Synthesis of Cationic Trigonal-bipyramidal Clusters $[MRh_4(\eta\text{-}C_5H_5)_4(PPh_3)(\mu_3\text{-}CO)_2]^+ PF_6^-$ (M = Cu, Ag, Au)

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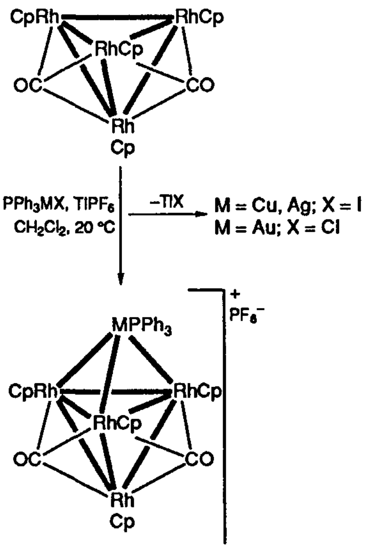
Novel mixed trigonal-bipyramidal clusters $[MRh_4(\eta\text{-}C_5H_5)_4(PPh_3)(\mu_3\text{-}CO)_2]^+ PF_6^-$ (M = Cu, Ag, Au) have been prepared by the reaction of $Rh_4(\eta\text{-}C_5H_5)(\mu_3\text{-}CO)_2$ with $[M(PPh_3)]^+$ fragments, generated *in situ* in CH_2Cl_2 from $M(PPh_3)Hal$.

The majority of stable transition metal clusters have deltahedral faces. It is interesting to study the addition of coordinatively unsaturated fragments, and in particular the addition of cationic metal fragments to the triangulated faces. There are some previous examples of the addition of cationic fragments to isolated triangular metal units. Mingos *et al.* have synthesized the cationic tetrahedral clusters $[AuPt_3(PR_3)_4(\mu\text{-}L)_3]^+$ *via* the addition of $[Au(PR_3)]^+$ fragments to the 42-electron clusters $[Pt_3(PR_3)_3(\mu\text{-}L)_3]$ (L = CO, SO_2).[1]

We have studied the reactions of the 48-electron cluster $[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CO)_3]$ with the 12-electron fragments $[M(PPh_3)]^+$ (M = Cu, Ag, Au)[2,3] and $[M(\eta\text{-}C_5R_5)]^+$ (M = Fe, R = H; M = Ru, R = H, Me).[4] We now report the reactions of $[M(PPh_3)]^+$ (M = Cu, Ag, Au) with the tetranuclear cluster $[Rh_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}CO_2)]$.[5] Such reactions take place at room temperature and selectively lead to new pentanuclear trigonal-bipyramidal clusters **1–3** (Scheme 1).



Scheme 1

The cations $[M(PPh_3)]^+$ were generated *in situ*, as reported previously,[1–3] by halogen-anion abstraction from $M(PPh_3)X$ (M = Cu, Ag, X = I; M = Au, X = X = Cl) with $TlPF_6$. The cations were then treated with $[Rh_4(\eta\text{-}C_5H_5)_4(\mu\text{-}CO)_2]$ at room temperature, to give the air-stable complexes $[Rh_4(\eta\text{-}C_5H_5)_4(\mu\text{-}CO)_2](MPR_3)]PF_6$ (M = Cu, X = I, **1**; M = Ag, X = I, **2**; M = Ag, X = Cl, **3**. The complexes were obtained as black crystals by precipitation from CH_2Cl_2 solution upon the addition of ether. The complexes dissolve in CH_2Cl_2 or acetone to give air-stable green solutions. This stability is greater than that observed for $[MRh_3(\eta\text{-}C_5H_5)_3(PPh_3)(\mu\text{-}CO)_3]PF_6$ (M = Cu, Ag, Au),[2,3] which decompose quickly in solution. The enhanced stability of **1–3** may be connected with the possibility of greater delocalization of positive charge within the higher nuclearity clusters.

The formulations for **1–3** have been confirmed by elemental analysis,† spectroscopic measurements,‡ and in the case of **3** by an X-ray crystal structure.§ The IR spectra for the complexes exhibit ν(CO) frequencies in the range 1700–1750 cm^{-1} which is consistent with the presence of μ_3-CO groups in cationic species. The ^1H NMR spectra, at 20 °C, show broad signals for the cyclopentadienyl H-atoms associated with the equatorial Rh atoms, while the signal for the cyclopentadienyl H-atoms associated with the apical Rh atom is sharp. These signals may be explained in terms of a fluxional process which involves the migration of the two μ_3-CO groups over three faces of the cluster. This process is confirmed by the results of a variable-temperature ^1H NMR study.¶

The molecular structure of **3** is shown in Fig. 1 which

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† Satisfactory elemental analysis data were obtained for all new compounds.

‡ ^1H NMR (200 MHz, $CDCl_3$, δ in ppm, relative to $SiMe_4$) and IR (CH_2Cl_2 solution) data for **1–3**:

1: 5.55 (s, br, 15H, $CpRh_{eq}$), 5.66 (s, 5H, $CpRh_{ax}$) and 7.38 (m, 6H) and 7.58 (m, 9H) (Ph_3PCu); $\nu_{(CO)}/cm^{-1}$; 1722 (m) and 1710 (s).

2: 5.57 (s, br, 15H, $CpRh_{eq}$), 5.66 (s, 5H, $CpRh_{ax}$) and 7.46 (m, 6H) and 7.57 (m, 9H) (Ph_3PAg); $\nu_{(CO)}/cm^{-1}$; 1725 (m) and 1710 (s).

