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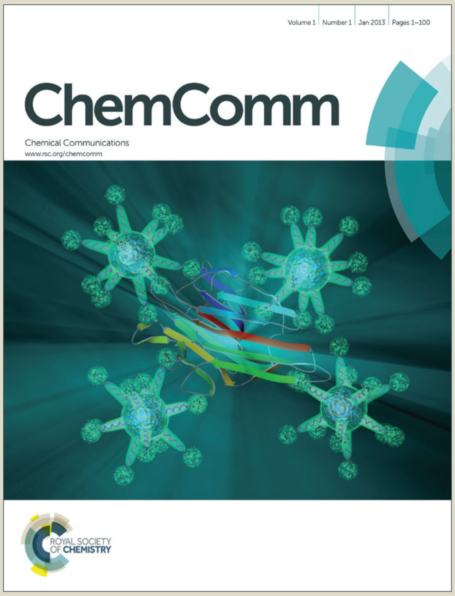

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A reversible two-electron redox system involving a divalent lead species[$]

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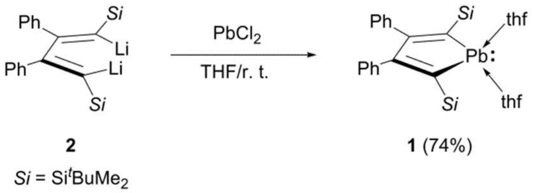
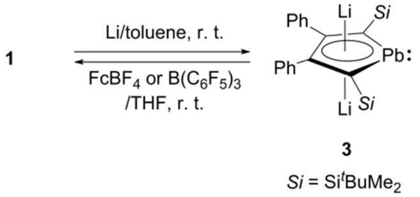
Reduction of THF-stabilized plumbacyclopentadienylidene with lithium afforded dilithioplumbole. On the other hand, oxidation of the dilithioplumbole provided the starting plumbacyclopentadienylidene. This is the unprecedented example of a reversible interconversion between group 14 M(II) and its dianionic species bearing organic substituents.

The group 14 divalent species, tetrylenes, are highly reactive and undergo oligomerization and/or insertion reactions to afford the corresponding oligomers and/or adducts, respectively.[1] On the other hand, using appropriate substituents to suppress their oligomerization enables to use the tetrylenes as key intermediates to activate small molecules[2] and therefore the tetrylenes are receiving considerable interest. In contrast, redox reactions of the tetrylenes have been remarkably limited. Reduction of tetrylenes with alkali metals afforded the corresponding anion radicals, which were identified by EPR spectroscopy or X-ray diffraction analysis.[3] However, further reduction of the anion radicals to dianionic species has never been reported. We report herein the first example of redox reaction of a tetrylene: reduction of a plumbylene to afford the corresponding dianionic species and oxidation of the resulting dianionic species to recover the starting tetrylene.

The starting plumbacyclopentadienylidene stabilized by two THF molecules **1** was previously prepared by the reaction of the corresponding 1,4-dilithio-1,3-butadiene **2**[4] with Lappert's diaminoplumbylene in 34% yield.[5, 6] Using lead dichloride instead of the diaminoplumbylene here did not require repetitive recrystallization to remove lithium disilazide from the crude product and improved the yield of **1** to 74% (Scheme 1). When compound **1** was then treated with an excess of lithium in toluene at room temperature, the color of the solution turned from deep red to light green during stirring for 9 h. After recrystallization of the crude product, dilithioplumbole **3** was obtained in 73% yield as green crystals (Scheme 2). The compound **3** is the second example of a dilithioplumbole.[7] As the reaction did not proceed in THF, the elimination of THF molecules from **1** to make a p-orbital of the central Pb atom vacant is essential for the reduction of **1** to **3**. Such dissociation behaviour was already supported by theoretical calculations.[6, 8] Dilithioplumbole **3** is regarded as a dianionic equivalent of **1**, and therefore two-electron reduction of **1** occurred, which is a novel reduction mode of a tetrylene.



Scheme 1 Improved synthesis of THF-stabilized plumbacyclopentadienylidene **1**.



Scheme 2 Redox reaction between plumbacyclopentadienylidene **1** and dilithioplumbole **3**.

