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SOME PLATINUM(II)-METAL BONDED COMPLEXES

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SUMMARY

The compound $Pt(C_2H_4)(PPh_3)_2$ provides a convenient route to platinum-metal bonded derivatives. Thus, from reaction with hexamethylditin $Pt(SnMe_3)_2(PPh_3)_2$ is obtained; its reactions with hydrogen, bromine, and hydrogen chloride have been examined. The reaction of $Pt(C_2H_4)(PPh_3)_2$ with metal halides constitutes a general synthetic route to products of which $PtCl(SnMe_3)(PPh_3)_2$ and $\{PtCl[Fe(CO)_2(\pi\text{-}C_5H_5)]PPh_3\}_2$ are typical examples.

INTRODUCTION

At present there is considerable experimental and theoretical interest in compounds containing metal–metal bonds[1,2]. Those containing a transition metal and a Group IVB element are of particular interest due to their use as catalysts in homogeneous hydrogenations[3]. Such compounds containing covalent Pt–Si[2,4–9], Pt–Ge[2,4–8], Pt–Sn[2,10] and Pt–Pb[10,11] bonds have been investigated in detail. Most have been prepared by the reactions of metallic halides with derivatives of Group IVB elements of the type R_3MLi.

Although $Pt(C_2H_4)(PPh_3)_2$ is stable in the solid state, loss of ethylene occurs on treatment with a number of reagents[12,14]. We have now found that it reacts with hexamethylditin to give a platinum(II)–tin bonded complex, $Pt(SnMe_3)_2(PPh_3)_2$. The same product is also formed by the reaction of hexamethylditin with $Pt(PPh_3)_4$. The properties and reactions of $Pt(SnMe_3)_2(PPh_3)_2$ with a number of reagents are reported. Moreover, we find that the reactions of $Pt(C_2H_4)(PPh_3)_2$ with organometallic halides provide a general synthetic route to compounds with platinum–metal bonds, which is more convenient than the corresponding reactions with $Pt(PPh_3)_4$[15,16].

RESULTS AND DISCUSSION

$Pt(C_2H_4)(PPh_3)_2$ reacts with hexamethylditin, under extremely mild conditions, with rupture of the tin–tin bond, to give a stable crystalline trinuclear product *trans*-$Pt(SnMe_3)_2(PPh_3)_2$, accompanied by the evolution of ethylene. The same product is also formed by the reaction of hexamethylditin with $Pt(PPh_3)_4$. The

$$\mathrm{Pt(C_2H_4)(PPh_3)_2 + Me_6Sn_2 \rightarrow \textit{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2 + C_2H_4}$$
$$\mathrm{Pt(PPh_3)_4 + Me_6Sn_2 \rightarrow \textit{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2 + 2\ PPh_3}$$

configuration *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ is assigned on the basis of an observed single medium intensity band at 420 cm^{-1}, characteristic of ν(Pt–P). Usually *trans*-phosphine complexes have a single band due to the Pt–P stretching vibration in the range 420–406 cm^{-1}, while the *cis* complexes have a doublet at approximately 440 and 425 cm^{-1} (refs. 17 and 18). The *trans* configuration is also observed for the analogous lead complexes, *trans*-$Pt(PbPh_3)_2(PEt_3)_2$[11] and *trans*-$Pd(PbPh_3)_2(PEt_3)_2$[19]. The trimethyltin protons in *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ cause absorption at τ 9.3 ppm ($CDCl_3$) in the proton NMR spectrum; the expected splitting due to coupling to ^{119}Sn and ^{117}Sn could not be observed due to limited solubility. The complete spectroscopic data are given in Table 1.

