

Notes

A Heterotopically Chelated Low-Valent Lead Amide¹

Alexander Murso, Michal Straka, Martin Kaupp, Rüdiger Bertermann, and Dietmar Stalke*

Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany

Received March 9, 2005

Summary: The solid-state structure and NMR parameters of the heavier carbene analogue $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**), obtained in the reaction of the phosphane $\text{Ph}_2\text{P}(\text{CH}_2\text{Py})$ with $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$, are discussed.

Plumbylenes usually occur as reactive intermediates in the preparation of plumbanes R_4Pb and undergo polymerization and/or disproportionation in the absence of stabilizing groups at the lead(II) center.² Thus, only a few examples of low-valent plumbylenes have been reported so far,³ although the first diamino- and dialkylplumbylenes were already described by Lappert et al. in the 1970s.⁴ Recently, some heteroleptic plumbylenes with a dimeric structure in the solid state were published.⁵ In this paper a low-valent lead(II) complex, stabilized by sidearm donation, is communicated. This heavier carbene analogue is one of the rare examples of heterotopically chelated monomeric lead(II) complexes.

The reaction of $\text{Ph}_2\text{P}(\text{CH}_2\text{Py})$ ⁶ with $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ^{4c} in a 1:1 ratio gives the phosphanamide $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**). One amide anion of the starting material deprotonates the phosphane at the C_α -position, while the other remains coordinated to the lead(II) cation. A heteroleptic lead(II) complex is formed (Scheme 1).

Dissolving **1** in various solvents results in decomposition and formation of elemental Pb^0 . However, dark red

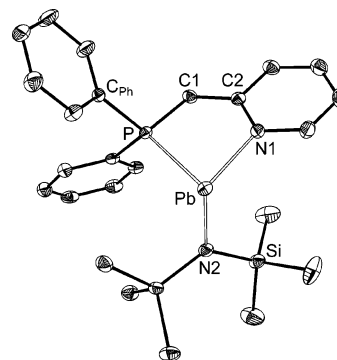
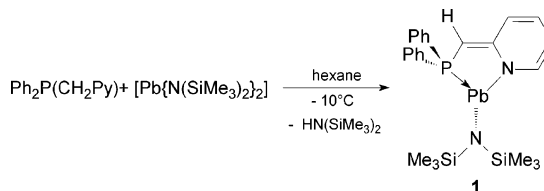


Figure 1. Solid-state structure of $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**). Only one of the two molecules in the asymmetric unit is shown. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [pm] and angles [deg]: Pb–P 275.01(7), Pb–N1 236.32(19), Pb–N2 223.31(18), P–C1 173.9(2), C1–C2 139.4(3), C2–N1 138.4(3), av. P–C_{Ph} 182.3; P–C1–C2 122.46(17), P–Pb–N1 73.78(5), N1–Pb–N2, 100.37(7), P–Pb–N2 93.30(5).

Scheme 1. Synthesis of $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (1**) by Deprotonation of $\text{Ph}_2\text{P}(\text{CH}_2\text{Py})$ with $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$**



blocks of crystalline $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**) could be grown from a solution of **1** in hexane at -24°C .

The asymmetric unit contains two independent molecules of **1**. As the structural parameters of the two molecules are almost identical within their estimated standard deviations (esd's), the bond lengths and angles given in the caption of Figure 1 are averages; the esd's are maxima. The molecular structure of **1** is depicted in Figure 1. In $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**), the central cation is 3-fold coordinated. The $[\text{Ph}_2\text{PC}(\text{H})\text{Py}]^-$ anion (*P,N*)-chelates the metal, forming a five-membered planar metallacycle. The cation is displaced only by 1.8 pm from the best plane of the anion. The

* To whom correspondence should be addressed. Fax: +49-551-39-3373. Tel: +49-551-39-3000. E-mail: dstalke@chemie.uni-goettingen.de.

(1) Dedicated to Professor Johann Weis on the occasion of his 60th birthday.

(2) (a) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 2, p 670.

(b) Harison, P. G. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 3, p 185. (c) Harison, P. G. In *Comprehensive Organometallic Chemistry II*; Pergamon: New York, 1995; Vol. 2, p 305.

(3) (a) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 827. (b) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, 210, 251.

(4) (a) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (c) Gyane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

(5) (a) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. *Organometallics* **1998**, 17, 4425. (b) Klinkhammer, K. W.; Fässler, T. F.; Grützmacher, H. *Angew. Chem., Int. Ed.* **1998**, 37, 124. (c) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, 38, 187. (d) Stürmann, M.; Saak, W.; Weidenbruch, M.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 579.

