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Synthesis and Characterization of Stable N-Heterocyclic Plumbylenes

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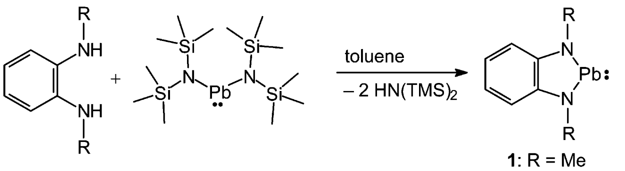
The reaction of *N*,*N*′-dialkyl-1,2-diaminobenzenes with bis[bis(trimethylsilyl)amido]lead(II) leads to the corresponding N-heterocyclic plumbylenes (R = Me: **1**; R = Et: **2**; R = isobutyl: **3**; R = neopentyl: **4**). The steric demand of the *N*,*N*′-dialkyl substituents determines the mode of aggregation of the plumbylenes. X-ray diffraction analyses show both **3** and **4** to form dimers in the solid state with intermolecular [η^2-(C_6H_4)···Pb]$_2$ contacts for **3** and [η^6-(C_6H_4)···Pb]$_2$ contacts for **4**.

Introduction

The heavier analogues of diaminocarbenes E[N(SiR$_3$)$_2$]$_2$ (E = Ge, Sn, Pb) have been described as early as 1974 by Lappert et al.[1] They are highly reactive, but thermally stable, coloured and mostly diamagnetic compounds. Later, the heavier analogues of the Arduengo carbene[2] with divalent silicon,[3] germanium[4] and tin[5] have been synthesized. In addition, benzannulated N-heterocyclic carbenes,[6] silylenes,[7] germylenes[8] and stannylenes[9] are known. While some monomeric diaryl- and bis(trimethylsilyl)plumbylenes[10] and -diplumbenes[11] have been reported, no N-heterocyclic plumbylenes have been described in the literature. Lappert et al. mention a benzannulated N-heterocyclic plumbylene and its carbene adduct[12] but no spectroscopic or structural data about the plumbylene are given. We describe here the preparation of four benzannulated N-heterocyclic plumbylenes with different *N*,*N*′-substituents and the molecular structures of two of these derivatives.

Results and Discussion

The preparation of the benzimidazolin-derived plumbylenes **1**–**4** (Scheme 1) was achieved by the transamination reaction of bis[bis(trimethylsilyl)amido]lead(II)[1] with a suitable 1,2-diaminobenzene derivative in toluene. The preparation of various differently *N*,*N*′-alkylated 1,2-diaminobenzene precursors has been described.[8d,8e,9c] The driving forces for the transamination reaction are believed to be a combination of chelate and entropy effects. The reaction rate decreases with increasing steric bulk of the *N*,*N*′-disubstituents at the 1,2-diaminobenzene. However, the yields are generally very good (89–92%) in all cases. Initiation of the reaction can be monitored visually by a color change of the reaction mixture from yellow-orange to red or purple, respectively. The benzimidazolin-derived plumbylenes were isolated as intensely red (**1**, **2**) or purple (**3**, **4**) crystalline solids. They are very sensitive towards oxygen and moisture.



1: R = Me
2: R = Et
3: R = *i*Bu
4: R = neopentyl

Scheme 1. Transmetalation of Pb[N(SiMe$_3$)$_2$]$_2$ with *N*,*N*′-dialkyl-1,2-diaminobenzene derivatives.

Compound **1** precipitates directly from the reaction solution and was isolated in pure form by filtration. The plumbylenes **2**–**4** were isolated by filtration after concentration of the reaction solution. The EI mass spectra of all four plumbylenes show a peak for the molecular ion as the most abundant signal exhibiting the correct isotope pattern.

Plumbylene **1** is insoluble in polar and nonpolar organic solvents, while **2**–**4** are sparingly soluble in toluene and benzene. The solubility increases with the steric bulk of the *N*,*N*′-disubstituents. The ^{1}H NMR spectroscopic data for compounds **2**–**4** show a downfield shift of about 1.8 ppm for the signal of the methylene protons next to the nitrogen atoms relative to the free 1,2-diaminobenzenes. Plumbylene formation was also detected in the ^{13}C NMR spectra by the downfield shift of the resonance signal of the *ipso*-carbon atoms from $\delta \approx 137$ ppm for the 1,2-diaminobenzenes to $\delta \approx 156$ ppm for the plumbylenes.

