New Plumbylenes and a Plumbylene Dimer with a Short Lead−Lead Separation[†,1]

Martin Stürmann and Manfred Weidenbruch*

Fachbereich Chemie der Universität Oldenburg, Carl-von-Ossietzky-Strasse 9-11,
D-26111 Oldenburg, Germany

Karl W. Klinkhammer* and Falk Lissner

Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany

Heinrich Marsmann

Fachbereich Chemie der Universität (GH) Paderborn, Warburger Strasse 100,
D-33095 Paderborn, Germany

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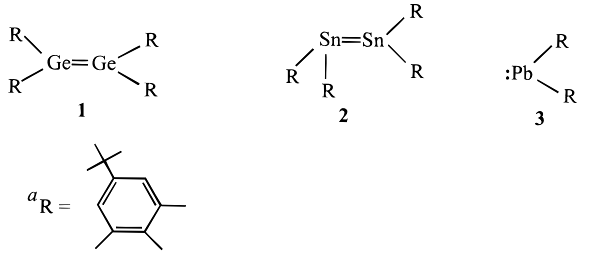
The diarylplumbylene R_2Pb: (**3**), R = 2-*t*Bu-4,5,6-Me_3C_6H, and the rearranged alkylarylplumbylene RR′Pb:, R = 2,4,6-*t*$Bu_3C_6H_2$, R′ = $CH_2C(CH_3)_2$-3,5-*t*$Bu_2C_6H_3$, were synthesized and characterized by NMR and UV/vis spectroscopy, as well as by X-ray crystallography. Treatment of **3** with the disilylplumbylene R''_2Pb:, R″ = $Si(SiMe_3)_3$, furnished the heteroleptic plumbylene RR″Pb: (**8**), which, in the solid state, forms the plumbylene dimer RR″PbPbRR″ (**9**). The X-ray structure analysis of **9** reveals a *trans*-bent angle of 46.5° and a $Pb\cdots Pb$ separation of 3.37 Å, the shortest observed so far between the lead atoms of two plumbylenes.

Introduction

Only few dialkyl- and diarylplumbylenes have been synthesized and structurally characterized in the past years. One of these is the diarylplumbylene R_2Pb:, R = 2,4,6-$(CF_3)_3C_6H_2$, which experiences an intramolecular stabilization through contacts between the lead atom and the fluorine atoms of the *ortho*-CF_3 groups.[2] Another is the sterically extremely overcrowded plumbylene with 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$ substituents.[3] The first dialkylplumbylene, :$Pb[CH(SiMe_3)_2]_2$, was prepared as early as 1973,[4] but its structure has still not been published.[4c] The synthesis and structure of a dialkylplumbylene with a similar substitution pattern was reported recently in which the lead atom is part of a seven-membered ring.[5]

We now report on the syntheses and structures of a further diarylplumbylene, the first ever alkylarylplumbylene, and an arylsilylplumbylene which, in the solid state, exists as a dimer with the shortest lead−lead separation observed to date in such systems.

Scheme 1



Results and Discussion

Reaction of lead(II) chloride with the Grignard reagent 2-*t*Bu-4,5,6-Me_3C_6HMgBr furnishes red crystals of the diarylplumbylene **3** (Scheme 1) in 81% yield. The constitution of **3** was confirmed by its analytical and spectral data. With a value of $\delta[^{207}Pb] = 6927$ ppm, the chemical shift is in the typical region for diarylplumbylenes that ranges from 3870 to 8888 ppm.[2,3,6] The electronic spectrum of **3** with an absorption at longest wavelength of 490 nm is in full accord with the data for other compounds of this type.

The results of an X-ray crystallographic analysis of **3** (Figure 1) with Pb−C bond lengths of 2.357 and 2.376 Å and a C−Pb−C bond angle of 103.0° are similar to

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[†] Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday.

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S0276-7333(98)00447-6 CCC: $15.00

