STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 4, 2009

HYPERVALENT TETRA- AND TRIORGANOLEAD(IV) COMPOUNDS CONTAINING 2-(R_2NCH_2)C_6H_4 GROUPS (R = Me, Et)

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ABSTRACT. Reaction of [2-(R_2NCH_2)C_6H_4]Li with R'_3PbCl or Ph_2PbCl_2, in 1:1 molar ratio, gave the new organolead(IV) compounds [2-(R_2NCH_2)C_6H_4]R'_3Pb [R = Me, R' = Me (**1**), Ph (**2**); R = Et, R' = Ph (**3**)] and [2-(Me_2NCH_2)C_6H_4]Ph_2PbCl (**4**). Treatment of [2-(R_2NCH_2)C_6H_4]Ph_3Pb with iodine resulted in isolation of [2-(R_2NCH_2)C_6H_4]Ph_2PbI [R = Me (**5**), Et (**6**)]. The iodide **5** was also obtained by halogen exchange reaction between **4** and KI. The compounds were characterized in solution by ^1H and ^{13}C NMR. The molecular structure of **2** and **4** was established by single-crystal X-ray diffraction. In both cases the nitrogen atom from the pendant Me_2NCH_2 arm is coordinated intramolecularly to the lead atom [Pb-N 3.051(9) Å in **2** and 2.635(8) Å in **4**, respectively] leading to distorted trigonal bipyramidal geometry around the metal atom and thus to hypervalent 10-*Pb*-5 species. Compounds **2** and **4** crystallize as 1:1 mixtures of *R*- and *S*-isomers (planar chirality induced by the non-planar PbC_3N chelate ring).

Keywords: organoleadIV) compounds, hypervalent, solution NMR studies, single-crystal X-ray diffraction

INTRODUCTION

Aromatic ligands with pendant arm containing nitrogen as donor atom, such as 2-(Me_2NCH_2)C_6H_4 or related organic compounds have been largely used in organotin chemistry in last years [1-17]. By contrast, such ligands were only sparingly used in organolead chemistry. Only one lead(II) compound, [2-(Me_2NCH_2)C_6H_4]$_2$Pb [18], and few organoled(IV) derivatives, *i.e.* [2-(Me_2NCH_2)C_6H_4]$_4$Pb [18], [2-(Me_2NCH_2)C_6H_4](4-MeC_6H_4)$_2$PbI [19] and [2-(Me_2NCH_2)C_6H_4](4-MeC_6H_4)(4-$MeOC_6H_4$)PbI [19,20], were described in early works and the structure of the latter chiral compound was established by single-crystal X-ray diffraction. Some related derivatives, *i.e.* [CpFe{C_5H_3(CH_2NMe_2)-2}]$_2$Pb [21] and [CpFe{C_5H_3(CH_2NMe_2)-2}]$_2$PbM(CO)$_5$ (M = Cr, Mo, W) [22], were also recently described.

We report here on the synthesis and solution behavior of new tetraorganolead(IV) compounds, [2-(R_2NCH_2)C_6H_4]R'_3Pb [R = Me, R' = Me (**1**), Ph (**2**); R = Et, R' = Ph (**3**)], and triorganolead(IV) halides, [2-(Me_2NCH_2)C_6H_4]Ph_2PbCl (**4**), [2-(R_2NCH_2)C_6H_4]Ph_2PbI [R = Me (**5**), Et (**6**)], as well as the molecular structure of **2** and **4**.

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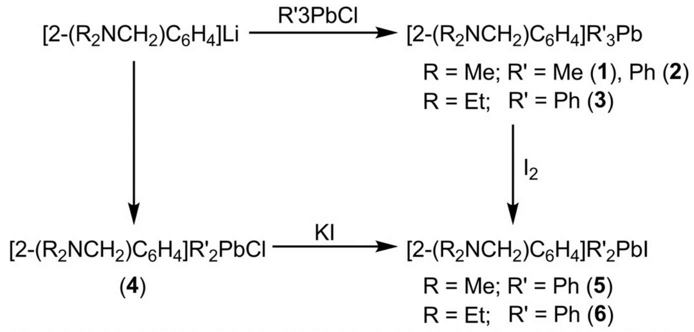
RESULTS AND DISCUSSION

The new tetraorganolead(IV) compounds **1-3** were obtained by reacting R'$_3$PbCl with [2-(R$_2$NCH$_2$)C$_6$H$_4$]Li in 1:1 molar ratio, in hexane, at at –78 ^{o}C, while reaction of Ph$_2$PbCl$_2$ with [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li in 1:1 molar ratio, in same conditions, resulted in isolation of the chloride **4** (Scheme 1).

