

ORGANOPLUMBIO COMPLEXES OF PLATINUM(II) *

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Summary

The complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ reacts with Pb_2Ph_6 to give *cis*- $[\text{PtPh}(\text{Pb}_2\text{Ph}_5)(\text{PPh}_3)_2]$; this decomposes in solution to *cis*- $[\text{PtPh}(\text{PbPh}_3)(\text{PPh}_3)_2]$, which may also be obtained from the ethylene complex and PbPh_4 . Lead compounds PbPhMe_3 and PbPh_3Br also give products of insertion into $\text{Pb}-\text{Ph}$ bonds, but PbMe_3Cl gives *cis*- and *trans*- $[\text{PtCl}(\text{PbMe}_3)(\text{PPh}_3)_2]$. The complex *trans*- $[\text{Pt}(\text{PbPh}_3)_2(\text{PEt}_3)_2]$ reacts with 1,2-bis(diphenylphosphino)ethane (DPPE) to give $[\text{Pt}(\text{PbPh}_3)_2(\text{DPPE})]$ which readily decomposes in dichloromethane in presence of PEt_3 to give $[\text{Pt}(\text{PbPh}_3)(\text{PEt}_3)(\text{DPPE})]\text{Cl}$ and $[\text{PtPh}(\text{PEt}_3)(\text{DPPE})]\text{Cl}$. The complex *trans*- $[\text{PtCl}(\text{PbPh}_3)(\text{PEt}_3)_2]$ was detected in the products of reactions between *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ and *trans*- $[\text{Pt}(\text{PbPh}_3)_2(\text{PEt}_3)_2]$ or less than 2 moles of LiPbPh_3 ; it was not detected in the mixture after treatment of *trans*- $[\text{Pt}(\text{PbPh}_3)_2(\text{PEt}_3)_2]$ with HCl . In contrast to an earlier report, we were unable to detect lead-containing complexes in the products of the reaction between *trans*- $[\text{PtHCl}(\text{PPh}_3)_2]$ and Ph_3PbNO_3 . The complexes and their decomposition products were identified by $^{31}\text{P}-\{^1\text{H}\}$ NMR spectroscopy.

Introduction

Examination by $^{31}\text{P}-\{^1\text{H}\}$ NMR spectroscopy of the products of oxidative-addition of SnR_3Cl to platinum(0) complexes showed that the originally assigned formulations *cis*- or *trans*- $[\text{PtCl}(\text{SnR}_3)\text{L}_2]$ (L = phosphine) [1] were incorrect and that the products were either the complexes *cis*- $[\text{PtR}(\text{SnR}_2\text{Cl})\text{L}_2]$ or mixtures containing them [2]. We now describe the results of a $^{31}\text{P}-\{^1\text{H}\}$ NMR spectroscopic examination of the products of oxidative-addition reactions of some organolead compounds with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$. Close analogues of some of these reactions have been studied previously [3] but the reported

* No reprints available.

spectra of the products did not include ^{31}P NMR, and in some instances the results were insufficient to give structural assignments which could be regarded as unequivocal in the light of our findings for the Sn—Pt complexes.

For completeness we have also re-examined by ^{31}P - $\{^1\text{H}\}$ NMR the products of a number of reactions reported to lead to Pt—Pb complexes [4,5]. A preliminary account of some of this work has been published [6].

Results and discussion

The complex *cis*-[PtPh(PbPh₃)(PPh₃)₂], whose structure has been determined by X-ray crystallography [3], was originally obtained from a compound formulated as [Pt(PbPh₃)₂(PPh₃)₂] [3], but we have found that it can also be obtained by the more direct reaction between PbPh₄ and [Pt(C₂H₄)(PPh₃)₂]. Its ^{31}P - $\{^1\text{H}\}$ NMR spectrum in dichloromethane is as expected; it comprises two doublets (δ 112.3, 120.0 ppm) from the non-equivalent phosphines [$^2J(\text{PPtP})$ 13 Hz]. The lines corresponding to δ 112.3 ppm have satellites from coupling to ^{195}Pt [$^1J(\text{Pt—P})$ 2944 Hz] and to ^{207}Pb [$^2J(\text{PbPtP})$ 3462 Hz], and those corresponding to δ 120.0 ppm have couplings $^1J(\text{Pt—P})$ 1968 Hz and $^2J(\text{PbPtP})$ 259 Hz. The larger indirect coupling $^2J(\text{PbPtP})$ is clearly associated with PPh₃ *trans* to Pb and the smaller coupling constant $^1J(\text{Pt—P})$ is of a magnitude expected for PPh₃ *trans* to a phenyl group [2].

