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Frustrated Lewis Pairs

Geminal Phosphorus/Aluminum-Based Frustrated Lewis Pairs: C–H versus C≡C Activation and CO_2 Fixation**

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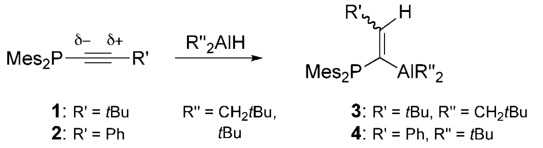
Frustrated Lewis pairs (FLPs),[1] which have donor and acceptor sites in close proximity, are of considerable interest for the dipolar activation of small molecules, such as hydrogen,[2] alkynes,[3] and the greenhouse gases carbon dioxide[4] and nitrous oxide.[5] So far, phosphines,[1,6] amines,[7] thioethers,[3c] and carbenes[2e,8] have been applied as Lewis base, while polyfluorinated boranes are the common Lewis acid in FLP chemistry. Surprisingly, alanes have only been rarely used,[3a,c,9] although these are generally better Lewis acids[10] that can circumvent the need for decorating the acceptor site with electron-withdrawing fluorinated substituents. Herein we present a simple one-step synthesis of geminal phosphorus/aluminum-based FLPs by hydroalumination[11,12] of readily available alkynylphosphines,[13] as well as on their propensity to activate small molecules.[14]

To illustrate the diversity of our general method, $Mes_2PC{\equiv}CtBu$ (**1**; Mes = 2,4,6-$Me_3C_6H_2$) was treated with di(neopentyl)aluminum hydride, and $Mes_2PC{\equiv}CC_6H_5$ (**2**) was treated with di(*tert*-butyl)aluminum hydride at room temperature, which afforded the respective adducts **3** and **4** as sole products (Scheme 1). Interestingly, phosphinoalanes **3** ($\delta(^{31}P) = -32.0$ ppm, $^3J(H,P) = 37.9$ Hz) and **4** ($\delta(^{31}P) = -14.2$ ppm, $^3J(H,P) = 17.7$ Hz) both have distinct $^3J(H,P)$ couplings, indicating different conformations of the double bond. The molecular structures of **3** and **4** were established unequivocally by X-ray crystal structure determinations (Figure 1),[15] which showed that **3** is the expected *cis* hydroalumination adduct with a *Z* configured C=C bond, while a *cis*/*trans* isomerization occurred in the case of *E*-**4**.[16] Such an isomerization requires intermolecular activation,[17] which is evidently impeded by the bulky *tert*-butyl group on the double bond in **3**. The highly selective attack of the positively charged aluminum atom at the α-carbon atom of the alkynylphosphines **1** and **2** is in accord with the charge separation in the starting alkyne (NBO values of **1**: α-C −0.49, β-C +0.03; **2**: α-C −0.35, β-C −0.004). Expectedly, the phosphorus atoms in **3** and **4** have a pyramidal coordination and the aluminum atoms are trigonal-planar. Furthermore, both heteroatoms are perfectly oriented for small-molecule activation.



Scheme 1. Synthesis of FLPs **3** and **4** by hydroalumination of **1** and **2**.

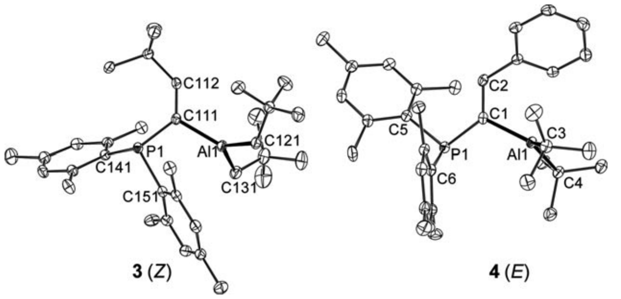


Figure 1. Molecular structures of **3** and **4**. Ellipsoids set at 30% probability; hydrogen atoms are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **3**: Al1–C111 198.0, P1–C111 183.0, C111–C112 133.6, Al1···P1 315.3; Al1-C111-P1 111.0. **4**: Al1–C1 199.2, P1–C1 182.2, C1–C2 134.3, Al1···P1 328.7; Al1-C1-P1 119.1.