TABLE 1

IR AND ^{1}H NMR DATA FOR PLATINUM(II) COMPLEXES[a]

Compound	ν(Pt–P) (cm^{-1})	ρ(Sn–CH_3) (cm^{-1})	ν(Pt–Cl) (cm^{-1})	ν(Pt–H) (cm^{-1})	τ(Sn–CH_3) (ppm)
trans-$Pt(SnMe_3)_2(PPh_3)_2$	420 m	760 vs, 745 vs			9.3
trans-$PtH(SnMe_3)(PPh_3)_2$	420 m	758 vs, 748 vs		2042 s δ 840 m	9.32
trans-$PtCl(SnMe_3)(PPh_3)_2$	418 m	756 vs, 749 vs	296 m		9.32
trans-$PtCl[Fe(CO)_2(\pi\text{-}C_5H_5)](PPh_3)_2$	415 m		283 s		

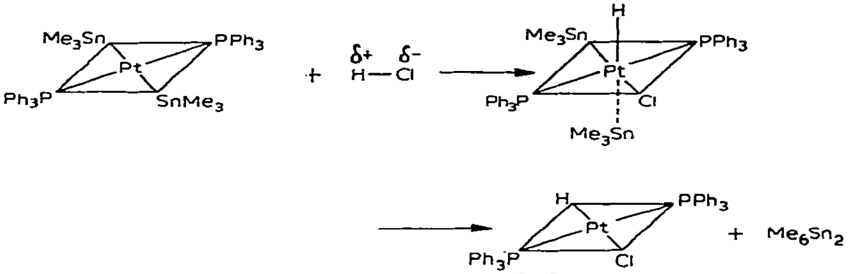
[a] ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as an external reference. IR spectra were recorded as Nujol mulls and absorptions other than those due to internal vibrations of ligands are given.

The reactions of *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ with molecular hydrogen, bromine and hydrogen chloride were investigated and can be described by the following equations:

$$\mathrm{\textit{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2 + H_2 \rightarrow \textit{trans}\text{-}PtH(SnMe_3)(PPh_3)_2 + Me_3SnH}$$
$$\mathrm{\textit{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2 + 2\ Br_2 \rightarrow \textit{cis}\text{-}PtBr_2(PPh_3)_2 + 2\ Me_3SnBr}$$
$$\mathrm{\textit{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2 + HCl \rightarrow \textit{trans}\text{-}PtHCl(PPh_3)_2 + Me_6Sn_2}$$

At room temperature, *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ reacts with molecular hydrogen in benzene to give the hydrido–platinum(II) complex, *trans*-$PtH(SnMe_3)(PPh_3)_2$, and trimethyltin hydride. The configuration *trans*-$PtH(SnMe_3)(PPh_3)_2$ was assigned due to the presence of a medium intensity band at 420 cm^{-1}, characteristic of ν(Pt–P). Absorption due to ν(Pt–H) was observed at 2042 cm^{-1} (Table 1). The latter frequency is close to ν(Pt–H) at 2056 cm^{-1} observed for *trans*-$PtH(SnCl_3)(PPh_3)_2$[10], but is higher than ν(Pt–H) at 1940 cm^{-1} for *trans*-$PtH(PbPh_3)(PEt_3)_2$[11]. The trimethyltin protons in *trans*-$PtH(SnMe_3)(PPh_3)_2$ appear as a weak signal at τ 9.32 ppm in the proton NMR spectrum, but unfortunately the high field signal due to the hydridic proton could not be observed on account of the limited solubility of the complex. The reactions of platinum(II) complexes containing Pt–Ge, Pt–Sn and Pt–Pb[11] bonds with molecular hydrogen probably proceed via octahedral platinum(IV) complexes, as suggested by Glocking[5,7,8].

