Journal of Organometallic Chemistry, 240 (1982) 143–151
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOSPHORUS-31, PLATINUM-195 AND LEAD-207 NMR STUDIES ON SOME PLATINUM-LEAD BONDED COMPOUNDS

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(Received June 15th, 1982)

Summary

Phosphorus-31, platinum-195 and lead-207 nuclear magnetic resonance studies have been carried out on a series of complexes of the type *cis*-$Pt(PPh_3)_2(R)(PbR_2R')$ and *trans*-$Pt(PBu_3)_2(PbR_3)_2$ (R = Ph, 4-MePh, 4-MeOPh, 4-ClPh, 4-FPh; R' = R, Br, I). Lead–platinum coupling constants, $^1J(^{207}Pb-^{195}Pt)$, range between 14.5 kHz and 18.5 kHz with the *trans* compounds having the smaller coupling constants. Variation of the phenyl group substituents has only a small effect on the lead chemical shift and virtually no effect on the other NMR parameters. However, variation of the substituents directly bonded to the lead atom significantly effects the ^{207}Pb chemical shift and causes corresponding, but weaker, effects in the other spectral parameters. Second order heteronuclear coupling effects between platinum-195 and lead-207 are observed for all the complexes and this is the first time that second order coupling has been observed between different elements.

Phosphorus-31, ^{195}Pt and ^{207}Pb NMR spectra have been used to confirm the identity of the intermediate *cis*-$Pt(PPh_3)_2(Ph)(Pb_2Ph_5)$ observed during the preparation of *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$.

Introduction

Although there are four reports of NMR studies involving ^{31}P, ^{119}Sn (or ^{117}Sn) and ^{195}Pt nuclei of platinum–tin bonded compounds [1–4], there has been little study of analogous platinum–lead bonded compounds. Al-Allaf et al. [5] used ^{31}P NMR to characterize several new platinum–lead bonded compounds, but no ^{195}Pt or ^{207}Pb NMR data have been reported for these complexes.

There are several reports [6] of ^{207}Pb NMR spectra of compounds of the type PbL_4, Pb_2L_6 (L = alkyl, aryl or halide in various permutations). There is also a single report [7] of directly bonded lead–tin compounds for which the NMR parameters were determined by double resonance methods. It was found that the coupling constant $^1J(^{207}Pb-^{119}Sn)$ was extremely sensitive to the nature of the groups attached to the lead atom and that this coupling constant could provide a

0022-328X/82/0000–0000/$02.75

useful probe for the study of such bonds. Similarly, for platinum–tin bonded compounds of the type $Pt(PR''_3)_2(SnCl_3)_nCl_{2-n}$ (R'' = alkyl, aryl; $n = 1, 2$) it was found that $\delta(^{195}Pt)$, $\delta(^{119}Sn)$ and $^1J(Pt-Sn)$ vary considerably with the substituent on the phosphine as well as the groups attached to the tin atom [1–4].

The object of this work was to investigate the usefulness of direct measurements of the ^{195}Pt ($I = \frac{1}{2}$, 33.8%) and ^{207}Pb ($I = \frac{1}{2}$, 22.6%) chemical shifts and the platinum–lead coupling constants in elucidation of the structures of these compounds. We describe the preparation of a series of platinum-lead compounds of the types *cis*-$Pt(PPh_3)_2(R)(PbR_2R')$ and *trans*-$Pt(PBu_3)_2(PbR_3)_2$ (R = Ph, 4-MePh, 4-MeOPh. 4-ClPh, 4-FPh; R' = R, Br, I) and describe the effects of substituents at the lead atom on the ^{31}P, ^{195}Pt and ^{207}Pb chemical shifts and the coupling constants $J(P-P)$, $J(Pt-P)$, $J(Pb-P)$ and $J(Pb-Pt)$. A preliminary report of the heteronuclear second order coupling effects has been given [8].

