# The Preparation of Some Manganese–Mercury Cluster Complexes and a Study of Their Redistribution Reactions

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The heterometallic cluster complexes  $[Mn_2(\mu-HgPh)(\mu-PPh_2)(CO)_8]$  (2),  $[Mn_2(\mu-HgCl)(\mu-PPh_2)(CO)_8]$  (3), and  $[Hg\{Mn_2(\mu-PPh_2)(CO)_8\}_2]$  (4) have been prepared by reaction of  $[N(PPh_3)_2][Mn_2(\mu-PPh_2)(CO)_8]$  (1) with, respectively, HgPhCl, HgCl<sub>2</sub>, and Hg(CN)<sub>2</sub>. Some redistribution reactions of (2), (3), and (4) (in which the Hg atom is three- or four-co-ordinate) have been investigated and are compared with previously studied redistribution reactions of transition-metal-mercury complexes containing two-co-ordinate mercury atoms.

Compounds containing mercury bonded to one or two mononuclear transition-metal centres were among the first heterometallic species to be reported <sup>1</sup> and many such complexes are now known.<sup>2-4</sup> It is only recently, however, that the first compound containing mercury bonded to a polynuclear transition-metal fragment,  $[Ru_3(\mu-HgBr)(\mu_3-C=CCMe_3)(CO)_9]$ , has been prepared.<sup>5</sup> An X-ray crystal structure determination of this complex revealed that the mercury atom bridges an edge of the ruthenium triangle and the Ru–Ru distances indicate that the bridged Ru atoms are also directly bonded to each other.

We have recently described the preparation of the triangulomixed-metal clusters,  $[Mn_2\{\mu-Au(PR_3)\}(\mu-PPh_2)(CO)_8]$ , by means of the reaction of the dinuclear anion  $[Mn_2(\mu-PPh_2) (CO)_8]^-$  (1) with cationic gold complexes.<sup>6</sup> The molecular structure of these compounds was shown by an X-ray determination<sup>6</sup> to be related to that of the hydrido-complex  $[Mn_2(\mu-H)(\mu-PPh_2)(CO)_8]^{6,7}$  with the gold phosphine moiety replacing the bridging hydride ligand. The isolobal nature of the  $[Au(PR_3)]^+$  and hydride ligands has been previously noted<sup>8,9</sup> and it seemed to us that this analogy could be extended to include  $[HgX]^+$  ligands (X = e.g. Ph or Cl). We have sought therefore to prepare mercurial analogues of the above manganese-gold complexes by reaction of the anion (1) with mercury(II) compounds. These reactions have led to the synthesis of the series of complexes  $[Mn_2(\mu-HgX) (\mu$ -PPh<sub>2</sub>)(CO)<sub>8</sub>] [X = Ph (2); X = Cl (3)] and [Hg{Mn<sub>2</sub>( $\mu$ - $PPh_2(CO)_{8}_2$  (4) which are obtained on treatment of (1) with HgPhCl, HgCl<sub>2</sub>, and Hg(CN)<sub>2</sub> respectively. Spectroscopic data indicate that in these complexes the mercurial ligand bridges the Mn-Mn bond, thus imposing three- or four-fold co-ordination on the mercury atom.

Redistribution reactions of transition-metal-mercury complexes have been intensively studied.<sup>2,10</sup> Such reactions have not been investigated, however, for any complex in which the mercury atom has a higher co-ordination number than two. We have therefore investigated some redistribution reactions of (2)—(4) in order to determine whether the higher coordination number of the mercury atom in these complexes has any effect on the course of the reactions. For two-coordinate mercury the position of equilibrium in reaction (i)

$$HgX_2 + M_2Hg \Longrightarrow 2MHgX$$
 (i)

(M = mononuclear transition-metal fragment; X = halide, alkyl, or aryl) lies, in general, far to the right for X = halide <sup>10</sup> and far to the left for X = alkyl or aryl.<sup>2,3</sup>

## **Results and Discussion**

(a) Preparation of the Complexes.—(i)  $[Mn_2(\mu-HgPh)(\mu-PPh_2)(CO)_8]$  (2). Addition of a stoicheiometric amount of  $[N(PPh_3)_2][Mn_2(\mu-PPh_2)(CO)_8]$  (1) to a dichloromethane solution of HgPhCl at -70 °C afforded a bright yellow solution. Chromatography on silica at -70 °C followed by rapid removal of solvent at -30 to -20 °C under high vacuum gave (2) in *ca*. 80% yield as a yellow powder. Solutions of (2) readily equilibrate at these temperatures (-30 to -20 °C) to give (4) and HgPh<sub>2</sub>, hence the solvent must be removed rapidly if (2) is to be obtained in a pure state. Once isolated in the solid state, however, (2) is stable with respect to symmetrisation to (4) and HgPh<sub>2</sub> and may be stored for several weeks in air without change.

