Unique Coordination of Two C=C Double Bonds to an Electron-Deficient Lead Center

Thomas Müller,*[a] Christian Bauch,[a] Michael Bolte,[b] and Norbert Auner*[a]

Abstract: Reaction of bis(cyclopentenemethyl)diethylplumbane (**2**) with trityl cation leads to the formation of the plumbyl cation bis(cyclopentenemethyl)plumbylium (**1**), in which the positively charged lead atom interacts with the two C=C double bonds of the cyclopentene ligands. The plumbyl cation **1** is characterized by NMR spectroscopy ($\delta(^{207}Pb) = 807$ ppm, $\delta(^{13}C(C{=}C)) = 136.1$ ppm, $^{1}J(Pb,C{=}C) = 14.4$ Hz) and X-ray crystallography. The structure of **1** reveals a distorted trigonal-bipyramidal coordination sphere for the lead atom with a unique coordination of two C=C double bonds in apical positions. According to quantum-mechanical calculations (MP2/6-311G(d,p) (C, H), SDD (Pb)//MP2/6-31G(d), SDD (Pb)) this interaction stabilizes **1** by 28.3 kcal mol^{-1} relative to the tricoordinated plumbylium ion **10**. An "atoms in molecules" (AIM) analysis indicates a π-type interaction between the lead atom and the C=C double bonds, reminiscent of that in the 2-norbornyl cation.

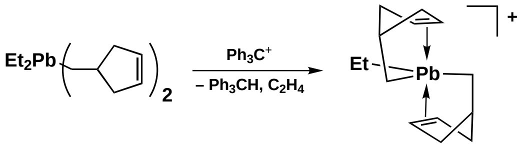
Keywords: alkene ligands · cations · computer chemistry · lead · NMR spectroscopy

Introduction

Intramolecularly stabilized triorgano-substituted cations of the heavier analogues of carbon have recently received considerable attention.[1, 2] Many examples with the central element stabilized by interaction with remote donor substituents having lone pairs are known, and this interaction leads to tetra-, and pentacoordination for the formally positively charged element atom.[3, 4] We have previously shown that the stabilization with a π-donor ligand, as it is provided in the norbornyl framework, is sufficient to generate and characterize organo-substituted cations of the Group 14 elements.[5, 6] This methodology is now extended to form a cationic pentacoordinated complex of lead **1** (see Scheme 1), which is intramolecularly stabilized by two C=C double bonds.

Results and Discussion

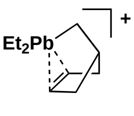
The synthesis of the plumbyl cation **1** exploits remote attack of a strong electrophile on an ethylplumbane. The cation **1** is formed from the bis(cyclopentenemethyl)plumbane **2** after hydride abstraction by trityl cation and ethene elimination (Scheme 1).[5, 7] Solutions of the salt **1**-[$B(C_6F_5)_4$] in dry [D_8]toluene are stable at room temperature for several weeks.



2 **1**

Scheme 1. Formation of plumbyl cation **1**.

During the synthesis of cation **1**, the plumbanorbornyl cation **3**[8a] and a third compound to which we assign structure **4**[9] are formed as minor by-products with varying yields (5–10 %). These cations are formed from triethyl(cyclopentenemethyl)lead (**5**)[8a] and from ethyltris(cyclopentenemethyl)lead, (**6**).[8b] Both plumbanes **5** and **6** are formed readily by a



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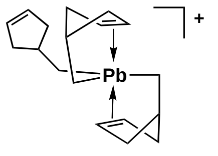

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fast ligand-exchange reaction[10] of the precursor **2** upon standing even at temperatures as low as –30 °C (Scheme 2).

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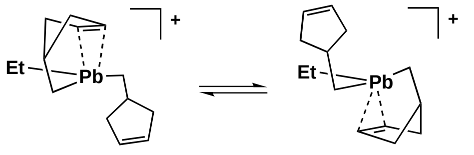
Scheme 2. Ligand disproportionation reaction of plumbane **2**.

