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Novel triphospholyl and diphosphastibolyl lead(II) complexes

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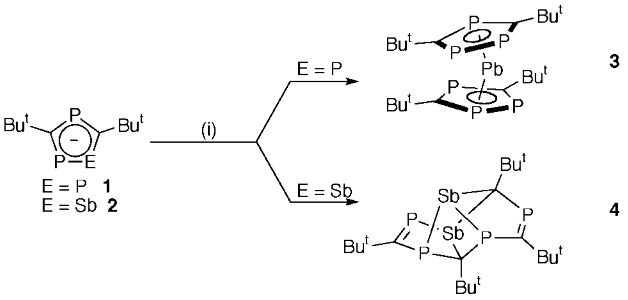
$PbCl_2$ reacted with the triphospholyl ring anion $[P_3C_2Bu^t_2]^-$ to afford the hexaphospha-plumbocene $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ **3** which has been characterised by multinuclear NMR spectroscopy. In contrast the reaction between $PbCl_2$ and the diphosphastibolyl ring anion $[P_2SbC_2Bu^t_2]^-$ led to the organo-antimony cage compound $[P_4Sb_2C_4Bu^t_4]$ **4** *via* an oxidative coupling route. Both the heteroleptic plumbocenes $[Pb(\eta^5\text{-}EP_2C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (E = P **5**, E = Sb **6**) could be prepared by treatment of the corresponding hetero-ring anion with a mixture of $PbCl_2$ and $Li(C_5Me_5)$ (for **5**) or the half sandwich complex $[Pb(\eta^5\text{-}C_5Me_5)Cl]$ (for **6**). Both complexes were characterised by multinuclear NMR spectroscopy and single crystal X-ray diffraction studies. The novel, structurally characterised, hetero-bimetallic complex $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)(\mu\text{-}Cl)_2Li(tmen)_2]$ **7** could be synthesised by carrying out the reaction of $PbCl_2$ with $[Li(dme)_3][P_3C_2Bu^t_2]$ in tmen rather than dme. This compound was found to be highly fluxional in solution even at low temperature.

Introduction

Recent years have seen considerable interest in the chemistry of cyclopentadienyl compounds of divalent Group 14 elements.[1] The structural information that is available indicates that, in general, such compounds exist as bent monomeric sandwich units, the centroid–metal–centroid angle being dependent upon both the central Group 14 atom and the degree of steric substitution of the cyclopentadienyl ring. In contrast, Group 14 metallocenes incorporating heteroatom substituted cyclopentadienyl rings are comparatively rare, except for a small number of tin complexes derived from boron containing heterocycles *e.g.* $[Sn\{\eta^5\text{-}N(Bu^t)B(Me)C(Me)(CH)_2\}_2]$[2] and one structurally characterised example of a 1,1′-diaza-plumbocene *viz.* $[Pb(\eta^5\text{-}NC_4H_2Bu^t_2)_2]$.[3] In response to the paucity of examples of compounds of this type we decided to employ the triphospholyl $[P_3C_2Bu^t_2]^-$ **1** and diphosphastibolyl $[P_2SbC_2Bu^t_2]^-$ **2** ring anions in the preparation of a range of homo- and hetero-leptic divalent lead(II) complexes. Our previous studies have shown that these Group 15 substituted cyclopentadienyl systems can be employed in the synthesis of main group compounds such as $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$[4] and $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}1,4,2\text{-}P_2SbC_2Bu^t_2)\}_\infty]$[5] and a host of transition metal complexes of which representative examples include $[M(\eta^5\text{-}EP_2C_2Bu^t_2)_2]$ (E = P, M = Fe[6] or Ru;[7] E = Sb, M = Fe[8] or Ru[8]); $[M(\eta^5\text{-}EP_2C_2Bu^t_2)(\eta^5\text{-}C_5R_5)]$ (E = P, R = H, M = Fe[9] or Ru;[7] E = Sb, R = Me, M = Fe[8] or Ru[10]).

Results and discussion

Treatment of a dme (1,2-dimethoxyethane) slurry of anhydrous $PbCl_2$ with two equivalents of $[Li(dme)_3][\mathbf{1}]$ at low temperature led, after workup, to the hexaphospha-plumbocene, $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, **3** in 48% yield (Scheme 1). In contrast, the reaction between $[Li(tmen)_2][\mathbf{2}]$ and $PbCl_2$ did not lead to the corresponding complex $[Pb(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ but yielded the cage compound, $[P_4Sb_2C_4Bu^t_4]$, **4** in approximately 60% yield. We have recently described the formation of this compound *via* the oxidative coupling of two molecules of **2** with $FeCl_3$.[11] The formation of metallic lead in the reaction between $[Li(tmen)_2][\mathbf{2}]$ and $PbCl_2$ attests to a redox mechanism.



Scheme 1 *Reagents and conditions*: (i) $PbCl_2$, dme, −45 °C, 30 min.

