Synthesis of Heterotrimetallic Complexes containing M–Hg–Pt (M = Pt, Fe, Mn, or Co) Arrays

Oriol Rossell,* Miquel Seco, and Immaculada Torra
Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Heterotrimetallic complexes $[Hg\{PtR(PPh_3)_2\}_2]$ (R = 2,3,4-$C_6H_2Cl_3$, 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4, or C_6Cl_5) have been prepared by reaction of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ with $[RHg{-}PtR(PPh_3)_2]$. From the reactions of $[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2]$ with $[Hg\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, $[Hg\{Mn(CO)_5\}_2]$, and $[Hg\{Co(CO)_4\}_2]$, the complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$, $[(CO)_5Mn{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$, and $[(CO)_4Co{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$ were isolated. The scope of these reactions is discussed. All the compounds were characterized by i.r. and ^{31}P n.m.r. spectroscopy.

The synthesis of heterobimetallic platinum–mercury metal–metal bonded complexes has been the subject of a number of recent studies.[1–3] Insertion of the 14-electron, carbene like PtL_2 (L = neutral ligand) fragment into Hg–X (X = halide) or Hg–E (E = Group 4B atom) is a general method for obtaining organoplatinum–mercury compounds having a metal–metal bond. These complexes can be isolated if the ligand attached to the mercury atom is a strongly electronegative group (*e.g.* CF_3[4]), or when steric crowding occurs near the intermetallic bond (*e.g.* C_6Cl_5[1]).

In this paper we describe the extension of the Pt^0 insertion into heterobimetallic $[RHg{-}PtR(PPh_3)_2]$ (R = polychloroaryl group) complexes in order to obtain heterotrimetallic $[Hg\{PtR(PPh_3)_2\}_2]$ derivatives. It is noteworthy that the insertion of the $Pt(PPh_3)_2$ fragment into one of the Hg–C bonds does not deactivate the second Hg–C bond, in contrast with the behaviour of the complex $[(C_6F_5)_3Ge{-}Hg{-}Pt(PPh_3)_2{-}Ge(C_6F_5)_3]$[5] where the $Pt(PPh_3)_2$ moiety completely deactivates the Hg–Ge bond. When this work was in progress a di-insertion of PtL_2 into $Hg[Ge(CF_3)_3]_2$ was published.[6] We have tried to apply the related method to other complexes M′–HgR (M′ = transition metal carbonyl fragment) in an effort to form metal–metal bonded heterotrimetallic complexes. Unfortunately the previous synthesis of M′–HgR [M′ = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$, $Mn(CO)_5$, or $Co(CO)_4$] was not accomplished, because these compounds spontaneously symmetrised giving HgR_2 and HgM'_2. However, we have been able to prepare the complexes with M′–Hg–Pt arrangements $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$, $[(CO)_5Mn{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$ and $[(CO)_4Co{-}Hg{-}Pt(C_6Cl_5)(PPh_3)_2]$, *via* an exchange process between HgM'_2 and $[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2]$. A preliminary account[7] had been given of the results described in this paper.

Results and Discussion

Synthesis and Properties.—Treatment of the complexes $[RHg{-}PtR(PPh_3)_2]$ (R = 2,3,4-$C_6H_2Cl_3$, 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4, or C_6Cl_5) with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ in boiling toluene affords the new yellow crystalline compounds (**1**)—(**4**) in *ca.* 90—95% yield, according to the stoicheiometry of the reaction (1). Complexes (**1**)—(**4**) can be also prepared by

$$[RHg{-}PtR(PPh_3)_2] + [Pt(CH_2{=}CH_2)(PPh_3)_2] \longrightarrow \underset{(\mathbf{1})\text{—}(\mathbf{4})}{[Hg\{PtR(PPh_3)_2\}_2]} + CH_2{=}CH_2 \quad (1)$$

a one-step synthesis, treating two moles of the Pt^0 complex with one mole of the corresponding HgR_2 derivative. Yields are similar.