Therefore, **3** and **4** are unavoidable by-products in the synthesis of cation **1**.

^{1}H, ^{13}C, and ^{207}Pb NMR spectra confirm the formation of cation **1**. The ^{207}Pb NMR signal for **1** is strongly shifted downfield compared to that of the precursor plumbane **2**($\delta(^{207}Pb) = 807$, $\Delta\delta(^{207}Pb(\mathbf{1}, \mathbf{2})) = 777$ ppm) indicating positive charge accumulation at the lead atom. It is, however, significantly less deshielded than the lead atom in the triethylplumbylbenzenium ion, $[Et_3PbC_6H_6]^+$ (**7**) ($\delta(^{207}Pb) = 1432$ ppm),[5] which rules out the possibility of the formation of a trialkylplumbylbenzenium ion in our experiment.

In addition, the appreciable difference in the ^{207}Pb NMR chemical shift between the spirocation **1** and the plumbanorbornyl cation **3**, ($\delta(^{207}Pb) = 1039$ ppm,[5] $\Delta\delta(^{207}Pb(\mathbf{1},\mathbf{3})) = 232$ ppm) discards a conceivable degenerate equilibrium of plumbanorbornyl cations **8** (Scheme 3), for which a ^{207}Pb NMR chemical shift near to that of **3** is to be expected.



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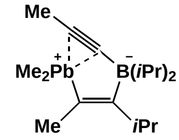
Scheme 3. Degenerate equilibrium between plumbanorbornyl cations **8**.

The presence of only six ^{13}C NMR signals for **1** suggest that both cyclopentenemethyl substituents in **1** are equivalent in solution and indicate a symmetric structure for **1**. The ^{13}C NMR chemical shifts of the saturated carbon atoms C2–C5 are typical for the norbornyl cage and are similar to those found for the norbornyl cation **3**.[5] The position of the ^{13}C NMR signal of the vinylic carbon atoms C6/C7 ($\delta(^{13}C(C6/7)) = 136.1$ ppm) is highly diagnostic for the bridged structure of the cation **1**. The small but significant lowfield shift ($\Delta\delta(^{13}C(C6/7))$, compared to the precursor plumbane **2** ($\Delta\delta(^{13}C(C6/7)) = 5.9$ ppm) is consistent with intramolecular coordination of the double bonds to the positively charged lead atom and indicates charge transfer from the element to the carbon atoms C(6/7). The direct bonding between the lead atom and the vinylic carbon atoms C6/7 is demonstrated by a significant scalar coupling constant ($^{1}J(C,Pb) = 14.4$ Hz) since an alternative coupling path along four bonds can not lead to substantial scalar coupling.[11] The observed $^{1}J(C,Pb)$ coupling is an order of magnitude smaller than regular couplings along a C–Pb single bond ($^{1}J(C,Pb) = 200–300$ Hz),[11] a fact that can be rationalized by the particular bonding situation in cation **1**. Similar strongly reduced $^{1}J(C,Pb)$ coupling constants have been found for zwitterionic compounds of the type **9** ($^{1}J(C,Pb) = 11–30$ Hz)[12] and for the norbornyl cation **3** ($^{1}J(C,Pb) = 16.2$ Hz).[5] An additional indication for the direct bonding between the lead atom and the vinyl groups is given by the small scalar coupling between the vinyl hydrogen atoms and the lead center ($^{2}J(H,Pb) = 18.8$ Hz).



