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

Josep Calvet, Oriol Rossell,* and Miquel Seco
Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
Pierre Braunstein*
Laboratoire de Chimie de Coordination, UA 416 du CNRS, Université Louis Pasteur, 4 Rue Blaise Pascal, 67070 Strasbourg Cedex, France

Heterotrimetallic complexes *cis*-[m–Pt(PPh$_3$)$_2$–Hg(C$_6$Cl$_5$)] [m = Mo(CO)$_3$(η-C$_5$H$_5$), W(CO)$_3$(η-C$_5$H$_5$), Fe(CO)$_2$(η-C$_5$H$_5$), Mn(CO)$_5$, or Co(CO)$_4$] have been prepared by the reaction of *trans*-[(C$_6$Cl$_5$)Hg–PtCl(PPh$_3$)$_2$] with the appropriate carbonylmetalate anions. The scope of this reaction is discussed. All the compounds have been characterised by ^{31}P n.m.r. spectroscopy. Linear correlations are obtained for plots of the coupling constant ratios $^1J(P_aPt)/^2J(P_aHg)$ or $^2J(P_aHg)/^2J(P_bHg)$ against either the nucleophilicity or the oxidation potential of the carbonylmetalate anions.

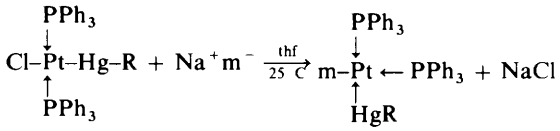
Interest in organometallic complexes with isomeric heteronuclear cores originates largely from the possible occurrence of selectivity effects in their synthesis and reactivity patterns.[1] Only a limited number of syntheses are available for obtaining oligomeric platinum compounds containing the M–M′–Pt or M–Pt–M′ arrangements (M, M′ = different metal atoms). This is partly due to the difficult access to carbonylplatinate anions,[2] which precludes their use in metathetical reactions, and to the easy replacement of both the chloride ions when [PtCl$_2$L$_2$] complexes are treated with carbonylmetalate anions, affording symmetrical M–Pt–M chains[3] or mixed-metal clusters if L is a bulky ligand such as PPh$_3$.[4]

We have recently described two methods to obtain complexes containing M–Hg–Pt arrays. One of them[5] is the selective insertion of the 14-electron, carbene-like PtL$_2$ fragment into the mercury–carbon bond of bimetallic compounds of the type [m–Hg(C$_6$Cl$_5$)] [m = transition metal carbonyl fragment, *e.g.* Mo(CO)$_3$(η-C$_5$H$_5$)];[6] the other[7] is based on the double-exchange reactions between [Hg{Pt(C$_6$Cl$_5$)(PPh$_3$)$_2$}$_2$][8] and [Hg(m)$_2$]. Both methods afford the compounds [m–Hg–Pt(C$_6$Cl$_5$)(PPh$_3$)$_2$] (L = PPh$_3$) in good yields. It is noteworthy that the facility with which redistribution and/or spontaneous symmetrisation reactions can occur in several mercury heterotrimetallic complexes can render their synthesis difficult.[7]

Having prepared several complexes with a M–Hg–Pt skeleton, we hoped to extend the class of linear trimetallic systems to a new series containing an isomeric M–Pt–Hg array. It was anticipated that interesting comparisons could be made between both series of complexes. In particular, we were interested in comparing their spectroscopic (*e.g.* ^{31}P n.m.r.) properties. With this in mind, we attempted the preparation of complexes [m–Pt(PPh$_3$)$_2$–Hg(C$_6$Cl$_5$)] by treating *trans*-[(C$_6$Cl$_5$)Hg–PtCl(PPh$_3$)$_2$] with the sodium salt of the carbonylmetalate anions [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$, [W(CO)$_3$(η-C$_5$H$_5$)]$^-$, [Fe(CO)$_2$(η-C$_5$H$_5$)]$^-$, [Mn(CO)$_5$]$^-$, and [Co(CO)$_4$]$^-$. We report in this paper the synthetic, reactivity, and spectroscopic studies on the complexes *cis*-[m–Pt(PPh$_3$)$_2$–Hg(C$_6$Cl$_5$)].

