STRUCTURE, PROPERTIES AND COMPARISON OF C,N-CHELATED AND AMIDO-STABILIZED PLUMBYLENES

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Received August 3, 2009 Accepted October 26, 2009 Published online February 10, 2010

Dedicated to Professor Pavel Kratochvíl on the occasion of his 80th birthday in recognition of his outstanding contributions to the area of macromolecular chemistry.

The molecular structure of $\{2-[(CH_3)_2NCH_2]C_6H_4\}_2Pb$ (1) in the solid state was determined by X-ray diffraction techniques on a single crystalline material. Bulky amido ligand stabilized complexes $[(i-C_3H_7)_2C_6H_3]NHLi$ (2) and $[(i-C_3H_7)_2C_6H_3N(Me_3Si)]_2Pb$ (3) were synthesized and characterized both in the solid state and solution by ¹H, ¹³C, ¹⁵N and ²⁰⁷Pb NMR and XRD techniques. The structure of both C,N-chelated and bulky amido plumbylenes is compared.

Keywords: Lead; Bulky amides; C,N-chelates; Plumbylenes; Organoelement chemistry; X-ray diffraction.

Organolead compounds have been known for almost 150 years. Tetraethyllead became an industrial commodity in the last century but is now being banned because of the negative environmental impact related to its toxicity^{1,2}.

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) center³. Thus, only a few examples of low-valent plumbylenes have been reported so far⁴, although the first diamino- and dialkylplumbylenes were already described by ¹H and ¹³C NMR spectroscopy^{5,6}. Another example of a lead(II) complex, stabilized by the intramolecular coordination, was described recently by Stalke⁷.

Besides, O,C,O- and similar chelated plumbylenes were described⁸. All of these compounds contain at least one electron-withdrawing substituent, which makes the lead atom a Lewis acid allowing intramolecular coordination. The most recent studies on the field of amido-stabilized plumbylenes with angular geometry and tendency to form dimers are published in papers of Hahn⁹.

We have recently reported reactivity and products of C,N-chelated plumbylene 1^{6} with a zirconocene derivative known as the Negishi reagent¹⁰ (Scheme 1) where the product is zircona complex 5 formed by C–H activation and C–C coupling, containing two five-membered rings¹¹. A different product of transmetallation, 6, the product of ligand transfer from lead to zirconium can be isolated if one equivalent of n-butyllithium instead of two is used for in situ generation of zirconocene¹².

The use of different stannylene (stabilized with bulky amide group) in the same reactions yields the same type of complex but one of the amido ligands on the tin atom is replaced by n-butyl group (Scheme 2)¹³.



SCHEME 1 Reactions of zirconocene dichloride derivatives with 1 and 4



SCHEME 2 Reactions of zirconocene dichloride derivatives with 7 and 8

In this paper, the crystal structure and ¹H, ¹³C, ¹⁵N and ²⁰⁷Pb NMR spectral description of the known C,N-chelated plumbylene and the mutual comparison of this compound to the new amido-stabilized plumbylene are described.

RESULTS AND DISCUSSION

The intramolecularly coordinated homoleptic organolead(II) compound 1^{6} and bisamido lead compound **3** have been obtained in good yields by reactions of the corresponding organolithium compounds with PbCl₂ at low temperature (for **2** and **3**, see Scheme 3).





Compound 1 was identified by ¹H and ¹³C NMR spectra in the past⁶. Two different polymorphs (1 and 1') were obtained from diethyl ether or THF solution. Both polymorphs crystallize in the same crystal system (monoclinic, $P2_1/c$, see Table I), but there are significant differences in the cell parameters found. The molecular structures of both polymorphs are slightly different and also the crystal packing differs significantly. The central lead atoms in both 1 and 1' are coordinated with four atoms two carbon and two nitrogen atoms (Fig. 1). The coordination geometry about lead atoms in 1 and 1' is ψ -distorted trigonal bipyramidal with two carbon atoms and the lone electron pair in equatorial and nitrogen atoms in axial positions. The Pb–N distances are slightly different (2.727(3) and 2.616(3) Å for 1 or 2.712(3) and 2.682(3) Å for 1'). The geometry of the lead central atom is very similar to the tin coordination vicinity in organotin(II) analogue¹⁴ of 1. Slightly longer distances between lead and carbon or nitrogen atoms are caused by a higher covalent radius of lead compared to tin. From the C11-Pb1-C21 angles (99.68(13)° for 1 and 92.01(11)° for 1'), which is the main difference between both polymorphs, we can conclude that the lone electron pairs in the compound are situated in radial s-orbital.