The precursor of this compound, formulated as [Pt(PbPh₃)₂(PPh₃)₂] with unassigned stereochemistry, was prepared by Crociani et al. by oxidative-addition of Pb₂Ph₆ to [Pt(PPh₃)₄] [3]. To record the ^{31}P - $\{^1\text{H}\}$ NMR spectrum of this compound we carried out the reaction between Pb₂Ph₆ and the more convenient starting material [Pt(C₂H₄)(PPh₃)₂] in dichloromethane in an NMR tube. Spectrum accumulation was commenced ca. 30 min. after mixing the reagents and the spectrum resulting after a further 20 min. showed the presence of two complexes in addition to the starting complex. One product, which was present in a minor proportion (ca. 30%), was identified from its parameters as *cis*-[PtPh(PbPh₃)(PPh₃)₂]. The major product of the reaction (70%) had a spectrum which was similar to that of *cis*-[PtPh(PbPh₃)(PPh₃)₂] except in the numerical values of the shift and coupling parameters. The presence of non-equivalent phosphines is clearly incompatible with either isomer of the original formulation, and from the magnitudes of the coupling constants we have assigned the formula *cis*-[PtPh(Pb₂Ph₅)(PPh₃)₂], a compound formed by insertion of platinum into a Pb—Ph bond of Pb₂Ph₆ rather than the Pb—Pb bond. This formula is, of course, in agreement with the analytical results obtained previously. Also, one phosphorus ligand is associated with a large value of $^2J(\text{PbPtP})$ (3516 Hz) and is clearly *trans* to a Pb donor atom; the other phosphorus ligand has $^1J(\text{Pt—P})$ 1926 Hz; a value similar to that in *cis*-[PtPh(PbPh₃)(PPh₃)₂] (1968 Hz), and indicative of a *trans* phenyl ligand. The presence of *cis*-[PtPh(PbPh₃)(PPh₃)₂] in the product mixture is consistent with the observation of Crociani et al. [3] that the product from oxidative-addition of Pb₂Ph₆ decomposes upon standing in dichloromethane to form this complex.

Complexes containing two triphenylplumbio-ligands have been prepared by the reaction of *cis*- or *trans*-[PtCl₂L₂] with LiPbPh₃ [4]. We have repeated the preparation for L = PEt₃ and the ^{31}P parameters (Table 1) confirm that the prod-

uct is *trans*-[Pt(PEt₃)₂(PbPh₃)₂]; the spectrum comprises a single resonance with ¹⁹⁵Pt satellites and the ²⁰⁷Pb satellites have ²J(PbPtP) 239 Hz indicating Pb *cis* to P and the intensity of the satellites further shows that there are two Pb donor atoms in a *cis* relationship to each P.

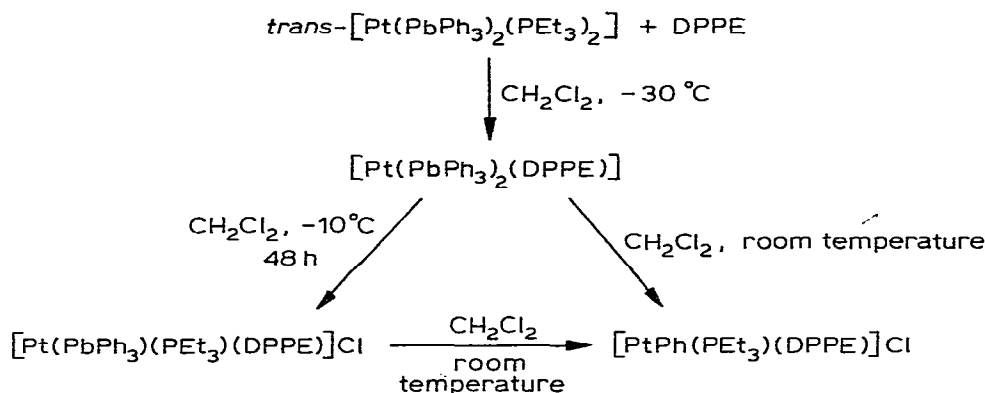
From a similar reaction in which a deficiency of LiPbPh₃ was used we obtained a product for which the ³¹P-{¹H} NMR spectrum showed the presence of *trans*-[Pt(PbPh₃)₂(PEt₃)₂] as the principal component and a small amount of a complex with parameters δ 131 ppm, ¹J(Pt—P) 2629 Hz, and ²J(PbPtP) 273 Hz. The intensity of the ²⁰⁷Pb satellites showed that the complex contained only one Pb attached to Pt, and this and the magnitudes of the coupling constants are consistent with the formula *trans*-[PtCl(PbPh₃)(PEt₃)₂], but we did not attempt to isolate this compound. This compound has been reported previously by Deganello et al., who obtained a white solid (with a satisfactory analysis [5] with ν(Pt—Cl) 285 cm⁻¹ by treating *trans*-[Pt(PbPh₃)₂(PEt₃)₂] with HCl (1 molar proportion) in benzene [4].