Results and Discussion

The reaction of *trans*-[(C$_6$Cl$_5$)Hg–PtCl(PPh$_3$)$_2$] with one equivalent of the sodium salt of each of the carbonylmetalate anions [M(CO)$_3$(η-C$_5$H$_5$)]$^-$ (M = Mo or W), [Fe(CO)$_2$(η-C$_5$H$_5$)]$^-$, [Mn(CO)$_5$]$^-$, and [Co(CO)$_4$]$^-$ in tetrahydrofuran (thf) affords, after 2 h, the new heterotrimetallic complexes [m–Pt(PPh$_3$)$_2$–Hg(C$_6$Cl$_5$)], according to equation (1) (R = C$_6$Cl$_5$). The nature of these heterotrimetallic complexes was deduced from analytical and spectroscopic data (Table). All these compounds are air-stable as solids but slowly decompose in solution. The i.r. spectra of (**1**)—(**5**) in the ν(CO) region are very similar to those of the corresponding [m–Hg–Pt(C$_6$Cl$_5$)(PPh$_3$)$_2$] isomeric compounds,[5,7] indicating that the permutation of the m and R groups in the skeleton does not markedly alter the ν(CO) force constants. The ^{1}H n.m.r. data confirm the presence of the η-C$_5$H$_5$ ligand for (**1**)—(**3**) and of two triphenylphosphine ligands in (**1**)—(**5**). The ^{31}P n.m.r. show in all cases two sets of resonances, each flanked with ^{195}Pt and ^{199}Hg satellites, indicating, together with the values of the coupling constants, a *cis* arrangement of inequivalent PPh$_3$ ligands attached to platinum. The ^1J(PPt) and ^2J(PHg) values fall in the expected range, as found for example in the complex *cis*-[(CO)$_4$Co–Hg–Pt(C$_6$Cl$_5$)(PPh$_3$)$_2$].[7]

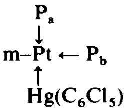


$$\mathrm{Cl{-}\overset{\overset{PPh_3}{\downarrow}}{\underset{\underset{PPh_3}{\uparrow}}{Pt}}{-}Hg{-}R} + \mathrm{Na^+m^-} \xrightarrow[25\,^\circ\mathrm{C}]{\mathrm{thf}} \mathrm{m{-}\overset{\overset{PPh_3}{\downarrow}}{\underset{\underset{HgR}{\uparrow}}{Pt}} \leftarrow PPh_3} + \mathrm{NaCl} \quad (1)$$

m = Mo(CO)$_3$(η-C$_5$H$_5$) (**1**)
m = W(CO)$_3$(η-C$_5$H$_5$) (**2**)
m = Fe(CO)$_2$(η-C$_5$H$_5$) (**3**)
m = Mn(CO)$_5$ (**4**)
m = Co(CO)$_4$ (**5**)

It is noteworthy that the formation of (**1**)—(**5**) according to equation (1) is a rational method to obtain trimetallic metal–metal bonded complexes containing a Pt(PPh$_3$)$_2$ fragment. In view of the isolobal analogy between Hg–R and H,[9] the reaction leading to (**1**) is formally analogous to the synthesis of *cis*-[(η-C$_5$H$_5$)(CO)$_3$Mo–PtH(PPh$_3$)$_2$] from *trans*-[PtH(Cl)(PPh$_3$)$_2$].[10]

It has been reported that the reaction of carbonylmetalate anions with *cis*- or *trans*-[PtX$_2$L$_2$] (X = halide) complexes depends markedly on the nature of L. When L is pyridine (py), a substituted pyridine, an isonitrile, or CO, complexes with m–PtL$_2$–m arrangements are obtained,[3,11] whereas when L is a tertiary phosphine, homo- or hetero-polymetallic clusters are

Table. Analytical data and spectroscopic parameters of the complexes 

$$\mathrm{m{-}}\overset{\displaystyle P_a\downarrow}{\underset{\displaystyle \uparrow Hg(C_6Cl_5)}{Pt}}\leftarrow P_b$$