3: 5.59 (s, br, 15H, $CpRh_{eq}$), 5.67 (s, 5H, $CpRh_{ax}$) and 7.43 (m, 6H) and 7.58 (m, 9H) (Ph_3PAu); $\nu_{(CO)}/cm^{-1}$; 1720 (m) and 1705 (s).

§ *Crystal data for* **3**: X-Ray measurements were performed on a black crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm. Crystal data for $C_{40}H_{35}AuF_6O_2P_2Rh_4$: $M = 1332.27$, orthorhombic, space group $P2_12_12_1$ with $a = 13.639(6)$, $b = 17.175(7)$, $c = 19.218(9)$ Å, $V = 4502(2)$ A^3, $Z = 4$, $\mu(MoK\alpha) = 4.81$ mm^{-1}, $F(000) = 2536$, $\lambda(MoK\alpha) = 0.71069$ Å, $d_{calc} = 1.966$ g cm^{-3}. Accurate unit-cell parameters were obtained by a least-squares fit of 15 reflections. Intensity data were measured on a Nicolet P3 diffractometer using graphite-monochromated MoKα radiation and ω-scan mode. Data collection range was $4.0° < 2\theta < 52.0°$, $0 \leq h \leq 16$, $0 \leq k \leq 21$, $0 \leq l \leq 23$. 4784 reflections were measured, of which 2126 were used in the refinement $[I > 3\sigma(I)]$. The data were corrected for Lorentz and polarization effects and absorption from empirical φ-scan data. The structure was solved by direct and Fourier methods using the SHELXS-86, SHELX-76 and SHELXTL-Plus programs[6–8] and refined with anisotropic temperature factors for Au, Rh, P atoms and isotropic temperature factors for F, O, C atoms. Phenyl (C–C 1.395 Å and C–C–C 120°) and cyclopentadienyl (C–C 1.420 Å and C–C–C 108°) rings, PF_6 (P–F 1.55 Å and F–P–F 90°) and CO (C–O 1.16 Å) groups were refined as rigid groups. On the basis of ^1H (and ^{13}C NMR spectra (two CO groups in the molecule) and rather large temperature factors for the C and O atoms in the three CO groups found by X-ray study, a population parameter of 0.67 was assigned to these atoms. Changing the population parameter from 1 to 0.67 lowered the temperature factors of the CO groups atoms and improved the R value from 0.060 to 0.059. Hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Final values for R and R_w with $w = 1/\sigma(F_0)$ are, respectively, 0.059 and 0.066 for 178 variables (the rejected enantiomeric structure had $R = 0.080$ and $R_w = 0.091$). Maximum and minimum heights in the final difference Fourier synthesis were 1.20 and −0.99 e $Å^{-3}$ and largest Δ/σ 0.11. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Centre (CCDC). See Notice to Authors, *Mendeleev Commun.*, 1993, Issue 1.

¶ The broad signal due to $C_5H_5Rh_{eq}$ at +20 °C is split into two sharp signals (intensity ratio 1:2) at −50 °C, whereas in the presence of three carbonyl groups only one sharp signal due to $C_5H_5Rh_{eq}$ should be observed at both temperatures.

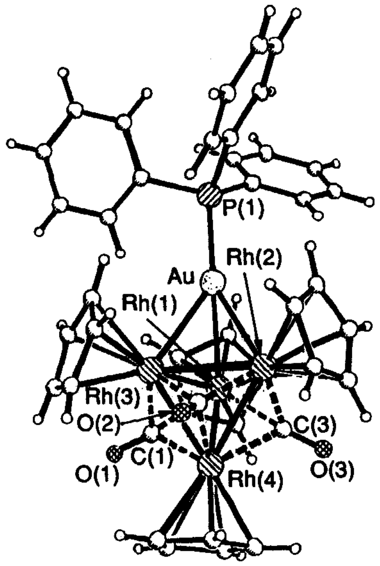

Fig. 1 Structure of cation $AuRh_4(\eta\text{-}C_5H_5)_4(PPh_3)(\mu_3\text{-}CO)_2{}^+$.

Several main bond lengths/Å: Au–Rh(1) 2.784(3), Au–Rh(2) 2.764(3), Au–Rh(3) 2.778(3), Rh(1)–Rh(2) 2.708(4), Rh(1)–Rh(3) 2.699(4), Rh(2)–Rh(3) 2.681(4), Rh(1)–Rh(4) 2.622(4), Rh(2)–Rh(4) 2.643(4), Rh(3)–Rh(4) 2.624(4), Rh(1)–C(1) 2.04(4), Rh(1)–C(3) 2.13(4), Rh(2)–C(2) 2.09(4), Rh(2)–C(3) 2.02(4), Rh(3)–C(1) 2.07(4), Rh(3)–C(2) 2.04(4), Rh(4)–C(1) 2.03(5), Rh(4)–C(2) 2.19(4), Rh(4)–C(3) 2.113(4) and Au–P 2.250(9); population factor for CO groups is 0.67 (see text).

includes selected bond parameters. The analysis confirms the trigonal-bipyramidal metal core geometry. The two μ_3-carbonyls were found to be disordered over the three Rh_3 triangular faces of the clusters and were consequently refined with site occupancies of 0.67.

The results of this work suggest that within the frontier molecular orbitals of the tetranuclear cluster $[Rh_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}CO)_2]$ there is an orbital with the appropriate symmetry and energy to interact with the unoccupied a_1 orbital *of the* $[MPPh_3]^+$ *fragment* ($M = Cu$, *Ag, Au*). *Thus, the* tetranuclear cluster behaves as a 2-electron donor group to the $[MPPh_3]^+$ fragment in a similar manner to that previously observed for $[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CO)_3]$.[2,3]

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