Compounds (**1**)—(**4**) were characterized by microanalyses and n.m.r. properties (Table 1). In the i.r. spectra, the bands of the polychlorophenyl groups appear at similar positions to those of $[RHg{-}PtR(PPh_3)_2]$.[1] The spectroscopic data for all compounds are very similar implying similar structures. An *X*-ray diffraction study on compound (**2**)[7] revealed a linear Pt–Hg–Pt array (Pt–Hg 2.637 Å, Pt–Hg–Pt 169.57°) with a *cis*

Table 1. Analytical[a] and physical data (n.m.r.: δ/p.p.m., *J*/Hz) for the complexes $[Hg\{PtR(PPh_3)_2\}_2]$

R	M.p.[b] (°C)	Analysis (%)		δP_A[c]	δP_B	$J(P_BPt)$	$^2J(P_AHg)$	$^2J(P_BHg)$	$^2J(P_AP_B)$
		C	H						
(**1**) 2,3,4-$C_6H_2Cl_3$[d]	196—198	(50.4) 50.9	(3.2) 3.3	40.2[d]	21.5[d]	2 688	1 880	218	8.2
(**2**) 2,4,6-$C_6H_2Cl_3$[e]	214—216	(50.4) 50.6	(3.2) 3.3	44.2	25.8	2 916	1 905	210	8.5
(**3**) 2,3,5,6-C_6HCl_4	209—211	(48.7) 48.8	(3.0) 3.2	47.0	24.9	2 980	1 870	200	8.9
(**4**) C_6Cl_5	202—203	(47.1) 47.7	(2.8) 2.9	45.5	22.4	2 970	1 875	205	8.3

[a] Required values are given in parentheses. [b] With decomposition. [c] P_A is *trans* to the Hg atom. [d] N.m.r. data for the *anti* isomer. For the *syn* isomer, $\delta P_A = 40.5$, $\delta P_B = 22.8$; similar coupling constants are observed in both isomers. [e] Other $^{31}P\text{-}\{^1H\}$ n.m.r. parameters: $J(P_APt) = 2\,129$, $^3J(P_APt) = 524$, $^4J(P_AP_{A'}) = 108$ Hz.

configuration of the bulky phosphines attached to the platinum atoms. All the compounds reported are air-stable as solids and in solution, but slow decomposition with mercury deposition is observed under strong sunlight.

Having established the structure of these complexes it was possible to devise a rational synthesis of trimetallic metal–metal bonded complexes with three different atoms by promoting a PtL_2 fragment insertion into a Hg–C bond of a bimetallic complex containing a preformed metal–mercury bond, *e.g.* M'–$Hg(C_6Cl_5)$ (M' = transition metal carbonyl fragment). However, this method could not be applied when M' = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$, $Mn(CO)_5$, or $Co(CO)_4$, because M'–$Hg(C_6Cl_5)$ derivatives underwent a spontaneous redistribution giving HgM'_2 and $Hg(C_6Cl_5)_2$ and, consequently, they were not isolable. We are examining now the action of zerovalent platinum complexes on other transition metal–mercury–carbon bonded compounds. Therefore the availability of the starting materials is a major limitation of the process described. However, we have been able to synthesize complexes containing M'–Hg–Pt arrays by the exchange of $[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2]$ with HgM'_2.

It has been reported that mixed organomercury compounds of the type XHgR and RHgR′ (X = halide; R,R′ = organic group) are obtained by the exchange of HgR_2 with HgX_2 or HgR'_2. The application of this process when R and R′ are different metallic fragments can afford a rational method for obtaining trimetallic M'–Hg–M' compounds.

