# Preparation of Silylplatinum Complexes by Interaction of Organosilicon Hydrides and Carbonatobis(phosphine)platinum(II) Complexes †

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The carbonatoplatinum complexes [Pt($CO_3$)$L_2$] (L = $PMe_2Ph$, $PEt_2Ph$, $PMePh_2$, and $PPh_3$) react in benzene with the silicon hydrides $SiHR_3$ ($R_3$ = $MePh_2$) or $SiH_2R_2$ ($R_2$ = $Ph_2$ or MePh) to give the bis(silyl) complexes [Pt($SiR_3$)$_2$$L_2$] or [Pt($SiHR_2$)$_2$$L_2$]. With $R_3$ = ($p$-$FC_6H_4$)$_3$ and L = $PMe_2Ph$, the product, formed in low yield, is [PtH($SiR_3$)$L_2$]. All the products have been shown to have *cis* configurations by $^{31}P\{^1H\}$ n.m.r. spectroscopy. The dihydrides ($Me_2HSi$)$_2$O, ($Ph_2HSi$)$_2$O, ($Ph_2HSiCH_2$)$_2$, $o$-($Me_2HSi$)$_2$$C_6H_4$, and $o$-$Me_2HSi{\cdot}C_6H_4{\cdot}CH_2SiHMe_2$ give chelated complexes such as [Pt($Me_2SiOSiMe_2$)$L_2$].

THE interaction of carbonatobis(phosphine)platinum(II) complexes with triorganostannanes was recently shown to provide a useful route to some complexes containing Pt–Sn bonds.[1] When ethanol is used as the solvent for the reaction, the $Pt^{IV}$ dihydrides [$PtH_2(SnR_3)_2L_2$] (L = tertiary phosphine) separate; in benzene the same species appear to be formed initially but lose dihydrogen (in a reversible reaction) to give the $Pt^{II}$ species *cis*-[$Pt(SnR_3)_2L_2$]. In view of the ready availability of a range of carbonatoplatinum complexes, we have now examined their use in the preparation of complexes containing Pt–Si bonds.

Ethanol is not a suitable solvent for the reactions involving silicon hydrides; a vigorous and copious gas evolution occurs, but no identifiable products have been isolated, and it seems likely that alcoholysis of the silicon hydride occurs under catalysis by the platinum complex (*cf.* ref. 2). A range of $Pt^{II}$ complexes can be obtained, however, with benzene as the solvent.

## RESULTS AND DISCUSSION

We concentrated mainly on reactions involving carbonatobis(dimethylphenylphosphine)platinum(II), since $Pt^0$ complexes such as [$Pt(PMe_2Ph)_2(C_2H_4)$] and [$Pt(PMe_2Ph)_4$], which would probably give silylplatinum complexes on treatment with silicon hydrides (*cf.* refs. 3—5), are not as readily available. Usually a suspension of the carbonato-complex in benzene was stirred with an excess of the silicon hydride at room temperature until a clear solution was obtained, the products being soluble in most cases. When reaction was too slow at room temperature the stirred mixture was heated; the conditions used in each case are specified in the Table, which also lists the yields and some properties of the products. The wide variation in yields is probably mainly due to variation in the ease with which the products form crystals, and no solid products could be obtained from reactions of [$Pt(CO_3)(PMe_2Ph)_2$] with the silanes $SiHR_3$ (R = Et, EtO, $PhCH_2$, $m$-$F_3C{\cdot}C_6H_4$, or

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[1] C. Eaborn, A. Pidcock, and B. R. Steele, *J.C.S. Dalton*, 1975, 809.

[2] See, for example, B.P. 842, 674/1960 (*Chem. Abs.*, 1961, **55**, 1066); E. Lukevitcs and M. G. Voronkov, *Latvijas PSR Zinatnu Akad. Vestis Kim. Ser*, 1961, 127 (*Chem. Abs.*, 1963, **58**, 2465); Yu I. Khudobin, M. G. D'yachenko, N. P. Kharitonov, and P. A. Vasil'eva, *J. Gen. Chem.* (*U.S.S.R.*), 1968, **38**, 180; Yu I. Khudobin, N. A. Sergeeva, and N. P. Kharitonov, *ibid.*, p. 404; G. H. Barnes and N. D. Daughenbaugh, *J. Org. Chem.*, 1966, **31**, 885; A. J. Chalk, *Chem. Comm.*, 1970, **847** and refs. therein.

