$[R\text{–}PLi_2(F\text{–}R)]_2$ [$R = SiPr^i{}_2(C_6H_2Pr^i{}_3\text{-}2,4,6)$] the first structural characterization of a dilithium phosphandiide in the form of a fluorosilane complex

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The preparation and spectroscopic characterization of the hexane-soluble, dimeric dilithium diisopropyl-(2,4,6-triisopropylphenyl)phosphandiide 1 and *ab initio* calculations of the corresponding parent compound 3 are reported; 1 reacts with diisopropyl(2,4,6-triisopropylphenyl)-fluorosilane to form the unusual complex 2, whose structure has been established by X-ray crystallographic analysis.

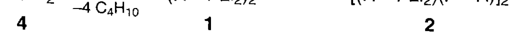
In initial studies on lithium phosphanides, Issleib and Tzschach reported in 1959 on the first synthesis of dilithium organophosphandiides, which were isolated in form of insoluble, amorphous solids.[1] Like phosphanides, they play an important role in organophosphorus synthesis. Until now, because of insolubility, proof of their existence was indirect, the species being characterized by derivatization reactions with electrophilic reagents such as MeI, Me_2SiCl_2 and Me_3SiCl.[2] Whereas the structures of monolithium phosphanides of the type $[R_2PLiL_n]$ (R = H, alkyl, silyl; L = donor solvent, n = 0–4)[3] and those of related systems such as bis(lithium phosphanidyl)silanes and tris(lithium phosphanidyl)silanes,[4] which form aggregates, are best investigated in solution and the solid state, the structures of dilithium phosphandiides remain unknown. In the series of dilithium compounds of the type $R\text{–}ELi_2$ (E = N, P, As) only the diethyl ether-solvated species $[(\alpha\text{-naphthyl-NLi}_2)_{10}(Et_2O)_6]\cdot Et_2O$ has been structurally characterized, isolated in form of a decamer, containing an $N_{10}Li_{20}$ aggregate framework.[5] Here we report on the hexane-soluble dilithium silylphosphandiide **1** and on the structural characterization of its dimeric fluorosilane complex **2**. Furthermore, *ab initio* calculations on the dimeric parent compound $(HPLi_2)_2$ **3** were carried out, which clearly show that the electronic structure is adequately described in terms of the ionic bonding model (Li^+P^-). The donor-solvent-free phosphandiide **1** was prepared *via* lithiiation of the primary silylphosphane **4** with 2 equiv. of Bu^nLi in toluene and diethyl ether as solvents, and isolated in the form of colourless crystals in 75% yield (Scheme 1). Cryoscopic measurements in benzene (c = 0.01–0.028 mol dm^{-3}) revealed that **1** is a molecular dimer of $R\text{–}PLi_2$ molecules; the relatively low aggregation is obviously due to the bulky silyl groups.

Multinuclear NMR spectroscopy clearly indicates that **1** partially dissociates in solution at room temperature: the ^{31}P NMR spectrum ($[^2H_8]$toluene) shows three broadened signals at 25 °C at characteristicly high field [δ −323.2, −328.6 (dissociation products) and −336.6 (**1**)] in the ratio 1 : 1 : 18, and in the ^7Li NMR spectrum only one signal was observed at δ 6.4 ($w_{\frac{1}{2}}$ 72 Hz). The single resonance in the ^7Li NMR spectrum reflects a fast exchange of Li centres within the NMR timescale. This is confirmed by low-temperature NMR studies: the ^{31}P NMR spectrum at −60 °C merely exhibits a signal at δ −336.6, which, therefore, we assigned to the dimer **1**, and the corresponding ^7Li NMR spectrum now shows an extremly broad signal at δ −3.0 ($w_{\frac{1}{2}}$ 336 Hz).