$[\text{N}(\text{SiMe}_3)_2]^-$ anion, completing the coordination sphere of the central metal ion, is arranged almost perpendicular to the five-membered metallacycle (P–Pb–N2: 93.30(5)°; N1–Pb–N2: 100.37(7)°). The sum of the angles at the cation of 267.45° illustrates the pyramidal coordination sphere and the presence of a stereochemically active lone pair at the lead(II) atom.

The P–C1–C2 angle of 122.46(17)° indicates sp^2 -hybridization of the C1 atom. The sum of the angles at C1 of 360° ascertains the planar coordination sphere. The Pb···C1 distance of 348.0 pm clearly shows that the cation is not interacting with the deprotonated “carbanionic” atom. The P–C_{Ph} distances in **1** (av 182.3 pm) are identical within their esd's and in the range normally quoted for standard P–C single bonds (185 pm).⁷ However, the P–C1 bond length of 173.9(2) pm is substantially shorter. This distance is similar to those observed in $[\text{Pb}\{\text{HC}(\text{PPh}_2)_2\}_2]$ (171.3–175.9 pm).⁸ Also the C1–C2 distance in **1** of 139.4(3) pm is shorter than a formal $\text{C}(\text{sp}^2)$ – $\text{C}(\text{sp}^2)$ single bond (146 pm).⁷ Therefore, the C2–N2 distance (138.4(3) pm) in the pyridyl substituent is ca. 5.2 pm longer than in the related $\text{Ph}_2\text{P}(\text{CH}_2\text{Py})(\text{NSiMe}_3)$ (133.17 pm).⁹ These structural parameters are consistent with a delocalization of the negative charge over the $[\text{P}–\text{C}(\text{H})–\text{Py}]$ moiety and charge transfer into the electron-deficient pyridyl substituent observed in the related zinc and iron complexes.¹⁰ Thus, the short P–C1 and C1–C2 distances in **1** originate from high electrostatic contributions and polarization effects.⁹ In **1**, the Pb–N1 distance of 236.32(19) pm is ca. 13 pm longer than the Pb–N2 bond (223.31(18) pm), indicating that the Pb–N1 interaction is weaker due to charge delocalization in the $[\text{P}–\text{C}(\text{H})–\text{Py}]^-$ residue. In the lead amide $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ the Pb–N distances are 226.0 pm.¹¹ A good example for Pb←N_{Py} donor interactions is $[(\text{C}_5\text{H}_5\text{N})\text{Pb}\{2,6-(2,4,6-\text{iPr}-\text{C}_6\text{H}_2)\text{C}_6\text{H}_3\}\text{Br}]$, with a Pb–N distance of 250.2 pm.¹² For the lead organic complex $[\text{Pb}(\text{o-C}_6\text{H}_4\text{PPh}_2-\text{NSiMe}_3)_2]$ a much longer Pb–N bond length of 263.6 pm is observed.¹³ Thus, in **1** the Pb–N2 bond is in the range for lead amides and the Pb–N1 interaction has a considerable amidic character, which is in accordance with a charge transfer toward the pyridyl nitrogen atom N1. The Pb–P bond in **1** is 275.01(7) pm long. Interestingly, this value is in the range found for Pb–P interactions in lead phosphanides with a tricoordinated lead(II) atom as in **1**. For example the Pb–P distances in $[\text{Pb}(\text{P}^t\text{Bu}_2)_2]$ are 278.1 and 281.2 pm;¹⁴ those in $[\text{Pb}_2\{\text{P}(\text{SiMe}_3)_2\}_4]$, 269.4 and 279.7 pm.¹⁵

