

Si/P Frustrated Lewis Pairs

Small Neutral Geminal Silicon/Phosphorus Frustrated Lewis Pairs

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Beate Neumann,^[a] Hans-Georg Stammler,^[a] and Norbert W. Mitzel*^[a]*Dedicated to Professor Lothar Weber on the occasion of his 75th birthday*

Abstract: Two new silicon/phosphorus-based frustrated Lewis pairs (FLP), $F_3SiCH_2PtBu_2$ (**1**) and $Cl_3SiCH_2PtBu_2$ (**2**) were prepared from lithiated di-*tert*-butylmethylphosphane, $LiCH_2PtBu_2$, and the corresponding silicon tetrahalides. They were characterised by NMR spectroscopy and by single-crystal X-ray diffraction. A gas phase electron diffraction study of **1** identified two conformers of similar energy in the vapor. The reactivity of both, **1** and **2**, towards a series of small molecules was investi-

gated. Phenyl isocyanate was found to undergo addition reactions of its C-N unit to afford five-membered SiCPC(O)N-ring structures. $Cl_3SiCH_2PtBu_2$ (**2**) was converted with perfluorophenyllithium and 3,5-bis(trifluoromethyl)phenyllithium. The reaction with LiC_6F_5 resulted in the ortho-fluoride substitution product $(C_6F_5)_2SiCH_2(C_6F_4)PtBu_2$ (**5**), while the aryl reagent without ortho-fluoride groups, leads to the intramolecular Lewis pair $(C_8H_3F_6)_3SiCH_2PtBu_2$ (**6**). The FLP reactivity of **6** was tested.

Introduction

Stephan's discovery of frustrated Lewis-pair (FLP) chemistry in 2006 is based on the principle that bulky substituents can prevent the adduct formation between Lewis acids and bases.^[1] The resulting frustrated Lewis pairs can react with substrates in a way that the unquenched reaction potentials of both, acid and base, act concertedly to bind and activate the substrate in this extremely polar surrounding.

The majority of FLP systems investigated so far contain phosphorus- and nitrogen-based Lewis bases,^[1,2] and boron-based Lewis acids.^[3] Alternatively, Lewis acids with aluminium,^[4] tin,^[5] the rare earth metals^[6] or transition metals^[7] have been reported. Silicon-based FLP have only recently been introduced.^[8] Most of them are intermolecular, using pentafluoroethyl- or triflate^[8a] substituents as electron-withdrawing groups. The only neutral intramolecular example is $(C_2F_5)_3SiCH_2PtBu_2$, reported by our group in 2015.^[9] In this compound, the pentafluoroethyl groups act as strongly electron-withdrawing substituents.^[10] The introduction of pentafluoroethyl groups requires special precautions due to the instability of pentafluoroethylolithium, and the pentafluoroethyl groups are not entirely stable during

the reactions with substrates. Occasionally, degradation reactions were observed, which led to the formation of Si-F functions by C_2F_4 extrusion.^[10]

This led us to the question whether a silicon-based intramolecular FLP can be realised without these groups, possibly with simple fluoride or chloride substituents? There is a broad knowledge on compounds containing trifluorosilyl (and trichlorosilyl) groups and geminal donor atoms. They have been investigated in the search for direct geminal interactions between silicon and the donor atoms, leading to three-membered ring motifs with weak dative bonds. Such compounds, the α -silanes, are also of industrial importance.^[11] Important findings in this context were the presence of pronounced geminal donor-acceptor interactions in Si-O-N units (silylhydroxylamines e.g. in $F_3SiONMe_2$,^[12] $F_3CF_2SiONMe_2$ ^[13]) and Si-N-N units (silylhydrazines, e.g. $F_3Si-NMeNMe_2$ ^[14]) units, with formations of three-membered rings. In contrast, the species F_3SiCH_2OMe ^[15] does not show such interactions and its O-C-Si angle is 107.1(1)° in the single crystal. Again different is the behaviour of $F_3Si-CH_2NMe_2$ ^[16] which has an open-chain structure (Si-C-N °) in the gas phase but forms a six-membered ring dimer with two head-to-tail Si...N dative bonds.

The above mentioned FLP $(C_2F_5)_3SiCH_2PtBu_2$ is monomeric in its single crystals and does not show a Si...P dative bond, i.e. it has an open Si-C-P unit with accessible acid and base functions. This was surprising in the light of the extreme electronegativity of the C_2F_5 substituents and the ability of $(C_2F_5)_3SiCH_2PtBu_2$ to bind a range of small substrates including CO_2 , SO_2 and to activate hydrogen, as was shown in H/D-scrambling experiments employing H_2/D_2 mixtures. $(C_2F_5)_3Si$ groups in geminal donor-acceptor systems were also shown to offer a variety of bonding motifs: without ring formation in

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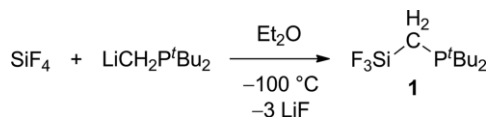
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(C₂F₅)₃SiCH₂OMe and (C₂F₅)₃SiCH₂NMe₂, and with ring formation in (C₂F₅)₃SiONMe₂.^[17]

Here we report about two simple silylmethylphosphanes, F₃SiCH₂P^tBu₂ (**1**) and Cl₃SiCH₂P^tBu₂ (**2**) and the Lewis pairs (C₆F₅)₂SiCH₂(C₆F₄)P^tBu₂ (**5**) and (C₈H₅F₆)₃SiCH₂P^tBu₂ (**6**) resulting from **2**. **1** and **2** represent simplified FLP analogues of (C₂F₅)₃SiCH₂P^tBu₂ with fluorine or chlorine substituents. The aim of this study was to compare the structures with above systems and to learn about their relationship to the reactivity of such systems, in particular the possibility to reduce the complexity of possible FLP systems. In addition, we wanted to vary Lewis acidity using different electron withdrawing groups.