Because of their slate-like morphology, crystals of **1** were unsuitable for an X-ray structure determination, and we therefore obtained evidence for our proposed structure of **1** by *ab initio* geometry optimization (MP2/6-31G*) of the dimeric parent compound $(HPLi_2)_2$ **3**.[6] The most stable arrangement for **3** turned out to have D_{4h} symmetry (Fig. 1) and an analysis of the harmonic frequencies confirmed this structure as an energy minimum. The four lithium and the two phosphorus centres constitute a octahedral framework, with P–P, Li–Li and Li–P distances of 3.191, 2.645 and 2.458 Å, respectively.

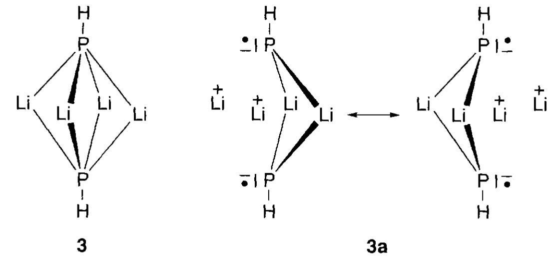
The natural bond orbital (NBO) analysis[7] clearly supports the electrostatic bonding model for this system, because the Li and P centres bear high net charges of the natural atomic orbitals (NAOs): Li 0.768, P −1.583. Furthermore, the NBO-Lewis resonance structure **3a** (Fig. 1) indicates stabilization by delocalization. The P atom in **3a** is triply bonded, and the Li–P bond contains 97% phosphorus contribution, of nearly 100% 3p orbital character. Each of the doubly bonded Li atoms possesses a pair of sp hybrids, and the P centre is 81% 3s in character.

Surprisingly, the reaction of **1** with the fluorosilane $Pr^i{}_2(C_6H_2Pr^i{}_3\text{-}2,4,6)Si\text{–}F$ in 1 : 1 molar ratio in toluene does not lead to the nucleophilic substitution of fluorine at silicon; instead, the unusual complex **2** was isolated in the form of colourless crystals in 58% yield. Compound **2** is much less soluble in hydrocarbons than **1**. The ^{31}P NMR spectrum of **2** at 25 °C revealed two broad signals at δ −307.3 and −319.6 in 1 : 1 ratio, and at −60 °C only the signal at δ −319.6 was observed; correspondingly, the ^7Li NMR spectrum at 25 °C shows one signal at δ = 6.1, owing to fast Li exchange, but two signals were observed at −60 °C (δ 5.6 and −4.8), in accord with the solid-state structure. The latter was elucidated by single-crystal X-ray diffraction.† The compound consists of a centrosymmetric dimer with a ladder-like $P_2Li_4F_2$ framework, in which, surprisingly, each fluorine atom acts as a bridging donor centre toward two lithium centres (Fig. 2).



$$\underset{\mathbf{4}}{2\ R\text{—}PH_2}\ \xrightarrow[-4\ C_4H_{10}]{4\ Bu^nLi}\ \underset{\mathbf{1}}{(R\text{—}PLi_2)_2}\ \xrightarrow{2\ R\text{—}F}\ \underset{\mathbf{2}}{[(R\text{—}PLi_2)(F\text{—}R)]_2}$$

Scheme 1 R = $SiPr^i{}_2(C_6H_2Pr^i{}_3\text{-}2,4,6)$



3 **3a**

Fig. 1 *Ab initio* optimized structure of **3**, and the NBO-Lewis resonance structures **3a**

