Selective Insertion of Mercury(II) Halides into the Ruthenium–Mercury Bonds of Trinuclear Ru_2Hg Clusters

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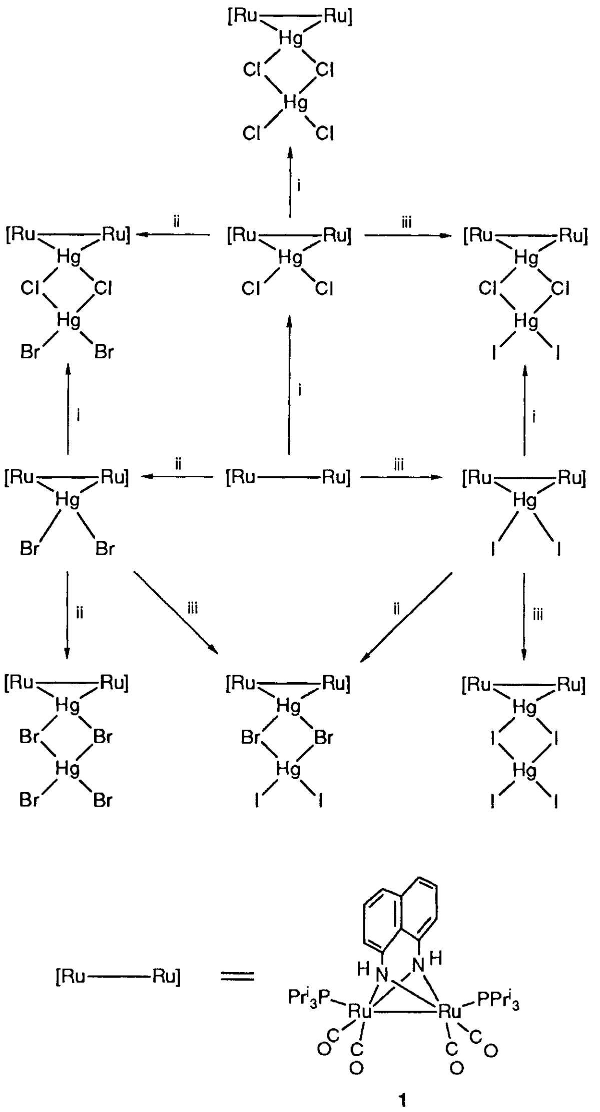
The complex $[Ru_2(\mu\text{-dan})(CO)_4(PPr^i_3)_2]$ **1** (H_2dan = naphthalene-1,8-diamine) reacts with HgX_2 (X = Cl, Br or I) to give the trinuclear clusters $[(\mathbf{1})HgX_2]$, which react with HgZ_2 (Z = Cl, Br or I) to form the insertion products $[(\mathbf{1})Hg(\mu\text{-}Z)_2HgX_2]$ only when Z is more electronegative than X, otherwise the addition products $[(\mathbf{1})Hg(\mu\text{-}X)_2HgZ_2]$ are obtained; the X-ray structure of $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]$ has been determined.

We have recently found that the readily accessible ruthenium(I) complex $[Ru_2(\mu\text{-dan})(CO)_6]$ (H_2dan = naphthalene-1,8-diamine)[1] reacts with electrophiles that attack at the Ru–Ru bond and with nucleophiles that substitute carbonyl ligands.[2] The X-ray structures of $[Ru_2(\mu\text{-dan})(CO)_4(L)_2]$ [L = $P(OPh)_3$,[2] PPh_3,[3]] have revealed very short Ru–Ru distances [2.571(1) and 2.579(1) Å, respectively]. Since the presence of triisopropylphosphine in the complex $[Ru_2(\mu\text{-dan})(CO)_4(PPr^i_3)_2]$ **1** increases the basic character of the Ru–Ru bond, and the dan ligand holds the two metal atoms very close together,[2–4] we decided to study the reactivity of complex **1** with mercury(II) halides. We also had in mind the fact that the synthesis of compounds containing transition metal–mercury bonds has been achieved (*a*) by treating mercury(II) halides or pseudohalides with anionic complexes,[5–7] (*b*) by the reaction of HgClPh with hydrido complexes,[8] (*c*) by forming adducts between mercury compounds and complexes containing electron-rich metals,[9] (*d*) through the oxidative addition of a mercury halide to a metal complex,[10] or (*e*) by reducing complexes with metal amalgams.[11] The uptake of several equivalents of HgX_2 by neutral complexes has been described;[9,12] however, the presence of lattice HgX_2 and the formation of ionic species through the abstraction of halide ions have been claimed as being responsible for the stability of such compounds.[12]

