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Synthesis and structures of tin(II) and lead(II) 1-aza-allyls; the $[N(SiMe_3)C(Ph)C(SiMe_3)_2]^-$ ligand [1]

Peter B. Hitchcock, Michael F. Lappert *, Marcus Layh

The Chemistry Laboratory, University of Sussex, Brighton, BN1 9QJ, UK

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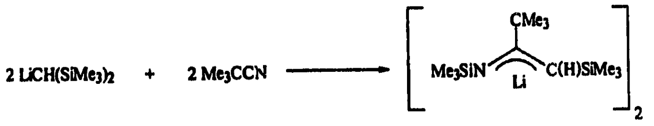
Abstract

The new lithium 1-aza-allyl $Li[N(R)C(Ph)CR_2](THF)$ (**1**) ($Li(LL'')(THF)$) has been prepared in high yield from $LiCR_3(THF)_2$ and benzonitrile ($R = SiMe_3$; THF = tetrahydrofuran). From **1** and MCl_2, the stable 1-aza-allyls $[M(\mu\text{-}Cl)(LL'')]$ (**2** (M = Sn); **3** (M = Pb)) and $M(LL'')_2$ (**4** (M = Sn); **5** (M = Pb)) were obtained. Each of the compounds **1**–**5** was fully characterised by multinuclear NMR spectroscopy (the compounds are fluxional in solution), mass spectrometry and for **3**, **4** and **5** single crystal X-ray diffraction. Crystalline **3** is a centrosymmetric dimer having terminal η^3-1-aza-allyl ligands with one bridging Cl^- strongly bonding, Pb–Cl = 2.609(3) Å, and the other much less so, Pb···Cl = 3.276(3) Å. Crystalline **4** and **5** are mononuclear (η^3-1-aza-allyl)metal(II) enamides, $M[N(R)C(Ph)CR_2][N(R)C(Ph){:}CR_2]$. Also reported are the synthesis and NMR spectra of $PbCl[N(R)C(Bu^t)CHR]$ (**6**).

Keywords: Crystal structures; Organotin complexes; Organolead complexes; 1-Aza-allyl complexes

1. Introduction

A series of recent papers (entitled, 'Transformation of the bis(bistrimethylsilyl)methyl into the 1-aza-allyl and β-diketiminato ligand'; for the latest, see Ref. [1]) has been devoted to the synthesis, structures and reactions of metal-1-aza-allyls and β-diketiminates. These stemmed from the discovery that treatment of bis(trimethylsilyl)methyl-lithium ($LiCHR_2$) with t-butyl nitrile [2] or benzonitrile [3] yielded $[Li\{N(R)C(Bu^t)CHR\}]_2$ ($[Li(LL')]_2$) (Eq. (1)) or $[Li\{N(R)C(Ph)C(H)C(Ph)N(R)\}]_2$, respectively ($R = SiMe_3$). A major part of the present study is concerned with the synthesis of a new and more bulky lithium 1-aza-allyl $Li\{N(R)C(Ph)CR_2\}$ (**1**) ($Li(LL'')$) and its role as a ligand transfer reagent in providing access to a range of tin(II) and lead(II) 1-aza-allyls, $M(\mu\text{-}Cl)(LL'')$ and $M(LL'')_2$ (M = Sn or Pb).



(1)

The following 1-aza-allyl-metal complexes have previously been prepared from $[Li(LL')]_2$: $[K(LL')]_n$ [2], *rac*-$[Sn(LL')]_2$ [4], *rac*-$[Zr(LL')_2Cl_2$ [2,5], $[\{Zr(LL')Cl_2\text{-}(\mu\text{-}Cl)\}]_2$ [5], *rac*-$[Th(LL')_2Cl_2]$ [6], *rac*-$[Ln(LL')]_2\text{-}X(THF)_n]$ (X = Cl, $n = 1$ and Ln = Ce or Nd; X = I, $n = 1$ and Ln = Sm; or X = I or OSO_2CF_3, $n = 0$ and Ln = Yb) [7], *rac*-$[Sm(LL')_2(THF)]$ or *rac*-$[Yb(LL')]_2$; while a Cu(I) derivative $[Cu(\mu\text{-}LL')]_2$ has been briefly mentioned [8].

Some lithium 1-aza-allyls related to $[Li(LL')]_2$ have been reported including $Li\{N(R)C(Bu^t){=}C(H)Ph](TMEDA)$ [9], $1,2\text{-}C_6H_4[\{C(H)C(Bu^t)NR\}Li(TMEDA)]_2$ and $Li[N(R)C(Bu^t)C(H)C_6H_3Me_2\text{-}2,5]$ [10].

In a recent communication we drew attention to the variable bonding modes in the homoleptic tin(II) 1-aza-allyls [4]; thus the crystalline compounds $Sn[N(R)C(Bu^t){=}C(H)C_6H_3Me_2\text{-}2,5]_2$, *rac*-$[Sn(LL')]_2$ and $Sn[N(R)C(Ph)CR_2][N(R)C(Ph){:}CR_2]$ were shown to be a bis(enamide), bis(η^3-1-aza-allyl) and an (η^3-1-aza-allyl) enamide, respectively. Details for the last of these, compound **4**, are reported herein.

2. Experimental

2.1. General procedures and instrumentation

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying

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* Corresponding author. Tel.: +44 1273 606 755; fax: +44 1273 677 196; e-mail: lappert@sussex.ac.uk

[1] Dedicated to Professor Dr Wolfgang Beck, as a mark of friendship and respect, on the occasion of his 65th birthday.

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agents and degassed. The NMR spectra were recorded in C_6D_6 or $CDCl_3$ at 298 K using the following Bruker instruments: AC-P 250 (^{1}H, 250.1; ^{13}C, 62.9; ^{207}Pb 52.2; ^{29}Si 49.7; ^{119}Sn 93.3 MHz), DPX 300 (^{1}H, 300.1; ^{13}C 75.5; ^{31}P, 121.5 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7; ^{207}Pb 104.4; ^{119}Sn 186.5 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{29}Si, ^{119}Sn and ^{207}Pb spectra were referenced externally to $SiMe_4$, $SnMe_4$ and $Pb(NO_3)_2$, respectively. Unless otherwise stated all NMR spectra other then ^{1}H were proton decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK.

2.2. *Li[N(R)C(Ph)CR$_2$](THF) (1)*

Benzonitrile (3.63 ml, 3.55 mmol) was added at room temperature by a pipette to a solution of tris(trimethylsilyl)methyllithium (13.59 g, 3.55 mmol) in diethyl ether (100 ml). The colour of the reaction mixture changed immediately from colourless to yellow. After the mixture was stirred for 15 h at r.t. the solvent was removed and the colourless solid dried for 4 h in vacuo at 60°C. The colourless residue was extracted with pentane (200 ml), the extract filtered and the filtrate cooled to −30°C to give colourless crystals of **1** (9.85 g, 67%). The procedure was repeated using pentane (100 ml), yielding a second crop of crystals (3.05 g, 21%), m.p.: 125°C (decomp.). *Anal.* Found: C, 59.4; H, 9.69; N, 3.17. Calc. for $C_{21}H_{40}LiNOSi_3$: C, 61.0; H, 9.74; N, 3.39%. MS: *m/z* (%) 335 (55) $[MH-Li-THF]^+$, 320 (22) $[MH-Li-THF-Me]^+$. ^{1}H NMR (C_6D_6): δ 0.11 (s, $NSiMe_3$), 0.26 (s, $SiMe_3$), 1.18 (t, THF), 3.36 (t, THF), 7.16–7.18 (Ph, 3H), 7.35–7.39 (Ph, 2H). ^{7}Li NMR (C_6D_6): δ 2.4. ^{13}C NMR (C_6D_6): δ 3.1 (s, $SiMe_3$), 3.6 (s, $SiMe_3$), 25.3 (s, CH_2, THF), 68.8 (s, OCH_2, THF), 77.0 (s, CSi_2), 127.4, 127.9 and 129.1 (s, Ph), 150.1 (s, *ipso*-C), 189.8 (s, CN).