Suitable single crystals for X-ray diffraction analyses could be obtained for **3** and **4** by cooling of a saturated

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toluene solution. Both compounds are found to be dimers in the solid state (Figures 1 and 2). However, the dimeric structures do not arise from intermolecular Pb–Pb or Pb–N contacts but from interactions of the lead atom of one molecule with the aromatic six-membered ring of a second molecule.

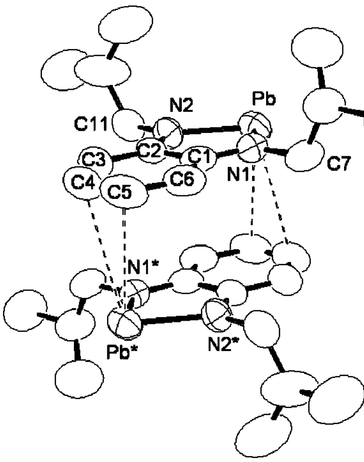

Figure 1. Molecular structure of dimeric **3** in the solid state. Selected bond lengths [Å] and angles [°] for molecule 1 [molecule 2]: Pb–N1 2.150(7) [2.164(8)], Pb–N2 2.160(7) [2.154(8)], N1–C1 1.379(11) [1.379(11)], N1–C7 1.448(13) [1.448(3)], N2–C2 1.359(11) [1.373(13)], N2–C11 1.453(13) [1.446(14)], C1–C2 1.462(14) [1.438(14)]; N1–Pb–N2 75.6(3) [75.8(3)], Pb–N1–C1 116.5(6) [115.5(6)], Pb–N1–C7 122.7(6) [123.0(7)], C1–N1–C7 120.6(8) [121.2(8)], Pb–N2–C2 116.5(6) [115.8(7)], Pb–N2–C11 122.8(6) [123.5(7)], C2–N2–C11 120.4(8) [120.3(9)].

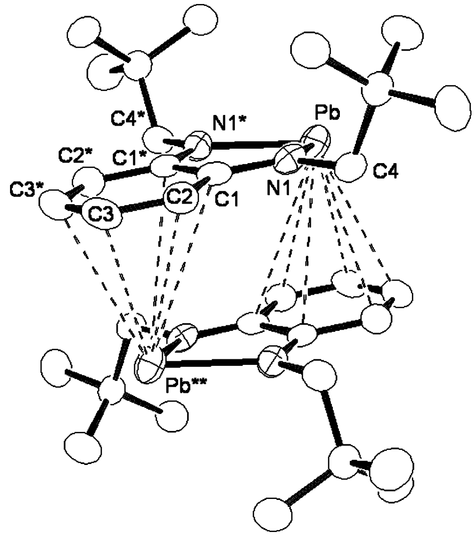

Figure 2. Molecular structure of dimeric **4**. Selected bond lengths [Å] and angles [°]: Pb–N1 2.180(4), N1–C1 1.373(7), N1–C4 1.457(6) C1–C1* 1.440(10); N1–Pb–N1* 75.4(2), Pb–N1–C1 115.3(3), Pb–N1–C4 121.8(4), C1–N1–C4 122.2(5).

Plumbylene **3** crystallizes with two essentially identical molecules in the asymmetric unit. Two identical molecules from neighbouring asymmetric units form one dimer (Figure 1). The five- and six-membered rings in **3** are planar, and the nitrogen atoms are surrounded in a trigonal-planar fashion (range of the sum of angles at N1 and N2 359.6–359.8°). The C_{ring}–N–Pb angles deviate most significantly from 120° [range 115.5–116.5(6)°]. The Pb–N distances in **3** [range 2.150(7)–2.164(8) Å] are, as expected, elongated when compared to the equivalent distances in heterocyclic benzannulated stannylenes (Sn–N ca. 2.08 Å)[9] and germylenes (Ge–N ca. 1.87 Å).[8] The N–E–N angle, however, becomes more acute for E = Pb (75.7°) when compared to E = Sn and E = Ge.

The dimer of **3** is formed by intermolecular interactions of ring atoms C4 (Pb*–C4 3.367 Å) and C5 (Pb*–C5 3.390 Å) with the symmetry-related atom Pb*. The other intermolecular Pb*–C distances are about 0.4 Å longer (Pb*–C3/C6 ca. 2.70 Å, Pb*–C1/C2 ca. 4.10 Å).