Results and discussion

(a) Preparations

The compounds *cis*-$Pt(PPh_3)_2(R)(PbR_3)$ (R = 4-MePh, 4-MeOPh, Ph) were prepared, following the method of Al-Allaf [5], from $Pt(PPh_3)_2C_2H_4$ and PbR_4 or Pb_2R_6 in benzene according to the equations:

$$Pt(PPh_3)_2C_2H_4 + PbR_4 \rightarrow cis\text{-}Pt(PPh_3)_2(R)(PbR_3) \qquad (1)$$

$$2\ Pt(PPh_3)_2C_2H_4 + 2\ Pb_2R_6 \rightarrow 2\ cis\text{-}Pt(PPh_3)_2(R)(PbR_3) + PbR_4 + Pb \qquad (2)$$

The presence of PbR_4 among the reaction products of the reaction (2) was verified using ^{207}Pb NMR spectroscopy and comparison with a genuine sample of PbR_4. The compounds with R = 4-ClPh and 4-FPh could not be prepared in benzene, but were readily generated in dichloromethane by reaction 2. For R = 2-MePh no reaction could be obtained in either benzene or dichloromethane, presumably because of severe steric hindrance about the lead atom in $Pb_2(2\text{-MePh})_6$.

The compounds Ph_3PbBr and Ph_3PbI reacted with $Pt(PPh_3)_2C_2H_4$ in dichloromethane at −30°C to give *cis*-$Pt(PPh_3)_2(Ph)(PbPh_2Br)$ and *cis*-$Pt(PPh_3)_2(Ph)(PbPh_2I)$, respectively, but elemental lead was precipitated on warming above −20°C. Triphenyl lead chloride, Ph_3PbSCN and $Ph_3PbSeCN$ did not react with $Pt(PPh_3)_2C_2H_4$ in dichloromethane at −30°C, presumably because of their low solubilities, and when the reaction was carried out at room temperature no compounds containing a platinum–lead bond could be isolated.

The compounds *trans*-$Pt(PBu_3)_2(PbR_3)_2$ (R = Ph, 4-MePh, 4-MeOPh, 2-MePh) were prepared from *trans*-$Pt(PBu_3)_2Cl_2$ and 2 mol of $LiPbR_3$ [9] (eq. 3)

$$trans\text{-}Pt(PBu_3)_2Cl_2 + 2\ LiPbR_3 \rightarrow trans\text{-}Pt(PBu_3)_2(PbR_3)_2 + 2\ LiCl \qquad (3)$$

(b) NMR Spectra

The NMR data for all the compounds studied are given in Tables 1 and 2. The compound *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$, which is a typical example of the monoplumbo compounds, has a ^{31}P NMR spectrum consisting of two main doublets ($\delta(^{31}P) = 24.8, 20.8$ ppm) arising from the non-equivalent phosphines ($^2J(P-P) = 13$ Hz). The doublet at higher frequency has two sets of satellites ($^1J(Pt-P) = 2940$ Hz, $^2J(Pb-P) = 3460$ Hz) consistent with a phosphine being *trans* to the lead atom, while

TABLE 1

$^{31}P\text{-}\{^{1}H\}$, ^{195}Pt AND ^{207}Pb NMR DATA FOR *cis*-$Pt(PPh_3)_2(R)(PbR_2R')^g$ AND *trans*-$Pt(PBu_3)_2(PbR_3)_2$ [a,b,c] AT 30°C IN CH_2Cl_2 AT 100 MHz

Compound	$\delta(^{195}Pt)$ (ppm)	$^{1}J(Pt\text{-}P_{trans})^h$ (Hz)	$^{1}J(Pt\text{-}P_{cis})^h$ (Hz)	$\delta(^{207}Pb)$ (ppm)	$^{2}J(Pb\text{-}P_{trans})^h$ (Hz)	$^{2}J(Pb\text{-}P_{cis})^h$ (Hz)	$^{1}J(Pb\text{-}Pt)^h$ (Hz)	$\delta(^{31}P)_{trans}$ (ppm)	$\delta(^{31}P)_{cis}$ (ppm)
cis-$Pt(PPh_3)_2(R)(PbR_2R')^g$									
R = R′ = Ph	−4610	2940	1965	−100	3460	260	18380	27.8	20.7
R = R′ = Ph [d]	−4595	2945	1965	−105	3460	260	18390	27.6	20.8
R = R′ = 4-MeOPh	−4610	2890	2000	−95	3585	255	18515	26.9	20.2
R = R′ = 4-MePh	−4595	2910	1995	−105	3480	250	18390	26.6	20.3
R = R′ = 4-ClPh	−4605	3020	2000	−80	3575	260	18285	27.0	19.2
R = R′ = 4-FPh [e]	−4605	2970	2005	−80	3615	265	18465	27.7	19.1
R = Ph, R′ = Br [f]	−4548	3460	2075	530	4015	245	17195	25.7	22.2
R = Ph, R = I [f]	−4568	3470	2075	515	3970	240	16855	24.8	24.1
trans-$Pt(PBu_3)_2(PbR_3)_2$									
R = Ph	−4915		2365	76		240	14395		−2.5
R = 4-MePh	−4925		2375	76		240	14200		−2.5
R = 4-MeOPh	−4880		2370	76		240	14425		−1.9

