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A Neutral Germanium/Phosphorus Frustrated Lewis Pair and its Contrasting Reactivity Compared to its Silicon Analogue

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Abstract. The chlorogermane $(C_2F_5)_3$ GeCl with very electronegative pentafluoroethyl groups was converted with LiCH₂P'Bu₂ to obtain the intramolecular frustrated Lewis pair (FLP) $(C_2F_5)_3$ GeCH₂P'Bu₂ – a neutral germanium-based FLP. Its reactivity was compared to its silicon homologue $(C_2F_5)_3$ SiCH₂P'Bu₂. Both FLP cleave NO but give cyclic (Si) and open-chain oxides (Ge). In reactions with HCl both FLP give the same adduct type in the solid state, while the proton seems more mobile in solution in the germanium case. Reactions with PhCNO and Me₃SiCHN₂ result in ring-type adducts. The structures of $(C_2F_5)_3$ GeCH₂P'Bu₂ and of five adducts with substrates were elucidated by X-ray diffraction. The study clearly features the germanium compound to have a more moderate Lewis acidity compared to the silicon analogue.

Frustrated Lewis pair (FLP) chemistry is investigated since only slightly more than a decade but already has a tremendous impact as powerful chemical concept. It explains the concerted activity of Lewis acids and bases in activation of small molecules.^[1] Besides reversible hydrogen binding and transfer,^[2] the reactions with several other small substrate molecules have been investigated. Activation of CO₂ is still a major aspect.^[3] With the hydroboration of diazomethane derivatives, Stephan et al. have recently opened a new field to FLP-chemistry and interpret this as potential prelude to FLP-N₂ chemistry in the sense of metal-free activation of dinitrogen-species.^[4]

Most FLP are based on combinations of boron Lewis acids and phosphorus Lewis bases, either in two independent molecules or as two functions within one intramolecular FLP system. Nitrogen bases are also frequently employed. Far less common are systems containing AI,^[5] C,^[6] Si,^[7] Ge,^[8] Sn,^[8,9] rare-earth^[10] or transition elements (e.g. Zr,^[11] Zn,^[12] Sc^[13]) as acid functions.

We have recently reported the synthesis of the first neutral silicon/phosphorus FLP, $(C_2F_5)_3SiCH_2P({}^{\prime}Bu)_2$ (1).^[7d] Its activity in H₂ splitting, and addition of CO₂ and SO₂ is due to the highly electron-withdrawing pentafluoroethyl groups, which turn the silane function into a strong Lewis acid. Hoge et al. explored the foundations of pentafluoroethyl element chemistry in detail and made a range of new Lewis acidic functions accessible.^[14] With

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 $(C_2F_5)_3GeCl + LiCH_2P'Bu_2 \longrightarrow (C_2F_5)_3Ge^{C}P'Bu_2$ 2

Compound 2 was obtained as a colourless liquid. Its ¹H NMR spectrum contains two doublets, one at 1.78 ppm with a coupling constant of 1 Hz for the methylene unit and at 0.85 ppm with a coupling constant of 12 Hz for the tert-butyl group. The ¹⁹F NMR shows the typical pattern for pentafluoroethyl groups.^[14] A ³¹P{¹H} NMR signal is observed at 14.9 ppm, similar to the shift of 1 (18.5 ppm).^[7d] This indicates three-coordinate phosphorus atoms and thus the presence of a FLP system without direct P...Ge interaction. This is not naturally so, because the geminal system 1 comprises an electronegatively substituted germanium atom and a potent donor function in close proximity. It is thus related to Ge/N systems such as Ge(ONMe₂)₄ H₃GeONMe₂ or Cl₃GeONMe₂^[16] or related Si/N systems^[17] with direct Ge…N or Si...N interactions. The absence of a P...Ge bond is confirmed by a P...Ge distance of 3.266(1) Å in the crystalline state (Figure 1). This was determined by X-ray diffraction of a single crystal generated in situ from the liquid compound 2 (details see Supporting Information). The angle Ge-C-P is wide at 117.8(1)°, but 2.7° narrower than the corresponding angle Si-C-P in FLP 1 (120.4(1)°). The coordination sphere of germanium is only slightly distorted from tetrahedral.



Figure 1. 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...Ge1 3.266(1), P1–C1 1.876(1), Ge1–C1 1.939(1), Ge1-C1-P1 117.8(1), C1-P1-C8 99.4(1), C1-P1-C12 101.6(1), C12-P1-C8 110.9(1).

