Formation of Platinum–Silicon, –Germanium, and –Tin Complexes by Cleavage of Platinum–Carbon Bonds and by Oxidative Addition of Trimethylstannane to Platinum Complexes

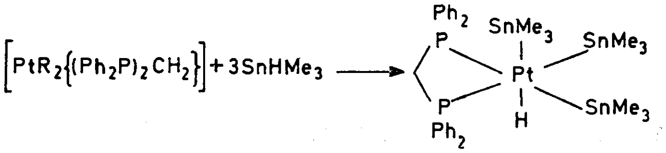
By **Frank Glockling** * and **R. J. Ivan Pollock**, Department of Chemistry, The Queen's University, Belfast TB9 5AG

Trimethylstannane displaces alkane from $[PtR_2\{(Ph_2P)_2CH_2\}]$ (R = Me or Et) at room temperature, or at 50 °C when R = Ph. The d^6 product, $[PtH(SnMe_3)_3\{(Ph_2P)_2CH_2\}]$ (I), reversibly dissociates in solution to $[Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$. Trimethyl-silane and -germane displace only 1 mol equiv. of alkane forming $[Pt(MMe_3)(Me)\{(Ph_2P)_2CH_2\}]$ (M = Si, Ge). The lead complex $[Pt(PbPh_3)_2\{(Ph_2P)_2CH_2\}]$ gives (I) and Pb_2Ph_6 with $SnHMe_3$. $[PtCl_2\{(Ph_2P)_2CH_2\}]$ on reaction with $SnHMe_3$ yields the d^6 complex $[PtClH(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$ (II) which dissociates to $[PtCl(SnMe_3)\{(Ph_2P)_2CH_2\}]$ (III) in solution. Similarly, oxidative addition of $SnHMe_3$ to $[Pt\{(Ph_2P)_2CH_2\}_2]$ produces $[Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$.

IN Pt–$SiMe_3$ bonded complexes [1] trimethyl-germane or -stannane readily displace the trimethylsilyl group as trimethylsilane. Similarly Pt–$GeMe_3$ complexes react with trimethylstannane with displacement of $GeHMe_3$.

$$[PtL_2(SiMe_3)_2] \xrightarrow{GeHMe_3} [PtL_2(GeMe_3)_2] \xrightarrow{SnHMe_3} [PtL_2(SnMe_3)_2] \xrightarrow{SnHMe_3} [PtHL_2(SnMe_3)_3]$$

These reactions are believed to proceed through successive oxidative addition and elimination stages, and if the equilibrium constants are determined largely by the M–H bond strength of the displaced hydride then organoplatinum complexes would be expected to undergo similar reactions. Eaborn and his co-workers have previously used the reaction between a dimethylplatinum(II) complex and organosilicon hydrides to make Pt–Si bonds.[2] In the present work the most striking examples encountered are the reactions between trimethylstannane and $[PtR_2\{(Ph_2P)_2CH_2\}]$ (R = Me and Et) where quantitative displacement of the R group as RH occurs at room temperature. The diphenylplatinum complex (R = Ph) is less reactive but at 50 °C both phenyl groups are converted into benzene. With an excess of trimethylstannane complex (I) is produced, the low value of ν(Pt–H) (1968 cm^{-1}) indicating the grouping *trans*-HPtSnMe$_3$ and thereby defining the stereochemistry. Complex (I) is stable in air during 6 months but in benzene solution it reversibly dissociates. These exchange reactions provide one of the cleanest and simplest methods of forming Pt–Sn bonds.

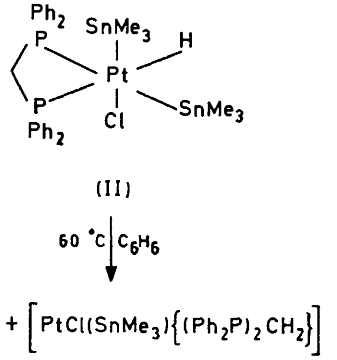


(I)

$$(I) \overset{C_6H_6}{\rightleftharpoons} [Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}] + SnHMe_3$$

The reaction between $[PtMe_2\{(Ph_2P)_2CH_2\}]$ and an excess of trimethyl-silane or -germane proceed much more slowly and even at 50 °C only 1 mol. equiv. of methane is formed together with the mixed complexes $[Pt(MMe_3)(Me)\{(Ph_2P)_2CH_2\}]$ (M = Si or Ge). This marked difference from the behaviour of trimethylstannane is probably a reflection of the lower tendency of Si–H and Ge–H compounds to undergo oxidative addition to Pt^{II}, though it might imply a different stereochemistry for an intermediate octahedral adduct.