In the ³¹P NMR spectrum of **1**, the phosphorus

nucleus resonates quite unexpectedly at $\delta = 61.17$. The observed lead satellites give a coupling constant of $^1J_{^{207}\text{Pb},^{31}\text{P}} = 2679.5$ Hz, which is quite large in comparison to other plumbynes, e.g., in $[\text{Pb}\{\text{HC}(\text{PPh}_2)_2\}_2]$ ($^1J_{^{207}\text{Pb},^{31}\text{P}} = 1970$ Hz),⁸ $[(\text{THF})\text{Li}(\mu_2-\text{P}^t\text{Bu}_2)_2\text{Pb}(\text{P}^t\text{Bu}_2)]$ ($^1J_{^{207}\text{Pb},^{31}\text{P}} = 1770$ Hz),¹⁶ or $[\text{Pb}\{\text{SiMe}_3\text{C}(\text{Ph}_2\text{P})_2\}_2]$ ($^1J_{^{207}\text{Pb},^{31}\text{P}} = 1510$ Hz).^{8b} The single proton at the C_α atom gives rise to a doublet at $\delta = 4.56$; the coupling constant is $^2J_{^1\text{H},^{31}\text{P}} = 6.4$ Hz. This signal shows satellites with a coupling constant of $^3J_{^{207}\text{Pb},^1\text{H}} = 33.0$ Hz. The ¹⁵N spectroscopical shifts were obtained from a ¹H, ¹⁵N-HMBC experiment. They reflect clearly the different bonding environment of the two nitrogen nuclei. Whereas the nitrogen atom of the $[\text{N}(\text{SiMe}_3)_2]^-$ moiety resonates upfield at $\delta = -268.0$, the resonance for the pyridyl nitrogen atom is shifted to lower field at $\delta = -145.3$. The resonance for the pyridyl nitrogen atom is located $\Delta\delta = 83.3$ upfield in comparison to the starting material $\text{Ph}_2\text{P}(\text{CH}_2\text{Py})$ ($\delta = -62.0$),¹⁷ consistent with an amidic character for this atom and in accordance with the observed structural parameters. To verify the experimental findings, the ³¹P and ¹⁵N shifts were calculated by density functional methods that include scalar relativistic effects on lead via an effective-core potential (ECP) and additionally spin–orbit (SO) corrections by a triple perturbation SO-ECP approach.¹⁸ The scalar relativistically obtained ³¹P shift of 19 ppm is moved to 60 ppm by large deshielding SO corrections, to give the computed shifts an excellent agreement with the experimental ones. Final SO-corrected ¹⁵N shifts are –129 ppm for the pyridyl nitrogen atom and –256 ppm for the $[(\text{Me}_3\text{Si})_2\text{N}]^-$ moiety, again in good agreement with the experiment. These values include more moderate deshielding SO corrections of ca. +12 ppm and ca. +11 ppm, respectively. The lesser importance of SO effects for the nitrogen nuclei compared to phosphorus is consistent with a relatively low nitrogen s-character in the Pb–N bonds.¹⁹ The more deshielded character of the pyridyl nitrogen atom reflects incorporation into an unsaturated π -system.

In summary, the $[\text{Ph}_2\text{PC}(\text{H})\text{Py}]^-$ anion in **1** should be regarded as an amide, although the Pb–P distance matches those of phosphanides and the Pb–N distance is considerably longer than that of the $[(\text{Me}_3\text{Si})_2\text{N}]^-$ ligand. This view is further substantiated by the experimental and theoretical NMR shifts.

Experimental Section

Preparation of $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (1**).** To a suspension of 0.50 g (1.80 mmol) of $\text{Ph}_2\text{PCH}_2\text{Py}$ in 40 mL of hexane was added 0.95 g (1.80 mmol) of $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in

(6) Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Dalton Trans.* **1994**, 2755.

(7) Rademacher, P. In *Strukturen Organischer Moleküle*; VCH: Weinheim, 1987.

(8) (a) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 215. (b) Balch, A. L.; Oram, D. E. *Inorg. Chem.* **1987**, *26*, 1906.

(9) Kocher, N.; Leusser, D.; Murso, A.; Stalke, D. *Chem. Eur. J.* **2004**, *10*, 3622.

(10) Murso, A.; Stalke, D. *Dalton Trans.* **2004**, 2563.

(11) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639.

(12) Pu, L.; Twamley, B.; Power, P. P. *Organometallics* **2000**, *19*, 2874.

(13) Wingerter, S.; Gornitzka, H.; Bertermann, R.; Pandey, S. K.; Rocha, J.; Stalke, D. *Organometallics* **2000**, *19*, 3890.

(14) Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *Polyhedron* **1988**, *7*, 1909.

(15) Goel, S. C.; Chiang, M. Y.; Rauscher, D. J.; Buhro, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 160.

(16) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1446.

(17) Assigned unambiguously in a ¹H, ¹⁵N-HMBC NMR experiment.

(18) Vaara, J.; Malkina, O. L.; Stoll, H.; Malkin, V. G.; Kaupp, M. *J. Chem. Phys.* **2001**, *114*, 61 (see this work for more computational details). Scalar relativistic shifts were calculated at the BP86-IGLO level, and SO corrections were computed with a common gauge on lead and a finite perturbation of $\lambda = 0.001$ au. A four-valence-electron ECP with (5s5p2d/4s4p2d) valence basis and matching SO-ECP was used on lead (Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245), with an IGLO-III basis on P, Si, and N (Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR—Basic Principles and Progress*; Springer: Heidelberg, 1990; Vol. 23, p 165) and a DZVD basis set on all other atoms (Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560).

(19) Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem. Eur. J.* **1998**, *4*, 118.

