Novel Metal Framework Rearrangements in Mercury-bridged Cluster Complexes: *X*-Ray Crystal Structures of $[Hg\{Fe_2M(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)\}_2]$ (M = Co and Rh)

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Differing metal connectivities are found for $[Hg\{Fe_2M(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)\}_2]$ (M = Co and Rh) in the solid state, whilst in solution ^{13}C and ^{199}Hg n.m.r. data suggest a novel polytopal rearrangement in the Rh compound with the Hg atom migrating around the Fe_2Rh triangles.

Complexes containing mercury–transition metal bonds are well known,[1] and several cluster species have been reported recently.[2,3] The cluster complexes have usually been prepared by treatment of the requisite carbonylate anion with Hg^{II} salts.[2] The mercury atom often adopts a co-ordination site commensurate with the orbital similarities between Hg^{2+}, $Au(PR_3)^+$, and H^+,[2a,2c,4] although more complex geometries *e.g.* planar condensed structures[2b] are sometimes observed. This communication reports an intermolecular elimination reaction[5] between $HgPh_2$ and hydrido clusters which provides

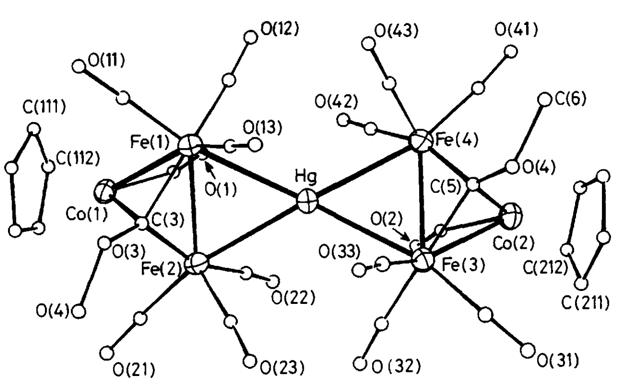

Figure 1. Molecular structure of $[Hg\{Fe_2Co(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)\}_2]$ (**3**). Dimensions Hg–Fe(1) 2.727(1), Hg–Fe(2) 2.735(1), Hg–Fe(3) 2.729(1), Hg–Fe(4) 2.726(1), Co(1)–Fe(1) 2.502(1), Co(1)–Fe(2) 2.503(1), Co(2)–Fe(3) 2.499(1), Co(2)–Fe(4) 2.494(1) Å; Fe(1)–Hg–Fe(2) 58.9(1), Fe(3)–Hg–Fe(4) 59.1(1), Fe(1)–Hg–Fe(3) 153.3(1), Fe(2)–Hg–Fe(4) 162.0(1)°.

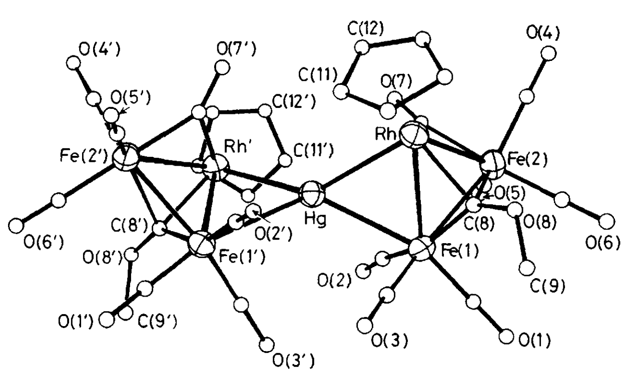

Figure 2. Molecular structure of $[Hg\{Fe_2Rh(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)\}_2]$ (**4**). Dimensions Hg–Rh 2.737(1), Hg–Fe(1) 2.775(2), Fe(1)–Rh 2.737(2), Fe(1)–Fe(2) 2.609(3), Fe(2)–Rh 2.570(2) Å; Fe(1)–Hg–Rh 59.5(1), Fe(1)–Hg–Rh′ 145.7(1)°.

a useful new synthetic route to mercury-bridged complexes.

Treatment of $[Fe_2M(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)]$ (**1**) M = Co[6] or (**2**) M = Rh[7] with $HgPh_2$ (toluene, 90 °C, 12 h) affords the mercury-bridged clusters $[Hg\{Fe_2M(\mu_3\text{-}COMe)(CO)_7(\eta\text{-}C_5H_5)\}_2]$ (**3**) M = Co or (**4**) M = Rh as the sole isolable products. Complexes (**3**) and (**4**) were characterised by spectroscopic† and crystallographic‡ methods, the molecular structures together with important geometrical parameters are shown in Figures 1 and 2. Although the precursor compounds (**1**) and (**2**) have similar solid state structures, with the hydrido ligand bridging the Fe–Fe vector in both cases,[6,7] complexes (**3**) and (**4**) have different metal framework geometries. Thus in (**3**) the Hg atom bridges the Fe(1)–Fe(2), Fe(3)–Fe(4) bonds, whilst in (**4**) it bridges the Fe(1)–Rh, Fe(1′)–Rh′ bonds.

