

## A new type of heteroleptic complexes of divalent lead and synthesis of the first *P*-plumbyleniophosphasilene, $R_2Si=P-Pb(L)$ : ( $L = \beta$ -diketimate)

Shenglai Yao, Stefan Block, Markus Brym and Matthias Driess \*

*Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin, Strasse des 17. Juni 135, Sekr. C2, D-10623 Berlin, Germany. Fax: +49(0)30-314-29732 Tel: +49(0)30-314-29731; E-mail: [matthias.driess@tu-berlin.de](mailto:matthias.driess@tu-berlin.de)*

### General Considerations.

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material [ $\{HC(CMeNAr)_2\}Li(OEt_2)$ ]<sup>1</sup> ( $Ar = C_6H_3Pr^i_{2-2,6}$ )  $^tBu_3SiSi(F)IsPH_2$ <sup>2</sup> ( $Is = C_6H_2Pr^i_{3-2,4,6}$ )  $Pb(OC_6H_3Bu^t_{2-2,6})_2$  (**1**)<sup>3</sup> were prepared according to literature procedure. The NMR spectra were recorded on Bruker Spectrometers AS 200 and AV 400 with residual solvent signals as internal reference (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) or with an external reference ( $SiMe_4$  for <sup>29</sup>Si,  $PbMe_4$  for <sup>207</sup>Pb, 85%  $H_3PO_4$  for <sup>31</sup>P, respectively). Elemental analyses were carried out at the Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin. The carbon content of compounds **2b**, **2c** and **3** determined by combustion analyses deviates from the expected values (ca. 1%) due to silicon carbide formation. Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad. The <sup>207</sup>Pb NMR signals observed for compound **2c** and **3** are broadened (half-width ca. 3000 Hz). Therefore, scalar  $J(Pb, P)$  couplings could not be resolved.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary and measured in a cold  $N_2$  flow. The data of **2a-2c** were collected on a Bruker-AXS SMART CCD diffractometer at 173(2) K (Mo- $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ), while those of **3** was collected on a Oxford Diffraction Xcalibur S Sapphire at 150 K (2) (Mo- $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and were refined on  $F^2$  with the SHELX-97<sup>4</sup> software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Crystals of **3** contain disordered toluene molecules.

*Synthesis of [ $\{HC(CMeNAr)_2\}PbOAr^*$ ] ( $Ar = C_6H_3Pr^i_{2-2,6}$ ,  $Ar^* = C_6H_3Bu^t_{2-2,6}$ ) (**2a**).*

A solution of [ $\{\text{HC}(\text{CMeNAr})_2\}\text{Li}(\text{OEt}_2)$ ] (1.54 g, 3.1 mmol) in *n*-hexane (40 mL) was added to a suspension of  $\text{Pb}[\text{OAr}^*]_2$  (1.91 g, 3.1 mmol) in *n*-hexane (30 mL) at ambient temperature and stirred for 48 h. After filtration, storage of the filtrate at  $-20^\circ\text{C}$  for 12 hours afforded yellow crystals of **2a**. (Yield: 2.13 g, 2.6 mmol, 83 %). Recrystallization from *n*-hexane/toluene (3/1 v/v) at  $-20^\circ\text{C}$  for 3 days afforded crystals suitable for X-ray diffraction analysis. M.p.  $147^\circ\text{C}$  (decomp.).  $^1\text{H}$  NMR (400.13 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 0.96 - 1.61$  (m, br, 42H  $\text{CMe}_3, \text{CHMe}_2$ ), 1.64 (s, 6H  $\beta\text{-Me}$ ), 2.94 - 3.06 (m, 2H  $\text{CHMe}_2$ ), 3.65 - 3.75 (m, 2H  $\text{CHMe}_2$ ), 4.95 (s, 1H  $\gamma\text{-CH}$ ), 6.73 - 7.46 (m, br, 9H  $\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ ,  $\text{C}_6\text{H}_3\text{Bu}^t\text{-2,6}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.61 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 24.5, 24.9, 25.4, 25.5, 26.2, 32.7, 35.6$  ( $\text{Bu}^t$ ,  $\text{CHMe}_2$ ,  $\beta\text{-Me}$ ); 28.0, 28.3 ( $\text{CHMe}_2$ ); 106.0 ( $\gamma\text{-C}$ ); 115.7, 124.0, 125.2, 125.5, 127.1, 142.8, 142.9, 145.2 (NC,  $\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ ,  $\text{C}_6\text{H}_3\text{Bu}^t\text{-2,6}$ ).  $^{209}\text{Pb}\{^1\text{H}\}$  NMR (83.67 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 1040$ . Anal. Calcd (%) for  $\text{C}_{43}\text{H}_{62}\text{N}_2\text{PbO}$ : C, 62.2; H, 7.5; N, 3.4. Found: C, 62.4; H, 7.4; N, 3.5. EI-MS:  $m/z$  (%): 625.3 [100,  $\text{Pb}[\text{HC}(\text{CMeNAr})_2]^+$ ], 403.3 [81,  $\text{HC}(\text{CMeNAr})_2]^+$ ].