10 mL of hexane at $-10\text{ }^{\circ}\text{C}$. The resulting dark red solution was stored at $-24\text{ }^{\circ}\text{C}$, yielding 1.10 g (1.71 mmol, 95%) of **1** as red blocks. The ^1H , ^{13}C , ^{15}N , ^{29}Si , and ^{31}P solution NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^1H , 300.1 MHz; ^{13}C , 75.5 MHz; ^{15}N , 30.4 MHz; ^{29}Si , 59.6 MHz; ^{31}P , 121.5 MHz). Toluene- d_8 was used as solvent. Chemical shifts [ppm] were determined relative to internal $\text{C}_6\text{D}_5\text{CHD}_2$ (^1H , $\delta = 2.09$; C_7D_8), C_7D_8 (^{13}C , $\delta = 20.4$; C_7D_8), external formamide (^{15}N , $\delta = -268.0$; C_7D_8), external TMS (^{29}Si , $\delta = 0$; C_7D_8), and external 85% H_3PO_4 (^{31}P , $\delta = 0$; C_7D_8). Analysis and assignment of the ^1H NMR data were supported by ^1H , ^1H COSY, ^{13}C , ^1H , ^{15}N , ^1H , and ^{31}P , ^1H correlation experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. ^1H NMR: δ 0.18 (s, 18H, SiMe_3), 4.56 (d, $^2J_{\text{H}^{31}\text{P}} = 6.4$ Hz, satellites, $^3J_{207\text{Pb}^{31}\text{P}} = 33.0$ Hz, 1H, H-1), 5.62 (ddd, 1H, H-5), 6.53 (dddd, 1H, H-4), 6.74 (d, 1H, H-3), 7.14 (overlap with m -, p -PhH, 1H, H-6), 7.07–7.46 (m, m -, p -PhH), 7.44–7.68 (m, o -PhH). ^{13}C NMR: δ 6.1 (s, SiMe_3) 61.8 (d, $^2J_{^{13}\text{C},^{31}\text{P}} = 55.6$ Hz, C-1), 105.1 (s, C-5), 121.0 (d, C-3), 134.6 (s, C-4), 144.6 (d, C-6), 172.6 (d, $^2J_{^{13}\text{C},^{31}\text{P}} = 22.5$ Hz, C-2), 127.5–129.8 (m, m -, p -PhH), 132.8 (d, o -PhH). ^1H , ^{15}N -HMBC NMR: δ -268.0 (N(SiMe_3) $_2$), -145.3 (NPy). ^{29}Si NMR: δ -1.72 (s). ^{31}P NMR: δ 61.17 (s, satellites, $^1J_{207\text{Pb},^{31}\text{P}} = 2679.5$ Hz). Anal. CHN, found, (calcd) [%]: C 44.98 (44.77), H 5.13 (5.17), N 4.45 (4.35). Mp: $43\text{ }^{\circ}\text{C}$.

Crystal Structure of $[\text{Pb}\{\text{Ph}_2\text{PC}(\text{H})\text{Py}\}\{\text{N}(\text{SiMe}_3)_2\}]$ (1**).** The dataset was measured at 100(2) K 20 using graphite-monochromated Mo K α radiation ($\lambda = 71.073$ pm) on a Bruker D8 goniometer platform, equipped with a Smart Apex CCD detector. The structure was solved using direct methods and

refined by full-matrix least-squares on F^2 using SHELXL. 21 The hydrogen atoms at the methylene bridges were taken from the difference Fourier map and refined freely. All other hydrogen atoms were refined using a riding model. All non-hydrogen atoms were refined anisotropically. **1**: $\text{C}_{24}\text{H}_{33}\text{N}_2\text{-PPbSi}_2$, $M_r = 643.86$ g/mol, triclinic, space group $P\bar{1}$, $a = 859.44(15)$ pm, $b = 1748.2(3)$ pm, $c = 1841.1(3)$ pm, $\alpha = 102.425(3)^{\circ}$, $\beta = 96.536(3)^{\circ}$, $\gamma = 95.131(3)^{\circ}$, $V = 2.6652(8)$ nm $^{-3}$, $Z = 4$, $\rho_{\text{calcd}} = 1.605$ Mg m $^{-3}$, $\mu = 6.493$ mm $^{-1}$, $F(000) = 1264$. Data were collected from $\theta = 2.29$ to 28.28° . A total of 73 736 reflections were measured, from which 13 243 were unique, $R(\text{int}) = 0.0266$, $\text{wR2}(\text{all data}) = 0.0412$, $R1(I > 2\sigma(I)) = 0.0179$, for 13 238 data and 561 parameters. Crystallographic data of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-234744. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: internat.) +44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgment. Continuous financial support of the DFG (grants no. STA 334/8, KA 1187/5 and the Graduiertenkolleg 690 Elektronendichte-Theorie und Experiment) is kindly acknowledged.

Supporting Information Available: Crystal data tables for **1**, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters in cif file format are available free of charge via the Internet at <http://pubs.acs.org>.

OM0501677

(20) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. (b) Kottke, T.; Lagow R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465. (c) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.

(21) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) SHELXTL-97; Bruker Nonius Inc.: Madison, WI, 1997.