The molecular structure of dilithioplumbole **3** was established by X-ray diffraction analysis (Fig. 1).[†] The plumbole ring is planar with no C–C bond alternation, suggesting that compound **3** possesses considerable aromatic character, as was observed in the corresponding tetraphenyl derivative.[7] Each of the two lithium atoms is coordinated by the plumbole ring in an η^5-fashion, which is retained in solution, as judged from a high-field resonance (–3.5 ppm in C_6D_6) in the ^{7}Li NMR resulting from its aromatic nature, similar to dilithiostannoles.[4b, 9] On the other hand, the molecular structure of tetraphenyldilithioplumbole reveals that one of the two lithium atoms is coordinated by its plumbole ring in an η^5-fashion, while the other lithium atom is coordinated by three DME molecules, and exchange of lithium cations was suggested by the ^{7}Li signal of –1.1 ppm.[7] As supporting this, the ^{7}Li NMR signal for **3** in THF shifted to a low field (–2.3 ppm), clearly indicating exchange of lithium cations. As expected, the ^{7}Li NMR spectrum for **3** in THF at 203 K exhibited two signals at –2.2 and –5.0 ppm, the former of which is assignable to a solvated lithium nucleus and the latter of which arises from an η^5-coordinated lithium nucleus. No remarkable effects of silyl substituents on the molecular structure of **3** were observed. However, the ^{207}Pb NMR signal for **3** (2573 ppm) shifted to a low field, compared with that for the tetraphenyl derivative (1713 ppm), which reflects its plumbylene character enhanced by silyl groups. A similar trend was also found in dilithiostannoles.[4b]

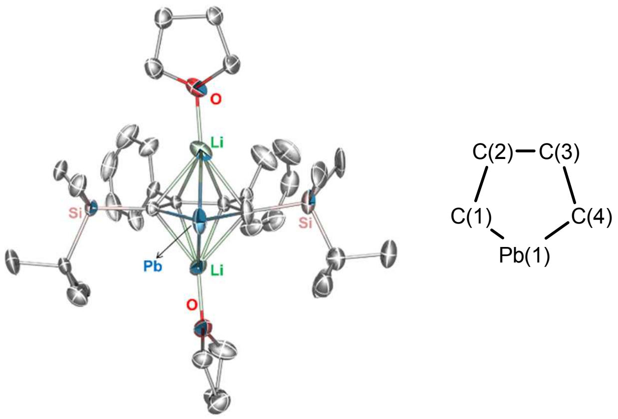
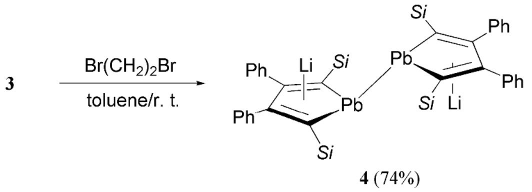


Fig.1 Molecular structure of dilithioplumbole **3** with thermal ellipsoid plots at 50% probability. Selected bond lengths (Å): C(1)–C(2): 1.424(5); C(2)–C(3): 1.452(5); C(3)–C(4): 1.423(5). Disorder around one of the silyl groups is found and only one part is shown here.

For the oxidation of dilithioplumbole **3**, ferrocenium tetrafluroborate ($FcBF_4$) was chosen, as in the case of tetraphenyldilithiostannole.[10] When THF was added to a mixture of **3** and two equivalents of $FcBF_4$ at room temperature, the reaction proceeded cleanly. After NMR analysis, compound **1** was generated quantitatively as a result of two-electron oxidation of **3** (Scheme 2). It is noted that oxidation of a dianionic species of group 14 elements to afford the corresponding divalent species was also unprecedented. Tris(pentaflurophenyl)borane ($B(C_6F_5)_3$) also functioned as an oxidant. Reaction of **3** with 2 equivalents of $B(C_6F_5)_3$ provided **1** quantitatively. This is a rare example of an oxidation reaction of main group compounds using $B(C_6F_5)_3$,[11,12] even though transition-metal compounds were known to be oxidized by $B(C_6F_5)_3$.[13]



4 (74%)

Si = Si^{t}BuMe$_2$

Scheme 3 Oxidation of dilithioplumbole **3** by dibromoethane.

In contrast to the formation of **1** from **3**, when using 0.5 equiv. of dibromoethane, which is a milder oxidant,[14] 1,1'-dilithiobiplumbole **4** was obtained in 74% yield as red crystals (Scheme 3),[15] the structure of which was established by X-ray diffraction analysis (Fig. 2).† Each of the two lithium atoms is coordinated by a THF molecule and a plumbole in an η^1- and η^5-fashions, respectively, and the plumbole rings, which are placed in an anti fashion, are nearly planar with the sum of the internal angles of 538.8°. The C–C bonds in the plumbole rings remarkably alter (1.375(6) to 1.495(6) Å), suggesting their non-aromatic character. Although such geometry was also found in 1,1'-dilithiobistannole,[9b] the angle between the vectors of Pb atoms and the plumbole ring centres each is 134°, whereas that of 1,1'-dilithiobistannole is linear because of its C*s* symmetry with regard to the Sn–Sn bond. Such deviation probably arises from considerable steric repulsion due to the bulky silyl group because the shortest C–C distance in the two *t*-butyldimethylsilyl groups is 3.6 Å, which is comparable to the sum of van der Waals radii of two methyl groups (3.4–4.4 Å).[16] Note that the Pb–Pb distance of 3.2056(3) Å is much longer than that of $Ph_3PbPbPh_3$ (2.848(4) Å)[17] and even longer compared to those in diplumbynes (3.1283(6)[18] and 3.1881(1)[19] Å) and cyclotriplumbane (3.1727(3) to 3.2014(2) Å),[20] reflecting the increase of p character of the Pb–Pb bond because of a lone pair on the lead atom with high s character. The ^{207}Pb NMR signal for **4** was observed at 1391 ppm, which is in a region similar to those of lithiomesitylplumbole (1096 ppm)[7] and lithiotriphenylplumbane (1060 ppm),[21] suggesting that an anionic charge of **4** should localize at the lead atom. Compound **4** is of considerable interest as the first example of a 1,1'-dianion equivalent of a diplumbane.[22] The formation of **4** is reasonably interpreted in terms of dimerization of the corresponding intermediary anion radical formed by the oxidation of **3**. In contrast, the reaction with an equimolar amount of dibromoethane did not proceed cleanly and the expected **1** was not obtained.[23] The liberated ethylene upon the redox reaction might make the reaction complicated.[24] The reaction of **4** with dibromoethane also afforded a complex mixture and did not produce **1**.

