Synthesis and Characterization of a Stable Organolead(II) Compound: Bis[2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]lead†

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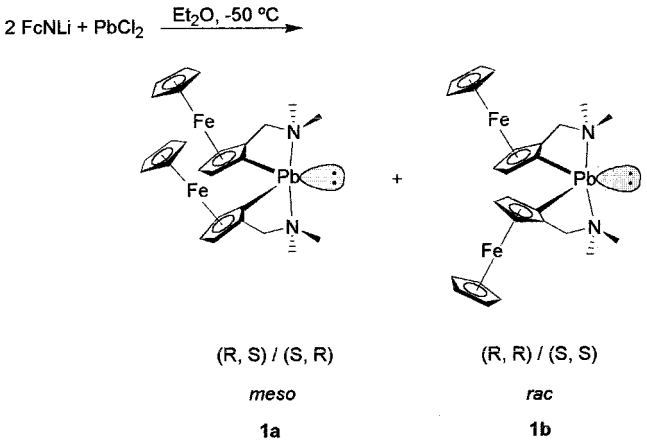
Summary: *The reaction of {C,N-[Fe(η^5-C_5H_5)(η^5-C_5H_3-(CH_2NMe_2)-2)]}Li, [FcN]Li, with $PbCl_2$ yields the new stable tetracoordinated diorganolead(II) compound $[FcN]_2Pb$, **1**, as a mixture of two diastereomers. In the solid state only the meso-diastereomer exists, which crystallizes in two polymorphs, $P2_1/c$ and $C2/c$. The ratio of meso/rac-diastereomers in solution is solvent- and temperature-dependent, consistent with an intermolecular exchange between diastereomers. This is the very first observation of such an exchange for lead(II) compounds. An intramolecular exchange process is responsible for equivalency of both FcN groups in solution. The NMR measurements of **1** revealed the authentic spectroscopical data: $^{13}C-^{207}Pb$ coupling constants in solid-state ^{13}C NMR spectra.*

Introduction

The chemistry of divalent organolead compounds, in which the organic groups are σ-bonded to the metal, was until recently very poorly investigated in comparison to lead(IV) organometallic chemistry. Although Lappert et al.[1] reported the isolation of the very first plumbylene $Pb[CH(SiMe_3)_3]_2$ already in 1973, its structure has not been determined yet.[2,3] The difficulty in isolating these compounds is their facile disproportionation to elemental lead and hexaorganodilead compounds. The few plumbylenes that could be isolated owe their stability to either steric shielding by voluminous alkyl[4] or aryl[2,5,6] groups, intramolecular stabilization,[2,7,8] or formation of diplumbenes.[7,9] We now report on the formation and characteristics of a new stable diorganolead(II) compound, $\{C,N\text{-}[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3(CH_2NMe_2)\text{-}2)]\}_2Pb$, $[FcN]_2Pb$, **1**, which is stabilized by intramolecular Pb−N interactions.

Scheme 1



Results and Discussion

The reaction of $PbCl_2$ with 2 equiv of [FcN]Li in diethyl ether yields a solution of **1** (Scheme 1). The ^1H and ^{13}C NMR data of **1** in C_6D_6 at 25 °C (after taking a sample and removal of ether in vacuo) show that $[FcN]_2Pb$ appears in solution as a mixture of diastereomers **1a** and **1b**, respectively, in the ratio of 7:1. After cooling the solution, only the major diastereomer **1a** crystallizes in the form of large deep-red prisms in 75% yield. The compound can be handled in air for a few minutes, but in solution it decomposes immediately when exposed to air. It is thermally stable to its melting point (123 °C). The EI mass spectrum shows a molecular peak at *m*/*z* 692 with 80% relative intensity. **1** is readily soluble in both polar and nonpolar solvents.

