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Saturated and unsaturated triruthenium clusters containing three sterically demanding phosphine ligands: synthesis and structure of $[Ru_3(CO)_9(PCy_3)_3]$ and $[Ru_3H_2(CO)_6(PCy_3)_3]$

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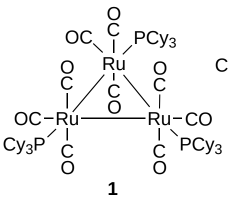
The reaction of $Na[Ru_3H(CO)_{11}]$ with an excess of tricyclohexylphosphine in methanol afforded, depending on the reaction conditions, the tri-substituted clusters $[Ru_3(CO)_9(PCy_3)_3]$ (48e) and $[Ru_3H_2(CO)_6(PCy_3)_3]$ (44e), inaccessible hitherto.

Ligand substitution reactions of dodecacarbonyltriruthenium with tertiary phosphines have been studied in great detail.[1] The thermal reaction of $Ru_3(CO)_{12}$ with PR_3 (R = Ph, Et, Bu^n, OPh) in general leads to the mono-, di- and tri-substituted derivatives $[Ru_3(CO)_{11}(PR_3)]$, $[Ru_3(CO)_{10}(PR_3)_2]$ and $[Ru_3(CO)_9(PR_3)_3]$.[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 substitution[5] 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 $[Ru_3(CO)_{12}]$ in the presence of $Na[Ph_2CO]$ gave only the mono- and the di-substituted complexes, but no $[Ru_3(CO)_9(PCy_3)_3]$.[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 $[Ru_3H_2(CO)_5(PBu^t_2)_2(Ph_2PCH_2PPh_2)]$ 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 $[Ru_3H(CO)_9(NSOMePh)]$,[7] and (very recently) $[Ru_3H_2(CO)_{10}]$ as well as its phosphine derivative $[Ru_3H_2(CO)_9(PPh_3)]$;[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 $[Ru_3(CO)_9(PCy_3)_3]$ **1** and the highly electron-deficient (44e) triruthenium cluster $[Ru_3H_2(CO)_6(PCy_3)_3]$ **2**, both accessible from $Na[Ru_3H(CO)_{11}]$ and PCy_3.



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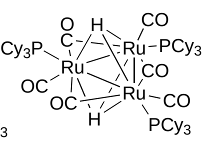

2

The reaction of $Na[Ru_3H(CO)_{11}]$, easily accessible from $[Ru_3(CO)_{12}]$ and $Na[BH_4]$,[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 $[Ru_3(CO)_9(PCy_3)_3]$ **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 $Ru–CO_{(eq)}$ distances of 1.876(7) Å are distinctly shorter than the $Ru–CO_{(ax)}$ distances [1.924(7) and 1.931(7) Å]. This is in keeping with the findings in the known cluster $[Ru_3(CO)_9(PMe_3)_3]$,[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 $[Ru_3(CO)_9(PMe_3)_3]$ [2.860(1), 2.862(1), 2.854(1) Å][10] and in $[Ru_3(CO)_{12}]$ [2.852(1), 2.851(1),

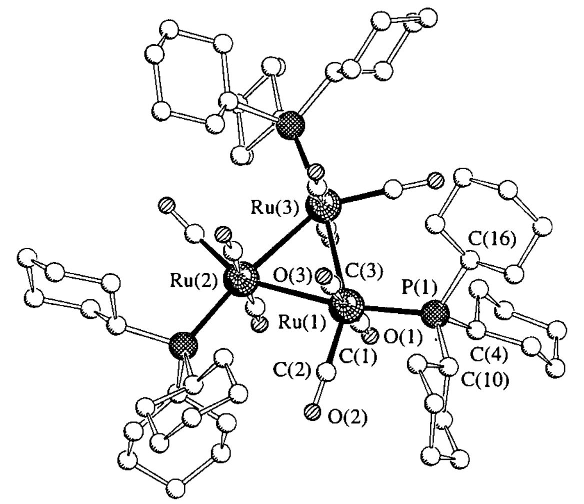

Fig. 1 Molecular structure of $[Ru_3(CO)_9(PCy_3)_3]$ **1** showing the atom numbering scheme; H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.9396(8), Ru(1)–Ru(3) 2.9396(8), Ru(2)–Ru(3) 2.9396(8), Ru(1)–P(1) 2.414(2), Ru(1)–C(2) 1.876(7), Ru(1)–C(1) 1.924(7), 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)

