Compounds of Germanium, Tin, and Lead, 30[+]
A Heteroleptic Diplumbene and a Magnesium Dibromide Stabilized Plumbylene Dimer

Martin Stürmann,[a] Wolfgang Saak,[a] Manfred Weidenbruch,*[a] and Karl W. Klinkhammer[b]

Keywords: Lead / Plumbylenes / Plumbanediyles / Diplumbene / Plumbylene dimers / Double-bond systems

Treatment of the diarylplumbylene R_2Pb: ($R = 2,4,6\text{-}i\mathrm{Pr}_3C_6H_2$) with the disilylplumbylene R'_2Pb: [$R' = Si(SiMe_3)_3$] furnishes the heteroleptic plumbylene RR′Pb: which exists as the diplumbene RR′Pb=PbRR′ (**7**) in the solid state. The X-ray structure analysis of **7** reveals a *trans*-bent angle of 42.7° and a Pb–Pb bond length of 298.99(5) pm, the shortest observed so far for diplumbenes with a lead–lead double bond. Reaction of mesitylmagnesium bromide with $PbCl_2$ yielded black crystals of an $MgBr_2$ stabilized dimesitylplumbylene dimer with a large *trans*-bent angle of 71°, a lead–lead separation of 335.49(6) pm, and long Pb···Br contacts of 315.71(8) pm.

Dialkyl-[1][2] and diarylplumbylenes[3−5] without intra- or intermolecular donor stabilization have become known and their structures have been elucidated only in the past few years.[6] They predominantly exist as V-shaped molecules without any contacts between the lead atoms of neighboring plumbylene molecules. The low tendency for dimerization (Figure 1) is probably a consequence of the available mechanism for bond formation which, unlike that for carbon, for example, is through donor-acceptor interactions between the doubly occupied 6s orbitals and the empty 6p orbitals of two singlet plumbylene molecules. This is corroborated by the low bond-dissociation energy, which was calculated to be merely 24 kJ mol^{-1}.[7]

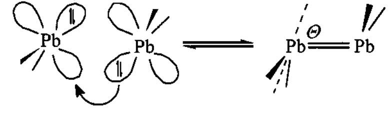
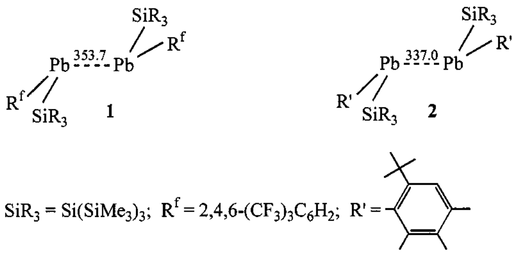
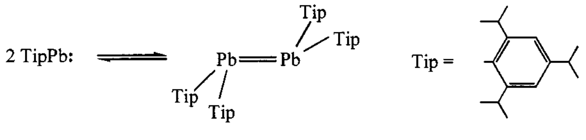


Figure 1. Formation of a diplumbene from two singlet plumbylenes

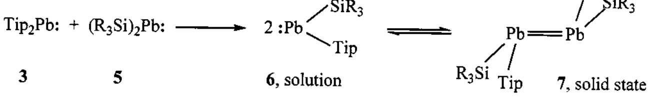
The first advances in the direction of lead−lead interactions were realized with the syntheses of compounds **1**[7] and **2**[5] which exhibited the theoretically required *trans*-bent arrangements. However, the observed Pb···Pb separations of 353.7(1) pm in **1** and 337.0(1) pm in **2** were markedly larger than the calculated values of around 295 pm for the parent compound $H_2Pb{=}PbH_2$ with a Pb−Pb double bond. Values of about 55° were determined for the corresponding *trans*-bent angles θ.[7−9] With the preparation of compound **4** we recently obtained the first diplumbene with a Pb−Pb bond length [305.15(3) pm] and *trans*-bent angles θ [43.9° and 51.2°] in good agreement with the theoretical predictions.[10]





3, solution **4**, solid state

We now describe the first heteroleptic diplumbene with a Pb−Pb bond even shorter than that of **4** as well as a plumbylene dimer stabilized by magnesium dibromide.