2.3. *[Sn(μ-Cl){N(R)C(Ph)CR$_2$}]$_n$ (2), [Pb(μ-Cl){N(R)C(Ph)CR$_2$]$_2$ (3) and [Pb(μ-Cl){N(R)C(Bu^t)CHR} (6)*

A solution of Li(LL")(THF) (**1**) (0.75 g, 1.81 mmol) in pentane (20 ml) was added dropwise to a suspension of $SnCl_2$ (0.34 g, 1.81 mmol) in pentane (15 ml) at −50°C. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. A colourless precipitate was filtered off and most of the solvent was removed from the yellow filtrate. After cooling, pale yellow crystals of **2** (0.58 g, 65%) were isolated. *Anal.* Found: C, 41.1; H, 6.53; N, 2.89. Calc. for $C_{17}H_{32}ClNSi_3Sn$: C, 41.8; H, 6.60; N, 2.87%. MS: *m/z* (%) 489 (35) $[M]^+$, 474 (8) $[M-Me]^+$, 454 (8) $[M-Cl]^+$. ^{1}H NMR (C_7D_8): δ −0.05 (s, $NSiMe_3$), 0.09 (s, broad, $SiMe_3$), 6.90–6.95 (Ph, 3H), 7.29 (d, Ph, 2H). ^{119}Sn NMR (C_6D_6/C_6H_6): δ −68. ^{29}Si NMR (C_6D_6/C_6H_6): δ −3.1 (s, broad, $SiMe_3$), 5.6 (s, $NSiMe_3$). ^{13}C NMR (C_6D_6): δ 1.1 (s, $NSiMe_3$), 3.2 (s, broad, $C(SiMe_3)_2$), 62.5 (s, CSi_2), 128.0 and 128.4 (s, *m/o*-C), 130.9 (s, *p*-C), 146.3 (s, *ipso*-C), 203.9 (s, CN).

In a low temperature ^{1}H NMR experiment on **2** in C_7D_8 the broad signal for the $SiMe_3$ groups observed at ambient temperature was replaced by two signals at δ 0.07 and 0.15; the coalescence temperature was 241 K.

The corresponding lead compound **3** was synthesised by an identical procedure from **1** (0.88 g, 2.12 mmol) and $PbCl_2$ (0.65 g, 2.34 mmol) at room temperature in diethyl ether (30 ml). After recrystallisation from pentane, yellow crystals of **3** (0.35 g, 30%) were isolated, m.p.: 144°C (decomp.). MS: *m/z* (%) 577 (19) $[M]^+$, 542 (22) $[M-Cl]^+$. ^{1}H NMR (C_6D_6): δ 0.00 (s, $NSiMe_3$), 0.11 (s, $SiMe_3$), 7.00–7.02 (Ph, 3H), 7.39–7.43 (Ph, 2H). ^{207}Pb NMR (C_6D_6/C_6H_6): δ 2105.1. ^{29}Si NMR (C_6D_6/C_6H_6): δ −5.2 (s, $C(SiMe_3)_2$), 2.9 (s, $NSiMe_3$). ^{13}C NMR (C_6D_6): δ 1.6 (s, $NSiMe_3$), 3.7 (s, $SiMe_3$), 89.3 (s, CSi_2), 128.3, 130.5 and 137.7 (s, Ph), 156.8 (s, *ipso*-C), 199.1 (s, CN).

Compound **6** was prepared in a similar manner from $PbCl_2$ (1.30 g, 4.65 mmol) and $[\overline{Li(LL')}]_2$ (1.16 g, 4.65 mmol) in diethyl ether (30 ml). After mixing the components at −30°C and stirring for 15 h at room temperature, pale yellow crystals of **6** (0.87 g, 40%) were obtained from pentane, m.p.: 110°C (decomp.). MS: already at room temperature without heating only fragments of oligomeric species and decomposition products were observed. ^{1}H NMR (C_6D_6): δ 0.15 (s, $SiMe_3$), 0.36 (s, $SiMe_3$), 1.14 (s, Bu^t), 2.93 (s, CH, $^2J(^1H-^{207}Pb) = 34.5$ Hz). ^{207}Pb NMR (C_6D_6): δ 1958.8. ^{29}Si NMR (C_6D_6): δ −12.8 (s, $SiMe_3$, $^2J(^{29}Si-^{207}Pb) = 58.0$ Hz), −3.5 (s, $SiMe_3$, $^2J(^{29}Si-^{207}Pb) = 51.6$ Hz). ^{13}C NMR (C_6D_6, ^{1}H coupled): δ 1.8 (q, $SiMe_3$, $^1J(^{13}C-^1H) = 118.3$ Hz), 4.5 (q, $SiMe_3$, $^1J(^{13}C-^1H) = 118.0$ Hz), 30.0 (q, $C(CH_3)_3$, $^1J(^{13}C-^1H) = 125.9$ Hz), 46.7 (s, *C*$(CH_3)_3$), 61.6 (d, CH, $^1J(^{13}C-^1H) = 128.7$ Hz), 200.0 (s, CN).

2.4. *Sn[N(R)C(Ph)CR$_2$]$_2$ (4) and Pb[N(R)C(Ph)CR$_2$]$_2$ (5)*

Solid Li(LL")(THF) (**1**) (1.31 g, 3.20 mmol) was added to a suspension of $SnCl_2$ (0.30 g, 1.58 mmol) in pentane (30 ml) at −40°C. The reaction mixture was stirred at room temperature for 18 h. A colourless precipitate was filtered off and most of the solvent was removed from the orange–red filtrate. By cooling to −30°C orange–red crystals of **4** (0.91 g, 73%) were obtained, m.p.: 125°C (decomp.). *Anal.* Found: C, 51.6; H, 8.15; N, 3.49. Calc. for $C_{34}H_{64}N_2Si_6Sn$: C, 51.8; H, 8.19; N, 3.55%. MS: *m/z* (%) 788 (1) $[M]^+$, 715 (0.5) $[M-SiMe_3]^+$, 454 (75) $[M-Me_3SiNC(Ph)C(SiMe_3)_2]^+$. ^{1}H NMR ($C_6D_6$): δ 0.12 (s, $NSiMe_3$), 0.32 (s, $SiMe_3$), 7.16 (m, Ph, 3H), 7.41 (d, Ph, 2H). ^{29}Si NMR (C_7D_8): δ 6.6 (s, $NSiMe_3$, $^2J(^{29}Si-^{119}Sn) = 8.9$ Hz, $^1J(^{29}Si-^{13}C) = 56.6$ Hz), −2.1 ($^2J(^{29}Si-^{119}Sn) = 16.7$ Hz, $^1J(^{29}Si-$

Table 1
Crystallographic data for compounds 3, 4 and 5

Compounds	3	4	5
Formula	$C_{17}H_{32}ClNPbSi_3$	$C_{34}H_{64}N_2Si_6Sn$	$C_{34}H_{64}N_2PbSi_6$
M	577.4	788.1	876.6
Temperature (K)	293(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	9.832(2)	19.249(4)	14.182(3)
b (Å)	15.911(3)	12.400(3)	17.770(3)
c (Å)	15.784(4)	19.820(5)	17.833(4)
β (°)	101.64(2)	112.83(2)	105.19(2)
U (Å^3)	2418.4(9)	4360(2)	4337(2)
Z	4	4	4
D_c (mg m^{-3})	1.59	1.20	1.34
$F(000)$	1128	1664	1792
μ (mm^{-1})	7.24	0.77	4.08
Crystal size (mm)	0.2×0.2×0.2	0.4×0.3×0.2	0.3×0.3×0.2
θ Min. and max. (°)	2 to 25	2 to 25	2 to 25
Index ranges	$0\leq h\leq 11, 0\leq k\leq 18, -18\leq l\leq 18$	$0\leq h\leq 22, 0\leq k\leq 14, -23\leq l\leq 21$	$0\leq h\leq 16, 0\leq k\leq 21, -21\leq l\leq 20$
Reflections collected	4497	7895	7941
Independent reflections (R_{int})	4243 (0.046)	7663 (0.42)	7622 (0.107)
Reflections with $I>2\sigma(I)$	2564	5008	3978
Structure solution	heavy atom method	direct methods	direct methods and difference map
No. variables	208	388	368
$R1$ ($I>2\sigma(I)$)	0.054	0.048	0.077
$wR2$ (all data)	0.097	0.106	0.148
Largest difference peak (e Å^{-3})	0.64	0.38	0.87
Absorption correction from psi scans (T_{max}, T_{min})	1.00, 0.82	1.00, 0.91	1.00, 0.89

