Frustrated Lewis Pairs

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A Neutral Silicon/Phosphorus Frustrated Lewis Pair

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Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 60th birthday

Abstract: *Frustrated Lewis pairs (FLPs) have a great potential for activation of small molecules. Most known FLP systems are based on boron or aluminum atoms as acid functions, few on zinc, and only two on boron-isoelectronic silicenium cation systems. The first FLP system based on a neutral silane, $(C_2F_5)_3SiCH_2P(tBu)_2$ (**1**), was prepared from $(C_2F_5)_3SiCl$ with C_2F_5 groups of very high electronegativity and $LiCH_2P(tBu)_2$. **1** is capable of cleaving hydrogen, and adds CO_2 and SO_2. Hydrogen splitting was confirmed by H/D scrambling reactions. The structures of **1**, its CO_2 and SO_2 adducts, and a decomposition product with CO_2 were elucidated by X-ray diffraction.*

Despite its young age, the chemistry of frustrated Lewis pairs (FLP) has sparked enormous scientific efforts over the last years and has also put numerous observations in chemistry into a new light as a powerful unifying concept. Lewis' definition of acids and bases has been a major concept in chemistry since its formulation in 1923.[1] Although Brown found the first FLPs in 1942, the vast possibilities they hold were only recently uncovered.[2] Stephan and co-workers have demonstrated their ability to reversibly store and release elemental hydrogen[3] and to transfer it onto reducible substrates.[4] Several other small molecules, such as CO_2 and olefins, have since been activated using a variety of FLP systems.[4] Besides reversible hydrogen binding, activation and transfer, the storage and chemical activation of carbon dioxide has also been of major interest in FLP chemistry. The first suitable FLPs in this context contained a boron atom as acidic and a phosphorus atom as basic site (B/P).[5] Many FLPs are capable of binding or activating CO_2, SO_2, N_2O, and other small molecules.[6] Besides fundamental interest in new chemical transformations and catalytic processes, this is also of current interest in the context of activation of greenhouse gases.[6] Up to now most common systems are those based on Group 13 elements such as boron or aluminum[7] as Lewis acids. Few exceptions include Si and P^V and a few transition and rare-earth elements as alternatives. Examples are the zinc-based FLP systems, namely those of the combinations Zn/P, Zn/NHC, and $Zn/R_2P{=}C{=}PR_2$,[8] zirconium-based compounds including $[Cp_2ZrOC_6H_4PtBu_2][B(C_6F_5)_4]$,[9] or the P^V-containing species;[10] more are described in a recent review.[4d] Isoelectronic to the boron systems are such employing cationic silicenium cations and also silylene/silicenium mixtures;[11] they have also been shown to exhibit FLP reactivity. Hydrogen splitting has also been demonstrated for single-site carbenes.[12]

Herein we present the first FLP system based on a neutral silane as the Lewis acidic function. Compound **1**, $(C_2F_5)_3SiCH_2P(tBu)_2$, is an intramolecular FLP with three strongly electron-withdrawing pentafluoroethyl groups at the silicon atom. Compounds with $(C_2F_5)_3Si$ units have already been demonstrated to be the basis for very Lewis-acidic silicon species.[13] In **1** the silicon atom is connected to the Lewis-basic tBu_2P group via a single methylene unit. It was prepared by a nucleophilic substitution of $(C_2F_5)_3SiCl$ with $LiCH_2P(tBu)_2$ [Eq. (1)].

$$(C_2F_5)_3SiCl + LiCH_2P(tBu)_2 \rightarrow LiCl + (C_2F_5)_3SiCH_2P(tBu)_2 \qquad (1)$$

The solid-state structure of the liquid compound **1**, gained by in situ crystallization and subsequent X-ray diffraction (Figure 1, crystallography details see Supporting Information) shows a large Si-C-P angle of 120.4(1)°. This is probably

