

Syntheses and structures of new diaryl lead(II) compounds PbR_2 (**1**, $\text{R} = 2,4,6$ -triphenylphenyl; **2**, $\text{R} = 2,6$ -bis(1'-naphthyl)phenyl)

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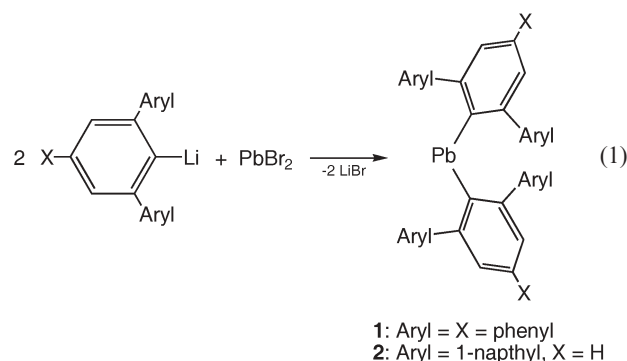
Reaction of RLi with lead(II) bromide affords the diaryl lead(II) compounds PbR_2 ($\text{R}^1 = 2,4,6$ -triphenylphenyl, **1**; $\text{R}^2 = 2,6$ -bis(1'-naphthyl)phenyl, **2**), which have monomeric, carbene-like structures with bent two-coordinate Pb(II) centers.

Aryl and alkyl compounds of the divalent heavier group 14 elements constitute an interesting area of research. A number of diorgano-group 14 compounds (*i.e.*, :ER_2 , E = Si, Ge, Sn, Pb; R = organic group), which are heavier analogs of carbenes :CR_2 , have been synthesized and reviewed.^{1–9} Compared to the lighter group 14 congeners (the silylenes SiR_2 ,^{9–12} germynes GeR_2 ,^{3,4,9,13,14} and stannyls SnR_2 ,^{4,9,15–17}), the chemistry of the heaviest carbene analogs, the plumbynes PbR_2 , has been less developed. Although the dialkyl-lead(II) species $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$ was reported in the early 1970s,^{18,19} its structure has not been reported yet, and the first structurally characterized lead(II) dialkyl compound, in which the Pb atom is part of a PbC_4Si_2 -seven-membered ring system, only appeared recently.²⁰ The first stable diaryl-lead(II) compound $\text{Pb}[\text{C}_6\text{H}_2-2,4,6-(\text{CF}_3)_3]_2$ was reported in 1991.²¹ However, the X-ray structural results suggested that the two-coordinate lead atom may be enhanced by four intramolecular Pb–F contacts. Plumbynes can form loosely bonded R_2PbPbR_2 dimers or a cyclic $(\text{PbR}_2)_3$ trimer.²² Diplumbenes are essentially ethylene analogs with Pb=Pb double bonds. However, such metal–metal interactions are usually quite weak often dissociating in solution into :PbR_2 monomers.^{23–28} Indeed, the two-coordinate lead(II) diaryl analogs are rare with the literature revealing few examples of structurally characterized monomeric diarylplumbynes.^{21,23,29–31}

Herein we report the syntheses and structures of two new monomeric, two-coordinated, diarylplumbynes PbR_2 containing terphenyl-based ligands ($\text{R}^1 = 2,4,6$ -triphenylphenyl, **1**; $\text{R}^2 = 2,6$ -bis(1'-naphthyl)phenyl, **2**). These ligands differ from the other terphenyls applied in the stabilization of low-valent diaryl-lead species^{32,33} in the lack of alkyl (*e.g.*, methyl or isopropyl) groups at the *ortho* and/or *para* positions of the flanking aryl rings. On the other hand, ligand R^1 bears an additional phenyl ring in the *para* position of the central ring, while R^2 has two flanking naphthyl groups attached to the central phenyl ring. It was hoped that these less crowding ligands could lead to aggregation of the :PbR_2 units to form novel $(\text{PbR}_2)_n$ compounds. However, both ligands resulted in monomeric products. The two ligands used in this work, R^1 and R^2 , have proven to be effective for the steric protection of germynes while leaving sufficient substituent motion to avoid destabilizing strain.¹³ Although $\text{Ge}[\text{C}_6\text{H}_3-2,6-(\text{naph})_2]_2$ has been

synthesized and structurally characterized, the analogous germylene with the $\text{C}_6\text{H}_2-2,4,6-\text{Ph}_3$ ligand, $\text{Ge}(\text{C}_6\text{H}_2-2,4,6-\text{Ph}_3)_2$, was not structurally characterized. The R^1 ligand has also been used to synthesize BiR_3 , an air-stable compound.³⁴