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While compound **1** was earlier shown to cleave dihydrogen, **2** turned out to be inactive in this respect. **1** also gave isolable adducts with CO_2 and SO_2 , while solutions of **2** showed no changes in NMR shifts when exposed to these reactants. However, **1** and **2** both react with nitrogen oxide, but afford rather different products. Both reactions lead to the cleavage of NO and only the oxygen atom is found in the products – unlike the reaction of a boron-based FLP with NO reported by Sajid et al., in which the entire NO unit is captured in the product.^[18]

The structures in the solid state (Figures 2 and 3) show that FLP 1 reacts with NO to afford a formal phosphane oxide; its oxygen atom –also a Lewis base site– is coordinated to the silicon atom. So, product **3** is not a frustrated Lewis pair, but one where acid and base functions joined to form a Si–O bond. The two molecules in the asymmetric unit of **3** differ only marginally in the structure of their four-membered rings; only the C_2F_5 and 'Bu groups are arranged slightly differently.



Figure 2. Molecular structure of compound **3** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms and second molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1...Si1 2.620(1), P1–O1 1.574(2), Si1–O1 1.869(2), P1–C7 1.779(2), Si1–C7 1.942(2), Si1–C1 1.964(2), Si1–C5 1.968(2), Si1–C3 2.049(2), Si1-O1-P1 98.8(1), Si1-C7-P1 89.4(1), O1-Si1-C3 164.0(1), C3-Si1-C1 92.4(1), C3-Si1-C5 96.2(1), C3-Si1-C7 88.6(1).

The silicon atom in **3** is trigonal bipyramidally coordinate with oxygen and C3 atoms adopting the axial positions (angle O-Si-C3 164.0(1)°). Si–C distances including carbon atoms C1/C5/C7 are almost 0.1 Å shorter than the axial bond Si–C3. Penta-coordination of silicon is conserved in solution as is proven by a ²⁹Si NMR chemical shift of -91.5 ppm. The ³¹P NMR resonance at 89.9 ppm is at lower field than that of **1** (18.5 ppm) The non-bonded Si-P distance within the four-membered ring at 2.620(1) Å is much shorter than that in **1** (3.248(1) Å). The Si–O distance at 1.869(2) Å is longer than standard Si–O bonds (e.g. 1.632(5) Å for (Me₃Si)₂O).^[19] The Si-O-P angle is 98.8(1)°.

The ³¹P NMR resonance of **4**, an oxidation product of **2** with NO, at 61.5 ppm is at higher field than that of **3**, but still at much lower field than that of **2**. This is consistent with the absence of a bond between the Lewis acid function (Ge) and oxygen in this case – in contrast to **3**. This fact from solution finds confirmation in the molecular structure determined in the crystalline state (Figure 3). The two molecules in the asymmetric unit (denoted a and b) vary drastically in their non-bonding Ge--O distances (a: 3.204(2), b: 2.860(2) Å) and Ge-C7-P angles (a: 116.8(1)°, b: 108.0(1)°). Their torsion angles O-P-C7-Ge are similar (a: 5.7(2)°, b: 4.1(1)°). The Ge1-C7-P1 angle of **4**a is similar to the corresponding angle in **2** at 116.8(1)°. The P–O bond in **4** at 1.491(2) Å is significantly shorter than that in **3**, and closer to the standard value of a phosphane oxide (Me₃PO: 1.489(6) Å).^[20]



Figure 3. Molecular structure of compound **4** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms and second molecule are omitted for clarity. Selected bond lengths [Å] and angles [°] (given for molecules a/b if markedly different, otherwise only for a): P1-··Ge1 3.056(1)/3.223(1), P1-O1 1.491(2), Ge1···O1 3.240(1)/2.860(2), P1-C7 1.832(2), Ge1-C7 1.951(2), Ge1-C1 2.027(2), Ge1-C5 2.029(2), Ge1-C3 2.014(2), Ge1-O1-P1 76.0(1)/82.7(1), Ge1-C7-P1 116.8(1), C7-Ge1-C1 103.3(1), C7-Ge1-C3 112.6(1), C7-Ge1-C5 114.9(1), O1-P1-C7-Ge1 5.7(2)/ 4.1(1).



Figure 4. Relaxed potential energy profiles along the E–O distances for compounds 3 (E = Si) and 4 (E = Ge), calculated at the B97-3c level of theory.