$^{13}C) = 49.3$ Hz, $^1J(^{29}Si-^{13}C(SiMe_3) = 52.0$ Hz). ^{119}Sn NMR (C_6D_6/C_6H_6): δ −37.3. ^{13}C NMR (C_7D_8): δ 8.4 (s, $NSiMe_3$, $^1J(^{29}Si-^{13}C) = 56.6$ Hz), 10.0 (s, $C(SiMe_3)_2$, $^1J(^{29}Si-^{13}C) = 52.0$ Hz), 102.9 (s, CSi_2, $^1J(^{29}Si-^{13}C) = 49.3$ Hz), 127.7, 129.6 and 130.1 (s, Ph), 153.4 (s, *ipso*-C, $^3J(^{13}C-^{119}Sn) = 23.4$ Hz), 185.7 (s, CN, $^2J(^{13}C-^{119}Sn) = 55.0$ Hz).

The corresponding Pb compound **5** was prepared in a similar way by reacting a solution of the lithium compound **1** (1.32 g, 3.19 mmol) in pentane (20 ml) with a suspension of $PbCl_2$ (0.44 g, 1.60 mmol) in pentane (30 ml) at −60°C. After warming up to room temperature, a yellow solution with a colourless precipitate was obtained. On further stirring at r.t. the colour of the reaction mixture changed to dark red. After 1 h the suspension was filtered and part of the solvent removed from the filtrate. Cooling to −30°C gave dark red crystals of **5** (1.00 g, 71%), m.p.: 105–108°C (decomp.). *Anal.* Found: C, 46.0; H, 7.41; N, 3.56. Calc. for $C_{34}H_{64}N_2Si_6Pb$: C, 45.6; H, 7.41; N, 3.20%. MS: m/z (%) 1738 (0.01) $[M_2-Me]^+$, 1223 (0.15) $[M_2-2Me]^+$, 1666 (0.15) $[M_2-Me-SiMe_3]^+$, 1649 (0.9) $[M_2-2Me-SiMe_3]^+$, 542 (27) $[M-Me_3SiNC(Ph)C(SiMe_3)_2]^+$. ^{1}H NMR ($C_6D_6$): δ 0.12 (s, $NSiMe_3$), 0.25 (s, $SiMe_3$), 7.04–7.12 (Ph, 3H), 7.37–7.40 (Ph, 2H). ^{207}Pb NMR (C_6D_6/C_6H_6): δ 1720. ^{13}C NMR (C_6D_6): δ 3.8 (s, $NSiMe_3$), 4.9 (s, $C(SiMe_3)_2$), 100.6 (s, CSi_2), 127.7, 129.6 and 130.1 (s, Ph), 153.4 (s, *ipso*-C), 185.7 (s, CN).

2.5. X-ray structure determinations for compounds 3, 4 and 5

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo Kα radiation. For compounds **3** and **4** the crystals were sealed in a capillary under argon, whilst for compound **5** the crystal was enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Cell dimensions were calculated from the setting angles for 25 reflections with $9<\theta<13°$. Intensities were measured by an ω-2θ scan. Corrections were made for Lorentz and polarisation effects and also for absorption by ψ-scans. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods or heavy atom methods using SHELXS-86 [11a] and refined on F^2 with anisotropic thermal parameters (except C(1), C(4), C(6) in compound **5**, which were refined isotropically) by full-matrix least-squares using SHELXL-93 [11b]. Further details are given in Table 1.

3. Results and discussion

3.1. Synthesis of Li[N(R)C(Ph)CR₂](THF) (1)

Past experience has shown that the stereo-electronic properties of a lithium 1-aza-allyl can to some degree be tuned by agents and degassed. The NMR spectra were recorded in C_6D_6 or $CDCl_3$ at 298 K using the following Bruker instruments: AC-P 250 (^{1}H, 250.1; ^{13}C, 62.9; ^{207}Pb 52.2; ^{29}Si 49.7; ^{119}Sn 93.3 MHz), DPX 300 (^{1}H, 300.1; ^{13}C 75.5; ^{31}P, 121.5 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7; ^{207}Pb 104.4; ^{119}Sn 186.5 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{29}Si, ^{119}Sn and ^{207}Pb spectra were referenced externally to $SiMe_4$, $SnMe_4$ and $Pb(NO_3)_2$, respectively. Unless otherwise stated all NMR spectra other then ^{1}H were proton decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK.

2.2. *Li[N(R)C(Ph)CR$_2$](THF) (1)*

Benzonitrile (3.63 ml, 3.55 mmol) was added at room temperature by a pipette to a solution of tris(trimethylsilyl)methyllithium (13.59 g, 3.55 mmol) in diethyl ether (100 ml). The colour of the reaction mixture changed immediately from colourless to yellow. After the mixture was stirred for 15 h at r.t. the solvent was removed and the colourless solid dried for 4 h in vacuo at 60°C. The colourless residue was extracted with pentane (200 ml), the extract filtered and the filtrate cooled to −30°C to give colourless crystals of **1** (9.85 g, 67%). The procedure was repeated using pentane (100 ml), yielding a second crop of crystals (3.05 g, 21%), m.p.: 125°C (decomp.). *Anal.* Found: C, 59.4; H, 9.69; N, 3.17. Calc. for $C_{21}H_{40}LiNOSi_3$: C, 61.0; H, 9.74; N, 3.39%. MS: *m/z* (%) 335 (55) $[MH-Li-THF]^+$, 320 (22) $[MH-Li-THF-Me]^+$. ^{1}H NMR (C_6D_6): δ 0.11 (s, $NSiMe_3$), 0.26 (s, $SiMe_3$), 1.18 (t, THF), 3.36 (t, THF), 7.16–7.18 (Ph, 3H), 7.35–7.39 (Ph, 2H). ^{7}Li NMR (C_6D_6): δ 2.4. ^{13}C NMR (C_6D_6): δ 3.1 (s, $SiMe_3$), 3.6 (s, $SiMe_3$), 25.3 (s, CH_2, THF), 68.8 (s, OCH_2, THF), 77.0 (s, CSi_2), 127.4, 127.9 and 129.1 (s, Ph), 150.1 (s, *ipso*-C), 189.8 (s, CN).