Fig. 1

Molecular structure of 1 (ORTEP 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) and angles (in °) of 1 (the appropriate parameters for the second polymorph 1' are given in parentheses): Pb1–N1 2.727(3) (2.712(3)), Pb1–N2 2.616(3) (2.682(3)), Pb1–C11 2.311(3) (2.319(3)), Pb1–C21 2.294(4) (2.311(3)); N11–Pb1–N21 163.54(9) (152.67(7)), C11–Pb1–C21 99.68(13) (92.01(11)) In ²⁰⁷Pb NMR spectrum, a signal at 2624 ppm was observed. An important tool in evaluation of coordination between donor nitrogen and metal atoms is the ¹⁵N NMR spectroscopy. The value of ¹⁵N NMR chemical shift (-351.11 ppm) indicates a weak interaction comparable to that found in tetraorganotin(IV) compounds bearing the same ligand¹⁵.

The synthesis of compound 3 and many other compounds of current interest includes the lithiation, silylation and further lithiation of bulky anilido ligands. Compound 2 was isolated after the first step of reaction procedure. The nitrogen atoms (N1, N1a) and lithium atoms (Li1, Li1a) in 2 (Fig. 2) are in the same plane, while the oxygen atoms of diethyl ether coordinated to lithium atoms are below or above this plane. The planes formed by phenyl rings are perpendicular to this plane and parallel to each other. The center of symmetry of this compound is in the cross point of Li1–Li1a and N1–N1a bisectors.

Compound 3 was prepared from 2 by silvlation and further reaction with 0.5 molar equivalent of $PbCl_2$. Both isopropylphenyl groups are oriented perpendicularly to the plane described by N1, Pb1 and N2 atoms (Fig. 3) because of high steric repulsion. In the comparison with the tin analogue, the geometry of this compound is almost the same¹⁶. Small differences in dis-



FIG. 2

The molecular structure of 2·Et₂O (ORTEP 40% probability level). Hydrogen atoms and ethyl groups of diethyl ether are omitted for clarity. Selected interatomic distances (in Å) and angles (in °): Li1–O1 1.918(2), Li1–N1 2.025(2), Li1–N1a 1.989(2), Li1–Li1a 2.473(3), N1–C1 1.3843(14), N1–N1a 3.1616(13); C1–N1–Li1 118.03(9), N1–Li1–N1a 103.93(10), Li1–N1–Li1a 76.07(9), O1–Li1–N1 129.47(11)

tances between lead or tin and nitrogen atoms are caused by a higher covalent radius of the lead atom. Judging from the value of the N1-Pb1-N2 angle $(111.34(10)^\circ)$, the structure can be described as singlet ${}^{1}\sigma^{2}$. Both nonbonding and bonding electron pairs occupy sp²-hybrid orbitals and the p orbital is unoccupied. An alternative description of the bonding situation is that the 6s² electrons, stabilized by relativistic effects, play no part, the bonding electrons are in 6p orbitals, and the large size of Pb atom leaves room for several weaker interactions that give apparent coordination numbers greater than 2. The difference from the theoretical model (120°) is caused by steric requirements of the ligands (mainly SiMe₃ groups). There is a weak interaction between lead and carbon atoms (or the aromatic system of the phenyl ring) in the molecule due to suitable orientation of lead and the ipso-carbon (dashed lines in Fig. 3). These interactions (2.877(3) and 2.940(3) Å) are weaker than those found in 1-plumba-closo-heptaboranes¹⁷, but much stronger than those found for dimeric plumbylenes of Hahn (3.367 Å). On the other hand, normal Pb–C bond lengths range from 2.3 to 2.4 Å ¹⁸.