We have repeated this procedure but the products we obtained were identified by ³¹P-{¹H} NMR as *trans*-[PtPh(Cl)(PEt₃)₂] [δ 126 ppm, ¹J(Pt—P) 2793 Hz] and *trans*-[PtCl₂(PEt₃)₂] [δ 128 ppm, ¹J(Pt—P) 2412 Hz], together with unreacted starting material. In CHCl₃ a similar procedure gave only *trans*-[PtCl₂(PEt₃)₂], so in the absence of full characterisation of the products of this reaction as obtained by Deganello et al., [4] it must be somewhat doubtful whether *trans*-[PtCl(PbPh₃)(PEt₃)₂] can be obtained by this method. A complex with ³¹P parameters [δ and ¹J(Pt—P) only] identical to those assigned to *trans*-[PtCl(PbPh₃)(PEt₃)₂] was detected in low yield from a reaction in benzene between *trans*-[Pt(PbPh₃)₂(PEt₃)₂] and a mixture of *cis*- and *trans*-[PtCl₂(PEt₃)₂]. After 24 h at ambient temperature the solution was shown by ³¹P-{¹H} NMR to contain *trans*-[PtCl(PbPh₃)(PEt₃)₂], the starting complexes, *cis*-[PtPh(Cl)(PEt₃)₂] [δ 129.6, 135.6 ppm, ¹J(Pt—P) 1616, 4180 Hz] and *trans*-[PtPh(Cl)(PEt₃)₂].

It has also been reported [4] that treatment of *trans*-[Pt(PbPh₃)₂(PEt₃)₂] with an excess of 1,2-bis(diphenylphosphino)ethane (DPPE) either in boiling benzene or in benzene or dichloromethane at room temperature gave a product with m.p. 255–260°C (decomp.) which was assigned the formula [Pt(PbPh₃)₂(DPPE)] on the basis of the analytical results [Analysis found: C, 51.8; H, 3.82. Calcd.: C, 50.5; H, 3.66%]. When we carried out the reaction in boiling benzene a metallic mirror was rapidly deposited so this mixture was not investigated further. The ³¹P-{¹H} NMR spectra of mixtures prepared in dichloromethane at room temperature gave no evidence for the presence of complexes containing Pt—Pb bonds, but such complexes were detected when dichloromethane solutions were prepared and maintained at temperatures below -10°C. Our results are summarized in Scheme 1. The products were identified from the ³¹P-{¹H} spectra as detailed below, and because the calculated carbon and hydrogen contents of all three products are closely similar, the identities of the solid complexes used for analytical determinations were established by recording ³¹P-{¹H} NMR spectra of their solutions in dichloromethane prepared and maintained at -30°C.

The initial product [Pt(PbPh₃)₂(DPPE)] has a ³¹P-{¹H} NMR spectrum which comprises a ca. 1 : 4 : 1 triplet from molecules containing inactive lead nuclei

SCHEME 1



together with an AA'X spectrum from molecules containing $\text{X} = {}^{207}\text{Pb}$ (21% abundance). The parameters of this spectrum are given in Table 1 together with those for the analogous complex $[\text{Pt}(\text{SnPh}_3)_2(\text{DPPE})]$; the principal features of the spectrum of this complex have been reported previously [7], but a spectrum of sufficient intensity to show tin satellites was obtained subsequently. Satisfactory analytical results were obtained for this and the lead complex (Table 1) which melted with decomposition at $110\text{--}116^\circ\text{C}$.