This type of reaction seemed to offer the possibility of forming organolead hydrides under mild conditions by the cleavage of Pt–Pb bonds but, as applied to the complex $[Pt(PbPh_3)_2\{(Ph_2P)_2CH_2\}]$, the observed products were (I), hydrogen, lead, and hexaphenyldilead. Dichlorobis(diphenylphosphino)methaneplatinum(II) also adds trimethylstannane but in a complex reaction since hydrogen, $SnClMe_3$, and Sn_2Me_6 are formed. The platinum-containing product is assigned structure (II), based on the values of ν(Pt–H) and ν(Pt–Cl) and on its ready conversion into (III). Complex (II) is considerably more stable in solution than (I) and comparison of ν(Pt–H) in the two compounds [1968 cm^{-1} in (I) and 2002 cm^{-1} in (II)] suggests that the difference in stability relates to the lower *trans*-labilising effect of phosphorus relative to that of the trimethylstannyl group.



(II)

(III)

The reaction between $[Pt\{(Ph_2PCH_2)_2\}_2]$ and trimethylstannane has previously [1] been shown to give a d^6 hydride, $[PtH(SnMe_3)_3\{(Ph_2PCH_2)_2\}]$, which reversibly dissociates in solution to $[Pt(SnMe_3)_2\{(Ph_2PCH_2)_2\}]$. Reaction of the four-membered chelate complex, $[Pt\{(Ph_2P)_2CH_2\}_2]$ and an excess of trimethylstannane gave as final product $[Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$ together

---

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

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

with a large amount of hydrogen produced by the catalytic decomposition of $SnHMe_3$. In one experiment an intermediate having ν(PtH) at 1998 cm^{-1} (*trans*-HPtP) and a further i.r. band at 1895 cm^{-1} was isolated. The latter band is more indicative of ν(SnH) than ν(PtH), but in solution this complex decomposed to $[Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$.

EXPERIMENTAL

Bis(diphenylphosphino)methanehydridotris(trimethylstannyl)platinum(II) *and Bis(diphenylphosphino)methanebis(trimethylstannyl)platinum*(II).—Trimethylstannane (0·21 g) and benzene (5 ml) were condensed onto the complex $[PtMe_2\{(Ph_2P)_2CH_2\}]$ [3] (0·10 g) in a break-seal tube. At room temperature considerable effervescence occurred and a pale yellow solution resulted. Work-up yielded methane (0·35 mmol) and the *complex* $[PtH(SnMe_3)_3\{(Ph_2P)_2CH_2\}]$ as a white solid (0·15 g, 88%) with ν(Pt–H) at 1968 cm^{-1} (Found: C, 36·85; H, 4·85. $C_{34}H_{50}P_2PtSn_3$ requires C, 38·09; H, 4·67%). Recrystallisation from benzene yielded $[Pt(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$ as a pale yellow solid, m.p. 226—229 °C (dec.) (Found: C, 40·65; H, 4·3. $C_{31}H_{40}P_2PtSn_2$ requires C, 41·05; H, 4·41%).

A similar reaction between $SnHMe_3$ (0·14 g) and $[PtPh_2\{(Ph_2P)_2CH_2\}]$ (0·07 g) in toluene (3 ml) at 50 °C for 6 h yielded hydrogen (0·14 mmol), benzene, and $[PtH(SnMe_3)_3\{(Ph_2P)_2CH_2\}]$ (0·076 g, 74%).

