Bis(trimethylsilyl)mercury and Bis(diphenylphosphino)methanedichloroplatinum(II): Formation of Pt–$SiMe_3$, Pt–$HgSiMe_3$ Bonds, and a Platinum(I) Complex

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The reaction between 2 mol equiv. of $[Hg(SiMe_3)_2]$ and $[PtCl_2\{(Ph_2P)_2CH_2\}]$ gives the complex $[Pt(SiMe_3)_2\{(Ph_2P)_2CH_2\}]$ (I), whilst with a deficiency of $[Hg(SiMe_3)_2]$ a bright red air-sensitive platinum(IV) complex can be isolated having the composition $[Pt(HgSiMe_3)_2(SiMe_3)_2\{(Ph_2P)_2CH_2\}]$ (II); this slowly decomposes in solution to give (I), mercury, and Si_2Me_6. Under different experimental conditions the reaction produces a yellow air-stable platinum(I) complex, $[Pt_2Cl_2\{(Ph_2P)_2CH_2\}_2]$ (III). Diphenylmercury also combines with $[PtCl_2\{(Ph_2P)_2CH_2\}]$ forming $[Pt(HgPh)_2Ph_2\{(Ph_2P)_2CH_2\}]$.

EARLIER work has reported that the reaction between $[Hg(SiMe_3)_2]$ or its germanium analogue and *cis*-$[PtCl_2(PEt_3)_2]$ proceeds cleanly to give *trans*-$[PtCl(SiMe_3)(PEt_3)_2]$ if equimolar ratios of the reactants are used.[1] An excess of $[Hg(SiMe_3)_2]$ leads to uncharacterized red air- and water-sensitive oily products. The analogous reaction with *cis*-$[PtCl_2(Ph_2PCH_2)_2]$ allows the introduction of one or two $SiMe_3$ groups giving $[PtCl(SiMe_3)(Ph_2PCH_2)_2]$ or $[Pt(SiMe_3)_2(Ph_2PCH_2)_2]$.[2] The related reaction between $[Hg(SiMe_3)_2]$ and $[Ir(CO)Cl(PEt_3)_2]$ produces an iridium(III) complex with an Ir–Hg bond,[3] *viz.* $[Ir(CO)(HgSiMe_3)(PEt_3)_2(SiMe_3)_2]$.

Here [4] we describe the reaction of a four-membered

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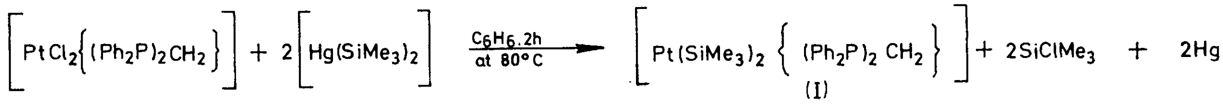
[1] F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1968, 826.

[2] F. Glockling and A. F. Clemmit, *J. Chem. Soc.* (*A*), 1971, 1164.

[3] K. A. Hooton, *J. Chem. Soc.* (*A*), 1971, 1251.

[4] F. Glockling and R. J. I. Pollock, *J.C.S. Chem. Comm.*, 1972, 467.

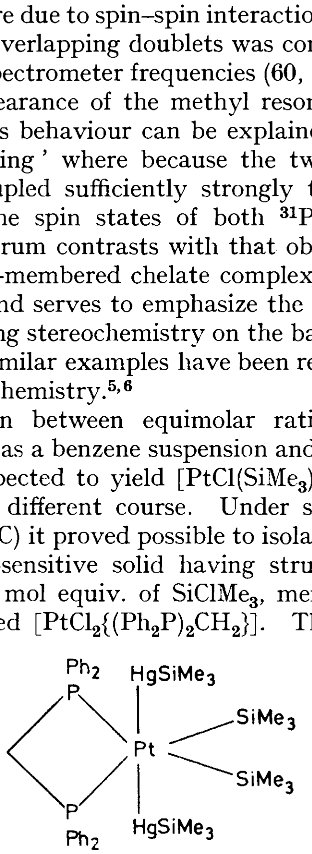
chelating diphosphine platinum dichloride complex with [Hg(SiMe$_3$)$_2$]. If 2 mol equiv. of the latter are used the reaction proceeds according to the following equation