When the reaction mixture was maintained at -10°C for 48 h the ${}^{31}\text{P}\text{--}\{{}^1\text{H}\}$ NMR spectrum was of ABX form with platinum satellites. The shifts and coupling constants show that a PEt_3 ligand is *trans* to one phosphorus of a DPPE ligand which is also associated with weak ${}^{207}\text{Pb}$ satellites, presumably from a PbPh_3 ligand in *cis* relationship [${}^2J(\text{PbP})$ 241 Hz]. The other phosphorus of DPPE is associated with ${}^1J(\text{Pt--P})$ 2397 Hz, which is somewhat smaller than for P *trans* in $[\text{Pt}(\text{PbPh}_3)_2(\text{DPPE})]$, but a change of ligand in *cis* relationship can cause differences in ${}^1J(\text{Pt--P})$ of this magnitude. Since we are able to eliminate the possible presence of a phenyl ligand (*vide infra*), it seems reasonable to assign the formula $[\text{Pt}(\text{PbPh}_3)(\text{PEt}_3)(\text{DPPE})]\text{Cl}$ to this complex.

When any of these reaction mixtures were allowed to warm to room temperature or when the mixture was prepared at room temperature, the ${}^{31}\text{P}\text{--}\{{}^1\text{H}\}$ NMR spectra obtained within 1 h showed complete conversion into $[\text{PtPh}(\text{PEt}_3)(\text{DPPE})]\text{Cl}$, the spectrum of which is also of ABX form with ${}^1J(\text{Pt--P})$ 1702 Hz for the P of DPPE assigned *trans* to the phenyl ligand. This complex was obtained with satisfactory analytical results (Table 1) and with m.p. $110\text{--}120^\circ\text{C}$ from a reaction mixture at room temperature after removal of PbCl_2 and PbPh_4 . It is evident that in dichloromethane the Pt–Pb bonds are labile and are probably replaced by Pt–Cl bonds in reactions with the solvent, after which the chloride is displaced by the excess of phosphine to form the cationic complexes.

We are unable to explain the results reported by Deganello et. al. [4] for the product of the reaction between *trans*- $[\text{Pt}(\text{PbPh}_3)_2(\text{PEt}_3)_2]$ and DPPE. Although it is possible that their product with m.p. $255\text{--}260^\circ\text{C}$ (decomp.) was $[\text{Pt}(\text{PbPh}_3)(\text{PEt}_3)(\text{DPPE})]\text{Cl}$, which has similar carbon and hydrogen contents to those reported [4] and which we did not isolate, our results imply that it is unlikely that any platinum complex other than $[\text{PtPh}(\text{PEt}_3)(\text{DPPE})]\text{Cl}$ could be

obtained from dichloromethane at room temperature by the procedure they report. In toluene at -20°C or benzene close to its m.p., $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of mixtures of *trans*- $[\text{Pt}(\text{PbPh}_3)_2(\text{DPPEt}_3)_2]$ and DPPE showed the presence of small amounts of $[\text{Pt}(\text{PbPh}_3)_2(\text{DPPE})]$, but in toluene at room temperature the solution contained mainly $[\text{PtPh}_2(\text{DPPE})]$ [δ -99.8 ppm, $^1J(\text{Pt}-\text{P})$ 1672 Hz, lit. [8] (in CH_2Cl_2) δ -99.4 ppm, $^1J(\text{Pt}-\text{P})$ 1704 Hz], so the complex is unstable in solution at room temperature even in an inert solvent.