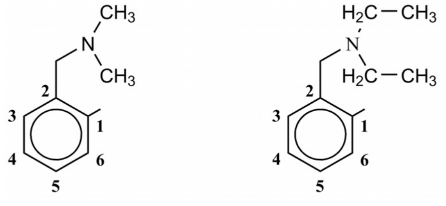


Scheme 1

Treatment of [2-(R$_2$NCH$_2$)C$_6$H$_4$]Ph$_3$Pb with iodine, in CH$_2$Cl$_2$, at room temperature, resulted in selective cleavage of one phenyl group and isolation of the iodides [2-(R$_2$NCH$_2$)C$_6$H$_4$]Ph$_2$PbI [R = Me (**5**), Et (**6**)]. This suggests that the presence of the CH$_2$NR$_2$ pendant arm on the aromatic ring stabilizes the Pb-C bond established by the [2-(Me$_2$NCH$_2$)C$_6$H$_4$] group with respect to that which involves the phenyl moiety, probably through the intramolecular N→Pb interaction. The same iodide **5** was obtained by halogen exchange when the chloride **4** was treated with excess of KI, in CH$_2$Cl$_2$/water.

The new organolead(IV) compounds were isolated in rather good yields (50-90%) as colorless (**1-4**) or yellowish (**5**, **6**) crystalline solids. They are air-stable compounds, soluble in common organic solvents. The compounds were investigated by NMR spectroscopy (^{1}H, ^{13}C, 2D) in solution and for compounds **2** and **4** the molecular structures were established by single-crystal X-ray diffraction.

The NMR spectra for the compounds **1-6** were recorded in CDCl$_3$, at room temperature. The assignment of the ^{1}H and ^{13}C chemical shifts was made according to the numbering schemes shown in Scheme 2, based on 2D experiments and the lead-carbon coupling constants.



Scheme 2

The NMR (^{1}H, ^{13}C) spectra of compounds **1**, **2**, **4** and **5** are very similar with respect to the [2-(Me_2NCH_2)C_6H_4] group attached to the lead atom, showing the expected resonances in the alkyl and the aryl regions. All four compounds show in the alkyl region singlet resonances for NMe_2 and CH_2 protons of the pendant arm, respectively, with the latter surrounded by lead satellites. The ^{1}H NMR spectrum of the mixed alkyl-aryllead(IV) derivative **1** exhibits in the alkyl region an additional singlet resonance for the protons of the methyl groups bonded to lead. The aromatic region is much better resolved for compound **1**, with four multiplet resonances (that for the H_3 proton is partially overlapped by the resonance of residual $CHCl_3$). For the mixed tetraaryllead(IV) compound **3** the aromatic region is more complicated due to overlapping of the resonances for the protons of the C_6H_4 group and those corresponding to the phenyl groups, respectively. The main influence of the halogen atom attached to lead in the chloride **4** and the iodide **5** is the downfield shift of the resonance for the proton H_6 with respect to the other *ortho* protons from the phenyl groups bonded to lead. For compounds **3** and **6**, containing the [2-(Et_2NCH_2)C_6H_4] group attached to lead, in addition to a broad signal for the benzylic CH_2 protons, one triplet and one quartet resonance were observed for the ethyl groups in the aliphatic region of the ^{1}H NMR spectra. The aromatic region exhibits a rather complex pattern due to partial overlapping of the resonance signals.

According to the ^{1}H NMR data, the ^{13}C NMR spectra of compounds **2-5** contain, in addition of six resonances for the different aromatic carbons of the [2-(R_2NCH_2)C_6H_4] group, a single set of four resonances for the phenyl groups, indicating their equivalence in solution. Most of these singlet resonances are surrounded by lead satellites due to lead-carbon coupling. The unambiguous assignment of the ^{13}C resonance signals for these organolead(IV) compounds was based on the 2D correlation spectra and carbon-lead coupling constants, respectively.

The NMR data suggest that in solution these compounds might have similar structures as found in solid state for **2** and the chloride **4**, *i.e.* a trigonal bipyramidal coordination geometry around the lead atom due to the intramolecular N→Pb coordination (assuming a fast conformational change in solution for the nonplanar, five-membered PbC_3N chelate ring, which gives averaged ^{1}H NMR signals). Alternatively, a tetrahedral geometry around the lead atom can also be considered, a behavior which will assume the lack of intramolecular coordination in solution. Unfortunately, the ^{207}Pb NMR spectra, which might provide further information on the coordination degree of the lead atom, could not be yet recorded.

Single-crystals suitable for X-ray diffraction studies were obtained by slow diffusion from a mixture of CH_2Cl_2 and hexane (1/4, v/v) for compounds [2-(Me_2NCH_2)C_6H_4]Ph_3Pb (**2**) and [2-(Me_2NCH_2)C_6H_4]Ph_2PbCl (**4**).