To investigate the reactivity of our new FLPs, we examined the reaction of **4** with terminal acetylenes, CO_2, and H_2 and we also analyzed the reaction profiles computationally. Treating FLP **4** with phenylacetylene in toluene at room temperature gave a 3:1 mixture of **5a** ($\delta(^{31}P) = -5.1$ ppm) and **6a** ($\delta(^{31}P) = 24.2$ ppm, $^3J(H,P) = 60.1$ Hz; Scheme 2), while at 50 °C a 1:1 mixture was obtained. Heating the mixture at 70 °C for 1 hour resulted in the full conversion of **5a** into **6a**, which after crystallization was isolated in 91% yield. Single-crystal X-ray diffraction analysis revealed that **6a** is formed by P/Al addition to the alkyne[3a,b] (Figure 2).[15] Whereas **5a** could not be obtained in pure form, its large $^1J(H,P)$ coupling of 503.5 Hz is characteristic for a P–H species, indicating that it is formed by C–H activation of the alkyne.[3a] This hypothesis was confirmed by the reaction of **4**

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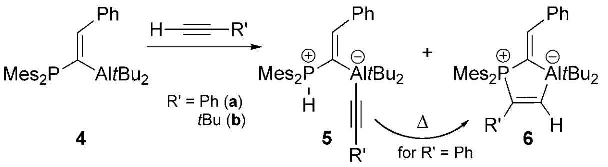

Scheme 2. Reaction of FLP **4** with terminal acetylenes.

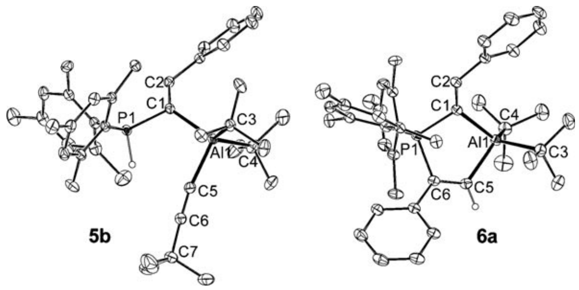

Figure 2. Molecular structures of **5b** and **6a**. Ellipsoids set at 30% probability; hydrogen atoms except at P1 (**5b**) and C5 (**6a**) and toluene (**5b**) or hexane (**6a**) solvent molecules are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **5b**: Al1–C5 198.7(3), P1–H1 127(2), C5–C6 120.3(3), C1–C2 135.0(3); Al1-C5-C6 171.1(2). **6a**: Al1–C5 202.6(3), P1–C6 181.9(3), C1–C2 134.1(4), C5–C6 134.1(4); Al1-C1-P1 106.1(1).

with *tert*-butylacetylene at 40 °C (2 h), which afforded only **5b** (92%; $\delta(^{31}P) = -5.2$ ppm, $^1J(H,P) = 507.5$ Hz) and could be characterized crystallographically (Figure 2). The molecular structure of **5b** reveals a phosphonium alkynylaluminate with typical Al–C and C≡C bond lengths of $\delta = 198.7$ and 120.3 pm, respectively.

To provide insight into the mode of activation and to establish whether **6a** is a primary product or formed by **5a**, we resorted to M06-2X/6-31 + G(d,p) calculations[18] on the full system. Three van der Waals complexes were observed upon reacting phenylacetylene with FLP **4** of which the most stable complex (**vdW**, $\Delta E = -5.7$ kcal mol^{-1}; Figure 3) has the alkyne positioned near the aluminum atom[3a,b,19] and orthogonal to the P-C-Al plane of **4**. Rotating the alkyne into the P-C-Al plane either clockwise or anticlockwise determines the reaction outcome by bringing about the other complexes, namely **5a-vdW** and **6a-vdW** ($\Delta\Delta E = 1.2$ and 2.2 kcal mol^{-1}, respectively). In **5a-vdW**, the acetylenic proton is oriented towards the Lewis base, which yields **5a** by deprotonation after initial formation of the Al–C bond and subsequent migration of H to P ($\Delta\Delta E^{\neq} = 7.6$, $\Delta\Delta E = -10.7$ kcal mol^{-1}; Figure 3). In **6a-vdW**, the C≡C bond is facing both phosphorus and aluminum atoms, facilitating an asynchronous 1,2-addition by Al–C and then P–C bond formation ($\Delta\Delta E^{\neq} = 4.5$, $\Delta\Delta E = -27.2$ kcal mol^{-1}; Figure 3). It can be concluded that products **5a** and **6a** are formed depending on the initial orientation of the alkyne. Upon heating, **5a** can interconvert via **vdW** into the thermodynamically favored **6a**, which corroborates with the experimental details. Using *tert*-butylacetylene as substrate, **5b** is the thermodynamic sink that does not rearrange into **6b** owing to steric crowding in the transition state (compare with **TS6a** in Figure 3), which precludes the formation of the P–C bond under the reaction conditions.