$$[PtCl_2\{(Ph_2P)_2CH_2\}] + 2[Hg(SiMe_3)_2] \xrightarrow[\text{at } 80^{\circ}C]{C_6H_6, 2h} \underset{(I)}{[Pt(SiMe_3)_2\{(Ph_2P)_2CH_2\}]} + 2SiClMe_3 + 2Hg$$

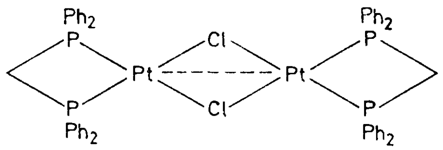
Complex (I) was characterized by elemental analysis and by its vibrational spectrum. Its ^{1}H n.m.r. spectrum in C_6D_6 showed the methylene resonance as a 1 : 2 : 1 triplet [^2J(PH) = 8·28 Hz], but the methyl resonance appeared as a triplet of triplets, in the ratio 1 : 2 : 1 : 4 : 8 : 4 : 1 : 2 : 1, centred on τ 9·38. Coupling of the methyl protons to ^{195}Pt produces a 1 : 4 : 1 triplet [$^3J(^{195}$PtH) = 31·5 Hz], each line being further split by the 'virtually coupled' ^{31}P nuclei into 1 : 2 : 1 triplets [^4J(PH) = 2·4 Hz]. That the triplets were due to spin–spin interactions and not the result of two overlapping doublets was confirmed by using different spectrometer frequencies (60, 100, 220 MHz) when the appearance of the methyl resonance was unchanged. This behaviour can be explained in terms of 'virtual coupling' where because the two phosphorus atoms are coupled sufficiently strongly this resonance depends on the spin states of both ^{31}P nuclei. The resulting spectrum contrasts with that observed for the analogous five-membered chelate complex [2] [Pt(SiMe$_3$)$_2$-(Ph$_2$PCH$_2$)$_2$] and serves to emphasize the caution necessary in deducing stereochemistry on the basis of 'virtual coupling'. Similar examples have been reported in iron and rhodium chemistry.[5,6]

The reaction between equimolar ratios of [PtCl$_2$-{(Ph$_2$P)$_2$CH$_2$}] as a benzene suspension and [Hg(SiMe$_3$)$_2$], which was expected to yield [PtCl(SiMe$_3$){Ph$_2$P)$_2$CH$_2$}], took a totally different course. Under suitable conditions (2 h, 50 °C) it proved possible to isolate a bright red extremely air-sensitive solid having structure (II) together with 2 mol equiv. of SiClMe$_3$, mercury, and *ca.* 75% unchanged [PtCl$_2${(Ph$_2$P)$_2$CH$_2$}]. The assignment of structure (II) to the compound is based on ^{1}H n.m.r. evidence and on its slow decomposition to (I), Si$_2$Me$_6$, and mercury. Initially the spectrum showed a low intensity CH$_2$ resonance, assigned to (I) [τ 6·00 (1 : 2 : 1), ^2J(PH) = 8·28 Hz] and a high intensity CH$_2$ resonance assigned to (II) [τ 4·83 (1 : 2 : 1), ^2J(PH) = 9·00 Hz]. A methyl resonance [τ 9·37 (1 : 2 : 1), ^4J(PH) = 2·1 Hz] is assigned to the two platinum-bonded SiMe$_3$ groups for which the low-field satellite was observed [^3J(PtH) = 31·0 Hz]. A further methyl resonance at τ 9·62 is assigned to the two mercury-bonded PtHgSiMe$_3$ groups for which the high-field satellite with ^3J(HgH) = 39·5 Hz was observed. The resonance at τ 9·62 is not due to [Hg(SiMe$_3$)$_2$] for which the values τ 9·80 and ^3J(HgH) = 41·0 Hz were obtained in C_6D_6. When allowance has been made for the low initial concentration of (I) the observed proton ratios in (II) were Ph : CH$_2$: CH$_3$ = 10·3 : 1 : 18·3 and HgSiMe$_3$: PtSiMe$_3$ = 1·1 : 1·0. During 35 days at 20 °C the ^{1}H n.m.r. spectrum of (II) changed to that of (I) together with an additional sharp singlet at τ 9·94, assigned to Si$_2$Me$_6$, and the correct weight of mercury was deposited. During this period the colour changed from bright red to yellow-brown. The i.r. spectrum of (II) contained bands at 327 and 335 cm^{-1}, probably due to ν(Pt–Si) and ν(Hg–Si).