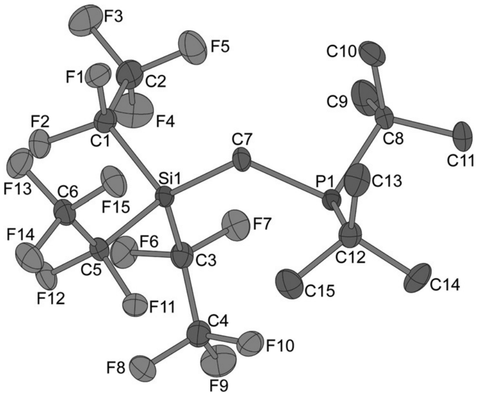

Figure 1. Molecular structure of compound **1** in the solid state.[23] Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C7 1.893(1), P1–C8 1.893(1), P1–C12 1.888(1), Si1–C7 1.850(1), Si1–C1 1.954(1), Si1–C3 1.947(2), Si1–C5 1.952(1); C8-P1-C7 99.4(1), C12-P1-C7 101.7(1), C12-P1-C8 110.4(1), C3-Si1-C1 104.6(1), C3-Si1-C5 105.7(1), C5-Si1-C1 102.0(1), C7-Si1-C1 109.7(1), C7-Si1-C3 117.5(1), C7-Si1-C5 115.7(1), Si1-C7-P1 120.4(1).

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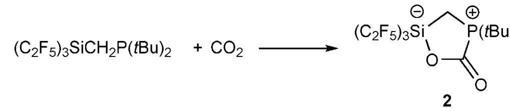
due to steric repulsion of the large substituents at the silicon as well as at the phosphorus atom. The result is a clear separation of the Lewis-acidic and -basic sites, thus prompting the desired frustrated character. The ^{29}Si NMR chemical shifts are almost identical in C_6D_6 and [D$_8$]THF solutions (-12.4 ppm in C_6D_6, -12.3 ppm in [D$_8$]THF), indicating that donor molecules like THF also do not bind to the silyl group of **1**. The absence of a P−Si bond is not necessarily to be expected, because compound **1** is a geminal system comprising an electronegatively substituted silicon atom and a donor site. It is therefore closely related to Si/N systems such as $F_3SiONMe_2$[14] and $(F_3C)F_2SiONMe_2$,[15] which show strong direct Si···N interactions, while the carbon-bridged $F_3SiCH_2NMe_2$[16] and the most closely related $(C_2F_5)_3SiCH_2NMe_2$[17] do not. $(C_2F_5)_3SiCH_2NMe_2$ did not show any reactivity towards hydrogen or CO_2, but the tBu$_2$P compound **1** reacts readily with CO_2 at room temperature and yields the addition product **2** in almost quantitative yield [Eq. (2)].



2

(2)

The formation of a five-coordinate silicon compound can be deduced from the ^{29}Si NMR spectrum. Compared to **1**, the resonance is shifted to high field at -100.1 ppm characteristic for five-coordinate silicon compounds. The ^{31}P NMR signal is observed at 43.8 ppm. The ^{13}C NMR resonance for the CO_2 unit is found at 161.9 ppm as a characteristic doublet ($^1J_{PC} =$ 85 Hz, compare for instance the CO_2 adduct of Mes$_2$P-(CH$_2$)$_2$B(C$_6$F$_5$)$_2$ $\delta(^{13}C)_{C=O} = 160.5$ ppm, $^1J_{PC} = 89.0$ Hz[5]).