2.3. *[Sn(μ-Cl){N(R)C(Ph)CR$_2$}]$_n$ (2), [Pb(μ-Cl){N(R)C(Ph)CR$_2$]$_2$ (3) and [Pb(μ-Cl){N(R)C(Bu^t)CHR] (6)*

A solution of Li(LL")(THF) (**1**) (0.75 g, 1.81 mmol) in pentane (20 ml) was added dropwise to a suspension of $SnCl_2$ (0.34 g, 1.81 mmol) in pentane (15 ml) at −50°C. The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. A colourless precipitate was filtered off and most of the solvent was removed from the yellow filtrate. After cooling, pale yellow crystals of **2** (0.58 g, 65%) were isolated. *Anal.* Found: C, 41.1; H, 6.53; N, 2.89. Calc. for $C_{17}H_{32}ClNSi_3Sn$: C, 41.8; H, 6.60; N, 2.87%. MS: *m/z* (%) 489 (35) $[M]^+$, 474 (8) $[M-Me]^+$, 454 (8) $[M-Cl]^+$. ^{1}H NMR (C_7D_8): δ −0.05 (s, $NSiMe_3$), 0.09 (s, broad, $SiMe_3$), 6.90–6.95 (Ph, 3H), 7.29 (d, Ph, 2H). ^{119}Sn NMR (C_6D_6/C_6H_6): δ −68. ^{29}Si NMR (C_6D_6/C_6H_6): δ −3.1 (s, broad, $SiMe_3$), 5.6 (s, $NSiMe_3$). ^{13}C NMR (C_6D_6): δ 1.1 (s, $NSiMe_3$), 3.2 (s, broad, $C(SiMe_3)_2$), 62.5 (s, CSi_2), 128.0 and 128.4 (s, *m*/*o*-C), 130.9 (s, *p*-C), 146.3 (s, *ipso*-C), 203.9 (s, CN).

In a low temperature ^{1}H NMR experiment on **2** in C_7D_8 the broad signal for the $SiMe_3$ groups observed at ambient temperature was replaced by two signals at δ 0.07 and 0.15; the coalescence temperature was 241 K.

The corresponding lead compound **3** was synthesised by an identical procedure from **1** (0.88 g, 2.12 mmol) and $PbCl_2$ (0.65 g, 2.34 mmol) at room temperature in diethyl ether (30 ml). After recrystallisation from pentane, yellow crystals of **3** (0.35 g, 30%) were isolated, m.p.: 144°C (decomp.). MS: *m/z* (%) 577 (19) $[M]^+$, 542 (22) $[M-Cl]^+$. ^{1}H NMR (C_6D_6): δ 0.00 (s, $NSiMe_3$), 0.11 (s, $SiMe_3$), 7.00–7.02 (Ph, 3H), 7.39–7.43 (Ph, 2H). ^{207}Pb NMR (C_6D_6/C_6H_6): δ 2105.1. ^{29}Si NMR (C_6D_6/C_6H_6): δ −5.2 (s, $C(SiMe_3)_2$), 2.9 (s, $NSiMe_3$). ^{13}C NMR (C_6D_6): δ 1.6 (s, $NSiMe_3$), 3.7 (s, $SiMe_3$), 89.3 (s, CSi_2), 128.3, 130.5 and 137.7 (s, Ph), 156.8 (s, *ipso*-C), 199.1 (s, CN).

Compound **6** was prepared in a similar manner from $PbCl_2$ (1.30 g, 4.65 mmol) and $[\overline{\mathrm{Li(LL}}')]_2$ (1.16 g, 4.65 mmol) in diethyl ether (30 ml). After mixing the components at −30°C and stirring for 15 h at room temperature, pale yellow crystals of **6** (0.87 g, 40%) were obtained from pentane, m.p.: 110°C (decomp.). MS: already at room temperature without heating only fragments of oligomeric species and decomposition products were observed. ^{1}H NMR (C_6D_6): δ 0.15 (s, $SiMe_3$), 0.36 (s, $SiMe_3$), 1.14 (s, Bu^t), 2.93 (s, CH, $^2J(^1H-^{207}Pb) = 34.5$ Hz). ^{207}Pb NMR (C_6D_6): δ 1958.8. ^{29}Si NMR (C_6D_6): δ −12.8 (s, $SiMe_3$, $^2J(^{29}Si-^{207}Pb) = 58.0$ Hz), −3.5 (s, $SiMe_3$, $^2J(^{29}Si-^{207}Pb) = 51.6$ Hz). ^{13}C NMR (C_6D_6, ^{1}H coupled): δ 1.8 (q, $SiMe_3$, $^1J(^{13}C-^1H) = 118.3$ Hz), 4.5 (q, $SiMe_3$, $^1J(^{13}C-^1H) = 118.0$ Hz), 30.0 (q, $C(CH_3)_3$, $^1J(^{13}C-^1H) = 125.9$ Hz), 46.7 (s, $\mathit{C}(CH_3)_3$), 61.6 (d, CH, $^1J(^{13}C-^1H) = 128.7$ Hz), 200.0 (s, CN).

2.4. *Sn[N(R)C(Ph)CR$_2$]$_2$ (4) and Pb[N(R)C(Ph)CR$_2$]$_2$ (5)*

Solid Li(LL")(THF) (**1**) (1.31 g, 3.20 mmol) was added to a suspension of $SnCl_2$ (0.30 g, 1.58 mmol) in pentane (30 ml) at −40°C. The reaction mixture was stirred at room temperature for 18 h. A colourless precipitate was filtered off and most of the solvent was removed from the orange–red filtrate. By cooling to −30°C orange–red crystals of **4** (0.91 g, 73%) were obtained, m.p.: 125°C (decomp.). *Anal.* Found: C, 51.6; H, 8.15; N, 3.49. Calc. for $C_{34}H_{64}N_2Si_6Sn$: C, 51.8; H, 8.19; N, 3.55%. MS: *m/z* (%) 788 (1) $[M]^+$, 715 (0.5) $[M-SiMe_3]^+$, 454 (75) $[M-Me_3SiNC(Ph)C(SiMe_3)_2]^+$. ^{1}H NMR ($C_6D_6$): δ 0.12 (s, $NSiMe_3$), 0.32 (s, $SiMe_3$), 7.16 (m, Ph, 3H), 7.41 (d, Ph, 2H). ^{29}Si NMR (C_7D_8): δ 6.6 (s, $NSiMe_3$, $^2J(^{29}Si-^{119}Sn) = 8.9$ Hz, $^1J(^{29}Si-^{13}C) = 56.6$ Hz), −2.1 ($^2J(^{29}Si-^{119}Sn) = 16.7$ Hz, $^1J(^{29}Si-$

Table 1
Crystallographic data for compounds 3, 4 and 5

Compounds	3	4	5
Formula	$C_{17}H_{32}ClNPbSi_3$	$C_{34}H_{64}N_2Si_6Sn$	$C_{34}H_{64}N_2PbSi_6$
M	577.4	788.1	876.6
Temperature (K)	293(2)	293(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	9.832(2)	19.249(4)	14.182(3)
b (Å)	15.911(3)	12.400(3)	17.770(3)
c (Å)	15.784(4)	19.820(5)	17.833(4)
β (°)	101.64(2)	112.83(2)	105.19(2)
U (Å^3)	2418.4(9)	4360(2)	4337(2)
Z	4	4	4
D_c (mg m^{-3})	1.59	1.20	1.34
F(000)	1128	1664	1792
μ (mm^{-1})	7.24	0.77	4.08
Crystal size (mm)	0.2×0.2×0.2	0.4×0.3×0.2	0.3×0.3×0.2
θ Min. and max. (°)	2 to 25	2 to 25	2 to 25
Index ranges	$0 \le h \le 11, 0 \le k \le 18, -18 \le l \le 18$	$0 \le h \le 22, 0 \le k \le 14, -23 \le l \le 21$	$0 \le h \le 16, 0 \le k \le 21, -21 \le l \le 20$
Reflections collected	4497	7895	7941
Independent reflections (R_{int})	4243 (0.046)	7663 (0.42)	7622 (0.107)
Reflections with $I > 2\sigma(I)$	2564	5008	3978
Structure solution	heavy atom method	direct methods	direct methods and difference map
No. variables	208	388	368
$R1$ ($I > 2\sigma(I)$)	0.054	0.048	0.077
$wR2$ (all data)	0.097	0.106	0.148
Largest difference peak (e Å^{-3})	0.64	0.38	0.87
Absorption correction from psi scans (T_{max}, T_{min})	1.00, 0.82	1.00, 0.91	1.00, 0.89

^{13}C) = 49.3 Hz, $^1J(^{29}\text{Si}-^{13}\text{C}(\text{SiMe}_3)$ = 52.0 Hz). ^{119}Sn NMR (C_6D_6/C_6H_6): δ −37.3. ^{13}C NMR (C_7D_8): δ 8.4 (s, NSiMe$_3$, $^1J(^{29}\text{Si}-^{13}\text{C})$ = 56.6 Hz), 10.0 (s, C(Si*Me*$_3$)$_2$, $^1J(^{29}\text{Si}-^{13}\text{C})$ = 52.0 Hz), 102.9 (s, CSi$_2$, $^1J(^{29}\text{Si}-^{13}\text{C})$ = 49.3 Hz), 127.7, 129.6 and 130.1 (s, Ph), 153.4 (s, *ipso*-C, $^3J(^{13}\text{C}-^{119}\text{Sn})$ = 23.4 Hz), 185.7 (s, CN, $^2J(^{13}\text{C}-^{119}\text{Sn})$ = 55.0 Hz).