The behavior of **4** with terminal alkynes encouraged us to examine the FLP activation of CO_2, for which there are only limited examples.[4,9] CO_2 was bubbled through a solution of **4** in toluene at room temperature for 30 seconds, which after crystallization afforded CO_2 adduct **7** in 74% yield ($\delta(^{31}P) = 5.6$ ppm; $\delta(^{13}C)$ $(CO_2) = 165.1$ ppm, $^1J(C,P) = 106.5$ Hz). A crystal structure determination confirmed the five-membered heterocycle (Figure 4)[15] bearing short C–O (128.0 pm) and C=O (120.6 pm) bonds,[4a] but an elongated P–C(O) bond (191.9 pm). This carbon dioxide binding can be reversed: Treatment of **7** in the solid state at 135 °C under vacuum for 2 minutes resulted in the complete reformation of FLP **4**.

Analysis of the formation of CO_2 adduct **7** at the M06-2X/6-31 + G(d,p) level of theory[18] showed the intermediacy of a

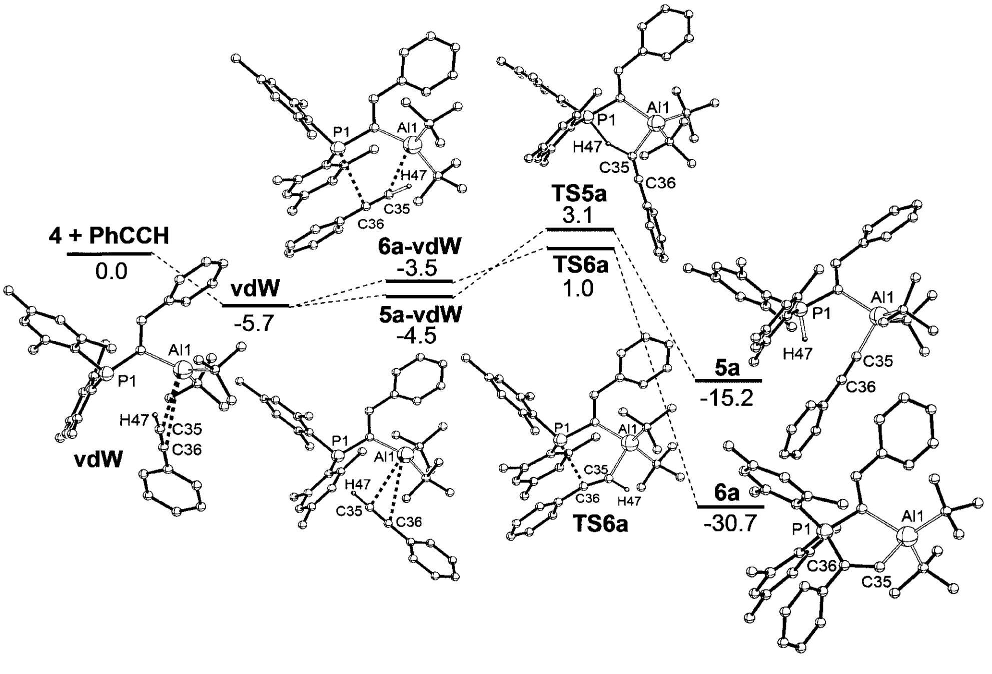

Figure 3. Relative M06-2X/6-31 + G(d,p) energies [kcal mol^{-1}] for the reaction of FLP **4** with phenylacetylene, yielding products **5a** and **6a**. Selected bond lengths [pm] for **vdW**: Al1–C35 299.8, Al1–C36 353.1, C35–C36 121.2. **5a-vdW**: Al1–C35 353.8, Al1–C36 389.3, C35–C36 121.1. **6a-vdW**: Al1–C35 359.3, P1–C36 317.1, C35–C36 121.1. **TS5a**: Al1–C35 214.9, P1–H47 175.0, C35–H47 129.6. **TS6a**: Al1–C35 283.5, P1–C36 217.6, C35–C36 124.8. **5a**: Al1–C35 200.4, P1–H47 139.3, C35–C36 122.6. **6a**: Al1–C35 203.4, P1–C36 183.6, C35–C36 134.8.

