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Preliminary communication

The formation of metal clusters by the facile condensation of electron-deficient metal centres; X-ray crystal structures of $(\eta\text{-}C_5H_5)_2Rh_4(CO)_4Cl_2(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$

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Abstract

When solutions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and $[Rh(CO)_2Cl]_2$ in hexane are mixed and left at room temperature, black crystals of the condensation product $(\eta\text{-}C_5H_5)_2Rh_4(CO)_4Cl_2(CF_3C_2CF_3)$ are deposited. X-ray structure determination shows that one rhodium atom of the $[Rh(CO)_2Cl]_2$ dimer has added to the Rh–Rh bond of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ to form a triangular Rh_3 cluster. This is capped on one side by a semi-face bridging carbonyl and on the other by a $\mu_3\eta^2$ bound alkyne. Variable temperature NMR data reveal that two isomers of the complex co-exist in solution and that they rapidly interconvert at room temperature. In similar reactions between $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ and $Pt(COD)_2$ in hexane at room temperature, there is loss of cyclooctadiene and the formation of two cluster products. One is formulated as $(\eta\text{-}C_5H_5)_2Rh_2Pt(CO)(COD)(CF_3C_2CF_3)$ and the other as $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$. Determination of the X-ray crystal structure of the latter establishes that the Pt is a common apex for two linked Rh_2Pt triangles. Within each Rh_2Pt unit, a semi-bridging carbonyl spans one Rh–Rh edge, and the hexafluorobut-2-yne occupies a $\mu_3\eta^2$ face bridging position.

The binuclear complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ is a remarkably versatile reagent for studying the addition and subsequent intramolecular reactions of organic substrates on a metal–metal bond. Reactions with both transient and stable species, including alkenes [1], alkynes [2,3], carbenes [4], isocyanates [5] and nitrenes [5] have been described previously. The dirhodium complex also promises to be an excellent site for the construction of cluster compounds [6]. The addition of nucleophilic or electron-deficient metal compounds to the Rh–Rh bond should lead to the designed syntheses of diverse Rh_2M_n clusters which incorporate a variety of labile or reactive ligands. The considerable current interest [7,8] in alkyne metal cluster chemistry prompts us to report some preliminary results on the facile formation of several such compounds. In this communication, we describe the additions of $[Rh(CO)_2Cl]_2$ and $Pt(COD)_2$ to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$.

Treatment of $(\eta\text{-}C_5H_5)_2Rh(CO)(CF_3C_2CF_3)$ with one equivalent of $[Rh(CO)_2Cl]_2$ in hexane at room temperature results in the deposition of large black crystals over 24 h. These were collected by filtration and washed thoroughly with hexane. Analytical and spectroscopic data indicate that the crystalline material is $(\eta\text{-}C_5H_5)_2Rh_4(CO)_4Cl_2(CF_3C_2CF_3)$; it is isolated in 60% yield. Three carbonyl peaks are observed at 2088, 2016 and 1796 cm^{-1} in the IR spectrum (CH_2Cl_2 solution). The NMR spectra ($CDCl_3$ solutions) are surprisingly simple at room temperature, and show just one C_5H_5 resonance at δ 5.67 in the ^1H spectrum and a single CF_3 resonance at δ 52.2 in the ^{19}F spectrum. Determination of the molecular structure by X-ray crystallography establishes that the structure is more complex than might be expected from the spectroscopic results.

Crystal data. $C_{18}H_{10}Cl_2F_6O_4Rh_4$, $M = 886.6$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 15.099(9), b 9.314(4), c 8.496(4) Å, α 95.78(4), β 93.60(4), γ 90.17(4)°, U 1186(1) Å^3, D_m 2.44(1), D_c $(Z = 2)$ 2.48 g cm^{-3}, $F(000) = 836$, μ_{Mo} 28 cm^{-1}, $A^{\star}_{min,max} = 1.23, 1.55$.

