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Some Unusual Gold- and Rhodium–Rhenium Clusters

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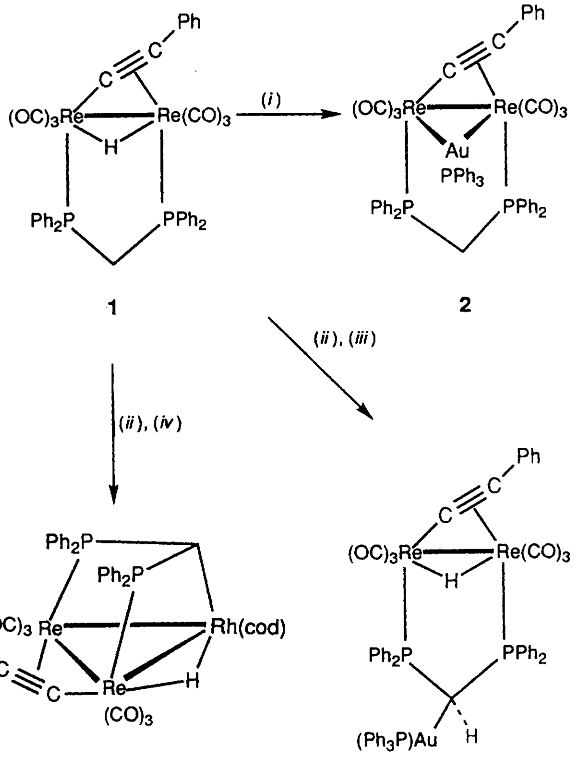
The isomeric complexes $[AuRe_2(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6(PPh_3)]$ [dppm = bis(diphenylphosphino)-methane] and $[Re_2(\mu\text{-H})\{\mu\text{-}(PPh_2)_2CH[Au(PPh_3)]\}(\mu\text{-}C_2Ph)(CO)_6]$ have been obtained from $[Re_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6]$ and $[AuMe(PPh_3)]$, or from LiMe and $[AuCl(PPh_3)]$ or $[\{Au(PPh_3)\}_3O]^+$, respectively; extension of the latter reaction to $[\{Rh(\mu\text{-Cl})(cod)\}_2]$ (cod = cycloocta-1,5-diene) gave $[Re_2Rh(\mu\text{-H})\{\mu_3\text{-}(PPh_2)_2CH\}(\mu\text{-}C_2Ph)(CO)_6(cod)]$ in which the Re_2Rh cluster is capped by the five-electron donor $(PPh_2)_2CH$.

Replacement of H by the isolobal $Au(PR_3)$ (R = alkyl or aryl) group in metal complexes is a now well established procedure: common sources of the $Au(PR_3)$ fragment are $[AuCl(PR_3)]$, $[AuMe(PR_3)]$ or $[\{Au(PR_3)\}_3O]^+$.[1] However, to our knowledge, there have been no reports describing the formation of isomeric products resulting from the use of different combinations of metal complex and $Au(PR_3)$ source. Herein we describe such a system which leads to substitution of metal-bonded H in one instance and ligand-bonded H in the other, and extension of the latter reaction to give a novel type of Re–Rh cluster.

The reaction between $[Re_2(\mu\text{-H})(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6]$ **1** [dppm = bis(diphenylphosphino)methane] (Scheme 1) and $[AuMe(PPh_3)]$ in refluxing tetrahydrofuran afforded bright yellow-green crystals of $[AuRe_2(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_6(PPh_3)]$ **2** (60%),* which has been characterised by a single-crystal X-ray structure determination, which will be reported in detail in the full paper. As expected, replacement of the μ-H ligand in **1** by an $Au(PPh_3)$ group has occurred with the formation of an $AuRe_2$ cluster. The dppm and C_2Ph ligands remain bridging the Re–Re vector.