	m	Decomp. temp./(°C)	I.r.[a] ν(CO)/cm^{-1}	Analysis[b] (%)		^{31}P-{^{1}H} N.m.r.[c]						
				C	H	δP$_a$	δP$_b$	^1J(P$_a$Pt)	^1J(P$_b$Pt)	^2J(P$_a$Hg)	^2J(P$_b$Hg)	^2J(P$_a$P$_b$)
(1)	$Mo(CO)_3(\eta\text{-}C_5H_5)$	211—215	1 955vs, 1 860vs	42.9 (42.4)	2.6 (2.5)	41.1[d]	16.8	2 639	2 725	2 930	290	11.5
(2)	$W(CO)_3(\eta\text{-}C_5H_5)$	245—248	1 955vs, 1 865vs	39.8 (39.9)	2.1 (2.2)	44.1[d]	16.8	2 604	2 742	2 804	278	11.5
(3)	$Fe(CO)_2(\eta\text{-}C_5H_5)$	258—261	1 960vs, 1 910s	43.6 (43.7)	2.6 (2.6)	38.5[d]	19.1	2 441	2 841	2 253	264	10.0
(4)	$Mn(CO)_5$	184—187	2 065vs, 1 970vs, 1 930(sh)	41.9 (41.3)	2.3 (2.2)	41.4[e]	16.6	2 669	2 727	2 941	287	12.0
(5)	$Co(CO)_4$	161—164	2 060m, 1 990m	40.7 (41.2)	2.1 (2.2)	25.4[e]	14.3	2 855	2 562	3 679	350	12.0

[a] KBr discs. [b] Calculated values in parentheses. [c] External reference 85% H_3PO_4. [d] In toluene. [e] In thf.

isolated instead. From these reactions, clusters containing the cores Pt_5,[12] Pt_2Co_2,[4] Pt_3Co_2,[13] Pt_2Cr_2,[11] Pt_2Mo_2,[11] and Pt_2W_2[11] have been characterised. The different course of these reactions has been interpreted in terms of the steric crowding and lability of the groups attached to the platinum atom (*e.g.*, py *vs.* PPh_3).[3,11] This interpretation is strengthened by the distortion observed in the square-planar environment of the platinum atom in *cis*-$[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}PtH(PPh_3)_2]$.[10]

In spite of the co-ordination of two triphenylphosphine ligands to the platinum atom, good yields of the trimetallic platinum compounds are obtained in reaction (**1**). Therefore, it is clear that the mercury atom plays a *decongestion effect* on the platinum centre because of its low co-ordination number of two, such that its presence reduces the steric hindrance due to the bulky PPh_3 ligands and the transition metal carbonyl fragment.

We have investigated the reactivity of complexes (**1**)—(**5**) towards zerovalent platinum complexes or visible light radiation, in an attempt to obtain heterotetranuclear m-Pt-Hg-Pt or bimetallic m-Pt compounds, respectively. In the first case, insertion of the $Pt(PPh_3)_2$ fragment into the Hg-C bond of these complexes does not take place as no change is observed when treating the trimetallic derivatives (**1**)—(**5**) with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ in toluene for several hours. This contrasts with the corresponding reactivity of the Hg-C bond in the related m-$Hg(C_6Cl_5)$ complexes.[5]

An alternative route to heterotetranuclear chain compounds would consist of the replacement of the halide ligand of $[(PPh_3)_2XPt\text{-}Hg\text{-}Pt(C_6Cl_5)(PPh_3)_2]$ by metal carbonylate anions. This is however prevented by the impossibility to isolate the X-Pt-Hg-Pt precursor since it undergoes spontaneous symmetrisation. The redistribution reactions of trimetallic compounds containing a mercury atom in the central position of the trinuclear chain have been discussed elsewhere.[7,14,15] On the other hand, the action of the visible light on toluene solutions of (**1**)—(**5**) does not induce the demercuriation of the derivatives and the starting materials are recovered unaltered.

N.M.R. Studies.—From an inspection of the Table, several interesting features emerge.

(*i*) The values of $^1J(P_aPt)$, $^2J(P_aHg)$, and $^2J(P_bHg)$ for complexes (**1**)—(**5**) ('type I' complexes) increase gradually in the order of M = Fe < W < Mo < Mn < Co, whereas $^1J(P_bPt)$ values decrease in the same order. In addition, we have been able to construct good correlations using any two of these parameters. For example, when $^1J(P_aPt)$ is plotted against $^2J(P_aHg)$ a linear correlation (regression coefficient $r = 0.997$) is observed, suggesting that similar factors influence the magnitude of both coupling constants.