Complex **1** reacted with one equivalent of HgX_2 (X = Cl, Br or I) in tetrahydrofuran (THF), at room temperature, to give the adducts $[(\mathbf{1})HgX_2]$ quantitatively (Scheme 1). The triangular arrangement of the Ru_2Hg framework was confirmed by IR and ^{31}P NMR spectroscopy. Their IR spectra in the ν(CO) region were nearly identical, showing three bands (C_{2v} symmetry) (*ca.* 2035m, 2020m and 1975s cm^{-1}, thf) at higher wavenumbers than those of complex **1** (1991s, 1953m and 1918s cm^{-1}, THF). Their ^{31}P NMR spectra (Table 1) were



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Scheme 1 *Reagents*: i, $HgCl_2$; ii, $HgBr_2$; iii, HgI_2

Table 1 $^{31}P\{^1H\}$ NMR data[a]

Complex	$\delta(^{31}P)$	$^2J(^{31}P-^{199}Hg)$/Hz
(**1**)	49.0	
[(**1**)$HgCl_2$]	56.5	1118
[(**1**)$HgBr_2$]	55.3	1087
[(**1**)HgI_2]	52.7	1004
[(**1**)$Hg(\mu-Cl)_2HgCl_2$]	60.2	1168
[(**1**)$Hg(\mu-Br)_2HgBr_2$]	60.4	1123
[(**1**)$Hg(\mu-I)_2HgI_2$]	60.3	1002
[(**1**$Hg(\mu-Cl)_2HgBr_2$]	60.3	1156
[(**1**)$Hg(\mu-Cl)_2HgI_2$]	60.1	1109
[(**1**)$Hg(\mu-Br)_2HgI_2$]	60.2	1076

[a] Spectra recorded at 121.5 MHz in [$^2H_6$]acetone solutions; chemical shifts (δ) referred to external 85% H_3PO_4; all resonances are singlets with satellites.

singlets with satellites due to coupling to ^{199}Hg (17% natural abundance). Interestingly, the ^2J ($^{31}P-^{199}Hg$) values varied regularly with the electronegativity of the halogens, ranging from 1004 Hz for [(**1**)HgI_2] to 1118 Hz for [(**1**)$HgCl_2$], indicating that the electron density on the Ru atoms is significantly affected by the nature of the halogen bonded to the Hg atom.