[3] J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 881; C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **43**, C5.

[4] C. Eaborn, B. Ratcliff, and A. Pidcock, *J. Organometallic Chem.*, 1974, **65**, 181.

[5] C. Eaborn, T. N. Metham, and A. Pidcock, *J. Organometallic Chem.*, 1973, **63**, 107.

$p$-MeOC$_6$H$_4$). Only in one case was a hydrido(silyl)platinum complex isolated, *viz. cis*-[PtH{Si(C$_6$H$_4$F-$p$)$_3$}(PMe$_2$Ph)$_2$], and this was obtained in low yield.* Of the silicon hydrides used, only two, the dihydrides SiH$_2$Ph$_2$ and SiH$_2$MePh, reacted at a significant rate with [Pt(CO$_3$)(PMe$_2$Ph)$_2$] in the absence of solvent, and these reactions were so vigorous that better results were obtained by using benzene as a moderator.

Preparation of complexes from silicon hydrides and carbonatobis(phosphine)platinum(II) complexes, [Pt(CO$_3$)L$_2$], in benzene [a]

| Hydride | L | Product [b] | Yield (%) | M.p. ($\theta_c$/°C) | Analyses [c] (%) | | $M$ [c,d] | Conditions [e] $\theta_c$/°C ($t$) |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | | |
| SiHMePh$_2$ | PMe$_2$Ph | *cis*-[Pt(SiMePh$_2$)$_2$L$_2$] [f] | 71 | 143—146 | 58.2<br>(58.25) | 5.6<br>(5.8) | 860<br>(865) | Reflux (1 h) |
| (Me$_2$HSi)$_2$O | | [Pt(Me$_2$SiOSiMe$_2$)L$_2$], (I) | 22 | 133—137 | 39.6<br>(39.8) | 5.6<br>(5.7) | 650<br>(604) | r.t. (6 h) |
| (Ph$_2$HSi)$_2$O | | [Pt(Ph$_2$SiOSiPh$_2$)L$_2$], (II) | 68 | 184—187 | 56.4<br>(56.4) | 5.1<br>(5.0) | | r.t. (20 h), then 95 (0.5 h) |
| $o$-(Me$_2$HSi)$_2$C$_6$H$_4$ | | [Pt{$o$-(Me$_2$Si)$_2$C$_6$H$_4$}L$_2$], (III) | 22 | 110—113 | 47.1<br>(47.0) | 6.0<br>(5.8) | 650<br>(663) | r.t. (2 d) |
| $o$-(Me$_2$HSiCH$_2$)(Me$_2$HSi)-C$_6$H$_4$ | | [Pt{$o$-(Me$_2$SiCH$_2$)(Me$_2$Si)C$_6$H$_4$}L$_2$], (IV) | 21 | 102—104 | 48.0<br>(47.8) | 6.2<br>(5.95) | | r.t. (16 h) |
| (Ph$_2$HSiCH$_2$)$_2$ | | [Pt(Ph$_2$SiCH$_2$CH$_2$SiPh$_2$)L$_2$], (V) [g] | 32 | 174—177 | 58.3<br>(58.4) | 5.4<br>(5.4) | 870<br>(864) | r.t. (24 h), then 75 (6 h) |
| SiH$_2$Ph$_2$ | | *cis*-[Pt(SiHPh$_2$)$_2$L$_2$] [h] | 81 | 11—121 | 57.1<br>(57.3) | 5.5<br>(5.3) | 830<br>(837) | r.t. (15 min), after warming to initiate |
| SiH$_2$MePh | | *cis*-[Pt(SiHMePh)$_2$L$_2$] [i] | 74 | 117—121 | 50.3<br>(50.5) | 5.7<br>(5.65) | 690<br>(714) | r.t. (15 min), after warming to initiate |
| SiH(C$_6$H$_4$F-$p$)$_3$ | | *cis*-[PtH{Si(C$_6$H$_4$F-$p$)$_3$}L$_2$] | 15 | 118—120 | 52.0<br>(52.0) | 4.5<br>(4.5) | | r.t. (3 d) |
| SiHMePh$_2$ | PPh$_3$ | *cis*-[PtH(SiMePh$_2$)L$_2$] | 60 | 121—125 | 64.1<br>(64.1) | 5.0<br>(4.8) | | r.t. (60 h), then 60 (22 h) |
| (Ph$_2$HSi)$_2$O | | [Pt(Ph$_2$SiOSiPh$_2$)L$_2$], (VI) | 50 | 166—167 | 64.4<br>(65.5) | 4.7<br>(4.6) | | r.t. (40 h), then 50 (30 h) |
| SiH$_2$Ph$_2$ | PEt$_2$Ph | *cis*-[Pt(SiHPh$_2$)$_2$L$_2$] [j] | 63 | 134—135 | 59.1<br>(59.1) | 6.0<br>(5.9) | | r.t. (48 h) |
| SiH$_2$MePh | | *cis*-[Pt(SiHMePh)$_2$L$_2$] [k] | 55 | 103—105 | 53.0<br>(53.0) | 6.4<br>(6.3) | | r.t. (40 h) |
| (Me$_2$HSi)$_2$O | | [Pt(Me$_2$SiOSiMe$_2$)L$_2$], (VII) [l] | 41 | 112—116 | 43.8<br>(43.7) | 6.4<br>(6.4) | | r.t. (30 h) |
| (Ph$_2$HSiCH$_2$)$_2$ | | [Pt(Ph$_2$SiCH$_2$CH$_2$SiPh$_2$)L$_2$] [m] | 58 | 147—149 | 60.0<br>(60.0) | 6.0<br>(5.9) | | r.t. (36 h), then 85 (23 h) |
| (Ph$_2$HSiCH$_2$)$_2$ | PMePh$_2$ | [Pt(Ph$_2$SiCH$_2$CH$_2$SiPh$_2$)L$_2$] | 34 | 165—167 | 63.8<br>(63.2) | 5.4<br>(5.1) | | 75 (3 h) |
| SiHMePh$_2$ | | *cis*-[Pt(SiMePh$_2$)$_2$L$_2$] [n] | 17 | 135—136 | 62.7<br>(63.1) | 5.4<br>(5.3) | | 80 (0.5 h), then r.t. (4 h) |

