

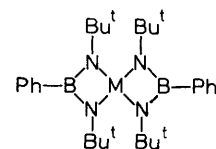
Synthesis and X-Ray Crystal Structure of a Tricyclic Lead–Nitrogen–Boron Heterocycle

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1,3,5,7-Tetra-*t*-butyl-4,8-diphenyl-1,3,5,7-tetra-aza-2,6-diplumba-4,8-diboratricyclo[4.2.0.0^{2,5}]octane-1,5-dium-2,6-diide (**1**) has been obtained from PhB(NBu^tLi)₂ and PbCl₄ in hexane or from PbCl₂ in tetrahydrofuran and structurally characterised by X-ray diffraction.

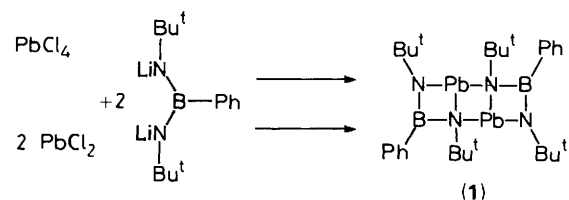
Several metal tetrahalides such as GeCl₄, SnCl₄, and TiCl₄ give corresponding spirocyclic species¹ (A) upon treatment with dilithiated di(*t*-butylamino)phenylborane; if, however, PbCl₄ is used in this reaction (solvent pentane) it is evidently reduced, and 1,3-di-*t*-butyl-4-phenyl-1,3-diaza-2-plumba-4-boracyclobutane is formed,[†] which adopts a dimeric structure (**1**) in the solid state.[‡]



M = Ge, Sn, Ti
(A)

[†] *Preparative details and spectroscopic data:* a solution of bis(*t*-butylamino)phenylborane² (0.034 mol) in *n*-hexane (60 ml) was mixed with a solution (46 ml) of *n*-butyl-lithium (0.070 mol) in hexane at 0 °C and stirred for 12 h under reflux. The suspension formed was added dropwise in the dark with stirring at –78 °C to PbCl₄ (0.017 mol) in pentane (200 ml). Stirring at –78 °C was continued for 12 h followed by 6 h at 20 °C. Alternatively PbCl₂ (0.034 mol) in tetrahydrofuran (200 ml) can be used and the reaction conducted at –10 °C (3 h) and then 20 °C (2 h). In due course the solvent is removed under reduced pressure, the residue sublimed at 175 °C and 0.01 mbar, and the sublimed (**1**) recrystallized from hexane. The yellowish crystals decompose above 185 °C: yield, 6.9 g (48% from PbCl₂); MS [*m/z* (%): EI 438 (8) (*M*⁺) and 57 (100); FI (field ionization) 438 (100); NMR (in C₆D₆): δ(¹¹B) 35.1 ppm from external BF₃·OEt; δ(¹H) 1.19 (s, 18 H) and 7.31–7.67 (br., 5 H); δ(¹³C) 36.1, 51.9 (Bu^t, 126.6, 127.5, 132.9, 158.3 (Ph)).

[‡] *Crystal data* for C₂₈H₄₆B₂N₄Pb₂: triclinic, space group *P* $\bar{1}$, *a* = 707.3(3), *b* = 1068.1(6), *c* = 1106.2(5) pm, α = 77.55(3), β = 88.50(4), γ = 72.56(2)°, *U* = 0.778 nm³, *Z* = 1, *D*_c = 1.867 g/cm³, μ = 10.91 mm⁻¹, *F*(000) = 416. A crystal (0.6 × 0.4 × 0.4 mm) was mounted on a Stoe-Siemens four-circle diffractometer, and 4326 reflections were measured at –85 °C using Mo-*K*_α radiation (λ 71.073 pm) giving 2722 independent data, of which 2546 with *F* > 3σ(*F*) were employed for all calculations. A Patterson synthesis located the Pb position. In view of the high absorption coefficient a semiempirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically, and a riding model starting from calculated positions was employed for the hydrogen atoms. 163 parameters were refined with a weighting scheme [*w*⁻¹ = σ²(*F*) + 0.0005 *F*_o²]. The final values for *R* and *R*_w were 0.029 and 0.030 respectively, with a final difference electron density maximum of 1850 and minimum of –2600 e nm⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Conditions: pentane, –78 °C, –4 LiCl, or THF, –10 °C, –4 LiCl.

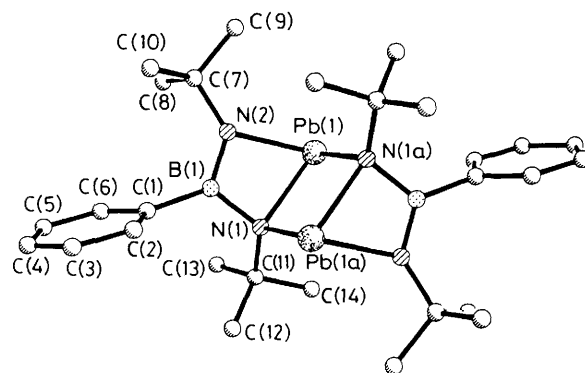


Figure 1. Molecular structure of (**1**); selected bond lengths (pm) and angles (°): Pb(1)–N(1) 232.9(6), Pb(1)–N(2) 225.0(5), N(1)–B(1) 149.8(8), N(2)–B(1) 139.3(10), B(1)–C(1) 159.9(9), Pb(1)–N(1a) 240.7(5), N(1)–Pb(1)–N(2) 62.8(2), N(1)–Pb(1)–N(1a) 83.8(2), Pb(1)–N(1)–B(1) 89.6(4), B(1)–N(1)–Pb(1a) 108.1(3), Pb(1)–N(2)–B(1) 95.6(4), N(2)–Pb(1)–N(1a) 98.2(2), N(1)–B(1)–N(2) 111.2(5).

Compound (**1**) can also be prepared using PbCl_2 as the starting material in tetrahydrofuran. Mass spectrometry indicates that (**1**) dissociates into two monomeric plumbanediyls in the gas phase; in solution the NMR data are also consistent with this dissociation into monomers. It is extremely sensitive towards air and hydrolysis. It shows thermochromic behaviour; the solution in hexane is orange at -15°C , but yellow at 20°C . Thermally it shows remarkable stability and can be sublimed at 175°C and 0.01 mbar. Attempted dissolution of (**1**) in chlorinated solvents leads to immediate decomposition.

The single-crystal X-ray structure of (**1**) (Figure 1) shows two monomer units with asymmetric kite-shaped PbNBN four-membered rings joined by additional Pb-N bonds [240.7(5) pm] which are not much longer than the Pb-N bonds

in the monomer units [232.9(6) and 225.0(5) pm]. The resulting PbNPbN four-membered ring lies on a crystallographic inversion centre and subtends an angle of 103.8° to the other ring mean planes.

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