see Section 4) and the noble gas rule (electron count $48 e^-$), and in the light of **4** being an intermediate in the reaction of **3** to **5**, we propose **4** to have the composition $\text{H}_2\text{Ru}_3(\text{CO})_8(\text{PCy}_3)_3$ (Fig. 4). The IR spectrum of **4** shows three absorptions in the region of the terminal carbonyl ligands only. In the ^1H -NMR spectrum, apart from the multiplet of the cyclohexyl substituents, **4** gives rise to two hydride resonances: the signal at δ

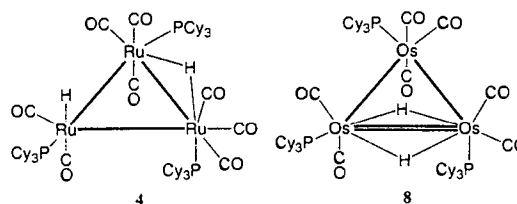


Fig. 4. Proposed structure of the $48 e^-$ cluster $\text{H}_2\text{Ru}_3((\text{CO})_8(\text{PCy}_3)_3)$ (**4**) and structural plot of the $46 e^-$ cluster $\text{H}_2\text{Os}_3((\text{CO})_7(\text{PCy}_3)_3)$ (**8**).

– 17.94 ppm, a doublet of doublets is coupled to two different phosphorus atoms (20.2 and 7.6 Hz) one being equatorial and the other on being axial, but not to the third one nor to the other hydride; it is assigned to the bridging hydrido ligand. The second signal at δ – 10.89 ppm is assigned to a terminal hydride; it appears as a doublet and shows only a coupling to one phosphorus atom (10 Hz). The $48 e^-$ cluster $\text{H}_2\text{Ru}_3(\text{CO})_8(\text{PCy}_3)_3$ which we propose for the intermediate **4** observed in solution is a derivative of the parent compound $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ obtained by Keister et al. from the protonation of $[\text{HRu}_3(\text{CO})_{11}]^-$ at low temperature; this cluster was also characterised spectroscopically in solution and could not be isolated [34,35]. Very recently, $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ has been prepared by reaction of $\text{Ru}_3(\text{CO})_{11}(\text{NCMe})$ with H_2 and carefully characterised by ^1H - and ^{13}C -NMR spectroscopy [36]. For **4** additional evidence comes from the ^{31}P -NMR spectrum showing three resonances for the three different phosphine ligands, and from the mass spectrum (ESI positive) showing a molecular peak at 1372 (calculated for ^{102}Ru) with the correct Ru_3 isotope pattern.

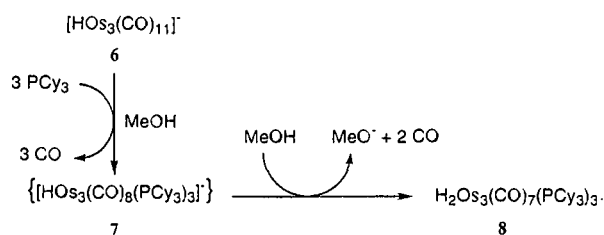
The reaction of the osmium analogue $[\text{HOs}_3(\text{CO})_{11}]^-$ (**6**) with an excess of tricyclohexylphosphine (1:5) in methanol leads, upon heating to 80°C for 3 h, to the neutral cluster $\text{H}_2\text{Os}_3(\text{CO})_7(\text{PCy}_3)_3$ (**8**) which precipitates directly from the reaction solution. The possible anionic intermediate $[\text{HOs}_3(\text{CO})_8(\text{PCy}_3)_3]^-$ (**7**) could not be detected in solution (Scheme 2). Also in this case, methanol acts as a source of protons, since the highest yield is obtained with thoroughly dried methanol and in the absence of air and moisture.

The complex $\text{H}_2\text{Os}_3(\text{CO})_7(\text{PCy}_3)_3$ (**8**) has an electron count of 46 electrons and derives from the famous unsaturated osmium cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [37,38] the

Table 2
Selected bond lengths (Å), angles ($^\circ$) and torsion angles ($^\circ$) for $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$ (**5**)

Bond lengths ^a		Angles ^a		Torsion angles ^a	
Ru(1)–Ru(1a)	2.9396(9)	Ru(2)–Ru(1)–Ru(3)	60.0	C(1)–Ru(1)–Ru(1a)–C(1a)	0
Ru(1)–P(1)	2.414(2)	Ru(3)–Ru(1)–P(1)	111.22(5)	C(1)–Ru(1)–Ru(1a)–C(1a)	3.6(3)
Ru(1)–C(1)	1.923(7)	P(1)–Ru(1)–C(2)	98.2(2)		
Ru(1)–C(2)	1.876(7)	P(1)–Ru(1)–C(1)	92.0(2)		
Ru(1)–C(3)	1.931(7)	P(1)–Ru(1)–C(3)	90.2(4)		

^a Estimated standard deviations in parentheses. Symmetry code: (a) y, z, x.



Scheme 2. Reaction of $[\text{HOs}_3(\text{CO})_{11}]^-$ (6) with PCy_3 in methanol. The intermediate {7} is hypothetical.

chemistry of which has been studied in great detail [39]. To our knowledge, **8** is the only trisubstituted derivative of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ reported so far; Deeming's comprehensive review of 1995 mentions only monosubstituted derivatives [1].

Complex **8** is characterised by spectroscopic and analytical data (see Section 4) and by X-ray diffraction (see below). While the IR spectrum shows only absorptions in the area of terminal carbonyls, the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum shows three singlets for the three non equivalent phosphorus ligands. In the ^1H -NMR spectrum, apart from the cyclohexyl multiplet, **8** gives rise to two hydride resonances which show only hetero-spin coupling: The pseudo triplet at $\delta - 8.64$ ppm is attributed to H(2) which is coupled (5.5 Hz) with P(2) and P(3), the angles H(2)–Os(2)–P(2) [94(2)°] and H(2)–Os(3)–P(3) [97(2)°] being very similar and small. The doublet of doublets at $\delta - 12.87$ ppm assigned to H(1), is also coupled to P(2) (8 Hz) and to P(3) (38 Hz), the angles H(1)–Os(2)–P(2) and H(1)–Os(3)–P(3) being different (83.9(2) and 169.7(2)°, respectively) (Fig. 5).