[a] $^{31}$P N.m.r. parameters for dichloromethane solutions are given in the footnotes. Shifts are quoted relative to external trimethyl phosphite dissolved in hexadeuteriobenzene; positive values indicate resonances to high field of the reference. [b] White or cream unless otherwise stated. [c] Calculated values are given in parentheses. [d] In benzene, using a Mechrolab vapour-pressure osmometer 301 A at 37 °C. [e] The bath temperature is given; r.t. denotes room temperature (*ca.* 21 °C). [f] Orange; $^1J$(Pt–P) 1 558 Hz, $\delta$ 148.3 p.p.m. [g] $^1J$(Pt–P) 1 563, $\delta$ 148.6 p.p.m. [h] $^1J$(Pt–P) 1 687, $\delta$ 145.5 p.p.m. [i] Mixture of *meso* and DL (see text): $^1J$(Pt–P) 1 638, $\delta$ 143.9; $^1J$(Pt–P) 1 626 Hz, $\delta$ 144.3 p.p.m. [j] Bright yellow, but darkens rapidly in air; $^1J$(Pt–P) 1 687 Hz, $\delta$ 128.4 p.p.m. [k] Orange, but darkens rapidly in air. [l] $^1J$(Pt–P) 1 560, $\delta$ 123.2 p.p.m. [m] $^1J$(Pt–P) 1 540, $\delta$ 132.8 p.p.m. [n] Orange-yellow.

The complex [Pt(SiMePh$_2$)$_2$(PMe$_2$Ph)$_2$] obtained from SiHMePh$_2$ after crystallization during 2 weeks at 0 °C had a m.p. of 143—146 °C, and that prepared from [PtMe$_2$(PMe$_2$Ph)$_2$] as described previously,[6] but again with prolonged crystallization at 0 °C, had a m.p. 136—139 °C (*cf.* 130—136 °C observed after a shorter crystallization time[6]). The same complex obtained on treatment of *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] with methyldiphenylsilyl-lithium had a m.p. of 124—126 °C.[8] Since these three sets of crystals were orange or yellow, whereas the great majority of analogous silylplatinum complexes are white or cream, we thought that *cis–trans* mixtures might be involved, with the degree of isomerization depending on the crystallization time, but $^{31}$P {$^1$H} n.m.r. spectra (see below) showed all three to be pure *cis* isomers in solution.