Single crystal X-ray diffraction data was measured to $2\theta_{max} = 50°$ with a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with graphite monochromated Mo-K_α radiation. For 3464 unique reflections ($I > 3\sigma(I)$), R is 0.032 *. A representation of the molecular structure, and some important geometrical parameters, are given in Fig. 1. This shows that one rhodium atom (Rh(1)) of the $[Rh(CO)_2Cl]_2$ has added to the Rh(2)–Rh(3) bond of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. The remaining rhodium atom (Rh(4)) is linked to Rh(1) through two bridging chlorides. There are two terminal carbonyl groups on Rh(4), and the geometry about this metal atom remains square planar. A further terminal carbonyl is attached to Rh(1). The remaining carbonyl and the hexafluorobut-2-yne ligands are attached on opposite sides of the triangular face presented by Rh(1)–Rh(2)–Rh(3). This carbonyl is asymmetrically bonded to the Rh_3 face, with the distances to Rh(2) and Rh(3) (av. 2.037 Å) being significantly shorter than that to Rh(1) (2.260 Å). The attachment of the alkyne is best described in terms of σ-bonding to Rh(1) and Rh(3) and π-bonding to Rh(2). There is an η^5-cyclopentadienyl group on each of Rh(2) and Rh(3). An especially interesting feature of the structure is the coplanarity of all four rhodium atoms plus the two chlorines.

Awareness of the solid state structure leads to further comment on the deceptively simple NMR spectra observed at room temperature. Measurement of the spectra over a temperature range reveals that a non-degenerate exchange process operates to provide a time averaged spectrum at room temperature. In the ^1H spectrum, four C_5H_5 signals are clearly distinguished at $-52°C$ and below, and these can be divided into two $(C_5H_5)_2$ sets of relative intensity 3/2. As the solution

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* A table of atomic coordinates and a full list of bond lengths and angles will be deposited by the authors with the Cambridge Crystallographic Data Centre.

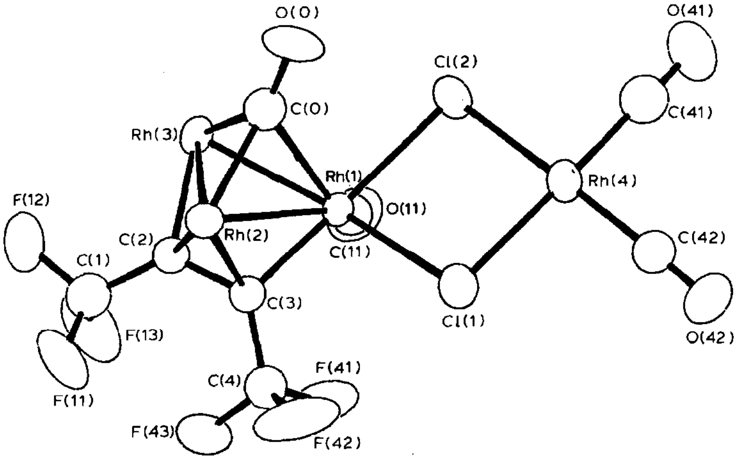

Fig. 1. Molecular structure of $(\eta\text{-}C_5H_5)_2Rh_4(CO)_4Cl_2(CF_3C_2CF_3)$; the C_5H_5 rings on Rh(2) and Rh(3) have been omitted for clarity. Important geometrical parameters are: Rh(1)–Rh(2) 2.736(1), Rh(1)–Rh(3) 2.619(1), Rh(2)–Rh(3) 2.665(1), Rh(1)— — —Rh(4) 3.664(1), Rh(1)–C(0) 2.260(6), Rh(2)–C(0) 2.030(6), Rh(3)–C(0) 2.044(6), Rh(1)–C(3) 1.985(5), Rh(2)–C(2) 2.096(5), Rh(2)–C(3) 2.120(5), Rh(3)–C(2) 2.014(5), C(2)–C(3) 1.395(8), Rh(1)–Cl(1) 2.551(2), Rh(1)–Cl(2) 2.548(2), Rh(4)–Cl(1) 2.349(2), Rh(4)–Cl(2) 2.353(2) Å.

is warmed, all peaks broaden and they eventually coalesce at about 35 °C. A similar effect is observed in the ^{19}F spectrum with four CF_3 quartets (of relative intensity 3/3/2/2) evident at −72 °C, but only one broad singlet at 40 °C. These phenomena can be explained in terms of rotation of the alkyne on the Rh_3 face, with two orientations (μ_3-∥ and μ_3-⊥) being frozen out at low temperature. Similar acetylene rotation processes have been discussed previously [9]. Further studies on the reactions of this complex, and on the formation of several related complexes, are in progress and will be reported in a full paper.