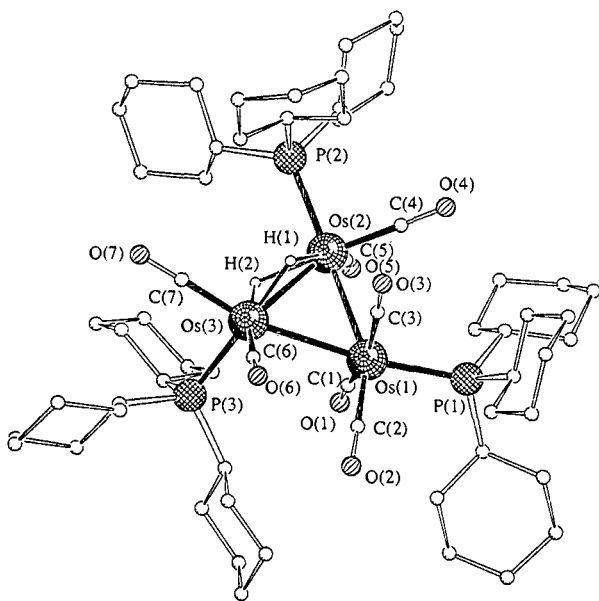


Fig. 5. Molecular structure of $\text{H}_2\text{Os}_3((\text{CO})_7)(\text{PCy}_3)_3$ (**8**). The hydrogen atoms of the cyclohexyl groups have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for $\text{H}_2\text{Os}_3(\text{CO})_7(\text{PCy}_3)_3$ (**8**)

Bond lengths ^a		Angles ^a	
Os(1)–Os(2)	2.8881(2)	Os(2)–Os(1)–Os(3)	56.00(3)
Os(1)–Os(3)	2.8920(2)	Os(3)–Os(2)–Os(1)	62.07(3)
Os(2)–Os(3)	2.7135(2)	Os(2)–Os(3)–Os(1)	61.93(3)
Os(1)–P(1)	2.395(2)	H(1)–Os(2)–P(2)	83.9(2)
Os(2)–P(2)	2.371(2)	H(2)–Os(2)–P(2)	94(2)
Os(3)–P(3)	2.364(2)	H(1)–Os(3)–P(3)	169.7(2)
Os(2)–H(1)	1.72(7)	H(2)–Os(3)–P(3)	97(2)
Os(3)–H(1)	1.77(7)	C(1)–Os(1)–P(1)	89.2(2)
Os(2)–H(2)	1.88(6)	C(2)–Os(1)–P(1)	93.0(2)
Os(3)–H(2)	1.92(6)	C(3)–Os(1)–P(1)	98.3(3)
Os(1)–C(1)	1.924(8)	C(4)–Os(2)–P(2)	90.9(2)
Os(1)–C(2)	1.873(8)	C(5)–Os(2)–P(2)	96.3(2)
Os(1)–C(3)	1.933(9)	C(6)–Os(3)–P(3)	92.5(3)
Os(2)–C(4)	1.87(1)	C(7)–Os(3)–P(3)	87.7(3)
Os(2)–C(5)	1.878(9)		
Os(3)–C(6)	1.89(1)		
Os(3)–C(7)	1.863(8)		

^a Estimated standard deviations in parantheses.

The single-crystal X-ray structure analysis of **8** reveals a tri-osmium framework with three phosphine ligands. All carbonyl ligands are terminal, and two μ_2 -hydride ligands are positioned on the same Ru–Ru edge. The three osmium atoms define an isosceles triangle in which the non-bridged osmium–osmium distances are 2.881(2) Å (Os(1)–Os(2)) and 2.8920 Å (Os(1)–Os(3)), they are longer than in the parent complex $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (average 2.815 Å) [40]. The short dihydrido-bridged osmium–osmium bond is 2.7135(2) Å, slightly longer than the corresponding distance in the parent compound $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (2.681 Å) [40] and in the mono-substituted derivatives $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ (2.683(2) Å) [41], $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPr}_3)$ (2.689(1) Å) [42] and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})$ (2.703(1) Å) [43]. Two phosphine ligands are equatorial, and one is axial. The osmium–phosphine distances (average 2.377 Å) are similar to that observed in $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ (2.361(2) Å) [41], $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PPr}_3)$ (2.384(5) Å) [42] and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})$ (2.347 Å) [43] (Table 3).

3. Theoretical analysis of the 44 e[−] Ru₃ species

In order to shed some light on the electronic structure and the bonding of the 44 e[−] cluster **3**, we have performed extended Hückel theory (EHT) and density functional theory (DFT) molecular orbital (MO) calculations on the isoelectronic models $\text{H}_2\text{Ru}_3(\text{CO})_9$ and $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PH}_3)_3$. The choice of the former hypothetical cluster comes from its high ideal D_{3h} symmetry which allows an easier MO analysis (see below). Details of the calculations are given in Section 4.

3.1. Stereochemical considerations

Before entering into a detailed analysis of the MO calculations, we would like to point out some important structural similarities and differences existing between the electron deficient cluster $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ and classical triangular $48 e^-$ compounds such as $\text{Ru}_3(\text{CO})_{12}$ [17] or **5**. Discarding for the moment the hydrogen atoms in **3**, one can say that in both types of clusters the Ru atoms are in a similar tetracoordinated ligand environment. This ML_4 -type local environment of approximate C_{2v} symmetry is often described as derived ideally from an octahedral ML_6 system from which two *cis* ligands have been removed [44,45]. In such a fragment, one of the LML angles is large, approaching the ideal value of 180° . In a $48 e^-$ species such as $\text{Ru}_3(\text{CO})_{12}$, the almost linear LML arrangements are perpendicular to the Ru_3 plane, while in **3** they lie in the Ru_3 plane, the corresponding ligands being the bridging carbonyls. This different orientation of the same ligand environment in both types of complexes is sketched in the bottom of Fig. 6.

3.2. Comparison of the bonding in the $44 e^-$ model $[\text{Ru}_3(\text{CO})_9]^{2-}$ and the $48 e^-$ cluster $\text{Ru}_3(\text{CO})_{12}$

The frontier orbitals of a C_{2v} octahedron-derived ML_4 unit are well known [44,45]. They are shown in the middle of Fig. 6 for the two considered orientations of the fragments. They consist in a set of five orbitals: The highest is a σ -type hybrid, lying above a π -type hybrid,

situated above a group of three closely spaced d-type levels, derived from the t_{2g} orbitals of the ML_6 parent, which are of σ -, δ - and π -type, respectively. Note that this latter π orbital is perpendicular to the π -type hybrid. The more diffuse and better oriented hybrids generally provide stronger interactions than the three d-type levels.