The chelated bis(silyl)complexes (I)—(V) obtained from [Pt(CO$_3$)(PMe$_2$Ph)$_2$] and the silicon dihydrides (Me$_2$HSi)$_2$O, (Ph$_2$HSi)$_2$O, $o$-(Me$_2$HSi$_2$)$_2$C$_6$H$_4$, $o$-Me$_2$HSi·C$_6$H$_4$·CH$_2$SiHMe$_2$, and (Ph$_2$HSiCH$_2$)$_2$ are very similar to the corresponding bis(triphenylphosphine) complexes obtained from [Pt(PPh$_3$)$_2$(C$_2$H$_4$)],[4] but complexes (I), (III), and (IV) decompose on storage in air during several weeks whereas the bis(triphenylphosphine) analogue of (I) appears to be indefinitely stable under

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* This complex was previously obtained by treatment of [PtMe$_2$(PMe$_2$Ph)$_2$] with tri-$p$-fluorophenylsilane, and had $\nu$(Pt–H) (Nujol mull) at 2 040 cm$^{-1}$,[6] whereas our product, apparently identical in other respects, had $\nu$(Pt–H) at 2 080 cm$^{-1}$. Crystal modifications may be involved, as noted for *trans*-[PtH(Cl)(PPh$_3$)$_2$].[7]

[6] C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1974, **66**, 23.

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[8] J. Chatt, C. Eaborn, S. Ibekwe, and P. N. Kapoor, *Chem. Comm.*, 1967, 869; *J. Chem. Soc.* (*A*), 1970, 1343.

these conditions. It is noteworthy that the disiloxane $(Me_2HSi)_2O$ reacts with $[Pt(CO_3)(PMe_2Ph)_2]$ at room temperature to give the chelate complex (I), whereas with $[Pt(PPh_3)_2(C_2H_4)]$ at 45 °C it gives the hydrido-complex $[PtH(Me_2SiOSiHMe_2)(PPh_3)_2]$, which undergoes cyclization with loss of hydrogen only at higher temperatures.[5] In view of this, and since the tin hydrides $SnHR_3$ react with the complexes $[Pt(CO_3)L_2]$ to give the dihydrides $[PtH_2(SnR_3)_2L_2]$, which in benzene lose dihydrogen to give $[Pt(SnR_3)_2L_2]$,[1] it is possible that the bis(silyl)complexes $[Pt(SiR_3)_2(PMe_2Ph)_2]$ and the related chelated bis(silyl) species are also usually formed by loss of dihydrogen from a $Pt^{IV}$ complex, rather than through the hydrido(silyl) complexes as in the reactions with $[Pt(PPh_3)_2(C_2H_4)]$.[4] However, hydrido(silyl)platinum(II) complexes can clearly also be formed (see above and below).

For the preparation of silylplatinum complexes containing triphenylphosphine ligands, the ethylene complex $[Pt(PPh_3)_2(C_2H_4)]$ is a much superior reagent to the carbonate, but the expected reactions do take place between silicon hydrides and $[Pt(CO_3)(PPh_3)_2]$ (see Table). Thus, while no significant reaction occurred between the carbonate and $SiHMePh_2$ during 60 h at room temperature, the hydrido(silyl) complex $[PtH(SiMePh_2)(PPh_3)_2]$ was obtained in 60% yield after 22 h at 60 °C. A similar yield of the expected chelated complex (VI) was obtained from the disiloxane $(Ph_2HSi)_2O$ after 30 h at 60 °C, and the reaction may have been complete in a shorter time since direct observation of completion of the reaction was prevented in this case by the partial insolubility of the product.

With the complex $[Pt(CO_3)(PMePh_2)_2]$, the reactions appeared to proceed as usual, but only in two cases were the products obtained crystalline, and these in low yield (see Table). Somewhat surprisingly, no difficulty was encountered in obtaining crystalline products from $[Pt(CO_3)(PEt_2Ph)_2]$ in the cases examined (see Table). Again the disiloxane $(Me_2HSi)_2O$ gave a chelated bis(silyl) complex, (VII), even at room temperature. The reactions of the dihydrides $SiH_2Ph_2$ and $SiH_2MePh$ with $[Pt(CO_3)(PEt_2Ph)_2]$ were much slower than those with $[Pt(CO_3)(PMe_2Ph)_2]$, and prolonged stirring at room temperature was required.