X-ray diffraction analysis revealed two monoclinic polymorphs of **1a**, with different space groups, $P2_1/c$ (Figure 1) and $C2/c$. Both polymorphs were obtained from the same crystallization. The structures are virtually identical. In the discussion below, the data of the

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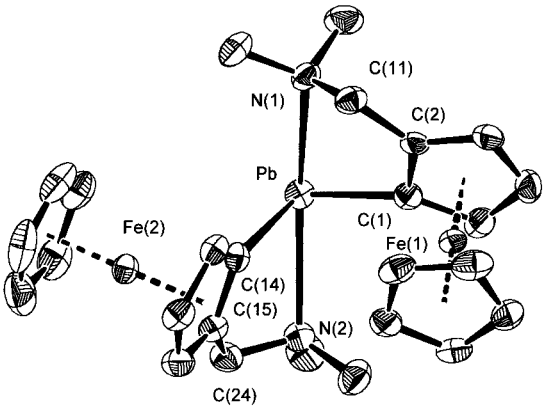

Figure 1. Molecular structure of **1** ($P2_1/c$ polymorph) with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [FcN]$_2$Pb, 1a

	$P2_1/c$	$C2/c$
Pb−C1	2.311(4)	2.301(4)
Pb−C14	2.284(4)	2.298(5)
Pb−N1	2.684(4)	2.708(5)
Pb−N2	2.728(4)	2.661(4)
C1−Pb−C14	94.8(1)	95.2(2)
N1−Pb−N2	158.6(1)	157.7(1)
C1−Pb−N1	71.5(1)	70.8(2)
C14−Pb−N2	71.3(1)	71.8(2)
C1−Pb−N2	96.5(1)	96.9(2)
C14−Pb−N1	91.6(1)	90.7(2)
Pb−N1−C11	103.7(3)	103.9(4)
Pb−N1−C12	114.9(3)	115.9(3)
Pb−N1−C13	106.4(3)	105.8(3)
Pb−N2−C24	99.2(2)	103.6(6)
Pb−N2−C25	115.4(3)	113.3(4)
Pb−N2−C26	111.4(3)	107.9(4)
Pb−C1−C2	115.3(3)	116.1(3)
Pb−C14−C15	114.8(3)	115.1(3)
Pb−C1−C5	136.4(3)	138.2(4)
Pb−C14−C18	139.2(3)	137.1(4)
C−N−C (mean)	110.4(3)	110.0(6)

centric monoclinic modification will be given in parentheses. Selected geometrical data of both polymorphs are listed in Table 1. The crystal structure in both polymorphs is built up from discrete monomers. The FcN ligand is chiral; in **1a** one of the ligands is in *R*- and the other in *S*-configuration (*meso*-diastereomer), and therefore it is assumed that the other, minor diastereomer **1b** possesses a set of *R*,*R* (or *S*,*S*)-configurated FcN ligands (*rac*-diastereomer). The shortest Pb−Pb separation is 6.74 Å, which is beyond bonding distance. The Pb−Pb distance in the second polymorph (5.54 Å) is significantly shorter and might indicate a weak interaction in the solid state reminiscent of other metal−metal bonded dimeric plumbylenes.[2,10,11] The lead atom is four-coordinated with two chelating *C*,*N*-bonded FcN groups. The molecule has a distorted trigonal bipyramidal geometry in which the localized lone pair occupies one of the equatorial positions, and the amino groups are axial. The N1−Pb−N2 angle is 157.6(1)° [157.7(1)°]. The distortion is mainly caused by the lead electron lone pair, which is in agreement with the VSEPR principle. It leads to an acute C1−Pb−C14 angle of 95.1(6)° [94.8(4)°]. The Pb−N bond lengths of 2.638(6) and 2.727(5) Å [2.660(5) and 2.707(5) Å] are significantly longer than those in nitrogen-centered lead(II) compounds, e.g., 2.24(2) Å in Pb[N(SiMe$_3$)$_2$]$_2$[12] or 2.465 Å (av) in Pb[{N(SiMe$_3$)$_2$}PPh$_2$]$_2$,[13] but may be compared to those of 2.678 Å (av) in Pb[CH$_2$PMe$_2$=NSiMe$_3$]$_2$.[8] The Pb−C(sp^2) bond lengths of 2.310(9) and 2.283(6) Å [2.301(2) and 2.298(1) Å] correspond well to the Pb−C(sp^2) distance of 2.336 Å in Pb[C$_6$H$_2$(CF$_3$)$_3$-2,4,6]$_2$[5] and that of 2.296(4) Å in {(2,4,6-*i*Pr$_3$C$_6$H$_2$)[(SiMe$_3$)$_3$Si]Pb}$_2$.[9] The small bite angle of the FcN ligand (C−Pb−N is about 71°) causes distortion around the α-carbon and nitrogen atoms. Whereas the C−N−C angles have ideal values, the Pb−N1−C11 and Pb−N2−C24 angles (103.6(6)° [103.9(4)°] and 99.2(2)° [103.6(5)°], respectively) are smaller than the other Pb−N−C angles. Similarly, the C2−C1−Pb and C15−C14−Pb (115.3(1)° [116.0(7)°] and 114.7(6)° [115.1(2)°], respectively) are smaller than the C5−C1−Pb and C18−C14−Pb angles (136.3(8)° [138.2(4)°] and 139.1(7)° [137.1(1)°], respectively).

