Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF *trans*-CHLORO(TRIPHENYLSILYL)BIS(DIMETHYLPHENYLPHOSPHINE)PLATINUM AND ITS ARSENIC ANALOGUE

J. CHATT, C. EABORN AND P. N. KAPOOR
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, (Great Britain)

(Received January 19th, 1970)

SUMMARY

The complexes *trans*-[PtCl($SiPh_3$)(QMe_2Ph)$_2$], where Q = P or As, have been shown to react with lithium or sodium salts, MX, in acetone to give *trans*-[PtX($SiPh_3$)(QMe_2Ph)$_2$], where X = Br, I, N_3, or NCS. The complex *trans*-[PtCl($SiPh_3$)(PMe_2Ph)$_2$] likewise reacts with phenyl- or pentafluorophenyllithium or with *m*- or *p*-fluorophenylmagnesium bromide to give [Pt(aryl)($SiPh_3$)(PMe_2Ph)$_2$], where aryl = C_6H_5, C_6F_5, *m*- or *p*-C_6H_4F; the C_6F_5 complex has a *cis*-configuration but the other three have *trans*-configurations. Tin(II) chloride and indium(I) chloride add to *trans*-[PtCl($SiPh_3$)(PMe_2Ph)$_2$] to give *trans*-[Pt($SnCl_3$)($SiPh_3$)(PMe_2Ph)$_2$] and *trans*-[Pt($InCl_2$)($SiPh_3$)(PMe_2Ph)$_2$], respectively. Tin(II) bromide and *trans*-[PtBr($SiPh_3$)(PMe_2Ph)$_2$] correspondingly give *trans*-[Pt($SnBr_3$)($SiPh_3$)(PMe_2Ph)$_2$]. Phenylacetylene appears to insert into the Pt–Si bond of *trans*-[PtCl($SiPh_3$)(PMe_2Ph)$_2$] to give *trans*-[PtCl{$C_2HPh(SiPh_3)$}(PMe_2Ph)$_2$].

INTRODUCTION

We have described some reactions of the complexes *trans*-[PtCl($SiMePh_2$)(QMe_2Ph)$_2$] in which Q = P or As, especially those involving cleavage of the Pt–Si bond[1]. We now report some reactions of the closely related *trans*-[PtCl($SiPh_3$)(QMe_2Ph)$_2$] complexes; these mainly involve replacement of the chlorine or insertion into the Pt–Cl bond without disruption of the Pt–Si bond, but, insertion of phenylacetylene into the latter bond is also described.

RESULTS AND DISCUSSION

Metathetical reactions

The complexes *trans*-[PtCl($SiPh_3$)(QMe_2Ph)$_2$] readily react with lithium or sodium salts to undergo replacement of the chloride ligand, as in eqn. (1). (Analogous reactions of *trans*-[PtCl($GeMe_3$)(PEt_3)$_2$] have been described[2].)

$$trans\text{-}[PtCl(SiPh_3)(QMe_2Ph)_2] + MX \rightarrow trans\text{-}[PtX(SiPh_3)(QMe_2Ph)_2] + MCl \quad (1)$$

$$(Q = P \text{ or } As; M = Na \text{ or } Li; X = Br, I, NCS, N_3)$$

TABLE 1

DERIVATIVES PREPARED FROM $[PtCl(SiPh_3)(QMe_2Ph)_2]$ BY METATHESIS

Reactants		Mole ratio	Product[a], yield (%) and m.p. (°C)	Analysis found (calcd.) (%)			Mol. wt. found (calcd.)
Q	MX			C	H	N	
P	NaI	1/10	$[PtI(SiPh_3)(PMe_2Ph)_2]$[b]	48.0	4.6		825
			82, 210–212 (dec.)	(47.6)	(4.3)		(858)
P	NaSCN	1/10	$[Pt(NCS)(SiPh_3)(PMe_2Ph)_2]$	53.1	4.7	1.9	781
			84, 156–157	(53.3)	(4.7)	(1.8)	(789)
P	NaN_3	1/15	$[PtN_3(SiPh_3)(PMe_2Ph)_2$[c]	53.4	4.8	5.0	
			80, 136–139 (dec.)	(52.8)	(4.8)	(5.4)	
As	LiBr	1/15	$[PtBr(SiPh_3)(AsMe_2Ph)_2]$[a]	45.1	4.1		908
			70, 185–188	(45.4)	(4.1)		(899)
As	NaI	1/12	$[PtI(SiPh_3)(AsMe_2Ph)_2]$[b,e]	43.3	3.8		953
			88, 191–194 (dec.)	(43.2)	(3.9)		(946)
As	NaSCN	1/15	$[Pt(NCS)(SiPh_3)(AsMe_2Ph)_2]$	47.9	4.4	1.8	
			77, 136–137 (dec.)	(47.9)	(4.2)	(1.6)	
As	NaN_3	1/15	$[PtN_3(SiPh_3)(AsMe_2Ph)_2]$[f]	47.2	4.1	4.4	
			80, 138–139 (dec.)	(47.4)	(4.3)	(4.9)	