A slightly different mode of dimerization was found for **4**. Here, one molecule of **4** (the asymmetric unit contains only 1/2 molcule of **4**, related to the other half by a mirror plane containing the lead atom and bisecting the C3–C3* bond) is placed on top of a second molecule with the lead atoms residing on top of the midpoint of the six-membered benzene ring of the adjacent molecule. This leads to six Pb–C separations which fall in the range from 3.348 Å for Pb–C3/C3* to 3.601 Å for Pb–C1/C1*. The distance between the lead atom and the midpoint of the six-membered ring of the adjacent molecule measures 3.17 Å. A similar type of $[\eta^6\text{-}(C_6H_4)\cdots Sn]_2$ dimerization has been described for a benzannulated N-heterocyclic stannylene.[9a]

Conclusions

Four benzannulated N-heterocyclic plumbylenes have been prepared and characterized. The solubility and dimerization behaviour of these plumbylenes is determined by the steric bulk of the *N*,*N′*-disubstituents. The plumbylenes **3** and **4** are dimeric in the solid state exhibiting intermolecular $[\eta^2\text{-}(C_6H_4)\cdots Pb]_2$ or $[\eta^6\text{-}(C_6H_4)\cdots Pb]_2$ contacts which are shorter than the sum of the van der Waals radii for carbon and lead (3.72 Å).

Experimental Section

Starting Materials, Reaction Conditions and Instrumentation: All manipulation were carried out under argon using Schlenk or glovebox techniques. Toluene was dried with sodium/benzophenone and was freshly distilled prior to use. C_6D_6 was dried with Na/K alloy. The preparation of differently substituted *N*,*N′*-dialkyl-1,2-diaminobenzenes has been described.[8d,8e,9c] $Pb[N(SiMe_3)_2]_2$ was prepared as described in the literature.[1]

General Procedure for the Synthesis of Plumbylenes 1–4: A sample of bis[bis(trimethylsilyl)amido]lead(II) (0.268 g, 0.5 mmol) was added to a solution of an *N*,*N′*-dialkyl-1,2-diaminobenzene (0.5 mmol) in toluene (8 mL). The reaction mixture was then stirred under argon at ambient temperature for 36 h. Subsequently, all volatiles were removed in vacuo, and the residue was recrystallized from toluene with the exception of **1** which is insoluble in toluene. Plumbylene **1** precipitated in analytically pure form from the toluene reaction solution.

[*N*,*N*′-Dimethylbenzene-1,2-diamido]lead(II) (1): Yield 0.151 g (89%) of a red crystalline solid. MS (EI, 70 eV): *m*/*z* (%) = 342 (100) $[M]^+$, 208 (4.3) $[Pb]^+$, 133 (65.7) $[M – Pb]^+$, 119 (16.5) $[M – Pb – CH_3]^+$.

[*N*,*N*′-Diethylbenzene-1,2-diamido]lead(II) (2): Yield 0.150 g (80%) of a dark red crystalline solid. ^1H NMR (200 MHz, C_6D_6): δ = 7.00 (m, 2 H, Ar-H), 6.68 (m, 2 H, Ar-H), 4.80 (q, ^3J = 6.7 Hz, 4 H, NCH_2CH_3), 0.92 (t, ^3J = 6.7 Hz, 6 H, NCH_2CH_3) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 155.5 (Ar-C_{ipso}), 117.4 (Ar-C_{meta}), 112.5 (Ar-C_{ortho}), 44.9 (NCH_2CH_3), 19.0 (CH_2CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 370 (100) $[M]^+$, 342 (44) $[M – Et]^+$, 208 (4.3) $[Pb]^+$, 164 (43) $[M – Pb]^+$.

[*N*,*N*′-Diisobutylbenzene-1,2-diamido]lead(II) (3): Yield 190 mg (88%) of a purple crystalline solid. ^1H NMR (200 MHz, C_6D_6): δ = 6.87 (m, 2 H, Ar-H), 6.68 (m, 2 H, Ar-H), 4.81 (d, ^3J = 6.5 Hz, 4 H, NCH_2CH), 1.95 [m, 2 H, $NCH_2CH(CH_3)_2$], 0.87 [d, ^3J = 6.5 Hz, 12 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 155.0 (Ar-C_{ipso}), 117.4 (Ar-C_{meta}), 113.3 (Ar-C_{ortho}), 58.2 (NCH_2CH), 29.8 [$NCH_2CH(CH_3)_2$], 21.2 [$NCH_2CH(CH_3)_2$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 426 (100) $[M]^+$, 383 (39.5) $[M – CH(CH_3)_2]^+$, 220 (30.1) $[M – Pb]^+$, 175 (22.8) $[M – Pb – CH(CH_3)_2]^+$.