In a $48 e^-$ cluster of D_{3h} symmetry, the way the frontier orbitals of the three metal centers interact is qualitatively schematized on the left side of Fig. 6, as obtained from EHT calculations on $\text{Ru}_3(\text{CO})_{12}$. The three metallic σ -type hybrids mix to give an in-phase $2a'_1$ and two out-of-phase $3e'^*$ combinations. Lying in the Ru_3 plane, the other hybrid is also of σ -type with respect to Ru–Ru bonding. It is labelled π_σ in Fig. 6. The d-type π orbital, which is perpendicular to the Ru_3 plane is labelled π_\perp . The π_σ frontier orbitals mix to give two bonding $2e'$ and one antibonding $1a'_2$ MO's. Similarly, the d-block leads to combinations of σ -type ($1a'_1$ and $1e'^*$), of δ -type ($1e''$ and $1a''_1$) and of π_\perp ($1a''_2$ and $2e''$). At the Ru–Ru separation of ca. 2.9 Å, the nine d-type combinations are only weakly bonding or antibonding and therefore remain at the rather low energy of a non-bonding d-type level. This is not the case for the hybrid combinations $3e'^*$ and $1a''_1$ which are high-lying antibonding levels. In a $48 e^-$ cluster, there are 8 electrons per metal center available for filling the metal combinations. Twelve metallic orbitals of $\text{Ru}_3(\text{CO})_{12}$ will be filled, leaving a large HOMO/LUMO gap separating the three bonding and nine more-or-less non-bonding orbitals from the three antibonding ones (2.04

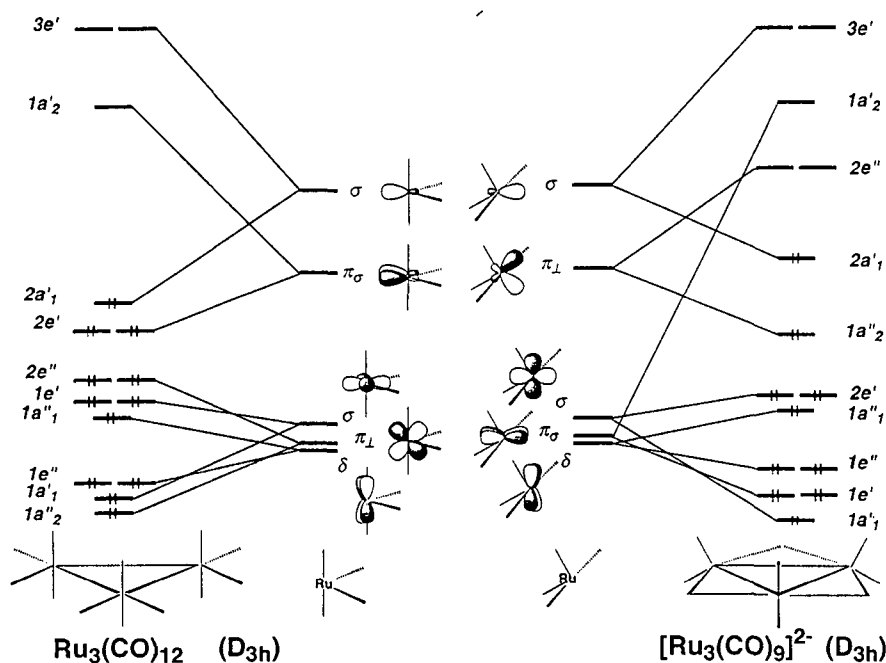


Fig. 6. Simplified MO diagrams of $\text{Ru}_3(\text{CO})_{12}$ (left) and $[\text{Ru}_3(\text{CO})_9]^{2-}$ (right) based on the interaction of the frontier orbitals of the three metal centres considered as octahedrally-derived ML_4 'monomers'. The second-order mixing between combinations of the same symmetry is not considered.

eV from EHT calculations). Considering all the other occupied levels as nonbonding, the three occupied bonding combinations of the hybrid orbitals, namely $2e'$ and $2a'_1$ in Fig. 6, can be associated with the three 2-electron 2-center Ru–Ru bonds. The computed EHT Ru–Ru overlap population is 0.216, a value in agreement with a bond order of 1.

We now apply the same symmetry considerations to the $44 e^-$ deprotonated model of $H_2Ru_3(CO)_9$, namely the D_{3h} fragment $[Ru_3(CO)_9]^{2-}$. As compared to $Ru_3(CO)_{12}$, the different orientation of the local ligand environment around the metal atoms exchanges the roles of the two π -type frontier orbitals (see Fig. 6). The hybrid is now π_\perp , leading to the $2e''^*$ and $1a''_2$ combinations, while the now in-plane π_σ d-level gives rise to the $1e'$ and $1a''_2$ combinations. Due to the good overlap ability of the involved hybrid and to the shorter Ru–Ru bonds, the π_\perp interaction is much stronger than in $Ru_3(CO)_{12}$. EHT calculations indicate that the π_σ interaction is also significant. The other metallic frontier orbitals, of σ and δ local symmetries, barely unchanged upon the rotation of the local metallic framework, interact more or less similarly (i.e. weakly) as in $Ru_3(CO)_{12}$. The resulting level ordering of the $[Ru_3(CO)_9]^{2-}$ fragment is schematized on the right side of Fig. 6, as obtained from EHT calculations. In $[Ru_3(CO)_9]^{2-}$, there are 20 electrons left available for filling the metal combinations. For this electron count, the two highest occupied MO's are the $2a'_1$ and $1a''_2$ bonding combinations of the two high-lying hybrids. Comparing the metallic configurations of the $48 e^- Ru_3(CO)_{12}$ and $44 e^- [Ru_3(CO)_9]^{2-}$ systems (Fig. 6), it appears that the main difference is that the $2e''^*$ out-of-phase π_\perp combination is almost nonbonding and populated in the former but significantly antibonding and unoccupied in the latter. As a result, $[Ru_3(CO)_9]^{2-}$ contains three σ -type bonding electron pairs (located in the $2a'_1$ HOMO and in the $1e'$ π_σ combination) and one π -type significantly bonding pair in the $1a''_2$ level. This situation corresponds to a Ru–Ru bond order of 4/3. The corresponding EHT overlap population is 0.279, a value in agreement with a bond order larger than 1. $[Ru_3(CO)_9]^{2-}$ could be described simply with three equivalent canonical formulae exhibiting two R–Ru single bonds and one Ru=Ru double bond, with one electron-pair vacancy on the singly bonded Ru atom. The computed EHT HOMO/LUMO gap of $[Ru_3(CO)_9]^{2-}$ (0.71 eV) is not very large suggesting some instability. As shown below, the presence of two capping hydrogen atoms brings significant additional stability to the cluster.