The corresponding Pb compound **5** was prepared in a similar way by reacting a solution of the lithium compound **1** (1.32 g, 3.19 mmol) in pentane (20 ml) with a suspension of $PbCl_2$ (0.44 g, 1.60 mmol) in pentane (30 ml) at −60°C. After warming up to room temperature, a yellow solution with a colourless precipitate was obtained. On further stirring at r.t. the colour of the reaction mixture changed to dark red. After 1 h the suspension was filtered and part of the solvent removed from the filtrate. Cooling to −30°C gave dark red crystals of **5** (1.00 g, 71%), m.p.: 105–108°C (decomp.). *Anal.* Found: C, 46.0; H, 7.41; N, 3.56. Calc. for $C_{34}H_{64}N_2Si_6Pb$: C, 45.6; H, 7.41; N, 3.20%. MS: m/z (%) 1738 (0.01) $[M_2-\text{Me}]^+$, 1223 (0.15) $[M_2-2\text{Me}]^+$, 1666 (0.15) $[M_2-\text{Me}-\text{SiMe}_3]^+$, 1649 (0.9) $[M_2-2\text{Me}-\text{SiMe}_3]^+$, 542 (27) $[M-\text{Me}_3\text{SiNC(Ph)C(SiMe}_3)_2]^+$. ^{1}H NMR ($C_6D_6$): δ 0.12 (s, NSiMe$_3$), 0.25 (s, SiMe$_3$), 7.04–7.12 (Ph, 3H), 7.37–7.40 (Ph, 2H). ^{207}Pb NMR (C_6D_6/C_6H_6): δ 1720. ^{13}C NMR (C_6D_6): δ 3.8 (s, NSiMe$_3$), 4.9 (s, C(Si*Me*$_3$)$_2$), 100.6 (s, CSi$_2$), 127.7, 129.6 and 130.1 (s, Ph), 153.4 (s, *ipso*-C), 185.7 (s, CN).

2.5. *X-ray structure determinations for compounds 3, 4 and 5*

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo Kα radiation. For compounds **3** and **4** the crystals were sealed in a capillary under argon, whilst for compound **5** the crystal was enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Cell dimensions were calculated from the setting angles for 25 reflections with $9 < \theta < 13°$. Intensities were measured by an ω-2θ scan. Corrections were made for Lorentz and polarisation effects and also for absorption by ψ-scans. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods or heavy atom methods using SHELXS-86 [11a] and refined on F^2 with anisotropic thermal parameters (except C(1), C(4), C(6) in compound **5**, which were refined isotropically) by full-matrix least-squares using SHELXL-93 [11b]. Further details are given in Table 1.

3. Results and discussion

3.1. *Synthesis of Li[N(R)C(Ph)CR$_2$](THF) (1)*

Past experience has shown that the stereo-electronic properties of a lithium 1-aza-allyl can to some degree be tuned by

Table 2
Selected bond lengths (Å) and angles (°) for compounds **4** and **5**

	4 (M = Sn)	5 (M = Pb)
M–N1	2.153(4)	2.336(9)
M–N2	2.288(4)	2.412(11)
M–C19	2.531(5)	2.534(12)
M–C18	2.775(4)	2.835(12)
N1–C1	1.432(5)	1.40(2)
N2–C18	1.317(6)	1.28(2)
C1–C2	1.365(6)	1.38(2)
C18–C19	1.461(6)	1.47(2)
N1–M–N2	109.9(1)	106.2(4)
N1–M–C19	113.2(2)	115.4(4)
N2–M–C19	59.3(1)	57.3(4)
C1–N1–Si1	116.4(4)	124.8(9)
C1–N1–M	105.0(3)	97.4(7)
Si1–N1–M	137.6(2)	132.1(5)
C18–N2–Si4	130.4(3)	132.6(10)
C18–N2–M	97.0(3)	95.3(9)
Si4–N2–M	130.9(2)	131.0(6)
C2–C1–N1	126.6(4)	123(1)
C2–C1–C3	121.3(4)	122(1)
N1–C1–C3	112.0(4)	115(1)
C1–C2–Si2	123.0(4)	120(1)
C1–C2–Si3	121.1(4)	122(1)
Si2–C2–Si3	115.7(2)	118.3(8)
N2–C18–C19	119.0(4)	119(1)
N2–C18–C20	118.7(4)	122(2)
C19–C18–C20	122.3(4)	119(1)
C18–C19–Si5	116.2(3)	122(1)
C18–C19–Si6	116.3(3)	113.0(10)
Si5–C19–Si6	114.6(3)	114.6(7)
C18–C19–M	83.5(3)	85.8(8)
Si5–C19–M	92.3(2)	119.8(6)
Si6–C19–M	129.5(2)	95.0

the η^1 bonded ligand which prevents a shorter metal–ligand contact; and (ii) the large deviation of the Si(1)–N(1)–M angle (for **4**: 137.6(2); for **5**: 132.1(5)°) from the sp^3 value.

3.4. The crystal structure of [Pb(μ-Cl)LL″]$_2$ (3)

The X-ray molecular structure of the heteroleptic 1-azaallyllead(II) chloride **3** is illustrated in Fig. 3, with the atom numbering scheme. Selected bond lengths and angles are listed in Table 6 and non-hydrogen atom coordinates are in Table 7.

While in the gas phase monomeric **3** may be the predominant species (parent ion only for monomer observed; no fragments of higher molecular weight, which is also true for the corresponding Sn-compound **2**), in the solid state **3** consists of a loosely bonded centrosymmetric dimer. The distances between the metal and the bridging chlorides are unequal with one close (Pb–Cl = 2.609(3) Å) and the other much more remote, (Pb···Cl = 3.276(3) Å). In the recently published dinuclear alkyllead(II) chloride [Pb(μ-Cl)-C(SiMe$_3$)$_3$]$_2$ [36], the Pb–Cl distances are much more nearly equal, 2.729(3) and 2.962(3) Å, while in PbCl$_2$, having Pb surrounded by nine chlorides, a value of 2.42 Å is observed [37].