Compounds **1** and **2** were synthesized by reaction of PbBr_2 with RLi in diethyl ether at -78°C (eqn (1)).[†]



The initially orange mixture was warmed to r.t. overnight, during which time the color deepened to red (**1**) or orange–red (**2**). After removing the volatiles *in vacuo*, the products could be recrystallized from toluene solution as purple (**1**) or orange (**2**) crystals in moderate yields. **1** and **2** were characterized by elemental analyses, ^1H NMR spectroscopy, and single crystal X-ray diffraction.[‡]

The compounds are air- and moisture-sensitive. In the solid state, **1** decomposes at 190°C upon melting, while **2** is much more thermally stable, melting at 215°C without decomposition. The solutions of **1** and **2** undergo disproportionation slowly under argon at room temperature as indicated by the appearance of a black precipitate of lead metal. Both compounds are readily soluble in benzene, toluene and THF, and are less soluble in diethyl ether and hexane. The ^1H NMR spectrum of **1** recorded in C_6D_6 indicates the presence of $\text{Pb}(\text{C}_6\text{H}_2-2,4,6-\text{Ph}_3)_2$ and the co-crystallized triphenylbenzene (TPB) molecule in a 2 : 1 ratio. The singlet occurring at 8.06 ppm is assigned to the *m*-protons of the central phenyl rings of $\text{Pb}(\text{C}_6\text{H}_2-2,4,6-\text{Ph}_3)_2$, while the singlet at 7.77 ppm is attributed to the central phenyl protons of the co-crystallized TPB molecule. The two singlets have an integral ratio of 8 : 3. The incorporation of half a molecule of TPB per $\text{Pb}(\text{C}_6\text{H}_2-2,4,6-\text{Ph}_3)_2$ unit was also confirmed by elemental analysis and X-ray diffraction. The TPB hydrocarbon may have originated from hydrolysis of RLi with a trace of water in the lithiation (or subsequent steps), and was accommodated during the crystallization process. The ^1H NMR spectrum of **2** (in C_6D_6) shows extensively overlapped multiplets in the aromatic region (7.0–8.0 ppm).

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Compound **1** crystallizes in the triclinic space group *P*-1. The asymmetric unit cell contains two independent $\text{Pb}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)_2$ molecules (Fig. 1; For clarity, only one PbR_2 molecule is shown) and one molecule of triphenylbenzene with the overall composition of $\text{C}_{120}\text{H}_{86}\text{Pb}_2$. The diaryl lead(II) centers have a V-shaped coordination geometry. The two plumblylene molecules have slightly different structural parameters. For instance, the $\text{C}(1)\text{-Pb}(1)\text{-C}(25)$ bond angle is $95.8(5)^\circ$, while $\text{C}(73)\text{-Pb}(2)\text{-C}(49)$ angle of another PbR_2 is $92.7(6)^\circ$. The ligands are readily arranged around the lead centers and all the phenyl rings exhibit a nearly perfect planar conformation with negligible deviations. The nearest $\text{Pb}\cdots\text{Pb}$ separation is 11.34 \AA , indicating unambiguous monomeric, two-coordinate feature of the compound. In an extended structure, the $\text{Pb}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)_2$ molecules pack in layers, and the TPB molecules are filled between the layers.

Compound **2** is monoclinic, space group $P2_1/n$ with one PbR_2 molecule per asymmetrical unit cell. There are no solvent or organic molecules in the lattice. The Pb(II) center also resides at a bent, two-coordinate environment with a $\text{C}(1)\text{-Pb}(1)\text{-C}(27)$ bond angle of $100.40(13)^\circ$ (Fig. 2). The nearest $\text{Pb}\cdots\text{Pb}$ separation of 8.09 \AA excludes any dimerization of the PbR_2 units.