Results and Discussion

The reaction of SiF₄ with di-*tert*-butylphosphanyl-methyl lithium, LiCH₂P^tBu₂,^[18] at –100 °C in diethyl ether afforded the colourless liquid (di-*tert*-butylphosphanyl-methyl)trifluorosilane, F₃SiCH₂P^tBu₂ (**1**, Scheme 1). Its ²⁹Si NMR resonance at 59.2 ppm is, under proton decoupling, split into a diagnostic quartet of doublets with coupling constants of 273.5 Hz (¹J_{SiF}) and 24.7 Hz (²J_{PSi}). Under ¹⁹F decoupling the signal is a doublet of triplets with coupling constants of 24.7 Hz and 11.9 Hz (²J_{SiH}). The ³¹P NMR quartet resonance at 13.8 ppm (³J_{PF} = 9.9 Hz) is shifted to high field compared to the earlier reported (C₂F₅)₃SiCH₂P^tBu₂ (18.5 ppm).^[9] Both, ²⁹Si and ³¹P NMR chemical shifts provide no indication of a direct interaction between the silicon and phosphorus atoms in deuterated benzene solution. The ¹H NMR spectrum contains a doublet at 0.88 ppm for the *tert*-butyl group and a quartet at 0.49 ppm for CH₂ group; this means that a ²J_{PH} coupling is not observed.



Scheme 1. Preparation of (di-*tert*-butylphosphanyl-methyl)trifluorosilane, F₃SiCH₂P^tBu₂ (**1**).

The molecular structure of **1** was determined in the solid state by X-ray diffraction (XRD) of an in situ grown single crystal and in the gas phase by electron diffraction (GED). While the crystal contains only one conformer (Figure 1), the *anti*-conformer of nearly C_s symmetry, the gas phase is a conformational mixture of 61(11)% *anti*- and 39(11)% *gauche*-conformer at the temperature of measurement, 398 K (Figure 2). This shows that the relative energies of *anti*- and *gauche*-conformer are very similar; in fact, a range of different quantum-chemical methods (TPSS-D3BJ, M06–2X, PBE0-D3, MP2(fc)) prefer the one or the other conformer slightly, but the maximum energy difference was never predicted to be larger than 1.6 kJ mol^{–1}. The energy of a third conformer, *syn*, was predicted between 10.0 and 11.1 kJ mol^{–1} higher in energy and even found not to represent a minimum by one DFT method (details see Supporting information). The GED experiment provided no evidence of the presence of this *syn*-conformer.

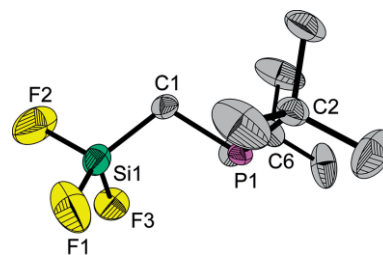


Figure 1. Molecular structure of compound **1** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–Si1 3.007(1), P1–C1 1.879(2), P1–C2 1.880(2), P1–C6 1.875(3), Si1–C1 1.806(2), Si1–F1 1.563(2), Si1–F2 1.556(2), Si1–F3 1.564(2), C2–P1–C6 112.2(1), C2–P1–C1 101.9(1), C1–P1–C6 100.8(1), P1–C1–Si1 109.4(1), C1–Si1–F1 113.0(1), C1–Si1–F2 113.0(1), C1–Si1–F3 112.7(1), F1–Si1–F2 105.9(2), F1–Si1–F3 105.8(1), F2–Si1–F3 105.7(1).

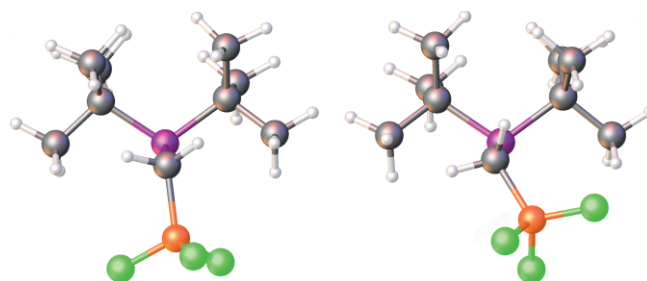


Figure 2. Molecular structures of the *anti* (left) and *gauche* (right) conformers (rel. abundance *anti/gauche*, 61:39(11%)) of F₃SiCH₂P^tBu₂ determined by gas electron diffraction.

Figure 3 contains a radial distribution curve for the GED experiment, Table 1 lists structural parameters in both phases for comparison. In both phases the distances between the silicon and phosphorus atoms indicate the absence of a direct bonding Si...P interaction. This Si1...P1 distance in the solid state at 3.007(1) Å, is significantly shorter than that in the FLP (C₂F₅)₃SiCH₂P^tBu₂ (3.248(1) Å).^[9] The absence of a significant attractive Si...P interaction in **1** follows also from the virtually undistorted tetrahedral coordination geometries at the silicon atoms and the P–C–Si angles in the *anti*-conformers in the gaseous and solid state: they are close to the tetrahedral angle of 109.47°. The *gauche*-conformer in the gas has a significantly wider P–C–Si angle of 118.0(12)°. Furthermore, the Si–F bonds are all of the same length (XRD: 1.556(2) Å – 1.564(2) Å), and similar to those in other geminal silicon/donor compounds (F₃SiCH₂OCH₃: 1.562(2) Å – 1.572(1) Å),^[15] for which no geminal interactions were concluded.