[a] $\delta(^{195}Pt)$ measured relative to external 1.0 *M* H_2PtCl_6; estimated error ±2 ppm. $\delta(^{207}Pb)$ relative to 85% Me_4Pb; estimated error ±2 ppm. $\delta(^{31}P)$ relative to 85% H_3PO_4; estimated error 0.1 ppm. [b] *Cis* refers to phosphine adjacent to the lead. *Trans* refers to phosphine opposite the lead. [c] At 100 MHz $\gamma(H_2PtCl_6)-\gamma(Me_4Pb) = 573.8$ kHz. [d] Recorded at 200 MHz. $\gamma(H_2PtCl_6)-\gamma(Me_4Pb) = 1149.5$ kHz. [e] $^{5}J(Pt\text{-}F) = 12$ Hz, $^{4}J(Pb\text{-}F) = 8$ Hz. [f] Measured at −30°C. [g] $^{2}J(P\text{-}P) = 12 \pm 1$ Hz. [h] Estimated error ±5 Hz.

TABLE 2

$^{31}P\{^1H\}$ NMR DATA FOR *cis*-$Pt(PPh_3)_2(R)(Pb^aR_2Pb^bR_3)$ IN CH_2Cl_2 SOLUTION AT 30°C

	$\delta(^{31}P)$ (ppm)	$^1J(Pt-P)$ (Hz)	$^2J(Pb^a-P)$ (Hz)	$^3J(Pb^b-P)$ (Hz)	$^2J(P-P)$ (Hz)
R = Ph [a]					
P_{cis}	19.4	1945	220	13 [b]	12
P_{trans}	29.4	3095	3440	465	
R = 4-ClPh					
P_{cis}	18.5	1955	235	[c]	13
P_{trans}	28.8	3280	3630	560	
R = 4-FPh					
P_{cis}	19.1	1965	[c]	[c]	12
P_{trans}	27.7	2955	3615	380	

[a] $\delta(^{207}Pb^a) = 90$ ppm; $\delta(^{207}Pb^b) = -120$ ppm and $\delta(^{195}Pt) = -4520$ ppm. [b] Not observed in the phosphorus spectrum, but derived from the ^{207}Pb spectrum. [c] Not observed.

the doublet at lower frequency has couplings ($^1J(Pt-P) = 1965$ Hz, $^2J(Pb-P) = 260$ Hz) indicating a phosphine *cis* to the lead atom. These results are very similar to those previously observed [5]. The ^{195}Pt NMR spectrum (represented by Fig. 1a) has a central doublet of doublets, due to coupling to the different phosphines, together with lead satellites (with the same platinum–phosphorus couplings). However, the lead satellites are not symmetrically disposed about the central multiplet, their median position being 180 Hz above the frequency of the central multiplet. The ^{207}Pb NMR spectrum at 20.84 MHz (Fig. 1b) is of similar appearance (with different lead-phosphorus couplings) with the ^{195}Pt satellites unsymmetrically disposed about the central multiplet by 180 Hz to the low frequency side of the spectrum. The ^{195}Pt and ^{207}Pb spectra of *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$ at higher field strength (^{195}Pt at 42.70 MHz; ^{207}Pb at 41.76 MHz) show that the asymmetry is reduced to 85 Hz.

Two explanations of this phenomenon are possible; either there are second order coupling effects between platinum and lead or there is a very large isotope effect. However, all the evidence suggests that the former is the correct explanation. The above variation with increasing magnetic field is exactly opposite to that expected for an isotope effect. The central multiplets of both spectra are very sharp, and in the platinum-195 spectrum correspond to those molecules in which platinum-195 is bound to lead nuclei with spin zero (^{206}Pb 24%; ^{208}Pb 52%). The magnitude of the asymmetry of the lead-207 satellites suggests that for a genuine isotope effect the peaks of the central multiplet should be broadened, if not split into two multiplets, corresponding to platinum bonded to each of the spin zero nuclei. Similar arguments apply to the central lead-207 multiplet which corresponds to lead bonded to platinum isotopes with spin zero (^{194}Pt 33%; ^{196}Pt 25%; ^{198}Pt 7%). Furthermore, it also seems very unlikely that asymmetry due to isotope effects would have exactly the same magnitude in both ^{195}Pt and ^{207}Pb spectra.