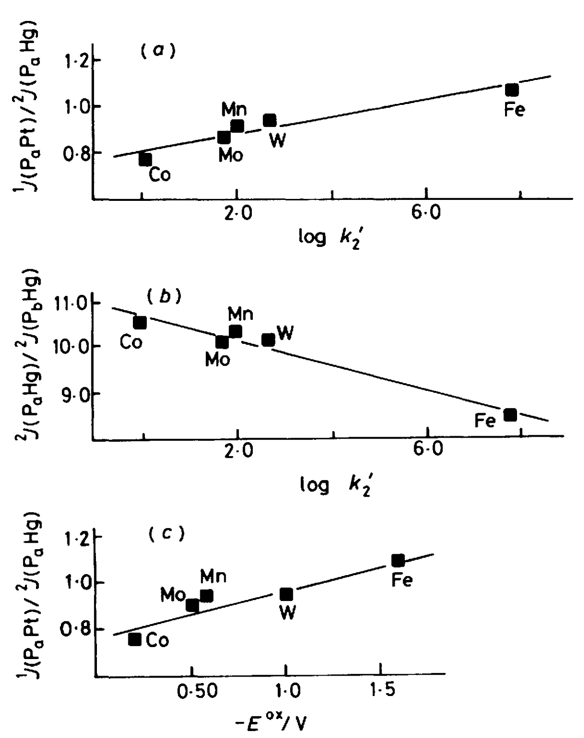


Figure. (*a*) Plot of $^1J(P_aPt)/^2J(P_aHg)$ *vs.* log k_2' [$k_2' = k_2/k_{2(Co)}$]; (*b*) plot of $^2J(P_aHg)/^2J(P_bHg)$ *vs.* log k_2'; (*c*) plot of $^1J(P_aPt)/^2J(P_aHg)$ *vs.* $-E^{ox}$ ($m^- \longrightarrow m^\bullet$)

(*ii*) We have reported previously the ^{31}P n.m.r. data of complexes $[m\text{-}Hg\text{-}Pt(C_6Cl_5)(PPh_3)_2]$ [m = $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$, or $Co(CO)_4$] ('type II' complexes)[5,7] and have now found good linear correlations when combining both series of complexes. For instance, the plot of $^2J(P_bHg)$ (type I complex) *vs.* $^2J(P_bHg)$ (type II complex) gives a linear correlation ($r = 0.999$). Similar results are obtained for $^2J(P_aHg)$ ($r = 0.999$). It is obvious that the obtention of good linear correlations using only three points is easy but, as already indicated, the complexes of type II in which m = $Fe(CO)_2(\eta$-

C_5H_5) and $Mn(CO)_5$ display, unfortunately, a *trans* arrangement of the phosphines attached to platinum. However, it is clear from the reported data that the permutation of the m and C_6Cl_5 groups in going from the complexes of type I to the complexes of type II does not essentially alter their n.m.r. parameters.

(*iii*) In order to relate the n.m.r. parameters of the complexes of type I with other physical properties, it seemed interesting to correlate their coupling constants with the nucleophilicity of the corresponding carbonylmetalate anions. Other significant parameters such as the ν(CO) energies were rejected owing to the very different ν(CO) patterns exhibited by the complexes (**1**)—(**5**).

The nucleophilicity of many carbonylmetalate anions has been established by comparison of their relative rates of reactivity with alkyl halides.[16] Thus, from the reaction $m^- + RX \longrightarrow m\text{-}R + X^-$, it is possible to obtain k_2, the pseudo first-order rate constant. With $k_2' = k_2/k_{2(Co)}$, k_2' values for each organometallic fragment have been estimated. In this way, it has been shown that the nucleophilicity of metal anions decreases as follows: m = $Fe(CO)_2(\eta\text{-}C_5H_5) > W(CO)_3(\eta\text{-}C_5H_5) > Mn(CO)_5 > Mo(CO)_3(\eta\text{-}C_5H_5) > Co(CO)_4$. In this paper, the plot of $^1J(P_aPt)/^2J(P_aHg)$ *vs.* log k_2' gives a linear correlation ($r = 0.969$) [Figure (*a*)]. A good correlation ($r = 0.988$) is also found when the ratio $^2J(P_aHg)/^2J(P_bHg)$ is plotted against log k_2' [Figure (*b*)]. From Figure (*a*) and (*b*) it is seen that increasing the nucleophilicity of the carbonylmetalate anion causes an increase of the ratio $^1J(P_aPt)/^2J(P_aHg)$ and a decrease of the ratio $^2J(P_aHg)/^2J(P_bHg)$.

(*iv*) Given the fact that there is a linear correlation between log k_2' and the potential required to oxidize the anion m^- to the radical $m^\bullet$ at a Pt electrode,[16] we have also been able to observe a linear correlation [Figure (*c*)] between the oxidation potentials of m^- and the $^1J(P_aPt)/^2J(P_aHg)$ ratio ($r = 0.960$). We believe that such correlations can be useful and could be extended to other anions not investigated in this work.