The $^{31}P\{^1H\}$ NMR spectrum of **3** displays multiplets at 275.1 ppm and 273.1 ppm arising from a distorted $[AB_2]_2$ spin system with a typical $^2J_{PP}$ value of 47.5 Hz. Clearly resolved ^{207}Pb satellites are visible from which $^1J_{PbP}$ values of 365.7 Hz ($^1J_{PbP(A)}$) and 231.5 Hz ($^1J_{PbP(B)}$) can be evaluated. The downfield shift of the $^{31}P\{^1H\}$ resonances of **1** upon ligation to the lead centre (*cf.* 247.7 ppm and 243.5 ppm in the free **1**)[12] is in contrast to the generally observed upfield shift upon ligation of **1** to transition metals *e.g.* in $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ the triphospholyl resonances appear at 38.9 ppm and 37.9 ppm, over 200 ppm upfield of the signals in the free ion.[6] Interestingly, when the spectrum is recorded in thf a minor signal is seen shadowing the major signal and shifted slightly upfield of it. This does not appear when the spectrum is recorded in a hydrocarbon solvent and it is therefore possible that the species responsible for this signal originates as a result of solvation effects. Indeed, Wright and co-workers have shown that both stannocene and plumbocene can form weakly bonded Lewis base adducts in solution and in the solid state.[13] The retention of an $[AB_2]_2$ line pattern in **3** is indicative of an intact $[P_3C_2Bu^t_2]^-$ ring but this

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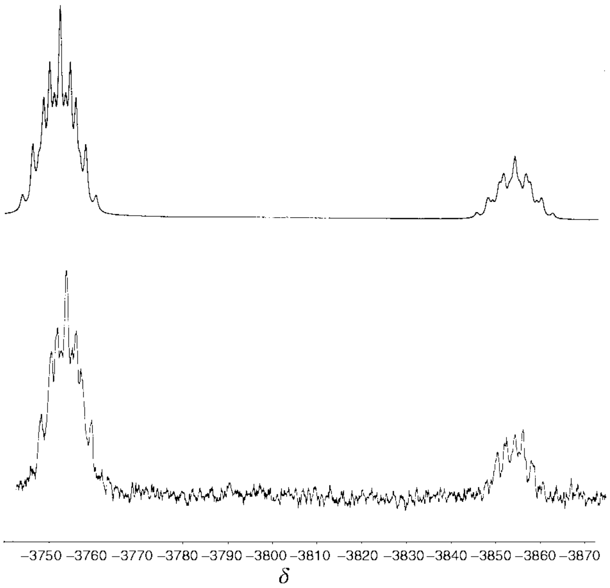


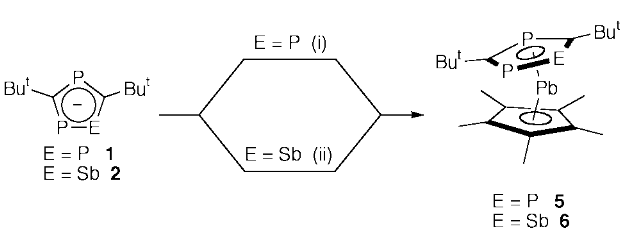
Fig. 1 PANIC and experimentally recorded ^{207}Pb{^{1}H} spectra of **3**.

cannot alone distinguish between an η^5 or fluxional η^1 ligation mode. We are, however, inclined to favour an η^5 bonding mode based on the magnitude of the J_{PbP} coupling constants. These couplings of 365.7 Hz and 231.5 Hz are of a similar order of magnitude suggesting that the three phosphorus centres have a similar degree of association with the lead. Moreover the magnitude of these couplings is surprisingly small. Direct comparison is precluded by the lack of available literature data relating to one bond lead–phosphorus couplings but an η^1 interaction between a phosphorus centre and a large, heavy metal typically gives rise to a coupling constant of the order of thousands of Hz. One of the few structurally characterised examples available for comparison is the monomeric three coordinate lead(II) complex [Pb{CH(PPh$_2$)$_2$}$_2$] in which the $^1J_{PbP}$ coupling constant is 1970 Hz.[14]

The ^{207}Pb{^{1}H} NMR spectrum of **3** displays a broad high field multiplet at −3752 ppm which is the region seen for the shifts of related carbocyclic plumbocenes (−4756 ppm in [Pb(η^5-C$_5$H$_3$Bu$^t_2$)$_2$][15] and −4930 ppm in [Pb(η^5-C$_5$Me$_5$)$_2$][16]). As in the ^{31}P{^{1}H} spectrum, a minor signal is also seen in the ^{207}Pb{^{1}H} spectrum when it is recorded in thf. A PANIC[17] simulation of the ^{207}Pb{^{1}H} NMR spectrum of **3** using coupling constant data from the ^{31}P{^{1}H} NMR spectrum is depicted in Fig. 1 along with the experimentally observed spectrum. The two are in excellent agreement and are consistent with the presence of a species containing a lead centre sandwiched between two planar η^5 bound [P$_3$C$_2$Bu$^t_2$]$^-$ rings. The minor signal was also simulated and it appears in Fig. 1.

The FAB mass spectrum of **3** shows no molecular ion, consistent with the mass spectra of other Group 14 metallocenes which generally show a parent molecular ion with an intensity of <1%. A base peak at *m*/*z* = 439 is seen corresponding to the fragment [Pb(η^5-P$_3$C$_2$Bu$^t_2$)]$^+$.