Quantum-chemical investigations for the reasons of the different structures of products **3** and **4** were undertaken by calculating the potential of a series of optimized structures with increasing fixed E–O distances (E = Si, Ge, Figure 4, details see Supporting Information). Surprisingly, **3** shows a double-minimum potential; that means the structure found in the crystalline state represents the absolute minimum, with a slightly longer calculated Si–O distance of 1.962 Å (B97-3c, compare solid state: 1.869(2) Å),

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while a structure with a Si–O distance of 3.207 Å represents a second minimum, but is 4.6 kJ mol⁻¹ higher in energy. Germanium compound **4**, in contrast, shows a single minimum at a Ge–O distance of 3.132 Å, in the range of experimental values in the solid state (3.240(1)/2.860(2) Å).

Expectedly both FLPs, **1** and **2**, react with hydrogen chloride gas: in the products the chloride is linked to the silicon and germanium sites, respectively, but the protons are found at different positions in solution.



NMR spectra for product **5** are consistent with expectation of a P–H bonded system. One of three observed ¹H NMR signals can be assigned to a P–H unit (doublet of triplets at 5.97 ppm; ¹*J*_{PH} = 482.9 Hz, ³*J*_{HH} = 4.7 Hz). The other two resonances, a doublet of doublets at 1.89 ppm (²*J*_{PH} = 16.5 Hz and ³*J*_{HH} = 4.7 Hz), and a doublet at 0.91 ppm, belong to the CH₂ and *tert*-butyl groups, respectively. Consistently, the ³¹P NMR resonance at 47.5 ppm shows a characteristic doublet splitting of 482.9 Hz and nonet splitting of 16.5 Hz; the ²*J*_{HH} coupling to the CH₂ protons is – as frequently observed for such compounds– not observed.

By contrast, product **6**, resulting from the reaction of FLP **2** with HCl, has different NMR characteristics. Its ¹H NMR spectrum contains two doublets at 2.19 and 1.52 ppm and a broad signal at 7.07 ppm (low-temperature experiments did not markedly improve the line-width). This indicates that the proton is not directly bound to the phosphorus atom. Consistently, ³¹P and ³¹P{¹H} NMR spectra feature broadened resonances, but no doublet signal indicating a P–H bond. However, a hydrogen atom at phosphorus was located in the molecular structures of both, **5** and **6**, in the solid state by low-temperature X-ray diffraction (Figures 5 and 6).



Figure 5. Molecular structure of compound **5** in the solid state. Hydrogen atoms, disordered atoms and second molecule are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°] (given for molecules *a/b/c* if markedly different, otherwise only for a): P1–Cl1 3.294(1)/ 3.307(1)/3.375(1), P1–Si1 3.249(1), Si1–Cl1 2.268(1), Si1-C7-P1 122.8(1)/ - 121.0(1)/ 121.3(1), C3-Si1-Cl1 178.4(1)/178.5(1)/179.3(1), C5-Si1-Cl 123.7(1)/122.9(1)/ 124.0(1), C8-P1-C7 109.7(1), C8-P1-C12 116.2(1), C7-P1-C12 112.7(1).



Figure 6. Molecular structure of one molecule in compound **6** in the solid state. Hydrogen atoms, disordered atoms and second molecule are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°] (given for molecules a/b if markedly different, otherwise only for a): P1–Ge1 3.343(1)/ 3.296(1), P1–Cl1 3.292(2)/ 3.426(2), Ge1–Cl 2.510(2)/2.442(1), P1–C7 1.805(4), Ge1–C7 1.988(4), Ge1–C1 2.054(4), Ge1–C5 2.028(5), Ge1–C3 2.132(5), Ge1-C7-P1 123.5(2)/120.4(2), Cl1-Ge1-C3 177.5(2)/179.5(1), C7-Ge1-C1 123.1(2)/123.4(2), Cl2-P1-C8 117.4(2), C7-P1-C8 111.2(2), C7-P1-C12 107.4(2), C1-Ge1-C7-P1 3.0(3)/52.6(3).

Crystals of **5** contain three molecules in the asymmetric unit; they slightly differ in their P–Cl distances. Compound **6** contains two molecules (a and b) in the asymmetric unit; they differ in their torsion angles Cl-Ge-C7-P (a: $52.6(3)^\circ$, b: $39.0(3)^\circ$) and subsequently in their P···Cl distances (a: 3.292(2), b: 3.426(2) Å).

The complexed Lewis acid functions adopt trigonal bipyramidal coordination, indicated by their *r* parameters:^[21] it is 0.91–0.94 for **5** and 0.92/0.94 for **6**. The averaged Si–Cl bond at 2.260 Å and the averaged Ge–Cl bond at 2.476 Å are longer than in the related five-coordinate silicate [PNP][(C₂F₅)₄SiCl] 2.218(1) Å^[22] and germanate [PNP][(C₂F₅)₃GeCl₂] 2.322(1) Å),^[23] respectively. Hydrogen chloride can be removed from both adducts by reacting them with a hydride source such as 'Bu₃SnH, whereby elemental dihydrogen is released.