[a] All *trans*. Colourless unless otherwise specified. [b] Yellow. [c] $\nu(N_3)$ 2030; ν(Pt–P) 424 cm^{-1}. [d] Pale yellow; ν(Pt–Br) 158; ν(Pt–As) 313 cm^{-1}. (Found: Br, 8.7. Calcd.: Br, 8.9%.) [e] ν(Pt–As) 310 cm^{-1}. [f] $\nu(N_3)$ 2030; ν(Pt–As) 312 cm^{-1}.

Some properties of the new complexes thus obtained are listed in Table 1. The *trans*-configuration of the derivatives with Q = P was indicated by the appearance in ^1H NMR spectrum of three triplets centred at τ 8.40 and τ 8.35 for X = Br and I, respectively, and at τ 8.71 for $X = N_3$. *trans*-Configurations are tentatively assigned to the compound with Q = P, X = NCS and to the $[PtX(SiPh_3)(AsMe_2Ph)_2]$ compounds on the basis of the similarity between their properties, including the IR frequencies in the common regions, and those of the other derivatives. The compounds with X = NCS have an IR band at 2095 cm^{-1} attributable to ν(C=N) and one at 813 cm^{-1} attributable to ν(C=S); these values indicate that the complexes are isothiocyanates (*cf.* ref. 2).

The compound *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ likewise reacted with PhLi, C_6F_5Li, *m*-FC_6H_4MgBr and *p*-FC_6H_4MgBr to give the corresponding $[Pt(aryl)(SiPh_3)(PMe_2Ph)_2]$ complexes. The ^1H NMR spectra of the compounds with aryl = Ph, *m*-FC_6H_4 and *p*-FC_6H_4 included three triplets, centred at τ 8.95, τ 8.98, and τ 8.96, respectively, indicating a *trans*-configuration, but that of the complex $[Pt(C_6F_5)(SiPh_3)(PMe_2Ph)_2]$ showed three doublets, centred at τ 8.92, characteristic of a *cis*-configuration[3].

The complex $[Pt(Ph)(SiPh_3)(PMe_2Ph)_2]$ reacted with hydrogen in tetrahydrofuran to give an oil; this contained a Pt–H bond [ν(Pt–H) 2040 cm^{-1}] and appeared to be identical with the oil obtained by reduction of *trans*- $[PtCl(SiPh_3)(PMe_2Ph)_2]$ with sodium borohydride; it was possibly $[PtH(SiPh_3)(PMe_2Ph)_2]$. Hydrogenolysis of the Pt–Ph bond is known to occur with *cis*-$[Pt(Ph)(GeMe_3)(PEt_3)_2]$[2].

Insertion reactions with tin(II) halides and indium(I) chloride

Tin(II) chloride and bromide react readily with *trans*-$[PtX(SiPh_3)(PMe_2Ph)_2]$

in ether to give the crystalline complexes *trans*-$[Pt(SnX_3)(SiPh_3)(PMe_2Ph)_2]$, where X = Cl or Br. A suspension of indium(I) chloride in tetrahydrofuran similarly gives *trans*-$[Pt(InCl_2)(SiPh_3)(PMe_2Ph)_2]$. The products are stable in the air as solids. They are insoluble in non-polar solvents, but dissolve in polar organic solvents, possibly with dissociation; thus the complex *trans*-$[Pt(SnCl_3)(SiPh_3)(PMe_2Ph)_2]$ was found to regenerate the starting materials when dissolved in acetone, indicating the existence of equilibrium (2), analogous to that observed with $[PtCl(SnCl_3)(PPh_3)_2]$[4].

