Lead Chemistry

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A Base-Stabilized Lead(I) Dimer and an Aromatic Plumbylidenide Anion**

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Heavier Group 14 alkyne analogues with the composition REER (R = supporting ligand; E = Si, Ge, Sn, Pb) have attracted much attention in the past decades owing to their unique structures and reactivities.[1] A series of stable disilynes, digermynes, and distannynes stabilized kinetically by bulky aryl and silyl ligands was synthesized.[1] X-ray crystallography showed that they have a *trans*-bent and planar geometry in which the R-E-E angle decreases from silicon to tin. Recent theoretical studies and UV/Vis spectroscopy showed that they adopt a multiply bonded structure **M** in solution (Scheme 1).[2] The reactivity of stable disilynes, digermynes, and distannynes has been investigated extensively.[1d,3] One of the well-studied cases is reduction. Stable disilynes, digermynes, and distannynes can undergo one-electron and two-electron reduction to give the radical anions $[\mathrm{REER}]^{\bullet -}$ and the doubly reduced species $[\mathrm{REER}]^{2-}$, respectively.[1f,4] Comparison of their structural data with those of the heavier alkyne analogues can provide insight into the E–E bonding.[2,5] In contrast, a diplumbyne is rare. Only [Ar*PbPbAr*] (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$) was synthesized and structurally characterized by Power et al. in 2000.[1e] X-ray crystallography showed that it has a strongly bent structure, a long Pb–Pb single bond, and a lone pair of electrons on each lead atom (singly bonded structure **S**). However, theoretical studies and UV/Vis spectroscopy showed that [Ar*PbPbAr*] has a multiply bonded structure **M** in solution.[6] The singly bonded structure of [Ar*PbPbAr*] in the solid state is ascribed to packing effects. Moreover, little is known about its reactivity,[7] and the reduction of [Ar*PbPbAr*] has not yet been reported.

M **S**

E = Si, Ge, Sn
R = silyl or terphenyl ligand

Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$

Scheme 1. Multiply bonded **M** and singly bonded structures **S**.

Recently, a series of novel base-stabilized Group 14 element(I) dimers [LË–ËL] (E = Si, Ge, Sn, L = amidinate, quanidinate, β-diketiminate, N-functionalized aryl, P-functionalized amide) was synthesized.[8] They comprise an Ë–Ë single bond and a lone pair of electrons on each E atom. Their structures resemble the singly bonded structure **S**. Thus, they are considered as base-stabilized heavier alkyne analogues. Their reactivities showed that they are powerful reagents for the activation of small molecules and unsaturated substrates.[8b,c,g,9] In contrast, no examples of a base-stabilized lead(I) dimer have yet been reported because of the synthetic difficulties in preparing such molecules. For example, Jones et al. reported that an attempt to isolate a β-diketiminate or amidinate Pb^I dimer by the reduction of the corresponding lead(II) chloride or triflate with the magnesium(I) dimer failed, which led to the formation of homoleptic Pb^{II} complex [HC(C*t*BuNMes)$_2$Pb:] (Mes = 2,4,6-$Me_3C_6H_2$) or lead metal, respectively.[8a,f] However, the lighter analogues were synthesized in very high yield by a similar method. It seems that a lead(I) dimer is unstable towards disproportionation.

Although lead(I) dimers are still unknown, they are worthwhile synthetic targets both for fundamental reasons and small-molecule activation. Moreover, they could show different properties and reactivity compared with those of the multiply bonded derivative [Ar*PbPbAr*], which has also been little investigated compared with the lighter analogues. Recently, a 2,6-diiminophenyl ligand has been shown to stabilize a germanium(I) and tin(I) dimer.[8d,e] We anticipate that the ligand is capable of stabilizing a lead(I) radical or its dimeric derivative. Herein, we report the preparation of a 2,6-diiminophenyllead(I) dimer [{LPb:}$_2$] (L = 2,6-(CH=NAr)$_2C_6H_3$, Ar = 2,6-*i*$Pr_2C_6H_3$) by the oxidation of a 2,6-diiminophenylplumbylidenide anion $[\mathrm{LPb}]^-$, which is the first example of aromatic low-valent lead analogue of an indenyl anion. The reduction of [{LPb:}$_2$] with lithium regenerated $[\mathrm{LPb}]^-$.