#### Synthesis of [ $\{\text{HC}(\text{CMeNAr})_2\}\text{PbN}(\text{SiMe}_3)_2$ ] (**2b**).

To a solution of **2a** (1.43 g, 1.7 mmol) in *n*-hexane (20 mL) was added a solution of  $\text{LiN}(\text{SiMe}_3)_2$  (0.28 g, 1.7 mmol) in *n*-hexane (20 mL) with stirring at ambient temperature. A white precipitate was formed during a period of 48 h. After filtration, storage of the filtrate at  $-20^\circ\text{C}$  for 12 h afforded pale yellow crystals of **2b**. (Yield: 1.19 g, 1.5 mmol, 88 %). M.p.  $157^\circ\text{C}$  (decomp.).  $^1\text{H}$  NMR (400.13 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 0.17, 0.43$  (br, 18H  $\text{SiMe}_3$ ), 1.14 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H  $\text{CHMe}_2$ ), 1.27 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6H  $\text{CHMe}_2$ ), 1.47 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6H  $\text{CHMe}_2$ ), 1.60 (s, 6H  $\beta\text{-Me}$ ), 3.10 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2H  $\text{CHMe}_2$ ), 3.75 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2H  $\text{CHMe}_2$ ), 4.94 (s, 1H  $\gamma\text{-CH}$ ), 7.03 - 7.23 (m, br, 6H  $\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.61 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 7.1$  ( $\text{SiMe}_3$ ); 23.0, 24.5, 25.2, 26.7 ( $\text{CHMe}_2$ ); 25.7 ( $\beta\text{-Me}$ ); 27.8, 28.2 ( $\text{CHMe}_2$ ); 105.1 ( $\gamma\text{-C}$ ); 124.4, 124.8, 126.7, 143.3, 143.8, 144.8 ( $\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$ ); 165.3 (NC).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = -3.1, -2.4$  ( $\text{SiMe}_3$ ).  $^{209}\text{Pb}\{^1\text{H}\}$  NMR (83.67 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta = 1824$ . Anal. Calcd (%) for  $\text{C}_{35}\text{H}_{59}\text{N}_3\text{PbSi}_2$ : C, 53.5; H, 7.6; N, 5.3. Found: C, 54.5; H, 7.5; N, 5.2. EI-MS:  $m/z$  (%): 625.3 [6,  $\text{Pb}[\text{HC}(\text{CMeNAr})_2]^+$ ], 403 [38,  $\text{HC}(\text{CMeNAr})_2]^+$ ].

#### Synthesis of [ $\{\text{HC}(\text{CMeNAr})_2\}\text{PbP}(\text{SiMe}_3)_2$ ] (**2c**).

A solution of **2a** (0.94 g, 1.1 mmol) in diethyl ether (15 mL) was added a solution of  $\text{LiP}(\text{SiMe}_3)_2\cdot\text{DME}$  (0.31 g, 1.1 mmol) in diethyl ether (15 mL) at  $-60^\circ\text{C}$  and stirred for 2 h. The mixture was then allowed to warm up to room temperature and stirred for another 2 h.