(ii)  $[Mn_2(\mu-HgCl)(\mu-PPh_2)(CO)_8]$  (3). A CH<sub>2</sub>Cl<sub>2</sub> solution of (1) was added to a vigorously stirred MeOH solution of HgCl<sub>2</sub> (ten-fold excess) at 20 °C. [N(PPh<sub>3</sub>)<sub>2</sub>]Cl, excess HgCl<sub>2</sub>, and a small amount of (4) (11%) [presumably formed from attack of (1) on (3), see below] were removed by chromatography to afford (3) in 89% yield as an orange-yellow powder. Microanalytical, and i.r. and <sup>1</sup>H n.m.r. spectroscopic data for (2) and (3) are given in the Table. The close similarity between the v(CO) absorption patterns in the i.r. spectra (Figure 1) of (2), (3), and  $[Mn_2{\mu-Au(PMe_2Ph)}(\mu-PPh_2)(CO)_8]$  suggests that both (2) and (3) possess a similar structure (Figure 2) to that determined crystallographically for the gold complex, in which the hetero-metal symmetrically bridges the Mn-Mn bond.<sup>6</sup> The <sup>13</sup>CO n.m.r. spectrum of (3) (recorded at  $-40 \degree C$ in CDCl<sub>3</sub>, <sup>1</sup>H noise decoupled) shows three resonances of relative intensities 1:1:2 and is consistent with the structure proposed:  $\delta$  221.3 (s, 2 CO), 222.1 [d, <sup>2</sup>J(PC) = 16, 2 CO],

Table 1. Spectroscopic and microanalytical data for the complexes

• • •	-		Analysis * (%)	
Compound	v(CO)/cm <sup>-1</sup>	<sup>1</sup> H N.m.r. (δ)	C	—————————————————————————————————————
(2) $[Mn_2(\mu-HgPh)(\mu-PPh_2)(CO)_8]$ (3) $[Mn_2(\mu-HgCl)(\mu-PPh_2)(CO)_8]$ (4) $[Hg_1^{\prime}Mn_2(\mu-PPh_2)(CO)_8_2]$	2 043m, 2 003s, 1 979m, 1 955m 2 061m, 2 017s, 1 998m, 1 976m 2 061w, 2 045s, 2 011s, 1 998 (sh), 1 979m, 1 955m	7.7 (m, 15 H, Ph) 7.6 (m, 10 H, Ph) 7.7 (m, 20 H, Ph)	39.1 (39.2) 32.0 (31.8) 38.5 (38.8)	2.0 (1.9) 1.4 (1.3) 1.6 (1.6)

Calculated values are given in parentheses.



Figure 1. Infrared spectra of  $[Mn_2(\mu-ML)(\mu-PPh_2)(CO)_8]$  complexes: (a)  $ML = Au(PMe_2Ph)$ ; (b) ML = HgCl; (c) ML = HgPh

205.4 [d,  ${}^{2}J(PC) = 14$  Hz, 4 CO]. Mercury-199 satellites were observed on the resonance of the phosphido-bridge in the  ${}^{31}P$  n.m.r. spectrum of (3) [relative to P(OMe)\_3]: 65.2 p.p.m. [t,  ${}^{2}J(HgMnP) = 258$  Hz, 1 P]. Since this coupling is larger than other  ${}^{2}J(HgP)$  couplings reported in the literature [ ${}^{2}J(HgSeP) = 122$ —141 Hz  ${}^{11}$  and  ${}^{2}J(HgCP) = 128$  Hz  ${}^{12}$ ] it



Figure 2. Proposed structures for the manganese-mercury complexes

seems unlikely that (3) dissociates significantly in solution to give, e.g., (1) and [HgCl]<sup>+</sup>.