3 **5** **6**, solution **7**, solid state

In the syntheses of the plumbylene dimers **1** and **2** the diarylplumbylene was allowed to react with the disilylplumbylene[11] to furnish the heteroleptic molecules **1** and **2** by substituent exchange. An analogous reaction of the plumbylene **3**, existing in solution, with the disilylplumbylene **5** also proceeded through rapid substituent exchange to afford a greenish-blue solution of the plumbylene **6** from

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[a] Fachbereich Chemie der Universität Oldenburg,
Carl-von-Ossietzky-Straße 9−11, D-26111 Oldenburg,
Germany

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

which reddish-brown crystals of the diplumbene **7** were isolated.

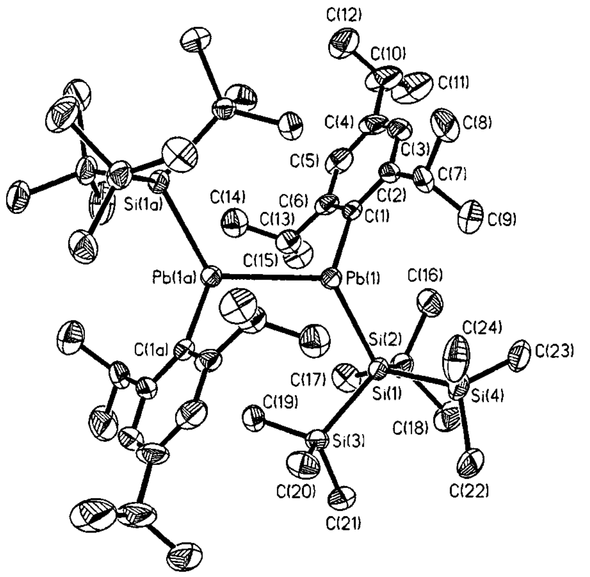
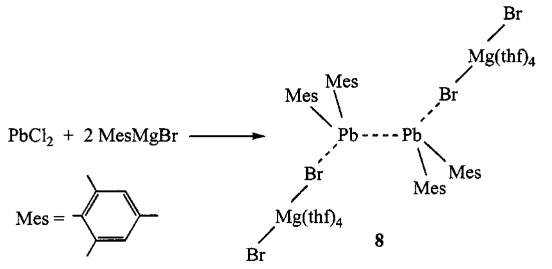


Figure 2. Molecular structure of **7** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at 50% probability; selected bond lengths [pm] and angles [°]: Pb(1)−Pb(1a) 298.99(5), Pb(1)−C(1) 229.6(4), Pb(1)−Si(1) 271.7(1); C(1)−Pb(1)−Si(1) 108.8(1), C(1)−Pb(1)−Pb(1a) 109.5(1), Si(1)−Pb(1)−Pb(1a) 120.72(3)

An X-ray crystal-structure analysis of compound **7** (Figure 2) revealed the existence of a centrosymmetrical molecule having a lead−lead bond length of 298.99(5) pm, a value even shorter than that of **4** and very close to the theoretically calculated value for the parent compound. The *trans*-bent angle θ in **7** of 43.7° (see Figure 1) is somewhat smaller than those of **4**, presumably as a consequence of the different substitution pattern. Thus, compound **7** is not only the second diplumbene ever to be prepared but is also the first heteroleptic molecule of this type.

It has been found for disilenes, digermenes, and distannenes that the steric requirements of the substituents must increase with increasing length of the element−element double bond in order to effectively shield the compounds from further reactions.[12][13] Thus, for example, the compounds $Tip_2Si{=}SiTip_2$ and $Tip_2Ge{=}GeTip_2$ (Tip = 2,4,6-$i\text{Pr}_3C_6H_2$) are thermally stable while $Tip_2Sn{=}SnTip_2$, although it can be generated thermally or photochemically from the cyclotristannane $(Tip_2Sn)_3$, reverts to the three-membered ring compound at room temperature.[14] The existence of compounds **4** and **7**, however, seems to suggest that steric shielding of the Pb−Pb double bond does not play such a dominating role. We have thus examined whether the use of smaller aryl groups would also permit the formation of this structural element or whether subsequent reactions would occur.