The reactions of PbMe_3Ph and PbPh_3Br with the complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ in CH_2Cl_2 were shown from the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of the product mixtures to involve formal insertion of platinum into the $\text{Pb}-\text{Ph}$ bonds. The reaction with PbMe_3Ph at ambient temperature gave *cis*- $[\text{PtPh}(\text{PbMe}_3)(\text{PPh}_3)_2]$ the spectrum and parameters of which are closely related to those of *cis*- $[\text{PtPh}(\text{PbPh}_3)(\text{PPh}_3)_2]$ (Table 1). With PbPh_3Br at -30°C the spectrum of the product shows the presence of a single *cis* complex with one PPh_3 *trans* to Ph [$^1J(\text{Pt}-\text{P})$ 2078 Hz] and one PPh_3 *trans* to Pb [$^2J(\text{PbPtP})$ 4019 Hz]. The magnitude of $^1J(\text{Pt}-\text{P})$ for PPh_3 *trans* to Pb [3457 Hz] is larger than that for PPh_3 *trans* to PbPh_3 [2944 Hz] in *cis*- $[\text{PtPh}(\text{PbPh}_3)(\text{PPh}_3)_2]$. The stoichiometry of the reaction and analogy with the complexes *cis*- $[\text{PtPh}(\text{X})(\text{PPh}_3)_2]$, where for PPh_3 *trans* to X $^1J(\text{Pt}-\text{P}) = 2717$ Hz for $\text{X} = \text{SnPh}_2\text{Br}$ and $^1J(\text{Pt}-\text{P}) = 2354$ Hz for $\text{X} = \text{SnPh}_3$ [2], then imply the formula *cis*- $[\text{PtPh}(\text{PbPh}_2\text{Br})(\text{PPh}_3)_2]$ for the product from PbPh_3Br . This complex decomposed in CH_2Cl_2 upon warming to room temperature and from the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum the product mixture was shown to comprise *trans*- $[\text{PtBr}(\text{Ph})(\text{PPh}_3)_2]$ (ca. 35%), *cis*- $[\text{PtBr}(\text{Ph})(\text{PPh}_3)_2]$ (ca. 39%), *cis*- $[\text{PtPh}_2(\text{PPh}_3)_2]$ (ca. 11%), and *cis*- $[\text{PtPh}(\text{PbPh}_3)(\text{PPh}_3)_2]$ (ca. 16%). The reaction was accompanied by the precipitation of metallic Pb ; the same product mixture was obtained when the oxidative-addition reaction was carried out at room temperature.

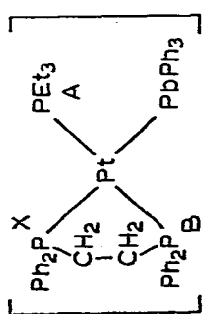
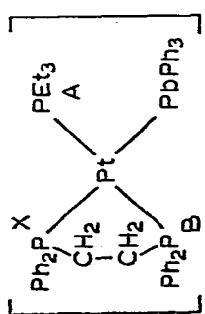
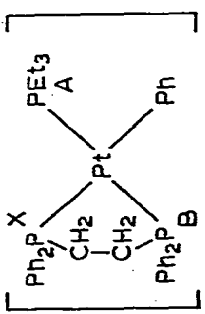
The spectrum of the product of the reaction between PbClMe_3 and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ in CH_2Cl_2 at -30°C indicated the presence of *cis*- $[\text{PbCl}(\text{PbMe}_3)(\text{PPh}_3)_2]$ (ca. 8%) and its *trans* isomer (ca. 92%). The *cis* complex has the expected form of spectrum, with coupling constants $^1J(\text{Pt}-\text{P})$ indicating PPh_3 *trans* to Cl (3991 Hz) and PbMe_3 (2731 Hz). Coupling constants $^1J(\text{Pt}-\text{P})$ *trans* to PbMe_3 are expected to be slightly smaller than those *trans* to PbPh_3 (Table 1) by analogy with results for PPh_3 *trans* to Sn in the related tin complexes *cis*- $[\text{PtPh}(\text{SnPh}_3)(\text{PPh}_3)_2]$ [$^1J(\text{Pt}-\text{P})$ 2354 Hz P *trans* to Sn] and *cis*- $[\text{PtPh}(\text{SnMe}_3)(\text{PPh}_3)_2]$ [$^1J(\text{Pt}-\text{P})$ 2036 Hz P *trans* to Sn]. Because of the low abundance of the *cis*-product, the ^{207}Pb -satellites were too weak to observe.

The identification of the *trans* product as *trans*- $[\text{PtCl}(\text{PbMe}_3)(\text{PPh}_3)_2]$ has been inferred from the value of $^1J(\text{Pt}-\text{P})$ (2688 Hz), which is typical of PPh_3 *trans* to P , and from the ^{207}Pb satellites which have a combined intensity of ca. 25% of the main peak intensity [Abundance of ^{207}Pb 21%], indicating one Pb atom per molecule, and a coupling constant $^2J(\text{PbPtP})$ (188 Hz) consistent with a *cis* relationship between the Pb and P donor atoms. In the ^1H NMR spectrum at -30°C signals from the PbMe_3 group [δ 0.67 ppm, $^2J(\text{PbCH}) = 60$ Hz] and unreacted PbClMe_3 [δ 1.37 ppm, $^2J(\text{PbCH})$ 68 Hz] were observed and there were no indications of $\text{Pt}-\text{Me}$ groups. When the oxidative addition reaction was carried out at room temperature in CH_2Cl_2 the products *cis*- $[\text{PtMe}(\text{Cl})(\text{PPh}_3)_2]$ and *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ were identified from the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum and