Second order coupling between different elements has not been previously reported, because the chemical shift difference between nuclei is usually vastly greater than the coupling constants, thus resulting in first order interactions. However, in the case of *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$ the coupling constant between

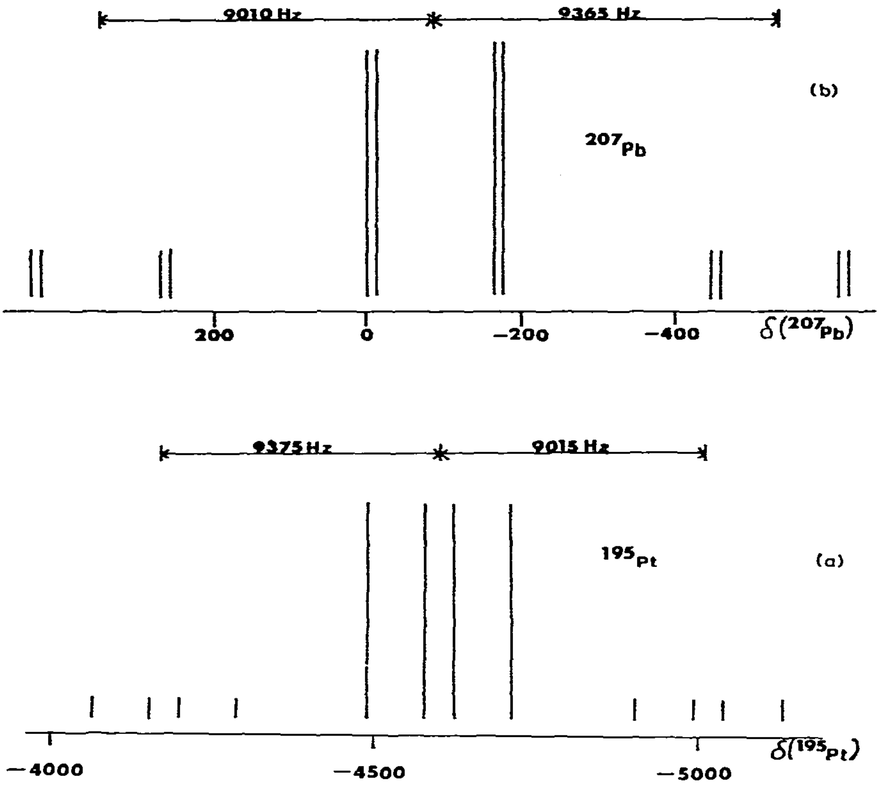

Fig. 1. (a) Platinum-195 spectrum; (b) Lead-207 spectrum for *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$.

platinum-195 and lead-207 has the very large value of 18375 Hz and, combined with the unusually small chemical shift difference between two different elements of 477310 Hz, gives a ratio of (J(Pb–Pt)/$\Delta\gamma = 0.038$ (where $\Delta\gamma = \gamma_{Pt} - \gamma_{Pb}$) which is sufficiently large to result in second order effects. For spectra recorded at higher magnetic field the ratio (J(Pt–Pt)/$\Delta\gamma$ is reduced to 0.019 and the spectra more closely approximate first order appearance. Calculated chemical shifts of platinum-195, lead-207 and phosphorus-31, based on the assumption that the satellite spectra are parts of an ABXZ spectrum, were found to agree within the experimental error (± 10 Hz) of the observed positions of the central multiplets. Similar second-order effects are observed for all the other monoplumbo complexes.

For compounds of the type *trans*-$Pt(PBu_3)_2(PbR_3)_2$ consider *trans*-$Pt(PBu_3)_2(PbPh_3)_2$ as a typical example. The ^{31}P NMR spectrum of *trans*-$Pt(PBu_3)_2(PbPh_3)_2$ consists of a single main resonance at $\delta = -2.48$ ppm flanked by a pair of platinum satellites (^1J(Pt–P) = 2365 Hz) and two sets of lead-207 satellites (^2J(Pb–P) = 240 Hz) corresponding to those molecules containing zero, one or two ^{207}Pb nuclei. The relative intensities of the lead-207 satellites and the value of the coupling constant confirms that the lead and phosphorus atoms are mutually *cis*.