The molecular structure of **2** in the crystal is shown in Figure 2. It shows an O1-Si1-C5 angle of 179.2(1)°, that is, a OC(O) ligand in axial position of a trigonal bipyramidal coordination sphere at the silicon atom. The Si1−C7 distance is increased by 0.06 Å relative to **1** and the C-Si-C angles enclosed by the equatorial pentafluoroethyl groups deviate slightly from ideal angles, but the angles enclosed by the equatorial groups sum up to 359.9°. The Si1-C7-P1 angle is 113.1(2)° and thus much closer to an ideal tetrahedral angle than in the starting material **1**. The bond from the Si atom to the axial C atom is increased by almost 0.12 Å compared to that of **1**. NMR investigations at increased temperatures up to 60 °C in [D$_8$]THF show a slow release of CO_2. In turn, solutions of **1** in typical hydrocarbons such as toluene do not absorb CO_2 as facilely as solutions in THF.

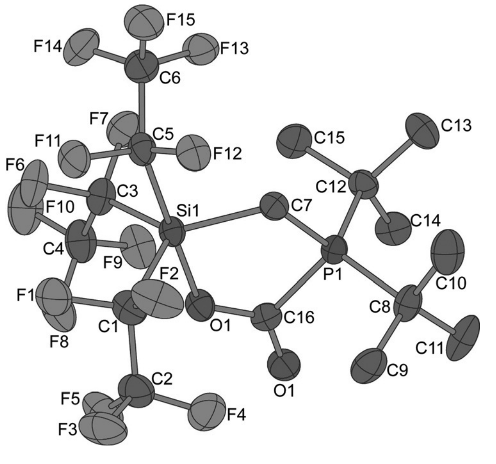


Figure 2. Molecular structure of compound **2** in the solid state.[23] Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C7 1.788(3), P1–C8 1.845(3), P1–C12 1.848(3), Si1–O1 1.853(2), Si1–C1 1.966(4), Si1–C3 1.959(4), Si1–C5 2.078(4), Si1–C7 1.911(3), O1–C16 1.303(4), O2–C16 1.217(4); O1-Si1-C1 89.8(1), O1-Si1-C3 88.1(1), O1-Si1-C5 179.2(1), O1-Si1-C7 89.5(1), P1-C7-Si1 113.1(2), O1-C16-P1 110.7(2), O2-C16-P1 122.9(3), O2-C16-O1 126.3(3).

The elongated Si−C bond to the axial pentafluoroethyl group indicates decreased stability of this bond. This is the likely reason why traces of a decomposition product (**3**) were found separated among the crystals of compound **2**. Single crystals of **3** were also investigated by X-ray diffraction (for details, see the Supporting Information, Figure S1). The molecular structure shows the axial pentafluoroethyl group of **2** replaced by a fluorine atom, while the coordination of the CO_2 unit remains intact. In an experiment carried out in an NMR tube at 60 °C, only traces of this decomposition product were observable, pointing towards a reasonable stability of the Si−C_2F_5 bond in solution.

An SO_2 adduct of **1**, compound **4**, was formed in analogy to compound **2** [Eq. (3)] in an NMR-tube experiment from which single crystals were also isolated. The solid-state structure of compound **4** (Figure 3) shows an Si1-C7-P1 angle of 117.7(1)° and an O1-Si1-C1 angle of 173.0(1)°, which indicates a more distorted trigonal bipyramidal configuration than in **3**, which is probably due to the higher steric demand of SO_2. The Si−C bond to the axial pentafluoroethyl group is again elongated by 0.1 Å compared to the corresponding bond of compound **1**. A decomposition product analogous to **3** could not be isolated in this case.

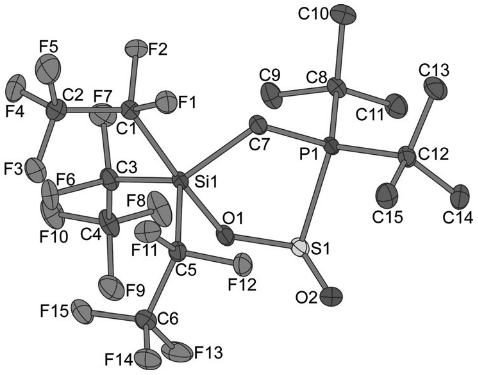
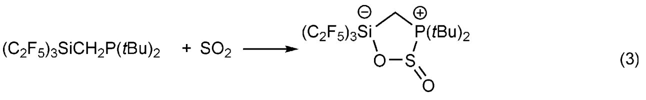


