Frustrated Lewis Pairs

International Edition: DOI: 10.1002/anie.201511048
German Edition: DOI: 10.1002/ange.201511048

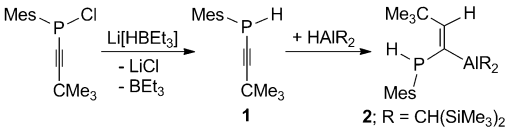
A P−H Functionalized Al/P Frustrated Lewis Pair: Substrate Activation and Selective Hydrogen Transfer

*Lukas Keweloh, Hans Klöcker, Ernst-Ulrich Würthwein, and Werner Uhl**

Abstract: *Hydroalumination of an alkynylphosphine gave an unprecedented P−H functionalized frustrated Lewis pair (FLP). The reactive P−H group does not influence the typical FLP properties, but the activation of substrates follows a new reaction pattern involving hydrogen transfer to yield unusual compounds with phosphaurea, iminophosphine, or phosphanyltriazene structural motifs.*

Frustrated Lewis pairs (FLPs) are in the focus of current research activities.[1] They have coordinatively unsaturated Lewis acidic and Lewis basic centers in single molecules or bimolecular systems and have been used in a vast number of stoichiometric or catalytic transformations. The heterolytic cleavage of H_2 is one of the most prominent examples,[1,2] but the ambiphilic nature of these FLPs allowed further remarkable activation or complexation reactions.[1] Recently we reported the synthesis of an Al/P-based FLP, $\mathrm{Mes_2P\text{-}C(Al^tBu_2){=}C(H)Ph}$, which was obtained by hydroalumination of an alkynylphosphine and was the first geminal FLP reported.[3] Al atoms have the advantage that their inherently high Lewis acidity does not require activation by electron-withdrawing groups. These compounds have been applied for the coordination of various substrates,[4] in phase-transfer catalysis (hydride transfer)[5] or the catalytic dehydrogenation of ammineboranes.[6] Functionalized compounds that have a protecting and a reactive group (X) attached to Al or P should open new perspectives in FLP chemistry. They may allow the ambiphilic coordination of substrates by the specific FLP properties and the transfer of X to the activated substrates.

Al/P-based FLPs are readily available by hydroalumination of alkynylphosphines.[3,7] A suitable starting compound for the synthesis of a P−H functionalized FLP is $\mathrm{Mes(H)P\text{-}C{\equiv}C\text{-}CMe_3}$ **1** which was obtained by treatment of $\mathrm{Mes(Cl)P\text{-}C{\equiv}C\text{-}CMe_3}$[8] with $\mathrm{Li[HBEt_3]}$ in 95% yield (Scheme 1). Compound **1** shows a $^1J_{\mathrm{PH}}$ coupling constant of 233.8 Hz which is characteristic of three-coordinate $\mathrm{P^{III}}$ atoms. It is thermally stable and does not decompose or rearrange in toluene or THF or in the melt upon heating to 80 °C. The X-ray crystal structure (Figure 1)[9] confirms the pyramidal coordination sphere of the P atom which is bound to an H atom, a mesityl, and an alkynyl group (angle C1-P1-C4 103.02(7)°).



Scheme 1. Synthesis of the P−H functionalized FLP **2**.

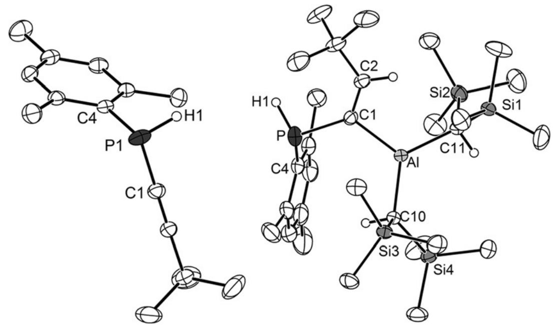


Figure 1. Molecular structures of **1** and **2** (thermal ellipsoids set at 40% probability).