The platinum-195 NMR spectrum should consist of three overlapping components resulting from different numbers of bonded lead-207 nuclei. These components are Pb–Pt–Pb (59.9%), ^{207}Pb–Pt–Pb (35.0%) and ^{207}Pb–Pt–^{207}Pb (5.1%). The first of these resonances appears as a strong central triplet due to coupling to the phosphorus atoms. The spectrum of those molecules with a single ^{207}Pb nucleus appear as two satellite triplets separated by ^{1}J(Pb–Pt) = 14395 Hz, but as before the satellites are asymmetric about the central multiplet, their median position being 120 Hz above the frequency of the centre of the main multiplet. Thus second order effects also occur in these molecules with J(Pb–Pt)/$\Delta\gamma = 0.031$. The ^{195}Pt NMR spectrum of those molecules containing two ^{207}Pb nuclei should therefore be of the ABXZ type, but this part of the spectrum is inherently expected to be of low intensity and was not observed.

The lead-207 NMR spectrum consisted of a central triplet with satellites, due to those molecules also containing ^{195}Pt, which were asymmetric by 120 Hz to the low frequency side of the main multiplet.

During the preparation of *cis*-Pt(PPh$_3$)$_2$(R)(PbR$_3$) using the Pb$_2$R$_6$ method (eq. 2), Al-Allaf et al. [5] observed an intermediate compound which slowly decomposed to the required product with simultaneous deposition of lead. This unstable intermediate had been previously reported by Crociani [10] as Pt(PPh$_3$)$_2$(PbR$_3$)$_2$, but the ^{31}P NMR spectrum reported [5] was not consistent with either possible isomer of that formulation. The intermediate proposed was analytically identical to *cis*-Pt(PPh$_3$)$_2$(R)(Pb$_2$R$_5$) and, although the reported ^{31}P NMR spectrum [5] was incomplete, the original formulation of the intermediate has now been confirmed by a combination of ^{31}P, ^{195}Pt and ^{207}Pb NMR spectra for R = Ph and by ^{31}P NMR when R = 4-ClPh and 4-FPh (Table 2).

The ^{31}P NMR spectrum of a freshly prepared solution of *cis*-Pt(PPh$_3$)$_2$(Ph)(Pb$_2$Ph$_5$) (shown diagrammatically in Fig. 2) consists of two phosphorus doublets, ^{2}J(P–P) = 12 Hz, both of which are flanked by platinum-195 satellites. The phosphorus resonance at lower frequency has only one set of observable ^{207}Pb satellites, ^{2}J(Pb^{a}–P) = 220 Hz, but the one at higher frequency has two sets of ^{207}Pb satellites, ^{2}J(Pb^{a}–P) = 3440 Hz and ^{3}J(Pb^{b}–P) = 465 Hz. This second set of satellites is crucial to the formulation of the complex as *cis*-Pt(PPh$_3$)$_2$(Ph)(Pb$_2$Ph$_5$) since it clearly demonstrates non-equivalent lead atoms in the molecule. The observed

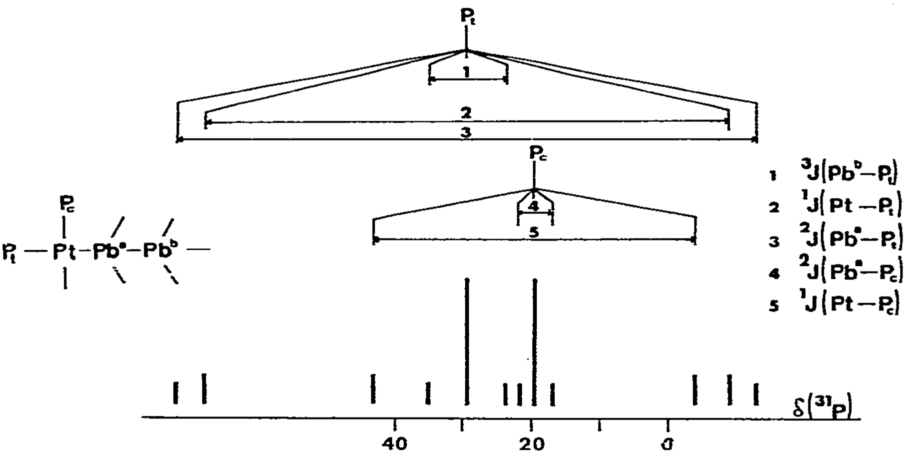

Fig. 2. Diagrammatic representation of the phosphorus-31 spectrum of *cis*-Pt(PPh$_3$)$_2$(Ph)(Pb$_2$Ph$_5$).