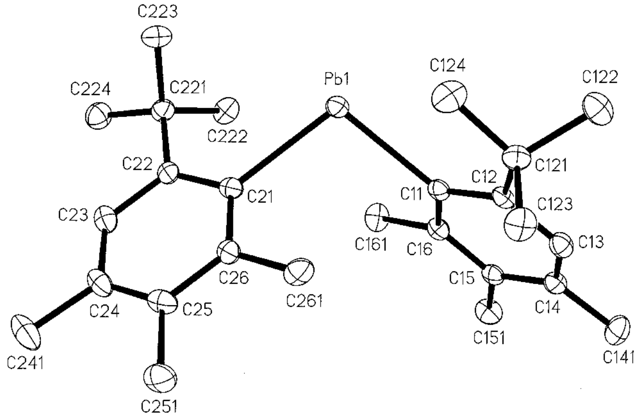
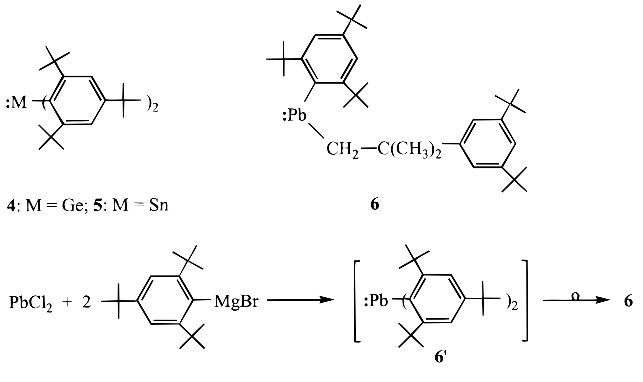


Figure 1. Molecule of **3** in the crystal (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (deg): Pb−C(11) 2.357(4), Pb−C(21) 2.376(4), C(11)−Pb−C(21) 103.04(13).

Scheme 2



those of the other two structurally characterized diarylplumbylenes. A comparison of **3** with the correspondingly substituted germanium and tin compounds is of more interest. Whereas germanium forms the digermene **1** with a short Ge−Ge bond length and a planar or almost planar arrangement of the substituents about the germanium atoms,[7] tin forms the distannene **2** characterized not only by an unusually long tin−tin bond length of 2.910(1) Å, markedly longer than a normal tin−tin single bond, but also by the differing environments at the two tin atoms. The one tin atom has an almost planar substituent arrangement, while the other is pyramidal with a *trans*-bent angle of 64.4°.[8] A comparison of the series of compounds **1**−**3** reveals that, in harmony with the decreasing element−element bond energy with increasing atomic mass of the element, compound **1** has a rather stable Ge=Ge double bond, compound **2** has a relatively loose bond in the solid state, and compound **3** is isolated exclusively as the monomeric plumbylene.

The ready formation of **3** prompted us to attempt the synthesis of the diarylplumbylene R_2Pb:, R = 2,4,6-$t\text{Bu}_3C_6H_2$, under otherwise identical reaction conditions (Scheme 2). The first attempt at this synthesis was made by Okazaki et al.,[9] who, however, only obtained the four-coordinate lead compounds $R'_3PbPbR'_3$ and R'_3-PbBr together with the alcohol R′OH, all with the aryl/alkyl-isomerized group $R' = CH_2\text{-}C(CH_3)_2\text{-}3,5\text{-}t\text{Bu}_2C_6H_3$ from the reaction of $PbCl_2$ with LiR or RMgBr.

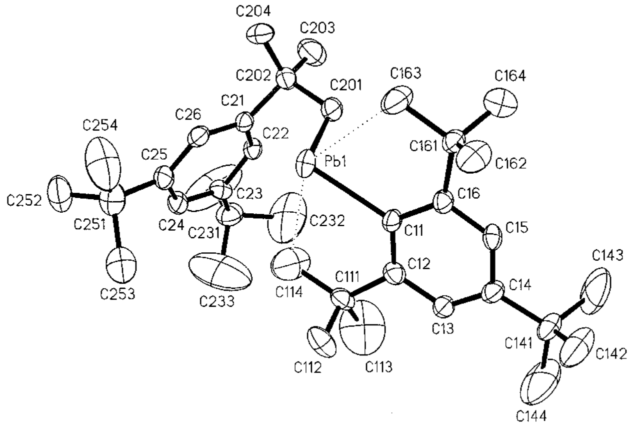


Figure 2. Molecule of **6** in the crystal (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (deg): Pb−C(11) 2.344(9), Pb−C(201) 2.476(14), C(11)−Pb−C(201) 94.8(4).

In our hands, the reaction of lead(II) chloride with the Grignard reagent RMgBr resulted in the formation of a yellow crystalline product in 61% yield. The analytical data, the ^{207}Pb NMR spectrum {$\delta[^{207}\text{Pb}]$ = 5067 ppm}, and the electronic spectrum were indicative of the constitution of a plumbylene. However, the ^{1}H and ^{13}C NMR spectra revealed instead that the plumbylene **6** with one aryl and one alkyl group had been formed; that is, rearrangement of one aryl group had occurred.