Solid-state ^{13}C MAS NMR measurements at 25 °C confirmed the results of the X-ray diffraction analysis. In the solid state only one diastereomer, *meso*-[FcN]$_2$Pb, **1a**, is present. Due to the unequivalency of the FcN groups, there is one set of signals for each group. Four slightly broadened signals for the methyl groups are present. The signals of the α-carbon atoms appear at 148.8 and 157.1 ppm, with coupling constants $^1J_{C,Pb}$ of 1260 and 1340 Hz, respectively [^{207}Pb has 22.7% abundance]. This is a rare example of ^{13}C,^{207}Pb coupling constants of plumbylene compounds determined in solid-state NMR measurements.

The ^{1}H and ^{13}C NMR data in C$_6$D$_6$ at 25 °C show only one set of signals for both FcN groups in each diastereomer, indicating intramolecular dynamics. In the ^{13}C-{^{1}H} NMR spectrum (C$_6$D$_6$, rt) several signals of both diastereomers are attended by satellites, due to coupling with ^{207}Pb. The chemical shift of the α-carbon atom of the main diastereomer **1a**, which appears at 151.1 ppm, shows a coupling constant $^1J_{C,Pb}$ = 1305 Hz. These data correspond nicely with the solid-state NMR data (vide supra). The only literature data are from Stürmann et al.,[2] with a value of 1288 Hz in a diarylplumbylene. Further couplings are found for the signal at 46.3 ppm attributed to the NMe$_2$ group ($^2J_{C,Pb}$ = 21 Hz) and for the signals of the substituted Cp ring at 70.1 ppm (J = 33 Hz), 70.2 ppm (J = 47 Hz), and 78.2 ppm (J = 58 Hz). Due to its low abundance, satellites for the minor diastereomer **1b** were only observed for the signal of the methyl groups at 46.7 ppm ($^2J_{C,Pb}$ = 19 Hz) and for the α-carbon atom at 148.4 ppm ($^1J_{C,Pb}$ = 1272 Hz). The coupling constants are very similar to those of **1a**. By comparing the chemical shifts in the solution NMR spectra with those in the solid-state NMR spectrum, it is concluded that *meso*-[FcN]$_2$Pb is the main diastereomer **1a**.

At −50 °C in toluene-d_8 the signals of methyl and methylene groups of **1a** are slightly broadened. At −80 °C there are two signals for the methyl groups of **1a** in a ratio of 1:3 at 1.94 and 2.25 ppm, respectively. As one