In contrast, treatment of **1** with LiMe, followed by addition of either $[AuCl(PPh_3)]$ or $[\{Au(PPh_3)\}_3O][BF_4]$, gave the complex $[Re_2(\mu\text{-H})\{\mu\text{-}(PPh_2)_2CH[Au(PPh_3)]\}(\mu\text{-}C_2Ph)(CO)_6]$ **3** in 45 and 95% yields, respectively.* The ^1H NMR spectrum of **3** contained a characteristic high-field resonance at δ −9.91 and only one CH resonance at δ 4.15. A single-crystal X-ray structure determination† confirmed that one of the dppm protons had been replaced by the $Au(PPh_3)$ group. A molecule of **3** is shown in Fig. 1 and significant bond parameters are given in the caption. The molecular structure is very similar to that of **1**; the H atom (which was tentatively located in the X-ray determination) and C_2Ph ligands bridge the Re–Re vector, while the $Au(PPh_3)$ group is attached to C(0) [Au–C(0) 2.121(8) Å] of the bridging diphosphine ligand. The *endo* position of this substituent is dictated by steric interactions between the Ph



Scheme 1 (*i*) $[AuMe(PPh_3)]$, (*ii*) LiMe, (*iii*) $[AuCl(PPh_3)]$ or $[\{Au(PPh_3)\}_3O]^+$, (*iv*) $[\{Rh(\mu\text{-Cl})(cod)\}_2]$

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* Data for **2**: m.p. 248–253 °C (decomp.). IR (thf): ν(CO) 2018s, 1987vs, 1935m, 1914s and 1903s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.53–2.64 (1 H, m, CHP_2), 4.18–4.27 (1 H, m, CHP_2) and 6.92–7.56 (40 H, m, Ph). FAB mass spectrum: *m*/*z* 1485, M^+ and 1457–1317, $[M - n\text{CO}]^+$ (n = 1–6).

Data for **3**: IR (thf): ν(CO) 2035s, 2008m, 1994 (sh), 1941 (br) and 1917 (br) cm^{-1}. NMR ($CDCl_3$): ^1H, δ −9.91 [1 H, br s, Re–H], 4.15 [1 H, br s, CHP_2] and 6.78–8.09 (45 H, m, Ph); ^{13}C, δ 94.2 (s, *C*≡CPh), 102.0 (s, C≡*C*Ph), 127.2–140.85 (m, Ph), 187.41, 187.88, 188.21 and 191.72 (4 × s, CO). FAB mass spectrum: *m*/*z* 1408, $[M - \text{Ph}]^+$; 1026, $[M - \text{Au(PPh}_3)]^+$ and 998–858 $[M - \text{Au(PPh}_3) - n\text{CO}]^+$ (n = 1–6).

† Crystal data. $[Re_2(\mu\text{-H})\{\mu\text{-}(PPh_2)_2CH[Au(PPh_3)]\}(\mu\text{-}C_2Ph)(CO)_6]\cdot CH_2Cl_2$ **3**, $C_{57}H_{42}AuO_6P_3Re_2\cdot CH_2Cl_2$, $M = 1570.2$; triclinic, space group $P\bar{1}$, $a = 15.335(4)$, $b = 14.420(6)$, $c = 13.114(3)$ Å, $\alpha = 80.12(3)$, $\beta = 71.29(3)$, $\gamma = 87.74(3)°$, $U = 2705(2)$ Å^3, $Z = 2$, $D_c = 1.93$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 74.1$ cm^{-1}, $2\theta_{max} = 50°$, $A^*_{(min,max)} = 4.65$, 7.45 (analytical), crystal dimensions 0.45 × 0.60 × 0.26 mm. 8798 Data, 7324 having $I \geqslant 3\sigma(I)$ were refined to $R = 0.033$, $R' = 0.037$.