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for compound **4**

	x	y	z	U_{eq} [a]
Sn	2906.5(2)	846.4(3)	2477.7(2)	34(1)
Si(1)	2246.1(8)	−1864.6(13)	1853.2(8)	42(1)
Si(2)	4655.7(8)	−931.8(13)	2788.2(8)	41(1)
Si(3)	4526.6(9)	−334.9(13)	1172.4(9)	46(1)
Si(4)	3120.4(9)	578.0(13)	4408.4(8)	44(1)
Si(5)	1974.7(9)	−3034.3(12)	2381.1(8)	43(1)
Si(6)	666.5(8)	1295.7(14)	1720.1(9)	50(1)
N(1)	2808(2)	−718(3)	1978(2)	33(1)
N(2)	2566(2)	747(3)	3461(2)	33(1)
C(1)	3258(3)	−655(4)	1549(2)	31(1)
C(2)	4026(3)	−612(4)	1807(3)	33(1)
C(3)	2784(3)	−580(4)	746(3)	37(1)
C(4)	2785(3)	−1395(5)	262(3)	49(1)
C(5)	2335(4)	−1312(6)	−485(3)	68(2)
C(6)	1893(4)	−432(6)	−745(3)	70(2)
C(7)	1876(3)	378(6)	−284(3)	64(2)
C(8)	2312(3)	304(5)	459(3)	51(2)
C(9)	1998(3)	−1996(5)	2671(3)	63(2)
C(10)	1373(3)	−1877(5)	995(3)	65(2)
C(11)	2775(4)	−3108(5)	1797(4)	70(2)
C(12)	5368(3)	−1962(5)	2777(3)	66(2)
C(13)	4201(3)	−1539(5)	3380(3)	54(2)
C(14)	5195(3)	277(5)	3299(3)	62(2)
C(15)	5479(3)	281(5)	1671(4)	67(2)
C(16)	4047(3)	695(5)	443(3)	75(2)
C(17)	4692(4)	−1602(5)	732(4)	80(2)
C(18)	1874(3)	1113(4)	3127(3)	33(1)
C(19)	1657(3)	1601(4)	2403(3)	35(1)
C(20)	1337(3)	1032(4)	3513(3)	39(1)
C(21)	1240(3)	71(5)	3815(3)	55(2)
C(22)	779(4)	23(6)	4205(3)	71(2)
C(23)	436(4)	940(7)	4309(4)	85(2)
C(24)	520(4)	1894(7)	4002(4)	82(2)
C(25)	968(3)	1931(5)	3601(3)	61(2)
C(26)	3153(4)	−852(5)	4702(3)	71(2)
C(27)	2806(3)	1446(6)	4997(3)	68(2)
C(28)	4075(3)	1023(5)	4517(3)	62(2)
C(29)	2250(4)	3314(5)	1585(3)	71(2)
C(30)	2790(3)	3369(5)	3251(3)	59(2)
C(31)	1252(3)	4099(5)	2287(3)	67(2)
C(32)	−111(3)	2162(6)	1779(4)	101(3)
C(33)	355(3)	−95(5)	1818(4)	73(2)
C(34)	628(4)	1455(8)	769(3)	113(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

The coordination environment around the lead in **3** may be described as distorted trigonal bipyramidal with Cl and the free electron pair in axial and N, C(2) and Cl′ in equatorial positions. The metal [LL″]$^-$ ligand contacts are fairly symmetrical Pb–C = 2.447(10), Pb–N = 2.381(7) Å, indicating less steric strain in **3** than in **5** (see also Table 5). Another interesting feature is, that the central carbon C(1) in **3** is much more bent towards the metal (angle between the planes Pb,N,C(2) and N,C(1),C(2) 30°) as in a true η^3-1-aza-allyl, while in **4** (13°) and **5** (19°) the corresponding values are much smaller, attributed to the considerable steric hindrance for **4** and **5** imposed by the second 1-aza-allyl ligand. An even

Table 4
Atomic coordinates($\times 10^4$) and equivalent isotropic displacement parameters($Å^2 \times 10^3$) for compound **5**

	x	y	z	U_{eq} [a]
Pb	1534.9(4)	7248.6(3)	6365.8(3)	22(1)
Si(1)	563(3)	8233(2)	4475(2)	26(1)
Si(2)	4446(3)	7428(3)	5923(2)	34(1)
Si(3)	2766(3)	6308(3)	4968(3)	32(1)
Si(4)	1218(3)	8923(2)	7609(2)	26(1)
Si(5)	−1137(3)	6601(3)	5852(2)	31(1)
Si(6)	395(3)	6353(3)	7486(3)	31(1)
N(1)	1467(7)	7745(7)	5140(5)	18(2)
N(2)	744(8)	8155(6)	7004(6)	17(3)
C(1)	2474(9)	7854(8)	5252(7)	19(3)
C(2)	3129(9)	7267(9)	5369(7)	23(3)
C(3)	2792(10)	8654(8)	5258(7)	20(3)
C(4)	3416(10)	8870(8)	4822(7)	20(3)
C(5)	3688(12)	9611(9)	4786(9)	41(5)
C(6)	3337(11)	10151(9)	5215(9)	40(4)
C(7)	2721(10)	9939(8)	5676(9)	34(4)
C(8)	2441(10)	9193(8)	5676(8)	27(4)
C(9)	−353(9)	7571(7)	3872(7)	29(4)
C(10)	−90(10)	8901(8)	4948(8)	36(4)
C(11)	1097(11)	8746(9)	3765(7)	38(4)
C(12)	4607(11)	8241(10)	6628(9)	49(5)
C(13)	5344(10)	7548(9)	5330(9)	51(6)
C(14)	4838(11)	6583(9)	6553(9)	50(2)
C(15)	3780(12)	5909(9)	4590(10)	52(6)
C(16)	2490(13)	5624(8)	5651(9)	42(5)
C(17)	1660(11)	6318(9)	4098(8)	44(5)
C(18)	−74(10)	7803(10)	6866(8)	30(4)
C(19)	−105(10)	7006(7)	6637(7)	19(4)
C(20)	−994(10)	8172(9)	6928(8)	28(4)
C(21)	−1681(9)	7804(9)	7222(7)	29(4)
C(22)	−2504(11)	8150(8)	7300(9)	32(4)
C(23)	−2681(11)	8896(10)	7105(9)	43(5)
C(24)	−2021(11)	9275(10)	6796(9)	40(4)
C(25)	−1197(10)	8919(9)	6705(8)	30(4)
C(26)	2558(9)	8738(8)	7951(8)	32(4)
C(27)	676(12)	8941(9)	8450(8)	46(5)
C(28)	1066(11)	9865(7)	7137(9)	38(5)
C(29)	−606(10)	5983(8)	5211(8)	35(4)
C(30)	−2065(11)	6013(9)	6179(9)	48(5)
C(31)	−1890(9)	7365(9)	5235(8)	37(4)
C(32)	1512(11)	6739(9)	8185(8)	49(5)
C(33)	694(12)	5425(8)	7161(9)	42(5)
C(34)	−467(11)	6187(10)	8115(9)	51(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

larger angle of 37° is also reported for $\overline{\text{Sn}(\text{LL}')_2}$ [4], having the less bulky $[\text{N(R)C(Bu}^t\text{)CHR}]^-$ ligand.

3.5. *Dynamic processes in solution*

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the compounds **1**–**5** as well as the ^{29}Si{^{1}H} NMR spectra of M(μ-Cl)(LL″) (**2** (M = Sn) or **3** (M = Pb)) in $^2H_6$-benzene or $^2H_8$-toluene at ambient temperature were very similar and showed only a sharp signal for the $NSiMe_3$ group and a broader one of twice the intensity for the two inequivalent $SiMe_3$ groups bonded to carbon.

When a solution of **2** in $^2H_8$-toluene was cooled to 213 K, the broad singlet in the ^{1}H NMR spectrum split into two separate signals, thus indicating the freezing of a dynamic process. The coalescence temperature T_c was 241 ± 2 K corresponding to a $\Delta G_{T_c} = 51$ kJ mol^{-1}. A similar fluxional behaviour with the slightly lower T_c of 220 K was reported for $\overline{\text{Sn}[\text{NC}_5\text{H}_4\text{C}(\text{SiMe}_3)_2\text{-2}]}$Cl and $\overline{\text{Sn}[\text{NC}_5\text{H}_4\text{C}(\text{SiMe}_3)_2\text{-2}]}[\text{N(SiMe}_3)_2]$ [29], there attributed to the scission of the Sn–N bond and a subsequent rotation of the ligand around the Sn–C bond, making the two $SiMe_3$ groups equivalent. An analogous mechanism, involving M–C cleavage in **2** and **3**, followed by rotation about the M–N bond would account for the fluxionality observed not only for **2** and **3** but also for **1**. An alternative mechanism should be considered, involving a rapid monomer/dimer equilibrium (crystalline **3** is a dimer, see Section 3.4) with exchange of the bridging chlorides for **2** and **3** (or lithiums for **1**) and inversion at the metal centre during the dinuclear transition state. This latter view is supported by a recent study in our laboratory, where a 2D-EXSY-^{119}Sn NMR experiment on a sample containing a mixture of $\overline{\text{Sn}[\text{N(SiMe}_3\text{)C(Ph)C(H)C(Ph)N(SiMe}_3)]}$Cl and $\overline{\text{Sn}[\text{N(SiMe}_3\text{)C(Ph)C(H)C(Ph)N(SiMe}_3)]}$Br (both being monomers in the crystal), showed a strong correlation between the two tin signals, probably due to a rapid exchange of Cl$^-$ and Br$^-$ via a monomer/dimer equilibrium in solution [38].