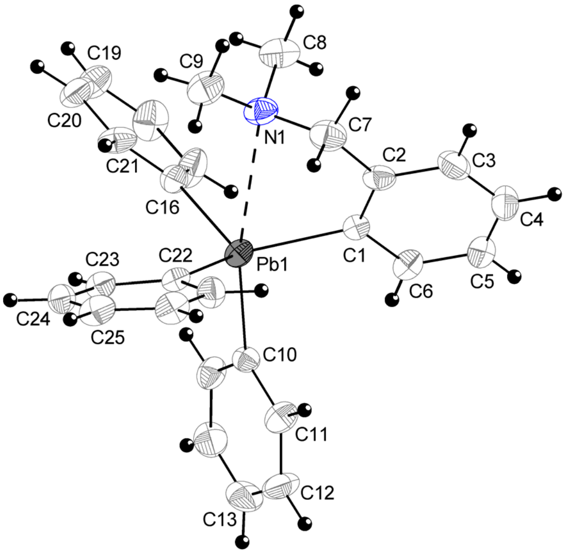


Figure 1. ORTEP representation at 30% probability and atom numbering scheme for R_N-**2** isomer.

The crystal of **2** consists of discrete monomers separated by normal van der Waals distances, while compound **4** has two independent, very similar, molecules (**4a** and **4b**) in the unit cell and therefore the subsequent discussion will refer only to molecule **4a**. The ORTEP diagrams of the molecular structures of **2** and **4a**, with the atom numbering scheme, are shown in Figures 1 and 2. Selected interatomic distances and angles are listed in Tables 1 and 2.

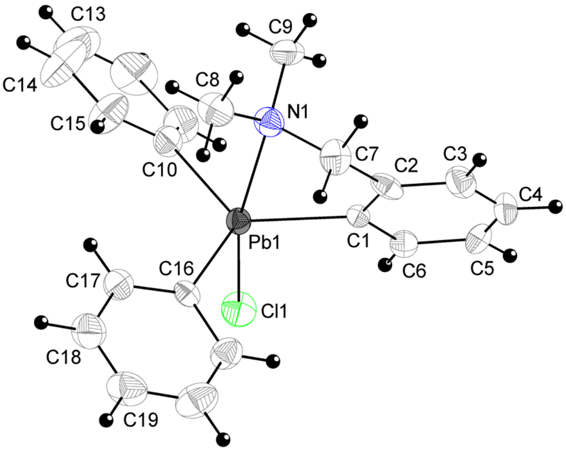


Figure 2. ORTEP representation at 30% probability and atom numbering scheme for R_N-**4a** isomer.

Table 1. Interatomic bond distances (Å) and angles (°) for compound **2**.

Pb(1)-C(1)	2.223(8)	Pb(1)-C(16)	2.222(8)
Pb(1)-C(10)	2.253(8)	Pb(1)-C(22)	2.207(8)
Pb(1)-N(1)	3.051(9)		
N(1)-C(7)	1.475(12)	N(1)-C(9)	1.453(11)
N(1)-C(8)	1.440(12)		
C(1)-Pb(1)-C(10)	102.2(3)	C(10)-Pb(1)-C(16)	105.7(3)
C(1)-Pb(1)-C(16)	118.6(3)	C(10)-Pb(1)-C(22)	104.9(3)
C(1)-Pb(1)-C(22)	114.2(3)	C(16)-Pb(1)-C(22)	109.6(3)
N(1)-Pb(1)-C(10)	169.1(3)		
N(1)-Pb(1)-C(1)	66.8(3)	N(1)-Pb(1)-C(22)	80.8(3)
N(1)-Pb(1)-C(16)	80.6(3)		
C(7)-N(1)-C(8)	109.0(8)	Pb(1)-N(1)-C(7)	94.8(6)
C(7)-N(1)-C(9)	111.0(8)	Pb(1)-N(1)-C(8)	110.3(6)
C(8)-N(1)-C(9)	111.3(8)	Pb(1)-N(1)-C(9)	119.2(7)

Table 2. Interatomic bond distances (Å) and angles (°) for compound **4**.