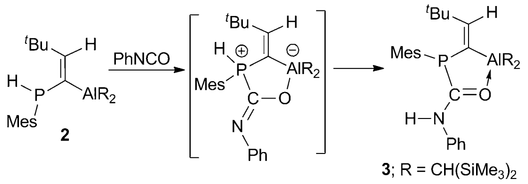
Hydroalumination of **1** with sterically shielded $\mathrm{H\text{-}Al[CH(SiMe_3)_2]_2}$[10] afforded selectively the new P−H functionalized FLP **2** in 73% yield. Deprotonation of the P−H group by the basic hydride as an unwanted competitive process was not observed. The bulky $\mathrm{CH(SiMe_3)_2}$ groups prevent secondary reactions, such as dimerization. The coupling constants $^1J_{\mathrm{PH}}$ and $^3J_{\mathrm{PH}}$ (221.4 and 31.8 Hz) confirmed the coordination number of three at P and the *trans*-arrangement of the P and H atoms across the C=C bond. The molecular structure of **2** in the solid state (Figure 1)[9] revealed the monomeric formula unit with a geminal arrangement of P and Al atoms which have a trigonal pyramidal and a planar coordination sphere, respectively. The long intramolecular Al···P distance of 333 pm is similar to dimesityl compounds (ca. 330 pm)[3] and indicates the absence of significant Al−P bonding interactions.

Treatment of **2** with phenyl isocyanate as a typical heterocumulene at −30 °C yielded the colorless compound **3** (Scheme 2) in 60% yield. The ^{31}P NMR spectrum showed only the coupling of the P atom to the vinylic H atom ($^3J_{\mathrm{PH}} =$ 47.1 Hz). The missing large $^1J_{\mathrm{PH}}$ coupling constant indicated the cleavage of the P−H bond. A resonance signal in the

---

[*] M. Sc. L. Keweloh, M. Sc. H. Klöcker, Prof. Dr. W. Uhl
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
E-mail: uhlw@uni-muenster.de
Prof. Dr. E.-U. Würthwein
Organisch-chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201511048.



Scheme 2. Reaction of **2** with phenyl isocyanate.

^{1}H NMR spectrum at $\delta = 7.19$ ppm was assigned to an N–H group. The molecular structure in the solid state (Figure 2)[9] confirmed the unprecedented reaction course with the coordination of the NCO moiety to the FLP via its C=O bond (127.0(2) pm) and the H transfer from P to N with the formation of a phosphaurea derivative (N–C 133.3(2) pm; P-C 183.8(2) pm). Only a single compound is known with a similar structural motif (H_2N-CO-PH_2 as a crown-ether complex)[11] which may be stabilized in **3** by the intramolecular interaction of the O with the Al atom. The reaction probably starts with coordination of the carbonyl group to the P and Al atoms of the FLP **2** which reflects the normal reaction course.[12] Coordination via the C=N bond was only achieved with a sterically less-shielded Al/P FLP.[12] Compound **3** may finally be formed by a 1,3-shift of the H atom from the four-coordinate P to the more basic N atom.

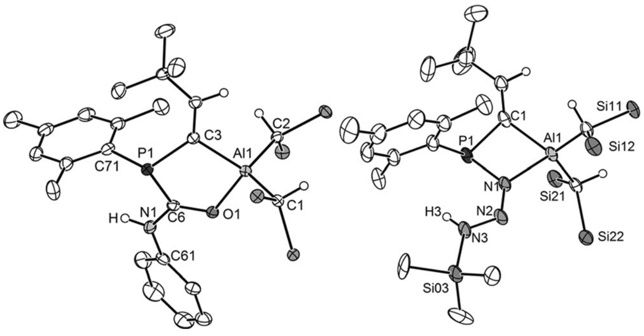
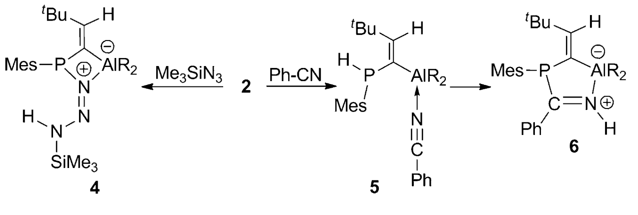


Figure 2. Molecular structures of **3** and **4** (thermal ellipsoids set at 40% probability). Important bond lengths [pm]; **3**: O1-C6 127.0(2), N1-C6 133.3(2), P1-C6 183.8(2); **4**: N1-N2 127.3(1), N2-N3 132.3(1), P1-N1 179.2(1).