Using a similar synthetic approach, the reaction between a thf slurry of PbCl$_2$ with a 1 : 1 mixture of [Li(dme)$_3$][**1**] and [Li(η^5-C$_5$Me$_5$)] afforded the heteroleptic complex [Pb(η^5-P$_3$C$_2$Bu$^t_2$)(η^5-C$_5$Me$_5$)] **5** in 45% yield after workup and subsequent recrystallisation from hexane (Scheme 2). Additionally, the analogous complex derived from **2** *viz.* [Pb(η^5-P$_2$SbC$_2$-Bu$^t_2$)(η^5-C$_5$Me$_5$)] **6** was prepared by the reaction between [Li(tmen)$_2$][**2**] and [Pb(η^5-C$_5$Me$_5$)Cl]. The latter synthesis also yielded a small (*ca.* 25%) amount of complex **5** arising from the unavoidable concomitant formation of **1** during the synthesis of **2**.[18] Unfortunately **6** could not be completely separated from **5** despite repeated attempts at fractional crystallisations. Both **5** and **6** were characterised by multinuclear NMR spectroscopy and single crystal X-ray diffraction studies (*vide infra*).



Scheme 2 *Reagents and conditions*: (i) PbCl$_2$, LiC$_5$Me$_5$, dme, −45 °C, 30 min; (ii) [Pb(η^5-C$_5$Me$_5$)Cl], dme, −50 °C, 30 min.

The ^{31}P{^{1}H} NMR spectrum of **5** at 183 K consists of an [AB$_2$] spin system at 280.3 ppm and 255.3 ppm ($^2J_{PP}$ = 48.8 Hz) with clearly resolved ^{207}Pb satellites indicating a $^1J_{PbP(A)}$ coupling of 470 Hz and a $^1J_{PbP(B)}$ coupling of 212 Hz. At 298 K a marginal broadening of the resonances is observed and the satellites become poorly resolved. These data suggest that a fluxional process is occurring at room temperature in which the P$_3$C$_2$Bu$^t_2$ ring is exchanging intermolecularly between lead sites. This process is clearly suppressed or partially suppressed at lower temperature. The ^{207}Pb{^{1}H} NMR spectrum of **5** consists of a doublet of triplets with couplings matching those derived from the ^{31}P{^{1}H} NMR spectrum. The shift of this multiplet (−3951 ppm) lies in between that of its homoleptic analogues (*cf.* −3752 ppm for **3**, −4390 ppm for [Pb(η^5-C$_5$Me$_5$)$_2$][16]).

The ^{31}P{^{1}H} NMR spectrum of complex **6** shows a simple AB pattern with doublets at 334.3 ppm and 297.0 ppm with a $^2J_{PP}$ coupling of 50.1 Hz. In a similar manner to complexes **3** and **5**, these chemical shifts are downfield of those seen in the parent lithium complex *i.e.* 277.9 ppm and 308.2 ppm in [Li(tmen)$_2$][**2**].[18] Additionally, the lower field doublet is considerably broader than the higher field doublet suggesting it originates from the phosphorus adjacent to the quadrupolar antimony centre. In contrast to complex **5**, ^{207}Pb satellites are clearly visible in the room temperature ^{31}P{^{1}H} NMR spectrum of **6** indicating $^1J_{PbP}$ couplings of 470 Hz and 212 Hz. Moreover, the spectrum remains essentially unchanged over the temperature range +25 °C to −60 °C. It is evident, therefore, that in contrast to **5**, complex **6** shows no intermolecular exchange process.

Single crystal X-ray diffraction studies were carried out on complexes **5** and **6** and their molecular structures are depicted in Figs. 2 and 3 with selected bond angles and distances collected in Tables 1 and 2 respectively. In the solid state both **5** and **6** exist as bent monomeric sandwich complexes. The ring centroid–lead–ring centroid angles of 142.2° in **5** and 144.2° in **6** are very close to those seen in other related systems *e.g.* 151.0° in [Pb(η^5-C$_5$Me$_5$)$_2$][19] and 142.7° in [Pb(η^5-NC$_4$H$_2$Bu$^t_2$)$_2$].[3] In both cases, the distance of the metal from the ring centroid is remarkably larger than the corresponding metal–C$_5$Me$_5$ ring centroid distance. In **5** these distances are 2.755 Å (mean) and 2.357 Å respectively while in **6** the corresponding distances are 2.761(4) Å and 2.356(5) Å. Initially, the steric bulk of the heterocyclopentadienyl rings may be seen as responsible for this extended distance. Increasing the steric bulk of rings in main group metallocenes, however, tends to force the rings into a more parallel orientation *e.g.* [Sn(η^5-C$_5$Ph$_5$)$_2$][20] and [Pb{η^5-C$_5$Me$_4$(SiBu^{t}Me$_2$)}$_2$].[21] In these types of complexes the rings are parallel as a result of steric hindrance but the Pb–ring centroid distance in the latter is only 2.460(5) Å. The most likely reason for the elongated Pb–heteroring centroid distances in **5** and **6** is that there is a significant degree of ionic character in the bonding of the two moieties. Unfortunately, the structure of **6** is disordered. This disorder was successfully modelled by assuming Sb(1) to have a partial antimony occupancy of 40% and a partial phosphorus occupancy of 60%. Similarly, the position P(1) was refined with a phosphorus occupancy of 75%

