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Heteronuclear Unsaturated Di- and Tri-nuclear Metal Complexes; Crystal Structures of $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$

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The reaction between $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Co(C_2H_4)_2(\eta\text{-}C_5Me_5)]$ affords $[CoRh(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, structurally characterised and compared with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ by *X*-ray crystallography; the cobalt–rhodium species gives $[CoRh(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ on treatment with diazomethane, and reacts with low valent metal complexes to give various tri- and tetra-nuclear metal cluster compounds.

The unsaturated (32 valence electron) homonuclear dimetal species $[M_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (M = Co,[1] M = Rh[2]) readily add co-ordinatively unsaturated metal ligand fragments, isolobal with CH_2, to afford saturated trinuclear metal compounds. Moreover, $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**1**) displaces ethylene from $[Pt(C_2H_4)_3]$ to give the pentanuclear cluster complex $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$.[3] The scope of these rational metal cluster syntheses would be considerably extended if 'mixed' dimetal compounds, formally[4] containing M=M′ bonds, were available as reagents. Herein we give a preliminary account of the chemistry of one such species.

Treatment of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ with $[Co(C_2H_4)_2(\eta\text{-}C_5Me_5)]$ in light petroleum gives an intense turquoise coloured solution which *via* column chromatography affords black crystals of (**2**) (*ca.* 80%).† The structure of this compound was established by *X*-ray crystallography.‡ The molecule (Figure 1) contains a cobalt-rhodium linkage [2.404 0(5) Å] bridged asymmetrically by two CO ligands. Unfortunately there is a disorder present in the solid state structure wherein the metal atom sites are occupied alternately by both elements in the ratios 2:3 and 3:2, respectively. The predominance of rhodium (*i.e.* 60%) at Rh (Figure 1) and of cobalt (60%) at Co(1) is reflected in the metal–C(O) separations of 1.913(3) and 1.888(3) Å, and in the mean metal–C(η-C_5Me_5) distances of 2.204(3) and 2.176(3) Å, respectively. The mean planes of the η-C_5Me_5 rings lie effectively parallel to one another and perpendicular to the metal–metal vector, and adopt an eclipsed conformation. The $CoRh(\mu\text{-}CO)_2$ skeleton is planar within 0.01 Å.

An *X*-ray diffraction study was also carried out on $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**1**). The overall structure is similar to that of (**2**) except that in the dirhodium species the η-C_5Me_5 rings

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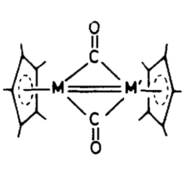
† Selected spectroscopic data, with coupling constants in Hz. Compound (**2**), ν_{CO} at 1 752 cm^{-1} (light petroleum); $^{13}C\text{-}\{^1H\}$ n.m.r. (CH_2Cl_2–CD_2Cl_2), δ 261.3 [d, CO, *J*(RhC) 52], 100.8 (*C*$_5$Me$_5$), 92.2 (*C*$_5$Me$_5$), 7.7 (C$_5$*Me*$_5$), and 6.9 p.p.m. (C$_5$*Me*$_5$). Compound (**3**), ν_{CO} at 1 695 cm^{-1} (thf); $^{13}C\text{-}\{^1H\}$ n.m.r. ($C_6D_5CD_3$), δ 261.4 [d, CO, *J*(RhC) 44, *J*(PtC) 217], 98.7 [d, *C*$_5$Me$_5$, *J*(RhC) 3], 93.7 (*C*$_5$Me$_5$), 88.1 [CH, *J*(PtC) 94], 85.3 [CH, *J*(PtC) 118], 33.2 [CH$_2$, *J*(PtC) 14], 30.5 (CH$_2$), 9.9 (C$_5$*Me*$_5$), and 9.1 p.p.m. (C$_5$*Me*$_5$). Compound (**4**), $^{13}C\text{-}\{^1H\}$ n.m.r. (CH_2Cl_2–CD_2Cl_2), δ 248.9 [d, CO, *J*(RhC) 44], 222.4 (CO), 103.8 [d, *C*$_5$Me$_5$, *J*(RhC) 5], 101.5 (*C*$_5$Me$_5$), 8.0 (C$_5$*Me*$_5$), and 6.5 p.p.m. (C$_5$*Me*$_5$). Compound (**5**), ν_{CO} at 1 957w and 1 938s cm^{-1} (light petroleum); n.m.r. ^1H ($CDCl_3$), δ 1.82 (s, 15 H, C$_5$Me$_5$), 1.91 (s, 15 H, C$_5$Me$_5$), and 5.72 (m, 2 H, CH$_2$); $^{13}C\text{-}\{^1H\}$ (CH_2Cl_2–CD_2Cl_2), δ 202.9 [d, CO, *J*(RhC) 44], 112.2 [d, CH$_2$, *J*(RhC) 29], 99.6 (*C*$_5$Me$_5$), 94.4 (*C*$_5$Me$_5$), and 9.5 p.p.m. (CoC$_5$*Me*$_5$ and RhC$_5$*Me*$_5$). Compound (**6**), ν_{CO} at 1 742 cm^{-1} (thf). Compound (**7**), ν_{CO} at 1 698s and 1 667vs cm^{-1} (thf). Compound (**8**), ν_{CO} at 1 682 cm^{-1} (thf); $^{13}C\text{-}\{^1H\}$ n.m.r. (CH_2Cl_2–CD_2Cl_2), δ 269.2 [q, CO, *J*(RhC) 37], 94.2 (*C*$_5$Me$_5$), and 9.6 p.p.m. (C$_5$*Me*$_5$). Compound (**9**), ν_{CO} at 1 678 cm^{-1} (thf); $^{13}C\text{-}\{^1H\}$ (CH_2Cl_2–CD_2Cl_2), δ 283.6 [t, CO, *J*(RhC) 35], 94.2 [d, *C*$_5$Me$_5$, *J*(RhC) 7], 92.5 (*C*$_5$Me$_5$), 9.6 (C$_5$*Me*$_5$), and 8.27 p.p.m. (C$_5$*Me*$_5$).