The shift of ca. 23 cm<sup>-1</sup> to higher energy of the v(CO) bands of (3) relative to those of (2) is comparable with that observed for the v(CO) absorptions of  $[Co(CO)_4(HgCl)]$  relative to those of  $[Co(CO)_4(HgMe)]$  (27 cm<sup>-1</sup>) and may be attributed to the variation in electron-donating and -withdrawing properties between the HgR and HgX ligands.<sup>13</sup>

(iii)  $[Hg\{Mn_2(\mu-PPh_2)(CO)_8\}_2]$  (4). Reaction of (1) in  $CH_2Cl_2$  with  $Hg(CN)_2$  in MeOH afforded, after removal of the  $CH_2Cl_2$  solvent, a red precipitate of  $[Hg\{Mn_2(\mu-PPh_2)(CO)_8\}_2]$  (4) in 89% yield. Compound (4) could also be prepared in essentially quantitative yield by reaction of (3) with one equivalent of (1) in  $CH_2Cl_2$  solution. Microanalytical and v(CO) i.r. data for (4) are given in the Table. As with the other manganese-mercury complexes, a mass spectrum of (4) could not be obtained, presumably because of its low volatility. Compound (4) is nearly insoluble in most common organic solvents except dichloromethane, in which it is sparingly soluble.

Complexes containing mercury bonded to four transitionmetal atoms are rare. Indeed, there has been only one previous report <sup>14</sup> in the literature of such a cluster, [{MoHgMo(CO)<sub>3</sub>-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)}<sub>4</sub>], the structure of which is based on a cubic core of Mo and Hg atoms with the mercury atoms being in a distorted tetrahedral environment.\* Although we have not been able to grow crystals of (4) suitable for an X-ray diffraction study, it seems reasonable to suppose that the coordination geometry of the mercury atom in (4) will also be distorted tetrahedral, resulting in a structure such as that shown in Figure 2.

(b) Redistribution Reactions.—The redistribution and interconversion reactions of (2), (3), and (4) are summarised in the Scheme.

Compound (2) redistributes rapidly in CH<sub>2</sub>Cl<sub>2</sub> solution to give the symmetrical mercurial (4) and HgPh<sub>2</sub>. Reaction is essentially complete within 2—3 min at room temperature, the v(CO) i.r. spectrum of the solution, recorded immediately after dissolution of (2), being superimposable on that of an authentic solution of (4) prepared from (1) and Hg(CN)<sub>2</sub>. Removal of solvent and extraction of the solid residue with diethyl ether afforded the stoicheiometrically required amount of HgPh<sub>2</sub>, identified by its mass and i.r. spectra. Reaction also occurred readily at low temperatures, being essentially complete within 60 min at -30 °C. The reaction is irreversible; thus stirring a CH<sub>2</sub>Cl<sub>2</sub> solution of (4) and a large excess of HgPh<sub>2</sub> at room temperature yielded no detectable amount of (2) as judged by t.l.c. and i.r. spectroscopy. This symmetrisation reaction [equation (ii), R = alkyl or aryl] is

<sup>\*</sup> Note added at proof: The recently reported crystal structure of  $[Hg{Ru_3(CO)_9(C_2Bu^i)}_2]$  provides a further example of a complex of this type.<sup>15</sup>

645



Scheme. (i) HgPhCl,  $CH_2Cl_2$ , -70 °C; (ii) Hg(CN)<sub>2</sub>, MeOH-CH<sub>2</sub>Cl<sub>2</sub> (1:1); (iii) [Mn<sub>2</sub>( $\mu$ -PPh<sub>2</sub>)(CO)<sub>8</sub>]<sup>-</sup>, CH<sub>2</sub>Cl<sub>2</sub>; (iv) CH<sub>2</sub>Cl<sub>2</sub>, dissolve,  $-\frac{1}{2}$ HgPh<sub>2</sub>; (v) HgCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>-MeOH (1:1); (vi) HgPhCl, CH<sub>2</sub>Cl<sub>2</sub>, -30 °C,  $-HgPh_2$ 

$$2MHgR \Longrightarrow M_2Hg + HgR_2 \qquad (ii)$$

entirely analogous to that undergone by most MHgR complexes where M is a mononuclear transition-metal fragment.<sup>2,3</sup> We have also investigated the redistribution reaction (iii),

which does not appear to have been studied for M = mononuclear fragment. We find that addition of (2) to a solution of HgPhCl in CH<sub>2</sub>Cl<sub>2</sub> or tetrahydrofuran at room temperature, or addition of two equivalents of HgPhCl to a dichloromethane solution of (1) at -30 °C, results in the formation of (3) and HgPh<sub>2</sub> identified by mass and i.r. spectroscopy, in the expected stoicheiometric amounts. Reaction is rapid in either case, being complete within the time required to make i.r. spectroscopic measurements. Attempts to drive this reaction in the opposite sense were unsuccessful. Thus, stirring a CH<sub>2</sub>Cl<sub>2</sub> solution of (3) and a large excess of HgPh<sub>2</sub> for 16 h at -70 °C [at which temperature any (2) formed would be stable with respect to redistribution to (4) and HgPh<sub>2</sub>] caused no change in the i.r. spectrum of the solution. On warming the solution to room temperature a small amount of (4) was formed and detected by i.r. spectroscopy. It is not clear, however, whether the formation of (4) under these conditions involves (2) as an intermediate.