3.3. The $44 e^-$ model $H_2Ru_3(CO)_9$

The EHT MO diagram of $H_2Ru_3(CO)_9$ is shown in Fig. 7, based on the interaction of $[Ru_3(CO)_9]^{2-}$ (left

side) with the $(H\cdots H)^{2+}$ bicapping fragment (right side) and assuming D_{3h} symmetry. The skeletal orbitals of the $[Ru_3(CO)_9]^{2-}$ unit have been described above. The frontier orbitals of the $(H\cdots H)^{2+}$ fragment are very simple. They are the in-phase (a'_1) and out-of-phase (a''_2) combinations of the 1s hydrogen orbitals, which are somewhat split due to the weak H \cdots H overlap (H \cdots H distance = 2.1 Å). They are vacant in the considered charge partitioning. Calculations indicate that they interact with the two highest occupied orbitals of $[Ru_3(CO)_9]^{2-}$, $2a'_1$ and $1a''_2$, which have the proper symmetry and a localization to favor strong overlap. The occupation after interaction of the a'_1 and a''_2 orbitals of the $[Ru_3(CO)_9]^{2-}$ fragment is 0.74 and 0.85, respectively. Being strongly Ru–Ru bonding, their depopulation upon interaction reduces the Ru–Ru overlap population to 0.096. This value is probably largely underestimated at the EHT level. Nevertheless, it is indicative of a significant electron transfer from the Ru–Ru bonds to the hydrogen atoms. The resulting net charge on the hydrogen atoms is -0.24 conferring to these atoms some hydrido character. The Ru–H overlap population is rather large (0.202). Interestingly, the H \cdots H overlap population is very small, but positive ($+0.002$). Because of their strong interactions with their hydrogen counterparts, the $2a'_1$ and $1a''_2$ orbitals of $[Ru_3(CO)_9]^{2-}$ are destabilized strongly, leaving a large HOMO/LUMO gap (1.81 eV) for the $H_2Ru_3(CO)_9$ cluster, in full agreement with the stability of the isoelectronic cluster **3**.

DFT calculations performed on $H_2Ru_3(CO)_9$ at the LDA level (see computational details) fully confirm the EHT MO qualitative analysis. Full geometry optimization without any symmetry constraint indicates no significant departure from the D_{3h} symmetry. One can see on the left side of Fig. 8 that the EHT and DFT one-electron level orderings are in a very good agreement, with similar HOMO–LUMO gaps. The major optimized bond distances are reported in Table 4. They are in satisfying agreement with the X-ray data of **3**, except for the Ru–Ru distances which are computed to be somewhat longer than the experimental ones (by ≈ 0.08 Å). The introduction of gradient corrections in the calculations (see computational details) does not change significantly these results.

3.4. The $H_2Ru_3(CO)_6(PH_3)_3$ model

Going from $H_2Ru_3(CO)_9$ to the less symmetrical cluster $H_2Ru_3(CO)_6(PH_3)_3$, does not change the major features of the bonding and electronic structure. EHT calculations were performed of the latter model assuming both the experimental structure of **3** and an averaged idealized geometry of C_s symmetry. Since only small insignificant differences were found between both calculations, we discuss below the results corresponding

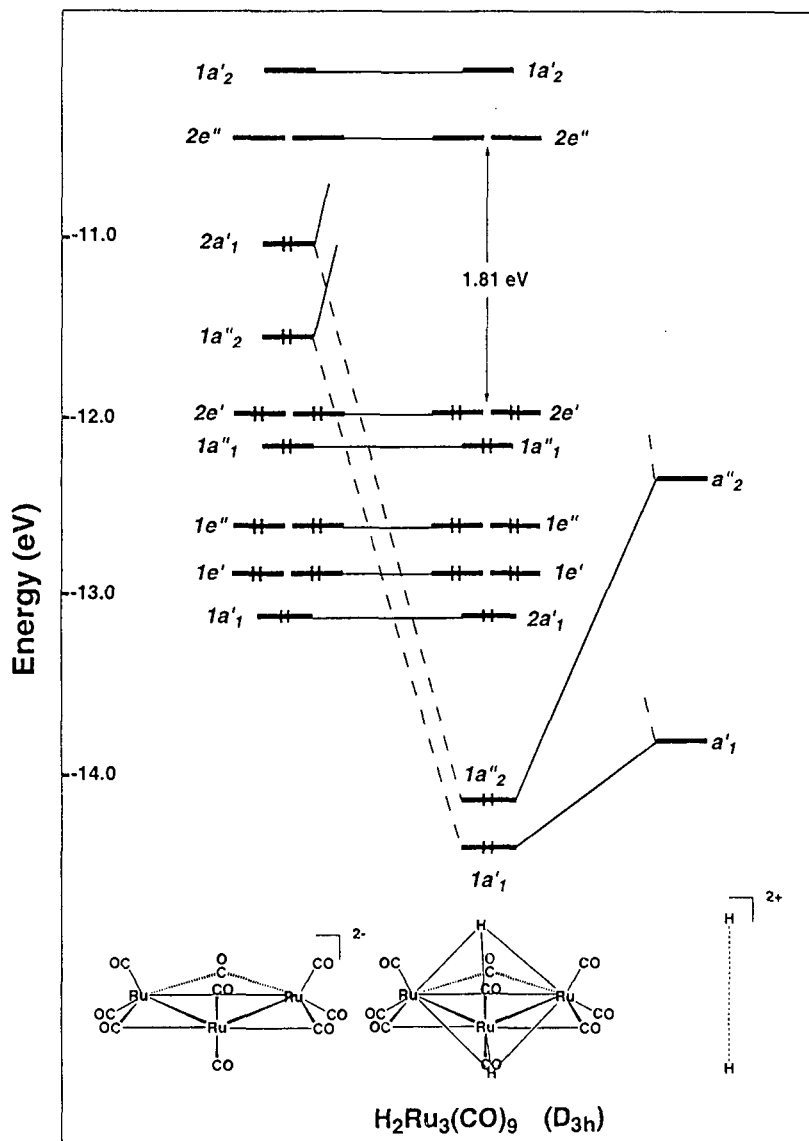


Fig. 7. Molecular orbital interaction diagram of $\text{H}_2\text{Ru}_3(\text{CO})_9$, from EHT calculations.