Table 1 Selected bond distances (Å) and angles (°) for compound **5** with estimated standard deviations (e.s.d.s) in parentheses

P(1)–C(1)	1.768(15)	Pb–P(1)	3.240(4)	Pb–C(11)	2.62(2)
C(1)–P(2)	1.72(2)	Pb–C(1)	3.11(2)	Pb–C(12)	2.609(14)
P(2)–P(3)	2.112(6)	Pb–P(2)	3.175(5)	Pb–C(13)	2.66(2)
P(3)–C(2)	1.735(15)	Pb–P(3)	3.160(4)	Pb–C(14)	2.71(2)
C(2)–P(1)	1.750(13)	Pb–C(2)	3.097(13)	Pb–C(15)	2.64(2)
Pb–Cent(a)[a]	2.755	Pb–Cent(b)[a]	2.357		
Cent(a)–Pb–Cent(b)	142.2	C(2)–P(1)–C(1)	100.0(7)	P(1)–C(1)–P(2)	120.3(8)
C(1)–P(2)–P(3)	99.7(5)	P(2)–P(3)–C(2)	99.8(4)	P(3)–C(2)–P(1)	120.2(7)

[a] Cent(a) = Centroid of $P_3C_2Bu^t_2$ ring; Cent(b) = Centroid of C_5Me_5 ring.

Table 2 Selected bond distances (Å) and angles (°) for compound **6** with estimated standard deviations (e.s.d.s) in parentheses

P(1)–C(11)	1.910(9)	Pb(1)–P(1)	3.266(4)	Pb(1)–C(1)	2.722(9)
C(11)–P(2)	1.758(9)	Pb(1)–C(11)	3.133(8)	Pb(1)–C(2)	2.671(10)
P(2)–C(12)	1.730(9)	Pb(1)–P(2)	3.239(4)	Pb(1)–C(3)	2.601(9)
C(12)–Sb(1)	1.972(8)	Pb(1)–C(12)	3.132(7)	Pb(1)–C(4)	2.579(9)
Sb(1)–P(1)	2.351(2)	Pb(1)–Sb(1)	3.3065(12)	Pb(1)–C(5)	2.637(10)
Pb(1)–Cent(a)[a]	2.761(4)	Pb(1)–Cent(b)[a]	2.356(5)		
Cent(a)–Pb(1)–Cent(b)	144.2(8)	Sb(1)–P(1)–C(11)	96.8(3)	P(1)–C(11)–P(2)	122.7(5)
C(11)–P(2)–C(12)	103.1(4)	P(2)–C(12)–Sb(1)	123.0(5)	C(12)–Sb(1)–P(1)	94.4(3)

[a] Cent(a) = Centroid of $P_2SbC_2Bu^t_2$ ring; Cent(b) = Centroid of C_5Me_5 ring.

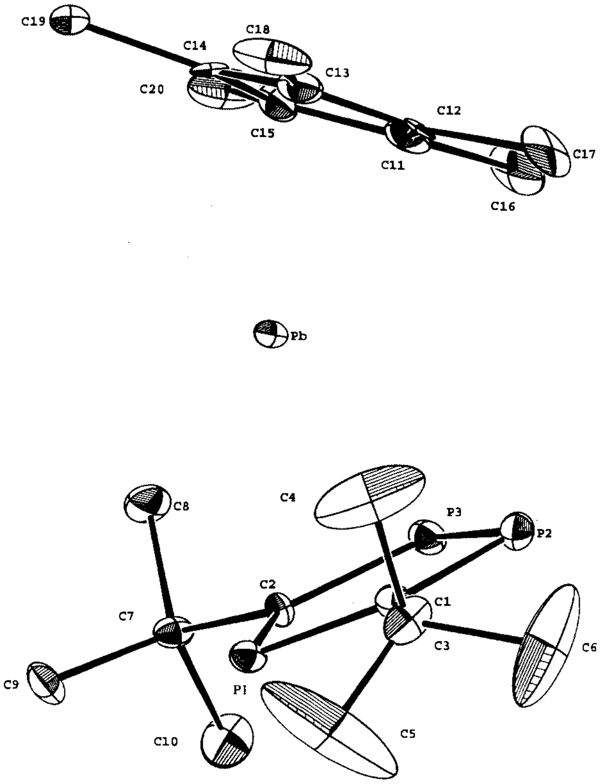


Fig. 2 Molecular structure of $[Pb(\eta^5-P_3C_2Bu^t_2)(\eta^5-C_5Me_5)]$ **5**.