(Continued on p. 342)

TABLE 1
 $^{31}\text{P}\{-^1\text{H}\}$ NMR AND ANALYTICAL DATA

Complex	Solvent	$^{31}\text{P}\{-^1\text{H}\}$ NMR Parameters a $-\delta(\text{ppm}), J(\text{Hz})$	Molecular formula	Analysis found (calc) (%)		
				C	H	Cl
<i>cis</i> -[PtPh(Pb ₂ Ph ₅)(PPh ₃) ₂]	C ₆ H ₆	P <i>trans</i> to Pb: δ 110.6, $^1J(\text{Pt-P})$ 3193, $^2J(\text{PbP})$ 3516 P <i>trans</i> to Ph: δ 120.7, $^1J(\text{Pt-P})$ 1926, $^2J(\text{PbP})$ 225 $^2J(\text{PP})$ 12				
<i>cis</i> -[PtPh(PbPh ₃)(PPh ₃) ₂]	CH ₂ Cl ₂	P <i>trans</i> to Pb: δ 112.3, $^1J(\text{Pt-P})$ 2944, $^2J(\text{PbP})$ 3462 P <i>trans</i> to Ph: δ 120.0, $^1J(\text{Pt-P})$ 1968, $^2J(\text{PbP})$ 259 $^2J(\text{PP})$ 13				
<i>cis</i> -[PtPh(PbMe ₃)(PPh ₃) ₂]	CH ₂ Cl ₂	P <i>trans</i> to Pb: δ 113.0, $^1J(\text{Pt-P})$ 2795, $^2J(\text{PbP})$ 3323 P <i>trans</i> to Ph: δ 118.4, $^1J(\text{Pt-P})$ 1985, $^2J(\text{PbP})$ 256 $^2J(\text{PP})$ 12	C ₄₅ H ₄₄ P ₂ PbPt	56.2 (56.5)	4.4 (4.1)	
<i>cis</i> -[PtCl(PbPh ₂ Br)(PPh ₃) ₂]	CH ₂ Cl ₂	P <i>trans</i> to Pb: δ 112.5, $^1J(\text{Pt-P})$ 3457, $^2J(\text{PbP})$ 4019 P <i>trans</i> to Ph: δ 116.2, $^1J(\text{Pt-P})$ 2073, $^2J(\text{PbP})$ 239 $^2J(\text{PP})$ 12				
<i>cis</i> -[PtCl(PbMe ₃)(PPh ₃) ₂]	CH ₂ Cl ₂	P <i>trans</i> to Pb: δ 103.3, $^1J(\text{Pt-P})$ 2731 P <i>trans</i> to Cl: δ 127.0, $^1J(\text{Pt-P})$ 3991 $^2J(\text{PP})$ 14				
<i>trans</i> -[PtCl(PbMe ₃)(PPh ₃) ₂]	CH ₂ Cl ₂	δ 119.5, $^1J(\text{Pt-P})$ 2688, $^2J(\text{PbP})$ 188				
<i>trans</i> -[Pt(PbPh ₃) ₂ (PEt ₃) ₂]	CH ₂ Cl ₂	δ 132.5, $^1J(\text{Pt-P})$ 2397, $^2J(\text{PbP})$ 239				
<i>trans</i> -[PtCl(PbPh ₃)(PEt ₃) ₂]	CHCl ₃	δ 130.9, $^1J(\text{Pt-P})$ 2629, $^2J(\text{PbP})$ 273				
[Pt(PbPh ₃) ₂ (DPPE)]	CH ₂ Cl ₂	δ 80.0, $^1J(\text{Pt-P})$ 2732, $^2J(\text{PbP})$ 2834, 201, $^2J(\text{PP})$ 6	C ₆₂ H ₅₄ P ₂ Pb ₂ Pt	49.9 (50.7)	3.7 (3.7)	