In the solid state structures of [M(LL″)]$_2$ (**4** (M = Sn) or **5** (M = Pb)) each of the six trimethylsilyl groups in **4** or **5** are inequivalent, but again only two signals were observed in the ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra at ambient temperature, one for the *N*- and one for the *C*-bound $SiMe_3$ groups. When a solution of **4** in $^2H_8$-toluene was cooled to 193 K, the two signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra became broader, but no separation into individual lines was observed. In the ^{13}C{^{1}H} NMR spectrum a broadening of the lines for CN and *C*(SiMe$_3$)$_2$ was also detected. These findings are in agreement with a rapid fluxional process in solution even at low temperature, whereby there is exchange between the η^3- and the η^1-[LL″]$^-$ coordinated ligand. This requires that C(2), which in the solid state is already within the van der Waals bonding range of the metal (Sn···C(2) = 3.45, Pb···C(2) = 3.22 Å), has only to approach slightly closer to the metal and eventually form a bond, while concomitantly the M–C(19) bond is weakened and hence causes inversion at the metal. This is schematically shown in Eq. (5). The observation of Sn satellites (see Section 2) in the ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra of **4** further supports this interpretation. A solid state ^{13}C NMR experiment on **4** showed four signals in the trimethylsilyl region, but the resolution was inadequate to distinguish clearly between the η^1- and η^3-coordinated ligand. A similar mechanism, Eq. (6), was proposed to explain the fluxional behaviour in solution of $\overline{\text{Pb}[\text{P(Ph}_2\text{)C(H)P(Ph}_2)]}$-[C(H)(PPh$_2$)$_2$] [35a].

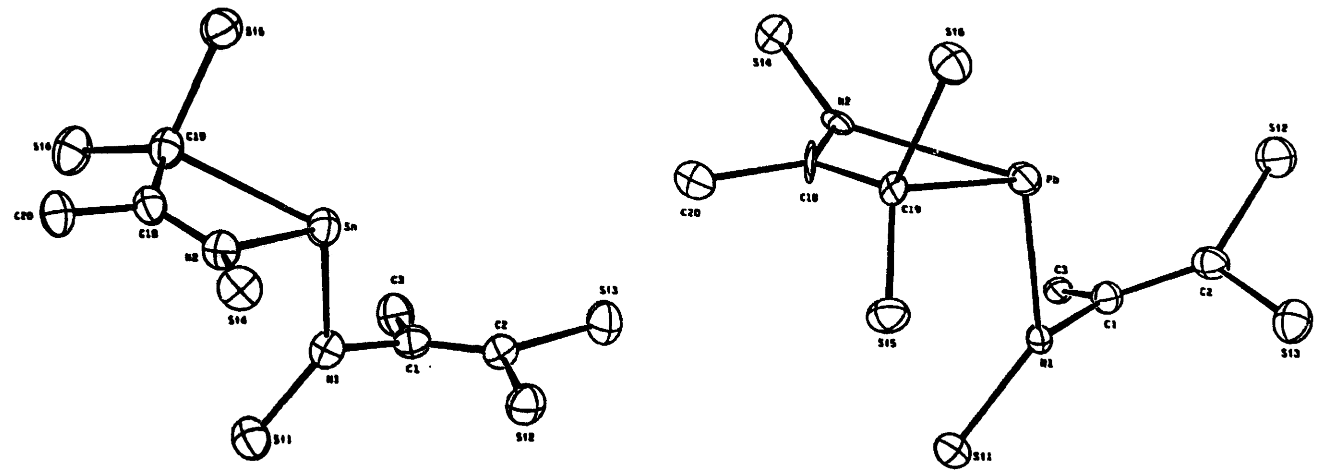


Fig. 2. Molecular structure of compounds 4 and 5 (core atoms only).

Table 5
Some bond distances (Å) of selected Sn and Pb compounds (R = $SiMe_3$)

Compound	M–N [M–C] [a] (η^1)	M–N (η^3)	M–N [M–C] [a] (η^3)	CN [b]
$Sn[N(R)C(Bu^t)C(H)C_6H_3Me_2\text{-}2,5]_2$ [4]	2.130(3)			2
$Sn[N(H)C_6H_2Bu^t_3\text{-}2,4,6]_2$ [14]	2.03(2)			2
$Sn[N(Me_2)(CH_2)_3CMe_2]_2$ [15]	2.102(6)			2
$1,2\text{-}C_6H_4[N(CH_2Bu^t)]_2Sn$ [16]	2 059(5)			2
$SnN(Bu^t)SiMe_2N(Bu^t)$ [17]	2.091(8)			2
$Sn[NR_2]_2$ [18]	2.092(6)			2
trans-$C_6H_4[N(R)SnNR_2]_2$ [19]	2.074(7)			2
$R_2NSnN[C_6H_2Me_3\text{-}2,4,6][B(Bu^t)NR_2]$ [20]	2.138(6)			2
$Sn[N(R)SiR_3]_2$ [21]	2.098(3)			2
$Sn[CR_2(CH_2)_2CR]_2$ [22]	[2.221(7)]			2
$Sn(CHR_2)_2$ [32]	[2.281(3)]			3
$Pb(NR_2)_2$ [18]	2.24(2)			2
$Pb[C_6H_2(CF_3)_3\text{-}2,4,6]_2$ [23]	[2.366(4)]			2
$Pb(CHR_2)_2$ [24]	[2.315(5)]			2
4	2.153(4)	2.288(4)	[2.531(5)]	3
$Sn[NC_5H_4CR_2\text{-}2][NR_2]$ [29]	2.144(5)	2.299(5)	[2.356(8)]	3
$Sn[NC_5H_4CR_2\text{-}2]Cl$ [29]		2.27(2)	[2.32(2)]	3
$Sn[N(Pr^i)C_7H_5N(Pr^i)]Cl$ [34]		2.164(5)	2.164(5)	3
$Sn[N(R)C(Ph)C(H)C(Ph)N(R)][NR_2]$ [38]	2.16(1)	2.21(1)	2.23(1)	3
5	2.34(1)	2.41(1)	[2.53(1)]	3
$Sn[N(R)C(Bu^t)=C(H)R]_2$ [4]		2.510(2)	[2.295(2)]	4
$Sn[C_6H_4(CH_2NMe_2\text{-}2)]_2$ [26]		2.588(3)	[2.222(3)]	4
$Sn[C_{10}H_6(NMe_2\text{-}8)]_2$ [27]		2.587(5)	[2.184(4)]	4
$Sn[C(R)P(Ph)\{C_6H_4(SiMe_2\text{-}2)N\}]_2$ [28]		2.503(6)	[2.344(7)]	4
$Pb[C(R)P(Ph)\{C_6H_4(SiMe_2\text{-}2)N\}]_2$ [28]		2.601(6)	[2.440(7)]	4
$Pb[C(R)P(Ph)_2N(R)]_2$ [28]		2.678(4)	[2.448(5)]	4
$Sn[NC_5H_4CR_2\text{-}2]_2$ [29]		2.418(7)	[2.352(7)]	4
$Sn[N(Me)C_7H_5N(Me)]_2$ [30]		2.220(2)	2.298(2)	4
$Sn[N(R)P(Ph)_2N(R)]_2$ [31]		2.233(5)	2.494(6)	4
$Pb[N(R)P(Ph)_2N(R)]_2$ [31]		2.347(4)	2.584(4)	4
$Pb[N(R)C\{C_6H_4(CF_3)\text{-}4\}N(R)]_2$ [31]		2.35(1)	2.49(1)	4
3		2.381(7)	[2.447(10)]	4

[a] Values in brackets refer to metal–carbon distances.