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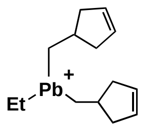

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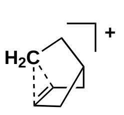

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Crystals of **1** suitable for X-ray structure analysis were grown under solvothermal conditions in pentane. The structure of the salt, **1**-$[B(C_6F_5)_4]$, reveals well-separated cations and anions. No fluorine atom of the anion is closer than 380 pm to the lead atom. The lead atom in cation **1** has a distorted trigonal-bipyramidal coordination geometry (Figure 1). The planarity of the trigonal base is indicated by summation of the three C-Pb-C angles (123.9, 119.9 and 116.2⁰) to 360.0⁰. The coordination sphere of lead is completed by the C=C double bonds of the two cyclopentenemethyl substituents, which take up the apical positions. The steric requirements of this intramolecular interaction enforces the deviations from the ideal trigonal-bipyramidal coordination. That is: 1) the axis along the centers of the two C=C double bonds is tilted by 14° towards the basal C_3Pb plane, and 2) the centers form an angle α, which differs markedly from 180° ($\alpha = 163.6°$, Figure 1), with the central lead atom. This spatial arrangement places seven carbon atoms at distances less than 290 pm around the positively charged lead atom.

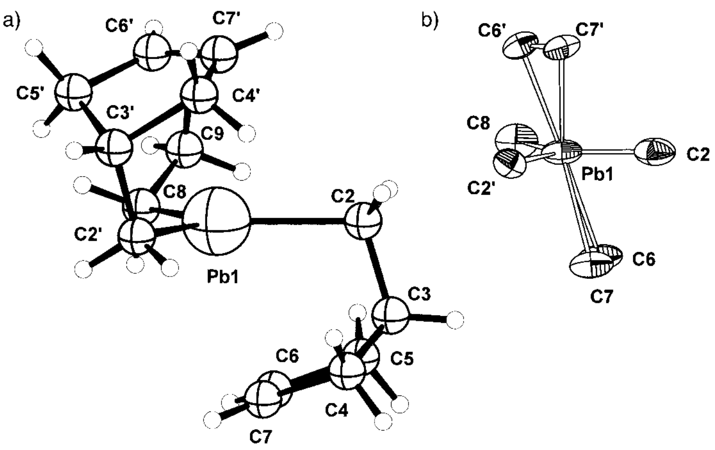

Figure 1. a) Molecular structure of cation **1** in the crystal. b) Coordination sphere of the lead atom in cation **1**. Selected interatomic distances [pm] and angles [°]: Pb1–C6 285.5(14), Pb1–C7 293.4(14), Pb-(center C6, C7) 281.7, Pb1–C6′ 287.7(15), Pb1–C7′ 287.7(15), Pb-(center C6′, C7′) 280.7, Pb1–C2 227(2), Pb1–C2′ 221.1(15), Pb1–C8 231.0(19), C6–C7 133(2), C6′–C7′ 132(2); C6-Pb-C7 26.6(4), C6′-Pb-C7′ 26.4(4), C2-Pb-C8 123.9(7), C8-Pb-C2′ 116.2(6), C2′-Pb-C2 119.9(6), (center C6, C7)-Pb-(center C6′, C7′) 163.6.

A comparison of the calculated structure[13] of cation **1** (at the MP2/6-31G(d) (C,H), SDD(Pb) level of theory, see Figure 2a)[14, 15] and the solid-state structure reveals a close agreement: the important bond lengths around the lead center deviate in the theoretical structure by less than 3% from the experimental data, thereby validating the theoretical