to the C_s geometry. The HOMO–LUMO gap (1.60 eV) is of the same order of magnitude as the one computed for $\text{H}_2\text{Ru}_3(\text{CO})_9$. The averaged Ru–Ru and Ru–H overlap populations, respectively 0.094 and 0.202 are also quite similar. DFT geometry optimization of $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PH}_3)_3$ under the constraint of C_s symmetry lead to a similar level ordering (see Fig. 8) and HOMO–LUMO gap. The corresponding bond distances are listed in Table 4 in which the atoms are labelled as in the X-ray structure of **3** (see Fig. 2). The agreement with the X-ray data of **3** is good, with the Ru–Ru distances closer to the experimental values than to that computed for $\text{H}_2\text{Ru}_3(\text{CO})_9$. The range of the Ru–H optimized distances (1.92–1.98 Å) is smaller than the corresponding experimental one found for **3** (1.61–2.04 Å). It is likely that the X-ray values are less accurate than the theoretical ones. H(1), which is close

to two phosphine ligands is less tightly bonded than H(2) which is close to only one phosphine. Although the DFT calculations do not modelize the steric hindrance of the bulky PCy_3 phosphines, these results suggests a rather symmetrical μ_3 -bonding of both hydrogen atoms in **3**.

3.5. Comparison with other electron deficient triangular clusters

From the above analysis one can describe the $44 e^-$ cluster **3** or its hypothetical relative $\text{H}_2\text{Ru}_3(\text{CO})_9$ as a symmetrically protonated trinuclear system having three σ -bonds, one delocalized π -bond and one delocalized electron-pair vacancy. The difference with the $46 e^-$ clusters **8** and $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is that the latter have no electron vacancy and present a localized double bond

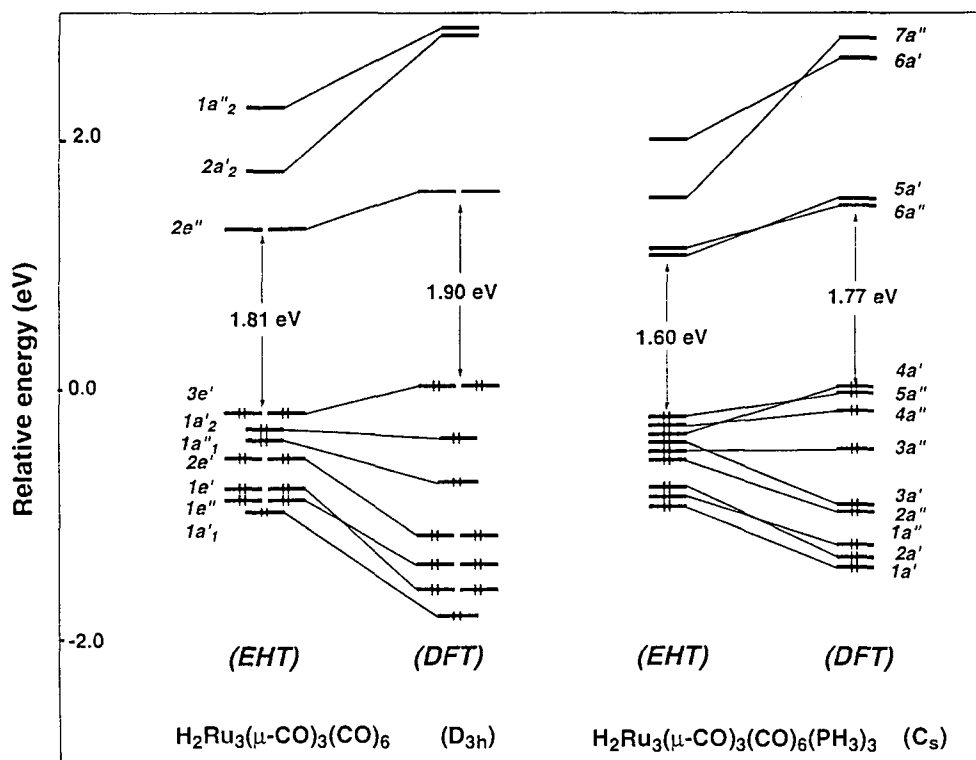


Fig. 8. EHT and DFT one-electron level ordering of $\text{H}_2\text{Ru}_3(\text{CO})_9$ (left) and $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PH})_3$ (right).

which is bridged by the protons. One may wonder why the double bond is not localized in the $44 e^-$ systems. Although the potential energy surfaces of the $\text{H}_2\text{Ru}_3(\text{CO})_6\text{L}_3$ ($\text{L}=\text{CO}, \text{PH}_3$) models were not explored fully, our calculations suggest that stability is favored by the presence of three bridging carbonyls which in turns favour π -delocalization.

As stated above, **3** is not the only $44 e^-$ triangular cluster characterized so far. Several $44 e^-$ Pd and Pt compounds are known [19–28]. Although they possess the same number of electrons, their electronic structure is different. In most of these compounds the local ligand environment is planar. Assuming a $16 e^-$ count per metal center, the existence of three M–M single bonds would correspond to $42 e^-$ for the whole cluster. Thus, the $44 e^-$ Pd₃ and Pt₃ planar or near-planar systems [19–27] are electron rich with respect to this count. Previous calculations [46,47] have shown that they bear three σ -bonding pairs (in MOs of e' and a'_1 symmetry) and one σ -antibonding pair (in a MO of a'_2 symmetry). This latter orbital is high-lying and vacant in the Ru₃ systems (see Figs. 6 and 7). Some of the above-mentioned clusters have only two metal centers lying in a planar environment [20,23,27,28]. They are better described as resulting from the assembly of two $16 e^-$ Pt centers and one $18 e^-$ Fe center, which corresponds to a localized M–M bonding with three σ -bonding pairs. Nevertheless, without any significant M–M π -bonding, none of these $44 e^-$ clusters is electronically similar to **3**.