$^{31}P$–$^{195}Pt$ *Coupling Constants and Configurations of Products*.—Representative complexes were examined by $^{31}P\{^1H\}$ n.m.r. spectroscopy (see footnotes to Table). The spectra comprised simple 1 : 4 : 1 triplets, indicating equivalent phosphines with coupling $^1J(Pt-P)$ to the $^{195}Pt$ nucleus (abundance 33.7%). The spectrum of $[Pt(SiHMePh)_2(PMe_2Ph)_2]$ comprised two such triplets of equal intensity with closely similar $^{31}P$ parameters: the triplets can be assigned to DL and *meso* forms, each of which has equivalent phosphines.

The parameters of the complex $[Pt(SiMePh_2)_2(PMe_2Ph)_2]$ are virtually identical to those reported previously for a complex assigned to a *cis* configuration by comparison of the magnitude of $^1J(Pt-P)$ with those for *cis*-$[PtPh_2(PEt_3)_2]$ [$^1J(Pt-P)$ 1 704 Hz] and *trans*-$[PtPh_2(PEt_3)_2]$[$^1J(Pt-P)$ 2 824 Hz].[9] This assignment is confirmed by the present results for three complexes containing chelating bis(silyl) ligands (Table, footnotes *g*, *l*, and *m*), which must have *cis* configurations with P *trans* to Si, and which have $^1J(Pt-P)$ *ca.* 1 550 Hz. All the complexes examined have similar values of $^1J(Pt-P)$, and therefore have *cis* configurations in solution. The magnitudes of $^1J(Pt-P)$ reflect the greater *trans* influence of silyl compared with phenyl ligands.[9,10]

## EXPERIMENTAL

The preparations of the silicon hydrides and the carbonatobis(phosphine)platinium(II) complexes have been described elsewhere.[1,5] Benzene was dried over sodium wire and distilled under dry nitrogen before use. The $^{31}P\{^1H\}$ n.m.r. spectra were obtained with a JEOL PFT-100 Fourier-transform spectrometer.

*Silicon Hydride–Platinum Carbonate Interactions*.—Three illustrative preparations are described below, and details for the related reactions are shown in the Table. In all cases, most of the benzene was removed under reduced pressure at the end of the reaction and n-hexane was added. All the reactions were conducted under dry nitrogen.

(a) A mixture of $[Pt(CO_3)(PMe_2Ph)_2]$ (420 mg, 0.79 mmol), methyl(phenyl)silane (*ca.* 2.0 cm³, excess), and benzene (5 cm³) was warmed gently until a vigorous effervescence began, then cooled in cold water, and stirred at room temperature until effervescence had ceased (*ca.* 15 min). After filtration, the filtrate was evaporated under reduced pressure and n-hexane (20 cm³) was added, to give a solid. The mixture was kept overnight in a refrigerator, then the solid was filtered off, washed with n-hexane (6 × 3 cm³), dried *in vacuo* and shown to be *cis*-$[Pt(SiHMePh)_2(PMe_2Ph)_2]$ (420 mg, 74%), m.p. 117—121 °C (decomp.); ν(SiH) at 2 030 cm$^{-1}$, with sharp shoulder at 2 015 cm$^{-1}$. There were no bands attributable to the $CO_3$ group.

(b) When a suspension of $[Pt(CO_3)(PMe_2Ph)_2]$ (135 mg, 0.25 mmol) in benzene (3.0 cm³) containing *sym*-tetraphenyldisiloxane (337 mg, 0.88 mmol) was stirred at room temperature for 20 h no visible reaction occurred. The stirred mixture was heated under reflux for 30 min to give a yellow solution and a white solid. The solid was filtered off, washed with n-hexane (3 × 5 cm³), and dried *in vacuo*, to give $[Pt(Ph_2SiOSiPh_2)(PMe_2Ph)_2]$, (II) (148 mg, 68%), m.p. 184—187 °C. There were no bands in the i.r. spectrum attributable to the $CO_3$ group.

(c) There was no apparent reaction when a suspension of $[Pt(CO_3)(PEt_2Ph)_2]$ (144 mg, 0.25 mmol) in a mixture of benzene (3.0 cm³) and 1,2-bis(diphenylsilyl)ethane (2.0 cm³) was stirred at room temperature for 36 h. Heating under reflux for 23 h gave a clear solution which was evaporated to small volume. Addition of n-hexane (10 cm³) gave a solid, which was filtered off, washed with n-hexane (3 × 5 cm³), and dried *in vacuo* to give $[Pt(Ph_2SiCH_2CH_2SiPh_2)(PEt_2Ph)_2]$ (130 mg, 58%), m.p. 147—149 °C.

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