The X-ray crystallographic analysis of **6** not only confirmed the structure deduced from the spectral data but also revealed some unusual features. Even with consideration of its large standard deviation, the Pb−C(alkyl) bond is conspicuously long (2.48 Å), and the C−Pb−C bond angle is very small (94.8°). The short contacts of 2.796 and 2.826 Å between the lead atom and the carbon atoms of the *ortho*-*tert*-butylmethyl groups are indicative of weak agostic interactions (Figure 2). A similar situation had been observed only for the *ortho*-CF_3 groups of 2,4,6-$(CF_3)_3C_6H_2$-substituted plumbylenes.[2,16]

A comparison with the correspondingly substituted germylene **4** and stannylene **5** and compound **6** is also of interest. Thus, the structurally characterized compound **4** is stable at low temperature,[10] whereas, in the presence of Lewis acids, an insertion of the germanium atom into the C−H bond of an *ortho*-*tert*-butyl group

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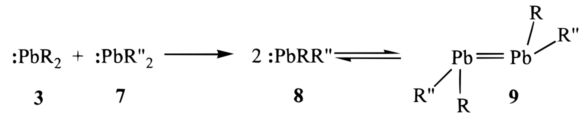
Scheme 3



^{a} R'' = Si(SiMe$_3$)$_3$

occurs with formation of a germaindan.[10,11] The stannylene **5** behaves differently: in the solid state the compound is completely stable at room temperature,[12] whereas in solution it undergoes a slow rearrangement to yield an alkylarylstannylene with identical substituents as in **6**.[13] The decreasing M−C bond dissociation energy in the series from germanium to lead apparently favors the isomerization of one of the aryl groups.

The color change of the solution from orange-red to yellow during the course of the reaction suggests the initial formation of the diarylplumbylene R$_2$Pb: (**6′**) which then undergoes the above-mentioned isomerization from about −30 °C. How this aryl → alkyl rearrangement, first observed in the reactions of tin tetrahalides with aryllithium compounds,[14] actually proceeds is still not clear. Since compounds **1** and **2** form stable radicals R$_3$M•, R = aryl, merely on exposure to light,[15] an intermolecular transfer of the aryl group R with concomitant isomerization is probable. Surprising in any case is the fact that under almost identical reaction conditions either only four-coordinated lead compounds are formed,[9] or—as observed in the present work—the plumbylene **6** is obtained in acceptable yield.

The formation of the arylsilylplumbylene RR″Pb, R = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, R″ = Si(SiMe$_3$)$_3$, was recently described in a short communication. In the solid state this compound forms a dimer with the short Pb···Pb contact of 3.537(1) Å.[16] Since the interactions between the *ortho*-CF$_3$ groups and the lead atom should hinder rather than favor such lead−lead contacts, we have allowed the plumbylene **3** to react with the disilylplumbylene **7**[17] and thereby observed spontaneous formation of a green-blue color in the solution. In this case again a substituent exchange has occurred with formation of the heteroleptic arylsilylplumbylene **8** (Scheme 3). This assumption is supported by the position of the ^{207}Pb NMR signal at 7545 ppm as well as the electronic spectrum of (λ_{max} = 610 nm) **8**.

The X-ray crystallographic analysis of the green crystals, isolated in 92% yield, revealed that the compound exists in the solid state as the dimer **9** of two plumbylene molecules with a very short lead−lead separation of 3.3695(11) Å. Although this distance represents the shortest separation between two plumbylene molecules reported to date, it is still markedly longer than the theoretically predicted bond length of 2.82−3.00 Å for the parent compound H$_2$Pb=PbH$_2$.[16,18,19] On the other hand, the *trans*-bending of 46.5° between the substituents and the Pb−Pb vector shown in Figure 4 approaches the theoretically predicted value of 53−56°. However, it cannot yet be decided with certainty if compound **9** really is a diplumbene with a formal lead−lead double bond.

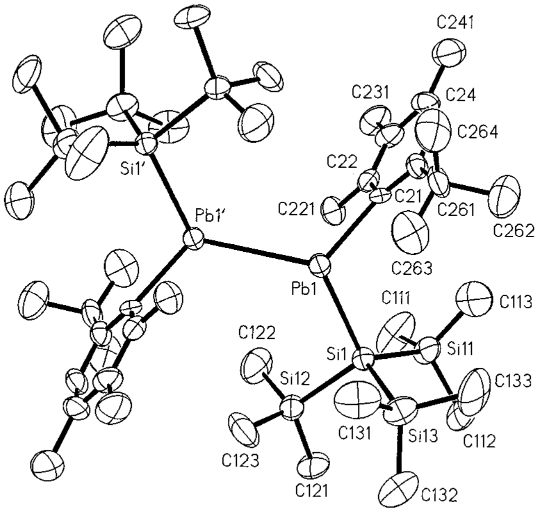


Figure 3. Molecular view of the plumbylene dimer **9** in the solid state (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (deg): Pb(1)···Pb(1a) 3.3695(11), Pb−C(21) 2.37(2), Pb−Si(1) 2.709(4), C(21)−Pb−Si(1) 106.0(3).