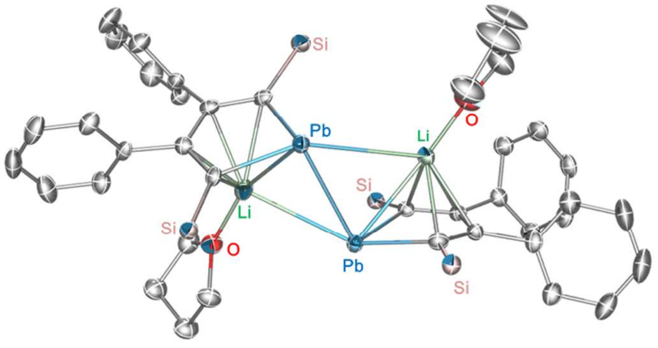


Fig.2 Molecular structure of 1,1'-dilithiobiplumbole **4** with thermal ellipsoid plots at 50% probability. All the carbon substituents on the silicon atoms are omitted for clarity.

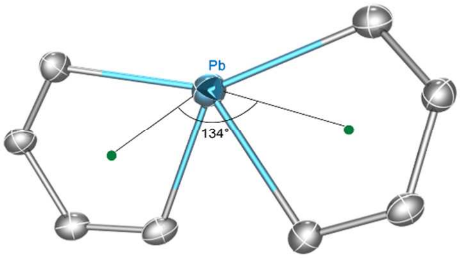


Fig.3 Orientation of the plumbole rings of **4** on the Pb–Pb axis. All the substituents on the ring carbon atoms are omitted for clarity.

In conclusion, we found reduction of a plumbylene to the corresponding dianionic species, which is the first example of conversion of a group 14 divalent compound to the corresponding dianion. The driving force of this reaction mode is probably aromatic stabilization of the dianionic species. The dilithioplumbole was oxidized to provide the starting plumbylene, stabilized by two THF molecules. When using a mild oxidant, the intermediary anion radical dimerized to afford 1,1'-dilithiobiplumbole. The present reversible redox reaction would give new insight into the difference and similarity between main group and transition-metal compounds.

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Notes and references

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$ Dedicated to the memory of Professor M. F. Lappert in the University of Sussex.

† Crystal data for **3**: triclinic, space group *P*-1, a = 12.4117(13) Å, b = 12.4449(15) Å, c = 13.7628(16) Å, α = 82.874(2)°, β = 67.352(2)°, γ = 75.447(3)°, V = 1898.1(4) Å^3, Dc = 1.396 g cm^{-3}, 100 K, Mo-K$_\alpha$ radiation (λ = 0.71073 Å) for Z = 2. Least-squares refinement based on 7098 reflections with $I > 2.0\sigma(I)$ (out of 8708 unique reflections) led to a final value of R ($_wR_2$) = 0.035 (0.083). CCDC 1030691. Crystal data for **4**: triclinic, space group *P*-1, a = 12.2658(10) Å, b = 16.7325(13) Å, c = 20.3750(16) Å, α = 99.2540(10)°, β = 107.1500(10)°, γ = 107.8820(10)°, V = 3654.6(5) Å^3, Dc = 1.385 g cm^{-3}, 150 K, Mo-K$_\alpha$ radiation (λ = 0.71073 Å) for Z = 2. Least-squares refinement based on 10861 reflections with $I > 2.0\sigma(I)$ (out of 13609 unique reflections) led to a final value of R ($_wR_2$) = 0.030 (0.074). CCDC 1030690.

Electronic Supplementary Information (ESI) available: experimental procedures and NMR charts of compounds **3** and **4**. See DOI:10.1039/c000000x/

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