Related cluster complexes were formed when two equivalents of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ were treated with $Pt(COD)_2$ in hexane. After 2 d at room temperature, two crystal types were evident in the deposited material. The very large rhomboids were identified on the basis of analytical and spectroscopic data as $(\eta\text{-}C_5H_5)_2Rh_2Pt(CO)(CF_3C_2CF_3)COD$, and the needle aggregates as $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$. The product mixture was conveniently separated by TLC (silica, 1/1 hexane/diethyl ether as eluent); this gave the Rh_2Pt and Rh_4Pt cluster compounds in yields of 30 and 10% respectively.

The structure of the Rh_4Pt complex has been determined by X-ray crystallography.

Crystal data. $C_{30}H_{20}F_{12}O_2PtRh_4$, $M = 1247.2$, monoclinic, space group $P2_1$ (C_2^2, No. 4), a 11.796(6), b 15.178(7), c 9.765(5) Å, β 113.32(11)°, U 1605.5 Å, D_m 2.57(2), D_c $(Z = 2)$ 2.58 g cm^{-3}, $F(000)$ 1164, μ_{Mo} 64 cm^{-1}, $A^{\star}_{max,min} = 0.488$, 0.771.

Single crystal X-ray diffraction data was measured to $2\theta_{max} = 60°$ with a Philips PW1100 diffractometer in conventional $2\theta/\theta$ scan mode with graphite monochromated Mo-K_α radiation. For 3328 unique reflections ($I > 3\sigma(I)$), R is 0.045 (see footnote).

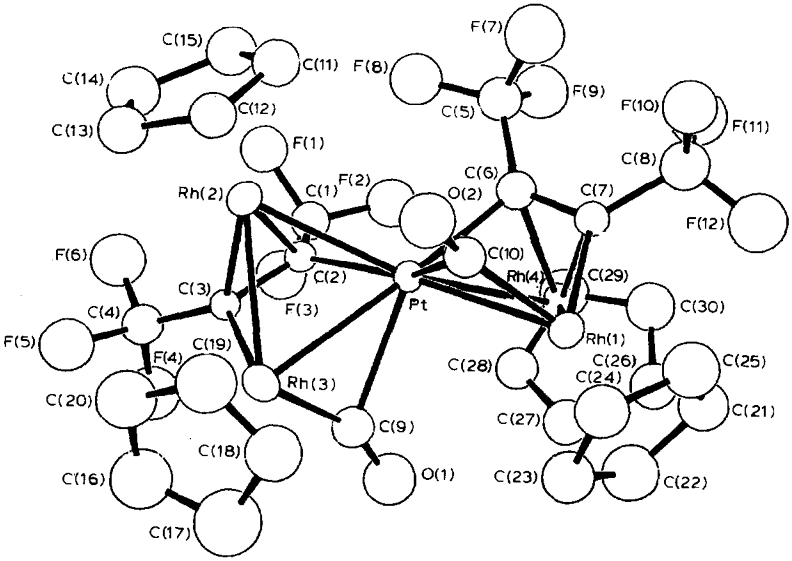

Fig. 2. Molecular structure of $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$.

Figure 2 shows the full molecular structure and Fig. 3a reveals the geometry of the cluster core more clearly. Two Rh_2Pt triangles are linked through a common platinum atom, with a dihedral angle of 70.0° between the two planes. The attachment of the carbonyl and hexafluorobut-2-yne ligands to one of the Rh_2Pt units is indicated in Fig. 3b. The bridging carbonyl spans the longer Rh–Pt bond and is asymmetrically bound, with strong bonding to Rh(3) and a much weaker attachment to Pt. The alkyne is σ-bonded to Rh(3) and Pt and π-bonded to Rh(2), and the alkyne C=C bond is approximately parallel to the Rh(3)–Pt edge. There is an analogous arrangement of the ligands in the second Rh_2Pt unit (see Fig. 2).