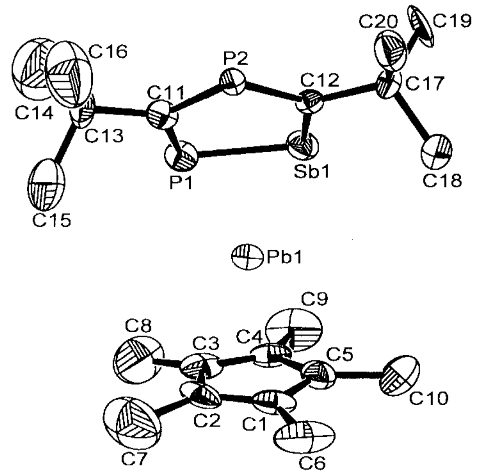
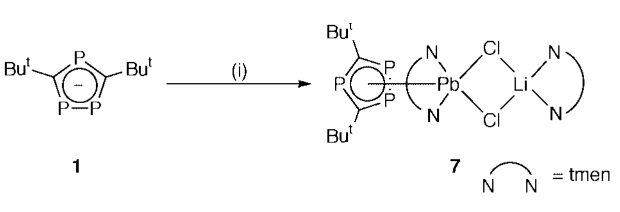


Fig. 3 Molecular structure of $[Pb(\eta^5-P_2SbC_2Bu^t_2)(\eta^5-C_5Me_5)]$ **6**.

and an antimony occupancy of 25%. This disorder arises from the co-crystallisation of both enantiomers of **6** as well as a moderate amount of **5** which unavoidably forms during the synthesis of **6**. From the refinement it would appear that there is a disparity in the amount of each enantiomer *i.e.* 40% of one and 25% of the other. The centrosymmetric nature of the structure, however, means that one pair of molecules in the unit cell has one percentage distribution (40%:25%) whilst the centrosymmetric pair has the reverse distribution (25%:40%). Thus, overall, there is a racemic mixture present in which complex **6** accounts for 65% of the total molecules present in the crystal. This disorder means it is not possible to comment on the bond angles and distances within the $P_2SbC_2Bu^t_2$ and those parameters in Table 2 cannot be considered reliable.

Interestingly, if the reaction between $PbCl_2$ and $[Li(dme)_2]$[**1**] is carried out in tmen rather than dme, the product formed is not the homoleptic plumbocene **3** but the novel heterobimetallic compound $[Pb(\eta^5-P_3C_2Bu^t_2)(\mu-Cl)_2Li(tmen)_2]$ **7** which can be isolated as an air sensitive powder in 18% yield (Scheme 3).



Scheme 3 *Reagents and conditions*: (i) $PbCl_2$, tmen, −45 °C, 15 min.

Complex **7** was found to be highly fluxional in solution as evidenced by its variable temperature $^{31}P\{^1H\}$ NMR spectra (Fig. 4). At ambient temperature, the triphospholyl ring resonance is seen only as a broad signal at 274.7 ppm with no apparent multiplicity visible. This broadness is likely to be the result of a dynamic process involving rapid ring rotation and/or intermolecular ring exchange between lead sites. At the solvent limiting temperature of −96 °C the broad signal has clearly split into three resonances at 273.5 ppm (P_M), 253.6 ppm (P_A) and 225.8 ppm (P_B) although the resonances remain broad

Table 3 Selected bond distances (Å) and angles (°) for compound **7** with estimated standard deviations (e.s.d.s) in parentheses

Pb–C(1)	3.17(4)	P(1)–P(2)	2.11(2)	Pb–Cl(1)	2.765(9)
Pb–P(3)	3.273(13)	P(2)–C(2)	1.83(4)	Pb–Cl(2)	2.901(11)
Pb–C(2)	3.16(4)	C(2)–P(3)	1.71(4)	Li–Cl(1)	2.47(5)
Pb–P(2)	3.230(13)	P(3)–C(1)	1.71(4)	Li–Cl(2)	2.30(5)
Pb–P(1)	3.223(10)	C(1)–P(1)	1.70(4)	Pb–Cent[a]	2.820(2)
Li–Cl(1)–Pb	88(1)	Cl(1)–Li–Cl(2)	101(2)	C(2)–P(2)–P(1)	98(1)
Li–Cl(2)–Pb	89(1)	C(1)–P(3)–C(2)	100(2)	P(2)–P(1)–C(1)	98(1)
Cl(1)–Pb–Cl(2)	80.7(3)	P(3)–C(2)–P(2)	119(2)	P(1)–C(1)–P(3)	125(2)

[a] Cent = Centroid of $P_3C_2Bu^t_2$ ring.

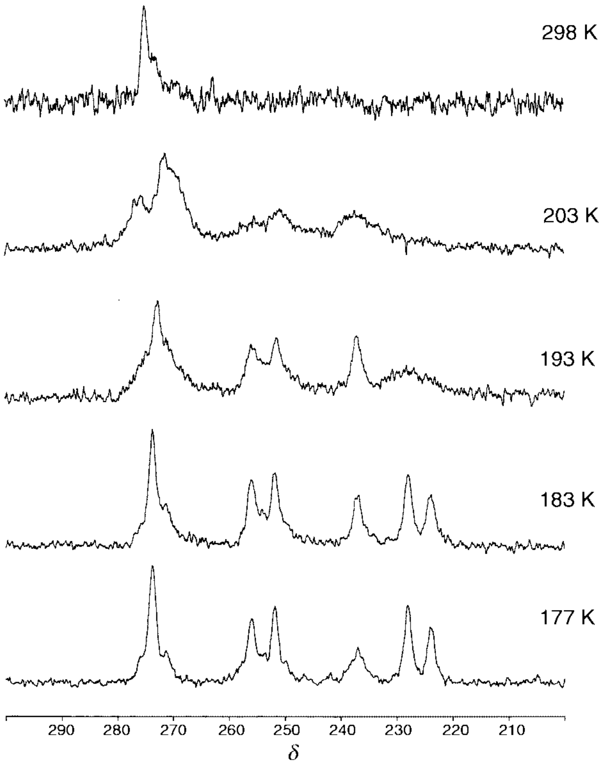


Fig. 4 Variable temperature $^{31}P\{^1H\}$ NMR spectra of **7**.