In contrast to nitrogen oxide and hydrogen chloride, both FLP react with phenylisocyanate under formation of the same type of adducts, **7** and **8**: here the oxygen atoms coordinate to the Lewis acid functions and the carbon atom to the phosphane unit. This binding pattern has also been observed for other FLP systems.^[24] This leads to five-membered rings. Low-field NMR shifts of the ³¹P nuclei of **7** (40.9 ppm) and **8** (31.2 ppm) were observed relative to the free FLPs **1** and **2**, respectively. The ¹H NMR spectra show CH₂ resonances at 1.80 (**7**) and 2.07 ppm (**8**) split into doublets – characteristic for adduct formation of the FLP. Adequate crystals for X-ray diffraction were not obtained.



FLP 1 reacts –in contrast to its germanium analogue 2– with trimethylsilyldiazomethane (Me₃SiCHNN) under 1,1-addition. Its terminal nitrogen atom becomes coordinated between the silicon and phosphorus atoms of 1. This binding type is the same as for Uhl's FLP 'Bu₂AIC(CHPh)PMes₂ in its Me₃SiCHNN adduct^[25] and related to the potential metal-free activation of dinitrogen described by Stephan and Melen.^[4] The four ¹H NMR signals of 9 include a singlet at 0.05 ppm for the TMS group, two doublets at 0.87 ppm for the *tert*-butyl groups, a doublet at 2.07 ppm for the

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methylene and a singlet at 7.91 ppm for the N₂CH group. Pentacoordination at the silicon atom follows from a ^{29}Si resonance at –88.6 ppm.



Final proof for the formation of a four-membered ring (similar to the product of the reaction with NO: **3**) stems from X-ray crystallography (Figure 7). The ring angle Si1-N1-P is 99.0(1)° while Si1-C7-P is 94.5(1)°. The Si1--P distance at 2.736(1) Å is 0.11 Å longer compared to compound **3**.



Figure 7. Molecular structure of compound **9** in the solid state. Ellipsoids are set at 50% probability; only hydrogen atom at C16 is shown for clarity. Selected bond lengths [Å] and angles [°]: P1–Si1 2.736(1), P1–N1 1.655(2), Si1–N1 1.933(2), P1–C7 1.785(2), Si1–C7 1.939(2), Si1–C1 2.012(3), Si1–C5 1.999(2), Si1–C3 2.054(2), C16–N2 1.290(3), N1–N2 1.398(3), Si1-N1-P1 99.0(1), Si1-C7-P1 94.5(1), C16-N2-N1 119.2(2), Si2-C16-N2 116.5(2).

Herein we demonstrated the neutral Ge/P FLP-system $(C_2F_5)_3$ GeCH₂P(*t*Bu)₂ (2) to be capable of cleaving NO and HCl, as well as to bind Ph-NCO, the same applies to the silicon analogue $(C_2F_5)_3SiCH_2P(tBu)_2$ (1). However, unlike the latter, 2 does not react with H₂, CO₂ or SO₂ under comparable conditions. There are a number of facts that demonstrate clearly that the germanium function is the reason for the weaker Lewis acidity in comparison to the silicon analogue: a) the different structures of the NO oxidation products, b) the predicted double-minimum potential for the SiCPO ring-type oxidation product 3 (E = Si) while 4 (E = Ge) has a single minimum and open-chain structure, c) the fact that only 1 but not 2 is able to split Me₃Si-CHN₂. In addition, we calculated free enthalpies for the addition of HCI (ΔG_{HCI}) and the fluoride ion affinities (FIA) for **1** and **2** (ΔG_{HCI} [kJ mol⁻¹] = -77 (1), -63 (2); FIA [kJ mol⁻¹] = 378 (1), 308 (2)) which fully confirm this trend (details see Supporting Information). This feature can allow a fine tuning of Lewis acidity in future applications.

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Conflict of interest

The authors declare no conflict of interest.

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Frustrated as well is the germanium Lewis Pair $(C_2F_5)_3GeCH_2P(tBu)_2$, but compared to its silicon homologue it shows contrasting behaviour in its reactivity to certain substrates as HCI and NO featuring the germanium function to be less Lewis acidic.



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XXX – XXX

A Neutral Germanium/Phosphorus Frustrated Lewis Pair and its Contrasting Reactivity Compared to its Silicon Analogue