After removal of all volatiles the residue was extracted with *n*-hexane (20 mL). Storage of the extract at -20°C for 48 h afforded orange crystals of **2c**. (Yield: 0.72 g, 0.90 mmol, 79 %). M.p. 135°C (decomp.). <sup>1</sup>H NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 0.25 (d, <sup>3</sup>J<sub>PH</sub> = 4.2 Hz, 18H SiMe<sub>3</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H CHMe<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H CHMe<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H CHMe<sub>2</sub>), 1.47 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 6H CHMe<sub>2</sub>), 1.58 (s, 6H β-Me), 3.23 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H CHMe<sub>2</sub>), 3.86 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H CHMe<sub>2</sub>), 4.70 (s, 1H γ-CH), 6.98 - 7.18 (m, 6H C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 6.6 (d, <sup>2</sup>J<sub>PC</sub> = 9.8 Hz SiMe<sub>3</sub>); 24.2, 24.3, 25.2, 27.4, 27.5, 27.6, 27.7, 28.2 (CHMe<sub>2</sub>, β-Me); 102.2 (γ-C); 123.6, 124.8, 126.2, 142.8, 143.9, 144.6 (C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>); 165.3 (NC). <sup>31</sup>P{<sup>1</sup>H} NMR (81.01 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = -116.6 (<sup>207</sup>Pb satellites, <sup>1</sup>J<sub>PPb</sub> = 2852 Hz). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 7.4 (d, <sup>1</sup>J<sub>PSi</sub> = 36 Hz). <sup>209</sup>Pb {<sup>1</sup>H} NMR (83.67 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = -1737. Anal. Calcd (%) for C<sub>35</sub>H<sub>59</sub>N<sub>3</sub>PbPSi<sub>2</sub>: C, 52.4; H, 7.4; N, 3.5. Found: C, 53.5; H, 7.4; N, 3.3. EI-MS: m/z (%): 625.3 [100, Pb[HC(CMeNAr)<sub>2</sub>]<sup>+</sup>], 403.3 [11, HC(CMeNAr)<sub>2</sub>]<sup>+</sup>].

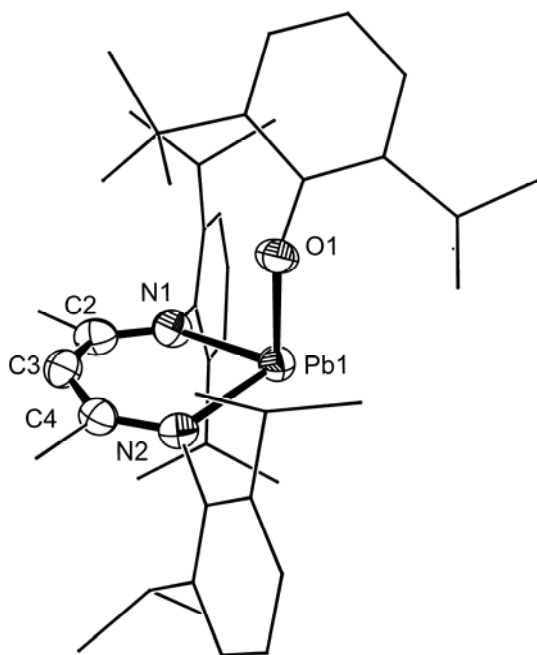
### Synthesis of [{HC(CMeNAr)<sub>2</sub>}PbP=Si(Is)Si(Bu<sup>*i*</sup>)<sub>3</sub>] (Is = C<sub>6</sub>H<sub>2</sub>Pr<sup>*i*</sup><sub>3-2,4,6</sub>) (**3**):