$$trans\text{-}[Pt(SnCl_3)(SiPh_3)(PMe_2Ph)_2] \rightleftharpoons trans\text{-}[PtCl(SiPh_3)(PMe_2Ph)_2] + SnCl_2 \qquad (2)$$

The *trans*-configuration of the tin- and indium-containing complexes was inferred from the observation that their IR spectra were essentially identical with that of *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ in the region 400–4000 cm^{-1} and showed an intense ν(Pt–P) bond at 425–420 cm^{-1} (*cf.* ref. 1). The spectrum of *trans*-$[Pt(SnCl_3)(SiPh_3)(PMe_2Ph)_2]$ includes three bands, at 348, 320, and 292 cm^{-1}, which are absent from that of *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$, and since the last two bands are absent in the case of the corresponding tribromotin-complex they are assigned to ν(Sn–Cl). Values of 341 and 325 cm^{-1} have been reported for ν(Sn–Cl) in $[PtCl(SnCl_3)(PPh_3)_2]$[5], and the somewhat lower frequencies in our compounds may be associated with the large *trans*-influence of the Ph_3Si group.

The spectrum of *trans*-$[Pt(InCl_2)(SiPh_3)(PMe_2Ph)_2]$ similarly shows a band at 292 cm^{-1} not present in that of *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$, and this is probably attributable to an (In–Cl) frequency.

Reaction with phenylacetylene

Phenylacetylene reacted with *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ in boiling benzene to give a white solid of formula $[PtCl\{C_2HPh(SiPh_3)\}(PMe_2Ph)_2]$ in 46% yield. The occurrence of three triplets centred at τ 8.75 in the ^1H NMR spectrum indicated a *trans*-configuration. The new complexes $[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ and $[PtCl(C{\equiv}CPh)(PMe_2Ph)_2]$ were prepared for comparison by Chatt and Shaw's method[6]; the ^1H NMR spectrum of the former included three triplets centred at τ 7.9, indicating a *trans*-configuration, while that of the latter showed three triplets with three overlapping doublets in this general region, indicative of a *cis*/*trans* mixture. In the IR, the complexes $[PtCl(R)(PMe_2Ph)_2]$ where R = Ph_3Si or $C_2HPh(SiPh_3)$ both show an intense band at 425–420 cm^{-1}, attributable to ν(Pt–P) and consistent with a *trans*-configuration.

The IR spectrum of the product $[PtCl\{C_2HPh(SiPh_3)\}(PMe_2Ph)_2]$ does not show an absorption near 2110 cm^{-1} which is characteristic of a C≡CR group σ-bonded to platinum and which is present for both of the σ-(phenylalkynyl)platinum complexes prepared. It shows intense bands at 1510 cm^{-1} and 600 cm^{-1} and a weak-shoulder at 3070 cm^{-1} which are not present in the spectrum of either *trans*-$[(PtCl)(SiPh_3)(PMe_2Ph)_2]$ or *trans*-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$; it is likely that the band at 1510 cm^{-1} is associated with the C=C stretching vibration and the shoulder at 3070 cm^{-1} with a C–H stretching vibration. The band at 600 cm^{-1} may possibly be associated with the out-of-plane C–H bending vibration. There seems little doubt that the phenylacetylene has inserted into the Pt–Si bond to give a substituted-vinyl complex, but on the evidence available we cannot distinguish between structures (I), (II), and (III) for the vinyl–platinum system.

$Pt{-}CH{=}C(Ph)(SiPh_3)$ (I) $Pt{-}C(Ph){=}C(SiPh_3)H$ (II) $Pt{-}C(SiPh_3){=}CHPh$ (III)

The resonance of the C=C–H proton expected to show up in the NMR spectrum is masked by the phenyl protons, which give rise to a complex multiplet centred at τ 2.7. A strong absorption at 270 cm^{-1} in the IR is attributed to ν(Pt–Cl) and indicates that the substituted vinyl ligand has a large *trans*-influence, though smaller than that of the Ph_3Si group.

There is insufficient evidence at present to enable us to speculate in detail on the mechanism of the insertion; one possibility, involving replacement of the Pt–$SiPh_3$ bond by a Pt–C≡CPh bond, with elimination of triphenylsilane which then adds to the alkyne, appears to be ruled out by the observation that triphenylsilane does not react with *trans*-$[PtCl(C{\equiv}CPh)(PMe_2Ph)_2]$ under the conditions employed for the insertion.