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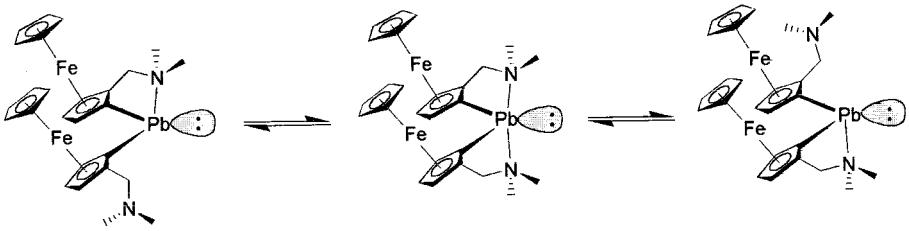
Scheme 2



expects four signals for these groups, the chemical shifts of three methyl groups probably coincide. The signals of the methylene groups are split into four doublets. The signal of the C_5H_5 group is also split into two signals at 3.91 and 4.21 ppm. We could not observe the decoalescence of the methyl signals of **1b**, because of overlap with signals of the *meso*-diastereomer. Due to C_2 symmetry, only two signals for the methyl groups should be seen. The temperature-dependent NMR data can be explained by a rapid dissociation of one of the Pb−N bonds and recoordination (Scheme 2).

As mentioned before, solution NMR data show the presence of both diastereomers, in contrast to the solid-state NMR data. Their ratio measured in different solvents (C_6D_6, toluene-d_8, $CDCl_3$, THF-d_8) at 25 °C was within the range 6:1 to 8:1. The ratio is temperature-dependent as well and suggests an intermolecular exchange between diastereomers. The proportion of **1a** is higher at lower temperatures. To our knowledge, this is the first observation of such a process for plumbylene compounds. The equilibrium constant K (**1a**/**1b**) gradually changes from 4.8 at +90 °C to 22.2 at −80 °C in toluene-d_8. Plotting ln K against $1/T$ gives a straight line (r = 0.998) from which the thermodynamical parameters ΔH = 5.1 kJ mol^{-1} and ΔS = 0.99 J K^{-1} mol^{-1} were obtained.

Two mechanistic pathways can be considered for the observed intermolecular exchange. Both of them invoke at first the interaction of two $[FcN]_2Pb$ units. In the first one, this is followed by a concerted intramolecular migration of two σ-bonded FcN groups. That is, a dyotropic rearrangement of two FcN groups, as considered probable for a similar exchange of aryl groups in tetraaryldisilenes.[14] In the second one, the migration of only one FcN group generates a zwitterionic form, followed by the shift of a second FcN group back to the incipient lead atom. The unimolecular mechanism of the interconversion is considered to be highly unlikely, because it should involve a 1,3-exchange along the Cp ring of a C−Pb bond against a C−H bond, to convert one enantiomer of the FcN ligand into the other.

In corroborating the stabilizing effect of the CH_2NMe_2 side chain in **1**, we reacted 2 equiv of ferrocenyllithium, FcLi, with $PbCl_2$ in ether. No Fc_2Pb is formed; instead decomposition took place with formation of ferrocene (FcH), elemental lead, and LiCl. In the presence of triethylborane $[FcN]_2Pb$ decomposed after a few hours at room temperature. The weak B→N coordination is obviously strong enough to decompose the compound **1** completely. With methanol-d_4 **1** reacted immediately, giving a white precipitate of Pb(II) methanolate and a solution of (1-deuterio)(2-*N*,*N*-dimethylaminomethyl)-ferrocene, FcND. $[FcN]_2Pb$ can also act as an organylating reagent: reaction with $HgCl_2$ afforded $[FcN]_2Hg$[15] as a 1:1 mixture of diastereomers.

Using cyclic voltammetry $[FcN]_2Pb$ in CH_2Cl_2 undergoes a single-stepped two-electron oxidation at $E^{\circ\prime}$ = +0.40 V (accompanied by yellow-to-blue color change) having features of chemical reversibility (at 0.05 V s^{-1} Δe_p = 80 mV, blue-to-yellow change accompanies reduction). The redox process takes place on the FcN ligand of $[FcN]_2Pb$ and not on the Pb center of the molecule. The oxidation potential may be compared with that of free FcNH, which oxidizes reversibly at $E^{\circ\prime}$ = +0.38 V; in addition, the blue color is typical for the formation of ferricinium cation. After several cycles of exhaustive oxidation/reductions the compound decomposes.