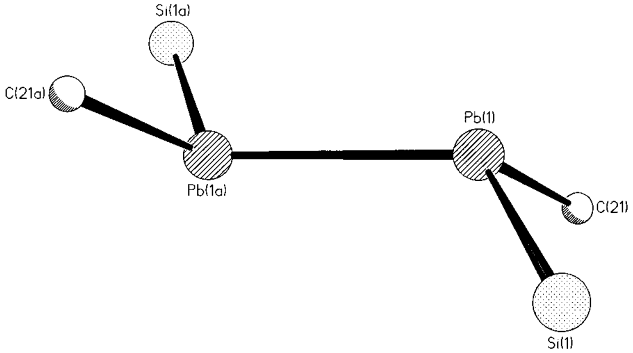


Figure 4. Side view of the Pb$_2$C$_2$Si$_2$ framework of **9**.

Similar to the bonding situation in **9**, the route by which the substituent transfer between the plumbylenes **3** and **7** proceeds is also unknown. One possibility would be the formation of a loose adduct between **3** and **7**, followed by a dyotropic rearrangement; such a mechanism is considered probable for the isomerization of tetraaryldisilenes.[20]

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon.

The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AM 300 spectrometer, the ^{29}Si and ^{207}Pb spectra on a Bruker AMX 300 spectrometer using C$_6$D$_6$ as solvent. Mass spectra were recorded on a Varian MAT 212 or Finnigan MAT 95 instrument. UV/vis spectra were taken on a ConSpec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

Bis(2-*tert*-butyl-4,5,6-trimethylphenyl)plumbylene (3). At −110 °C, solid PbCl$_2$ (2.88 g, 10.4 mmol) was added to the Grignard compound, which was prepared from 1-bromo-2-*tert*-butyl-4,5,6-trimethylbenzene (5.30 g, 20.8 mmol) and magnesium turnings (1.5 g, 60 mmol) in 60 mL of THF. The mixture was allowed to warm to room temperature over a period of 1 h with vigorous stirring. The solvent was distilled off, and the residue was extracted with three portions of 30 mL of

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Table 1. Crystallographic Data for 3, 6, and 9

	3	**6**	**9**
empirical formula	$C_{26}H_{38}Pb\cdot 1/2$ DME	$C_{36}H_{58}Pb$	$(C_{22}H_{46}PbSi_4)_2$
fw	602.81	698.01	1260.28
a (Å)	15.281(2)	15.2315(8)	14.075(1)
b (Å)	11.862(1)	11.4277(6)	17.352(1)
c (Å)	28.616(2)	41.207(3)	13.386(1)
β (deg)	90.631(7)	92.518(7)	111.978(9)
V (Å^3)	5186.5(10)	7165.6(7)	3031.5(4)
Z	8	8	2
D(calcd) (g cm^{-3})	1.544	1.294	1.381
cryst size (mm)	0.3 × 0.3 × 0.2	0.6 × 0.4 × 0.1	0.2 × 0.2 × 0.1
cryst syst	monoclinic	monoclinic	monoclinic
temp (K)	173(2)	296(2)	295(2)
space group	$C2/c$	$C2/c$	$P2_1/c$
data collection mode	ω		
$2\theta_{\max}$ (deg)	58	55	41
no. of rflns measd	8269	18 703	12 451
no. of unique rflns	6848	6874	3081
lin abs coeff (mm^{-1})	6.522	4.728	2.865
parameters	327	338	224
R [$I > 2\sigma(I)$]	0.0310	0.0769	0.0501
wR2 (all data)	0.0679	0.1893	0.1198
GOF (F^2)	0.769	1.054	0.883

n-hexane. Concentration of the solution to a volume of 30 mL and cooling at −50 °C afforded a red-violet solid, which was recrystallized from a minimum amount of DME to furnish 4.7 g (81% yield) of red crystals of **3**: mp 99−101 °C (dec); ^{1}H NMR δ 1.35 (s, 18 H), 1.98 (s, 6 H), 2.06 (s, 6 H), 2.12 (s, 6 H), 8.03 (s, 2 H); ^{13}C NMR (toluene-d_8) δ 16.28, 21.91, 23.61, 34.00, 40.97, 131.74, 135.67, 139.17, 144.00, 157.86, 275,6 ($^1J_{C,Pb}$ = 1288 Hz); ^{207}Pb NMR δ 6927; mass spectrum (CI, isobutane) *m*/*z* 578 (M$^+$, 5); UV/vis $\lambda_{\max}(\epsilon)$ 490 (33900) nm. Anal. Calcd for $C_{26}H_{38}Pb$: C, 55.99; H, 6.87; Pb, 37.15. Found: C, 55.87; H, 6.94; Pb, 37.05.