The reaction of [LBr][10] (**1**) with *n*BuLi in THF at −78 °C, followed by the treatment with $PbBr_2$, afforded [LPbBr] in 48.1% yield (**2**; Scheme 2).[11] It was isolated as a highly air- and moisture-sensitive yellow crystalline solid. It is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **2** show one set of signals owing to the 2,6-diiminophenyl ligand. No ^{207}Pb NMR resonance could be observed because the quadrupolar $^{79/81}Br$ nuclei may broaden the signal. The result is in accord with reported problems in recording ^{207}Pb NMR spectra of

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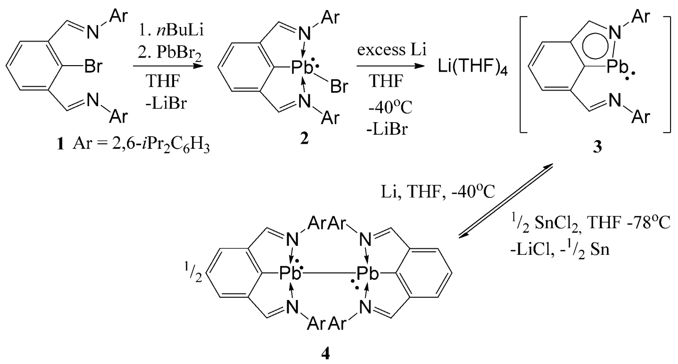

Scheme 2. Synthesis of **2**–**4**.

organolead(II) halides, such as $[\{Ar^*PbBr\}_2]$,[12] $[Ar^*Pb(NC_5H_5)Br]$,[12] and $[4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{P(OEt)_2{=}O\}_2C_6H_2PbCl]$.[13] X-ray crystallography showed that the 2,6-diiminophenyl ligand is bonded in tridentate fashion to the lead atom, which adopts a seesaw geometry with the N atoms at the axial positions and the C1 and Br1 atoms at the equatorial positions (Figure 1). The C1-Pb1-Br1 (95.0(4)°) and N-Pb-Br (average 88.2°) angles indicate little hybridization of the lead valence orbitals as well as the presence of a lone pair with high s character at the lead atom. The Pb−C (2.289(19) Å) and Pb−Br bonds (2.701(2) Å) are comparable with those in the pyridine-stabilized terphenyllead(II) bromide $[Ar^*Pb(NC_5H_5)Br]$ (Pb−C 2.322(4), Pb−Br 2.7063(6) Å).[12] Furthermore, the Pb−N bonds (2.637(16), 2.691(17) Å) are longer than the intermolecular Pb−N bond in $[Ar^*Pb(NC_5H_5)Br]$ (2.502(4) Å).[12]

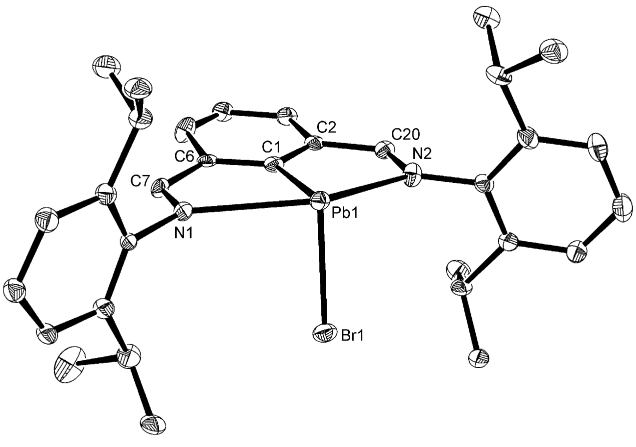

Figure 1. Molecular structure of compound **2** (ellipsoids set at 50% probability). Hydrogen atoms and disorder in the *i*Pr substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1–C1 2.289(19), Pb1–Br1 2.701(2), Pb1–N1 2.637(16), Pb1–N2 2.691(17), N1–C7 1.27(2), N2–C20 1.25(3), C2–C20 1.46(3), C6–C7 1.48(3), C1–C6 1.36(3), C1–C2 1.38(3); C1-Pb1-Br1 95.0(4), C1-Pb1-N1 68.6(6), C1-Pb1-N2 68.0(6), N1-Pb1-N2 135.9(5), N1-Pb1-Br1 88.1(4), N2-Pb1-Br1 88.2(4).