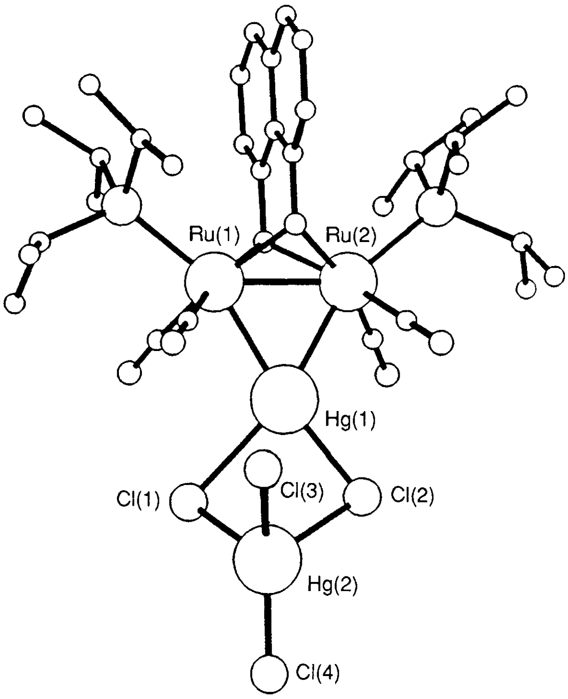

Fig. 1 The molecular structure of [(**1**)$Hg(\mu-Cl)_2HgCl_2$]; bond lengths: Ru(1)–Ru(2), 2.827(2); Ru(1)–Hg(1), 2.758(1); Ru(2)–Hg(1), 2.775(2); Hg(1)–Cl(1), 2.834(6); Hg(1)–Cl(2), 2.537(4); Hg(2)–Cl(1), 2.652(5); Hg(2)–Cl(2), 2.685(5); Hg(2)–Cl(3), 2.427(6); Hg(2)–Cl(4), 2.301(9) Å; bond angles: Ru(1)–Hg(1)–Ru(2), 61.5(0); Cl(1)–Hg(1)–Cl(2), 82.9(2)

The addition of one equivalent of HgX_2 (X = Cl, Br or I) to THF solutions of [(**1**)HgX_2] led to the isolation of yellow solids (Scheme 1). Although their IR spectra did not differ significantly from those of the parent compounds, their microanalysis and ^{31}P NMR spectra confirmed the incorporation of a second mercury halide fragment.

The way in which the second HgX_2 fragments are attached to the parent compounds was indicated by an X-ray structure determination of [(**1**)$Hg(\mu-Cl)_2HgCl_2$]·CH_2Cl_2† (Fig. 1). The structure shows an $HgCl_2$ fragment attached through the Hg atom to the two Ru atoms of the original complex **1** and to the Hg atom of the second $HgCl_2$ fragment through both Cl atoms. The coordination around Hg(1) is distorted square planar [dihedral angle between the Ru(1)–Ru(2)–Hg(1) and Cl(1)–Hg(1)–Cl(2) planes 22.2(1)°], whereas that around Hg(2) is tetrahedral. Although the observed Ru–Ru distance, 2.827(2) Å, is *ca.* 0.3 Å longer than that found in [$Ru_2(\mu$-dan$)(CO)_4(L)_2$] [L = $P(OPh)_3$,[2] PPh_3,[3]], it is still rather short. The Hg···Hg distance is out of the bonding range. Many compounds containing Hg atoms in a tetrahedral environment are known,[13] but mercury compounds with a distorted square-planar co-ordination are rare; three examples are the complexes [$Hg\{Ru_3(NO)(CO)_{10}\}_2$],[5b] [$Hg\{Ru_3(CO)_9(C_6H_9)\}_2$][7] and [$Hg_2Br_2\{Ru_3(CO)_9(C_6H_9)\}_2$].[8]

The relative positions (bridging or terminal) of the halogen atoms in the complexes containing two different mercury(II) halide fragments were deduced from the values of their ^2J

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† *Crystal data*: $C_{32}H_{50}Cl_4Hg_2N_2O_4P_2Ru_2 \cdot CH_2Cl_2$, M = 1418.77, monoclinic, space group $P2_1/n$, a = 15.840(7), b = 12.694(4), c = 23.366(2) Å, β = 105.74(2)°, V = 4522(2) Å^3, Z = 4, D_c = 2.08 g cm^{-3}. Mo-Kα radiation (graphite monochromator, λ = 0.71073 Å), μ(Mo-Kα) = 78.75 cm^{-1}, $F(000)$ = 2704, T = 273 K. Final conventional R factor = 0.054 for 4435 'observed' reflections [$I > 3\sigma(I)$] and 535 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

(^{31}P–^{199}Hg) coupling constants (Table 1). Since the effect of the electronegativity of the bridging halogens on the coupling constants should be greater than that of the electronegativity of the terminal halogens, and since the higher the electronegativity of the halogens in the complexes the greater the coupling constant, the observed data clearly indicate that the most electronegative halogens always occupy bridging positions, as represented in Scheme 1. Therefore, it can be concluded that mercury(II) halides insert into the Ru–Hg bonds of [(**1**)HgX$_2$] (X = Cl, Br or I) only when the new halogen is more electronegative than X, otherwise they simply coordinate to both X atoms of [(**1**)HgX$_2$]. Further work in this area, including mechanistic studies and the use of organometallic mercury compounds, is in progress.

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