4a		**4b**	
Pb(1)-C(1)	2.202(8)	Pb(2)-C(22)	2.205(9)
Pb(1)-C(10)	2.191(10)	Pb(2)-C(31)	2.197(9)
Pb(1)-C(16)	2.190(9)	Pb(2)-C(37)	2.198(9)
Pb(1)-Cl(1)	2.597(3)	Pb(2)-Cl(2)	2.616(2)
Pb(1)-N(1)	2.636(8)	Pb(2)-N(2)	2.646(9)
N(1)-C(7)	1.489(13)	N(2)-C(28)	1.478(15)
N(1)-C(8)	1.481(13)	N(2)-C(29)	1.458(14)
N(1)-C(9)	1.462(13)	N(2)-C(30)	1.452(14)
Cl(1)-Pb(1)-N(1)	166.11(19)	Cl(2)-Pb(2)-N(2)	167.2(2)
Cl(1)-Pb(1)-C(1)	94.9(2)	Cl(2)-Pb(1)-C(22)	93.3(3)
Cl(1)-Pb(1)-C(10)	93.4(3)	Cl(2)-Pb(1)-C(31)	99.1(2)
Cl(1)-Pb(1)-C(16)	98.5(2)	Cl(2)-Pb(1)-C(37)	93.9(3)
N(1)-Pb(1)-C(1)	72.9(3)	N(2)-Pb(1)-C(22)	74.2(3)
N(1)-Pb(1)-C(10)	89.0(3)	N(2)-Pb(1)-C(31)	89.0(3)
N(1)-Pb(1)-C(16)	92.6(3)	N(2)-Pb(1)-C(37)	91.3(3)
C(1)-Pb(1)-C(10)	126.7(4)	C(22)-Pb(1)-C(31)	117.0(3)
C(1)-Pb(1)-C(16)	113.7(3)	C(22)-Pb(1)-C(37)	124.3(3)
C(10)-Pb(1)-C(16)	116.8(4)	C(31)-Pb(1)-C(37)	116.1(4)
C(7)-N(1)-C(8)	108.8(9)	C(28)-N(1)-C(29)	109.6(10)
C(7)-N(1)-C(9)	111.2(9)	C(28)-N(1)-C(30)	108.3(10)
C(8)-N(1)-C(9)	110.0(9)	C(29)-N(1)-C(30)	111.0(10)
Pb(1)-N(1)-C(7)	98.0(6)	Pb(2)-N(1)-C(28)	97.7(6)
Pb(1)-N(1)-C(8)	118.4(6)	Pb(2)-N(1)-C(29)	111.8(7)
Pb(1)-N(1)-C(9)	109.8(7)	Pb(2)-N(1)-C(30)	117.4(8)

The molecule of **2** contains an intramolecular N→Pb interaction [Pb(1)-N(1) 3.051(9) Å] placed *trans* to the carbon atom of a phenyl group attached to lead. The strength of this interaction is enough strong to be taken into account [c.f. the sum of the van der Waals radii, Σr_{vdW}(Pb,N) 3.54 Å] [23]. The overall geometry at the lead atom is distorted trigonal bipyramidal, with the axial positions occupied by the nitrogen and the carbon atom [N(1)-Pb(1)-C(10) 169.1(3)°], while the carbon atoms of the other two phenyl groups and that of the pendant arm aryl ligand are in the equatorial positions. The distortion of the coordination geometry is due to the small bite of the *C,N*-ligand [N(1)-Pb(1)-C(1) 66.8(3)°]. The C_3PbN chelate ring is not planar, the nitrogen atom being out of the plane defined by the remaining C_3Pb unit. This results in coordination isomers, *i.e.* planar chirality, with C(1)-C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively [24]. As result compound **2** crystallizes as a 1:1 mixture of R_N and S_N isomers.

In the molecule of the chloride **4a** a much stronger intramolecular N→Pb interaction is established in the *trans* to the chlorine atom and the overall molecular structure is very similar to that reported for the related tin compound, $[2\text{-}(Me_2NCH_2)C_6H_4]Ph_2SnCl$ [4]. The lead-nitrogen interatomic distance [Pb(1)-N(1) 2.636(8) Å] is of similar magnitude as observed in the related chiral iodide, $[2\text{-}(Me_2NCH_2)C_6H_4](4\text{-}MeC_6H_4)(4\text{-}MeOC_6H_4)PbI$ [2.686(8) Å] [20], pointing out the lack of significant influence of the electronegativity of the atom placed in the *trans* position relative to nitrogen in the N→Pb-X fragment.

The axial positions in the resulted distorted trigonal bipyramidal geometry achieved around the metal centre are occupied by nitrogen and chlorine atoms [Cl(1)-Pb(1)-N(1) 166.11(19)°], while the aromatic carbon atoms are in the equatorial positions.

The *trans* effect is reflected in the length of the Pb-Cl bond, considerably shorter in **4a** [Pb(1)-Cl(1) 2.597(3) Å] than in the polymeric Ph_3PbCl [2.7059(7) Å] [25]. This is consistent with the stronger *trans* influence of the more electronegative chlorine atom in the Cl→Pb-Cl bridge in Ph_3PbCl than in the N→Pb-Cl system.