In the gas phase there is a striking difference between the different kind of P–C distances. The one to the central methylene unit is shorter by 0.016 Å than that to the *tert*-butyl units for the *anti*-conformer and even smaller (0.031 Å) for the *gauche*-conformer. This finding is supported by quantum-chemical calculations (see Supporting Information). In contrast, the corresponding solid state P–C distances are identical within experimental error.

In essence the structural studies in the gaseous and solid phases show the absence of direct interactions between silicon and phosphorus atoms, both intramolecular and intermolecular.

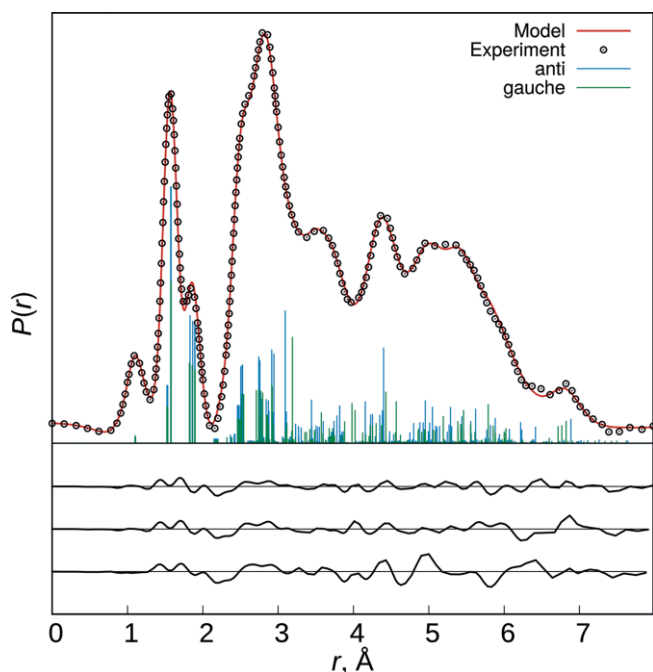


Figure 3. Experimental (dots) and model (line) radial distribution curve as well as delta curves (below) for the refinement of GED data of $F_3SiCH_2P^tBu_2$ using three different models: anti/gauche, 61:39 (top), anti (middle) and gauche (bottom). Vertical bars indicate interatomic distances in the anti (blue) and gauche (green) conformer, respectively.

Table 1. Molecular structure parameter values of compound **1** in the solid state and its two conformers in the gas phase in comparison (distances in Å, angles in deg). All errors given as 1σ .^[a]

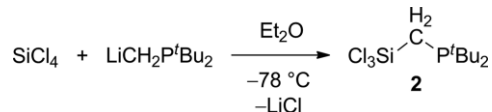
Parameter	XRD	GED	
	Solid state	Gas phase	
Conformer		<i>anti</i>	<i>gauche</i>
P...Si	3.007(1)	3.011(7)	3.133(7)
P–C(Si)	1.879(2)	1.856(1)	1.845(1)
P–C('Bu)	1.880(2)	1.872(1)	1.876(1)
Si–C(P)	1.806(2)	1.810(1)	1.811(1)
Si–F1	1.563(2)	} 1.570(1)	1.571(1)
Si–F2	1.556(2)		
Si–F3	1.564(2)		
P–C1–Si	109.4(1)	110.4(4)	118.0(4)
Si–C1–P–C6 ^[a]	–120.6(1)	343(2)	271(2)
Si–C1–P–C2 ^[a]	123.8(1)	129(2)	159(2)
$\chi^2/\%$	100	61(11)	39(11)

[a] The GED atom labels were adapted according to the XRD labelling system.

NMR spectra confirm this for the solution phase; for example the ^{31}P NMR resonance at 13.8 ppm is close to that of $(C_2F_5)_3SiCH_2P^tBu_2$ (18.5 ppm).^[9] In this sense compound **1** fulfils the prerequisite to be a frustrated Lewis pair.

Similar to the synthesis of **1**, the reaction of $LiCH_2P^tBu_2$ with $SiCl_4$ afforded (di-*tert*-butylphosphanyl-methyl)trichlorosilane,

$Cl_3SiCH_2P^tBu_2$ (**2**), as a colourless crystalline solid (Scheme 2). The ^{29}Si NMR chemical shift of **2** in C_6D_6 solution is detected at 10.8 ppm and is thus significantly shifted to high field compared to **1**, but similar to that of $(C_2F_5)_3SiCH_2P^tBu_2$ (–12.3 ppm).^[9] In contrast, the ^{31}P NMR resonance of **2** at 15.1 ppm is close to that of compound **1** (13.8 ppm).



Scheme 2. Preparation of (di-*tert*-butylphosphanyl-methyl)trichlorosilane, $Cl_3SiCH_2P^tBu_2$ (**2**).