Figure 3. Molecular structure of compound **4** in the solid state.[23] Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–P1 2.277(1), S1–O1 1.564(1), S1–O2 1.459(1), P1–C7 1.790(1), P1–C8 1.852(1), P1–C12 1.859(1), Si1–O1 1.822(1), Si1–C1 2.057(1), Si1–C3 1.974(1), Si1–C5 1.967(1), Si1–C7 1.931(1); P1-C7-Si1 117.7(1), C7-P1-S1 99.9(1), O1-S1-P1 92.0(1), O2-S1-P1 105.7(1), O2-S1-O1 111.1(1), S1-O1-Si1 136.5(1), O1-Si1-C1 173.0(1), O1-Si1-C3 85.7(1), O1-Si1-C5 90.8(1), O1-Si1-C7 91.0(1).



4 (3)

Attempts to prepare a stable adduct of dihydrogen to **1** failed. However, the activity of **1** to cleave hydrogen was proven by exposing a solution in CD_2Cl_2 to an atmosphere of a 1:1 mixture of H_2 and D_2 and observing the formation of HD by its characteristic 1:1:1 triplet at 4.64 ppm and a coupling constant $^1J_{DH}$ of 42.7 Hz. The formation of HD is rather slow and weakly observable after about five hours. In any case, H/D scrambling[18] (here in the variant using the cheaper H_2/D_2 mixture instead of HD)[19] requires bimolecular interaction of two molecules, one containing a cleaved H_2 and the other a cleaved D_2 molecule. It does not allow any conclusion on the reversible binding of H_2, which could be a process solely involving a single molecule of **1**, but this would regenerate H_2.

In conclusion, we have shown the first neutral Si/P FLP system, which is capable of binding CO_2 and SO_2 and splitting hydrogen at ambient temperature. The possibility to isolate the CO_2 and SO_2 adducts prompts us to aim in future work at testing the susceptibility of the trapped CO_2 towards conversion reactions as well as the capability of this class of compounds to activate other small molecules.

Experimental Section

$(C_2F_5)_3SiCH_2P(tBu)_2$ (1): (Lithiomethyl)bis(*tert*-butyl)phosphane[20] (2.16 g, 13.0 mmol) was suspended in *n*-pentane (100 mL). Tris(pentafluoroethyl)chlorosilane[21] (5.220 g, 12.4 mmol), prepared from LiC_2F_5[22] and Et_2NSiCl_3 and Si–N cleavage by HCl, was condensed onto the frozen suspension (−196 °C), allowed to warm to −100 °C and it was then stirred at this temperature for 2 h. Slow warming to room temperature overnight yielded a gray-green suspension. After filtration of the solid, fractionated distillation (80 °C, 0.1 mbar) yielded 1.7 g (3.1 mmol, 25 %) of the product. ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 1.33$ (d, $^2J_{PH} = 1.7$ Hz, CH_2), 0.94 ppm (d, $^3J_{PH} = 11.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C): $\delta = 122.5$–114.3 (m, C_2F_5), 32.1 (d, $^1J_{PC} = 27.7$ Hz, CCH_3), 28.3 (d, $^2J_{PC} = 15.2$ Hz, CH_3), −4.0 ppm (d, $^1J_{PC} = 56.2$ Hz, CH_2). $^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, 25 °C): $\delta = -80.5$ (CF_3), −119.0 ppm (CF_2). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 25 °C): $\delta = -12.4$ ppm (d sep, $^2J_{PSi} = 33.4$ Hz, $^2J_{SiF} = 33.4$ Hz). $^1H/^{29}Si$ HMBC ($[D_8]$THF): $\delta(^{29}Si) = -12.3$ ppm $^{31}P\{^1H\}$ NMR (245 MHz, C_6D_6, 25 °C): $\delta = 18.5$ ppm (m).