$[\text{Pt}(\text{SnPh}_3)_2(\text{DPPE})] \text{ } ^b$		CH_2Cl_2	δ 83.3, $^1\text{J}(\text{Pt}-\text{P})$ 2291, $^2\text{J}(\text{Pt}-\text{P})$ 1545, 127 $^2\text{J}(\text{PP})$ 11, $^2\text{J}(\text{Pt}-\text{P})$ 1619, 141	$\text{C}_{63}\text{H}_{56}\text{Cl}_2\text{P}_2\text{PtSn}_2 \text{ } ^b$	54.9 (54.9)	4.1 (4.1)	5.0 (5.1)
CH_2Cl_2		CH_2Cl_2	P_A : δ 134.8, $^1\text{J}(\text{Pt}-\text{P})$ 2471 c P_B : δ 89.2, $^1\text{J}(\text{Pt}-\text{P})$ 2297, $^2\text{J}(\text{Pt}-\text{P})$ 241 P_X : δ 82, $^1\text{J}(\text{Pt}-\text{P})$ 2397 c $^2\text{J}(\text{PP})$: 320 (AB), 19.5 (AX), 9.8 (BX)				
CH_2Cl_2		CH_2Cl_2	P_A : δ 129.7, $^1\text{J}(\text{Pt}-\text{P})$ 2634 P_B : δ 93.8, $^1\text{J}(\text{Pt}-\text{P})$ 2180 P_X : δ 96.3, $^1\text{J}(\text{Pt}-\text{P})$ 1702 $^2\text{J}(\text{PP})$: 356 (AB), 19.5 (AX), 5.0 (BX)	$\text{C}_{38}\text{H}_{44}\text{P}_3\text{ClPt}$	55.7 (55.4)	5.7 (5.4)	

a Positive chemical shifts are to high frequency of the external reference $(\text{MeO})_3\text{P}$ in C_6D_6 ; some spectra were recorded at low temperature, see text. b Solid contains 1 mol. CH_2Cl_2 of crystallization which was also detected by ^1H NMR spectroscopy. c Signal to noise ratio insufficient for the detection of ^{207}Pb satellites.

there were no signals corresponding to the complexes containing PbMe_3 ligands.

The complex $[\text{PtCl}(\text{PbPh}_3)(\text{PPh}_3)_2]$ has been reported to be obtained as white crystals after treatment of *trans*- $[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$ with an equimolar quantity of triphenyllead nitrate in tetrahydrofuran under reflux [9]. The compound was reported to be difficult to obtain pure since it tended to decompose rapidly to $[\text{PtPh}(\text{Cl})(\text{PPh}_3)_2]$. We examined the products of reactions between *trans*- $[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$ and PbPh_3NO_3 conducted under a variety of conditions: (a) as reported previously [9]; (b) in dichloromethane under reflux for 10, 30, 45 and 120 min. periods; (c) in dichloromethane at -50°C and -10°C , and (d) under reflux in benzene for 10 min. In all instances the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of the product mixture showed the presence of *cis*- and *trans*- $[\text{PtPh}(\text{Cl})(\text{PPh}_3)_2]$, and in benzene and in dichloromethane at -10°C some unreacted *trans*- $[\text{PtHCl}(\text{PPh}_3)_2]$ was present together with a complex whose formula is tentatively assigned as *trans*- $[\text{PtH}(\text{NO}_3)(\text{PPh}_3)_2]$ on the basis of the magnitude of $^1J(\text{Pt}-\text{P})$ [3143 (C_6H_6), 3103 (CH_2Cl_2) Hz]. None of the resonances were associated with ^{207}Pb satellites and the spectra were of a signal to noise ratio which was easily adequate for the detection of such satellites. We were therefore, unable to obtain spectroscopic evidence for the formation of $[\text{PtCl}(\text{PbPh}_3)(\text{PPh}_3)_2]$ or other lead-containing complexes, though it is probable that some such complexes are intermediates in the processes leading to the complexes *cis*- and *trans*- $[\text{PtPh}(\text{Cl})(\text{PPh}_3)_2]$. It may be noted that the analogous reaction between *trans*- $[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$ and SnPh_3NO_3 , which was reported [9] to give $[\text{PtCl}(\text{SnPh}_3)(\text{PPh}_3)_2]$, has been shown to give a mixture of phenylplatinum complexes and *cis*- $[\text{PtPh}(\text{SnPh}_2\text{Cl})(\text{PPh}_3)_2]$ [2].