In contrast with our results, reaction of phenylacetylene with *trans*-$[PtCl(SiMe_3)(PEt_3)_2]$ did not give insertion products, but instead the complexes $[PtCl(C{\equiv}CPh)(PEt_3)_2]$, $[PtH(C{\equiv}CPh)_2(PEt_3)_2]$, and $[Pt(C{\equiv}CPh)_2(PEt_3)_2]$, and a compound of empirical formula, as indicated by mass spectrometry, corresponding with $[PtCl(SiMe_3, Ph_2C_2H_4)(PEt_3)_2]$[2]. Under the conditions used with phenylacetylene we observed no reaction between *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ and diphenylacetylene, cyclohexene, styrene, acrylonitrile, or benzaldehyde; tetracyanoethylene reacted very rapidly but the oil formed could not be crystallised.

EXPERIMENTAL

General

All reactions were carried out under dry nitrogen. IR spectra were determined with Nujols mulls on a Perkin–Elmer 337 grating spectrophotometer or (unless otherwise stated) with Nujol mulls between polythene plates on a Grubb–Parsons DM4 grating spectrometer. Proton NMR spectra were recorded, in hexadeuteriobenzene unless otherwise stated, on a Varian HA 100 spectrometer at 100 Hz. Molecular weights were determined by osmometry in benzene. The light petroleum used was of b.p. 60–80°.

trans-Chloro(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II), m.p. 169–171°, was prepared as previously described[1].

trans-Bromo(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II)

Lithium bromide (0.52 g, 6.0 mmoles) in acetone (5 ml) was added to *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ (0.34 g, 0.44 mmole) in acetone (5 ml). The mixture was set aside at room temperature for 2 h then evaporated to dryness. The residue was extracted with benzene (20 ml), the extract was filtered and concentrated, and light petroleum was added to give the yellow *trans*-$[PtBr(SiPh_3)(PMe_2Ph)_2]$ (0.30 g, 83%), m.p. 197–198°; ν(Pt–P) 423 cm^{-1}; ν(Pt–Br) 161 cm^{-1} (polythene disc). (Found: C, 50.1; H, 4.6; Br, 9.8; mol.wt., 806. $C_{34}H_{37}BrP_2PtSi$ calcd.: C, 50.4; H, 4.6; Br, 9.9%; mol.wt., 811.) In the ^1H NMR spectrum there were three triplets centred at τ 8.4, with J(P–H) 3.5 and J(Pt–H) 29.0 Hz.

Metathetical reactions

Details of other preparations by the procedure of the preceding paragraph are given in Table 1.

trans-Phenyl(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II)

An ethereal solution of phenyllithium (0.75 mmole) was added dropwise to *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.50 g, 0.65 mmole) in benzene (10 ml) at 0°. After 1 h the mixture was allowed to warm to room temperature, the solvent was removed under reduced pressure, and the residue was extracted with benzene. The extract was filtered and concentrated and light petroleum was added, to give *trans*-[Pt(Ph)-(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.22 g, 42%), m.p. 165–166° (decompn.); ν(C=C) 1575, 1562 cm^{-1}; ν(Pt–P) 422 cm^{-1}. (Found: C, 59.5; H, 5.2% mol.wt., 836. $C_{40}H_{42}P_2PtSi$ calcd.: C, 59.5; H, 5.2%; mol.wt., 806.) In the ^{1}H NMR spectrum there were three triplets centered at τ 8.95, with J(P–H) 3.5 and J(Pt–H) 32.0 Hz.

A solution of the product (0.30 g) in benzene (10 ml) was shaken under hydrogen at atmospheric pressure for 40 h. Removal of the solvent at room temperature left a yellow-brown oil, which could not be crystallized. The IR spectrum showed a band at 2040 cm^{-1} which is probably attributable to ν(Pt–H). A similar oil, with a band at this frequency, was obtained after treatment of *trans*-[PtCl(SiPh$_3$)(PMe$_2$-Ph)$_2$] in benzene with aqueous sodium borohydride.

cis-Pentafluorophenyl(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II)

