

Preliminary communication

THE CRYSTAL STRUCTURE OF $[\text{Rh}_3(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_3]$ AND REACTIONS OF THE UNSATURATED METAL CLUSTERS $[\text{MM}'_2(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_3]$ ($\text{M} = \text{M}' = \text{Rh}$; $\text{M} = \text{Co}$ or Ir , $\text{M}' = \text{Rh}$) WITH HYDROGEN*

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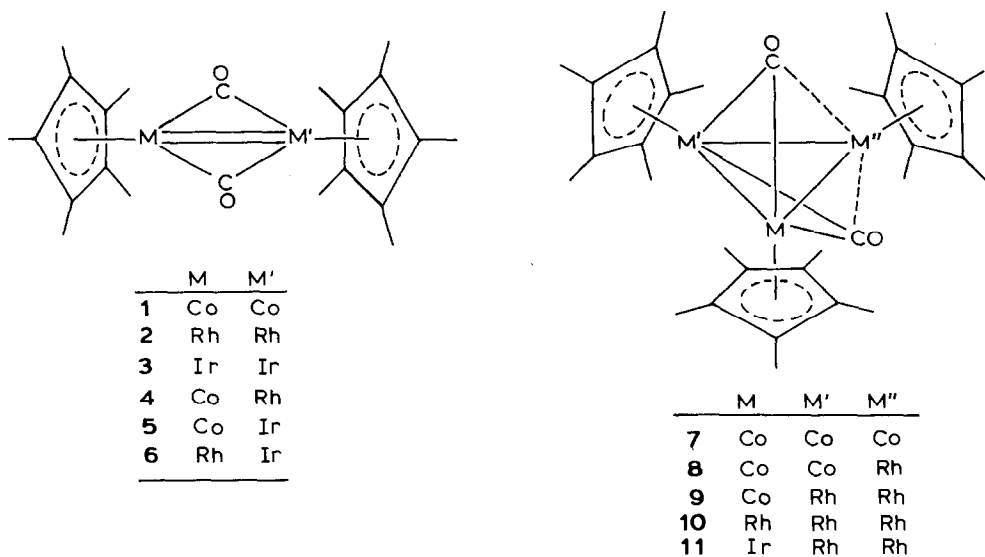
Summary

An X-ray crystallographic study of the complex $[\text{Rh}_3(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_3]$ has revealed that the CO ligands asymmetrically bridge the Rh_3 triangle in accord with theoretical predictions. Treatment of the trirhodium compound, or the related mixed-metal complexes $[\text{MRh}_2(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_3]$ ($\text{M} = \text{Co}$ or Ir), with hydrogen gas gives the species $[\text{MRh}_2(\mu\text{-H})_2(\mu\text{-CO})(\mu_3\text{-CO})(\eta\text{-C}_5\text{Me}_5)_3]$; the molecular structure of the dihydridotrirhodium cluster has been established by X-ray diffraction.

The unsaturated dimetal compounds 1–5 [1] are known to undergo a variety of interesting reactions, notably in combination with metal-ligand fragments to afford metal clusters [1d,1e,2,3]. Herein we report the synthesis of complex 6, thus completing this family of dimetal compounds. We also describe studies on the trimetal species 7–11.

A mixture of equimolar amounts of $[\text{Rh}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ and $[\text{Ir}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ in refluxing toluene (1 h) affords red purple crystals of 6 (60%) [4]. We have previously shown [1d] that 2 reacts with the mononuclear metal compounds $[\text{M}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ ($\text{M} = \text{Co}$ or Rh) to give the trimetal clusters 9 and 10, respectively. Extension of this procedure to reactions between $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ and 1 or 4, and between $[\text{Rh}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ and 6, affords the complexes 7, 8 and 11 [5].

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Consideration of the bonding in the hypothetical molecule $[\text{Rh}_3(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{H}_5)_3]$ in terms of a combination of frontier orbitals of the fragments $\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Rh}(\eta\text{-C}_5\text{H}_5)$ has led to the conclusion that the CO ligands would asymmetrically bridge the Rh_3 triangle in the tricyclopentadienyltrirhodium compound [6]. We were able to test this prediction by an X-ray crystallographic study of the pentamethylcyclopentadienyl compound 10. The structure is shown in Fig. 1 [7]. The results show that the two CO ligands adopt bonding modes intermediate between μ_2 and μ_3 , with C(1a)