Experimental

General

All the solvents were dry and oxygen-free, and reactions were carried out under nitrogen. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were recorded at 40.48 MHz on a JEOL PFT 100 instrument. Solutions in dichloromethane at 25°C in 8 mm outside diameter tubes were used except where stated otherwise. The magnetic field was locked to the ^2H resonance of a solution of trimethyl phosphite in deuteriobenzene or trimethyl phosphate in deuteriodichloromethane. These solutions served as external reference; chemical shifts are quoted with respect to trimethyl phosphite and positive values are to high frequency of the reference. Proportions of complexes were inferred directly from the relative peak heights in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra. Analytical and spectroscopic results for the complexes are given in Table 1.

Lead compounds

Lead compounds PbPh_4 and PbMe_3Cl were obtained from commercial sources; Pb_2Ph_6 , PbPh_3Br and PbPh_3Me were available in this laboratory. Triphenyllead nitrate has been obtained previously from PbPh_3Cl via initial conversion to PbPh_3OH [10] but the direct method (as follows) is superior.

A solution of AgNO_3 (0.85 g, 0.05 mol) in ethanol (50 cm^3) was added dropwise to a solution of PbPh_3Cl (2.4 g, 0.05 mol) in warm ethanol (150 cm^3). Silver chloride was removed by filtration, the filtrate evaporated to dryness,

and the white residue washed three times with n-hexane to give the crude product (2.25 g, 89%). Recrystallization from ethanol gave white crystals m.p. 220–225°C (decomp.) (lit [10] 220–225°C) (Analysis found: C, 43.6; H, 3.6; N, 2.7. $C_{18}H_{15}PbCl$ calcd.: C, 43.2; H, 3.0; N, 2.8%).

Complexes

The complexes $[Pt(C_2H_4)(PPh_3)_2]$ [11], *trans*- $[Pt(PbPh_3)_2(PEt_3)_2]$ [4] and *trans*- $[PtH(Cl)(PPh_3)_2]$ were prepared by established methods.

cis- $[PtPh(PbPh_3)(PPh_3)_2]$. Tetraphenyllead (0.27 g, 0.0054 mol) was added to a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.4 g, 0.0054 mol) in benzene (50 cm³) and the resulting orange-yellow solution boiled under reflux for 15 min. Addition of hexane gave *cis*-phenyl(triphenylplumbio)bis(triphenylphosphine)platinum(II) (0.29 g, 43%), m.p. 167°C (lit. [3] 168°C).

cis- $[PtPh(PbMe_3)(PPh_3)_2]$. A solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.4 g) in toluene (5 cm³) was treated with $PbMe_2Ph$ and the mixture stirred at room temperature for 15 min. Addition of n-hexane (20 cm³) gave a white precipitate which was washed with n-hexane to give *cis*-phenyl(trimethylplumbio)bis(triphenylphosphine)platinum(II) as a white powder (62%), m.p. 154°C.

$[Pt(PbPh_3)_2(DPPE)]$. A solution of *trans*- $[Pt(PbPh_3)_2(PEt_3)_2]$ (0.65 g, 0.5 mmol) in dichloromethane (20 cm³) was cooled to -30°C and treated with a solution of DPPE (0.26 g, 0.65 mmol) in dichloromethane (10 cm³) also at -30°C. The solution was stirred for 6 h at -30°C after which the dichloromethane was evaporated at -30°C and the residue washed with three portions of cold hexane (20 cm³). The crude material was dissolved in dichloromethane at -30°C and cold hexane added to the point of turbidity. The crystals which deposited were filtered off, washed with cold hexane, and dried to give the product as off-white crystals, m.p. 110–116°C (decomp.).

$[PtPh(PEt_3)(DPPE)]Cl$. A mixture of *trans*- $[Pt(PbPh_3)_2(PEt_3)_2]$ (0.65 g, 0.5 mmol) and DPPE (0.26 g, 0.65 mmol) in dichloromethane (20 cm³) was shaken for 5 min. then put aside at room temperature for 24 h. Colourless needles of $PbPh_4$, m.p. 221–222°C (lit. [12] 223–225°C), and a white solid, probably $PbCl_2$, were deposited. After filtration, the solution was treated with hexane to the point of turbidity and cooled. A further quantity of $PbPh_4$ was removed by filtration, the solution was evaporated to dryness, and the residue washed several times with hexane to remove PEt_3 . The crude product was recrystallised from dichloromethane-hexane to give white crystals, m.p. 110–120°C.

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