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 $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were measured on a Bruker WP 80SY spectrometer in toluene or thf solutions. Positive phosphorus chemical shifts are downfield relative to external H_3PO_4. Infrared spectra were recorded on a Beckman IR 20A spectrophotometer with KBr pellets.

Compounds $[(C_6Cl_5)Hg\text{-}PtCl(PPh_3)_2]$[17] and $[Pt(CH_2{=}CH_2)(PPh_3)_2]$[18] were prepared according to the methods described previously. The sodium salts of the carbonylmetalate anions $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, and $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, were prepared by Na/Hg reduction of the corresponding binuclear complexes. The salts $Na[M(CO)_3(\eta\text{-}C_5H_5)]\cdot 2dme$ (M = Mo or W, dme = 1,2-dimethoxyethane) were obtained by direct synthesis.[19]

Preparation of the Complexes $[m\text{-}Pt(PPh_3)_2\text{-}Hg(C_6Cl_5)]$ [m = $Mo(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_3(\eta\text{-}C_5H_5)$, $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mn(CO)_5$, *or* $Co(CO)_4$].—All these compounds were prepared by the following method. The appropriate carbonylmetalate anion (0.4 mmol) was added dropwise to a solution of $[(C_6Cl_5)Hg\text{-}PtCl(PPh_3)_2]$ (0.50 g, 0.4 mmol) in thf (50 cm^3) at −40 °C. The resulting mixture was allowed to reach room temperature whereupon it turned brown. It was then stirred for 1 h and the solvent was evaporated under reduced pressure. The residue was recrystallised from toluene–hexane, with the exception of $[(OC)_4Co\text{-}Pt(PPh_3)_2\text{-}Hg(C_6Cl_5)]$ owing to its slow decomposition in both solvents.

Acknowledgements

We thank the Comisión Asesora Científica y Técnica for financial support and Dr. P. S. Pregosin for a preprint (A. Albinati, U. von Gunten, P. S. Pregosin, and H. J. Ruegg, *J. Organomet. Chem.*, 1985, **295**, 239).

References

1 E. Sappa, A. Tiripicchio, and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219.
2 H. C. Clark and V. K. Jain, *Coord. Chem. Rev.*, 1984, **55**, 151.
3 O. Bars, P. Braunstein, and J. M. Jud, *Nouv. J. Chim.*, 1984, **8**, 771 and refs. therein.
4 See, for example, P. Braunstein, J. Dehand, and J. F. Nenning, *J. Organomet. Chem.*, 1975, **92**, 117; P. Braunstein, *Nouv. J. Chim.*, 1986, **10**, 365.
5 P. Braunstein, O. Rossell, M. Seco, I. Torra, X. Solans, and C. Miravitlles, *Organometallics*, 1986, **5**, 1113.
6 O. Rossell, M. Seco, and P. Braunstein, *J. Organomet. Chem.*, 1984, **273**, 233.
7 O. Rossell, M. Seco, and I. Torra, *J. Chem. Soc., Dalton Trans.*, 1986, 1011.
8 O. Rossell, M. Seco, I. Torra, X. Solans, and M. Font-Altaba, *J. Organomet. Chem.*, 1984, **270**, C63.
9 P. Braunstein, J. Rosé, A. Dedieu, Y. Dusausoy, J. P. Mangeot, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1986, 225.
10 O. Bars and P. Braunstein, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 308.
11 R. Bender, P. Braunstein, J. M. Jud, and Y. Dusausoy, *Inorg. Chem.*, 1984, **23**, 4489 and refs. therein.
12 J. P. Barbier, R. Bender, P. Braunstein, J. Fischer, and L. Ricard, *J. Chem. Res.*, 1978, (*S*) 230, (*M*) 2913.
13 J. P. Barbier, P. Braunstein, J. Fischer, and L. Ricard, *Inorg. Chim. Acta*, 1978, **31**, L361.
14 M. J. Mays and J. D. Robb, *J. Chem. Soc. A*, 1968, 329.
15 J. A. Iggo and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1984, 643.
16 R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, 1966, **88**, 5121.
17 J. Calvet, O. Rossell, and M. Seco, *Transition Met. Chem.*, 1984, **9**, 208.
18 U. Nagel, *Chem. Ber.*, 1982, **115**, 1998.
19 R. Bender, P. Braunstein, J. M. Jud, and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 3394.

Received 7th February 1986; *Paper* 6/265