As in the case of **2**, the C_3PbN chelate ring in the molecule of **4** is not planar, resulting in planar chirality. The crystal of the chloride **4** consists of a 1:1 mixture of R_N-**4a** / S_N-**4a** and R_N-**4b** / S_N-**4b** isomers, separated by normal van der Waals distances between heavy atoms. However, a closer check of the crystal structure revealed that weak intermolecular Cl···H interactions are established between neighboring molecules. This results in helicoidal chain polymers formed by alternating R_N-**4a** / R_N-**4b** and S_N-**4a** / S_N-**4b** isomers (Figure 3), respectively, supported by $Cl(1)\cdots H(30A)_{methyl}$ (2.95 Å) and $Cl(2)\cdots H(13b)_{phenyl}$ (2.87 Å) interactions [c.f. Σr_{vdW}(Cl,H) ca. 3.01 Å] [23]. No inter-chain contacts are present between parallel polymeric chains developed along the *b* axis.

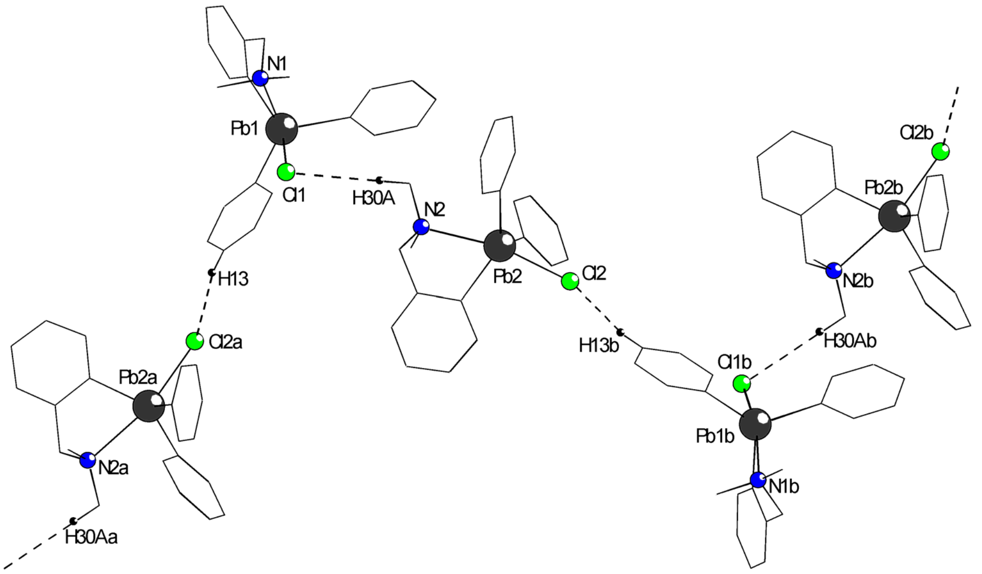


Figure 3. View of a chain polymer based on Cl···H contacts between S_N-**4a** and S_N-**4b** isomers in the crystal of **4** (only hydrogens involved in intermolecular interactions are shown) [symmetry equivalent atoms: Pb2a (1.5 – *x*, 0.5 + *y*, 0.5 – *z*); Pb1 (–0.5 + *x*, 0.5 – *y*, –0.5 + *z*); Pb1b (2 – *x*, –*y*, 1 – *z*) and Pb2b (1.5 – *x*, –0.5 + *y*, 0.5 – *z*)].

CONCLUSIONS

Six new hypervalent organolead(IV) compounds of the type $[2\text{-}(R_2NCH_2)C_6H_4]R'_3Pb$ (R = Me, R' = Me, Ph; R = Et, R' = Ph) and $[2\text{-}(R_2NCH_2)C_6H_4]Ph_2PbX$ (R = Me, X = Cl, I; R = Et, X = I) were obtained. All compounds were characterized in solution using multinuclear and 2D NMR spectroscopy. For both type of compounds single-crystal X-ray diffraction studies provide evidence for an intramolecular N→Pb interaction, resulting in distorted trigonal bipyramidal geometry around the lead atom (hypervalent 10-*Pb*-5 species). It was also found that cleavage of a phenyl group under treatment with iodine is preferred *versus* cleavage of the pendant arm aryl ligand, probably due to the intramolecular N→Pb interaction. All compounds crystallize as 1:1 mixtures of R_N- and S_N isomers (planar chirality induced by the non-planar PbC_3N chelate ring).

EXPERIMENTAL SECTION

All compounds were prepared under an inert atmosphere of argon (Linde, 99.999%) using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. Ph_3PbCl, Me_3PbCl and Ph_2PbCl_2 were commercially available. The other starting materials were prepared accordingly to literature methods: $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ [26] and $[2\text{-}(Et_2NCH_2)C_6H_4]Li$ [27]. The ^1H, ^{13}C and 2D NMR spectra were recorded at room temperature, in dried $CDCl_3$, on Bruker Avance 300 instrument. The chemical shifts are reported in ppm relative to the residual peak of the solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm). The NMR spectra were processed using the *MestReC* and *MestReNova* software [28].