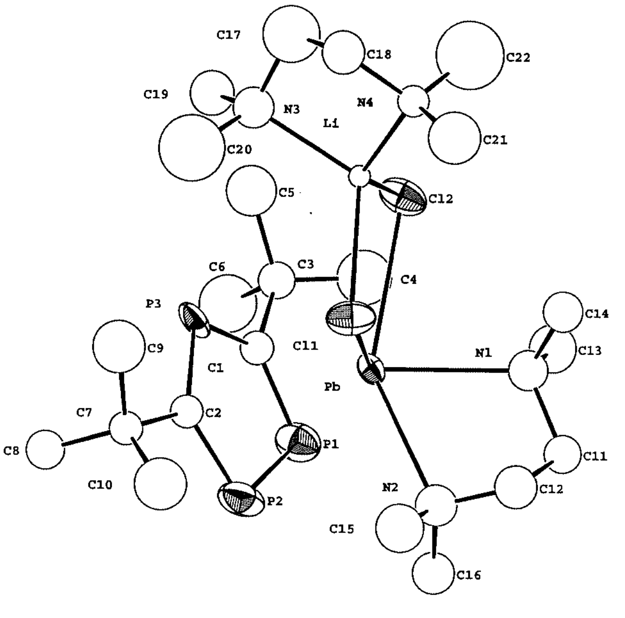


Fig. 5 Molecular structure of $[Pb(\eta^5\text{-}P_3C_2Bu^t_2)(\mu\text{-}Cl)_2Li(tmen)_2]$ **7**.

presumably due to the persistence of fluxional behaviour. The coupling constants cannot be accurately determined although the large $^1J_{PP}$ between P_A and P_B is clearly evident and is approximately 416 Hz.

The solid state structure of **7** was determined by a single crystal X-ray diffraction study and is depicted in Fig. 5 along with selected bond distances and angles in Table 3. The familiar bent motif of plumbocene species is retained in this half sandwich structure, with the planar delocalised $P_3C_2Bu^t_2$ ring η^5 ligated to the lead centre. The four membered bimetallic [PbClLiCl] unit is also an important feature and contributes to the reduction in the centroid–metal–chloride angles [centroid–Pb–Cl(1) = 120.4°, centroid–Pb–Cl(2) = 106.6°] compared with those in complexes **5** and **6**. The [PbClLiCl] unit is non planar and distorted, the asymmetric bond lengths reflecting the relative sizes of the two metals. This type of complex with a solvated LiCl molecule is unprecedented in Group 14 chemistry although it is encountered in lanthanide chemistry and in complexes of Group 13 elements such as $[Li(thf)_2(\mu\text{-}Cl)_2\text{-}GaCl\{C(SiMe_2Ph)_3\}]\cdot thf$.[22]

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove-box methods under an atmosphere of high purity argon or dinitrogen. The solvents tetrahydrofuran, 1,2-dimethoxyethane and hexane were refluxed over sodium–potassium alloy and distilled under nitrogen followed by freeze–thaw degassing prior to use. The solvent tmen was refluxed over and distilled from sodium. The ^1H, ^{31}P, ^{13}C, ^{207}Pb and ^7Li NMR spectra were recorded on either a Bruker WM-250, AC-400 or AC-P250 spectrometer. Variable temperature experiments were controlled by a Bruker B-VT 1000 variable temperature unit. ^{13}C and ^1H NMR spectra were referenced to the residual solvent references. ^{31}P, ^{207}Pb and ^7Li NMR spectra were referenced to external 85% H_3PO_4, $Pb(NO_3)_2$ and $LiNO_3$ respectively. Mass spectra were recorded on a VG 12-253 quad (70 eV) or MS80RF double focussing instrument. Elemental analyses were obtained from Medac Ltd. The starting materials $[Li(tmen)_2][P_2SbC_2Bu^t_2]$,[18] $[Li(dme)_3][P_3C_2Bu^t_2]$,[12] $Li(C_5Me_5)$[23] and $[Pb(\eta^5\text{-}C_5Me_5)Cl]$[16] were synthesised according to published procedures. $PbCl_2$ was purchased from Aldrich and chemically dried before use by refluxing over $SOCl_2$.