The group VIb $44 e^-$ bicapped triangular clusters $\text{Cr}_3(\mu_3\text{-S})_2(\mu\text{-S})_3(\text{dppe})_3$, $[\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-S})_3(\mu\text{-Cl})_3\text{Cl}_6]^{3-}$ and $\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-S})_3(\text{PMe}_3)_6$ have also an electronic configuration different from that of **3** [29–32]. They have been shown to bear three σ -bonding pairs and one non-bonding δ -type combination of a'_1 or e'' symmetry

Table 4
Major DFT-optimized bond distances of $\text{H}_2\text{Ru}_3(\mu\text{-CO})_3(\text{CO})_6$ and $\text{H}_2\text{Ru}_3(\mu\text{-CO})_3(\text{CO})_3(\text{PH}_3)_3$

	$\text{H}_2\text{Ru}_3(\mu\text{-CO})_3(\text{CO})_6$ (D_{3h})	$\text{H}_2\text{Ru}_3(\mu\text{-CO})_3(\text{CO})_3(\text{PH}_3)_3$ (C_s)
Ru(1)–Ru(3)	2.760	2.736
Ru(2)–Ru(1,3)		2.733
Ru(2)–H(1)	1.960	1.917
Ru(1,3)–H(1)		1.984
Ru(2)–H(2)		1.985
Ru(1,3)–H(2)		1.931
Ru(2)–C(2,3)	2.147 (bridg.)	2.133
Ru(1,3)–C(3,2)		2.145
Ru(1,3)–C(1)		2.132
Ru(2)–C(6)	1.884 (term.)	1.856
Ru(1,3)–C(4,5)		1.862
Ru(2)–P(3)		2.269
Ru(1,3)–P(1,2)		2.278
C(1)–O(1)	1.160 (bridg.)	1.156
C(2,3)–O(2,3)		1.170
C(4,5)–O(4,5)	1.146 (term.)	1.156
C(6)–O(6)		1.157
H...H	2.281	2.281

[29,30,48]. On the other hand, the monocapped species $[\text{W}_3(\mu_3\text{-O})(\text{Oac})_6(\text{H}_2\text{O})_3]^{2+}$ has been shown to possess three σ -type W–W bonding pairs and an additional weakly bonding σ -type pair [32]. Clearly, among all the 44 e^- trinuclear systems, cluster **3** is so far unique with respect to bonding and electronic configuration.

4. Experimental

4.1. General methods

The reactions were performed under nitrogen using standard Schlenk or vacuum-line techniques. The organic solvents were refluxed over appropriate desiccants [49], distilled and saturated with nitrogen prior to use. The NMR spectra were recorded on a Varian Gemini 200 BB instrument or on a Bruker AMX 400, chemical shifts were measured relative to SiMe_4 (^1H , ^{13}C) and to 85% H_3PO_4 (^{31}P). The IR spectra were recorded with a Perkin–Elmer FT IR 1720X spectrometer (4000–400 cm^{-1}). Micro-analytical data were obtained from the Mikroelementaranalytisches Laboratorium der ETH Zürich. Mass spectra were obtained with a LCQ Finnigan instrument using the ESI method. The starting compounds $[\text{Na}][\text{HRu}_3(\text{CO})_{11}]$ [50,51] and $[\text{PPN}][\text{HOs}_3(\text{CO})_{11}]$ [52] were synthesised according to the published methods. Tricyclohexylphosphine was purchased from Aldrich and used without further purification.

4.2. Synthesis of $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ (**3**)

$\text{Ru}_3(\text{CO})_{12}$ (0.200 g, 0.31 mmol) was dissolved in 20 ml of dry THF, an excess of NaBH_4 was added. The solution was stirred at room temperature for 30 min and then filtered. The THF was evaporated and the remaining $[\text{Na}][\text{HRu}_3(\text{CO})_{11}]$ was dissolved in 30 ml of MeOH. After addition of tricyclohexylphosphine (0.33 g, 1.2 mmol), the solution was heated to reflux (110°C bath temperature) in a Schlenk tube connected to a reflux condenser for 1 h. The product **3** precipitated directly from the reaction solution during the reaction as a purple powder. The solution was filtered hot, and the solid product was recrystallised from dichloromethane–methanol to give dark red, block-shaped crystals which are slightly air-sensitive (0.30 g, 73%).

IR(CH_2Cl_2): $\nu(\text{CO})$ 2027vw, 1949m, 1917vs, 1871w, 1855w, 1819vs, 1757w cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.27–2.30 (99H, m, C_6H_{11}), –19.46 [1H, dtd, $J(\text{H1-P3}) = 28.3$ Hz, $J(\text{H1-P1,P2}) = 5.3$ Hz, $J(\text{H1-H2}) = 2.2$ Hz, $\mu^3\text{-H1}$], –21.02 [1H, tdd, $J(\text{H2-P1,P2}) = 26.4$ Hz, $J(\text{H2-P3}) = 5.4$ Hz, $J(\text{H1-H2}) = 2.1$ Hz, $\mu^3\text{-H2}$], $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3): δ 74.8 (s, 1P), 71.3 (s, 2P) no coupling observed; FAB-MS: m/z 1316 (based on

^{102}Ru); Found: C 53.63, H 7.45; Calc. for $\text{C}_{60}\text{H}_{101}\text{O}_6\text{P}_3\text{Ru}_3 \cdot 2 \text{H}_2\text{O}$: C 53.36, H 7.84.

4.3. Synthesis of $\text{Ru}_3(\text{CO})_9(\text{PCy}_3)_3$ (**5**)

$\text{Ru}_3(\text{CO})_{12}$ (0.150 g, 0.23 mmol) was dissolved in 20 ml of dry THF, an excess of NaBH_4 was added. The solution was stirred at room temperature for 30 min, then filtered and transferred into a pressure Schlenk tube. The THF was evaporated, the remaining $[\text{Na}][\text{HRu}_3(\text{CO})_{11}]$ was dissolved in 30 ml of MeOH. After addition of tricyclohexylphosphine (0.33 g, 1.2 mmol), the solution was heated for 1 h in the closed vessel (80°C bath temperature). The product **5** precipitated directly from the reaction solution during the reaction as a purple powder which was filtered off hot and recrystallised from dichloromethane–methanol to give dark red, air-stable, cube-like crystals which contain two water molecules (from methanol) (0.18 g, 55%).