spectrum also shows the presence of a small proportion of *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$, but when the spectrum was re-recorded about twenty minutes later the proportion of monoplumbo complex had increased to about 30%.

The lead-207 NMR spectrum of *cis*-$Pt(PPh_3)_2(Ph)(Pb_2Ph_5)$ was difficult to observe because the longer time scale involved for data collection meant that most of the product in solution was the monoplumbo complex, *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$. The weak spectrum due to the intermediate complex was identified (Table 2) from the two markedly different lead signals whose couplings $J(Pb-P)$ agree with those derived from the phosphorus spectrum. The magnitude of the coupling $^3J(Pb^b-P_c) =$ 13 Hz, (obtained from the lead-207 spectrum) explains why an accompanying second set of satellites was not observed for the lower frequency phosphorus resonance because they are obscured by the phosphorus–phosphorus coupling of 12 Hz. The signal to noise ratio for this spectrum was insufficient to observe platinum and lead satellites as resolution decreased with increasing amounts of elemental lead precipitation (eq. 2).

The platinum-195 NMR spectrum consists of a doublet of doublets as expected, but no lead satellites were detected because of poor signal to noise ratio.

(c) Discussion of the spectra

For the series of compounds *cis*-$Pt(PPh_3)_2(R)(PbR_3)$ (R = Ph, 4-MePh, 4-MeOPh, 4-ClPh, 4-FPh) there is little variation in the NMR parameters (Table 1). As the electron-withdrawing nature of the substituent on the phenyl groups attached to the lead atom increases there is a corresponding increase in the lead-207 resonance frequency but this appears to be a local effect as there are no other significant variations caused by these changes. The phenyl group does exert a slight *trans* substituent effect which causes $^1J(Pt-P_c)$ and $^2J(Pb-P_c)$ to increase as the substituent becomes more electron withdrawing.

Significant changes do occur in the spectral data as the substituent directly bonded to the lead atom is changed. In the series *cis*-$Pt(PPh_3)_2(Ph)(PbPh_3)$, $Pt(PPh_3)_2(Ph)(PbPh_2Br)$ and $Pt(PPh_3)_2(Ph)(PbPh_2I)$ there are large changes in $\delta(^{207}Pb)$ compared to the parent compounds $PbPh_4$, $PbPh_3Br$ and $PbPh_3I$ (Table 3). In this series a phenyl group of the parent compound is in each case being replaced by a *cis*-$Pt(PPh_3)_2(Ph)$-group. As the change $\Delta\delta(^{207}Pb)$ increases, $^1J(Pb-Pt)$ decreases in the series, the *cis* and *trans* phosphorus resonances become more similar and there are corresponding variations in $\delta(^{195}Pt)$ and the coupling constants of both lead and platinum to phosphorus. These observations are consistent with bromine and iodine being more electron withdrawing than the phenyl group, thus withdrawing electron density from the platinum-lead bond as well as from the lead atom. This apparent weakening of the platinum–lead bond allows the platinum–phosphine bonds to become stronger as evidenced by the changes in $^1J(Pt-P)$ in the series.

For the *trans* complexes $Pt(PBu_3)_2(PbR_3)_2$ the NMR parameters do not vary as the substituent on the aryl groups attached to lead is varied. In these compounds the coupling constant $^1J(Pb-Pt)$ is reduced compared to the monoplumbo compounds, which is typical behaviour as the number of ligands of one type increases [6].