Reaction of the Grignard reagent MesMgBr with solid lead(II) chloride at low temperature in THF furnished a red-brown solution from which, among other products, black crystals of a very sensitive, thermolabile compound were isolated. Satisfactory characterization of this product by spectroscopic methods was not possible on account of its properties.



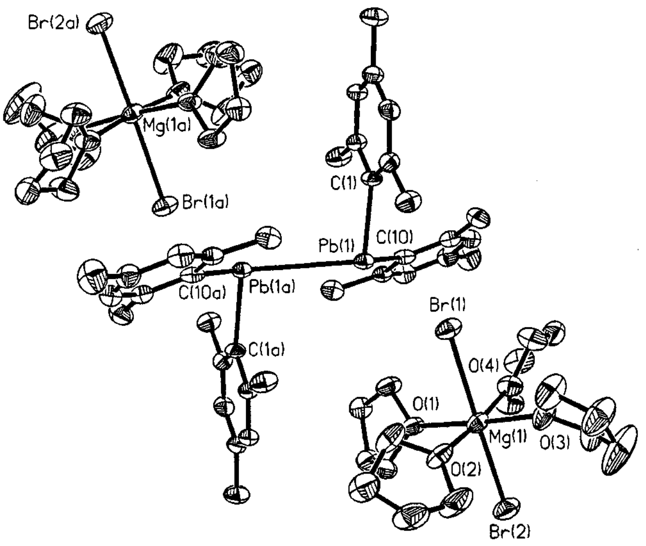


Figure 3. Molecular structure of **8** in the crystal (hydrogen atoms omitted); ellipsoids are drawn at 50% probability; selected bond lengths [pm] and angles [°]: Pb(1)···Pb(1a) 335.49(6), Pb(1)−C(1) 232.2(5), Pb(1)−C(10) 230.4(6), Mg(1)−Br(2) 262.6(2), Mg(1)−Br(1) 279.7(2), Pb(1)···Br(1) 315.71(8); C(1)−(Pb1)−Pb(1a) 99.6(2), C(10)−Pb(1)−Pb(1a) 118.0(2), Br(1)−Pb(1)−Pb(1a) 133.44(2), Br(2)−Mg(1)−Br(1) 178.04(9)

However, a low-temperature X-ray crystallographic analysis of these black crystals revealed that a magnesium bromide stabilized plumbylene dimer **8** had been formed (Figure 3). The Pb···Pb separation of 335.49(6) pm is in the same range as that for compound **2**. The *trans*-bent angle θ of 71° is unusually large. A further surprising feature is that a bromine atom of an $MgBr_2(thf)_4$ molecule experiences a weak interaction with each lead atom and not the THF present in a large excess. Although the respective Pb···Br separations are about 50 pm larger than those of a Pb−Br single bond,[15] these interactions are characterized not only by a large *trans* arrangement but also by the Mg−Br bond lengths within the almost linear Br−Mg−Br units. Thus, the Br−Mg bond weakly coordinated to the lead atom is around 17 pm longer than the other Mg−Br bond.

The novel molecules **7** and **8** described here indicate that further interesting and unexpected results may be expected in the field of low-coordinated lead compounds.

Experimental Section

General: All manipulations were performed by using standard Schlenk techniques under dry argon. − ^{1}H and ^{13}C NMR: Bruker AM 300. − MS: Finnigan MAT 212. − UV/Vis: ComSpec with fiber optics. − Elemental analyses: Analytische Laboratorien, D-51789 Lindlar, Germany.