A determination of the molecular structure of free molecules of **2** in the gas phase was attempted but prevented by decomposition during evaporation in the gas electron diffractometer. However, a single crystalline specimen of **2** was obtained by recrystallization in dichloromethane and was used for structure elucidation by X-ray diffraction (Figure 4). Molecules of **2** have C_s point group symmetry and reside on the mirror plane of the space group $P2_1/m$. The distance $P1...Si1$ of **2** is 3.106(1) Å, 0.1 Å longer than that of **1**, but slightly shorter than in $(C_2F_5)_3SiCH_2P^tBu_2$ (3.248(1) Å).^[9] The $Si1-C1-P1$ angle of **2** at 113.8(1)° is slightly wider than that of **1**, but not as much as in $(C_2F_5)_3SiCH_2P^tBu_2$ (120.4(1)°).^[9]

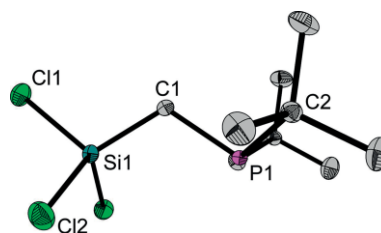


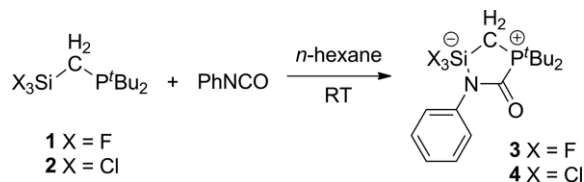
Figure 4. Molecular structure of compound **2** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: $P1...Si1$ 3.106(1), $P1-C1$ 1.876(1), $P1-C2$ 1.889(1), $Si1-C1$ 1.834(1), $Si1-C11$ 2.040(1), $Si1-C12$ 2.033(1), $C2-P1-C2$ 111.4(1), $C2-P1-C1$ 100.9(1), $P1-C1-Si1$ 113.7(1), $C1-Si1-C11$ 109.1(1), $C1-Si1-C12$ 113.1(1), $C11-Si1-C12$ 107.2(1).

Compounds **1** and **2** both feature structures in the solid and solution phases, **1** additionally in the gaseous phase, showing the Lewis acid (halosilyl group) and base sites (phosphanyl group) not to interact with one another. In this sense they can be regarded as non-interacting Lewis pairs. In order to test, whether they behave as frustrated Lewis pairs (FLP) in the sense of addition or activation of small molecules we tested them for reactivity towards a range of different substrates.

Both, **1** and **2**, are not capable of binding or activating the small molecules dihydrogen (H_2) and carbon dioxide (CO_2). In fact, no reactions were observed, which means no visible changes, no changes in the NMR spectra upon addition of the substrates and, in the case of hydrogen, also no H/D scrambling when H_2/D_2 mixtures were exposed to solutions of **1** and **2** for prolonged periods of time. **1** and **2** are also unreactive towards the 1,2-diketone benzil and towards phenylacetylene. Visible reactions occur with sulfur dioxide, hydrogen chloride and trimethylsilyldiazomethane, but we were not able to isolate or

identify defined products in these cases; rather, mixtures were obtained, however, too complicated to be separated.

Only in a conversion with phenylisocyanate, PhNCO, we were able to isolate and identify the stable adducts **3** and **4** (Scheme 3). In both cases five-membered rings are formed with PhNCO by coordination of the nitrogen atom to the silicon site of **1** or **2** and of the carbon atom to the phosphorus site, so that a penta-coordinated silane is formed. Such a binding pattern has also been observed for other FLP systems.^[19]



Scheme 3. Adduct formation of **1** and **2** with PhNCO, yielding **3** and **4**.

The pentacoordination of the silicon atoms in **3** and **4** can be observed by ²⁹Si NMR spectroscopy with resonances at -111.9 (**3**) and -88.1 ppm (**4**), respectively. The ³¹P chemical shifts of **3** (31.7 ppm) and **4** (42.5 ppm) compare well with the related systems (C₂F₅)₃SiCH₂P^tBu₂·PhNCO (40.8 ppm).^[20] The ¹H NMR spectrum of **3** shows a CH₂ resonance at 1.65 ppm and a C(CH₃)₃ resonance at 1.54 ppm with characteristic doublet splitting. Three further multiplets at 7.37, 7.26 and 7.11 ppm result from the phenyl protons. The ¹H NMR spectrum of **4** contains a double doublet resonance at 2.85 ppm for the CH₂ group and a doublet resonance at 1.58 ppm for the C(CH₃)₃ group. Three multiplets at 7.45, 7.27 and 7.15 ppm represent the protons at the phenyl unit.

The molecular structures of compounds **3** and **4** in the solid state were determined by X-ray diffraction (Figure 5 and Figure 6). Table 2 lists selected distances and angles for **3** and **4**, which are very similar for most parameters. For example, the non-bonded distance P1...Si1 is about 3.06 Å in both cases. The coordination sphere of the penta-coordinated silicon atoms can be characterised by their τ parameters.^[21] These are 0.90 for **3** and 0.89 for **4**, that is almost equivalent. A τ parameter close to unity characterises a coordination sphere as trigonal bipyramid; this is what is observed for **3** and **4**. The pentacoordination of the silicon atoms leads to significantly longer Si-F and Si-Cl bond lengths for the axial halogen atoms (**3** Si-F₂: 1.665(1), **4** Si-Cl₃: 2.250(1) Å) compared to the equatorial ones (average **3** Si-F: 1.605, **4** Si-Cl: 2.080 Å), respectively.