Compounds **1** and **2** show similar structural parameters about the lead(II) center. It is convenient to compare them with other diorgano lead(II) compounds. The Pb–C bond distances of **1** (2.321 \AA , average) and **2** (2.334 \AA , average) are comparable to those reported for other diarylplumblylenes, e.g., 2.37 \AA for $\text{Pb}(\text{C}_6\text{H}_2\text{-}2\text{-}^i\text{Bu-}4,5,6\text{-Me}_3)_2$,²³ $2.334(12) \text{ \AA}$ for $\text{Pb}(\text{C}_6\text{H}_3\text{-}2,6\text{-Me}_2)_2$,²⁹ 2.36 \AA for $\text{Pb}[\text{C}_6\text{H}_2\text{-}2,4,6\text{-(CF}_3)_3]_2$ ²¹ and $2.327(13) \text{ \AA}$ for $\text{Pb}[\text{C}_6\text{H}_2\text{-}2,4,6\text{-}\{\text{CH}(\text{SiMe}_3)_2\}_3]_2$.³¹ These values, however, are much longer than those of the tetravalent organolead compounds, e.g., the Pb–C bond length of 2.19 \AA in PbPh_4 ³⁵ and 2.20 \AA in $\text{Bp}_3\text{Pb-PbBp}_3$ (Bp = biphenyl).³⁶ The C–Pb–C bond angle of **1** (94.2°) is compared to that in $\text{Pb}[\text{C}_6\text{H}_2\text{-}2,4,6\text{-(CF}_3)_3]_2$ ($94.5(1)^\circ$)²¹ while the C–Pb–C angle of **2** ($100.40(13)^\circ$) is a little wider. However, both C–Pb–C angles of **1** and **2** are smaller than those in $\text{Pb}(\text{C}_6\text{H}_2\text{-}2\text{-}^i\text{Bu-}4,5,6\text{-Me}_3)_2$ ($103.04(13)^\circ$),²³ $\text{Pb}(\text{C}_6\text{H}_3\text{-}2,6\text{-Me}_2)_2$ ($114.5(6)^\circ$)²⁹ and $\text{Pb}[\text{C}_6\text{H}_2\text{-}2,4,6\text{-}\{\text{CH}(\text{SiMe}_3)_2\}_3]_2$ ($116.3(7)^\circ$),³¹ which bear bulky substituents on the aryl rings. It is noteworthy that the C–Pb–C bond angle of **1**, which lacks alkyl substituents on

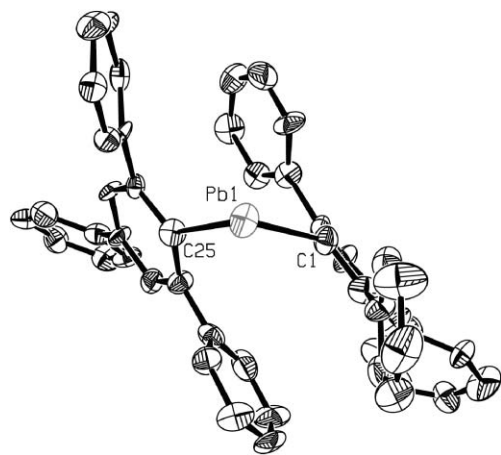


Fig. 1 Molecular structure of **1** (Thermal ellipsoids are shown at 30% probability levels). Selected bond distances (\AA) and angles ($^\circ$): $\text{Pb}(1)\text{-C}(1)$, $2.322(13)$; $\text{Pb}(1)\text{-C}(25)$, $2.327(13)$; $\text{C}(1)\text{-Pb}(1)\text{-C}(25)$, $95.8(5)$.

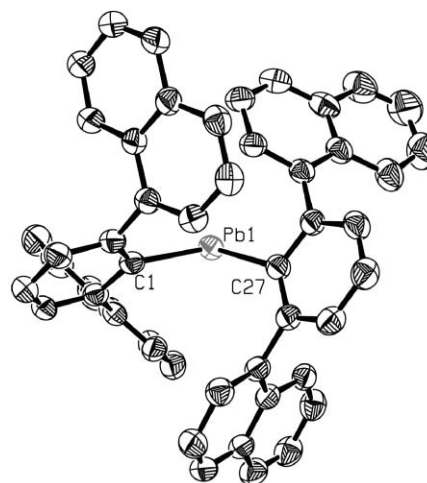


Fig. 2 Molecular structure of **2** (Thermal ellipsoids are shown at 30% probability levels). Selected bond distances (\AA) and angles ($^\circ$): $\text{Pb}(1)\text{-C}(1)$, $2.347(4)$; $\text{Pb}(1)\text{-C}(27)$, $2.322(4)$; $\text{C}(27)\text{-Pb}(1)\text{-C}(1)$, $100.40(13)$.