Hydrogen chloride (1/1 molar ratio) reacts with *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ in benzene to give *trans*-$PtHCl(PPh_3)_2$, hexamethylditin and a trace of trimethyltin chloride. The reaction is rapid, reaching completion while the reaction mixture attains room temperature from −196°. The reactions of HCl with compounds containing platinum(II)–Group IVB metal bonds probably proceed via an oxidative addition–elimination process involving electrophilic attack on platinum(II) by H^+ from HCl[5–8,11]. Such reactions (1/1 molar ratio) usually give *trans*-$PtCl(MR_3)(PR_3)_2$ and R_3MH, M = Ge, Pb, as the initial products[5–8,11] and thus differ from the reactions of HCl with *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ where *trans*-$PtHCl(PPh_3)_2$ and hexamethylditin are the main reaction products, indicating the selectivity of HCl attack on platinum–Group IVB metal bonds, which has been attributed to the nature and electronegativity of Group IVB elements[11]. However, bromine easily ruptures such bonds, to give a platinum(II) bromide and the corresponding bromide of Group IVB elements, without differentiating between the Pt–Ge, Pt–Sn and Pt–Pb bonds. These reactions most probably proceed through an electrophilic attack of the halogen leading to oxidative addition on platinum(II), thus forming a hexa-coordinated intermediate complex formally of platinum(IV)[5–8,11].



The reactions of trimethyltin hydride with $Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_4$ were investigated in an effort to prepare hydrido–platinum complexes of the type $PtH(SnMe_3)(PPh_3)_2$ or $PtH_2(SnMe_3)_2(PPh_3)_2$. Similar reactions involving the addition of R_3MH (M = Si, Ge, Sn and R = alkyl, alkoxy or halide) to d^8 complexes of iridium(I) are known[20–23]. When the organotin hydride and $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_4$ were allowed to react in 1/1 molar ratio, neat or in benzene solution, immediate reaction occurred with the formation of reddish colorations in the case of neat reactions or pale yellow colorations in the case of reactions carried out in benzene solution, accompanied by the evolution of hydrogen. In no case could the formation of the molecule $PtH(SnMe_3)(PPh_3)_2$ be detected. From the reaction mixtures, light yellow products of composition $Pt(SnMe_3)_2(PPh_3)_2$ were isolated in low yield. Similar products were also obtained when excess trimethyltin hydride was used. These compounds are relatively more insoluble in benzene and deuteriochloroform and decompose at a higher temperature (>200°), than the analogous products obtained from the reactions of hexamethylditin with $Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_4$ which decompose at 180°. These new complexes show IR absorptions due to $(CH_3)_3$-Sn at 760 and 745 cm^{-1}, but no single sharp absorption at 410–420 cm^{-1} characteristic of ν(Pt–P) in *trans*-$Pt(SnMe_3)_2(PPh_3)_2$. The IR spectra in the region 400–500 cm^{-1} are broad and complex, apparently containing a number of absorptions. These differences in properties can be explained in terms of mixtures of *cis* and *trans* isomers[10].

Organometallic halides react with $Pt(PPh_3)_4$ to give compounds containing covalent platinum(II)–metal bonds[15]. Similarly, $AuClPPh_3$ and $CuClPPh_3$ react with Rh^I and Ir^I carbonyl derivatives of the type *trans*-$MCl(CO)(PPh_3)_2$ to give metal–metal bonded complexes *e.g.* $(PPh_3)_2(CO)Cl_2Ir-AuPPh_3$, $(PPh_3)_2(CO)Cl_2Ir-CuPPh_3$ and $(PPh_3)_2(CO)Cl_2Rh-CuPPh_3$[24]. The reactions of organometallic halides with $Pt(C_2H_4)(PPh_3)_2$ provide a general method of considerable utility for the syntheses of compounds containing covalent platinum(II)–metal bonds. This method is more convenient than the corresponding reactions with $Pt(PPh_3)_4$[15,24] since it offers the following advantages[2,10,11,19]: (*i*) the reaction conditions are extremely mild and good yields are obtained; (*ii*) the only by-product, ethylene, is gaseous and is easily removed from the reaction site; so that no further purification of the products is required.