The occurrence of ill-defined addition products of compounds **1** and **2** with some substrates made us curious, whether the fluoride and chloride substituents in **1** and **2** are possibly too mobile and whether this could be the reason for product mixtures. Therefore, we set out to replace them by other electron withdrawing groups, namely by pentafluorophenyl (C₆F₅) or *meta*-bis(trifluoromethyl)phenyl (C₈H₃F₆) groups. In boron-based FLP chemistry, C₆F₅ is frequently used as a substituent.^[1i,2b,2c]

We converted Cl₃SiCH₂P^tBu₂ (**2**) using LiC₆F₅ which afforded the heterocyclic phosphasilylylid **5** (Scheme 4). It was identified by NMR spectroscopy, X-ray diffraction and elemental analysis. Compound **5** is the result of a nucleophilic aromatic *ortho*-fluor-

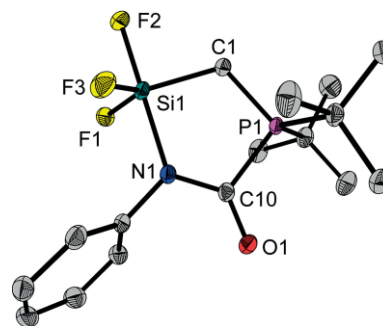


Figure 5. Molecular structure of compound **3** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted. Angles and distances are listed in Table 2.

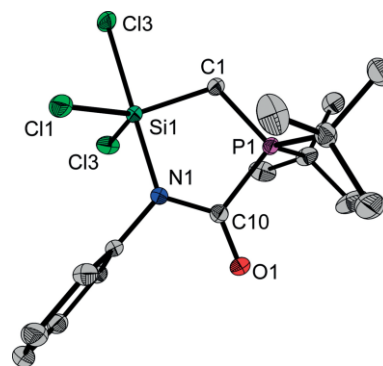


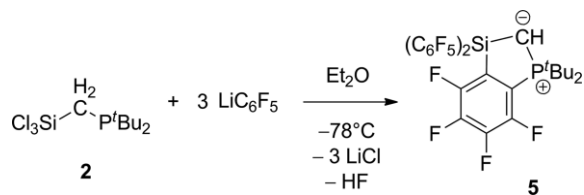
Figure 6. Molecular structure of compound **4** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted. Angles and distances are listed in Table 2.

Table 2. Molecular structure parameters of compounds **3** and **4** in the solid state (distances in Å, angles in deg).

Parameter	3	4
P1...Si1	3.062(1)	3.063(1)
P1-C1	1.779(1)	1.786(1)
P1-C10	1.850(1)	1.848(1)
Si1-N1	1.923(1)	1.909(1)
Si1-C1	1.897(1)	1.897(1)
N1-C10	1.338(1)	1.345(2)
O1-C10	1.230(1)	1.228(1)
Si1-Hal _{eq}	1.609(1)	2.079(1)
Si1-Hal _{ax}	1.601(1)	2.081(1)
Si1-Hal _{ax}	1.665(1)	2.250(1)
P1-C10-N1	110.2(1)	110.8(1)
P1-C1-Si1	112.8(1)	112.5(1)
τ Parameter ^[21]	0.90	0.89

ide substitution at one of the C₆F₅ rings introduced in this reaction. Related reactions have earlier been observed for C₆F₅ groups bound to boron atoms in FLP systems.^[22]

The ³¹P NMR resonance of **5** at 71.8 ppm is comparable with those of related compounds such as C₆F₅B(CH₂)(C₆F₄)P^tBu₂: (84.8 ppm).^[22b] The ¹H NMR spectrum shows a CH resonance at 0.41 ppm and a C(CH₃)₃ resonance at 0.90 ppm with characteristic doublet splitting. The ¹⁹F NMR spectrum of **5** contains three resonances at -128.0, -150.6 and -161.1 ppm from the intact C₆F₅ groups and four more resonances at -120.5, -121.5, -147.7 and -149.8 ppm from the C₆F₄ unit. ¹³C and ²⁹Si-NMR



Scheme 4. Preparation of the heterocyclic phosphasilylylid **5**.

spectra could not be obtained due to the limited solubility of compound **5**.

A single crystalline specimen of **5** was obtained by recrystallization from benzene and was used for structure elucidation via X-ray diffraction (Figure 7). The distance P1...Si1 with 2.894(1) Å of **5** is 0.17 Å shorter than that of the five-member ring systems **3** and **4**. The P1–C19 distance is 1.696(1) Å and typical for an ylide (Me₃P=CH₂ 1.678(2) Å).^[23] This confirms the significantly changed bonding situation, compared to (C₂F₅)₃SiCH₂P^tBu₂.^[9]

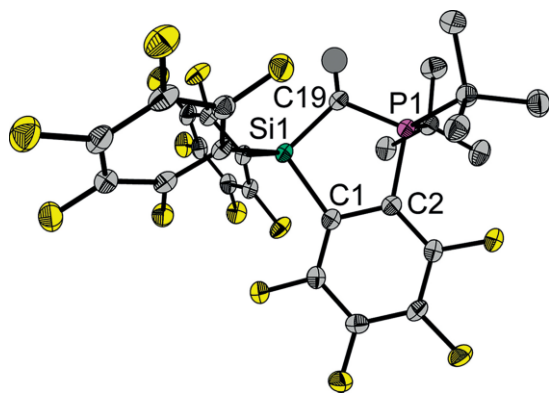
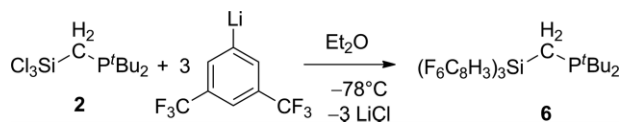


Figure 7. Molecular structure of compound **5** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1–C19 1.696(1), Si1–C19 1.763(2), P1...Si1 2.894(1), P1–C2 1.827(2), Si1–C1 1.890(2), P1–C19–Si1 113.6(1), C2–P1–C19 100.8(1), C1–Si1–C19 98.3(1), H19–C19–Si1 127.7(2), H19–C19–P1 118.3(2).