An attempt to isolate the 2,6-diiminophenyllead(I) dimer $[\{LPb{:}\}_2]$ (**4**) by the reduction of **2** with alkali metals or the magnesium(I) dimer[14] failed. The reaction of **2** with one equivalent of Li in THF at −40 °C afforded a mixture of 2,6-diiminophenyllithium $(LLi)_2$ (major product), lead(I) dimer $[\{LPb{:}\}_2]$, homoleptic plumbylene $[L_2Pb{:}]$,[15] and unidentified products, which was confirmed by NMR spectroscopy. Only $(LLi)_2$ can be isolated from the mixture by recrystallization (Supporting Information, Figure S1). Similarly, the reaction of **2** with 0.5 equivalent of $[HC(CMeNMes)_2Mg]_2$ in THF at −40 °C afforded $[L_2Pb{:}]$ and $[HC(CMeNMes)_2MgBr]$, which was confirmed by NMR spectroscopy. The results are consistent with the reduction of amidinate- or β-diketiminate lead(II) halides.[8a,f]

In contrast, the reaction of **2** with excess Li in THF at −40 °C afforded the plumbylidenide anion $[Li(thf)_4][LPb]$ (**3**), in which the negative charge is aromatically delocalized in the PbC_3N five-membered ring.[11] Compound **3** is the first aromatic low-valent lead analogue of an indenyl anion. The results indicate that 2p orbitals of C/N atoms and a 6p orbital of a low valent Pb atom can sufficiently overlap to form an aromatic compound. In contrast, a similar tetravalent lead analogue of a cyclopentadienyl anion, which is the lithiomesitylplumbole $[C_4Ph_4Pb(Mes)Li]$,[16] does not show any aromatic character. Until now, only one tetravalent lead compound, which is the dianionic plumbole $[Li(dme)_3][(dme)Li(\eta^5\text{-}PbC_4Ph_4)]$, shows considerable aromaticity.[16]

Compound **3** was isolated as a light-sensitive dark-red crystalline solid in 12.6% yield. It is stable in ether solvents and the solid state. It decomposes in toluene and C_6D_6 to form LLi and lead metal, which was confirmed by NMR spectroscopy. Thus, the spectroscopic analyses of **3** can only be performed in $[D_8]$THF. The ^{1}H NMR spectrum at room temperature shows a doublet and septet at δ 1.12 and 3.35 ppm for the *i*Pr substituents. It also displays signals for phenyl protons at δ 6.37–7.04 ppm. It is noteworthy that the signal for *H*CNAr (δ 7.92 ppm) shows an upfield shift compared with that of **2** (δ 9.15 ppm) and falls in the aromatic proton region. Moreover, the ^{1}H NMR spectrum of **3** was also acquired at −60 °C, whereupon two sharp doublets (δ 1.05, 1.10 ppm) and two septets (δ 3.12, 3.24 ppm) for the non-equivalent *i*Pr protons were resolved. The results indicate that compound **3** retains its solid-state structure at −60 °C in solution, and the imino substituents are fluxional in solution at room temperature. Moreover, the ^{207}Pb{^{1}H} NMR signal (δ 3415 ppm) at room temperature shows a significant downfield shift compared with that of the 2,6-diiminophenyllead(I) dimer $[\{LPb{:}\}_2]$ (**4**, δ 1684 ppm). The results indicate that the negative charge at the Pb atom is stabilized by an aromatic delocalization in the PbC_3N five-membered ring. It is also supported by DFT calculations of $\mathbf{3}^-$ (Supporting Information, Figure S3, M06-2x/LanL08(d) level),[17] which reveal pronounced aromaticity of the PbC_3N ring, indicated by the negative nucleus independent chemical shift value[18] (NICS(1) = −6.33 ppm). Furthermore, the NICS(1) value of the PbC_3N ring is comparable with that of the dianionic plumbole $[Li(dme)_3][(dme)Li(\eta^5\text{-}PbC_4Ph_4)]$ (NICS(1) = −6.28 ppm).[16]

X-ray crystallography showed that compound **3** is monomeric (Figure 2). The 2,6-diiminophenyl ligand is bonded in a bidentate fashion to the lead atom. The PbC_3N ring is planar and the sum of the internal bond angles is 540.0°. The Li1