To a stirred solution of Bu<sup>*i*</sup><sub>3</sub>SiSi(F)IsPH<sub>2</sub> (250 mg, 0.52 mmol) in toluene (15 ml) was added *n*-BuLi (0.21 ml, 2.5 M in hexane) at ambient temperature. An immediate colour change from colourless to greenish-yellow was observed. After stirring for 10 minutes the solution was cooled down to -78°C (dry ice-acetone) and a yellow solution of **2b**, (40.8 mg, 0.52 mmol) in toluene was added via syringe. A colour change to dark red brown was observed. After stirring for 12h at ambient temperature all volatiles were removed *in vacuo*. The remaining solid was extracted with hexane. Concentration and slow cooling of this solution led to the formation of red-brown crystals of **3**. (Yield: 0.36 g, 0.33 mmol, 65 %). M.p. 118°C (decomp.). <sup>1</sup>H NMR (400.13 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 1.12 -1.28 (m, 42H CHMe<sub>2</sub>), 1.36 (s, 27H Si(CMe<sub>3</sub>)<sub>3</sub>), 1.64 (s, 6H β-Me), 2.55 – 3.80 (m, 7H CHMe<sub>2</sub>), 4.95 (s, 1H γ-CH), 7.01 - 7.13 (m, 8H C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>, C<sub>6</sub>H<sub>2</sub>Pr<sup>*i*</sup><sub>3-2,4,6</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 23.1, 23.9, 24.4, 24.5, 25.1, 25.2, 25.3 (s, CHMe<sub>2</sub>, β-Me); 32.1 (s, Si(CMe<sub>3</sub>)<sub>3</sub>); 32.9 (s, Si(CMe<sub>3</sub>)<sub>3</sub>); 98.4 (γ-C); 120.1, 122.3, 142.1, 144.7, 145.3, 150.5, 152.4, (C<sub>6</sub>H<sub>3</sub>Pr<sup>*i*</sup><sub>2-2,6</sub>, C<sub>6</sub>H<sub>2</sub>Pr<sup>*i*</sup><sub>3-2,4,6</sub>); 163.8 (NC). <sup>31</sup>P NMR (81.01 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 292.5 (<sup>29</sup>Si satellites, <sup>1</sup>J<sub>P=Si</sub> = 206 Hz, <sup>207</sup>Pb satellites, <sup>1</sup>J<sub>PPb</sub> = 1052 Hz). <sup>31</sup>P {<sup>1</sup>H} NMR (81.01 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 292.5 (<sup>29</sup>Si satellites, <sup>1</sup>J<sub>P=Si</sub> = 206 Hz, <sup>207</sup>Pb satellites, <sup>1</sup>J<sub>PPb</sub> = 1052 Hz). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.49 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 19.0 (d, <sup>2</sup>J<sub>SiP</sub> = 3 Hz), 227.0 (d, <sup>1</sup>J<sub>Si=P</sub> = 206 Hz). <sup>209</sup>Pb {<sup>1</sup>H} NMR (83.67 MHz, *d*<sub>8</sub>-toluene, 298K): δ = 1068 (br). Anal. Calcd (%) for

C<sub>56</sub>H<sub>91</sub>N<sub>2</sub>PbPSi<sub>2</sub>: C, 61.89; H, 8.44; N, 2.58. Found: C, 59.3; H, 8.21; N, 2.59. EI-MS: m/z (%): 1086 [1, M<sup>+</sup>], 625 [10, Pb[HC(CMeNAr)<sub>2</sub>]<sup>+</sup>], 403 [95, HC(CMeNAr)<sub>2</sub>]<sup>+</sup>].

### Crystallographic data for compound 2a

Empirical formula	C <sub>43</sub> H <sub>62</sub> N <sub>2</sub> O Pb	
Formula weight	830.15	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 19.6849(6) Å	α = 90°.
	b = 10.9636(4) Å	β = 91.3040(10)°.
	c = 36.7625(12) Å	γ = 90°.
Volume	7931.9(5) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.390 Mg/m <sup>3</sup>	
Absorption coefficient	4.287 mm <sup>-1</sup>	
F(000)	3392	
Crystal size	0.40 x 0.30 x 0.25 mm <sup>3</sup>	
Theta range for data collection	1.94 to 25.00°.	
Index ranges	-23 ≤ h ≤ 23, -13 ≤ k ≤ 12, -30 ≤ l ≤ 43	
Reflections collected	47359	
Independent reflections	13905 [R(int) = 0.0615]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.4137 and 0.2789	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	13905 / 0 / 879	
Goodness-of-fit on F <sup>2</sup>	1.035	
Final R indices [I > 2σ(I)]	R1 = 0.0445, wR2 = 0.1029	
R indices (all data)	R1 = 0.0672, wR2 = 0.1122	
Largest diff. peak and hole	1.213 and -1.600 e.Å <sup>-3</sup>	