Thus, the complexes M'–Hg–$Co(CO)_4$, where M' = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$, $Mo(CO)_3(\eta^5\text{-}C_5H_5)$, or $W(CO)_3(\eta^5\text{-}C_5H_5)$ were obtained by redistribution reactions between $[Hg\{Co(CO)_4\}_2]$ and the corresponding HgM'_2.[8] This type of redistribution reaction has also been used to prepare compounds in which the co-ordination number of mercury is higher than two.[9]

The above facts prompted us to investigate the synthetic applicability of the process (2). We have found by ^{31}P n.m.r.

$$[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2] + Hg\text{–}M'_2 \longrightarrow 2[M'\text{–}Hg\text{–}Pt(C_6Cl_5)(PPh_3)_2] \quad (2)$$

$$(\mathbf{5});\ M' = Fe(CO)_2(\eta^5\text{-}C_5H_5)$$
$$(\mathbf{6});\ M' = Mn(CO)_5$$
$$(\mathbf{7});\ M' = Co(CO)_4$$

spectroscopy that the mixed metal–mercury compound is the only product detectable at room temperature, indicating that the equilibrium lies far to the right of reaction (2).

In the light of these results, it is possible to conclude that the reaction (2) follows the pattern given by Mays and Robb[8] in the sense that very different metallic fragments attached to mercury atoms move the equilibrium to the right. This conclusion is strengthened by the fact that all attempts to form unsymmetrical $[(PPh_3)_2RPt\text{–}Hg\text{–}PtR'(PPh_3)_2]$ derivatives from $[RHg\text{–}PtR'(PPh_3)_2]$ and $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ were unsuccessful since the high similarity between the $PtR(PPh_3)_2$ and $PtR'(PPh_3)_2$ fragments led to the redistribution of the former compound.

In our opinion, reaction (2) is specially interesting because it allows platinum complexes containing metal–metal bonds to be obtained and it is well known that the lack of platinum metallate anions has been an important limitation for building bi- and tri-metallic metal–platinum bonded derivatives. Analyses, decomposition temperatures, i.r. and n.m.r. spectra are given in Table 2. Compounds (**5**)—(**7**) are air-stable as solids, but their toluene solutions are not so.

N.M.R. Studies.—Because of the limited natural abundance of ^{195}Pt (33.7%) and ^{199}Hg (16.8%), the ^{31}P n.m.r. spectra of the trinuclear $HgPt_2$ compounds consist of superimposed spectra due to the following mixture of isotopomers: (**A**) PtHgPt (36.5%), (**B**) $^{195}PtHgPt$ (37.15%), (**C**) $^{195}PtHg^{195}Pt$ (9.4%), (**D**) $^{195}Pt^{199}HgPt$ (7.5%), (**E**) $Pt^{199}HgPt$ (7.4%), and (**F**) $^{195}Pt^{199}Hg^{195}Pt$ (1.9%). Isotopomer (**A**) shows two signals due to an A_2M_2 spin system with *J*(PP) not resolved; for (**D**) and (**F**) the combination of low natural abundance and spectral complexity results in signals too weak to be observed. (**E**) shows two doublets corresponding to the two ^{31}P–^{199}Hg couplings. Finally, (**B**) and (**C**) must be analysed in the second order since the ^{195}Pt nuclei exhibit magnetic non-equivalence in relation to the phosphorus nucleus. Thus, (**B**) affords an AA′MM′X spin system and shows eight signals due to the AA′ part and three signals due to the MM′ part. On the other hand, (**C**) can be analysed as an AA′MM′XX′ spin system, and therefore could give ten signals for the AA′ part as has been observed for $[Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)]$.[10] In our case, the limited solubility of these complexes in all solvents only permitted the two external more intense signals to be seen. This fact has precluded the determination of *J*(PtPt) by spectral simulation.

It is important to point out that the signals due to isotopomers (**B**) and (**C**) appear as doublets because of the increase of phosphorus–phosphorus coupling constants in the isotopomers containing ^{195}Pt.