Syntheses

$[Pb(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ 3. To a dme slurry of $PbCl_2$ (0.204 g, 0.73 mmol) at −45 °C was added a dme solution of $[Li(dme)_3]$-$[P_3C_2Bu^t_2]$ (4 cm³, 0.4 M solution, 1.6 mmol) dropwise, with the exclusion of light. The mixture was stirred at −45 °C for 30 min and was then allowed to warm to ambient temperature. Volatiles were removed *in vacuo* and the residue extracted with hexane and filtered. The hexane filtrate was evaporated to afford **3** as a red-orange oil (0.234 g, 48%). NMR (C_7D_8, 298 K): δ_H (250 MHz) 1.46 (s, Bu^t); δ_C (62.9 MHz) 37.5 [m, $C(CH_3)_3$], 42.7 [m, $C(CH_3)_3$], 228.1 [m, PCP, $^1J_{PC} = 71.7$ Hz, $\Sigma^1J_{PC} + {}^2J_{PC} = 93.9$ Hz]; $^{31}P\{^1H\}$ (101.4 MHz) δ 273.1 (d, CPC, $^2J_{PP} = 47.5$ Hz, $^1J_{P\text{-}Pb} = 485$ Hz), 275.1 (d, CPSb, $^2J_{PP} = 47.5$ Hz, $^1J_{P\text{-}Pb} = 303$ Hz); $^{207}Pb\{^1H\}$ (52.3 MHz) δ −3752 (m, $^1J_{PbP(A)} = 358$ Hz, $^1J_{PbP(B)} = 250$ Hz); FAB mass spectrum (25

Table 4 Crystal data for compounds **5**, **6** and **7**

	5	**6**	**7**
Formula	$C_{20}H_{33}P_3Pb$	$C_{20}H_{33}P_{2.3}PbSb_{0.65}$ [a]	$C_{22}H_{50}LiN_4P_3Pb$
M	573.6	632.57	748.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
$\beta/°$	102.39(6)	102.540(10)	106.88(3)
a/Å	10.235	10.2780(7)	37.859(17)
b/Å	12.517(5)	12.7250(7)	9.871(4)
c/Å	18.683(18)	18.597(4)	18.695(6)
V/Å^3	2338(3)	2374.2(5)	6685(5)
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
Z	4	4	8
μ/cm^{-1}	74.7	79.89	54.0
T/K	173	150	173
λ/Å	0.71073	0.71073	0.71073
Reflections collected	4547	10147	4458
Unique reflections	4313	3621	4391
R ($I > 2\sigma I$)	0.059	0.0377	0.094
R (all data)	0.060	0.0887	0.085

[a] Non integral stoichiometry arises from co-crystallisation of **6** with a small amount of **5**, see Results and discussion.

kV) *m*/*z* 439 ($[Pb(\eta^5\text{-}P_3C_2Bu^t_2)]^+$), 343 ($[C_5Me_5Pb]^+$, 72%), 208 ($[Pb]^+$, 100%).

$[Pb(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ 5. To a solution of 1,2,3,4,5-pentamethylcyclopentadiene (0.16 cm^3, 1.0 mmol) in dme (10 cm^3) at −45 °C was added *n*-BuLi (0.65 cm^3 of 1.6 M hexane solution, 1.0 mmol) dropwise with stirring. The resulting solution was warmed to room temperature and a dme solution of $[Li(dme)_3][P_3C_2Bu^t_2]$ (3.1 cm^3, 0.32 M, 1.0 mmol) was added with stirring. The resulting mixture was added to a slurry of $PbCl_2$ (0.278 g, 1.0 mmol) in dme (5 cm^3) at −45 °C with the exclusion of light and stirred for 30 min. The suspension was then warmed to room temperature and volatiles were removed *in vacuo* and the residue extracted with hexane and filtered. The filtrate was concentrated and cooled to −5 °C to yield **5** as orange-red needles (0.231 g, 45%), mp 157–158 °C (Found: C, 41.6%; H, 5.83%; $C_{20}H_{33}P_3Pb$ requires C, 41.88%; H, 5.80%). NMR: δ_H (250 MHz, C_6D_6) 1.62 (s, 18H, Bu^t), 2.05 (s, 15H, $C_5(CH_3)_3$, $^2J_{PbH} = 15.1$ Hz); δ_C (62.9 MHz, C_7D_8) 8.8 [s, $C_5(CH_3)_3$, $^2J_{PbC} = 22.4$ Hz], 37.7 [dd, $C(CH_3)_3$, $^3J_{PC} = 10$ Hz and 5 Hz], 41.6 [dd, $C(CH_3)_3$, $^2J_{PC} = 21.0$ Hz and 6.5 Hz], 119.3 [s, $C_5(CH_3)_5$, $^1J_{PbC} = 6.9$ Hz], 223.9 [m, P*C*P, $^1J_{PC} = 68.1$ Hz, $\Sigma^1J_{PC} + {}^2J_{PC} = 92.6$ Hz]; $^{31}P\{^1H\}$ (101.3 MHz, 183 K, C_7D_8) δ 280.3 (t, C*P*C, $^2J_{P(A)P(B)} = 48.8$ Hz, $^1J_{P\text{-}Pb} = 470$ Hz), 255.3 (d, C*P*P, $^2J_{P(A)P(B)} = 48.8$ Hz, $^1J_{P\text{-}Pb} = 212$ Hz); FAB mass spectrum (25 kV) *m*/*z* 574 (M^+), 439 ($[Pb(P_3C_2Bu^t_2)]^+$), 343 ($[Pb(C_5Me_5)]^+$), 277 ($[PbCBu^t]^+$), 231 ($[P_3C_2Bu^t_2]^+$), 208 ($[Pb]^+$), 169 ($[PC_2Bu^t_2]^+$), 135 ($[C_5Me_5]^+$).