For *cis*-$Pt(PPh_3)_2(Ph)(Pb_2Ph_5)$ the lead-207 shift of Pb^b (Table 2) at -120 ppm is moved to slightly lower frequency than those of compounds of the type *cis*-$Pt(PPh_3)_2(Ph)(PbR_3)$ (Table 1). However, there is a very large chemical shift change

TABLE 3

THE LEAD-207 SHIFTS OF *cis*-$Pt(PPh_3)_2(R)(R_2R'Pb)$ AND PbR_3R' [a]

Compound	$\delta(^{207}Pb)$ (ppm)	Compound	$\delta(^{207}Pb)$ (ppm)	$\Delta\delta(^{207}Pb)$ [b] (ppm)
cis-$Pt(PPh_3)_2(Ph)(Ph_3Pb)$	−100	$PbPh_4$	−180	80
cis-$Pt(PPh_3)_2(Ph)(Ph_2BrPb)$	530	$PbPh_3Br$	10	540
cis-$Pt(PPh_3)_2(Ph)(Ph_2IPb)$	515	$PbPh_3I$	−115	630

[a] Footnotes as per Table 1. [b] $\Delta\delta(^{207}Pb)$ is the chemical shift difference between *cis*-$Pt(PPh_3)_2(R)(R_2R'Pb)$ and PbR_3R'.

for Pb^{a} at +90 ppm, compared with the precursor Pb_2Ph_6 which has a shift of −80 ppm.

Experimental

All reactions were carried out under nitrogen in dried solvents. Microanalyses (Table 4) were performed by the Australian Microanalytical Service, Melbourne.

The complexes Pb_2Ph_6, $Pb_2(4\text{-}MePh)_6$, $Pb_2(2\text{-}MePh)_6$, and $Pb_2(4\text{-}MeOPh)_6$ were prepared by published methods [11]. $Pb_2(4\text{-}ClPh)_6$ and $Pb_2(4\text{-}FPh)_6$ were prepared by the same method with the minor modification that only five minutes was allowed after addition of the 1,2-dibromoethane since a longer time resulted in the formation of significant quantities of PbR_4. $Pb_2(4\text{-}ClPh)_6$ was characterized by its melting point (178°C, lit. 186°C [12]) and $Pb_2(4\text{-}FPh)_6$ melted with decomposition at 147°C.

The compounds $Pt(PPh_3)_2C_2H_4$ [13], *trans*-$Pt(PBu_3)_2Cl_2$ [14], *cis*-$Pt(PPh_3)_2(R)(PbR_3)$ [5], $Pt(PPh_3)_2(Ph)(Pb_2Ph_5)$ [5] and *trans*-$Pt(PBu_3)_2(PbR_3)_2$ [9] were prepared as detailed in the literature except that for the latter compounds higher

TABLE 4

ANALYTICAL DATA

Compound	Analysis (Found (calcd.) (%))	
	C	H
cis-$Pt(PPh_3)_2(4\text{-}MePh)[(4\text{-}MePh)_3Pb]$	58.1	5.1
	(59.1)	(5.0)
cis-$Pt(PPh_3)_2(4\text{-}MeOPh)[(4\text{-}MeOPh)_3Pb]$	56.6	4.4
	(56.3)	(4.3)
trans-$Pt(PBu_3)_2(Ph_3Pb)_2$	48.6	5.6
	(48.5)	(5.7)
trans-$Pt(PBu_3)_2[(4\text{-}MePh)_3Pb]_2$	50.6	5.7
	(50.5)	(6.1)
trans-$Pt(PBu_3)_2[(4\text{-}MeOPh)_3Pb]_2$	47.4	5.6
	(47.5)	(5.8)
$(4\text{-}FPh)_6Pb_2$	41.8	2.3
	(42.0)	(2.5)

yields were obtained when the *trans*-$Pt(PBu_3)_2Cl_2$ was added to the $LiPbR_3$ cooled to −40°C.

The NMR spectra were recorded in CH_2Cl_2 using an external ^7Li lock on a JEOL FX 100 spectrometer at 2.3 T. Spectra at higher field were observed using a JEOL FX 200 instrument. The references used were external 85% H_3PO_4, external 1 *M* H_2PtCl_6 in concentrated HCl and external 85% $PbMe_4$. High frequency positive convention is used. Phosphorus-31 spectra were typically recorded after 500 transients whereas platinum-195 and lead-207 after 60000 transients. Tris(acetylacetonato)chromium(III) was used as a paramagnetic relaxation agent.

Acknowledgement

We thank Dr. D.P. Kelly for helpful discussions and Dr. R. Brownlee of LaTrobe University, Melbourne for access to the JEOL FX 200.

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