Whereas $J(P_APt)$, $J(P_BHg)$, and $J(P_AHg)$ can be obtained by a simple first-order analysis, the other coupling constants must be obtained with computer assistance. Figure 1 shows the ^{31}P n.m.r. spectrum of $[Hg\{Pt(2,4,6\text{-}C_6H_2Cl_3)(PPh_3)_2\}_2]$ and its analyses based on the superposition of three kinds of spin

Table 2. Analytical[a] data and physical parameters of complexes $[M'\text{–}Hg\text{–}Pt(C_6Cl_5)(PPh_3)_2]$

M′	M.p.[b] (°C)	Analysis (%) C	Analysis (%) H	$\nu(CO)$[c]/ cm^{-1}	δP_B/ p.p.m.	$J(P_BPt)$/ Hz	$^2J(P_BHg)$/ Hz
(**5**) $Fe(CO)_2(\eta^5\text{-}C_5H_5)$[d]	205—207	(43.7) 43.9	(2.6) 2.4	1 945vs, 1 895s, 1 880s	25.2	3 160	332
(**6**) $Mn(CO)_5$	223—225	(41.4) 40.9	(2.2) 2.0	2 050s, 1 960vs,br	23.5	3 050	347
(**7**) $Co(CO)_4$[e]	218—219	(41.2) 41.3	(2.3) 2.3	2 040s, 1 970 (sh), 1 950vs,br	14.7	2 857	350

[a] Required values are given in parentheses. [b] With decomposition. [c] In KBr. [d] δH (C_6D_6) = 3.7 (5 H, s, C_5H_5). [e] Other n.m.r. data: δP_A = 25.3; $J(P_APt)$ = 2 561, $^2J(P_AHg)$ = 3 696, $^2J(P_AP_B)$ = 11 Hz; P_A *trans* to the Hg atom.

systems. Spectral simulation of (**B**) gives the values reported in Table 1. Additional information was obtained by examining the spectrum of (**1**) (Figure 2). For this compound, two rotational isomers (*syn* and *anti*) can exist due to the asymmetry of 2,3,4-$C_6H_2Cl_3$ (Figure 3) and its ^{31}P n.m.r. spectrum shows two well differentiated signal groups. One group corresponds to the *syn* isomer and the other can be attributed to the *anti* isomer. The slightly more intense signal group can be assigned to the *anti* isomer because it is the less hindered one. Finally, it is remarkable that the values of the coupling constants for platinum fall in the expected range[11] although phosphorus–mercury coupling constants are in general smaller than those found, for example, in the related *cis*-[RHg–PtR(PPh_3)$_2$] (R = 2,3,4-$C_6H_2Cl_3$, 2,3,5,6-C_6Cl_4, or C_6Cl_5).[1]