The co-ordination geometry of the mercury atom in these systems is best thought of as linear. Thus the MPT–Hg–MPT angles are 174.8° for (**3**) and 174.7° for (**4**) (MPT = mid-point of bridged M–M vector), while the dihedral angles between the HgM_2 triangles are 46.2° for (**3**) and 71.9° for (**4**). The colinear sp hybrids of Hg^{2+} (and those of Ag^+ and Au^+) provide an isolobal relationship to H^+, and if π effects are not important[8] the electronic barrier to rotation about the MPT–Hg–MPT axis should be small, with the equilibrium geometry determined mainly by steric considerations. The solid state structure observed for (**3**) minimises the non-bonded interactions between the forward pointing carbonyl oxygens O(12), O(13), O(22), and O(23) on Fe(1), Fe(2), and the corresponding ones on Fe(3), Fe(4), and a similar effect is seen in (**4**) and in other compounds with bridged Hg,[2a,2c,2e] Au,[9a] and Ag[9b] atoms. In solution however, these compounds are likely to have a low barrier to rotation about the central 'naked' atom, and n.m.r. evidence[2f] of free rotation about the central Hg–Ru bond in $[cis\text{-}Ru(CO)_4\{HgRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9\}_2]$ supports this view.

The two triangular sub-units in complexes (**3**) and (**4**) are related by a twofold axis through Hg [approximate for (**3**), crystallographically defined for (**4**)] and are thus equivalent. Solution ^1H and ^{13}C n.m.r. data† for (**3**) are consistent with rapid rotation of each sub-unit about the MPT–Hg–MPT axis. The ^{199}Hg n.m.r. spectrum shows a temperature dependent singlet resonance. N.m.r. data for (**4**) however indicate several exchange processes. The four signals observed† in the ^{199}Hg spectrum (213 K) are assigned to isomers (I) (δ 848), (II) (δ 588), (IIIa) (δ 138), and (IIIb) (δ 54) on the basis of multiplicities due to ^{103}Rh coupling. Broadening is observed at higher temperatures, and no signal is seen above 263 K. The unsymmetrical isomer (II) is the major solution component. Isomers (IIIa) and (IIIb) presumably both have the same metal–metal connectivities observed in the crystal structure of (**4**) and may differ from each other either by a rotational component about MPT–Hg–MPT (as drawn), a variation in the methoxymethylidyne bonding mode,[6] or in the butterfly angle of the $HgFe_2Rh$ sub-unit.[10] The ^{13}C and ^1H spectra are consistent with rapid exchange of all isomers at 298 K, whilst at 213 K distinct signals due to the three major species (II),

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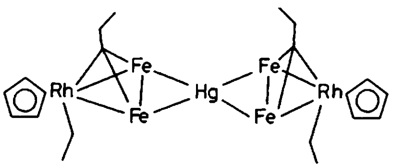
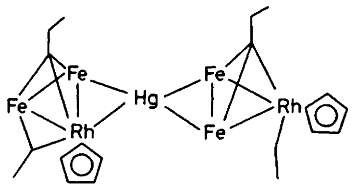
† *Selected spectroscopic data* (n.m.r. in $CDCl_3$ or CD_2Cl_2, *J* in Hz, ^{199}Hg chemical shifts to high frequency of Ξ = 17.910 841 MHz): (**3**) ν_{CO} (max., CH_2Cl_2) 2 054w, 2 023s, 2 017s (sh), 1 991m, 1 971m, 1 829 vw(br) cm^{-1}; n.m.r.: ^1H (213 K) δ 5.36 (C_5H_5), 4.58 (Me); $^{13}C\{H\}$ (213 K) δ 320.3 (*C*OMe), 230.9 (CoCO), 213.8, 209.8, 205.1 (FeCO), 90.7 (C_5H_5) 68.5 (Me); ^{199}Hg (223 K) δ 891, (298 K) δ 803. (**4**) ν_{CO} (cyclohexane) 2 060s, 2 051vs, 2 023vs, 2 014vs, 2 007(sh), 1 990m, 1 982s, 1 961m, 1 955m, 1 802w, 1 787w cm^{-1}; n.m.r.: ^1H (298 K) δ 5.63 [d, C_5H_5, *J*(Rh–H) 0.7], 4.34 (Me); (178 K) δ 5.69, 5.60, 5.54, 5.46 (C_5H_5), 4.33, 4.27, 4.19 (Me); $^{13}C\{^1H\}$ (298 K) δ 328.0 (*C*OMe), 210.5 (br,CO), 94.0 [d, C_5H_5, *J*(Rh–C) 2], 69.3 (Me); (213 K) δ 332.0 [d, *C*OMe, *J*(Rh–C) 40], 331.1 [d, *C*OMe, *J*(Rh–C) 40], 320.7 [d, *C*OMe, *J*(Rh–C) 22], 241.2 [d, μ-CO, *J*(Rh–C) 37], 235.0 [d, μ-CO, *J*(Rh–C) 40], 231.8—204.7 (CO), 94.6, 93.8, 93.3 (C_5H_5), 69.7, 69.3, 68.8, 68.4 (Me); ^{199}Hg (213 K), δ 848, 588 [d, *J*(Rh–Hg) 279], 138 [t, *J*(Rh–Hg) 333], 54 [t, *J*(Rh–Hg) 290]. Relative abundances of isomers (I), (II), (IIIa), (IIIb) are *ca.* 1 : 10 : 6 : 2 as judged from intensities in the ^{199}Hg spectrum. ^{13}C N.m.r. signals due to the μ_3-*C*OMe and μ-*C*O nuclei of isomer (IIIb) are not observed at 213 K; resonances in the C_5H_5 region are overlapping.