$[Pb(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ 6. The compounds $[Pb(\eta^5\text{-}C_5Me_5)Cl]$ (0.672 g, 1.78 mmol) and $[Li(tmen)_2][P_2SbC_2Bu^t_2]$ (1.0 g, 1.78 mmol) were stirred together at −50 °C in dme (18 cm^3). The resulting mixture was warmed to room temperature and stirred in the absence of light for 30 min. Volatiles were removed *in vacuo* and the residue extracted with hexane and filtered to afford a deep red solution. The hexane filtrate was concentrated and cooled slowly to −30 °C to afford red/brown co-crystals of **6** (*ca.* 71%) and **5** (*ca.* 29%) (0.15 g, 12%), mp 122–124 °C (with decomposition). NMR (C_7D_8, 298 K): δ_H (250 MHz) 1.83 (s, 9H, Bu^t), 1.91 (s, 9H, Bu^t), 2.37 (s, 15H, C_5Me_5); δ_C (100.6 MHz) 20.6 [s, $C_5(CH_3)_3$], 37.8 [virtual triplet, $C(CH_3)_3$, $^3J_{PC} = 14.7$ Hz], 39.1 [d, $C(CH_3)_3$, $^3J_{PC} = 12.1$ Hz], 45.8 [d, $C(CH_3)_3$, $^2J_{PC} = 18.6$ Hz], 46.7 [dd, $C(CH_3)_3$, $^2J_{PC} = 16.5$ Hz and 23.1 Hz], 118 [s, C_5Me_5], 200.7 [d, P*C*Sb, $^1J_{PC} = 72$ Hz], 217.5 [dd, P*C*P, $^1J_{PC} = 74.9$ Hz and 94.6 Hz]; $^{31}P\{^1H\}$ (101.4 MHz) δ 297.0 (d, C*P*C, $^2J_{PP} = 50.1$ Hz, $^1J_{P\text{-}Pb} = 470$ Hz), 334.3 (d, C*P*Sb, $^2J_{PP} = 50.1$ Hz, $^1J_{P\text{-}Pb} = 212$ Hz); FAB mass spectrum (25 kV) *m*/*z* 343 ($[C_5Me_5Pb]^+$, 72%), 208 ($[Pb]^+$, 100%).

$[Pb(\eta^5\text{-}P_3C_2Bu^t_2)(\mu\text{-}Cl)_2Li(tmen)_2]$ 7. To a slurry of $PbCl_2$ (0.124 g, 0.447 mmol) in tmen (2 cm^3) at −45 °C was added $[Li(dme)_3][P_3C_2Bu^t_2]$ (2.0 cm^3, 0.47 M solution, 0.94 mmol) with rapid stirring. The resulting mixture was stirred for 15 min and was then warmed to room temperature. Volatiles were removed *in vacuo* and the residue extracted with hexane and filtered. The filtrate was concentrated and cooled to −5 °C to yield **7** as orange-yellow plates (0.048 g, 18%). NMR δ_H (250 MHz, C_7D_8, 298 K) 1.57 (s, 18 H, Bu^t), 2.05 (s, 8H, CH_2), 2.1 (s, 24 H, $N(CH_3)_2$); δ_C (62.9 MHz, C_7D_8, 298 K) 37.5 [m, $C(CH_3)_3$], 42.5 [m, $C(CH_3)_3$], 46.0 [m, $N(CH_3)_2$], 57.0 [m, CH_2] ring quaternary not observed; δ_{Li} (97.25 MHz, C_7D_8, 298 K) 0.91 (s); $^{31}P\text{-}\{^1H\}$ δ_P (101.3 MHz, C_7D_8, 183 K) 225.8 (br d, $^1J_{PP} = 416$ Hz), 253.6 (br d, $^1J_{PP} = 413$ Hz), 273.5 (br m).

Crystallography

Crystals of compounds **5**, **6** and **7** suitable for structure determination were grown from hexane solutions and mounted in oil. Intensity data were measured on a CAD4 diffractometer (compounds **5** and **7**) or FAST[24] area-detector diffractometer (compound **6**) using Mo-Kα radiation. All structures were solved by heavy atom methods (SHELXS-86)[25] and refined by full matrix least squares. Empirical absorption corrections were carried out by the DIFABS[26] method. Crystal data, details of the data collection and refinement are given in Table 4.

All non hydrogen atoms in compounds **5** and **6** were refined anisotropically. In compound **7** the Pb, Cl and P atoms were refined anisotropically. Hydrogens were included in calculated positions. During refinement of compound **6** a site disorder was found to exist in which the sites labelled Sb(1) and P(1) are partially occupied by phosphorus (60%) and antimony (25%) respectively.

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