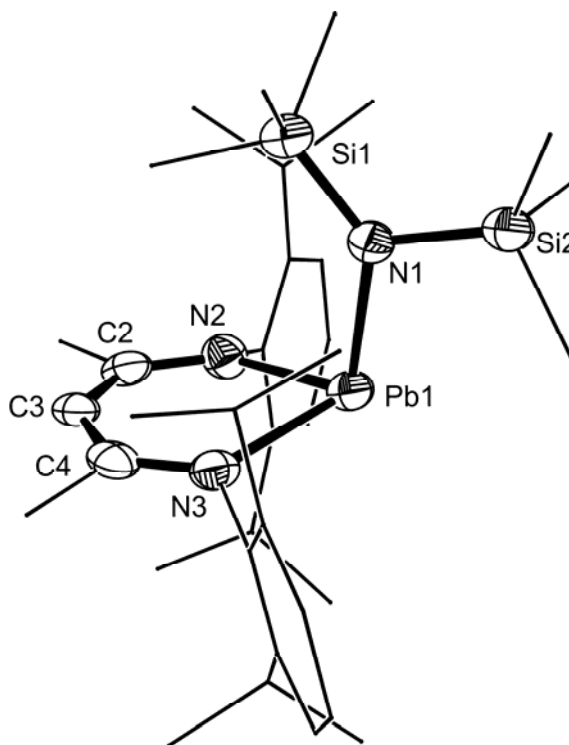


**Figure 1.** Molecular structure of **2a**. Thermal ellipsoids (C2-C4, N1, N2, Pb1, O1) are drawn at 50% probability level (one of the two molecules in the asymmetric unit). H atoms are omitted for clarity. Selected distances (pm) and angles ( $^{\circ}$ ): Pb1-O1 221.6(5), Pb1-N1 230.3(6), Pb1-N2 228.9(6), N1-C2 132.8(10), N2-C4 132.6(10), C2-C3 143.1(10), C3-C4 139.8(10), N2-Pb1-N1 83.6(2), O1-Pb1-N1 97.9(2), O1-Pb1-N2 93.31(18);  $\Sigma$  bond angles(Pb): 274.81.

### Crystallographic data for compound **2b**

Empirical formula	C <sub>38</sub> H <sub>66</sub> N <sub>3</sub> Pb Si <sub>2</sub>	
Formula weight	828.31	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.9877(7) Å	$\alpha$ = 76.037(2) $^{\circ}$ .
	b = 12.6789(8) Å	$\beta$ = 89.319(2) $^{\circ}$ .
	c = 15.1520(10) Å	$\gamma$ = 65.115(2) $^{\circ}$ .
Volume	2016.9(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.364 Mg/m <sup>3</sup>	
Absorption coefficient	4.270 mm <sup>-1</sup>	
F(000)	850	
Crystal size	0.40 x 0.40 x 0.40 mm <sup>3</sup>	
Theta range for data collection	1.88 to 25.00 $^{\circ}$ .	