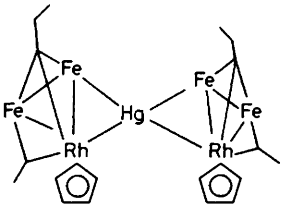
‡ *Crystal data* for (**3**): $C_{28}H_{16}O_{16}Co_2Fe_4Hg$, *M* = 1 150.3, orthorhombic, space group *Pbca* (D_{2h}^{15} No. 61), *a* = 16.572(4), *b* = 19.846(3), *c* = 20.224(5) Å, *U* = 6 651(2) Å^3, *Z* = 8, D_c = 2.30 g cm^{-3}, *F*(000) = 4 400 electrons, μ(Mo-K_α) = 59.7 cm^{-1}. (**4**): $C_{28}H_{16}O_{16}Fe_4HgRh_2$, *M* = 1 238.2, monoclinic, space group *C*2/*c* (C_{2h}^6 No. 15), *a* = 25.293(11), *b* = 9.084(3), *c* = 15.541(5) Å, β = 100.97(3), *U* = 3 505(2) Å^3, *Z* = 4, D_c = 2.35 g cm^{-3}, *F*(000) = 2 344 electrons, μ(Mo-K_α) = 69.5 cm^{-1}. Data were measured at ambient temperatures on an Enraf–Nonius CAD4-F diffractometer using graphite monochromated Mo-K_α *X*-radiation (λ = 0.71069 Å) for $2 \leqslant \theta \leqslant 25°$. Structures were corrected for absorption, solved by direct methods, and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were included in calculated positions. For (**3**) using 3 744 observed [$I \geqslant 2.5\,\sigma(I)$] data final residuals *R* (R_w) were 0.029 (0.035), whilst for (**4**) with 1 534 observed [$I \geqslant 2.5\,\sigma(I)$] data *R* ($R_w$) were 0.040 (0.043). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



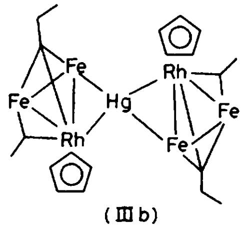
(I)



(II)



(IIIa)



(IIIb)

(IIIa), and (IIIb) are observed. These data imply a facile migration of the Hg atom around the edges of the Fe_2Rh triangles in (**4**), with the major solution component having a different structure to that in the solid state.

At an intermediate temperature (225 K) signals for two alkylidyne C (δ 332.0 and 320.7) and methyl (δ 69.3, 68.8) environments and one bridging (δ 234.9) CO resonance are broad, whilst other signals remain sharp, indicating a fluxional exchange between the inequivalent Hg bridged sites within the unsymmetrical isomer (II).

The hydride complexes $M_3(\mu\text{-H})(\mu\text{-COMe})(CO)_{10}$ (M = Fe, Ru) also afford $[Hg\{M_3(\mu\text{-COMe})(CO)_{10}\}_2]$ on treatment with $HgPh_2$; preliminary *X*-ray data for M = Ru shows a symmetrical structure with the Hg atom replacing the hydride ligand site in the precursor. This route to mercury-bridged complexes appears to have general applicability.

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