IR(CH_2Cl_2): $\nu(\text{CO})$ 1959vs, 1949vs cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.29–2.04 (m, C_6H_{11}); $^{31}\text{P-NMR}$ (CDCl_3): δ 47.3 (s, PCy_3); FAB-MS: m/z 1398 (related to ^{102}Ru); Found: C 52.64, H 7.00; Calc. for $\text{C}_{63}\text{H}_{99}\text{O}_9\text{P}_3\text{Ru}_3 \cdot 2 \text{H}_2\text{O}$: C 52.82, H 7.25.

4.4. Synthesis of $\text{H}_2\text{Os}_3(\text{CO})_7(\text{PCy}_3)_3$ (**8**)

$[\text{PPN}][\text{HOs}_3(\text{CO})_{11}]$ (0.20 g, 0.14 mmol) was dissolved in 50 ml of MeOH. After addition of tricyclohexylphosphine (0.19 g, 0.7 mmol) the solution was heated for 3 h to reflux in a Schlenk tube equipped with a reflux condenser (110°C bath temperature). The product **8** precipitated directly from the reaction solution during the reaction as a green–yellow powder which was filtered off and recrystallised from dichloromethane–methanol to give green, air-stable crystals (0.17 g, 75%).

IR(CH_2Cl_2): $\nu(\text{CO})$ 2001w, 1969vs, 1942w, 1923s, 1907m cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.27–2.09 (99H, m, C_6H_{11}), –8.64 [1H, t, $J(\text{H-P}) = 5.5$ Hz, $\mu^2\text{-H2}$], –12.87 [1H, dd, $J(\text{H-P}) = 38$ Hz, $J(\text{H-P}) = 8$ Hz, $\mu^2\text{-H1}$], $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3): δ 37.5 (s, 1P), 21.8 (s, 1P), 14.2 (s, 1P), no coupling observed; FAB-MS: m/z 1610 (based on ^{190}Os); Found: C 43.79, H 5.98; Calc. for $\text{C}_{61}\text{H}_{101}\text{O}_7\text{Os}_3\text{P}_3\text{CH}_2\text{Cl}_2$: C 43.93, H 6.12.

4.5. Reaction of $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ (**3**) with CO

The complex $\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3$ (0.100 g, 76.2 μmol) was dissolved in 20 ml of CH_2Cl_2 in a pressure Schlenk tube, which was pressurised with 1.5 bar of carbon monoxide. The solution was stirred at room temperature until the colour of the solution became red. Then the solution was evaporated to dryness. The residue contained **4**.

IR(CH₂Cl₂): 2071w, 2026w, 1997s cm⁻¹; ¹H-NMR (C₆D₆): δ 1.27–2.22 (99H, m, C₆H₁₁), -10.89 [1H, d, *J*(H–P) = 10 Hz], -17.94 [1H, dd, *J*(H–P) = 20.2 Hz, *J*(H–P) = 7.6 Hz]; ³¹P-NMR (C₆D₆): δ 64.7 (m, 1P), 32.9 (m, 1P), 11.4 (m, 1P), no coupling observed; FAB-MS: *m/z* 1372 (based on ¹⁰²Ru).

4.6. Reaction of Ru₃(CO)₉(PCy₃)₃ (**5**) with H₂

The complex Ru₃(CO)₉(PCy₃)₃ (0.100 g, 71.7 μmol) was dissolved in 20 ml of CH₂Cl₂ in a closed pressure Schlenk tube, which was pressurised with 1.5 bar of hydrogen. The solution was stirred at room temperature until the colour of the solution became red. Then the solution was evaporated to dryness. The residue contained **4**.

IR(CH₂Cl₂): 2071w, 2026w, 1997s cm⁻¹; ¹H-NMR (C₆D₆): δ 1.27–2.22 (99H, m, C₆H₁₁), -10.89 [1H, d, *J*(H–P) = 10 Hz], -17.94 [1H, dd, *J*(H–P) = 20.2 Hz, *J*(H–P) = 7.6 Hz]; ³¹P-NMR (C₆D₆): δ 64.7 (m, 1P), 32.9 (m, 1P), 11.4 (m, 1P), no coupling observed; FAB-MS: *m/z* 1372 (based on ¹⁰²Ru).

4.7. Crystal structure of H₂Ru₃(CO)₆(PCy₃)₃ (**3**)

Intensity data for an orange crystal of **3** were collected using a Stoe imaging plate diffractometer system (Stoe and Cie, 1995) equipped with a one-circle goniometer and a graphite-monochromator. Data collection was performed using Mo–K_α radiation (λ = 0.71073 Å). 200 exposures (3 min per exposure) were obtained at 70 mm with 0 < φ < 200° and with the crystal oscillated through 1° in φ. The structure was solved by direct methods using the program SHELXS-97 [53] and refined by full matrix least squares on *F*² with SHELXL-97 [54]. The positions of the two hydrides were derived from Fourier difference maps and refined while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. Crystallographic details are given in Table 4 and significant bond lengths and bond angles are listed in Table 1. The figure was drawn with SCHAKAL [55].

4.8. Crystal structure of Ru₃(CO)₉(PCy₃)₃ (**5**)

Suitable crystals of **5** were obtained as indicated in the synthetic section. Intensity data were collected on a Stoe–Siemens AED2 4-circle diffractometer at -50°C (Mo–K_α graphite monochromated radiation, λ = 0.71073 Å; ω/2θ scans). Table 1 summarises the crystallographic and selected experimental data for **5**. The structure was solved by direct methods using the program SHELXS-86 [56]. The refinement, using weighted full-matrix least-square on *F*², was carried out using the program SHELXL-93 [57]. No absorption correction was

applied. The hydrogen atoms of the cyclohexylphosphine ligands were included in calculated positions and treated as riding atoms using the SHELXL 93 default parameters. One disordered molecule of methanol and five molecules of water were found per asymmetric unit. Crystallographic details are given in Table 4 and significant bond lengths and bond angles are listed in Table 2. The figure was drawn with SCHAKAL 92 [55]. Full tables of atomic parameters and bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.