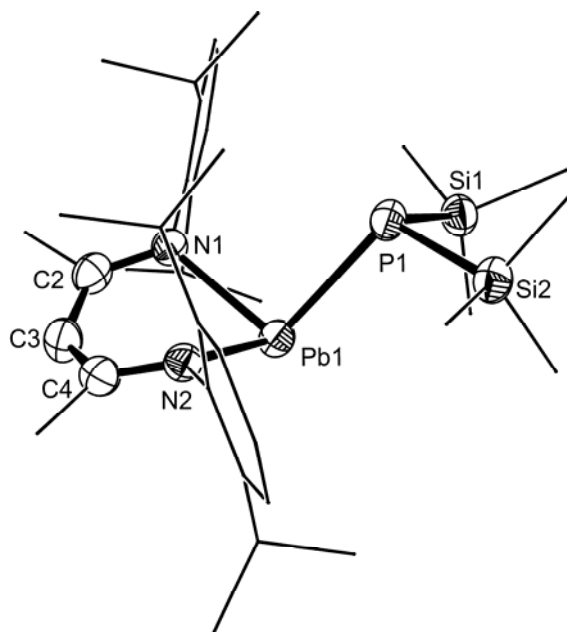
Index ranges	-14<=h<=14, -14<=k<=15, -11<=l<=18
Reflections collected	12160
Independent reflections	6989 [R(int) = 0.0441]
Completeness to theta = 25.00°	98.5 %
Absorption correction	Empirical
Max. and min. transmission	0.2800 and 0.2800
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6989 / 0 / 414
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1674
R indices (all data)	R1 = 0.0713, wR2 = 0.1809
Largest diff. peak and hole	2.837 and -2.401 e.Å <sup>-3</sup>



**Figure 2.** Molecular structure of **2b**. Thermal ellipsoids (C2-C4, N1-N3, Pb1, Si1, Si2) are drawn at 50% probability level. H atoms are omitted for clarity. Selected distances (pm) and angles (°): Pb1-N1 227.1(8), Pb1-N2 233.4(8), Pb1-N3 231.5(8), N1-Si1 171.5(8), N1-Si2 174.6(8), C2-C3 142.0(13), C3-C4 140.1(14), N2-C2 133.9(13), N3-C4 132.7(13), N1-Pb1-N3 99.2(3), N1-Pb1-N2 106.6(3), N3-Pb1-N2 83.2(3);  $\Sigma$  bond angles (Pb1) 289.0;  $\Sigma$  bond angles (N1) 358.4.

## Crystallographic data for compound 2c

Empirical formula	C <sub>35</sub> H <sub>59</sub> N <sub>2</sub> P Pb Si <sub>2</sub>
Formula weight	802.18
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.5295(3) Å                      α = 90.1280(10)° b = 10.2387(3) Å                     β = 90.4550(10)° c = 21.1917(6) Å                    γ = 109.5890(10)°
Volume	1947.91(10) Å <sup>3</sup>
Z	2
Density (calculated)	1.368 Mg/m <sup>3</sup>
Absorption coefficient	4.457 mm <sup>-1</sup>
F(000)	816
Crystal size	0.46 x 0.35 x 0.14 mm <sup>3</sup>
Theta range for data collection	0.96 to 25.00°
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 12, -23 ≤ l ≤ 25
Reflections collected	11779
Independent reflections	6757 [R(int) = 0.0309]
Completeness to theta = 25.00°	98.5 %
Absorption correction	Empirical
Max. and min. transmission	0.5742 and 0.2336
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6757 / 0 / 386
Goodness-of-fit on F <sup>2</sup>	1.054
Final R indices [I > 2σ(I)]	R1 = 0.0414, wR2 = 0.1274
R indices (all data)	R1 = 0.0509, wR2 = 0.1361
Largest diff. peak and hole	1.713 and -1.206 e.Å <sup>-3</sup>