FIG. 3

The molecular structure of **3** (ORTEP 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) and angles (in °): Pb1–N1 2.204(3), Pb1–N2 2.198(3), Pb1–C1 2.877(3), Pb1–C21 2.940(3), C1–N1 1.432 (4), C21–N2 1.430(4), N1–N2 3.635(4), N1–Si1 1.735(3), N2–Si2 1.732(3); N1–Pb1–N2 111.34(10), C1–Pb1–C21 164.39(9), Pb1–N1–Si1 137.73(16), Pb1–N2–Si2 132.05(16), Pb1–N1–C1 102.6(2), Pb1–N2–C21 106.3(2)

The structure of 3 in solution seems to be very close to that in the solid state judging from the ¹H NMR spectra pattern with non-equivalent isopropyl groups. From the ²⁰⁷Pb NMR chemical shift value (4070 ppm) can be concluded that the ²⁰⁷Pb NMR shift is strongly dependent on the coordination geometry of lead atom compared with the chemical shift 2624 ppm found for 1, which has a distorted trigonal bipyramidal geometry (ψ -TBP) of the lead central atom, where the organic substituents together with lone electron pair occupy the equatorial positions and intramolecularly coordinated amino groups axial ones. The chemical shifts of other kinetically stabilized monomeric dialkyl- and diarylplumbylenes (δ (²⁰⁷Pb) = 10050-8884 ppm)¹⁹ are much greater than those for plumbylenes in which the lead atom has a coordination number greater than 2 (1981–4878 ppm)^{19c,20} and diaminoplumbylene (4916 ppm)^{19b}. Diarylplumbylene (δ (²⁰⁷Pb) = 3870 ppm) bearing bulky terphenyl substituents resonates at a much higher fields than other kinetically stabilized plumbylenes²¹. Similar discrepancy has been found for four-coordinated plumbylene with one O,C,O-chelating and one bulky alkyl ligands of Jurkschat^{8a} (δ (²⁰⁷Pb) = 6874 ppm).

EXPERIMENTAL

All procedures were carried out using the modified Schlenk techniques under an argon atmosphere. The resulting plumbylenes need to be protected from light.

Synthesis of 1

2-[(CH₃)₂NCH₂]C₆H₄Li (1.5 g, 0.011 mol) in diethyl ether (100 ml) was added slowly to a mixture of PbCl₂ (1.67 g, 0.006 mol) with diethyl ether (50 ml) and stirred at room temperature for 24 h. The slightly green solution was filtered off, concentrated to about half of the initial volume and placed in a freezer at -20 °C for 1 day. Compound 1 was obtained as colorless crystals suitable for X-ray crystallography, which decompose in solution on daylight to elemental lead and an unidentified green solution. Yield 2.06 g (0.0043 mol, 78%). For C₁₈H₂₄N₂Pb (475.58) calculated: 45.46% C, 5.09% H, 5.89% N; found: 45.38% C, 5.06% H, 5.93% N. The compound was identified by NMR spectroscopy as a single product: ¹H NMR (360 MHz, toluene-*d*₈, 300 K): 2.41 (s, 12 H, CH₃); 3.83 (s, 4 H, CH₂); 7.37 (t, 2 H, CH(6), ³*J*(¹H, ¹H) = 5.6); 7.51 (d, 2 H, CH(4), ³*J*(¹H, ¹H) = 5.7); 7.62 (t, 2 H, CH(5), ³*J*(¹H, ¹H) = 6.0); 8.37 (d, 2 H, CH(3), ³*J*(¹H, ¹H) = 7.0). ²⁰⁷Pb NMR (75 MHz, toluene-*d*₈, 300 K): 2624. ¹⁵N NMR (36.5 MHz, toluene-*d*₈, 300 K): -351.11.