[b] CN = coordination number.

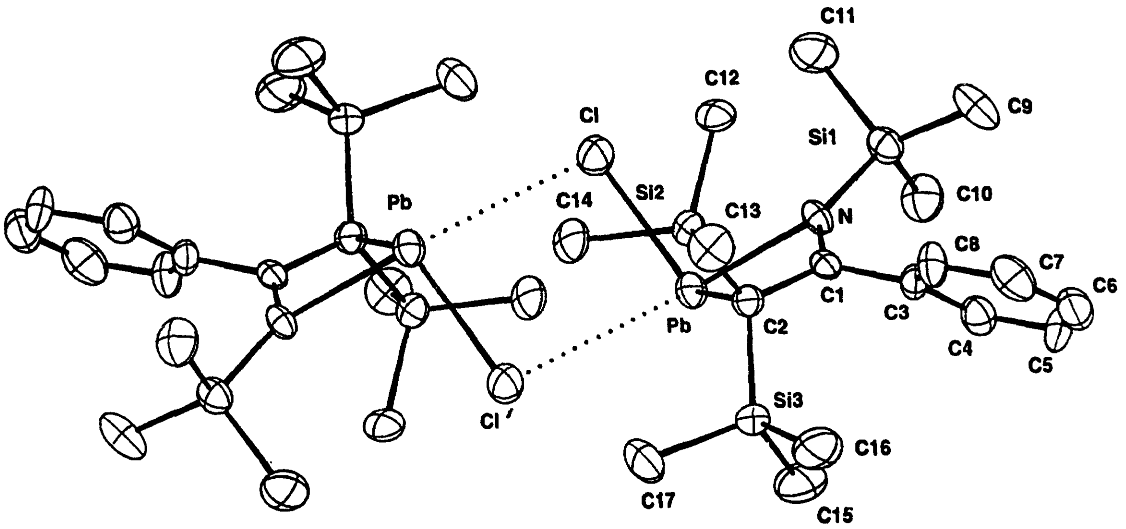
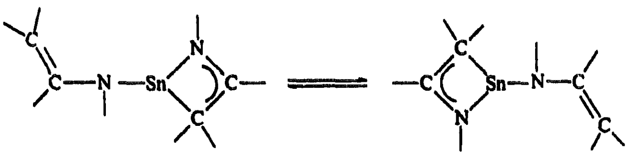


Fig. 3. Molecular structure of compound **3**.

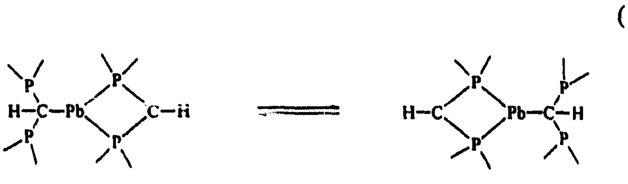
Table 6
Selected bond lengths (Å) and angles (°) for compound **3**

Pb–Cl	2.609(3)	Pb···Cl′	3.276(3)
Pb–N	2.381(7)	Pb–C(1)	2.750(10)
Pb–C(2)	2.447(10)	N–C(1)	1.317(11)
C(1)–C(2)	1.461(13)	C(1)–C(3)	1.509(13)
N–Pb–C(2)	58.9(3)	N–Pb–Cl	96.6(2)
C(2)–Pb–Cl	109.2(2)	Cl–Pb···Cl′	80.50(9)
N–Pb···Cl′	164.1 (2)	C(2)–Pb···Cl′	107.1(2)
Pb–Cl···Pb′	99.50(9)	C(1)–N–Si(1)	134.6(7)
C(1)–N–Pb	91.5(6)	Si(1)–N–Pb	132.6(4)
N–C(1)–C(2)	117.2(9)	N–C(1)–C(3)	120.3(8)
C(2)–C(1)–C(3)	122.4(9)	C(1)–C(2)–Pb	85.5(6)

Symmetry transformations used to generate equivalent atoms: ′ $-x$, $-y$, $-z$.



(5)



(6)

The ^{119}Sn{^{1}H} NMR spectra of **2** and **4** showed the chemical shift ($\delta = -68$ for **2** and -37 for **4**) shifted to lower frequency than in related three- [29] or four- [26,27,29] coordinated tin compounds, but similar values were observed for $\overline{\mathrm{Sn}[\mathrm{N}(\mathrm{SiMe}_3)\mathrm{C}(\mathrm{Ph})\mathrm{C}(\mathrm{H})\mathrm{C}(\mathrm{Ph})\mathrm{N}}(\mathrm{SiMe}_3)]\mathrm{Cl}$ (-67) [38] and $\overline{\mathrm{Sn}[\mathrm{N}(\mathrm{Pr}^i)\mathrm{C}_7\mathrm{H}_5\mathrm{N}}(\mathrm{Pr}^i)]\mathrm{Cl}$ (-68) [34]. Using the relation between ^{119}Sn and ^{207}Pb shifts of Eq. (7) [39], the calculated ^{207}Pb NMR chemical shifts of **3** and **5** are in good agreement with experiment for **3** (exp.: $\delta = 2105$; calc.: $\delta = 2112$) but less so for **5** (exp.: $\delta = 1720$; $\delta = 2214$).

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for compound **3**

	x	y	z	U_{eq} [a]
Pb	938.8(5)	−855.5(3)	−867.6(3)	46(1)
Cl	−509(3)	529(2)	−1111(2)	60(1)
Si(1)	1200(3)	−801(2)	−3239(2)	49(1)
Si(2)	−2413(3)	−1695(2)	−1662(2)	44(1)
Si(3)	−46(4)	−2976(2)	−704(2)	50(1)
N	619(8)	−1245(5)	−2351(5)	37(2)
C(1)	110(10)	−1982(7)	−2193(6)	36(3)
C(2)	−550(10)	−2041(6)	−1445(6)	40(3)
C(3)	274(12)	−2732(6)	−2749(6)	41(3)
C(4)	1588(12)	−2963(7)	−2873(7)	55(3)
C(5)	1742(15)	−3630(8)	−3400(8)	69(4)
C(6)	588(17)	−4055(8)	−3807(8)	72(4)
C(7)	−682(16)	−3849(9)	−3679(8)	76(4)
C(8)	−853(12)	−3191(7)	−3149(7)	56(3)
C(9)	618(13)	−1365(8)	−4272(6)	75(4)
C(10)	3120(11)	−748(8)	−2958(7)	74(4)
C(11)	456(14)	276(7)	−3349(8)	80(4)
C(12)	2758(10)	−981(7)	2612(6)	56(3)
C(13)	−3666(12)	−2596(7)	−1892(7)	74(4)
C(14)	−2907(11)	−1152(7)	−718(7)	62(4)
C(15)	1904(13)	−3069(9)	−449(8)	98(5)
C(16)	−748(16)	−4026(7)	−1126(8)	94(5)
C(17)	−628(14)	−2783(8)	329(7)	82(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

$$\delta(^{207}\mathrm{Pb}) = 3.30\cdot\delta(^{119}\mathrm{Sn}) + 2336 \qquad (7)$$

4. Supplementary material

Hydrogen atom positions, anisotropic thermal parameters and structure factors are available from author P.B.H.

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