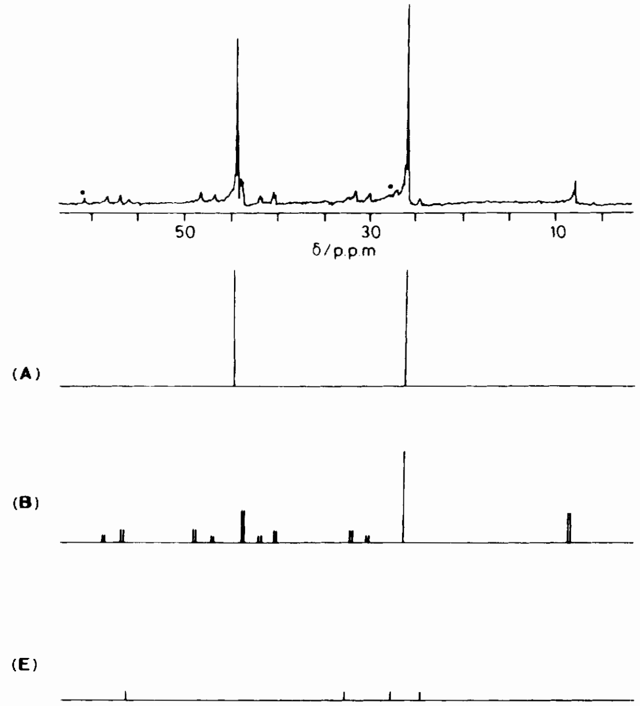

Figure 1. ^{31}P-{^1H} N.m.r. spectrum of [Hg{Pt(2,4,6-$C_6H_2Cl_3$)(PPh_3)$_2$}$_2$] (**2**) and its analyses based on the superposition of (**A**), (**B**), and (**E**) isotopomers. (●) Signals due to the isotopomer (**C**) (see text)

The ^{31}P n.m.r. spectrum of [$(CO)_4$Co–Hg–Pt(C_6Cl_5)(PPh_3)$_2$] is easier to analyse; two sets of resonances are observed, each flanked with ^{195}Pt and ^{199}Hg satellites, indicating a *cis* arrangement for the PPh_3 ligands (Table 2). Surprisingly, the two phosphine ligands remain *trans* in the complexes [$(CO)_5$Mn–Hg–Pt(C_6Cl_5)(PPh_3)$_2$] and [(η^5-C_5H_5)$(CO)_2$Fe–Hg–Pt(C_6Cl_5)(PPh_3)$_2$] consistent with the single signal flanked by ^{195}Pt and ^{199}Hg satellites observed in their spectra. The different arrangement for the ligands in both series of complexes remains unexplained.

Experimental

Solvents were dried by standard methods, and all manipulations and reactions were performed in Schlenk-type flasks under nitrogen. Elemental analyses of C and H were carried out at the Institut de Bio-Orgànica de Barcelona. The ^{31}P-{^1H} n.m.r. spectra (benzene solutions) were obtained on a Varian XL-200 FT spectrometer. Positive phosphorus chemical shifts are downfield relative to external H_3PO_4. Spectral simulations were performed on a Bruker FT 80SY spectrometer using the program PANIC. Infrared spectra were recorded on a Beckman IR 20A spectrophotometer with KBr pellets.

[RHg–PtR(PPh_3)$_2$][1] (R = 2,3,4-$C_6H_2Cl_3$, 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4, or C_6Cl_5), [Hg{Fe$(CO)_2$(η^5-C_5H_5)}$_2$],[12] [Hg{Mn$(CO)_5$}$_2$],[13] [Hg{Co$(CO)_4$}$_2$],[14] and [Pt(CH_2=CH_2)(PPh_3)$_2$][15] were prepared according to methods described previously.

Preparation of [Hg{PtR(PPh_3)$_2$}$_2$] (R = 2,3,4-$C_6H_2Cl_3$, 2,4,6-$C_6H_2Cl_3$, 2,3,5,6-C_6HCl_4, *or* C_6Cl_5).—*Method A.* [Pt(CH_2=CH_2)(PPh_3)$_2$] (0.74 g, 1.0 mmol) was added under nitrogen to a solution of [RHg–PtR(PPh_3)$_2$] (1.0 mmol) in toluene (25 cm^3) and the mixture was refluxed for 2 h to afford