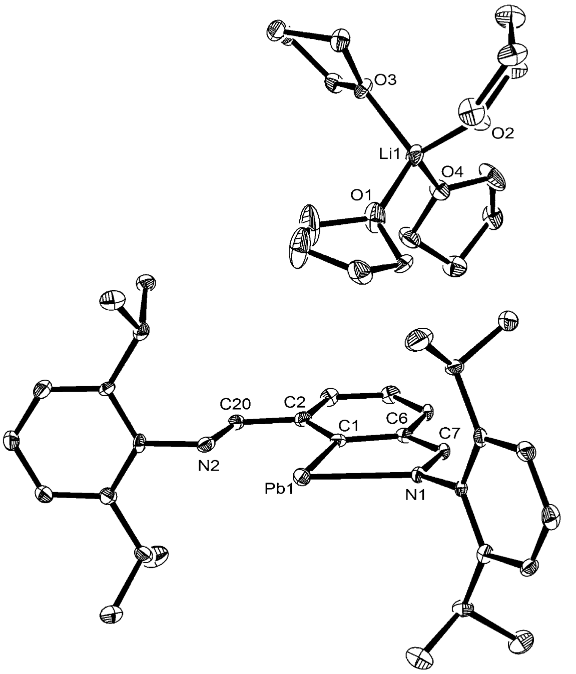

Figure 2. Molecular structure of compound **3** (ellipsoids set at 50% probability). Hydrogen atoms and disorder in THF molecules omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1–N1 2.425(5), N1–C7 1.347(10), C6–C7 1.380(10), C1–C6 1.444(9), Pb1–C1 2.180(5), N2–C20 1.293(11), C20–C2 1.456(10); C1-Pb1-N1 73.2(2), Pb1-N1-C7 111.3(4), C1-C6-C7 118.8(7), C6-C7-N1 120.1(7), Pb1-C1-C6 116.6(5).

atom is coordinated with four THF molecules. The Pb1–Li1 distance (8.041(8) Å) is longer than the sum of van der Waals radii, which suggests that there is no interaction between these atoms. Comparing the bonding in the PbC$_3$N five-membered ring (Pb1–N1 2.425(5) Å, N1–C7 1.347(10) Å, C6–C7 1.380(10) Å, C1–C6 1.444(9) Å, Pb1–C1 2.180(5) Å) with those in compound **2** (Pb–N average 2.664 Å, N1–C7 and N2–C20 average 1.26 Å, C6–C7 and C2–C20 average 1.47 Å, C1–C2 and C1–C6 average 1.37 Å, Pb–C 2.289(19) Å), it is suggested that there is an aromatic delocalization in the PbC$_3$N five-membered ring. Moreover, the Pb1–N1 bond is still longer than reported Pb^{II}–N$_{amide}$ single bonds (2.07(5)–2.35(5) Å).[19]

Recently, Sekiguchi et al. reported that a stannylsodium intermediate [*t*Bu$_2$MeSi]$_3$SnNa underwent an oxidation with SnCl$_2$·dioxane to form a stable stannyl radical.[20] It is anticipated that a lead(I) radical or its dimeric derivative can be prepared by a similar strategy. The reaction of two equivalents of **3** with SnCl$_2$ in THF at −78 °C afforded the 2,6-diiminophenyllead(I) dimer [{LPb:}$_2$] (**4**).[11] The ^{1}H and ^{13}C NMR spectra of **4** show one set of signals for the 2,6-diiminophenyl ligand. The ^{207}Pb NMR signal of **4** (δ 1684 ppm) shows an upfield shift compared with that of **3**. Compound **4** was isolated as a light-sensitive dark-green crystalline solid in 12.1% yield. It is stable in hydrocarbon solvents and the solid state. The UV/Vis spectrum of **4** in THF shows three absorption bands at 396, 473, and 526 nm in the visible light region, which shows a hypsochromic shift compared with that of the lighter congeners [{2,6-(CR=NAr)$_2$C$_6$H$_3$E:}$_2$] (E = Ge, R = H: 438, 586 and 702 nm; E = Sn, R = Me: 425, 457 and 561 nm).[8b,e] The shift is comparable with that observed in the amidinate-stabilized Group 14 element(I) dimers [{[R^{1}C(NAr)$_2$]E:}$_2$] (R^1 = C$_6$H$_4$-4-*t*Bu, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; E = Si: 629, Ge: 502, Sn: 388 nm).[8a] Moreover, this is opposite to the electronic spectra of multiple-bonded heavier Group 14 alkyne analogues [Ar*EEAr*] (E = Ge: 365, 490; Sn: 409, 593; Pb: 397, 719 nm) in which there is a bathochromic shift on descending the group.[1e,g] The results imply that the Pb–Pb bond in **4** has little π character in solution, which is different from [Ar*PbPbAr*] comprising a multiply bonded structure **M** in solution. X-ray crystallography showed that the 2,6-diiminophenyl ligand is bonded in tridentate fashion to the lead atoms, which adopt a seesaw geometry with the N atoms at the axial positions and the C atoms at the equatorial positions (Figure 3). The C-Pb-Pb angles (average 108.5°) indicate that there is a lone pair of electrons at the lead atoms. Moreover, compound **4** has a *gauche*-bent structure (C-Pb-Pb-C 102.2°), which is different from [Ar*PbPbAr*] comprising a *trans*-bent structure. The Pb–Pb bond (3.1283(6) Å) is comparable with that in [Ar*PbPbAr*] (3.1881(1) Å), which indicates that the Pb–Pb bond is a single bond. The C$_{imine}$–N bonds (average 1.270 Å) are shortened and the Pb–N (average 2.671 Å) and Pb–C (average 2.264 Å) bonds are lengthened compared with those of **3**, which indicate that