[*N*,*N*′-Dineopentylbenzene-1,2-diamido]lead(II) (4): Yield 209 mg (92%) of a purple crystalline solid. ^1H NMR (200 MHz, C_6D_6): δ = 7.16 (m, 2 H, Ar-H), 6.83 (m, 2 H, Ar-H), 4.90 [s, 4 H, $NCH_2C(CH_3)_3$], 0.88 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 155.6 (Ar-C_{ipso}), 116.8 (Ar-C_{meta}), 113.5 (Ar-C_{ortho}), 60.2 [$NCH_2C(CH_3)_3$], 34.6 [$CH_2C(CH_3)_3$], 28.3 [$CH_2C(CH_3)_3$] ppm. MS (EI, 70 eV): *m*/*z* (%) = 454 (100) $[M]^+$, 397 (11.0) $[M – C(CH_3)_3]^+$, 248 (6.4) $[M – Pb]^+$.

X-ray Diffraction Studies: Diffraction data for **3** and **4** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[13] program package. Structures were solved with the SHELXS-97[14] package using the heavy-atom method and were refined with SHELXL-97[15] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated positions. CCDC-673663 (**3**) and CCDC-673664 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif.

Crystal Data for Plumbylene 3: $C_{14}H_{22}N_2Pb$, M = 425.53, triclinic, $P\bar{1}$, Z = 4, a = 10.529(3), b = 11.398(3), c = 13.280(3) Å, α = 73.398(4), β = 89.522(4), γ = 76.447(5)°, V = 1481.8(6) Å^3, 12061 measured reflections, 5250 unique reflections (R_{int} = 0.0332), R = 0.0424, wR = 0.1082 for 3833 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions. The asymmetric unit contains two almost identical molecules of **3**.

Crystal Data for Plumbylene 4: $C_{16}H_{26}N_2Pb$, M = 453.58, tetragonal, $P4_2mbc$, Z = 8, a = 12.4313(11), c = 21.323(4) Å, V = 3295.2(7) Å^3, 21823 measured reflections, 1341 unique reflections (R_{int} = 0.0944), R = 0.0294, wR = 0.0491 for 1146 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms in calculated positions. The molecule resides on a crystallographic mirror plane orientated perpendicularly to the ring plane. The mirror plane contains the Pb atom and passes through the C3–C3* bond.

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[1] D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 895–896.

[2] A. J. Arduengo III, M. Kline, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1991**, *113*, 9704–9705.

[3] a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692; b) M. Haaf, T. A. Schmedake, R. West, *Acc. Chem. Res.* **2000**, *33*, 704–714.

[4] W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489–1492; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485–1488.

[5] T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* **2002**, *114*, 1966–1969; *Angew. Chem. Int. Ed.* **2002**, *41*, 1888–1891.

[6] a) F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935; b) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352.

[7] a) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932; b) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* **1996**, *521*, 211–220; c) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386.

[8] a) J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.* **1989**, *122*, 245–252; b) J. Pfeiffer, M. Noltemeyer, A. Meller, *Z. Anorg. Allg. Chem.* **1989**, *572*, 145–150; c) O. Kühl, P. Lönnecke, J. Heinicke, *Polyhedron* **2001**, *20*, 2215–2222; d) A. V. Zabula, F. E. Hahn, T. Pape, A. Hepp, *Organometallics* **2007**, *26*, 1972–1980; e) F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, *Eur. J. Inorg. Chem.* **2007**, 2405–2408.

[9] a) H. Braunschweig, B. Gehrhus, P. B. Hitchcook, M. F. Lappert, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922–1928; b) F. E. Hahn, L. Wittenbecher, M. Kühn, T. Lügger, R. Fröhlich, *J. Organomet. Chem.* **2001**, *617–618*, 629–634; c) F. E. Hahn, L. Wittenbecher, D. Le Van, A. V. Zabula, *Inorg. Chem.* **2007**, *46*, 7662–7667.

[10] M. Stürmann, M. Weidenbruch, K. W. Klinkhammer, F. Lissner, H. Marsmann, *Organometallics* **1998**, *17*, 4425–4428.

[11] a) M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem.* **1999**, *111*, 145–147; *Angew. Chem. Int. Ed.* **1999**, *38*, 187–189; b) M. Stürmann, W. Saak, M. Weidenbruch, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 579–582.

[12] B. Gehrhus, P. B. Hitchcook, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **2000**, 3094–3099.

[13] *SMART*, Bruker AXS, **2000**.

[14] *SHELXS-97*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[15] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

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