As **1** is a nonreducing reagent, it might be a promising starting material for the synthesis of early transition metal complexes bearing the FcN ligand.

Experimental Part

General Comments. All operations were carried out under a purified argon atmosphere in Schlenk tubes. Solvents used in reactions were distilled under argon and carefully dried over conventional drying agents.

The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Varian GEMINI XL-300 spectrometer, the ^{1}H low-temperature NMR spectra on a Varian Unity 500. ^{13}C MAS NMR spectra were recorded on a Varian INOVA 400 MHz. Mass spectra were recorded on a AMD 402 by EI at 70 eV. Materials and apparatus for electrochemistry have been described elsewhere;[16] all potential values are referenced to the saturated calomel electrode.

The organolithium reagents FcNLi[17] and FcLi[18] were prepared as solids as previously described.

Bis[2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]lead (1). To a suspension of FcNLi (5.48 g, 22.0 mmol) in 250 mL of diethyl ether cooled at −50 °C was slowly added a suspension of $PbCl_2$ (2.79 g, 10.0 mmol) in 100 mL of diethyl ether with vigorous stirring. The reddish reaction mixture was stirred overnight, being allowed to warm to room temperature. LiCl was filtered off and the filtrate stripped to dryness. The deep-red solid was isolated by exhaustive extraction of the residue with pentane. Yield: 80%. Anal. Calcd for $C_{26}H_{32}N_2Fe_2Pb$: C, 45.18; H, 4.63; N, 4.05. Found: C, 45.21; H, 4.76; N, 3.90. NMR data for **1a** (**1b** in brackets): ^{1}H NMR (C_6D_6, 25 °C): δ 2.22 [2.29] (12H, NMe_2), 2.86 [2.80] (d, 2H, CH_2N, $^1J_{C,H}$ = 13 Hz [14 Hz]), 3.93 [3.71] (d, 2H, CH_2N, $^1J_{C,H}$ = 13 Hz [14 Hz]), 3.91 [4.31] (2H, C_5H_3), 3.95 [4.32] (2H, C_5H_3), 4.02 (10H, C_5H_5), 4.12 [4.33] (2H, C_5H_3). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 46.3 [46.7] (NMe_2, $^2J_{C,Pb}$ = 21 Hz [19 Hz]), 63.5 [62.8] ($-CH_2N$), 69.0 [68.8]

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(C_5H_5), 70.1 [70.4] (C_5H_3, $J_{C,Pb}$ = 33 Hz), 70.2 [70.4] (C_5H_3, $J_{C,Pb}$ = 47 Hz), 78.2 [78.1] (C_5H_3, $J_{C,Pb}$ = 58 Hz), 97.8 [98.2] ($C_5H_3-CH_2NMe_2$), 152.1 [147.3] ($Pb-C_5H_3$, $^1J_{C,Pb}$ = 1305 Hz [1276 Hz]). Solid-state ^{13}C MAS NMR: δ 44.7/48.4 (NMe_2), 62.6/63.7 (CH_2N), 68.9/69.3 (C_5H_5), 70.0/77.2 (C_5H_3), 79.1 (C_5H_3), 97.1/100.1 ($C_5H_3-CH_2NMe_2$), 148.8 ($^1J_{C,Pb}$ = 1260 Hz)/ 157.1 ($Pb-C_5H_3$, $^1J_{C,Pb}$ = 1340 Hz). ^1H NMR (toluene-d_8, −80 °C): 1.94 (9H, NMe_2) 2.17 (3H, NMe_2) [2.25 (12H, NMe_2)], 2.63 (d, 1H, CH_2N, $^1J_{C,H}$ = 13 Hz) 2.86 (d, 1H, CH_2N, $^1J_{C,H}$ = 13 Hz) [2.72 (d, 2H, CH_2N, $^1J_{C,H}$ = 14 Hz)], 3.82 (d, 1H, CH_2N, $^1J_{C,H}$ = 13 Hz) [3.63 (d, 2H, CH_2N, $^1J_{C,H}$ = 14 Hz)], 3.91 (5H, C_5H_5), 4.21 (5H, C_5H_5), 3.95 [4.10] (2H, C_5H_3), 4.18 [4.32] (2H, C_5H_3), 4.44 [4.38] (2H, C_5H_3). MS (EI, 70 eV): *m*/*z* 692 (M^+, 80), 484 (($FcN)_2$, 70), 450 (FcNPb, 100), 242.8 (FcN, 35).