*Preparation of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Me$_3$Pb (**1**)*

A suspension of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.72 g, 5.1 mmol) in hexane (30 ml) was added dropwise, under stirring, to a solution of Me_3PbCl (1.49 g, 5.1 mmol) in hexane (50 ml), cooled (–78 °C). After the organolithium suspension was added, the reaction mixture was stirred for 1 h at –78 °C, and then left over night to reach the room temperature. The reaction mixture was filtered in open atmosphere and the solvent was removed in vacuum from the clear filtrate. The white solid residue was recrystallized from hexane to give the title compound as colorless crystals. Yield: 1.3 g (65%), m.p. 234 °C. ^1H NMR (300 MHz, 20 °C): δ 1.60s (9H, Pb-CH_3, $^2J_{PbH}$ 82.6 Hz), 2.33s (6H, N-CH_3), 3.64s (2H, -CH_2-N, $^4J_{PbH}$ 16.1 Hz), 7.25m (1H, H_3, partially overlapped by $CDCl_3$ resonance), 7.32ddd (1H, H_4, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.3 Hz), 7.42ddd (1H, H_5, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.4 Hz), 8.31dd (1H, H_6, $^3J_{HH}$ 7.4, $^4J_{HH}$ 0.9, $^3J_{PbH}$ 115.5 Hz). ^{13}C NMR (75.4 MHz, 20 °C): δ 16.28s (Pb-CH_3), 45.39s (N-CH_3), 65.78s (-CH_2-N), 128.16s (C_3), 129.00s (C_4), 129.24s (C_5), 137.78s (C_6), 142.28s (C_2), 156.67s (C_1).

*Preparation of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Ph$_3$Pb (**2**)*

A suspension of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.69 g, 4.9 mmol) in hexane (30 ml) was added dropwise, under stirring, to a cooled (–78 °C) solution of Ph_3PbCl (1.9 g, 4.9 mmol) in hexane (50 ml). After the organolithium suspension was added, the reaction mixture was stirred for 1 h at –78 °C, and then left over night to reach the room temperature. The reaction mixture was filtered and the solvent was removed in vacuum from the clear filtrate. The white solid residue was recrystallized from hexane to give the title compound as colorless crystals. Yield: 1.1 g (47%), m.p. 245 °C. ^1H NMR (300 MHz, 20 °C): δ 1.76s (6H, N-CH_3), 3.35s (2H, -CH_2-N, $^4J_{PbH}$ 9.0 Hz), 7.39m (12H, $H_{3\text{-}5}$ + C_6H_5-*meta+para*), 7.69m (7H, H_6 + C_6H_5-*ortho*, $^3J_{PbH}$ 78.7 Hz). ^{13}C NMR (75.4 MHz, 20 °C): δ 44.96s (N-CH_3), 66.07s (-CH_2-N, $^3J_{PbC}$ 31.5 Hz), 127.78s (C_5, $^3J_{PbC}$ 92.9 Hz), 127.88s (C_6H_5-*para*, $^4J_{PbC}$ 18.2 Hz), 128.35s (C_4, $^4J_{PbC}$ 19.7 Hz), 129.05s (C_6H_5-*meta*, $^3J_{PbC}$ 78.1 Hz), 130.22s (C_3, $^3J_{PbC}$ 75.6 Hz), 137.38s (C_6H_5-*ortho*, $^2J_{PbC}$ 65.3 Hz), 138.51s (C_6, $^2J_{PbC}$ 78.1 Hz), 145.98s (C_2, $^2J_{PbC}$ 51.6 Hz), 151.59s (C_1, $^1J_{PbC}$ 579.8 Hz), 153.40s (C_6H_5-*ipso*, $^1J_{PbC}$ 484.8 Hz).

Preparation of $[2\text{-}(Et_2NCH_2)C_6H_4]Ph_3Pb$ (**3**)

A solution of Ph_3PbCl (2.52 g, 6.5 mmol) in hexane (20 ml) was added during 1 h to a stirred suspension of $[2\text{-}(Et_2NCH_2)C_6H_4]Li$ (1.1 g, 6.65 mmol) in hexane (50 ml), kept at –78 °C. The reaction mixture was stirred at this temperature for 1 h and then over night to reach the room temperature. The reaction mixture was filtered under argon and the solvent was removed in vacuum from the clear filtrate. The white solid residue was recrystallized from hexane to give the title compound as colorless crystals. Yield: 2.0 g (58%), m.p. 223 °C. ^1H NMR (300 MHz, 20 °C): δ 0.68t (6H, N-CH_2-CH_3, $^3J_{HH}$ 7.1 Hz), 2.20q (4H, N-CH_2-CH_3, $^3J_{HH}$ 7.1 Hz), 3.50s (2H, -CH_2-N, $^4J_{PbH}$ 10.6 Hz), 7.33m (12H, $H_{3\text{-}5}$ + C_6H_5-*meta+para*), 7.63m (7H, H_6 + C_6H_5-*ortho*, $^3J_{PbH}$ 79.4 Hz). ^{13}C NMR (75.4 MHz, 20 °C): δ 9.84s (N-CH_2-CH_3), 44.80s (N-CH_2-CH_3), 60.85s (-CH_2-N, $^3J_{PbC}$ 41.1 Hz), 127.53s (C_5, $^3J_{PbC}$ 90.2 Hz), 128.11s (C_6H_5-*para*, $^4J_{PbC}$ 18.4 Hz), 128.53s (C_4, $^4J_{PbC}$ 19.4 Hz), 129.19s (C_6H_5-*meta*, $^3J_{PbC}$ 78.4 Hz), 129.89s (C_3, $^3J_{PbC}$ 72.0 Hz), 137.49s (C_6H_5-*ortho*, $^2J_{PbC}$ 65.9 Hz), 138.19s (C_6, $^2J_{PbC}$ 77.5 Hz), 146.90s (C_2, $^2J_{PbC}$ 54.0 Hz), 151.02s (C_1, $^1J_{PbC}$ 542.0 Hz), 152.32s (C_6H_5-*ipso*, $^1J_{PbC}$ 472.2 Hz).