The complexes $[(Ph_3P)Pt(Cl)Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ and $(Ph_3P)_2Pt(Cl)SnMe_3$ were prepared by adding the appropriate halide to benzene solutions of $Pt(C_2H_4)(PPh_3)_2$. These complexes are tentatively assigned *trans* configurations, by analogy with related tin and lead complexes[10,11] and also with the alkyl- and arylplatinum complexes of the type *trans*-$PtCl(R)(PR_3)_2$[25]. The spectroscopic data are given in Table 1. The complex $(Ph_3P)_2Pt(Cl)Fe(CO)_2(\pi\text{-}C_5H_5)$ showed $\nu(CO)$ at 2050 and 2002 cm^{-1} and three strong bands at 1003, 874 and 835 cm^{-1}, characteristic of the $(\pi\text{-}C_5H_5)-Fe$ group[26].

The reactions of various compounds containing metal–metal bonds and metal carbonyls *e.g.* $Co_2(CO)_8$ and $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ etc. with low valent phosphine complexes of platinum are under investigation and will be reported in a forthcoming publication.

EXPERIMENTAL

Reactions were carried out under a nitrogen atmosphere or under vacuum using standard high vacuum techniques. The volatile components of reaction mixtures were separated by trap-to-trap fractionation and identified by their IR spectra.

IR spectra were recorded with a Beckman IR 10 double beam spectrophotometer using CsI plates, while proton NMR spectra were obtained with a Varian A60 spectrometer. Molecular weights were determined in benzene solution using a Hitachi Perkin–Elmer Model 115 osmometer. Analyses were done by Dr. A. B. Gygli, Microanalyses Laboratory, Toronto, and by Schwarzkopf Microanalytical Laboratory, New York.

$Pt(PPh_3)_4$ was prepared by the procedure of Malatesta and Cariello[27] from K_2PtCl_4, KOH, and excess PPh_3 in aqueous ethanol, and $Pt(C_2H_4)(PPh_3)_2$ through the oxide $Pt(PPh_3)_2O_2$, according to the procedure of Cook and Jauhal[13]. $(\pi\text{-}C_5H_5)(CO)_2FeCl$ was prepared by the reaction of $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ with HCl[26]. The product was crystallized from a benzene/hexane mixture and finally sublimed over a cold probe. Trimethyltin hydride was prepared by the reduction of $(CH_3)_3SnCl$ by $LiAlH_4$ in n-butyl ether[28], and hexamethylditin according to the procedure described by Clark and Willis[29].

I. Reactions of $Pt(C_2H_4)(PPh_3)_2$ *and* $Pt(PPh_3)_4$ *with hexamethylditin*

(*a*). $Pt(C_2H_4)(PPh_3)_2$ (0.318 g, 0.72 mmoles) was dissolved in dry benzene

(3 ml) and the solution of Me_6Sn_2 (0.24 g, 0.72 mmole) in dry ether (2 ml) was added dropwise under nitrogen. The reaction mixture immediately became red and was degassed and allowed to stand at room temperature for 24 h under vacuum. After about 10 min, pale yellow crystals formed. The solvents and some ethylene were removed under vacuum. The pale yellow crystalline material was washed twice with an ether/benzene (5/1) mixture, then with ether, and dried under vacuum. Yield 0.375 g (48%). The compound decomposed at 180° to a black material. Analysis proved this pale yellow compound to be $Pt(SnMe_3)_2(PPh_3)_2$. (Found: C, 47.61; H, 4.32. $C_{42}H_{48}P_2PtSn$ calcd.: C, 48.17; H, 4.62%.) Spectroscopic data are given in Table 1.

(*b*). $Pt(PPh_3)_4$ (0.89 g, 0.72 mmole) was dissolved in dry benzene (3 ml) and a solution of Me_6Sn_2 (0.24 g, 0.72 mmole) in ether was added under nitrogen. The reaction mixture was degassed and allowed to stand at room temperature for 24 h, during which pale yellow material was deposited. The solvents were decanted and the residue washed with an ether/benzene (5/1) mixture, then with ether, and dried under vacuum. Yield 0.32 g (40%). This compound also decomposed at 180° and analysis showed it to be $Pt(SnMe_3)_2(PPh_3)_2$. (Found: C, 48.86; H, 4.98. $C_{42}H_{48}P_2PtSn_2$ calcd.: C, 48.17; H, 4.62%.) The IR and ^1H NMR spectra were the same as for the material prepared under (*a*) above.