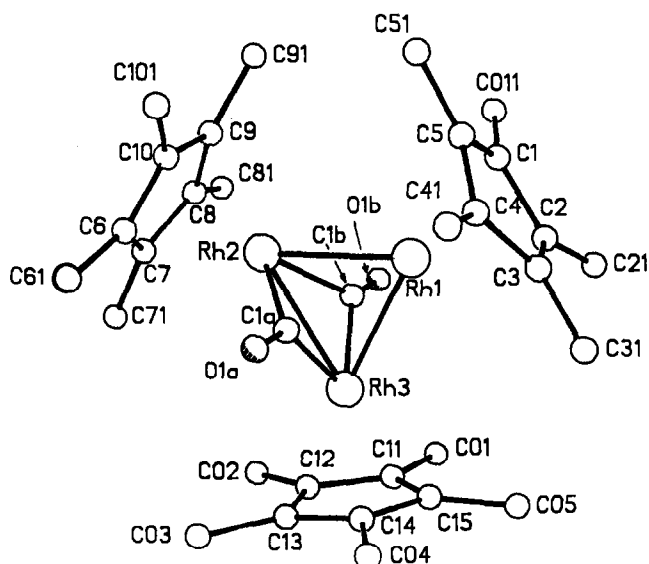


Fig. 1. The molecular structure of $[\text{Rh}_3(\mu_3\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_3]$ (10). Rh(1)—Rh(2) 2.572(2), Rh(1)—Rh(3) 2.553(2), Rh(2)—Rh(3) 2.639(2), Rh(1)—C(1a) 2.32(2), Rh(2)—C(1a) 1.97(2), Rh(3)—C(1a) 1.99(2), Rh(1)—C(1b) 2.37(2), Rh(2)—C(1b) 2.02(2), Rh(3)—C(1b) 1.96(2) Å.

and C(1b) essentially equidistant from Rh(2) and Rh(3) and significantly further from Rh(1) [8]. The uniqueness of Rh(1) is also reflected in the metal-metal separations with Rh(2)–Rh(3) (2.639(2) Å) being longer than Rh(1)–Rh(2) or Rh(1)–Rh(3) ((mean) 2.563(2) Å). Moreover, the Rh(1)–C₅Me₅ separations are slightly shorter (mean 2.17(2) Å) than those between Rh(2) or Rh(3) and their respective C₅Me₅ groups (mean 2.26(2) Å).

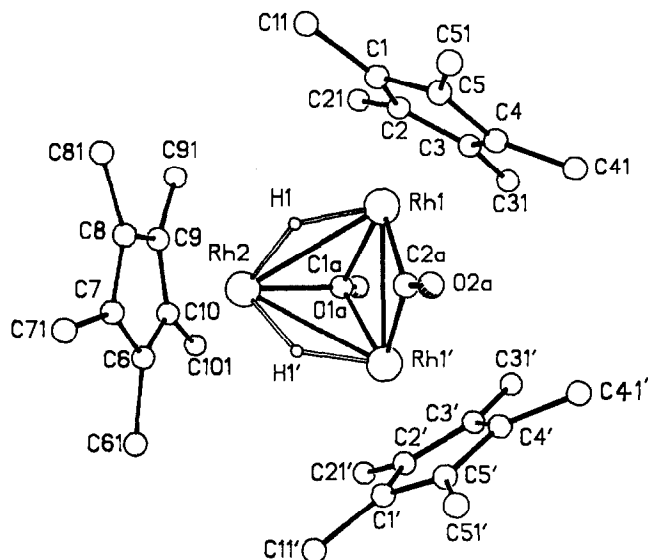
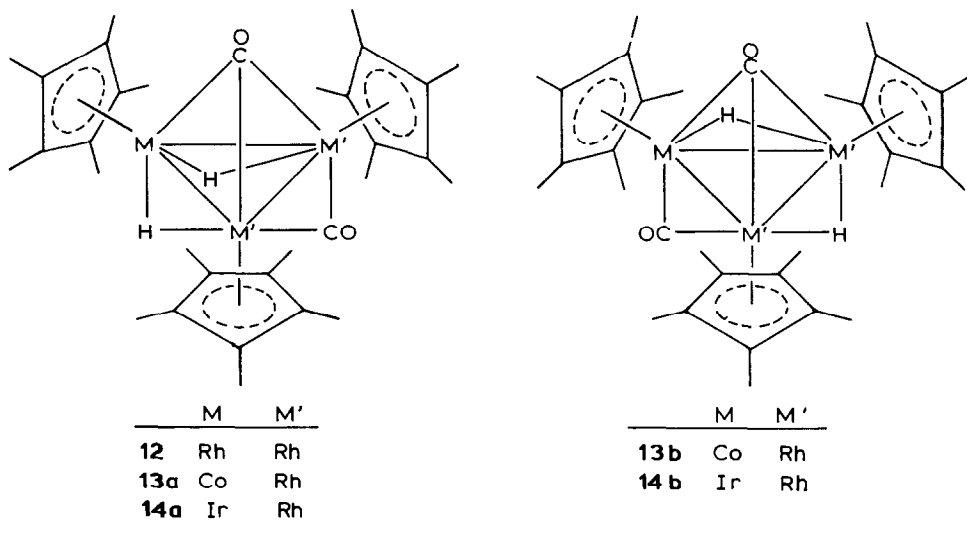