Preparation of $[2\text{-}(Me_2NCH_2)C_6H_4]Ph_2PbCl$ (**4**)

A suspension of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.69 g, 3.8 mmol) in hexane (30 ml) was added dropwise, under stirring, to a cooled (–78 °C) solution of Ph_2PbCl_2 (1.62 g, 3.77 mmol) in hexane (50 ml). After the organolithium suspension was added, the reaction mixture was stirred for 1 h at –78 °C, and then left over night to reach the room temperature. The reaction mixture was filtered and the solvent was removed in vacuum from the clear filtrate. The white solid residue was recrystallized from hexane to give the title compound as colorless crystals. Yield: 1.33 g (66%), m.p. 225 °C. ^1H NMR (300 MHz, 20 °C): δ 2.02s (6H, N-CH_3), 3.57s (2H, -CH_2-N, $^4J_{PbH}$ 16.4 Hz), 7.44m (9H, $H_{3\text{-}5}$ + C_6H_5-*meta+para*), 7.77 d (4H, C_6H_5-*ortho*, $^3J_{HH}$ 7.8, $^3J_{PbH}$ 111.6 Hz), 8.60d (1H, H_6, $^3J_{HH}$ 7.4, $^3J_{PbH}$ 130.7 Hz). ^{13}C NMR (75.4 MHz, 20 °C): δ 45.72s (N-CH_3), 65.32s (-CH_2-N, $^3J_{PbC}$ 38.5 Hz), 128.96s (C_3, $^3J_{PbC}$ 44.5 Hz), 129.47s (C_6H_5-*para*, $^4J_{PbC}$ 24.1 Hz), 129.57s (C_4, $^4J_{PbC}$ 24.8 Hz), 130.06s (C_6H_5-*meta*, $^3J_{PbC}$ 110.6 Hz), 136.01s (C_6H_5-*ortho*, $^2J_{PbC}$ 87.3 Hz), 138.51s (C_6, $^2J_{PbC}$ 70.7 Hz), 142.66s (C_2, $^2J_{PbC}$ 68.4 Hz), 154.45s (C_1, $^1J_{PbC}$ 826.6 Hz), 157.92s (C_6H_5-*ipso*, $^1J_{PbC}$ 726.3 Hz) (the resonance for C_5 carbon is overlapped by the resonance for the C_6H_5-*para* carbon).

Preparation of $[2\text{-}(Me_2NCH_2)C_6H_4]Ph_2PbI$ (**5**)

Method A. The chloride **4** (0.2 g, 0.45 mmol) was suspended in CH_2Cl_2 (20 ml) and solvent was added until the solid compound was completely solved. An aqueous solution of KI (0.375 g, 2.26 mmol, 500% excess) was then added and the obtained mixture was stirred for 3 h at room temperature. The organic layer was separated from the water layer and the latter was washed with CH_2Cl_2 (2 x 5 ml). The organic solution was dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the remaining yellow material was recrystallized from a CH_2Cl_2/hexane mixture to give the title compound. Yield: 0.22 g (91%).

