Notes

A Heterotopically Chelated Low-Valent Lead Amide[1]

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*Summary: The solid-state structure and NMR parameters of the heavier carbene analogue [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (**1**), obtained in the reaction of the phosphane $Ph_2P(CH_2Py)$ with [Pb{$N(SiMe_3)_2$}$_2$], 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 $Ph_2P(CH_2Py)$[6] with [Pb{$N(SiMe_3)_2$}$_2$][4c] in a 1:1 ratio gives the phosphanamide [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (**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).

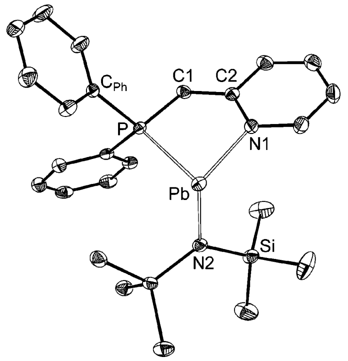
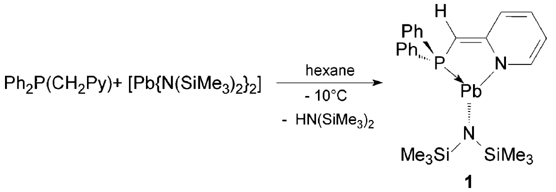


Figure 1. Solid-state structure of [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (**1**). Only one of the two molecules in the asymmetric unit is shown. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [pm] and angles [deg]: Pb−P 275.01(7), Pb−N1 236.32(19), Pb−N2 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 [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (1) by Deprotonation of $Ph_2P(CH_2Py)$ with [Pb{$N(SiMe_3)_2$}$_2$]



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Dissolving **1** in various solvents results in decomposition and formation of elemental Pb^0. However, dark red blocks of crystalline [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (**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 [Pb{$Ph_2PC(H)Py$}{$N(SiMe_3)_2$}] (**1**), the central cation is 3-fold coordinated. The [$Ph_2PC(H)$-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

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$[N(SiMe_3)_2]^-$ 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 $[Pb\{HC(PPh_2)_2\}]_2$ (171.3−175.9 pm).[8] Also the C1−C2 distance in **1** of 139.4(3) pm is shorter than a formal $C(sp^2)-C(sp^2)$ 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 $Ph_2P(CH_2Py)(NSiMe_3)$ (133.17 pm).[9] These structural parameters are consistent with a delocalization of the negative charge over the [P−C(H)−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 $[P-C(H)-Py)]^-$ residue. In the lead amide $[Pb\{N(SiMe_3)_2\}_2]$ the Pb−N distances are 226.0 pm.[11] A good example for $Pb \leftarrow N_{Py}$ donor interactions is $[(C_5H_5N)Pb\{2,6\text{-}(2,4,6\text{-}{}^iPr-C_6H_2)C_6H_3\}Br]$, with a Pb−N distance of 250.2 pm.[12] For the lead organic complex $[Pb(o\text{-}C_6H_4PPh_2\text{-}NSiMe_3)_2]$ 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 $[Pb(P^tBu_2)_2]_2$ are 278.1 and 281.2 pm;[14] those in $[Pb_2\{P(SiMe_3)_2\}_4]$, 269.4 and 279.7 pm.[15]

In the ^{31}P NMR spectrum of **1**, the phosphorus nucleus resonates quite unexpectedly at $\delta = 61.17$. The observed lead satellites give a coupling constant of $^1J_{^{207}Pb,^{31}P} = 2679.5$ Hz, which is quite large in comparison to other plumbylenes, e.g., in $[Pb\{HC(PPh_2)_2\}_2]$ ($^1J_{^{207}Pb,^{31}P} = 1970$ Hz),[8] $[(THF)Li(\mu_2\text{-}P^tBu_2)Pb(P^tBu_2)]$ ($^1J_{^{207}Pb,^{31}P} = 1770$ Hz),[16] or $[Pb\{SiMe_3C(Ph_2P)_2\}_2]$ ($^1J_{^{207}Pb,^{31}P} = 1510$ Hz).[8b] The single proton at the C_α atom gives rise to a doublet at $\delta = 4.56$; the coupling constant is $^2J_{^1H,^{31}P} = 6.4$ Hz. This signal shows satellites with a coupling constant of $^3J_{^{207}Pb,^1H} = 33.0$ Hz. The ^{15}N spectroscopical shifts were obtained from a $^1H,^{15}N$-HMBC experiment. They reflect clearly the different bonding environment of the two nitrogen nuclei. Whereas the nitrogen atom of the $[N(SiMe_3)_2]^-$ 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 $Ph_2P(CH_2Py)$ ($\delta = -62.0$),[17] consistent with an amidic character for this atom and in accordance with the observed structural parameters. To verify the experimental findings, the ^{31}P and ^{15}N 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 ^{31}P 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 ^{15}N shifts are −129 ppm for the pyridyl nitrogen atom and −256 ppm for the $[(Me_3Si)_2N]^-$ 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 $[Ph_2PC(H)Py]^-$ 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 $[(Me_3Si)_2N]^-$ ligand. This view is further substantiated by the experimental and theoretical NMR shifts.

Experimental Section

Preparation of $[Pb\{Ph_2PC(H)Py\}\{N(SiMe_3)_2\}]$ (1). To a suspension of 0.50 g (1.80 mmol) of Ph_2PCH_2Py in 40 mL of hexane was added 0.95 g (1.80 mmol) of $[Pb\{N(SiMe_3)_2\}_2]$ in

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10 mL of hexane at −10 °C. The resulting dark red solution was stored at −24 °C, yielding 1.10 g (1.71 mmol, 95%) of **1** as red blocks. The ^{1}H, ^{13}C, ^{15}N, ^{29}Si, and ^{31}P solution NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^{1}H, 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 $C_6D_5CHD_2$ (^{1}H, $\delta = 2.09$; 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 ^{1}H NMR data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H, ^{15}N,^{1}H, and ^{31}P,^{1}H correlation experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. ^{1}H NMR: δ 0.18 (s, 18H, SiMe$_3$), 4.56 (d, $^2J_{^1\mathrm{H},^{31}\mathrm{P}} = 6.4$ Hz, satellites, $^3J_{^{207}\mathrm{Pb},^1\mathrm{H}} = 33.0$ 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, $^2J_{^{13}\mathrm{C},^{31}\mathrm{P}} = 55.6$ 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, $^2J_{^{13}\mathrm{C},^{31}\mathrm{P}} = 22.5$ Hz, C-2), 127.5−129.8 (m, *m*-,*p*- PhH), 132.8 (d, *o*-PhH). ^{1}H,^{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, $^1J_{^{207}\mathrm{Pb},^{31}\mathrm{P}} = 2679.5$ Hz). Anal. CHN, found, (calcd) [%]: C 44.98 (44.77), H 5.13 (5.17), N 4.45 (4.35). Mp: 43 °C.

Crystal Structure of [Pb{Ph$_2$PC(H)Py}{N(SiMe$_3$)$_2$}] (1). The dataset was measured at 100(2) K[20] using graphite-monochromated Mo Kα 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**: $C_{24}H_{33}N_2PPbSi_2$, $M_r = 643.86$ g/mol, triclinic, space group $P\bar{1}$, $a = 859.44(15)$ pm, $b = 1748.2(3)$ pm, $c = 1841.1(3)$ pm, $\alpha = 102.425(3)°$, $\beta = 96.536(3)°$, $\gamma = 95.131(3)°$, $V = 2.6652(8)$ nm^{-3}, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.605$ 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, $R(\mathrm{int}) = 0.0266$, wR2(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].

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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.

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