Fig. 2. The molecular structure of $[\text{Rh}_3(\mu\text{-H})_2(\mu\text{-CO})(\mu_3\text{-CO})(\eta\text{-C}_5\text{Me}_5)_3]$ (**12**). Atoms labelled with a prime are related to those not so marked by a crystallographic mirror plane which bisects the positionally disordered C₅Me₅ ring bonded to Rh(2) (only one such ring is shown). Rh(1)–Rh(2) 2.785(1), Rh(1)–Rh(1') 2.674(1), Rh(1)–C(1a) 2.13(1), Rh(2)–C(1a) 1.99(1), Rh(1)–C(2a) 1.98(1) Å; Rh(1)–C(2a)–O(2a) 137.5(1)°.

Compound **10** in thf reacts readily with hydrogen gas (25°C, 1 atm) to give the dihydridotrirhodium complex **12** [9], the molecular structure [7] of which was established by an X-ray diffraction study (Fig. 2). The three rhodium atoms form an isosceles triangle, and whilst one CO ligand remains essentially triply bridging, the other CO group has been displaced to an edge-bridging site so as to accommodate the two hydrido ligands, which were located on the long Rh–Rh vectors by a low-angle electron density difference map.

The reaction between hydrogen and the heteronuclear clusters **9** and **11** afforded the isomeric species **13** and **14**, respectively. On warming solutions of these compounds, hydrogen is released and compounds **9** and **11** are regenerated. On the basis of relative peak intensities in the ¹H NMR spectra [9], it was observed that **13a** and **13b** were formed in the ratio ca. 15/85, and **14a** and **14b** in the ratio ca. 45/55. On the present evidence it is not possible to say whether these are the kinetically or thermodynamically controlled product ratios.

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References and notes

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- L.M. Cirjak, J.-S. Huang, Z.-H. Zhu, and L.F. Dahl, *J. Am. Chem. Soc.*, **102** (1980) 6626.
- Selected spectroscopic data for **6**: $\nu_{\max}(\text{CO})$ at 1713 cm^{-1} (PhMe). NMR: ^1H (in C_6D_6 for all complexes reported), δ 1.46 (d, 15 H, RhC_5Me_5 , $J(\text{RhH})$ 0.5 Hz), and 1.65 (s, 15 H, IrC_5Me_5); ^{13}C - $\{^1\text{H}\}$ (in C_6D_6 for all complexes reported), δ 239.8 (d, CO, $J(\text{RhC})$ 48 Hz), 96.6 (IrC_5Me_5), 100.6 (d, RhC_5Me_5 , $J(\text{RhC})$ 7 Hz), 9.1 (C_5Me_5), and 8.5 ppm (C_5Me_5).
- Selected spectroscopic data: Compound **7**, $\nu_{\max}(\text{CO})$ 1675 cm^{-1} (thf). NMR: ^1H , δ 3.38 (s, 45 H, C_5Me_5); Compound **8**, $\nu_{\max}(\text{CO})$ 1677 cm^{-1} (thf). NMR: ^1H , δ 0.98 (s, 15 H, RhC_5Me_5), and 1.95 (s, 30 H, CoC_5Me_5); ^{13}C - $\{^1\text{H}\}$, δ 94.6 (d, RhC_5Me_5 , $J(\text{RhC})$ 6 Hz), 94.3 (CoC_5Me_5), 11.1 (RhC_5Me_5), and 9.8 ppm (CoC_5Me_5); Compound **11**, $\nu_{\max}(\text{CO})$ 1661 cm^{-1} (PhMe). NMR: ^1H , δ 1.63 (d, 30 H, RhC_5Me_5 , $J(\text{RhH})$ 0.5 Hz), and 2.08 (s, 15 H, IrC_5Me_5); ^{13}C - $\{^1\text{H}\}$, δ 94.9 (d, RhC_5Me_5 , $J(\text{RhC})$ 6 Hz), 94.4 (IrC_5Me_5), 10.4 (RhC_5Me_5), and 9.5 ppm (IrC_5Me_5).
- A.R. Pinhas, T.A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, **63** (1980) 29.
- For **10**, crystal data. $\text{C}_{32}\text{H}_{48}\text{O}_3\text{Rh}_3$, $M = 770.4$, orthorhombic, space group *Pbca* (no. 61), a 17.85(4), b 21.85(1) Å, c 15.45(1), U 6028 Å³, $Z = 8$, D_x 1.70 g cm^{-3} , $F(001) = 3104$, Mo- K_α (graphite monochromator) λ 0.71069 Å, $\mu(\text{Mo}-K_\alpha)$ 16.2 cm^{-1} . Current $R = 0.05$ ($R_w = 0.05$) for 2067 absorption-corrected intensities (293 K, ω scans, $2\theta \leq 50^\circ$, $F \geq 4\sigma(F)$), Nicolet P3m diffractometer. For **12**, $\text{C}_{32}\text{H}_{47}\text{O}_3\text{Rh}_3$, $M = 772.5$, orthorhombic, space group *Pnam* (no. 62 non-standard setting), a 12.029(3), b 13.403(3), c 19.031(5) Å, U 3068(1) Å³, $Z = 4$, D_x 1.68 g cm^{-3} , $F(000) = 1560$, $\mu(\text{Mo}-K_\alpha)$ 15.96 cm^{-1} . Current $R = 0.043$ ($R_w = 0.047$) for 3221 absorption corrected intensities, 200 K, $2\theta \leq 60^\circ$, $F \geq 5\sigma(F)$.
The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.
- Using the terminology of ref. 6, the dihedral angles (θ) between the Rh(1)Rh(2)Rh(3) plane and the two Rh(2)Rh(3)C(1) planes in **10** are 75.6 and 77.5°, respectively, compared with θ 90° for an unsymmetrical trimer and θ 60° for a symmetrical trimer. Calculations [6] suggest θ 65° for a structure