Compound **4** was obtained by reaction of **2** with trimethylsilyl azide, a representative homonuclear cumulene (Scheme 3). Compound **4** has a four-membered Al-C-P-N heterocycle and results from coordination of the terminal N atom to P and Al and the shift of the P bound H atom to the N atom attached to Si. A ^{1}H NMR resonance at $\delta = 7.52$ ppm was assigned to the N–H proton. The N1–N2 distance (127.3(1) pm, Figure 2)[9] corresponds to an N=N bond, the N2–N3 bond length is slightly longer (132.3(1) pm) and indicates a delocalized π-bonding. The P–N bond length (179.2(1) pm) corresponds to the typical value of P–N single bonds. Both compounds **3** and **4** show a short intramolecular distance between the N–H hydrogen atom and the *ipso*-C atom of the mesityl group ($\delta = 245$ and 248 pm; N–H⋯π-interaction) which may help to stabilize the respective configuration in the solid state and may influence the chemical shifts of these protons in the ^{1}H NMR spectra in solution. Compounds **3** and **4** did not decompose in benzene solution upon warming to 70 °C for several hours. The unique structure of **4** may be derived from triazene, R-N=N-NH_2, or an unknown phosphanyltriazene, R_2P-N=N-NH_2,[13] which is stabilized by coordination to the Al atom. Upon cooling to 210 K resonance signals of a second species were seen in the ^{1}H and ^{31}P NMR spectra with low, but steadily increasing intensity. They may arise from *cis*/*trans* isomers or a change in ring size. The reaction of phenyl azide seems to result in the formation of a similar four-membered heterocycle (see the Supporting Information). The observation of a doublet of doublets in the ^{1}H NMR spectrum with a large $^1J_{PH}$ coupling constant of 472.9 Hz confirmed the presence of a P–H group with a four-coordinate P atom [$\delta(^{31}P) = 71.1$ ppm (**4**) vs. -11.8]. Rearrangement is probably hindered by mesomeric delocalization of the lone pair of electrons at N into the aromatic ring and the low basicity of the phenyl bound N atom.



Scheme 3. Reactions of **2** with trimethylsilyl azide and benzonitrile; R = CH(SiMe$_3$)$_2$.

Benzonitrile with its isolated C≡N triple bond reacted with **2** in *n*-pentane to yield adduct **5** in the first step, which rearranges to yield compound **6** after 7 days at room temperature or 12 h at 50 °C (73% yield). The coordination number of three at the P atom of **5** is confirmed by an only slight shift of the ^{31}P NMR resonance from $\delta = -80.8$ ppm in **2** to $\delta = -76.2$ ppm and a $^1J_{PH}$ coupling constant of 228.0 Hz (**2**: 221.4 Hz). The increased coordination number of the Al atom causes a shift of the inner hydrogen atom of the CH(SiMe$_3$)$_2$ group (AlC*H*Si$_2$) to a higher field ($\delta = -0.50$ vs. -0.69 ppm). In the ^{1}H NMR spectrum of **6** the characteristic doublet of the P–H group disappeared, and a new resonance was detected at $\delta = 8.80$ ppm which was assigned to an N–H proton. The coupling constant between the P and the vinylic H atom increased from 34.7 to 47.8 Hz. Crystal structure determination (Figure 3)[9] revealed an almost planar five-membered C_2NAlP heterocycle with an endocyclic C=N bond (130.4(1) pm), an N–H group and a three-coordinate P atom. Compound **6** may be described as an iminophosphine derivative (H-N=C(R)-PR$_2$).[14] This reaction helps to suggest a general reaction course. The substrates approach the Lewis acidic Al atoms via a lone pair of electrons of a heteroatom (O or N). Adduct formation (**5**) increases the polarity of the bonds and favors the formation of the P–C bond. H shift from P to the more-basic N atoms affords the finally isolated products.