(II)

Under different conditions (3h in refluxing benzene) the reaction between equimolar concentrations of [PtCl$_2${(Ph$_2$P)$_2$CH$_2$}] and [Hg(SiMe$_3$)$_2$] took yet another course. The initial red solution turned to yellow-brown with deposition of mercury, and formation of a yellow solid formulated as the dimeric platinum(I) complex (III).



(III)

This structure is based on elemental analysis, the presence of bridging ν(Pt–Cl) at 249 cm^{-1} and the correct Ph : CH$_2$ proton ratio. The CH$_2$ resonance consisted of nine lines (1 : 2 : 1 : 4 : 8 : 4 : 1 : 2 : 1) with ^2J(PH) = 3·8 Hz and ^3J(PtH) = 56·6 Hz. Its mass spectrum contained a molecular ion centred on 1229 a.m.u. with the correct isotope pattern; it is diamagnetic and produced no e.s.r. signal. Its E.S.C.A. spectrum,* indicated that only one type of platinum atom was present since only one peak was observed in the Pt($4f_{7/2}$) binding-energy region. Thus on the available evidence (III) is best regarded as a platinum(I) complex with significant Pt–Pt interaction. It is surprisingly inert chemically being unaffected by air, water, *p*-toluidine, CO at 1 atm, or (Ph$_2$P)$_2$CH$_2$. Binuclear platinum(I) anionic complexes have more recently been fully characterized by Goggin and Goodfellow [7] but these involve a Pt–Pt electron-pair bond with non-bridging chlorine and carbonyl groups. Several other possible Pt^{I} complexes have been reported,[8,9] and a

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* Examined by Dr. D. T. Clark, University of Durham.

[5] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685, 1693.

[6] W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 1971, **10**, 843.

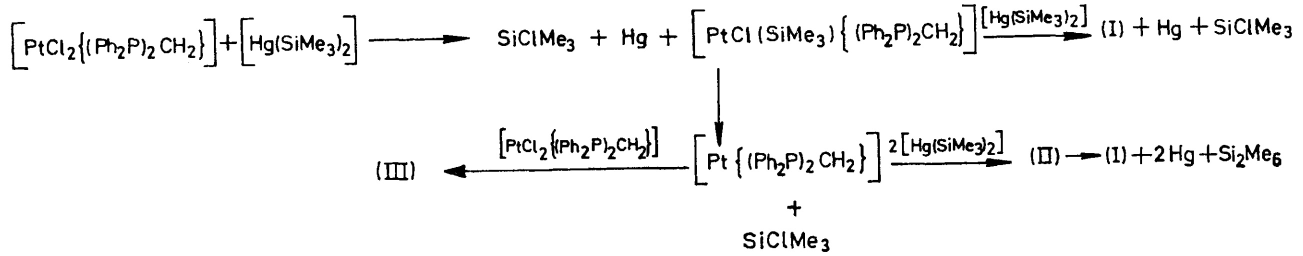
[7] P. L. Goggin and R. J. Goodfellow, *J.C.S. Dalton*, 1973, 2355.

[8] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1969, 170.

