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A zwitterionic carbene–plumbylene adduct

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4,5-Dimethyl-1,3-diisopropylimidazol-2-ylidene reacts with bis(2,4,6-triisopropylphenyl)plumbylene to furnish the adduct 4 as yellow crystals; an X-ray structure analysis of 4 revealed a very long lead–carbon bond of 254.0(5) pm and a pyramidal lead centre with a bending angle of 70.5°.

Since the first isolation of thermally stable carbenes of the imidazol-2-ylidene type[1] the chemistry of this class of compounds has undergone vigorous developments, which were recently reviewed.[2] The nucleophilicity of these molecules is reflected, for example, in the formation of adducts with GeI_2,[3] $SnCl_2$,[4] and even a diarylstannylene.[5] Lead(II) derivatives of this carbene system were previously unknown. We now report on the formation and structure of the first adduct between a plumbylene and an imidazol-2-ylidene.

Compound **1** (Scheme 1) which we recently prepared[6] is the first diplumbene having a Pb=Pb double bond length and *trans*-bending angle of the sizes predicted by theoretical calculations.[7–9] Although **1** is indefinitely stable in the solid state under exclusion of light and air, it decomposes in solution to furnish predominately the plumbylene molecules **2** as a consequence of the low Pb=Pb bond dissociation energy, calculated to be merely 24 kJ mol^{-1} for the parent compound $H_2Pb{=}PbH_2$.[9] Addition of the carbene **3**[10] to a violet solution of **2** in toluene results in a spontaneous change in the colour of the solution to orange. Replacement of the toluene by *n*-hexane and cooling to −30 °C then affords compound **4** as yellow crystals in 43% yield. The adduct **4** is sensitive to light and air and the solid decomposes at room temperature. It is only stable in solution in the presence of an excess of **2**. All attempts to record NMR and electron spectra of pure **4** have failed because deposition with formation of 1,3,5-triisopropylbenzene occurs even at −70 °C in C_7D_8 solution.

Accordingly, our determination of the constitution of **4** is based solely on a low-temperature, X-ray crystallographic analysis (Fig. 1)† which, however, does reveal some interesting features. The Pb–C(carbene) bond length of 254.0(5) pm is unusually long and is probably one reason for the lability of the molecule. While the carbon atom C(1) exhibits an almost planar environment, the lead atom shows a pyramidal arrangement of its substituents as reflected by the bending angle of θ = 70.5° between the plane of the atoms C(12)–Pb–C(27) and the Pb–C(1) vector.

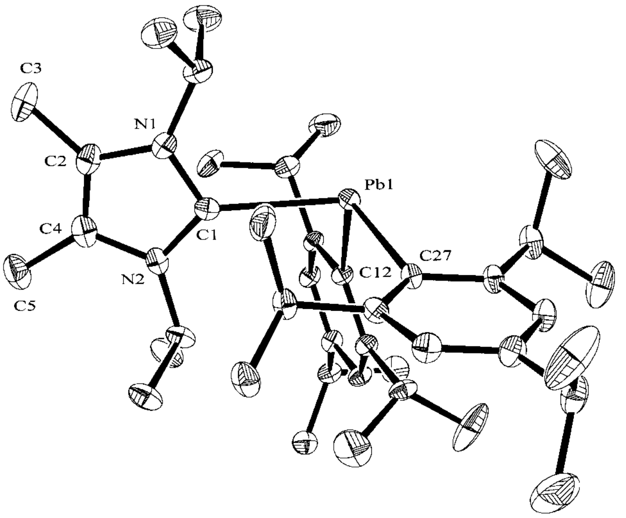
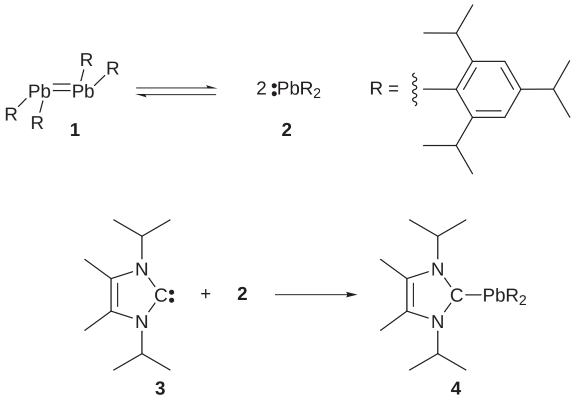


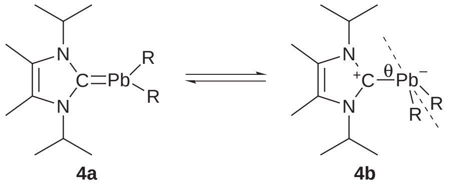
Fig. 1 Molecular structure of **4** (50% probability, hydrogen atoms omitted). Selected bond lengths (pm) and angles (°): C(1)–Pb 254.0(5), C(12)–Pb 237.6(4), C(27)–Pb 238.3(4), C(1)–N(1) 135.7(6), C(1)–N(2) 136.3(6), N(1)–C(2) 139.3(7), N(2)–C(4) 140.3(7), C(2)–C(4) 134.0(8), C(12)–Pb–C(27) 105.3(1), C(12)–Pb–C(1) 90.1(1), C(27)–Pb–C(1) 108.8(1), N(1)–C(1)–N(2) 104.6(4).

These results clearly indicate that, of the two possible electronic forms of the molecule **4** (Scheme 2) (the plumbene form **4a** and the zwitterionic form **4b**), the latter dominates. Further evidence in support of the existence of **4b** is provided by the Pb–C(*ipso*) bond lengths which are 8 pm longer than those in **1**.[6] Similarly, density functional theory calculations for the parent compound $H_2Pb{=}CH_2$, predicting a planar molecule with a Pb=C bond length of 204.5 pm,[8] are also suggestive of the loose adduct **4b** rather than a molecule with a Pb=C double bond of type **4a**. A bonding situation formally similar to that of **4b** may be present in the cyclopropylidene adduct of a diaminoplumbylene in which, however, the Pb=C bond length is 12 pm shorter such that the molecule is accordingly more stable.[11]

Although germenes and stannenes are now well-established,[12] molecules with Pb=C double bonds remain unknown. All attempts to achieve this goal by reaction of **2** and similarly constructed plumbylenes[13] with electrophilic carbenes of the cryptodiborylcarbene type[14] have been unsuccessful. This seems to indicate that diarylplumbylenes preferably participate in bond-forming reactions with nucleophilic rather than electro-



Scheme 1



Scheme 2

philic carbenes, a consequence of the relativistic contraction of the 6s electron pair of lead.[15]

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Notes and references

† *Crystal data* for **4**: $C_{41}H_{66}N_2Pb$, M = 794.15, crystal dimensions 0.71 × 0.63 × 0.30 mm^3, triclinic, space group $P\bar{1}$, a = 1056.88(7), b = 1108.20(6), c = 1791.80(8) pm, α = 72.784(6), β = 88.671(7), γ = 85.959(8)°, V = 1999.6(2) × 10^6 pm^3, Z = 2, D_c = 1.319 g cm^{-3}, λ(Mo-Kα) = 71.033 pm, T = 193(2) K, $2\theta_{max}$ = 52°, unique reflections 7260, observed [$I > 2\sigma(I)$] 6313, parameters 397. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically; R = 0.0311, $wR2$ (all data) = 0.0733. CCDC 182/1254. See http://www.rsc.org/suppdata/cc/1999/1131/ for crystallographic data in .cif format.

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