Method B. Compound **2** (0.2 g, 0.4 mmol) was suspended in CH_2Cl_2 (20 ml) and solvent was added until the solid compound was completely solved. A solution of iodine (0.1 g, 0.4 mmol) in CH_2Cl_2 was added and the mixture was stirred for 2 h at room temperature. The solvent was removed under vacuum and the remaining yellow solid was recrystallized from a CH_2Cl_2/hexane mixture to give the title compound. Yield: 0.15 g (68%), m.p. 236 °C. ^{1}H NMR (300 MHz, 20 °C): δ 1.95s (6H, N-CH_3), 3.54s (2H, -CH_2-N, $^4J_{PbH}$ 15.0 Hz), 7.42m (9H, H_{3-5} + C_6H_5-*meta+para*), 7.77dd (4H, C_6H_5-*ortho*, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.2, $^3J_{PbH}$ 111.6 Hz), 8.66dd (1H, H_6, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.0, $^3J_{PbH}$ 134.4 Hz). ^{13}C NMR (75.4 MHz, 20 °C): δ 45.72s (N-CH_3), 65.18s (-CH_2-N, $^3J_{PbC}$ 33.3 Hz), 128.86s (C_3), 129.29s (C_6H_5-*para*), 129.55s (C_4), 129.61s (C_5), 129.96s (C_6H_5-*meta*, $^3J_{PbC}$ 108.7 Hz), 135.88s (C_6H_5-*ortho*, $^2J_{PbC}$ 84.3 Hz), 140.67s (C_6, $^2J_{PbC}$ 74.0 Hz), 142.61s (C_2), 150.51s (C_1), 157.21s (C_6H_5-*ipso*).

*Preparation of [2-(Et_2NCH_2)C_6H_4]Ph_2PbI (**6**)*

Compound **3** (0.25 g, 0.4 mmol) was suspended in CH_2Cl_2 (20 ml) and solvent was added until the solid compound was completely solved. A solution of iodine (0.1 g, 0.4 mmol) in CH_2Cl_2 was added and the mixture was stirred for 2 h at room temperature. The solvent was removed under vacuum and the remaining yellow solid was recrystallized from a CH_2Cl_2/hexane mixture to give the title compound. Yield: 0.18 g (67%), m.p. 223 °C. ^{1}H NMR (300 MHz, 20 °C): δ 0.69t (6H, N-CH_2-CH_3, $^3J_{HH}$ 7.1 Hz), 2.30q (4H, N-CH_2-CH_3, $^3J_{HH}$ 7.1 Hz), 3.63s (2H, -CH_2-N, $^4J_{PbH}$ 12.8 Hz), 7.44m (9H, H_{3-5} + C_6H_5-*meta+para*), 7.78d (4H, C_6H_5-*ortho*, $^3J_{HH}$ 7.4, $^3J_{PbH}$ 110.7 Hz), 8.66d (1H, H_6, $^3J_{HH}$ 7.4, $^3J_{PbH}$ 129.9 Hz).

X-ray Crystallographic Study

Data were collected with a SMART APEX diffractometer (*National Center for X-Ray Diffractometry*, “Babes-Boyai” University, Cluj-Napoca, Romania) at 297 K, using a graphite monochromator to produce a wavelength (Mo-$K\alpha$) of 0.71073 Å. The crystal structure measurement and refinement data for compounds **2** and **4** are given in Table 3. Absorption correction was applied for **2** (semi-empirical from equivalents). The structure was solved by direct methods (full-matrix least-squares on F^2). All non hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement a software package SHELX-97 was used [29]. The drawings were created with the Diamond program [30].

Table 3. Crystallographic data for compounds **2** and **4**.

	2	**4**
chemical formula	$C_{27}H_{27}NPb$	$C_{21}H_{22}ClNPb$
crystal habit	colorless block	colorless block
crystal size [mm]	0.30 x 0.20 x 0.15	0.20 x 0.19 x 0.18
crystal system	monoclinic	monoclinic
space group	*P2(1)/c*	*P2(1)/n*
a [Å]	9.5351(12)	9.3153(5)
b [Å]	27.172(3)	24.2365(13)
c [Å]	10.1510(12)	17.8184(10)
α [deg]	90	90
β [deg]	117.036(2)	97.286(1)
γ [deg]	90	90
U [Å^3]	2342.6(5)	3990.4(4)
Z	4	8
D_c [g cm^{-3}]	1.624	1.768
M	572.69	531.04
F(000)	1112	2032
θ range [deg]	1.50 – 25.00	1.43 – 25.00
μ(Mo Kα) [mm^{-1}]	7.214	8.591
no. of reflections collected	16748	28670
no. of independent reflections	4114 (R_{int} = 0.0534)	7016 (R_{int} = 0.0463)
R_1 [$I > 2\sigma(I)$]	0.0490	0.0567
wR_2	0.0955	0.1048
no. of parameters	264	437
no. of restraints	0	0
GOF on F^2	1.133	1.292
largest difference electron density [e Å^{-3}]	0.987, –2.018	1.768, –1.675

CCDC-750465 (**2**) and -750466 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

ACKNOWLEDGEMENTS

We thank the Ministry of Education and Research of Romania (CNCSIS, Research Project No. 709/2007 and TD-342/2007) for financial support. We also thank the NATIONAL CENTER FOR X-RAY DIFFRACTION (”Babes-Bolyai” University, Cluj-Napoca, Romania) for the support in the solid state structure determinations.

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