The reaction of **2** with benzonitrile was studied by quantum chemical gas-phase DFT calculations (Scheme 4).

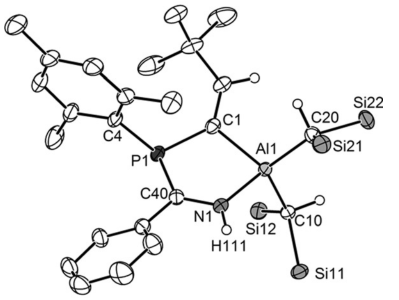
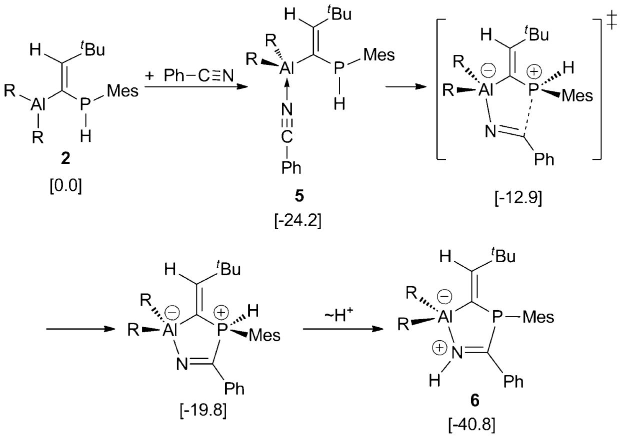


Figure 3. Molecular structures of **6** (thermal ellipsoids set at 40% probability). Important bond lengths [pm]: N1-C40 130.4(2), P1-C40 181.6(2).



Scheme 4. Calculated mechanism for the reaction of **2** with benzonitrile; relative energies in square brackets [kcal mol^{-1}]; M062x/6-311+G(d,p)+GD3+ZPE; R=CH(SiMe$_3$)$_2$.

The formation of adduct **5** was calculated to be exothermic by 24.2 kcal mol^{-1} (including zero point correction). 1,5-Cyclization affords a cyclic intermediate with the H atom still bonded to the P atom. This reaction was calculated to be exothermic by 19.8 kcal mol^{-1} with respect to **2** and benzonitrile, but slightly endothermic with respect to **5** (4.4 kcal mol^{-1}). The moderate barrier for the cyclization was 11.3 kcal mol^{-1} (with respect to **5**). Finally, H migration from P to N yields compound **6** in an exothermic reaction (−40.8 kcal mol^{-1} with respect to **2** and benzonitrile, −16.6 kcal mol^{-1} with respect to **5**). Experimentally the H shift may be facilitated by intermolecular interactions with the solvent or with reaction components, such as **5**, its cyclic form, or even by already formed **6** (autocatalysis). The calculations suggested an alternative chemical pathway starting with deprotonation of compound **2** or **5** at P using a rather strong base (**2** and **5** are relatively weak acids) which should result in highly reactive anions. The anion derived from **5** cyclizes in a facile and exothermic reaction (−33.6 kcal mol^{-1} with respect to the anion of **5**) via a negligible barrier. The final product **6** is then obtained by re-addition of the proton (see the Supporting Information).

