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LETTER

Synthesis and structural characterization of tetrakis(tert-butyldimethylsilyl)-diphosphine

Hermann Westermann
and **Martin Nieger***
Anorganisch-Chemisches Institut der Universität Bonn, Gerhard-Domagk-Strasse 1, O-5300 Bonn 1 (F.R.G.)

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In the light of chemical and structural studies of tetrakis(amino)diphosphines as well as unsymmetrically substituted aminosilyldiphosphines [1] we are also interested in the investigation of diphosphines bearing only σ-donator ligands, e.g. silyl groups. Compounds of this class normally are difficult to handle but show a great reactivity [2–4]. A representative, which is stabilized by bulky ligands, might allow a study of the solid state, as well as serve as a potential precursor for the generation of stable halogeno-substituted disilylphosphines.

The preparation of tetrakis(tert-butyldimethylsilyl)diphosphine from lithio-di-(tert-butyldimethylsilyl)phosphid, which is analogous to the method known for tetrakis(trimethylsilyl)diphosphine [5], yields, after evaporation, subsequent solution, and crystallisation in diethyl ether, colourless crystals of $(Bu^tMe_2Si)_2P{-}P(SiMe_2Bu^t)_2$ in 38% yield.

δ ^{31}P NMR (toluol d_8): -224.6; δ ^{13}C (C_6D_6): 27.9 (t, 2.2 Hz), 20.8 (t, 11.0 Hz), -0.7 (t, 3.7 Hz); δ ^1H (C_6D_6): 1.2 (s), 0.4 (t, 3.6 Hz); MS (160 °C, 50 eV): m/e 552(14) $[M]^+$; 507(6) $[M-Me]^+$; 465(13) $[M-Bu^t]^+$; 407(2) $[M-SiMe_2Bu^t]^+$; 115(9) $[SiMe_2Bu^t]^+$; 73(100) $[PSiCh_2]^+$.

Crystal data: orthorhombic, *Pbcn* (No. 60); $a=15.826(5)$, $b=10.743(3)$, $c=20.347(6)$ Å; $V=3.459$ nm^3; $Z=4$; $D_{calc}=1.01$ g cm^{-3}. Structure solution and refinement based on 1620 reflections with $|F|>4\sigma(F)$ (Mo Kα, $\lambda=0.71069$ Å, μ(Mo Kα) $=0.20$ mm^{-1}) converged at $R=0.066$.

The reaction of $LiP(SiMe_2Bu^t)_2$ with 1,2-dibromoethane at low temperature in unpolar solvents probably proceeds by the reaction sequence discussed in the case of dialkylphosphides [6]. In the first step formation of $(Bu^tMe_2Si)_2PBr$, LiBr and ethene (from intermediate $Li(CH_2)_2Br$) can be postulated. Subsequent S_N reaction of the bromophosphine with present lithio-phosphide yields the title compound.

The ^{31}P NMR shift of the molecule (-224.6 ppm) shows no abnormalities and lies in the region known for silyl-substituted diphosphines [2, 5].

The structure of $(Bu^tMe_2Si)_2P{-}P(SiMe_2Bu^t)_2$ is shown in Fig. 1, and relevant bond lengths and angles

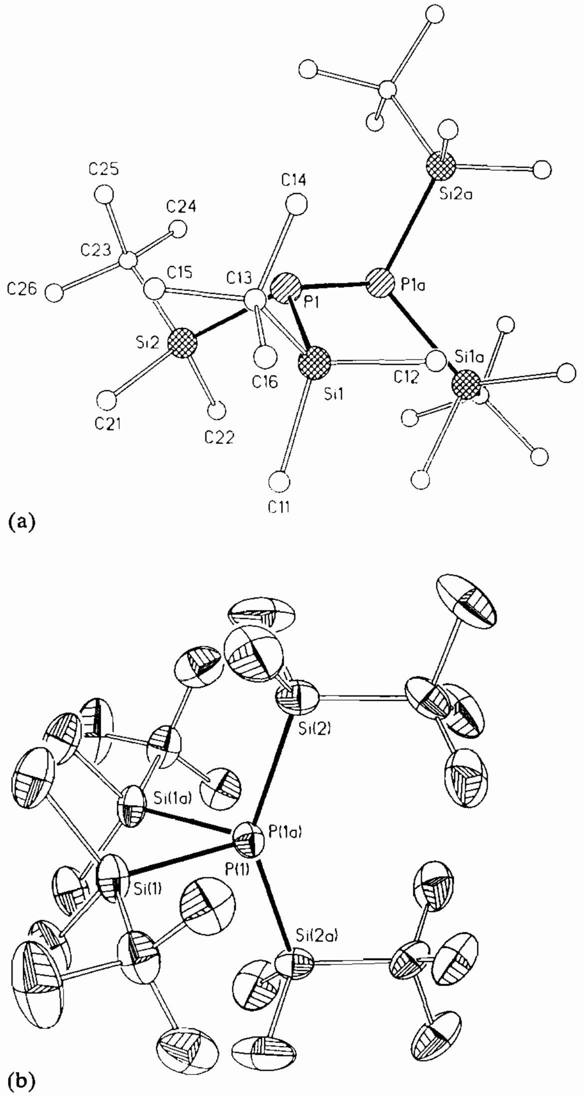

Fig. 1. (a) View of the structure of $(Bu^tMe_2Si)_2P{-}P(SiMe_2Bu^t)_2$. Bond length (pm) and angles (°): P1–P1a, 220.0(2); P1–Si1, 227.8(2); P1–Si2, 227.7(2); Si1–P1–P1a, 117.4(<1); Si2–P1–P1a, 103.9(1); Si1–P1–Si2, 111.6(1); Si1–P1–P1a–Si1a, 28.9(1); Si2–P1–P1a–Si2a, 141.3(1). (b) Newman-like projection of the molecule, illustrating the coordination geometry.

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*Author to whom correspondence should be addressed.

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are presented in the caption. With respect to the P1–P1a bond the molecule adopts a nearly half-ecliptic conformation of the silyl groups in the solid state. Two substituents are arranged nearly synperiplanar (torsion angle τ Si1–P1–P1a–Si1a = 28.9(1)°), while the other ones assume an almost anticlinal conformation (τ Si2–P1–P1a–Si2a = 141.3(1)°). For the electron pairs of the phosphorus atoms therefore an orthogonal orientation (τ = 95°) could be assumed. The steric congestion present in the molecule leads to an enlargement of one pair of P–P–Si angles, e.g. those with nearly ecliptic conformation, with Δ PPSi = 14°. The sum of the angles at the phosphorus atoms (333°), which is larger than the values observed for other diphosphanes [1, 7, 8], indicates that the lone pairs at the phosphorus atoms acquire a high p-character. The P–P (220.0(2) pm) as well as the P–Si (227.7(2)–227.8(2) pm) bond lengths are in the same magnitude predicted for diphosphine and trisilylphosphine, respectively [9].

Further work in view of the generation and isolation of stable halogenodisilylphosphines from silyl-substituted diphosphines is in preparation.

Supplementary material

Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, O-7514 Eggenheim-Leopoldshafen (F.R.G.), on quoting the depositary number CSD 7320174, the names of the authors, and the journal citation.

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