[9] W. Fink and A. Wenger, *Helv. Chim. Acta*, 1971, **54**, 2186.

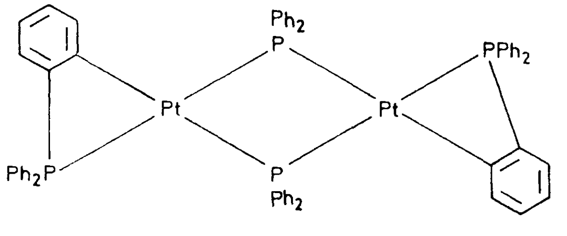
palladium(I) iodide, [$\{PdI(Ph_2PCH_2)_2\}_2$] has been described.[10]

On the basis of the foregoing evidence it appears that [$Hg(SiMe_3)_2$] can react with [$PtCl_2\{(Ph_2P)_2CH_2\}$] in a variety of ways, summarized in the following scheme:



Isolation of (II) implies that all stages proceed through oxidative addition of $HgSiMe_3$ and $SiMe_3$ to platinum. Direct evidence for the 2-co-ordinate Pt^0 species [$Pt\{(Ph_2P)_2CH_2\}$] is lacking though [$Pt(PPh_3)_2$] has been widely postulated as a reaction intermediate in many systems. The great ease with which *ortho*-metallation reactions take place in phenylphosphine metal complexes makes it unlikely that [$Pt\{(Ph_2P)_2CH_2)\}$] can exist other than as a reactive intermediate.[11] The complex [$PtCl_2Me(HgMe)(CO)(PPh_3)$] has been postulated as an intermediate in the reaction between [$PtCl_2(CO)(PPh_3)$] and [$HgMe_2$] [12] and we find that [$PtCl_2\{(Ph_2P)_2CH_2\}$] combines with diphenylmercury giving in low yield an analogue of (II), *i.e.* [$Pt(HgPh)_2Ph_2\{(Ph_2P)_2CH_2\}$].

Other attempts to form neutral platinum(I) complexes have so far proved unsuccessful. The reaction between [$Pt(PPh_3)_4$] and *cis*-[$PtCl_2(PPh_3)_2$] has been reported [13] as yielding [$(Ph_3P)_2ClPt-PtCl(PPh_3)_2$], but we find that no reaction occurs under the conditions described. Similarly no reaction was observed between [$Pt(PPh_3)_4$] and [$PtCl_2\{(Ph_2P)_2CH_2\}$] in refluxing benzene, and the reaction between [$Pt(C_2H_4)(PPh_3)_2$] and [$PtCl_2\{(Ph_2P)_2CH_2\}$] yielded the *ortho*-metallated complex (IV).[11]



(IV)

EXPERIMENTAL

Bis(diphenylphosphino)methanebis(trimethylsilyl)platinum(II), [$Pt(SiMe_3)_2(Ph_2PCH_2PPh_2)$], (I).—Bis(trimethylsilyl)mercury (1·10 g, 3·17 mmol) in benzene (20 ml) was added dropwise to a suspension of [$PtCl_2\{(Ph_2P)_2CH_2\}$] (1·00 g, 1·54 mmol) in refluxing benzene (500 ml) to give an immediate blood red colour which persisted until the end of the addition. After being refluxed for 3 h the reddish brown solution was filtered to remove mercury. The solvent, separated *in vacuo*, contained chlorotrimethylsilane (v.p.c.). The pale-brown solid was recrystallized from benzene to give [$Pt(SiMe_3)_2\{(Ph_2P)_2CH_2\}$] as a yellow solid, m.p. 165—168 °C (decomp.), $\rho(CH_3)$ 825 cm^{-1}, ν(Pt–Si), at 332 cm^{-1} (0·85 g, 76%) (Found: C, 51·0; H, 5·4. $C_{31}H_{40}P_2PtSi_2$ requires C, 51·3; H, 5·5%).