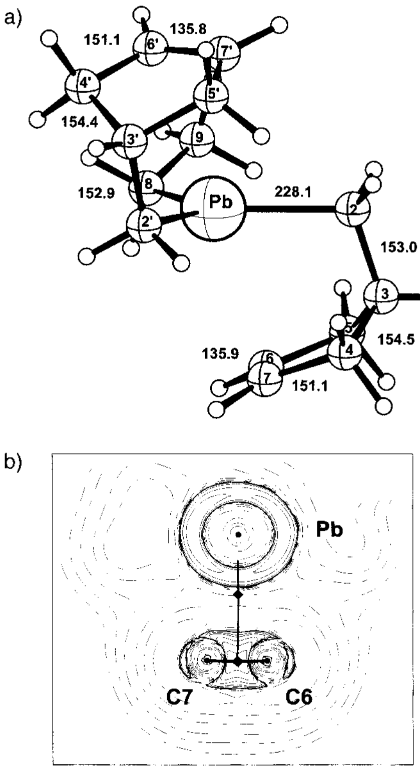

Figure 2. a) Calculated structure of **1** (at MP2/6–31G(d) (C,H), SDD (Pb)). Additional interatomic distances [pm] and angles [°]: Pb–C6 294.0, Pb–C7 294.5, Pb–(center C6, C7) 286.3, Pb–C6′ 296.3, Pb–C7′ 295.0, Pb–(center C6′, C7′) 287.8; C6-Pb-C7 26.6, C6′-Pb-C7′ 26.7, C2-Pb-C8 119.1, C8-Pb-C2′ 121.4, C2′-Pb-C2 119.5, (center C6, C7)-Pb-(center C6′, C7′) 171.3. b) Contour plots of the Laplacian distributions $\nabla^2\rho(r)$ in the plane containing the atoms Pb, C6, and C7. Solid and dotted lines designate regions of local charge concentration and depletion, respectively. The bond paths are indicated by the solid black lines, bond critical points are marked with a black square.

results. The intramolecular interaction between the positively charged lead atom and the two C=C double bonds markedly stabilizes the cation **1** by 16.8 and 28.3 kcal mol^{-1} relative to the norbornyl cation **8** and the trivalent plumbylium ion **10**, respectively (at MP2/6-311G(d,p) (C,H), SDD(Pb)//MP2/6-31G(d) (C,H), SDD(Pb)). An NBO analysis[16] of the MP2/6-311G(d,p) (C,H), SDD(Pb) wave function suggests a significant charge transfer from the C=C double bonds to the lead center in **1**, which leads to considerable occupation of the formally empty 6p(Pb) orbital (0.20 e in **1**, versus 0.06 e in **10**) and modestly depleted π orbitals of the C=C double bonds (1.87 e (**1**), 1.93 e (**10**)). This interaction reduces the electron deficiency of the lead atom in **1** slightly compared to that in the trivalent plumbylium ion **10**, as shown by the calculated NBO charges for the lead atom (**1**: +1.90; **10**: +1.94). The most significant result of a topological "atoms in molecules" (AIM) analysis[17, 18] of the MP2/6-311G(d,p) electron density is graphically shown in Figure 2b. The AIM analysis indicates T-shaped paths of maximum electron density, the so-called bond paths, which connect the lead atom with the bond critical point[19] of the C=C double bonds (shown in Figure 2b for one double bond). No bond critical point and no bond path exists between the lead atom and the vinylic carbon atoms. This situation is reminiscent to that in the norbornyl cation,[20] and is typical for π complexes between an electron-deficient center and a C–C multiple bond.[21] Therefore, the topological analysis of the electron density reveals that **1** is best described as a double π complex with a central pentacoordinated lead atom.

Conclusion

The plumbyl cation **1** is synthesized in aromatic solvents by electrophilic attack of trityl cation on an ethylplumbane **2** in the presence of a weakly coordinating anion. Hydride abstraction from the ethyl substituent is followed by ethene elimination and leads to the formation of the plumbyl cation **1**. The lead atom in **1** adopts a distorted trigonal-bipyramidal coordination polyhedron and the two C=C double bonds of the cyclopentenemethyl substituents adopt the apical positions. Quantum-mechanical calculations indicate a π-type interaction between the Pb atom and the C=C double bonds. Therefore, the plumbyl cation **1** is an example of an unique coordination of lead to two C=C double bonds. Investigations on other examples for Group 14 congeners of **1** are currently in progress in our laboratories.