The somewhat unusual donor stabilization of the Li centres through the Lewis-basic fluorine atoms leads to a relatively short distance between the Li(1) and Li(2′) centres [2.569(9) Å], whereas the Li(1)–Li(1′) distance is significantly longer [3.433(13) Å], and the P atoms are located on top of a shallow tetragonal pyramid. The P(1) centre is 0.4 Å out from the best Li(1)–Li(1′)–Li(2)–Si(2) plane. The unusual coordination geometry implies that the lone-pair electrons at phosphorus are not involved in the coordination of the Li centres close by. This may explain the relatively short Li(1)–Li(2′) distance and the acute Li(2)–F(1)–Li(1′) [90.4(3)°] and Li(1′)–P(1)–Li(2) angles [58.8(2)°], respectively, and further indicates that the Li centres prefer Li(1)–Li(2)–P three-centre–two-electron interactions. The Li–F distances [1.795(7), 1.825(7) Å] are little different but distinctly shorter than in related aggregates and lithium (fluorosilyl) phosphanides.[8] The fluorine atom is flattened pyramidal with a sum of bonding angles of 348.4°. The electronic stabilization of the Li(1) centre is also achieved by Li–H–C interactions with a nearby methyl group [C(36′)], and the Li(2) centre is η^2-coordinated at the C(16) and C(17) atoms of the aryl ring; the latter interaction pushes the crowded silyl substituent into an unusual position, resulting in a remarkable small Li(2)–P(1)–Si(2) angle of 80.4(1)°.

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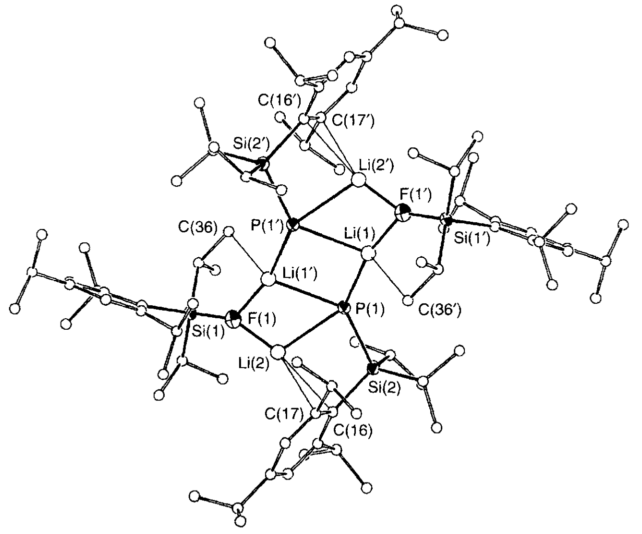

Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): P(1)–Li(1) 2.517(6), P(1)–Li(2) 2.564(7), P(1)–Li(1′) 2.668(6), Li(1)–Li(2′) 2.569(9), Li(1)–Li(1′) 3.433(13), P(1)–Si(2) 2.244(2), Li(1′)–F(1) 1.824(7), Li(2)–F(1) 1.795(7), Li(1′)–C(36) 2.719(10), Li(2)–C(17) 2.700(7), Li(2)–C(16) 2.586(7); Li(1)–P(1)–Li(2) 136.5(2), Li(1)–P(1)–Li(1′) 82.9(2), P(1′)–Li(1)–P(1) 97.1(2), Li(1′)–P(1)–Li(2) 58.8(2), Li(1)–F(1′)–Li(2′) 90.4(3), Li(1)–P(1)–Si(2) 131.1(2).

Footnotes

† *Crystal data* for compound **2**: monoclinic, space group $P2_1/n$, a = 10.292(7), b = 17.692(12), c = 25.267(16) Å, β = 94.46(5)°, U = 4587 Å^3, Z = 4. Intensity data were collected on a four-circle diffractometer (Mo-Kα radiation, ω-scan, T = 203 K), $2\theta_{max}$ = 50°, 8080 measured reflections, 506 parameters, $R1$ = 0.0566 for 5007 observed reflections $\{I > 2\sigma(I)$, $wR2$ = 0.1577 (all reflections, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{\frac{1}{2}}\}$. The structure was solved by direct methods[9a] and refined on F^2 with all measured reflections.[9b] Anisotropic displacement factors were used for all non-hydrogen atoms except for lithium. Methyl H atoms were refined as part of a rigid group. The other H atoms were inserted in calculated positions. Three isopropyl groups are disordered, which were refined with two sets for the methyl carbon groups using geometrical restraints. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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