Synthesis of (i-C₃H₇)₂C₆H₃NHSiMe₃

To $(i-C_3H_7)_2C_6H_3NH_2$ (9.5 g, 0.052 mol) in diethyl ether (30 ml) was added CH_3SiCl (5.91 g, 0.055 mol) and the reaction mixture stirred at -30 °C for 1 h. The orange solution was filtered and the solvents were evaporated. The product was obtained as an orange oil. Yield 11.68 g (0.0466 mol, 89.7%).

128

Synthesis of 2

To a mixture of $(i-C_3H_7)_2C_6H_3$ NHSiMe₃ (11.68 g, 0.047 mol) and hexane (100 ml) was added n-butyllithium (30 ml) in hexane (*c* = 1.6 mol/l, 0.048 mol). The mixture was stirred for at room temperature for 3 h. The solid state product was filtered off, washed with hexane and dried in vacuo. Yield 10.48 g (0.041 mol, 87%).

Synthesis of 3

To PbCl₂ (5.06 g, 0.018 mol) in THF (50 ml) was added **2** (9.33 g, 0.036 mol) in THF (100 ml) at room temperature. The mixture was stirred for 4 h, its color changed to red. The solvents were removed under reduced pressure, and the residue was extracted with hexane. The extract was filtered, concentrated to ca. 60% of the initial volume and placed in a freezer at –20 °C for 2 days. Compound **3** was obtained as red crystals. Yield 10.29 g (0.0146 mol, 81%), m.p. 220.1 °C (decomp.). The compound was identified by NMR as a single product. ¹H NMR (360 MHz, toluene- d_8 , 300 K): 0.32 (s, 18 H, Si-CH₃); 1.05, 1.23 (dd, 24 H, CH-CH₃, J(A,B) = 68.9, ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) = 6.9$); 3.68 (heptet, 4 H, CH, ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) = 6.9$); 6.85 (t, 2 H, CH(4), ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) = 7.8$); 7.09 (d, 4 H, CH(3), ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) = 5.7$. ²⁰⁷Pb NMR (75 MHz, toluene- d_8 , 300 K): 4070.

X-ray Diffraction

Single crystals of the studied compounds suitable for X-ray diffraction studies were obtained at -20 °C from solutions in various solvents (mainly diethyl ether). Crystallographic data were obtained on a Nonius KappaCDD diffractometer with an area detector, source of MoK α and a graphite monochromator. Suitable single crystals were mounted on glass fibre in an inert oil and measured at the wavelength 0.71073 Å.

The structures were solved by direct methods (SIR92)²². All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97)²³. Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of crystal treatment, all hydrogen atoms were recalculated in idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl group. Absorption corrections were made using the Gaussian integration from crystal shape²⁴.

CCDC 740899 (for 1), 740900 (for 1'), 740901 (for 2) and 740902 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

NMR Spectroscopy

NMR spectra of the studied compounds were measured in deuterated solvents (toluene- d_8 , benzene- d_6) at 220–360 K on Bruker AMX 360 and Bruker Avance 500 spectrometers in pulsed mode with Fourier transformation. ¹H, ¹⁵N and ²⁰⁷Pb NMR spectra were measured at frequencies 360.13 (500.14) MHz, 36.5 MHz and 75.34 MHz, respectively, in a 5 mm widezone tuneable sampler. The values of ¹H NMR chemical shifts were calibrated to internal inert standard tetramethylsilane (δ (¹H) = 0.00 ppm) or to residual signals of benzene C,N-Chelated and Amido-Stabilized Plumbylenes