A solution of *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.50 g, 0.65 mmole) in ether (60 ml) was added dropwise to a solution of pentafluorophenyllithium made from pentafluorobenzene (0.13 g, 0.71 mmole) and n-butyllithium (0.73 mmole) in ether and maintained at −78°. The mixture was allowed to reach room temperature during 2 h, the solvent was removed, and the residue was extracted with benzene. Filtration and concentration of the extract, followed by addition of light petroleum gave *cis*-[Pt(C$_6$F$_5$)(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.38 g, 65%), m.p. 183–185° (decompn.); ν(C=C) 1620, 1595; ν(C–F) 1042, 950; ν(Pt–P) 437, 423 cm^{-1}. (Found: C, 53.7; H, 4.1; mol.wt., 890. $C_{40}H_{37}F_5P_2PtSi$ calcd.: C, 53.5; H, 4.2%; mol.wt., 898.) In the ^{1}H NMR spectrum there were three doublets centered at τ 8.92, with J(P–H) 9.5 and J(Pt–H) 33.0 Hz.

m- and p-Fluorophenyl(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II)

A solution of *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.40 g, 0.52 mmole) in benzene (10 ml) was added during 1 h to a solution of *p*-fluorophenylmagnesium bromide (ca. 0.7 mmole) in ether. The mixture was stirred at room temperature for 2 h, then dioxane (20 ml) was added. The solution was filtered, and the filtrate was evaporated under reduced pressure to leave a yellow oil, which on extraction with light petroleum left a colourless solid. This was recrystallized from benzene/light petroleum to give *trans*-[Pt(C$_6$H$_4$F-*p*)(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.18 g, 42%); m.p. 166–167° (decompn.); ν(C=C) 1570; ν(C–F) 1208; ν(Pt–P) 422 cm^{-1}. (Found: C, 58.5; H, 5.0; mol.wt., 840. $C_{40}H_{41}FP_2PtSi$ calcd.: C, 58.2; H, 5.0% mol. wt., 826.) The ^{1}H NMR spectrum included three triplets centered at τ 8.98, with J(P–H) 3.5 and J(Pt–H) 32 Hz.

The *m*-isomer (33%), m.p. 162–163° (decompn.) was prepared analogously; ν(C=C) 1586, 1560; ν(C–F) 1192; ν(Pt–P) 423 cm^{-1}. (Found: C, 58.6; H, 5.1%, mol.wt., 816). The ^{1}H NMR spectrum included three triplets centred at τ 8.96, with the same couplings as the *p*-isomer.

trans-Bis(phenylethynyl)bis(dimethylphenylphosphine)platinum(II)

Phenylacetylene (0.45 g, 4.4 mmoles) in benzene (50 ml) was added to the Grignard reagent prepared from ethyl bromide (0.50 g, 4.6 mmoles) and magnesium (0.16 g, 6.6 g-atom) in ether (20 ml). The mixture was refluxed for 15 min, then cooled to 20°, and *cis*-$[PtCl_2(PMe_2Ph)_2]$ (1.0 g, 1.8 mmoles) was added. After 20 h at 20° the mixture was treated with ice and dilute hydrochloric acid, and the usual working up, culminating in recrystallization from benzene/light petroleum, gave the yellow *trans*-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ (0.8 g, 66%), m.p. 191–192°; $\nu(C{\equiv}C)$ 2110; $\nu(Pt\text{–}P)$ 422 cm^{-1}. (Found: C, 57.0; H, 4.8. $C_{32}H_{32}P_2Pt$ calcd.: C, 57.1; H, 4.8%.) The ^1H NMR spectrum in deuteriochloroform included three triplets centred at τ 7.9, with $J(P\text{–}H)$ 3.5 and $J(Pt\text{–}H)$ 32.0 Hz.

Chloro(phenylethynyl)bis(dimethylphenylphosphine)platinum(II) (cis/trans mixture)

A solution of *trans*-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ (0.50 g, 0.74 mmole) in benzene (10 ml) was treated with anhydrous hydrogen chloride (0.74 mmole) in benzene during 10 min. The solution was evaporated to dryness, and the residue recrystallized from benzene/light petroleum to give the pale-yellow $[PtCl(C{\equiv}CPh)(PMe_2Ph)_2]$ (0.4 g, 86%), m.p. 119–126°; $\nu(C{\equiv}C)$ 2110 cm^{-1}. (Found: C, 47.0; H, 4.6. $C_{24}H_{27}ClP_2Pt$ calcd.: C, 47.4; H, 4.5%.) The ^1H NMR spectrum (in deuteriochloroform) included three triplets with three overlapping doublets in the region around τ 8.0.