To avoid the *ortho*-substitution, it is indispensable that the substituent does not bear a fluorine substituent in *ortho*-position.^[24] Therefore, we reacted **2** with in situ generated 3,5-bis(trifluoromethyl)phenyllithium to afford (di-*tert*-butylphosphanyl-methyl)tris(bis(trifluoromethyl)phenyl)silane, (C₈H₃F₆)₃-SiCH₂P^tBu₂ (**6**) (Scheme 5).



Scheme 5. Preparation of (di-*tert*-butylphosphanyl-methyl)tris(*meta*-bis(trifluoromethyl)phenyl)silane, (C₈H₃F₆)₃SiCH₂P^tBu₂ (**6**).

The tetra-coordination of the silicon atom in **6** can be observed by ²⁹Si NMR spectroscopy with resonances at –11.2 ppm (compare: (C₂F₅)₃SiCH₂P^tBu₂ –12.3 ppm).^[9] The ³¹P NMR resonance of **6** at 10.2 ppm is at lower field than that of **5** and similar to **1**, **2** and (C₂F₅)₃SiCH₂P^tBu₂ (18.5 ppm).^[9] The ¹H NMR spectrum of **6** contains a doublet resonance at 1.45 ppm for CH₂ and a doublet resonance C(CH₃)₃ at 0.92 ppm. Two further

multiplets at 8.08 and 8.05 ppm result from the phenyl hydrogen atoms.

The molecular structure of compound **6** (Figure 8) in the solid state was determined by X-ray diffraction. The P1–C25 distance at 1.870(1) Å, is significantly longer than that of **5**; this indicates a single bond. The P1...Si1 distance at 3.126(1) Å is longer than those of **1** and **2**, but shorter than that of (C₂F₅)₃SiCH₂P^tBu₂ (3.248(1) Å)^[9] and the angle P1–C25–Si1 is 113.3(1)° wide but still 7.1° narrower than the corresponding angle in (C₂F₅)₃SiCH₂P^tBu₂ (120.4(1)°).^[9] As well as **1** and **2**, **6** is not capable of activating the small molecules H₂, CO₂, benzyl and phenylacetylene; it visibly reacts with SO₂, HCl and trimethylsilyldiazomethane, but the products could neither be isolated nor identified and rather mixtures were obtained, too complicated to be separable. In contrast to the reaction of **1** and **2** with phenylisocyanate, **6** does not react with PhNCO under comparable conditions.

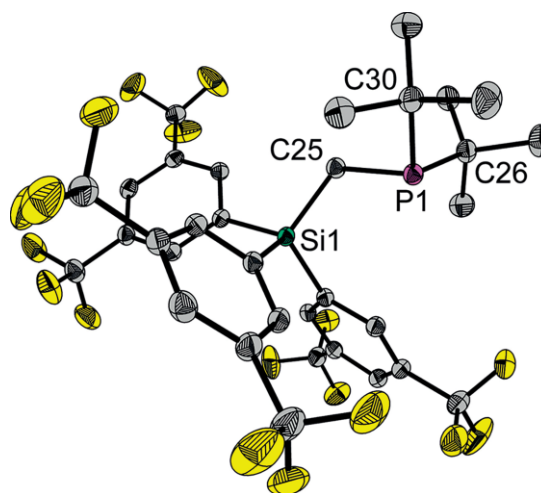


Figure 8. Molecular structure of compound **6** in the solid state. Ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1–C25 1.870(1), Si1–C25 1.872(2), P1...Si1 3.126(1), P1–C25–Si1 113.3(1), C26–P1–C30 110.5(1), C25–P1–C30 102.3(1), C25–P1–C26 101.0(1).

Conclusion

In this contribution we demonstrated that two simple silylmethylphosphanes with electronegatively substituted silicon atoms, F₃SiCH₂P^tBu₂ (**1**) and Cl₃SiCH₂P^tBu₂ (**2**) are easily accessible, in particular if compared to related molecules with complex fluorinated alkyl substituents at silicon. Compound **2** was further reacted with perfluorophenyllithium and 3,5-bis(trifluoromethyl)phenyllithium to introduce electron-withdrawing aryl groups. The reaction with LiC₆F₅ yielded in an ylidic heterocycle **5**, in which the Lewis acid and base functions are hindered, while the reaction with LiC₈H₃F₆ afforded (C₈H₃F₆)₃SiCH₂P^tBu₂ (**6**). Structural and spectroscopic analysis in the solid state (XRD), the gas phase (GED for **1**) and in solution phase (NMR) show that the Lewis acidic and basic sites in **1**, **2** and **6** are not directly interacting with one another – neither intramolecularly nor intermolecularly. Despite the unquenched availability of the

Lewis acid and base functions within **1**, **2**, **5** and **6**, they turn out to be unreactive towards H₂ and CO₂ and to yield very complicated product mixtures with other substrates. Only with phenyl isocyanate, **1** and **2** undergo adduct formation of adduct with the N–C unit of PhNCO being included into five-membered SiCPC(O)N rings.