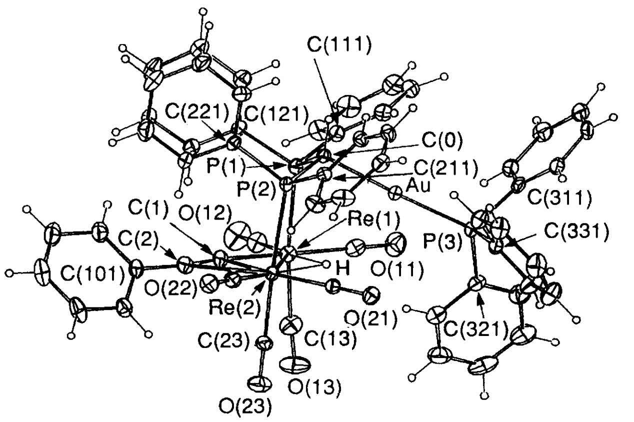

Fig. 1 Projection of a molecule of $[Re_2(\mu\text{-}H)\{\mu\text{-}(PPh_2)_2CH\text{-}[Au(PPh_3)]\}(\mu\text{-}C_2Ph)(CO)_6]$ **3** oblique to the Re(2)–C(1)–H plane, showing the atom numbering scheme. Important bond distances (Å) and angles (°): Re(1)–Re(2) 3.083 4(8), Re(1)–P(1) 2.461(2), Re(2)–P(2) 2.501(2), Re(1)–C(1) 2.11(1), Re(2)–C(1) 2.353(7), Re(2)–C(2) 2.529(8), Au–P(3) 2.279(2), Au–C(0) 2.121(8), P(3)–Au–C(0) 176.4(2), Re(1)–C(1)–C(2) 170.3(6), Re(1)–Re(2)–P(2) 89.81(8), Re(2)–Re(1)–P(1) 87.94(5), P(1)–C(0)–P(2) 111.1(4)

groups C(111)–C(116) and C(211)–C(216) of the substituted dppm and C(311)–C(316) and C(331)–C(336) of the PPh_3 ligands. However, there is no Au ··· Re interaction.

Complexes **2** and **3** are isomers but we have not been able to effect any interconversion.

A similar reaction between **1** and LiMe, followed by addition of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = cycloocta-1,5-diene) afforded the novel Re_2Rh cluster **4** in 30% yield.[*] A single-crystal structure determination [†] revealed the molecular structure depicted in Fig. 2. From this it is evident that although a similar metallation of the dppm ligand and addition of the Rh(cod) fragment has occurred, the latter has entered into a bonding arrangement with the two Re atoms to form a closed Re_2Rh cluster [Rh–Re(1,2) 3.096, 3.163(3) Å]. The C_2Ph ligand remains bridging the Re–Re vector [3.222(2) Å], while the five-electron $(PPh_2)_2CH$ ligand now caps the Re_2Rh cluster. The H atom was not located in the X-ray study, but appears to be bridging an Re–Rh vector, as it is coupled only to the Rh atom [δ −19.43; *J*(HRh) 13.5 Hz]. The CH proton (δ 3.45) is equally coupled to the two ^{31}P nuclei [*J*(HP) 10.1 Hz]. These data are also consistent with a fluxional process involving rapid σ,π interchange of the phenylethynyl ligand with concomitant migration of the hydride ligand between the Re(1)–Rh and Re(2)–Rh vectors; the former process has been well established in **1** and related complexes.[2]