Bis(diphenylphosphino)methanemethyl(trimethylgermyl)platinum(II).—Trimethylgermane (0·11 g, 0·93 mmol) and benzene (5 ml) were condensed onto the complex $[PtMe_2\{(Ph_2P)_2CH_2\}]$ (0·10 g, 0·16 mmol) in a break-seal tube. The colourless solution was heated at 50 °C overnight to give a light brown solution. Work-up yielded methane (0·14 mmol). The light brown residue was recrystallised from benzene to give yellow crystals of the *complex* $[PtMe(GeMe_3)\{(Ph_2P)_2CH_2\}]$ (0·07 g, 58%), m.p. 107—110 °C (decomp.) (Found: C, 49·35; H, 4·5. $C_{29}H_{34}GeP_2Pt$ requires C, 48·91; H, 4·78%).

A similar reaction using trimethylsilane (50 °C, 5 days) gave *bis(diphenylphosphino)methanemethyl(trimethylsilyl)platinum*(II), as an orange-yellow solid (68%), m.p. 105—108 °C (decomp.) (Found: C, 51·8; H, 4·8. $C_{29}H_{34}P_2PtSi$ requires C, 52·17; H, 5·10%).

Reaction of $[Pt(PbPh_3)_2\{(Ph_2P)_2CH_2\}]$ *with* $SnHMe_3$.—Trimethylstannane (0·19 g) and benzene (5 ml) were condensed onto the complex $[Pt(PbPh_3)_2\{(Ph_2P)_2CH_2\}]$ (0·08 g) in a break-seal tube. At room temperature some effervescence was observed and a yellow solution resulted. Within a few minutes the solution changed to light green with concomitant deposition of a small amount of lead. The tube was opened to a vacuum line, yielding hydrogen (0·06 mmol). The i.r. spectrum of the greenish residue showed it to be a mixture of hexaphenyldilead and $[PtH(SnMe_3)_3\{(Ph_2P)_2CH_2\}]$ [ν(Pt—H) at 1968 cm^{-1}].

Reaction of $[Pt\{(Ph_2P)_2CH_2\}_2]$ *with an Excess of* $SnHMe_3$.—Trimethylstannane (2 ml) was condensed onto the complex, $[Pt\{(Ph_2P)_2CH_2\}_2]$ (0·25 g) in a tube fitted with a break-seal. At room temperature slight effervescence was observed and the initially yellow solid became light green. After 2 h at 60 °C the contents darkened considerably. Hydrogen (1·25 mmol) was isolated and the light brown residue showed two strong peaks at 1998 and 1895 cm^{-1}. Crystallisation from benzene yielded $[\{Pt(SnMe_3)_2(Ph_2PCH_2PPh_2)\}]$ as a pale yellow solid (0·11 g, 47%).

Reaction of $[PtCl_2\{(Ph_2P)_2CH_2\}]$ *with an Excess of* $SnHMe_3$.—Trimethylstannane (0·69 g, 4·19 mmol) was condensed onto the complex, $[PtCl_2\{(Ph_2P)_2CH_2\}]$ (0·50 g, 0·77 mmol), in a tube fitted with a break-seal. When warmed to room temperature the solution became yellow. Heating of the mixture at 50 °C for 5 days gave a brown solution accompanied by some decomposition. The tube was opened to a vacuum line; hydrogen (1·8 mmol), Sn_2Me_6, and $SnClMe_3$ (mass spectrum and v.p.c. identification) were identified in the volatiles. The brown residue showed ν(Pt–H) at 2002 and ν(Pt–Cl) at 271 cm^{-1}, and is presumably $[PtClH(SnMe_3)_2\{(Ph_2P)_2CH_2\}]$; on crystallisation from benzene it gave the orange-yellow solid $\{PtCl(SnMe_3)(Ph_2PCH_2PPh_2)\}$, m.p. >315 °C, ν(Pt–Cl), 296 cm^{-1} (0·34 g, 57%) (Found: C, 42·8; H, 3·75. $C_{28}H_{31}ClP_2PtSn$ requires C, 43·18; H, 3·98%).

[4/925 *Received*, 9th *May*, 1974]

---

[3] F. Glockling, T. McBride, and R. J. I. Pollock, *Inorg. Chim. Acta*, 1974, **8**, 77.