Experimental Section

General methods: All reagents were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium/potassium alloy/benzophenone; [D$_6$]benzene and [D$_8$]toluene were distilled from sodium; trityl tetrakispentafluorophenylborate (TPFPB) was stored under vacuum for several hours prior to use. All reactions were carried out in oven-dried glassware under inert argon atmospheres. NMR spectra were recorded on Bruker AM-400 and DPX-250 instruments. ^{1}H NMR spectra were calibrated by using residual nondeuterated solvents as internal reference (C_6D_5H at $\delta = 7.15$ ppm, $C_6D_5CD_2H$ at $\delta = 2.03$ ppm), ^{13}C NMR spectra by using the central line of the solvent signal (C_6D_6 at $\delta = 128.0$ ppm, $C_6D_5CD_3$ at $\delta = 20.4$ ppm). Assignments were made with the aid of 2D correlation spectroscopy (HSQC) experiments. ^{207}Pb NMR spectra were calibrated by using external $(H_5C_2)_4Pb$ ($\delta(^{207}Pb) = 71.0$ ppm). Chloromethyl-3-cyclopentene,[22] TPFPB[23] and dibromodiethylplumbane[24] were prepared as described in the literature.

2: Cyclopentenemethylmagnesium chloride (6.54 mmol) in dry THF (30 mL) was added to dibromodiethylplumbane (1.4 g, 3.31 mmol), and the mixture was stirred overnight, then dried in vacuum. The resulting slurry was extracted pentane (3 × 10 mL). The combined solutions were cooled to −130 °C and filtered through Celite. Removal of solvent in vacuum yielded a greenish oil (0.68 g, 1.59 mmol). Purification was achieved by bulb-to-bulb distillation to give **2** as a colorless oil; yield 14.8 % (0.21 g, 0.49 mmol).

^{1}H NMR (250.133 MHz, [D$_6$]benzene, 303 K, $\delta(C_6D_5H) = 7.15$ ppm): $\delta =$ 5.65 (s, 4 H; -CH=CH-), 2.69 (hept, $^3J(H,H) = 7.1$ Hz, 2 H; -CH-), 2.51 (m, 4 H; -CH_2-CH-CH_2-), 1.91 (m, 4 H; -CH_2-CH-CH_2-), 1.66 (d, $^3J(H,H) =$ 7.1 Hz, 4 H; -CH-CH_2-Pb-), 1.48 (s, $^3J(Pb,H) = 127$ Hz, 10 H; -Pb-CH_2-CH$_3$; ^{13}C NMR (62.860 MHz, [D$_6$]benzene, 303 K, $\delta(C_6D_6) = 128.0$ ppm): $\delta =$ 130.2 (^1J (C,H) = 161.4 Hz; -CH=CH-), 43.8 ($^3J(Pb,C) = 57.1$ Hz; -CH$_2$-CH-CH$_2$), 38.5 ($^2J(Pb,C) = 28.6$ Hz; -CH-), 27.5 ($^1J(Pb,C) = 181.6$ Hz; -CH-CH$_2$-Pb-), 14.0 ($^2J(Pb,C) = 30.2$ Hz, -CH$_3$), 11.1 ppm ($^1J(Pb,C) = 197.0$ Hz, -CH$_2$-CH$_3$); ^{207}Pb NMR (52.304 MHz, [D$_6$]benzene, 303 K, $\delta(Et_4Pb) =$ 71.0 ppm): $\delta = 30.2$ ppm.

1-[B(C$_6$F$_5$)$_4$]: Plumbane **2** (210 mg, 0.49 mmol) was added slowly to a Schlenk flask charged with a vigorously stirred solution of trityl tetrakispentafluorophenylborate (TPFPB) (0.461 g, 0.5 mmol) in dry [D$_8$]toluene (3 mL). Immediately an evolution of gas accompanied by a noticeable increase in temperature was observed. The resulting brown, two-phase reaction mixture was allowed to settle down and the layers were separated by cannula transfer. The upper layer contained the by-product triphenylmethane. Treatment of the oily lower layer with pentane (3 × 10 mL) resulted in the formation of a white-brown solid (502 mg, 0.466 mmol, 95 %). Single crystals suitable for X-ray analysis were obtained by recrystallization from pentane under solvothermal conditions.