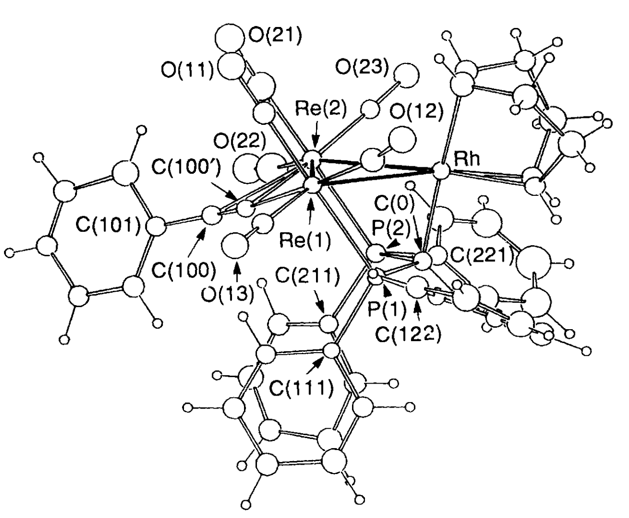

Fig. 2 Projection of a molecule of $[Re_2Rh(\mu\text{-}H)(\{\mu_3\text{-}(PPh_2)_2CH\}(\mu\text{-}C_2Ph)(CO)_6(cod)]$ **4** oblique to the Re_2Rh plane, showing the atom numbering scheme. Significant bond distances (Å) and angles (°): Re(1)–Re(2) 3.222(2), Re(1)–Rh 3.096(3), Re(2)–Rh 3.163(3), Re(1)–P(1) 2.441(8), Re(2)–P(2) 2.485(9), Re(1)–C(100′) 2.24(3), Re(2)–C(100) 2.52(3), Re(2)–C(100′) 2.32(3), Rh–C(0) 2.08(3), Re(1)–C(100′)–C(100) 174(2), Re(1)–P(1)–C(0) 105(1), Re(2)–P(2)–C(0) 106(1), Rh–C(0)–P(1) 100(2), Rh–C(0)–P(2) 97(1), P(1)–C(0)–P(2) 116(2)

The different reaction pathways are related to the ease of approach of the reagents to the respective H atoms and to the differing types of reactions. It is likely that the reaction with $[AuMe(PPh_3)]$ involves addition of $Au(PPh_3)$ and Me across the Re–Re bond with facile concomitant or subsequent elimination of CH_4. The LiMe reagent, on the other hand, is sufficiently basic to deprotonate the co-ordinated dppm ligand, as has been recently found in a related dimanganese system.[3] The extension to metals to the left of Group 11 offers a new route to heterometallic cluster formation; these materials may be stabilised by the capping $(PPh_2)_2CH$ ligand and retain the other functional ligands present in the precursor. The chemistry of these and related molecules will be the subject of a future report.

Acknowledgements

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[*] Data for **4**: m.p. 227–230 °C (decomp.). IR (cyclohexane): ν(CO) 2041vs, 2017vs, 2004w, 1955s, 1938s, 1931vs and 1920m cm^{-1}. ^1H NMR ($CDCl_3$): δ −19.43 [1 H, d, *J*(HRh) 13.5, Rh–H], 1.76 (6 H, m, cod), 2.21 (2 H, m, cod), 3.45 [1 H, t, *J*(HP) 10.1 Hz, CHP_2], 4.27 (2 H, s, $=CH_2$ of cod), 4.72 (2 H, s, $=CH_2$ of cod), 6.65 (3 H, m, C_2Ph), 6.82 (2 H, m, C_2Ph), 6.98 (5 H, m, Ph), 7.44–7.58 (10 H, m, Ph) and 7.96–8.01 (5 H, m, Ph). FAB mass spectrum: *m/z* 1237, M^+ and 1209–1069, $[M - nCO]^+$ (n = 1–6).

[†] Crystal data. $[Re_2Rh(\mu\text{-}H)\{\mu_3\text{-}(PPh_2)_2CH\}(\mu\text{-}C_2Ph)(CO)_6(cod)]\cdot 0.5CH_2Cl_2$ **4**, $C_{47}H_{39}O_6P_3Re_2Rh\cdot 0.5CH_2Cl_2$, $M = 1279.5$; orthorhombic, space group *Pcab*, $a = 23.470(8)$, $b = 21.199(6)$, $c = 18.814(5)$ Å, $U = 9361(5)$ Å^3, $Z = 8$, $D_c = 1.82$ g cm^{-3}, μ(Mo-Kα) = 56.2 cm^{-1}, $2\theta_{max} = 50°$, $A^*_{(min,max)} = 2.27, 8.19$ (analytical), crystal dimensions 0.24 × 0.17 × 0.31 mm. 7967 Data, 3602 having $I \geqslant 3\sigma(I)$ were refined to $R = 0.083$, $R' = 0.088$. Atomic coordinates, thermal parameters and bond lengths and angles for complexes **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.