the flanking phenyl rings, is *ca.* 20° more acute than that in $\text{Pb}(\text{C}_6\text{H}_3\text{-}2,6\text{-Me}_2)_2$,²⁹ which has $-\text{CH}_3$ groups at *ortho* and *para* positions of the flanking aryls. Also interesting is a comparison of the C–Pb–C angle of **2** (100.4°) with the C–Ge–C bond angle (102.7°) of its analogous germylene, $\text{Ge}[\text{C}_6\text{H}_3\text{-}2,6\text{-(naph)}_2]_2$.¹³ The Pb(II) and Ge(II) centers have similar bent structures with very close C–E–C angles.

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Notes and references

† **Syntheses.** All manipulations were performed under purified argon using Schlenk techniques in conjunction with an inert atmosphere dry-box (M-Braun LabMaster 130). **1:** A diethyl ether (30 mL) solution of $2,4,6\text{-Ph}_3\text{-C}_6\text{H}_2\text{Li}(\text{OEt})_2$ (4.2 mmol), which was *in situ* prepared by treating $2,4,6\text{-Ph}_3\text{-C}_6\text{H}_2\text{Br}$ with *n*-BuLi, was added to PbBr_2 (0.77 g, 2.1 mmol) at -78°C . The mixture was allowed to warm to r.t. overnight with constant stirring. All volatiles were removed and the residue extracted with toluene (15 mL) to give a purple–red solution. Concentration and standing of the solution at r.t. for 3 days afforded compound **1** as dark red–purple crystals (1.22 g, 60%). Mp: 190°C (decomp.). Anal.: Calc. for $\text{PbR}_2\cdot 0.5\text{C}_{24}\text{H}_{18}$ ($\text{C}_{60}\text{H}_{43}\text{Pb}$): C, 74.20; H, 4.46%. Found: C, 73.92; H, 4.71%. $^1\text{H NMR}$ (C_6D_6 , δ/ppm): 8.06 (s, 8H, C_6H_2 of PbR_2), 7.77 (s, 3H, C_6H_3 of TPB), 7.58 (dd, 8H, *ortho* protons of $4\text{-C}_6\text{H}_5$ in PbR_2), 7.52 (dd, 6H, *ortho* protons of C_6H_5 in TPB), 7.0–7.3 (m, 61H). **2:** This compound was synthesized by a similar method. Reaction of $2,6\text{-(Naph)}_2\text{C}_6\text{H}_3\text{Li}$ (5.0 mmol) with PbBr_2 (0.92 g, 2.5 mmol) gave a red–orange solution. Orange crystals were yielded from toluene (1.41 g, 65%). Mp: $215\text{--}220^\circ\text{C}$. Anal.: Calc. for $\text{C}_{52}\text{H}_{34}\text{Pb}$: C, 72.12; H, 3.96%. Found: C, 71.94; H, 3.95%. $^1\text{H NMR}$ (C_6D_6 , δ/ppm): 8.0–7.0 (m, 34H, aromatic protons).

‡ **Crystallographic data.** **1:** $\text{C}_{120}\text{H}_{86}\text{Pb}_2$ (1942.27), triclinic, space group *P*-1, $a = 11.337(4) \text{ \AA}$, $b = 14.978(5) \text{ \AA}$, $c = 26.833(9) \text{ \AA}$, $\alpha = 92.280(6)^\circ$, $\beta = 100.708(5)^\circ$, $\gamma = 90.038(6)^\circ$, $V = 4473(2) \text{ \AA}^3$, $Z = 2$, $\mu = 3.811 \text{ mm}^{-1}$, $D = 1.442 \text{ g cm}^{-3}$, $F(000) = 1940$. Final *R* indices (979 parameters) for 5509 observed reflections [$I > 2\sigma(I)$] are $R1 = 0.0744$, $wR2 = 0.1564$, and those for all unique reflections are $R1 = 0.1504$, $wR2 = 0.1951$. **2:** $\text{C}_{52}\text{H}_{34}\text{Pb}$ (865.98), monoclinic, space group $P2_1/n$, $a = 11.4487(9) \text{ \AA}$, $b = 16.1126(13) \text{ \AA}$, $c = 21.3687(18) \text{ \AA}$, $\beta = 100.3270(10)^\circ$, $V = 3878.0(5) \text{ \AA}^3$, $Z = 4$, $\mu = 4.386 \text{ mm}^{-1}$, $D = 1.483 \text{ g cm}^{-3}$, $F(000) = 1712$. Final *R* indices (478 parameters) for 5785 observed reflections [$I > 2\sigma(I)$] are $R1 = 0.0319$, $wR2 = 0.0789$, and those for all unique reflections are $R1 = 0.0372$, $wR2 = 0.0841$. CCDC 284966 and 284967. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513401c.