(2,4,6-Triisopropylphenyl)[tris(trimethylsilyl)silyl]plumbylene (6) and (*E*)-1,2-Bis(2,4,6-triisopropylphenyl)-1,2-bis[tris(trimethylsilyl)silyl]diplumbene (7): A solution of the plumbylenes **3** (0.34 g, 0.55 mmol) and **5** (0.39 g, 0.55 mmol) in 15 mL of *n*-pentane was stirred in the dark for 20 min at room temperature. The greenish-blue solution was concentrated to a volume of 15 mL and cooled at −65°C for 24 h. After this time, 0.53 g (73% yield) of reddish-brown crystals (green in thin layers) of **7** were isolated. M.p. 90°C (decomp.). − Spectroscopic data for **6** in solution: ^{1}H NMR ([D$_8$]toluene, 298 K): δ = 0.44 (s, 27 H), 1.34 (d, 6 H, ^{3}J = 6.85 Hz), 1.35 (d, 12 H, ^{3}J = 6.7 Hz), 2.15 (m, 2 H), 2.86 (m, 1 H), 7.29 (s, 2 H). − ^{13}C NMR ([D$_8$]toluene, 298 K): δ = 7.07, 24.50, 24.99, 33.81, 35.52, 124.74, 125.39, 127.58, 147.33, 158.53, 259.12. − ^{29}Si NMR ([D$_8$]toluene, 298 K): δ = −16.4 [*Si*(SiMe$_3$)$_3$], −4.3 (*Si*Me$_3$). − The ^{207}Pb-NMR signal could not be observed. − MS (CI, isobutane); *m/z* (%): 660 (5) [**6**$^+$]. − UV/Vis: $\lambda_{max}(\varepsilon)$ = 350 (670), 591 (80), 770 (175) nm. − $C_{48}H_{100}Pb_2Si_8$ (**8**) (1316.4): calcd. C 43.79, H 7.64; found C 43.48, H 7.43.

Bis(2,4,6-trimethylphenyl)plumbylene Dimer·2 MgBr$_2$(thf)$_4$ (8): At −110°C, solid PbCl$_2$ (4.7 g, 16.8 mmol) was added to the Grignard compound, prepared in turn from 1-bromo-2,4,6-trimethylphenylbenzene (6.8 g, 34 mmol) and magnesium turnings (3.2 g, 120 mmol) in 100 mL of THF. The mixture was allowed to warm to room temperature over a period of 30 min with vigorous stirring. THF was distilled off and the residue extracted with 10 mL of *n*-hexane in order to remove small amounts of 1,3,5-trimethylbenzene. The remaining residue was extracted with two portions of toluene (50 mL each), and the magnesium salts were filtered off. Concentration of the reddish-brown toluene solution to a volume of 60 mL and cooling at −50°C furnished 3.72 g (18% yield) of thermally unstable, black crystals of **8**. − ^{1}H NMR (C$_6$D$_6$, 298 K): δ = 2.15 (s, 6 H), 2.62 [s, 12 H, ^{4}J(^{1}H,^{207}Pb) = 5 Hz], 6.78 (s, 4 H); minor signals for THF at δ = 1.38 (m), 3.69 (m).

Table 1. Crystallographic data for **7** and **8**

	7	**8**
Empirical formula	$C_{48}H_{100}Pb_2Si_8$	$C_{68}H_{108}Br_4Mg_2O_8Pb_2$
Molecular mass	1316.38	1836.18
Crystal dimensions [mm]	0.55×0.50×0.42	0.50×0.50×0.30
Crystal system	monoclinic	triclinic
Space group	*P*2$_1$/*c*	*P*−1
a [pm]	1089.4(1)	1262.1(1)
b [pm]	2313.6(2)	1274.3(1)
c [pm]	1368.9(2)	1357.2(2)
α [°]	90	77.59(1)
β [°]	112.80(1)	81.11(1)
γ [°]	90	70.93(1)
V [× 10^6 pm^3]	3180.5(5)	2006.3(4)
Z	2	1
$d_{calcd.}$ [g cm^{-3}]	1.375	1.520
T [K]	193(2)	213(2)
μ [mm^{-1}]	5.464	6.242
2θ$_{max}$ [°]	52	52
No. of reflections	23407	27054
No. of unique reflections	6156	7351
No. of observed reflections	4552	6151
No. of parameters	262	379
R_1 [$I > 2\sigma(I)$]	0.0263	0.0361
wR_2 (all data)	0.0553	0.1031
GOF on F^2	0.895	1.008

X-ray Structure Analyses of 7 and 8: Crystal data and numerical data of the structure determinations are given in Table 1. In each case, the crystal was mounted in an inert oil. Data collection was performed with an STOE IPDS diffractometer using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The structures were solved by direct phase determination and refined by full-matrix least squares against F^2 with the SHELXL-97 program system.[16] Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically.[17]

Acknowledgments

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[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111750 (**7**) and -111751 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-093; E-mail: deposit@ccdc.cam.ac.uk].

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