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† Spectroscopic data for cluster **1**. IR(CH_2Cl_2): ν(CO) 1959vs, 1949vs 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 $C_{63}H_{99}O_9P_3Ru_3\cdot 2H_2O$: C, 52.82; H, 7.25%).

‡ Crystal data for cluster **1**. $C_{63}H_{99}O_9P_3Ru_3\cdot 2H_2O$, *M* 1474.52, cubic space group $Pa\bar{3}$, $a = 24.1347(12)$ Å, $U = 14\,058.1(12)$ Å^3, $T = 223(2)$ K, $Z = 8$, μ(Mo-Kα) = 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.

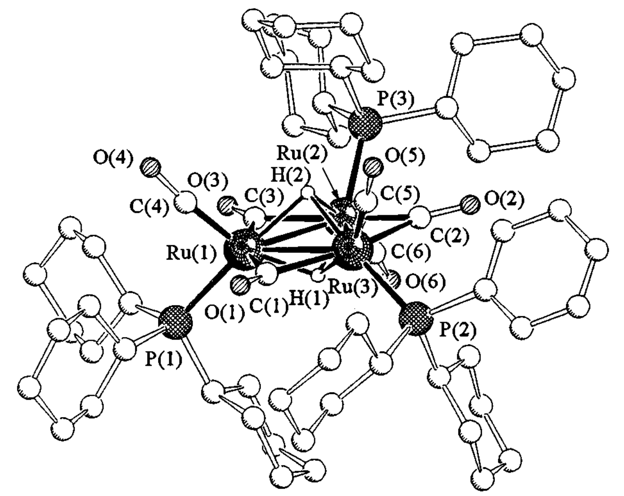

Fig. 2 Molecular structure of $[Ru_3H_2(CO)_6(PCy_3)_3]$ **2** showing the atom numbering scheme; H atoms on carbon have been omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2) 2.6702(6), Ru(1)–Ru(3) 2.7180(7), Ru(2)–Ru(3) 2.6931(7), Ru(1)–P(1) 2.332(2), Ru(2)–P(3) 2.336(2), Ru(3)–P(2) 2.344(2), 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 $Na[Ru_3H(CO)_{11}]$ 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 $[Ru_3H_2(CO)_6(PCy_3)_3]$ **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 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: $[Pd_3(SO_2)_2(Bu^tNC)_5]$,[12] $[Pt_3(CO)_3(PCy_3)_3]$[13] and $[FePt_2(CO)_5\{P(OPh)_3\}_3]$.[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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§ Spectroscopic data for cluster **2**. IR(CH_2Cl_2): ν(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 (H^2–P^3) = 28.3, J(H^2–P^1,P^2) = 5.3, J(H^1–H^2) = 2.2, μ_3-H^2], −21.02 [1 H, tdd, J(H^1–P^1,P^2) = 26.4, J(H^1–P^3) = 5.4, J(H^1–H^2) = 2.1 Hz, μ_3-H^1]; ^{31}P-{^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 ^{101}Ru) (Found: C, 53.63; H, 7.45. Calc. for $C_{60}H_{101}O_6P_3Ru_3{\cdot}2H_2O$: C, 53.36; H, 7.84%).

¶ Crystal data for cluster **2**. $C_{60}H_{101}O_6P_3Ru_3{\cdot}2H_2O$, M 1314.53, monoclinic, space group $P2_1/n$, $a = 10.561(1)$, $b = 36.649(2)$, $c = 15.957(1)$ Å, $\beta = 96.32(1)°$, $U = 6138.4(8)$ Å^3, $T = 223(2)$ K, $Z = 4$, μ(Mo-Kα) = 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.