II. Reactions of trans-$Pt(SnMe_3)_2(PPh_3)_2$ with H_2, HCl and Br_2

(*a*). Hydrogen was bubbled through a suspension of *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ (0.14 g) in 40 ml of benzene. The effluent gas was passed through a −78° trap and then through a mineral oil bubbler. After 4 h the reaction mixture had changed from pale yellow to colorless. Benzene was removed under vacuum and the residue washed with ether and dried. A whitish material was obtained, whose IR spectrum showed a strong band at 2042 cm^{-1} and a medium band at 840 cm^{-1} assigned to ν(Pt–H) and δ(Pt–H) respectively, and $Sn-CH_3$ rocking modes at 758 vs and 748 vs cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ showed very weak resonances at τ 2.7 and τ 9.32 ppm due to phenylphosphine and methyltin protons respectively. The high field resonance due to the hydridic proton could not be observed due to the limited solubility of the complex. It is stable in the solid state, but decomposition appeared to be complete in benzene or chloroform solution after 7 to 8 h. The −78° trap contained a small amount of trimethyltin hydride[30] [ν(Sn–H) = 1841 cm^{-1}] along with some benzene.

(*b*). *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ (0.144 g, 1.39 mmoles) was stirred in benzene (5 ml) under vacuum, and anhydrous HCl (0.05 g, 1.39 mmoles) was condensed in. The reaction mixture was allowed to come to room temperature slowly and then stirred continuously for 20 min after the solution had become colorless. The volatile fraction was separated under vacuum and the white residue washed with ether. The volatile fraction and ether washings were combined and solvent removed. Thus a small amount of hexamethylditin (mol.wt. found: 330.6; calcd.: 327.6) and a few crystals of trimethyltin chloride were obtained. The IR spectrum of the white residue confirmed it to be *trans*-$PtHCl(PPh_3)_2$[31]; ν(Pt–H) 2220 cm^{-1}, δ(Pt–H) 835 cm^{-1}, ν(Pt–Cl) 287 cm^{-1} and ν(Pt–P) 421 cm^{-1}. Decomposition point 218°.

(*c*). *trans*-$Pt(SnMe_3)_2(PPh_3)_2$ (0.104 g, 1.0 mmole) was stirred in benzene (6 ml) and a solution of bromine (0.328 g, 2 mmoles) in carbon tetrachloride was added dropwise with stirring at 0°. After the complete addition of bromine, the reaction mixture was stirred for 20 min. The volatile fraction was removed under vacuum and the residue washed with a carbon tetrachloride/ether mixture. The volatile fraction and washings were combined and solvent removed. Thus trimethyltin bromide (0.26 g, 80% yield) was recovered and identified by comparing its infrared spectrum with that of an authentic sample. The orange yellow residue (90% yield) was identified as *cis*-$PtBr_2(PPh_3)_2$[32].

III. Reactions of trimethyltin hydride with $Pt(C_2H_4)(PPh_3)_2$ and $Pt(PPh_3)_4$

(*a*). $Pt(C_2H_4)(PPh_3)_2$ (0.181 g, 0.41 mmole) was dissolved in benzene (3 ml) and Me_3SnH (0.25 g, 1.5 mmoles) was bubbled through the above solution under vacuum. The reaction mixture immediately became light yellow and after $\frac{1}{2}$ h turned dark yellowish. The reaction mixture was allowed to stand at room temperature overnight. The hydrogen present in the reaction flask was pumped off and excess Me_3SnH, a small amount of C_2H_4 and benzene were removed under vacuum. The yellow residue was washed with benzene and ether and dried under vacuum. Yield 0.115 g (27%). The compound decomposed at 200° without melting and was very insoluble in organic solvents. Analytical results were consistent with $Pt(SnMe_3)_2(PPh_3)_2$. (Found: C, 48.64; H, 4.68. $C_{42}H_{48}P_2PtSn_2$ calcd.: C, 48.17; H, 4.62%.)