Most of the redistribution reactions shown in the Scheme proceed rapidly at room temperature or below and the course of the reactions is determined by thermodynamic considerations. Kinetic factors can also be important, however, as is illustrated by reaction (iv). This reaction has been widely

$$M_2Hg + HgCl_2 \rightarrow 2MHgCl$$
 (iv)

studied for M = mononuclear transition-metal fragment and invariably proceeds rapidly to completion in solution at room temperature.<sup>10</sup> The reaction of (4) with HgCl<sub>2</sub> under these conditions, however, requires ca. 36 h for complete conversion of (4) to the unsymmetrical product (3). This observation can be readily accounted for it if is assumed that the preferred pathway for the redistribution reactions is via a bimolecular, associative process. The transition state for such a process would involve an increase in the co-ordination number of the mercury atom, and such a process is not unreasonable for complexes containing two- or three-co-ordinate mercury. Co-ordination numbers greater than four are not, however, normally observed for mercury in transition-metal complexes and, since the mercury atom in (4) is already four-co-ordinate, it is thus unlikely to react via an associative pathway. Hence redistribution reactions involving (4) may occur via a (slower) dissociative route.

#### Experimental

All reactions were performed under dry, oxygen-free nitrogen in nitrogen-saturated solvents freshly distilled off appropriate drying agents.

Infrared spectra were recorded in  $CH_2Cl_2$  solution in 0.5mm NaCl cells on a Perkin-Elmer 983 spectometer. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. spectra were recorded on a Bruker WM250 spectrometer in  $CD_2Cl_2$ solution using the solvent resonances or  $P(OMe)_3$ , as appropriate, as internal standards. Microanalyses were carried out at the University Chemical Laboratory, Cambridge.

Chromatography was performed on silica (Keiselgel 60, 70–230 mesh) using dichloromethane-hexane (10:1) as eluant.

 $[N(PPh_3)_2][Mn_2(\mu-PPh_2)(CO)_8]$  was prepared as previously described.<sup>6</sup>

(i)  $[Mn_2(\mu-HgPh)(\mu-PPh_2)(CO)_8]$  (2).— $[N(PPh_3)_2][Mn_2(\mu-PPh_2)(CO)_8]$  (1) (0.053 g, 0.05 mmol) was added to a vigorously stirred CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) solution of HgPhCl (0.016 g, 0.05 mmol) at -70 °C to afford a bright yellow solution of (2). This solution was immediately transferred to the top of a low-temperature chromatography column at -70 °C. Chromatography at -70 °C afforded a solution of (2) as the first fraction eluted. Rapid removal of solvent at -30 to -20 °C under high vacuum gave (2) (*ca*. 0.29 g, 80%) as a yellow powder. Subsequent fractions gave small quantities of (3) and (4). Redistribution of (2) to (4) and HgPh<sub>2</sub> occurs readily in solution even at temperatures of *ca*. -30 °C. In order to obtain (2) free from (4) and HgPh<sub>2</sub> it is therefore vital that removal of solvent following chromatography be accomplished rapidly and at low temperatures.

(ii)  $[Mn_2(\mu-HgCl)(\mu-PPh_2)(CO)_8]$  (3).—A solution of (1) (0.022 g, 0.021 mmol) in  $CH_2Cl_2$  (5 cm<sup>3</sup>) was added dropwise to a vigorously stirred MeOH (10 cm<sup>3</sup>) solution of HgCl<sub>2</sub> (0.052 g, 0.2 mmol). A golden orange solution resulted, with a slight precipitate of (4) also being formed. Chromatography on silica afforded, after removal of solvent (in order of decreasing  $R_f$  values) a red complex,  $[Hg\{Mn_2(\mu-PPh_2)-(CO)_8\}_2]$  (4) (0.0015 g, 11%), and an orange powder (3) (0.014 g, 89%).

(iii)  $[Hg{Mn_2(\mu-PPh_2)(CO)_8}_2]$  (4).—A solution of (1) (0.053 g, 0.05 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>) was added to a stirred solution of  $Hg(CN)_2$  (0.007 g, 0.028 mmol) in MeOH (10 cm<sup>3</sup>). Removal of the  $CH_2Cl_2$  solvent afforded a red precipitate of (4) which was collected by filtration, washed twice with 5-cm<sup>3</sup> aliquots of MeOH {to remove  $[N(PPh_3)_2]CN$  and excess  $Hg(CN)_2$  and dried (yield 0.027 g, 89%).

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