^{1}H NMR (250.133 MHz, [D$_8$]toluene, 303 K, $\delta(C_6D_5CHD_2) =$ 2.03 ppm): $\delta = 5.31$ (s, ^2J(Pb,H) = 18.8 Hz, 4H; -CH=CH-), 4.13 (m, ^3J(Pb,H) = 347.2 Hz, 2H; -CH-), 2.23 (m, 4H; -C*H*$_2$-CH-C*H*$_2$-), 1.99 (q, ^3J(H,H) = 8.0 Hz, 2H; -C*H*$_2$-CH$_3$), 1.67 (br, 4H; -CH-C*H*$_2$-Pb-), 1.58 (t, ^3J(H,H) = 8.0 Hz, 3H; -CH$_3$), 1.42 ppm (m, 4H; -C*H*$_2$-CH-C*H*$_2$-); ^{13}C NMR (62.860 MHz, [D$_8$]toluene, 303 K, $\delta(C_6D_5CD_3) =$ 20.4 ppm): $\delta = 136.1$ (^1J(Pb,C) = 14.4 Hz; -CH=CH-), 48.4 (^1J(Pb,C) = 74.3 Hz; -CH-*C*H$_2$-Pb-), 39.3 (^3J(Pb,C) = 50.1 Hz, -*C*H$_2$-CH-*C*H$_2$-), 35.6 (^2J(Pb,C) = 43.1 Hz; -CH-), 33.4 (^1J(Pb,C) = 82.7 Hz; -*C*H$_2$-CH$_3$), 13.0 (^2J(Pb,C) = 42.3 Hz, -CH$_3$); ^{207}Pb NMR (52.304 MHz, [D$_8$]toluene, 303 K, $\delta(Et_4Pb) = 71.0$ ppm) $\delta =$ 806.7 ppm.

Crystal data for **1** at 173 K with Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. Crystal dimensions: 0.40 × 0.12 × 0.07 mm, $C_{38}H_{23}BF_{20}Pb$, $M_W = 1077.57$, orthorhombic, Pbca, $a = 19.620(1)$, $b = 17.483(1)$, $c = 23.817(2)$, $V = 8169.6(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.752$ Mg m^{-3}, $2\Theta_{max} = 50.66$, $F(000) = 4144$, 78979 reflections, 7412 independent reflections, 541 parameters, GOF = 0.929, numerical absorption correction. The structure was solved by direct methods, and refined against F^2 using all data.[25] $R_1 = 0.0732$ [$I > 2\sigma(I)$], $wR_2 = 0.2007$, min./max. residual electron density −2.269/2.475 eÅ^{-3}.

CCDC-190170 (**1**) contains 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 CB21EZ, UK; fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

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[9] All three cyclopentenemethyl ligands in **4** are equivalent due to fast exchange of the coordinating C=C double bonds. Spectroscopic data for **4**: ^{13}C NMR (62.860 MHz, [D$_8$]toluene, 303 K, $\delta(C_6D_5CD_3) =$ 20.4 ppm): $\delta = 133.7$ (^1J(Pb,C) = 8.6 Hz, -CH=CH-), 50.1 (^1J(Pb,C) = 65.3 Hz, -CH-*C*H$_2$-Pb-), 40.5 (^3J(Pb,C) = 49.3 Hz, -*C*H$_2$-CH-*C*H$_2$-), 36.5 (^2J(Pb,C) = 46.0 Hz, -CH-); ^{207}Pb NMR (52.304 MHz, [D$_8$]toluene, 303 K, $\delta(Et_4Pb) = 71.0$ ppm): $\delta = 798.8$ ppm.

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