of optimum minimal energy, with transformation between this geometry and that with θ 60° requiring an energy change of 10 kJ mol^{-1} . It is not surprising, therefore, that variable temperature $^{13}\text{C}\{-^1\text{H}\}$ NMR studies [1d] reveal that **10** adopts the symmetrical structure even at -80°C .

- 9 Selected spectroscopic data: Compound **12**, $\nu_{\text{max}}(\text{CO})$ 1762 and 1634 cm^{-1} (thf). NMR: ^1H , δ -21.60 (d of d, 2 H, $\mu\text{-H}$, $J(\text{RhC})$ 28 and 20 Hz), 1.73 (s, 30 H, C_5Me_5), and 1.83 (s, 15 H, C_5Me_5); $^{13}\text{C}\{-^1\text{H}\}$, δ 245.2 (d of t, $\mu_3\text{-CO}$, $J(\text{RhC})$ 39 and 26 Hz), 237.5 (t, $\mu\text{-CO}$, $J(\text{RhC})$ 41 Hz), 101.7 (C_5Me_5), 98.5 (d, C_5Me_5 , $J(\text{RhC})$ 6 Hz), 11.1 (C_5Me_5), and 9.6 ppm (C_5Me_5). Compound **13a**, NMR: ^1H , δ -25.54 (d, 2 H, $J(\text{RhH})$ 32 Hz), 1.69 (s, 30 H, C_5Me_5), and 1.80 (s, 15 H, C_5Me_5). Compound **13b**, NMR: ^1H , δ -26.33 (d, 1 H, $\mu\text{-HCoRh}$, $J(\text{RhH})$ 20.8 Hz), -22.90 (d of d, 1 H, $\mu\text{-HRh}_2$, $J(\text{RhH})$ 31 and 21 Hz), 1.60 (s, 15 H, C_5Me_5), 1.71 (s, 15 H, C_5Me_5), and 1.80 (s, 15 H, C_5Me_5). Compound **14a**, NMR: ^1H , δ -21.67 (d, 2 H, $\mu\text{-HirRh}$, $J(\text{RhH})$ 27 Hz), 1.88 (br, 15 H, C_5Me_5), and 1.76 (s, 30 H, C_5Me_5); Compound **14b**, NMR: ^1H , δ -22.4 (d, 1 H, $\mu\text{-HirRh}$, $J(\text{RhH})$ 21 Hz), -21.21 (d of d, 1 H, $\mu\text{-HRh}_2$, $J(\text{RhH})$ 32 and 21 Hz), 1.88 (br, 15 H, C_5Me_5), 1.78 (s, 15 H, C_5Me_5), and 1.77 (s, 15 H, C_5Me_5).

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