TABLE I								
Crystallographic	parameters	for	compounds	1,	1′,	2	and	3

Parameter	1	1	2	3	
Empirical formula	$\mathrm{C}_{18}\mathrm{H}_{24}\mathrm{N}_{2}\mathrm{Pb}$	$\mathrm{C}_{18}\mathrm{H}_{24}\mathrm{N}_{2}\mathrm{Pb}$	C ₁₂ H ₁₈ LiN	$\mathrm{C_{30}H_{52}N_2PbSi_2}$	
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/c$	C2/c	$P2_{1}/c$	
<i>a</i> , Å	10.1091(3)	12.1570(2)	13.4343(3)	15.0339(2)	
<i>b</i> , Å	10.0179(4)	14.8668(3)	11.6970(2)	9.6941(2)	
<i>c</i> , Å	17.3922(6)	10.6320(3)	21.9955(5)	24.0312(4)	
α, °	90.00	90.00	90.00	90.00	
β, °	96.934(2)	113.702(1)	104.843(1)	103.954(1)	
γ, °	90.00	90.00	90.00	90.00	
Ζ	4	4	8	4	
<i>V</i> , Å ³	1748.44(11)	1759.52(7)	3341.32(12)	3398.91(10)	
D _c , g/cm	1.807	1.795	1.023	1.376	
Crystal size, mm	0.25×0.2×0.15	0.2×0.18×0.15	0.25×0.25×0.40	0.4×0.3×0.25	
Crystal shape	colorless block	colorless plate	colorless block	orange plate	
μ, mm ⁻¹	9.645	9.585	0.061	5.053	
<i>F</i> (000)	912	912	1136	1424	
h, k, l range	-13/13, -12/12, -22/22	-15/15, -19/19, -13/13	-17/17, -15/15, -18/28	-19/19, -12/12, -31/23	
θ range, °	3.56-27.47	1.83-27.52	1.92-27.46	1.75-27.45	
Reflections mea- sured	26322	30036	26526	41321	
Reflections independent $(R_{int})^a$	3988 (0.0499)	4034 (0.0401)	3819 (0.0202)	7763 (0.0495)	
Reflections ob- served $[I > 2\sigma(I)]$	3590	3144	2945	6177	
Parameters refined	195	195	172	331	
Max/min τ , e Å^{-3}	1.518/-1.311	0.806/-0.574	0.254/-0.210	1.001/-1.265	
GOF^b	1.039	1.123	1.028	1.027	
R^{c}/wR^{c}	0.0243/0.0561	0.0208/0.0454	0.0465/0.1278	0.0296/0.0594	

 ${}^{a}R_{\text{int}} = \Sigma |F_{o}{}^{2} - F_{\text{o,mean}}{}^{2}|/\Sigma F_{o}{}^{2}; {}^{b}S = [\Sigma(w(F_{o}{}^{2} - F_{c}{}^{2})^{2})/(N_{\text{diffs}} - N_{\text{params}})]^{1/2}; {}^{c}\text{ weighting scheme:} w = [\sigma^{2}(F_{o}{}^{2}) + (w_{1}P)^{2} + w_{2}P]^{-1}, \text{ where } P = [\max(F_{o}{}^{2}) + 2F_{c}{}^{2}], R(F) = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|, wR(F^{2}) = [\Sigma(w(F_{o}{}^{2} - F_{c}{}^{2})^{2})/(\Sigma w(F_{o}{}^{2})^{2})]^{1/2}.$

130

 $(\delta(^{1}\text{H}) = 7.16 \text{ ppm})$ or toluene $(\delta(^{1}\text{H}) = 2.09 \text{ ppm})$. The values of ¹⁵N chemical shifts were calibrated to a signal of external nitromethane standard in a coaxial capillary $(\delta(^{15}\text{N}) = 0.0 \text{ ppm})$. The values of ²⁰⁷Pb chemical shifts were calibrated to Pb(NO₃)₂ in water and recalculated to PbEt₄ $(\delta(^{207}\text{Pb}) = 0.00 \text{ ppm})$. Positive values of chemical shifts indicate a shift to lower field in compared with the standard. The coupling constants (*J*, Hz) were found in the spectra measured with digital resolution better than 0.5 Hz/point.

The Pardubice group would like to thank the Grant Agency of the Academy of Sciences of the Czech Republic (Grant KJB401550802) and the Ministry of Education, Youth and Sports of the Czech Republic (Grant VZ 0021627501) for financial support.

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