Bis(diphenylphosphino)methanebis(trimethylsilyl)bis[(trimethylsilyl)mercurio]platinum(IV), [$Pt(HgSiMe_3)_2(SiMe_3)_2\{(Ph_2P)_2CH_2\}$], (II).—Bis(trimethylsilyl)mercury (0·78 g, 2·25 mmol) in benzene (15 ml) was added dropwise to a suspension of [$PtCl_2\{(Ph_2P)_2CH_2\}$] (1·45 g, 2·23 mmol) in benzene (560 ml) at 50 °C. After being stirred for 2 h at 50 °C the bright red solution was cooled and filtered from deposited mercury and uncharged [$PtCl_2\{(Ph_2P)_2CH_2\}$] (1·19 g). Solvent was removed *in vacuo*; treatment with aqueous silver nitrate gave silver chloride derived from $SiClMe_3$ (0·131 g, 87·5% based on reacted [$PtCl_2\{(Ph_2P)_2CH_2\}$]). The bright red residue was washed with hexane (4 × 10 ml) to give [$Pt(HgSiMe_3)_2(SiMe_3)_2\{(Ph_2P)_2CH_2\}$] (0·67 g, 23·6%).

Bis[bis(diphenylphosphino)methane]-di-μ-chloro-diplatinum(I), (III).—Bis(trimethylsilyl)mercury (0·77 g, 2·22 mmol) in benzene (15 ml) was added dropwise to a suspension of [$PtCl_2\{(Ph_2P)_2CH_2\}$] (1·44 g, 2·22 mmol) in benzene (650 ml) at 60 °C. During addition the solution gradually became deep red. After being refluxed for 3 h the yellowish brown solution was cooled and filtered to remove mercury and [$PtCl_2\{(Ph_2P)_2CH_2\}$] (0·74 g). Solvent was removed *in vacuo*; treatment with aqueous silver nitrate gave silver chloride {0·130 g, 84% based on reacted [$PtCl_2\{(Ph_2P)_2CH_2\}$]}. The light brown residue recrystallized from benzene to give the *complex* as a yellow powder, m.p. 291 °C (dec.) {0·61 g, 92% based on reacted [$PtCl_2\{(Ph_2P)_2CH_2\}$]} (Found: C, 48·9; H, 3·6; Cl, 5·85; P, 9·65. $C_{50}H_{44}Cl_2P_4Pt$ requires C, 48·82; H, 3·58; Cl, 5·77; P, 10·09%).

Bis(diphenylphosphino)methanediphenyldi(phenylmercurio)platinum(IV), [$Pt(HgPh)_2Ph_2\{(Ph_2P)_2CH_2\}$].—Diphenylmercury (0·22 g, 0·62 mmol) and [$PtCl_2\{(Ph_2P)_2CH_2\}$] (0·40 g, 0·62 mmol) were refluxed in benzene (150 ml) for 17 h. Unchanged [$PtCl_2\{(Ph_2P)_2CH_2\}$] (0·33 g) was filtered off from the cold solution. The colourless benzene solution was evaporated *in vacuo* to give a white residue. Washing of this with hexane (4 × 10 ml) gave [$Pt(HgPh)_2Ph_2\{(Ph_2P)_2CH_2\}$] (0·13 g, 16·5%) (Found: C, 45·5; H, 3·25; Hg, 30·8. $C_{49}H_{42}Hg_2P_2Pt$ requires C, 45·65; H, 3·26; Hg, 31·13%). The hexane washings contained [$HgClPh$] and [$HgPh_2$].

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[10] S. Otsuka, Y. Tatsuna, and K. Ataka, *J. Amer. Chem. Soc.*, 1971, **93**, 6705.

[11] F. Glockling, T. McBride, and R. J. I. Pollock, *J.C.S. Chem. Comm.*, 1973, 650.

[12] R. J. Cross and R. Wardle, *J. Chem. Soc.* (*A*), 1970, 840.

[13] A. J. Layton, R. S. Nyholm, G. A. Pneumaticakis, and M. L. Tobe, *Chem. and Ind.*, 1967, 465.