Experimental Section

F₃SiCH₂P^tBu₂ (1): Diethyl ether (50 mL) was condensed onto (lithio-methyl)bis(*tert*-butyl)phosphane (2.98 g, 17.9 mmol). The suspension was degassed and silicon tetrafluoride (962 mbar, 660 mL, 26.0 mmol) was condensed onto the mixture. The resulting suspension was stirred overnight in a cold bath (–78 °C). The reaction vessel was warmed to –40 °C and the volatile components diethyl ether and excess SiF₄ were removed under static vacuum. Then the product was evaporated while the temperature was raised to 100 °C and condensed into a cold trap. It was isolated as a clear, colourless liquid (2.51 g, 8.81 mmol, 49 %). ¹H NMR (300 MHz, C₆D₆, 25 °C) δ = 0.88 ppm (d, ³J_{PH} = 11.6 Hz, CH₃), 0.48 ppm (q, ²J_{PH} = 3.1 Hz, CH₂). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C) δ = 31.6 ppm (d, ¹J_{PC} = 25.3 Hz, CCH₃), 28.8 ppm (d, ²J_{PC} = 14.8 Hz, CCH₃), –2.9 (dq, ¹J_{PC} = 44.3 Hz, ²J_{FC} = 16.2 Hz, CH₂). ¹⁹F{¹H} NMR (282 MHz, C₆D₆, 25 °C) δ = –134.0 (dt, ³J_{PF} = 10.1 Hz, ³J_{FH} = 3.2 Hz). ²⁹Si{¹H} NMR (60 MHz, C₆D₆, 25 °C) δ = –59.2 (dq, ²J_{PSi} = 273.5 Hz, ¹J_{SiF} = 24.7 Hz). ²⁹Si{¹⁹F} NMR (60 MHz, C₆D₆, 25 °C) δ = –59.2 (dt, ²J_{PSi} = 24.7 Hz, ²J_{SiH} = 11.9 Hz). ³¹P{¹H} NMR (282 MHz, C₆D₆, 25 °C) δ = 13.8 ppm (q, ³J_{PF} = 9.9 Hz). Elemental analysis calcd. (%) for C₉H₂₀F₃PSi (M_r = 244.31): C 44.25, H 8.25, F 23.33; found C 42.59, H 7.84, F 22.47.

Cl₃SiCH₂P^tBu₂ (2): (Lithio-methyl)bis(*tert*-butyl)phosphane (2.54 g, 15.3 mmol) was suspended in diethyl ether (100 mL) and cooled (–78 °C), silicon tetrachloride (1.76 mL, 15.3 mmol) was added slowly. The resulting suspension was stirred overnight in a cold bath, filtered and the solvent removed under slightly reduced pressure. The solid was purified by sublimation (subl.p. 0.01 mbar, 50 °C). A colourless crystalline solid (2.20 g, 7.49 mmol, 49 %) was obtained. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ = 1.47 ppm (d, ²J_{PH} = 1.0 Hz, CH₂), 1.15 ppm (q, ³J_{PH} = 11.6 Hz, CH₃). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C) δ = 32.6 ppm (d, ¹J_{PC} = 25.1 Hz, CCH₃), 29.8 ppm (d, ²J_{PC} = 14.5 Hz, CCH₃), 16.4 (d, ¹J_{PC} = 46.4 Hz, CH₂). ²⁹Si{¹H} NMR (60 MHz, CD₂Cl₂, 25 °C) δ = 10.9 (d, ²J_{PSi} = 50.5 Hz). ³¹P{¹H} NMR (282 MHz, CD₂Cl₂, 25 °C) δ = 15.1 ppm (s). Elemental analysis calcd. (%) for C₉H₂₀Cl₃PSi (M_r = 293.67): C 36.81, H 6.86; found C 37.52, H 7.12.

F₃SiCH₂P^tBu₂-PhNCO (3): **1** (249 mg, 1.02 mmol) was dissolved in *n*-hexane (10 mL) in an ampoule fitted with a Young greaseless tap. Phenylisocyanate (121 mg, 1.02 mmol) was slowly dropped into the tube at room temperature and the mixture was stirred. The volatile components were removed and a colourless solid (356 mg, 0.99 mmol, 97 %) was obtained. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ = 7.37 (m, o 2H), 7.26 (m, m H), 7.11 (m, p H), 1.65 ppm (d, ²J_{PH} = 10.8 Hz, CH₂), 1.54 ppm (d, ²J_{PH} = 15.7 Hz, CH₃). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, 25 °C) δ = 143.3 (d, ¹J_{PC} = 11.8 Hz, CO) 129.0 ppm (s, o-C), 127.5 ppm (s, m-C), 126.5 ppm (s, p-C), 124.7 ppm (s, i-C), 34.5 ppm (d, ¹J_{PC} = 32.5 Hz, CCH₃), 29.4 ppm (d, ²J_{PC} = 13.7 Hz, CCH₃), 0.87 (m, CH₂). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂, 25 °C) δ = –137.3 (m). ²⁹Si{¹H} NMR (60 MHz, CD₂Cl₂, 25 °C) δ = –111.9 (q, ¹J_{SiF} = 212.4 Hz). ³¹P{¹H} NMR (282 MHz, CD₂Cl₂, 25 °C) δ = 31.7 ppm (q, ³J_{PF} = 12.0 Hz). Elemental analysis calcd. (%) for C₁₆H₂₅F₃NOPSi (M_r = 363.44): C 52.88, H 6.99, F 15.68; found C 50.22, H 6.71, F 13.84.