The IR spectrum (Nujol) showed $Sn-CH_3$ rocking modes at 760 s and 745 s cm^{-1}, but no single band could be assigned to $\nu(Pt-P)$ due to overlapping broad bands in the 400–500 cm^{-1} region.

When $Pt(C_2H_4)(PPh_3)_2$ and $(CH_3)_3SnH$ were allowed to react (1/1 molar ratio), neat or in benzene, immediate reaction occurred with the evolution of H_2 and C_2H_4 and the formation of red (neat reaction) or pale green (reaction in benzene) colorations. From these reaction mixtures the same compound as described above, $Pt(SnMe_3)_2(PPh_3)_2$ was obtained in 10–15% yield.

(*b*). $Pt(PPh_3)_4$ (0.232 g, 0.18 mmole) and $(CH_3)_3SnH$ (0.25 g, 1.5 mmoles) were allowed to react in benzene under vacuum. Immediate reaction occurred at room temperature with the formation of a yellowish coloration. The reaction mixture was stirred for 2 h. Hydrogen present in the reaction flask and other volatiles, $(CH_3)_3SnH$ and benzene, were removed under vacuum. The pale yellow residue (0.031 g, 20% yield) was washed with benzene and ether and dried. This material was characterized as $Pt(SnMe_3)_2(PPh_3)_2$ and resembled in physical properties the compound prepared under (*a*) above.

An immediate reaction occurred when $Pt(PPh_3)_4$ and $(CH_3)_3SnH$ (1/1 molar ratio) were allowed to react neat. The reaction was essentially complete while coming from −196° to room temperature. Hydrogen was produced and the reaction mixture became red. After removing unreacted $(CH_3)_3SnH$, the residue was washed with benzene and ether and dried under vacuum. The same material, $Pt(SnMe_3)_2(PPh_3)_2$, as described above, was formed in 12% yield.

IV. Reactions of $Pt(C_2H_4)(PPh_3)_2$ with organometallic halides

(*a*). $Pt(C_2H_4)(PPh_3)_2$ (0.242 g, 0.55 mmole) was dissolved in benzene (3 ml) and $(CH_3)_3SnCl$ (0.11 g, 0.55 mmole, in 2 ml dry ether) was added dropwise under nitrogen. Immediately a white crystalline material was deposited. The reaction mixture was allowed to stand at 25° for 2 h, then the solvents were decanted, and the residue washed with benzene and ether and dried under vacuum.

Yield 0.22 g (43%). Decomposition point 280°. Spectroscopic data are given in Table 1. (Found: C, 50.56; H, 4.02. $C_{39}H_{39}ClP_2PtSn$ calcd.: C, 50.97; H, 4.27%.) Satisfactory chlorine analyses could not be obtained.

(*b*). $Pt(C_2H_4)(PPh_3)_2$ (0.318 g, 0.72 mmole) was dissolved in benzene (3 ml) and warmed to reflux with stirring under nitrogen. A solution of $(\pi\text{-}C_5H_5)(CO)_2FeCl$ (0.153 g, 0.72 mmole) in benzene (2 ml) was added dropwise with continuous stirring. The reaction mixture was allowed to stand at room temperature for 4 h under nitrogen. Pale brown crystalline material was deposited, solvent was decanted off and the residue washed with a benzene–chloroform mixture, and dried under vacuum. Yield 0.356 g (41%). The compound decomposed at 160°. It was insoluble in most organic solvents. The IR spectrum showed the frequencies associated with (π-C_5H_5–Fe), CO and Pt–P and Pt–Cl stretching vibrations (Table 1). (Found: C, 45.81; H, 3.19; P, 4.86. $C_{25}H_{20}ClFeO_2PPt$ calcd.: C, 44.83; H, 3.01; P, 4.63%.) Satisfactory chlorine analyses could not be obtained.

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