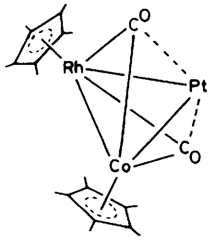
‡ *Crystal data for* (**2**): $C_{22}H_{30}CoO_2Rh$, $M = 488.3$, monoclinic, $a = 9.941(7)$, $b = 14.677(9)$, $c = 14.573(5)$ Å, $\beta = 104.30(4)^\circ$, $U = 2\,070(2)$ Å^3, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $F(000) = 999.9$. Space group $P2_1/c$ (No. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 16.0 cm^{-1}. Intensities [3 733 with $I \geqslant 1.5\sigma(I)$] were measured on a Nicolet *P*3*m* four-circle diffractometer at 200 K and corrected for Lorentz, polarisation, and *X*-ray absorption effects. The structure was solved by conventional heavy atom methods and refined to *R* 0.033 (*R′* 0.032) by blocked cascade least squares.

Crystal data for (**1**): $C_{22}H_{30}O_2Rh_2$, $M = 532.3$, monoclinic, $a = 9.779(6)$, $b = 7.254(4)$, $c = 15.038(10)$ Å, $\beta = 104.57(5)^\circ$, $U = 1\,032(1)$ Å^3, $Z = 2$, $D_c = 1.71$ g cm^{-3}, $F(000) = 535.9$. Space group $P2_1$ (No. 4), μ(Mo-K_α) = 15.9 cm^{-1}. Intensities [2 681 with $I \geqslant 2\sigma(I)$] measured as for (**1**), refining to *R* 0.039 (*R′* 0.041).

The atomic co-ordinates for both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



(1) M = M' = Rh
(2) M = Co, M' = Rh



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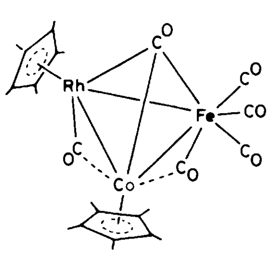
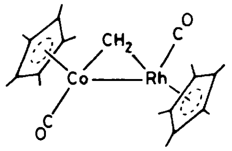


(4)



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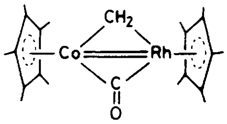