Cl₃SiCH₂P^tBu₂-PhNCO (4): **2** (255 mg, 0.870 mmol) was dissolved in *n*-hexane (10 mL) in an ampoule fitted with a Young greaseless tap. Phenylisocyanate (104 mg, 0.874 mmol) was slowly dropped into the tube at room temperature and the mixture was stirred. The volatile components were removed and a colourless solid was washed with pentane (15 mL) and benzene (5 mL). A colourless solid (71.9 mg, 0.17 mmol, 20 %) was obtained. ¹H NMR (300 MHz, THF[D₈], 25 °C) δ = 7.45 (m, o 2H), 7.27 (m, m H), 7.15 (m, p H), 2.58 ppm (dd, ²J_{PH} = 58.9 Hz, ²J_{HH} = 8.9 Hz, CH₂), 1.58 ppm (d, ²J_{PH} = 16.1 Hz, CH₃). ¹³C{¹H} NMR (75 MHz, THF[D₈], 25 °C) δ = 142.8 (d, ¹J_{PC} = 9.7 Hz, CO) 130.1 ppm (s, o-C), 128.6 ppm (s, m-C), 127.1 ppm (s, p-C), 125.7 ppm (s, i-C), 35.7 ppm (m, CCH₃), 27.3 ppm (d, ²J_{PC} = 6.3 Hz, CCH₃), 12.95 (m, CH₂). ²⁹Si{¹H} NMR (60 MHz, THF[D₈], 25 °C) δ = –88.1 (d, ²J_{SiP} = 5.9 Hz). ³¹P{¹H} NMR (282 MHz, THF[D₈], 25 °C) δ = 42.5 ppm (s). Elemental analysis calcd. (%) for C₁₆H₂₅Cl₃NOPSi (M_r = 412.79): C 46.56, H 6.10; found C 46.40, H 6.00.

(C₆F₅)₂SiCH₂(C₆F₄)P^tBu₂ (5): Bromopentafluorobenzene (5.95 g, 24.2 mmol) was dissolved in Et₂O (20 mL) and cooled to –78 °C *n*BuLi (14 mL, 23 mmol, 1.6 M in *n*-hexane) was added dropwise, and the solution was stirred for 1 h. Afterwards Cl₃SiCH₂P^tBu₂ (2.21 g, 7.6 mmol) was added. The resulting suspension was stirred overnight, filtered and the solvent was removed via distillation, the solid was washed over 7 days with *n*-pentane in a Soxhlet extractor, the residue was recrystallised from benzene (yield: 761 mg, 1.08 mmol, 15 %). ¹H NMR (300 MHz, C₆D₆, 25 °C) δ = 0.90 ppm (d, ³J_{PH} = 15.6 Hz, CH₃), 0.41 ppm (d, ²J_{PH} = 8.1 Hz, CH). ¹⁹F{¹H} NMR (282 MHz, C₆D₆, 25 °C) δ = –120.5 ppm (m, 1 F), –121.5 ppm (m, 1 F), –128.0 (m, 2F, C₆F₅), –147.7 (m, 1F), –149.8 (m, 1F), –150.6 (m, 2F, C₆F₅) –161.1 (m, 2F, C₆F₅). ³¹P{¹H} NMR (282 MHz, C₆D₆, 25 °C) δ = 71.8 ppm (s). Elemental analysis calcd. (%) for C₂₇H₁₉F₁₄PSi (M_r = 668.49): C 48.51, H 2.68; found C 48.58, H 3.07.

(C₈H₃F₆)₃SiCH₂P^tBu₂ (6): 3,5-Bis(trifluoromethyl)bromobenzene (2.72 g, 9.28 mmol) was dissolved in Et₂O (10 mL) and cooled to –78 °C *n*BuLi (5.5 mL, 8.8 mmol, 1.6 M in *n*-hexane) was added dropwise, the solution was stirred for 1.5 h. Afterwards Cl₃SiCH₂P^tBu₂ (770 mg, 2.62 mmol) was added. The resulting suspension was stirred overnight, filtered and the solvent was removed via distillation. The solid was evaporated, under reduced pressure and 100 °C, a colourless solid was retained into a cold trap (yield: 1.15 g, 1.39 mmol, 53 %, refer to **2**). **6** was recrystallised from benzene. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C) δ = 8.08 ppm (b, o H), 8.05 ppm (b, p H), 1.45 ppm (d, ²J_{PH} = 1.4 Hz, CH₂), 0.92 ppm (d, ³J_{PH} = 11.4 Hz, CH₃). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C) δ = 135.7 ppm (b, arom), 131.6 ppm (m, arom.), 124.4 (m, arom.), 121.4 ppm (b, arom.), 31.6 ppm (d, ¹J_{PC} = 25.1 Hz, CCH₃), 28.8 ppm (d, ¹J_{PC} = 13.8 Hz, CCH₃), 2.5 ppm (d, ¹J_{PC} = 46.9 Hz, CH₂). ¹³C{¹⁹F} NMR (75 MHz, C₆D₆, 25 °C) δ = 129.0 (s, CF₃). ¹⁹F{¹H} NMR (282 MHz, [D₈]THF, 25 °C) δ = –63.5 ppm (s). ²⁹Si{¹H} NMR (60 MHz, [D₈]THF, 25 °C) δ = –11.2 ppm (d, ³J_{PSi} = 24.8 Hz). ³¹P{¹H} NMR (282 MHz, CD₂Cl₂, 25 °C) δ = 10.2 ppm (s). Elemental analysis calcd. (%) for (C₈H₃F₆)₃SiCICH₂P^tBu₂ (M_r = 580.82): C 47.73, H 3.46, F 41.13; found C 47.95, H 3.54, F 41.37.

CCDC 1934501 (for **1**), 1934502 (for **2**), 1934503 (for **3**), 1934504 (for **4**), 1934505 (for **5**), and 1934506 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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