The spectroscopic properties are consistent with retention of this structure in solution. In the IR spectrum (CH_2Cl_2 solution), an edge-bridging carbonyl absorption is observed at 1862 cm^{-1}. The ^1H NMR spectrum shows two closely spaced C_5H_5 signals at δ 5.49 and 5.48, and two CF_3 multiplets are found at δ 47.4 and 56.3 in the ^{19}F spectrum; Pt–F coupling of 67 Hz is detected in the lower field CF_3 resonance, and this is typical of ^4J coupling.

Full characterization of the complex $(\eta\text{-}C_5H_5)_2Rh_2Pt(CO)(CF_3C_2CF_3)(COD)$ has so far proved more difficult, in part because there is dissociation of cyclooctadiene when the complex is left in solution. A carbonyl absorption in the IR spectrum (CH_2Cl_2 solution) is observed at 1748 cm^{-1}, and this is consistent with the presence of a face-bridging carbonyl. There is overlap of cyclopentadienyl and cyclooctadiene signals in the ^1H NMR spectrum ($CDCl_3$ solution), but it is evident that there is just one C_5H_5 signal at δ 5.34; apparent equivalence of the cyclopentadienyl group is confirmed by the single C_5H_5 resonance near δ 90 in the ^{13}C NMR spectrum. Some unusual features in the rest of the ^{13}C spectrum and in the ^{19}F spectrum have yet to be explained and will be important in the further characterization of this cluster complex. A tentative structure is proposed in Fig. 4.

Production of the complex $(\eta\text{-}C_5H_5)_2Rh_4(CO)_4Cl_2(CF_3C_2CF_3)$ establishes that

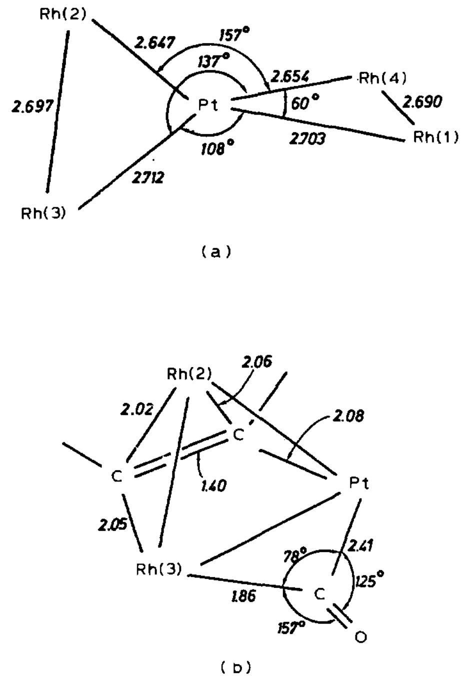

Fig. 3. Important geometric parameters for (a) the Rh_4Pt core and (b) the ligands attached to each Rh_2Pt unit within the complex $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$.

two formally electron deficient species can overcome their mutual electron deficiency through the formation of new metal–metal bonds. The formation of $(\eta\text{-}C_5H_5)_2Rh_2Pt(CO)(CF_3C_2CF_3)(COD)$ and $(\eta\text{-}C_5H_5)_4Rh_4Pt(CO)_2(CF_3C_2CF_3)_2$ is similar in the sense that one reactant, $Pt(COD)_2$, can readily lose its ligands to become the formally electron deficient species [PtCOD] or [Pt]. In each case, initial construction of the metal cluster framework is followed by rearrangement of the carbonyl and alkyne ligands to give an appropriate balance of electron density

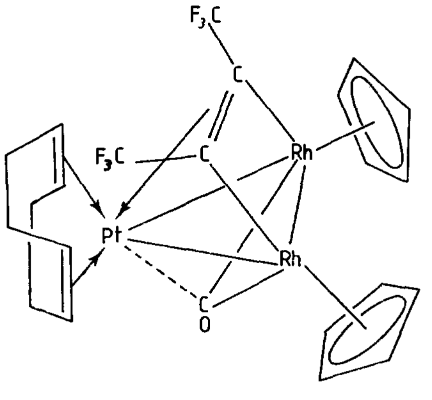

Fig. 4. Possible molecular structure for the complex $(\eta\text{-}C_5H_5)_2Rh_2Pt(CO)(CF_3C_2CF_3)(COD)$.

within the cluster. We note that in the complexes described here, the alkyne prefers a $\mu_3\eta^2$-|| orientation in which π-bonding is directed at the least electron-attracting metal.

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