The reaction between trans-chloro(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II) and phenylacetylene

Phenylacetylene (5 ml) was added to a solution of *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ (0.25 g, 0.33 mmole). The mixture was refluxed for 2 h and then evaporated to dryness under reduced pressure to give a yellow oil, which on extraction with light petroleum left a white solid. This was recrystallized from benzene/light petroleum to give *trans*-$[PtCl\{C_2HPh(SiPh_3)\}(PMe_2Ph)_2]$ (0.14 g, 46%), m.p. 191–192°; $\nu(C\text{–}H)$ 3070 (hexachlorobutadiene mull); $\nu(C{=}C)$ 1510; $\nu(Pt\text{–}P)$ 418; $\nu(Pt\text{–}Cl)$ 270 cm^{-1}. (Found: C, 58.0; H, 5.2; Cl, 3.9; mol.wt., 870. $C_{42}H_{43}ClP_2PtSi$ calcd.: C, 58.1; H, 5.0; Cl, 4.1%; mol.wt., 868.) The ^1H NMR spectrum included three triplets centred at τ 8.75, with $J(P\text{–}H)$ 3.5 and $J(Pt\text{–}H)$ 31 Hz.

The light petroleum extract was evaporated to leave an uncrystallizable yellow oil. The IR spectrum showed a band at 2110 cm^{-1} which is probably attributable to $\nu(C{\equiv}C)$.

trans-Trichlorostannyl(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II) and its bromine analogue

When a concentrated solution of stannous chloride in diethyl ether was added to a suspension of *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ (0.21 g, 0.27 mmole) in ether (5 ml), yellow needles rapidly separated. These were filtered off, washed with ether, and shown to be *trans*-$[Pt(SnCl_3)(SiPh_3)(PMe_2Ph)_2]$ (0.19 g, 70%), m.p. 150–152° (decompn.); $\nu(Pt\text{–}P)$ 423; $\nu(Sn\text{–}Cl)$ 320, 292 cm^{-1}. (Found: C, 42.7; H, 3.9; Cl, 11.0. $C_{34}H_{37}Cl_3P_2PtSiSn$ calcd.: C, 42.7; H, 3.9; Cl, 11.1%.)

Similarly from stannous bromide and *trans*-$[PtBr(SiPh_3)(PMe_2Ph)_2]$ was formed the orange-brown *trans*-$[Pt(SnBr_3)(SiPh_3)(PMe_2Ph)_2]$ (25%), m.p. 182–184°

(decompn.); ν(Pt–P) 424 cm^{-1}. (Found: C, 37.1; H, 3.4. $C_{34}H_{37}Br_3P_2PtSiSn$ calcd.: C, 37.5; H, 3.4%.)

trans-(Dichloroindium)(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II)

Finely powdered indium(I) chloride (0.11 g, 0.73 mmole) dissolved to form an orange solution when shaken with a solution of *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.52 g, 0.68 mmole) in tetrahydrofuran (10 ml) at room temperature for 1 h. Concentration followed by addition of light petroleum gave the orange *trans*-[Pt(InCl$_2$)-(SiPh$_3$)(PMe$_2$Ph)$_2$], (0.56 g, 93%), m.p. 145–148° (decompn.); ν(Pt–P) 421 cm^{-1}; ν(In–Cl) 292 cm^{-1}. (Found: C, 43.3; H, 4.1; Cl, 7.8. $C_{34}H_{37}Cl_2InP_2PtSi$ calcd.: C, 44.5; H, 4.1; Cl, 7.7%.)

ACKNOWLEDGEMENT

We thank Johnson Matthey and Co. Ltd. for the loan of platinum salts, the Shell International Petroleum Company Ltd, for financial support, and Dr. G.J. Leigh for helpful advice.

REFERENCES

1 J. Chatt, C. Eaborn, S. D. Ibekwe and P. N. Kapoor, *J. Chem. Soc. A*, (1970) in press.
2 F. Glockling and K. A. Hooton, *J. Chem. Soc. A*, (1967) 1066.
3 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, (1966) 770.
4 J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 5176.
5 M. C. Baird, *J. Inorg. Nucl. Chem.*, 29 (1967) 367.
6 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 4020.