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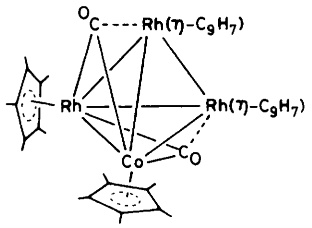
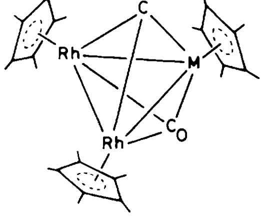


(7)



(8) M = Rh
(9) M = Co

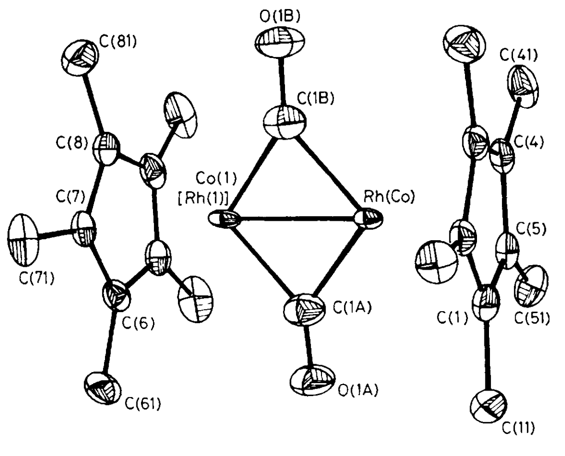


Figure 1. Molecular structure of $[CoRh(\mu-CO)_2(\eta-C_5Me_5)_2]$. Dimensions: Co–Rh 2.404 0(5), Co(Rh)–CO 1.888(3) and 1.913(3), Co(Rh)–C(η-C_5Me_5) 2.176(3) and 2.204(3) Å.

adopt a staggered conformation. Again there is a solid state disorder, but of a different nature wherein the molecule occupies one well defined site (96%) but small lateral displacements (±0.8 Å) reflect disorder (2%) of the major component. The rhodium–rhodium separation is 2.564(1) Å. Two *X*-ray diffraction studies[5,6] on the cobalt analogue $[Co_2(\mu-CO)_2(\eta-C_5Me_5)_2]$ gave cobalt–cobalt distances of 2.338(2) and 2.327(2) Å. Compound (**2**), formally with a Co=Rh bond, has a somewhat shorter metal–metal separation than expected on the basis of the data for the Co_2 and Rh_2 homonuclear complexes.

Compound (**2**) rapidly reacts [25 °C in tetrahydrofuran (thf)] with $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Fe_2(CO)_9]$, and CH_2N_2 giving the heteronuclear metal complexes (**3**) and (**4**), and the μ-CH_2 compound (**5**).[7]† The room temperature ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**3**) showed two signals having different ^{195}Pt–^{13}C couplings for the two ligated CH=CH groups, indicating that the Pt(cod) group is not rotating in solution. The ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**4**) shows only two CO resonances, with ^{103}Rh–^{13}C coupling to only the low field signal. The apparent equivalence of the Fe bonded CO groups implies a dynamic process in solution, which is possibly related to olefin-like rotation.[8]

Heating (**5**) in refluxing toluene (N_2 purge) affords the blue-green complex (**6**) (80%). Preliminary experiments suggest that $[Pt(cod)_2]$ and (**6**) react to give a compound structurally related to (**3**) with a μ-CH_2 ligand.

In refluxing thf, (**2**) reacts with bis(ethylene)indenylrhodium to give (**7**).† This can be rationalised by assuming that the latter is formed by addition of a Rh(η-C_9H_7) moiety to a 46 electron species $[CoRh_2(CO)_2(\eta-C_5Me_5)_2(\eta-C_9H_7)]$, formed by reaction of (**2**) with $[Rh(C_2H_4)_2(\eta^5-C_9H_7)]$. In accord with this idea, (**1**) reacts with $[M(C_2H_4)_2(\eta-C_5Me_5)]$ (M = Co or Rh) to give the trimetal compounds (**8**) and (**9**),† respectively. Steric crowding probably prevents these species reacting further to give tetranuclear metal clusters.

The ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**8**) is of interest in relation to possible structures of the unknown molecule $[Rh_3(CO)_2(\eta-C_5H_5)_3]$.[4] The CO resonance in the ^{13}C spectrum of (**8**)† is a quartet at room temperature and also at −70 °C, implying a D_{3h} structure for this molecule in solution.

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