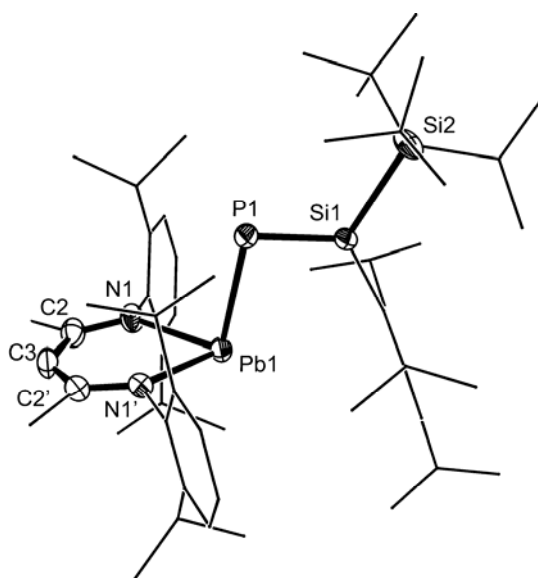
**Figure 3.** Molecular structure of **2c**. Thermal ellipsoids (C2-C4, N1, N2, Pb1, P1, Si1, Si2) are drawn at 50% probability level. H atoms are omitted for clarity. Selected distances (pm) and angles ( $^{\circ}$ ): Pb1-N2 232.5(6), Pb1-N1 235.9(6), Pb1-P1 271.5(2), P1-Si2 224.8(3), P1-Si1 226.0(3), C2-C3 142.7(11), C3-C4 139.8(11), N1-C2 131.8(10), N2-C4 134.6(10), N2-Pb1-N1 81.2(2), N2-Pb1-P1 103.18(16), N1-Pb1-P1 97.32(15);  $\Sigma$  bond angles (Pb1) 281.7;  $\Sigma$  bond angles (P1) 305.7.

### Crystallographic data for compound **3**•toluene

Empirical formula	C <sub>63</sub> H <sub>99</sub> N <sub>2</sub> P Pb Si <sub>2</sub>	
Formula weight	1178.78	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /m	
Unit cell dimensions	a = 12.4953(2) Å	$\alpha = 90^{\circ}$ .
	b = 18.9054(3) Å	$\beta = 109.2604(17)^{\circ}$ .
	c = 14.3412(2) Å	$\gamma = 90^{\circ}$ .
Volume	3198.18(8) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.224 Mg/m <sup>3</sup>	
Absorption coefficient	2.736 mm <sup>-1</sup>	
F(000)	1232	
Crystal size	0.52 x 0.46 x 0.28 mm <sup>3</sup>	



Theta range for data collection	3.13 to 25.00°.
Index ranges	-14<=h<=14, -22<=k<=22, -17<=l<=17
Reflections collected	17579
Independent reflections	5751 [R(int) = 0.0205]
Completeness to theta = 25.00°	98.8 %
Absorption correction	Analytical
Max. and min. transmission	0.5146 and 0.3303
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5751 / 188 / 443
Goodness-of-fit on F <sup>2</sup>	1.191
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0558
R indices (all data)	R1 = 0.0301, wR2 = 0.0616
Largest diff. peak and hole	0.645 and -0.674 e.Å <sup>-3</sup>



**Figure 4.** Molecular structure of **3**. Thermal ellipsoids (C2, C3, C2', N1, N1', Pb1, P1, Si1, Si2) are drawn at 50% probability level. All hydrogen atoms are omitted for clarity. The molecule lies about a mirror plane. The atom labels with the additional prime character (') indicate that these atoms are at equiv positions (x, 1/2-y, z). Selected distances (pm) and angles (°): P1-Pb1 267.06(11), Si1-Pb1 208.49(16), Si1-Si2 241.40(19), Pb1-N1 236.8(3), Pb1-N1' 236.8(3), N1-C2 132.7(4), C2-C3 139.6(4), C2'-C3 139.6(4), N1-Pb1-N1' 81.96(13), P1-Pb1-N1 97.23(6), Si1-P1-Pb1 97.10(5), Si2-Si2-P1 117.05(7);  $\Sigma$  bond angles (Pb1) 276.43;  $\Sigma$  bond angles (Si1) 360.

## References

<sup>1</sup> Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics*, **2001**, *20*, 1190.

<sup>2</sup> M. Driess, S. Block, M. Brym and M. T. Gamer, *Angew. Chem. Int. Ed.*, **2006**, *45*, 2293.

<sup>3</sup> B. Cetinkaya, I. Gumrukcu, M. F. Lappert, J. L. Atwood, R. D. Rogers, M. J. Zaworotko, *J. Am. Chem. Soc.* **1980**, *102*, 2088.

<sup>4</sup> Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.