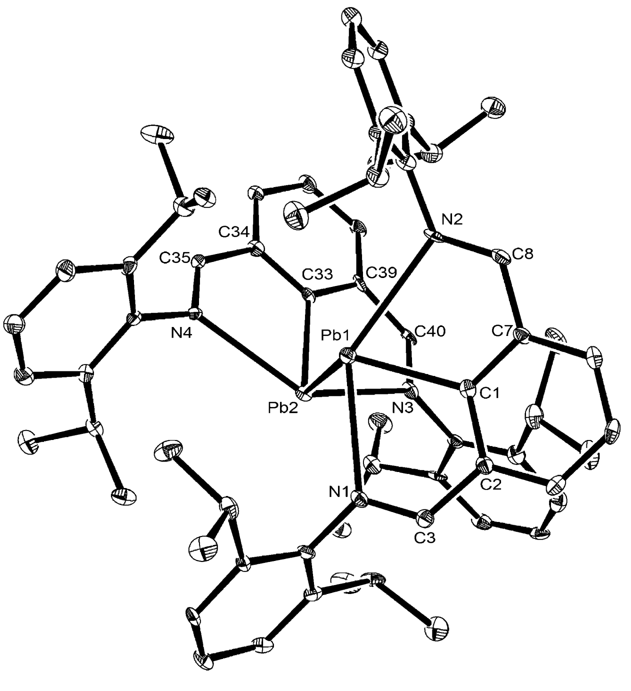

Figure 3. Molecular structure of compound **4** (ellipsoids set at 50% probability). Hydrogen atoms and disorder in the Ar substituents are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb1–Pb2 3.1283(6), Pb1–N1 2.613(10), Pb1–N2 2.706(9), Pb2–N3 2.715(9), Pb2–N4 2.650(8), Pb1–C1 2.287(11), Pb2–C33 2.240(11), N1–C3 1.276(14), N2–C8 1.287(14), C2–C3 1.455(17), C7–C8 1.463(16), C1–C2 1.423(16), C1–C7 1.400(16); C1-Pb1-Pb2 111.3(3), C1-Pb1-N1 69.5(4), C1-Pb1-N2 68.6(4), N1-Pb1-Pb2 81.2(2), N2-Pb1-Pb2 119.42(19), C33-Pb2-Pb1 105.7(3), C33-Pb2-N3 68.5(3), C33-Pb2-N4 68.7(3).

there is no electronic delocalization in the PbC$_3$N rings. Moreover, the bond lengths of the PbC$_3$N rings are comparable with those in **2**. It is concluded that compound **4** has a singly bonded structure **S** in both solution and the solid state.

To compare with the reactivity of multiply bonded heavier Group 14 alkyne analogues, the reduction of compound **4** with two equivalents of lithium in THF was performed, which quantitatively afforded compound **3**.[11] It is in contrast to the reduction of stable disilynes, digermynes, and distannynes to give the radical anions $[\mathrm{REER}]^{\bullet -}$ or the doubly reduced species $[\mathrm{REER}]^{2-}$. Moreover, the results imply that the reaction of **2** with excess Li in THF proceeds through the formation of a lead(I) radical intermediate, which then reacts with lithium to form **4**.

In conclusion, we have reported the synthesis of the first base-stabilized lead(I) dimer by a simple procedure. X-ray crystallography and NMR spectroscopy showed conclusively that compound **4** has a singly bonded structure **S** in both solution and the solid state. The reduction of **4** with lithium afforded the aromatic plumbylidenide anion **3**, which is in contrast to the outcome by the reduction of multiply bonded heavier Group 14 alkyne analogues. The small molecules activation of **4** and the utilization of **3** as an electron-rich ligand are currently under investigation.

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Keywords: aromaticity · carbene homologues · diiminophenyl ligands · lead · low-valent compounds

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