4.9. Crystal structure of H₂Os₃(CO)₇(PCy₃)₃ (**8**)

A green crystal of compound **8** was mounted on a Stoe–Siemens AED2 four-circle diffractometer. Intensity data were measured using graphite-monochromator Mo–K_α radiation (λ = 0.71073 Å). The ω/2θ scan technique was used to a maximum 2θ value of 50.0°. The cell parameters were determined from a least square treatment of the setting angles of 24 reflections with 12.2° < θ < 17.2°. The intensities of two representative reflections were measured every 60 min. During data collection the intensity of the standards decreased by less than 2%. A semi-empirical absorption correction was applied using psi-scans (*T*_{min} = 0.22, *T*_{max} = 0.35). The structure was solved by direct methods using the program SHELXS-97 [53] and refined by full matrix least squares on *F*² with SHELXL-97 [54]. The positions of the two hydrides both bridging Os2 and Os3 were derived from the Fourier difference maps and refined freely while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. One disordered molecule of methanol was found per asymmetric unit and refined isotropically. Crystallographic details are given in Table 4 and significant bond lengths and bond angles are listed in Table 3. The figure was drawn with SCHAKAL [55] (Table 5).

4.10. Computational details

EHT calculations have been carried out within the extended Hückel formalism [58] assuming the weighted *H*_{*ij*} formula [59] with the CACAO package [60]. The exponents (ξ) and the valence shell ionization potentials (*H*_{*ij*} in eV) were (respectively): 1.3, -13.6 for H 1s; 1.625, -21.4 for C 2s; 1.625, -11.4 for C 2p; 2.275, -32.3 for O 2s; 2.275, -14.8 for O 2p; 1.6, -18.6 for P 3s; 1.6, -14.0 for P 3p; 2.078, -8.6 for Ru 5s, 2.043, -5.1 for Ru 5p. *H*_{*ij*} value for Ru 4d was set equal to -12.2. A linear combination of two Slater-type orbitals of exponents ξ₁ = 5.378 and ξ₂ = 2.303 with the weighting coefficients *C*₁ = 0.5340 and *C*₂ = 0.6365 was used to represent the Ru 4d atomic

Table 5
Crystal data and data collection parameters for 3, 5 and 8

Compound	3	5	8
Formula	C ₆₀ H ₁₀₁ O ₆ P ₃ Ru ₃ 2H ₂ O	C ₆₃ H ₉₉ O ₉ P ₃ Ru ₃ 2H ₂ O	C ₆₁ H ₁₀₁ O ₇ Os ₃ P ₃ CH ₃ OH
<i>M</i>	1314.53	1474.52	1641.97
Crystal size (mm)	0.50 × 0.25 × 0.10	0.61 × 0.46 × 0.34	0.30 × 0.30 × 0.19
Temperature (K)	223(2)	223(2)	293(2)
Crystal system	Monoclinic	Cubic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>a</i> $\bar{3}$	<i>P</i> $\bar{1}$
Colour	Orange	Red	Green
<i>a</i> (Å)	10.561(1)	24.1347(12)	11.227(4)
<i>b</i> (Å)	36.649(2)	24.1347(12)	14.646(6)
<i>c</i> (Å)	15.957(1)	24.1347(12)	20.496(9)
α (°)	90	90	95.81(4)
β (°)	96.32(1)	90	93.26(3)
γ (°)	90	90	101.84(3)
Volume (Å ³)	6138.4(8)	14 058(12)	3 271(2)
<i>Z</i>	4	8	2
<i>D</i> _c (g/cm ³)	1.422	1.435	1.667
μ (mm ⁻¹)	0.854	0.765	5.935
<i>F</i> (000)	2 744	6 352	1 628
θ limits (°)	2.0.2 to 25.97	2.07 to 25.02	2.00 to 25.50
Reflections measured	38 984	4 157	12 165
Independent reflections	11 651	4 157	12 165
Observed reflections	6 231	3 224	9 953
Goodness-on-fit on <i>F</i> ²	0.801	1.186	1.135
<i>R</i> ₁ [<i>I</i> = 2 σ (<i>I</i>)]/ <i>R</i> ₁ (all data)	0.0487/0.1038	0.0579/0.0862	0.0434/0.0620
<i>wR</i> ₂ [<i>I</i> = 2 σ (<i>I</i>)]/ <i>wR</i> ₂ (all data)	0.0901/0.1028	0.1225/0.1727	0.0739/0.0825
residual e ⁻ -density min/max (e/Å ³)	-0.781/1.276	-0.648/1.336	-0.885/1.065

orbitals. The following bond distances (Å) were used in the H₂Ru₃(CO)₉ (*D*_{3h}) and H₂Ru₃(CO)₆(PH₃)₃ (*C*_s) models: Ru–Ru = 2.694, Ru– μ -CO = 2.138, Ru–CO = 1.840, C–O = 1.150, Ru–P = 2.337, P–H = 1.420 Å and Ru–H = 1.876 Å.

DFT calculations [61–64] were carried out on the H₂Ru₃(CO)₉ and H₂Ru₃(CO)₆(PH₃)₃ models using the ADF program developed in the group of Baerends [65]. Electron correlation was treated within the local density approximation (LDA) [66]. Test calculations with non local density approximation (NLDA) [67,68] were carried out on H₂Ru₃(CO)₉ assuming *D*_{3h} symmetry. Since they led to very similar results, the LDA level was considered for all the calculated models. The numerical integration procedure applied for the calculations was developed by te Velde et al. [63]. The standard ADF STO basis set IV, of triple- ξ quality for the valence orbitals was used for all the atoms. The frozen-core approximation was considered [61].

5. Conclusions

It is interesting to note that the analogous cluster anions [HRu₃(CO)₁₁]⁻ (**1**) and [HOs₃(CO)₁₁]⁻ (**6**) react both with tricyclohexylphosphine in methanol solution to give the trisubstituted, electron-deficient, neutral

clusters H₂Ru₃(CO)₆(PCy₃)₃ (**3**) and H₂Os₃(CO)₇(PCy₃)₃ (**8**), respectively. However, the ruthenium cluster **3** is a 44 e⁻ system, while the osmium cluster **8** is a 46 e⁻ system.

Acknowledgements

We thank the Fond National Suisse de la Recherche Scientifique for financial support of this work. Computing facilities were kindly provided by the IDRIS-CNRS computing center of Orsay (France). J.-Y.S. and M.T.G. are grateful to CNRS and to CONICYT for a cooperative French/Chilean travel grant. A generous loan of ruthenium trichloride hydrate by the Johnson Matthey Technology Centre (to G.S.-F.) is gratefully acknowledged.

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