In conclusion an interesting new reactivity mode of FLPs is reported starting with the P−H functionalized Al/P-based compound **2**. Unsaturated substrates are coordinated by the ambiphilic FLP and the activated species are reduced by H shift to achieve unusual structural motifs (phosphaurea, phosphanyltriazene, iminophosphine). As shown by control experiments the alkynylphosphine starting compound **1** is inert towards an attack of these substrates even at elevated temperatures. Cooperativity between the typical activation properties of the FLP and the reducing power of the P−H group is an essential component of this chemistry. Hydrogen transfer from the FLP to the activated substrates enables the generation of new functionalized phosphorus compounds, which are not easily accessible by other routes. This specific reactivity opens access to a promising new field of FLP chemistry. The interaction with the Al atoms, similar to that in **3**, **4**, and **6**, may help to stabilize reactive species, and the generation of the aluminium-free derivatives by hydrolysis or hydrogenation is an interesting challenge for future investigations.

Keywords: aluminum · cooperativity · density functional calculations · frustrated Lewis pairs · insertion reactions

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 3212–3215
Angew. Chem. **2016**, *128*, 3266–3269

---

[1] a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; c) "Frustrated Lewis Pairs, Vol. I and II": *Topics in Current Chemistry* (Eds.: G. Erker, D. W. Stephan), Springer, Heidelberg, **2013**.

[2] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[3] C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2011**, *50*, 3925–3928; *Angew. Chem.* **2011**, *123*, 4011–4014.

[4] "Frustrated Lewis Pairs, Vol. I and II": W. Uhl, E.-U. Würthwein, in *Topics in Current Chemistry*, *Vol. 334* (Eds.: G. Erker, D. W. Stephan), Springer, Heidelberg, **2013**, pp. 101–119.

[5] C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2012**, *51*, 5911–5914; *Angew. Chem.* **2012**, *124*, 6013–6016.

[6] C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2013**, *52*, 4256–4259; *Angew. Chem.* **2013**, *125*, 4350–4353.

[7] W. Uhl, C. Appelt, J. Backs, H. Westenberg, A. Wollschläger, J. Tannert, *Organometallics* **2014**, *33*, 1212–1217.

[8] H. Klöcker, M. Layh, A. Hepp, W. Uhl, *Dalton Trans.* DOI: 10.1039/c5dt02825f.

[9] CCDC 1437761 (**1**), CCDC 1437757 (**2**), CCDC 1437758 (**3**), CCDC 1437759 (**4**), and CCDC 1437760 (**5**) contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[10] W. Uhl, E. Er, A. Hepp, J. Kösters, J. Grunenberg, *Organometallics* **2008**, *27*, 3346–3351.

[11] A. Jupp, J. M. Goicoechea, *J. Am. Chem. Soc.* **2013**, *135*, 19131–19134; see also: M. Nieger, B. Klupfel, W. Malisch, private communication, CCDC 198134.

[12] S. Roters, C. Appelt, H. Westenberg, A. Hepp, J. C. Slootweg, K. Lammertsma, W. Uhl, *Dalton Trans.* **2012**, *41*, 9033–9045.

[13] A phosphonium triazenide has been published: A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, I. E. Boldeskul, M. P. Pono-

marchuk, L. F. Kasukhin, V. P. Kukhar, *J. Gen. Chem. USSR* **1988**, *58*, 249 – 254.

[14] Free iminophosphines: a) T. van Dijk, S. Burck, A. J. Rosenthal, M. Nieger, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *Chem. Eur. J.* **2015**, *21*, 9328 – 9331; coordinated derivatives: b) M. Ghalib, L. Könczöl, N. Nyulaszi, P. G. Jones, G. J. Palm, J. W. Heinicke, *Dalton Trans.* **2014**, *43*, 51 – 54; c) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J. Majoral, *Angew. Chem. Int. Ed.* **2000**, *39*, 4524 – 4528; *Angew. Chem.* **2000**, *112*, 4698 – 4702; d) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, A. Skowronska, *Chem. Eur. J.* **2001**, *7*, 221 – 229; e) N. E. Mansfield, M. P. Coles, P. B. Hitchcock, *Polyhedron* **2012**, *37*, 9 – 13; f) U. Segerer, S. Blaurock, J. Sieler, E. Hey-Hawkins, *J. Organomet. Chem.* **2000**, *608*, 21 – 26.

Received: November 27, 2015