(2,4,6-Tri-*tert*-butylphenyl)-[2-(3,5-di-*tert*-butylphenyl)-2-methylpropyl]plumbylene (6). At −110 °C, solid $PbCl_2$ (1.38 g, 4.96 mmol) was added to the Grignard compound, prepared from 1-bromo-2,4,6-tri-*tert*-butylbenzene (3.23 g, 9.93 mmol) and magnesium turnings (0.60 g, 25 mmol) in 60 mL of THF. The mixture was allowed to warm to room temperature over a period of 1 h with vigorous stirring. At approximately −30 °C, the color of the initially orange-red solution changed to yellow. The solvent was distilled off, and the residue extracted with 50 mL of *n*-hexane. The magnesium salts were filtered off, and the solution was concentrated to a volume of 15 mL. Cooling at −50 °C furnished 2.1 g (61% yield) of yellow crystals of **6**: mp 110 °C; ^{1}H NMR δ 1.14 (s, 18 H), 1.37 (s, 9 H), 1.38 (s, 18 H), 1.69 (s, 6 H), 1.86 (s, 2 H), 7.39 (t, 1 H, ^3J = 1.7 Hz), 7.53 (d, 2 H), 7.83 (s, 2 H); ^{13}C NMR δ 31.65, 31.91, 32.48, 34.57, 34.97, 36.32, 37.66, 41.69, 118.30, 119.63, 126.64, 146.52, 150.50, 152.73, 160.84, 231.64 ($^1J_{C,Pb}$ = 2697 Hz); ^{207}Pb NMR δ 5067; mass spectrum (CI, isobutane) *m*/*z* 699 (M$^+$, 5); UV/vis $\lambda_{\max}$ (ϵ) 406 (1080) nm. Anal. Calcd for $C_{36}H_{58}Pb$: C 61.94; H, 8.37. Found: C, 61.17; H, 8.53.

(2-*tert*-Butyl-4,5,6-trimethylphenyl)[tris(trimethylsilyl)-silyl]plumbylene (8). A solution of the plumbylenes **3** (0.28 g, 0.50 mmol) and **7** (0.35 g, 0.50 mmol) in 15 mL of *n*-pentane was stirred for 30 min at room temperature. Cooling of the greenish-blue solution for 12 h at −60 °C afforded 0.58 g (92% yield) of green crystals of **8**: mp 112 °C; ^{1}H NMR δ 0.36 (s, 27 H), 1.05 (s, 9 H), 1.51 (s, 3 H), 1.90 (s, 3 H), 2.13 (s, 3 H), 7.82 (s, 1 H); ^{13}C NMR δ 6.31, 14.72, 21.79, 29.33, 30.39, 42.25, 133.31, 134.16, 133.86, 142.62, 157.88, 239.46; ^{29}Si NMR (toluene-d_8) δ 1.06, 57.13; ^{207}Pb NMR δ 7545; mass spectrum (CI, isobutane) *m*/*z* 630 (M$^+$, 17); signals for the plumbylene dimer **9** were also observed at *m*/*z* 1260 (M$^+$, 25), 1085 (M$^+$ − R, 18), and 1012 (M$^+$ − R″, 54); UV/vis $\lambda_{\max}(\epsilon)$ 303 (34730), 341 (1750), 610 (1500) nm. Anal. Calcd for $C_{22}H_{46}PbSi_4$: C, 41.93; H, 7.36. Found: C, 41.75; H, 7.36.

Crystallographic Analyses. Crystal and numerical data of the structure determinations are given in Table 1. Single crystals were grown from saturated solutions in DME (**3**), *n*-hexane (**6**), and *n*-pentane (**9**) at −50 °C. In each case, the crystal was mounted in inert oil. Data were collected on a Siemens P4 (**3**) or STOE IPDS (**6**, **9**) diffractometer using graphite monochromated Mo Kα radiation (71.073 pm). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELX 93 program system.[21] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients for **3**, **6**, and **9** (19 pages). Ordering information is given on any current masthead page.

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