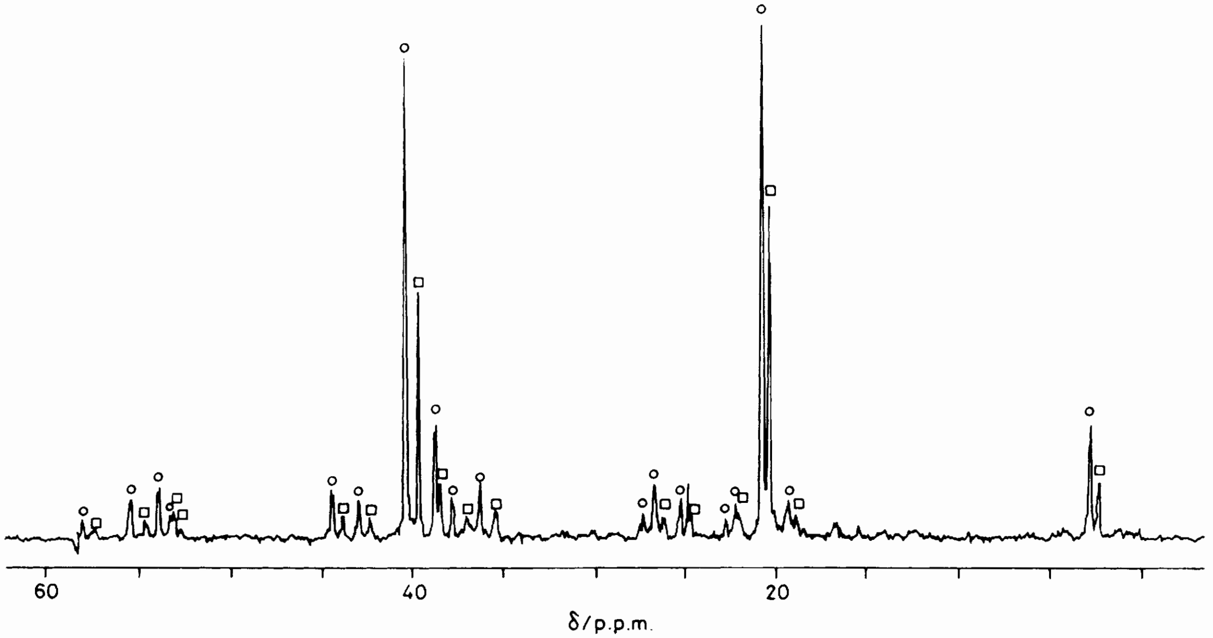

Figure 2. ^{31}P-{^1H} N.m.r. spectrum of [Hg{Pt(2,3,4-$C_6H_2Cl_3$)(PPh_3)$_2$}$_2$] showing the mixture of the *syn* (□) and *anti* isomers (○)

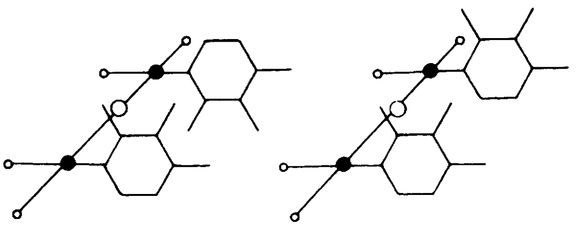

Figure 3. *syn* and *anti* isomers of $[Hg\{Pt(2,3,4\text{-}C_6H_2Cl_3)(PPh_3)_2\}_2]$ (**1**)

a yellow solid. The precipitate was recovered by filtration and recrystallized from benzene–hexane or acetone–ethanol. A second crop of slightly less pure material was obtained by further addition of n-hexane to the mother-liquor. The yields were *ca.* 90—95%.

Method B. An alternative method is as follows. $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (0.74 g, 1.0 mmol) was added to a toluene solution of HgR_2 (0.5 mmol) and the mixture was refluxed under nitrogen for 2 h. The resulting solution was worked up as described in method A.

Preparation of $[M'\text{-}Hg\text{-}Pt(C_6Cl_5)(PPh_3)_2]$ $[M' = Fe(CO)_2(\eta^5\text{-}C_5H_5)$, $Mn(CO)_5$, *or* $Co(CO)_4]$.—A mixture of $[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2]$ (0.213 g, 0.1 mmol) and the appropriate HgM'_2 (0.1 mmol) in toluene was refluxed for 2 h. After cooling, the solvent was removed *in vacuo*, and crystallization of the yellow residue from benzene–hexane gave the air-stable heterotrimetallic complexes. Yields were in all cases *ca.* 90%.

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