Reaction of $[FcN]_2Pb$ with CD_3OD. The $[FcN]_2Pb$ was dissolved in CD_3OD, and the white precipitate, presumably $(CD_3O)_2Pb$, was filtered off. From the solution ^1H and ^{13}C NMR spectra were taken, and the product was identified as (1-deuterio)(2-*N*,*N*-dimethylaminomethyl)ferrocene, FcND. ^1H NMR (CD_3OD, rt): 2.20 (6H, NMe_2), 3.38 (2H, CH_2N), 4.17 (5H, C_5H_5), 4.18 (2H, C_5H_3), 4.25 (1H, C_5H_3).

Reaction of $PbCl_2$ with FcLi. To the suspension of $PbCl_2$ (1.45 g, 5.2 mmol) in 50 mL of diethyl ether cooled at −50 °C was slowly added a suspension of FcLi (2.00 g, 10.4 mmol) in 100 mL of diethyl ether with vigorous stirring. After stirring the reaction mixture for 2 h and warming to room temperature, a dark gray precipitate was formed. It was filtered off and washed out with water to remove LiCl and dried in vacuo (0.85 g, 96% calcd on Pb). It was identified as elemental lead on the basis of the following experiments: a sample was dissolved in diluted HNO_3 and neutralized with soda, and the following reactions were done: with H_2SO_4 a white powder ($PbSO_4$) precipitated, with K_2CrO_4 a yellow one ($PbCrO_4$), and by adding of NaOH solution a white precipitate ($Pb(OH)_2$) was formed. The orange filtrate contained ferrocene, FcH. ^1H NMR (C_6D_6, rt): 4.16 (10H, C_5H_5).

Reaction of $[FcN]_2Pb$ with BEt_3. Triethylborane (0.21 mL, 1.4 mmol) was added to a solution of $[FcN]_2Pb$ (0.50 g, 0.7 mmol) in 3 mL of C_6D_6 with stirring at room temperature, and the reaction followed by NMR. The orange color of the solution was slightly discharged. After 2 h decomposition was complete, and elemental lead and FcNH had formed.

Crystal Structure Determination. Data were collected on a STOE IPDS diffractometer using Mo *K*α radiation (0.71073 Å) and corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct phase determination with SHELXS-97[19] and refined by a full-matrix least-squares refinement on F^2 with anisotropic temperature factors for all non-hydrogen atoms and isotropic factors for all hydrogen atoms using SHELXL-97.[20] All hydrogen atoms were found in the difference Fourier map.

Crystal data for *meso*-bis[2-(*N*,*N*-dimethylaminomethyl)-ferrocenyl]lead (the data for the other polymorph are given in brackets): $C_{26}H_{32}N_2Fe_2Pb$, **1a**, M = 691.43, monoclinic, $P2_1/c$ [$C2/c$], a = 11.643(4) [19.239(5)] Å, b = 10.994(3) [19.628(2)] Å, c = 20.086(6) [24.756(6)] Å, β = 104.54(4) [103.95(3)]°, Z = 4 [8], V = 2488.1(13) [4913(2)] Å^3, T = 193 K, μ = 7.916 [8.018] mm^{-1}, specimen 0.3 × 0.6 × 0.8 [0.1 × 0.3 × 0.4] mm, 22 778 [16 388] collected reflections, R1 = 0.0268 [0.0290] for 4664 [4773] [$I > 2\sigma(I)$], wR2 = 0.0676 (for all data) [0.0723].

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Supporting Information Available: Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, anisotropic displacement coefficients, and crystal packing diagrams for the two polymorphs of **1a**, as well as a figure of a molecular structure of the *C*2/*c* polymorph. Ordering information is given on any current masthead page.

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