- 1 W. Petz, *Chem. Rev.*, 1986, **86**, 1019.
- 2 M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267.
- 3 J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283.
- 4 W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311.
- 5 M. Kira, *Pure Appl. Chem.*, 2000, **72**, 2333.
- 6 T. Tsumuraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed.*, 1991, **30**, 902.
- 7 M. Driess and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 1996, **35**, 828.
- 8 M. Weidenbruch, *Eur. J. Inorg. Chem.*, 1999, 373.
- 9 M. Weidenbruch, *Organometallics*, 2003, **22**, 4348.
- 10 M. Weidenbruch, *J. Organomet. Chem.*, 2002, **646**, 39.
- 11 R. West, *Polyhedron*, 2002, **21**, 467.
- 12 R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 231.
- 13 G. L. Wegner, R. J. F. Berger, A. Schier and H. Schmidbaur, *Organometallics*, 2001, **20**, 418.
- 14 J. Barrau and G. Rima, *Coord. Chem. Rev.*, 1998, **178–180**, 593.
- 15 K. Klinkhammer, *Polyhedron*, 2002, **21**, 587.
- 16 B. E. Eichler, A. D. Phillips and P. P. Power, *Organometallics*, 2003, **22**, 5423.
- 17 B. E. Eichler and P. P. Power, *Inorg. Chem.*, 2000, **39**, 5444.
- 18 P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1973, 317.
- 19 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
- 20 C. Eaborn, T. Ganicz, P. B. Hitchcock, J. D. Smith and S. E. Sozerli, *Organometallics*, 1997, **16**, 5621.
- 21 S. Brooker, J. K. Buijink and F. T. Edelman, *Organometallics*, 1991, **10**, 25.
- 22 F. Stabenow, W. Saak, H. Marsmann and M. Weidenbruch, *J. Am. Chem. Soc.*, 2003, **125**, 10172.
- 23 M. Stürmann, M. Weidenbruch, K. W. Klinkhammer, F. Lissner and H. Marsmann, *Organometallics*, 1998, **17**, 4425.
- 24 K. W. Klinkhammer, T. F. Fassler and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 1998, **37**, 124.
- 25 M. Stürmann, W. Saak, H. Marsmann and M. Weidenbruch, *Angew. Chem., Int. Ed.*, 1999, **38**, 187.
- 26 M. Stürmann, W. Saak, M. Weidenbruch and K. W. Klinkhammer, *Eur. J. Inorg. Chem.*, 1999, 579.
- 27 M. Stürmann, W. Saak and M. Weidenbruch, *Z. Anorg. Allg. Chem.*, 1999, **625**, 705.
- 28 S. Hino, M. Olmstead, A. D. Phillips, R. J. Wright and P. P. Power, *Inorg. Chem.*, 2004, **43**, 7346.
- 29 R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, 1997, **16**, 1920.
- 30 L. Pu, B. Twamley and P. P. Power, *Organometallics*, 2000, **19**, 2874.
- 31 N. Kano, K. Shibata, N. Tokitoh and R. Okazaki, *Organometallics*, 1999, **18**, 2999.
- 32 T. Matsumoto, Y. Matsui, Y. Nakaya and K. Tatsumi, *Chem. Lett.*, 2001, 60.
- 33 M. M. Olmstead and P. P. Power, *J. Organomet. Chem.*, 1991, **408**, 1.
- 34 X. W. Li, J. Lorberth, W. Massa and S. Wocadlo, *J. Organomet. Chem.*, 1995, **485**, 141.
- 35 V. Busetti, M. Mammi, A. Signor and A. Del Pra, *Inorg. Chim. Acta*, 1967, **1**, 424.
- 36 Y. Wang, B. Quillian, P. Wei, X.-J. Yang and G. H. Robinson, *Chem. Commun.*, 2004, 2224.