$(C_2F_5)_3SiCH_2P(tBu)_2{\cdot}CO_2$: Compound **1** (0.281 g, 0.50 mmol) was dissolved in C_6D_6 in a Young NMR tube. CO_2 (0.50 mmol) was condensed into the tube and the solution was shaken. Single crystals that had precipitated from solution were taken for X-ray-diffraction. ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 1.05$ (d, $^2J_{PH} = 10.7$ Hz, CH_2), 0.90 ppm (d, $^3J_{PH} = 11.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C): $\delta = 161.9$ (d, $^1J_{PC} = 85$ Hz, CO_2), 123.7–116.3 (m, C_2F_5), 33.5 (d, $^1J_{PC} = 27.4$ Hz, CCH_3), 29.4 (d, $^2J_{PC} = 15.2$ Hz CH_3), 2.5 ppm (d, $^1J_{PC} = 37$ Hz, CH_2). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 25 °C): $\delta = -100.1$ ppm (m). $^{31}P\{^1H\}$ NMR (245 MHz, C_6D_6, 25 °C): $\delta = 43.8$ ppm. An analogous preparation in $[D_8]$THF was performed by using **1** (0.308 mg, 0.52 mmol) dissolved in THF (4.5 mL), degassing the solution and applying 1 atm of CO_2. Crystallization from THF was not successful. ^1H NMR (500 MHz, $[D_8]$THF, 25 °C): $\delta = 2.31$ (d, $^2J_{PH} = 11.2$ Hz, CH_2), 1.55 ppm (d, $^3J_{PH} = 16.4$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $[D_8]$THF, 25 °C): $\delta = 161.9$ (d, $^1J_{PC} = 84$ Hz, CO_2), 125.5–115.0 (m, C_2F_5), 33.5 (d, $^1J_{PC} = 27.4$ Hz, CCH_3), 29.4 (d, $^3J_{PH} = 15.2$ Hz CH_3), 2.5 ppm (d, $^1J_{PC} = 37.0$ Hz, CH_2). $^{19}F\{^1H\}$ NMR (470 MHz, $[D_8]$THF, 25 °C): $\delta = -81.0$ (very broad, CF_3), −119.4 ppm (very broad, CF_2). $^{29}Si\{^1H\}$ NMR (99 MHz, $[D_8]$THF, 25 °C): $\delta = -93.2$ ppm (m). $^{31}P\{^1H\}$ NMR (245 MHz, $[D_8]$THF, 25 °C): $\delta = 43.5$ ppm.

$(C_2F_5)_3SiCH_2P(tBu)_2{\cdot}SO_2$: Compound **1** (0.098 g, 0.18 mmol) was dissolved in C_6D_6 in a Young NMR tube. SO_2 (0.2 mmol) was condensed into the tube and the solution was shaken. Single crystals that had precipitated from solution were taken for X-ray-diffraction. The bulk sample was contaminated with some unidentified byproduct that could not as yet be separated. ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta = 1.88$ (d, $^2J_{PH} = 12.2$ Hz, CH_2), 0.91 ppm (d, $^3J_{PH} = 16.2$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C): $\delta = 123.7$–116.8 (m, C_2F_5), 37.2 (d, $^1J_{PC} = 31.3$ Hz, CCH_3), 25.8 (s, CH_3), −3.8 ppm (d, $^1J_{PC} = 27$ Hz, CH_2). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 25 °C): $\delta = -72.3$ ppm (m). $^{31}P\{^1H\}$ NMR (245 MHz, C_6D_6, 25 °C): $\delta = 71.8$ ppm.

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[23] CCDC 1063576 (**1**), 1063577 (**2**), 1063578 (**3**), and 1063579 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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