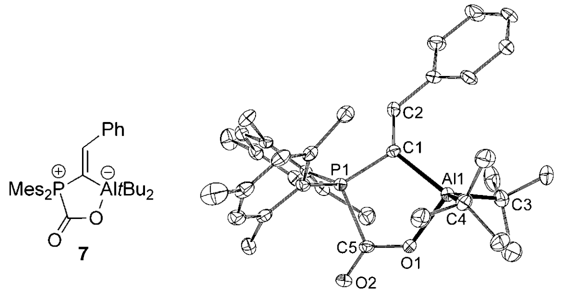

Figure 4. Molecular structure of **7**. Ellipsoids set at 30% probability; hydrogen atoms and toluene molecule are omitted for clarity. Selected average bond lengths [pm] and angles [°] for four independent molecules: Al1–C1 205.8, Al1–O1 185.9, P1–C1 178.8, P1–C5 191.9, C1–C2 134.6, C5–O1 128.0, C5–O2 120.6; Al1-C1-P1 108.6, O1-C5-O2 126.7.

van der Waals complex (**7-vdW**, $\Delta E = -6.52$ kcal mol^{-1}) with a nonlinear CO$_2$ fragment (171.0°) positioned perpendicular to the P-C-Al plane of **4** (Figure 5). Compound **7-vdW** has a short contact between the oxygen atom of CO$_2$ and aluminum (222.9 pm), but a rather long P–C distance (298.2 pm) that decreases smoothly upon conversion into **7** via an almost barrier-free transition ($\Delta\Delta E^{\neq} = 0.07$, $\Delta\Delta E = -16.9$ kcal mol^{-1}). Interestingly, it has been shown computationally that in the case of P/B-based FLPs, CO$_2$ interacts first with the Lewis base.[4a] Our computational analyses show that for the Al-based FLP **4**, both terminal alkynes and CO$_2$ are activated by initial interaction with the acceptor site, which underscores the fact that alanes are also potent Lewis acids for frustrated Lewis pair chemistry.

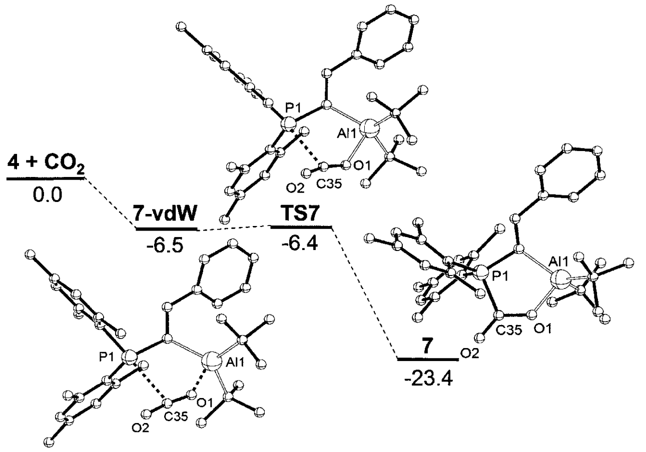

Figure 5. Relative M06-2X/6-31+G(d,p) energies [kcal mol^{-1}] for the reaction of FLP **4** with CO$_2$ to give **7**. Selected bond lengths [pm] and angles [°] for **7-vdW**: Al1–O1 222.9, P1–C35 298.2, C35–O1 117.6, C35–O2 115.6; O1-C35-O2 171.0. **7**: Al1-O1 187.9, P1-C35 193.4, C35-O1 127.8, C35-O2 120.8; O1-C35-O2 129.1.

Finally, preliminary studies showed that **4** is unreactive towards dihydrogen, but with a very modest endothermicity of $\Delta E = 5.9$ kcal mol^{-1}, calculated at M06-2X/6-31+G(d,p).[18] To increase the potential for H$_2$ activation, the Lewis acidity of the acceptor site and the Lewis basicity of the donor site can be enhanced easily by using differently substituted P-alkynes and aluminum hydrides.

In summary, hydroalumination of alkynylphosphines provides a facile approach to geminal phosphorus/aluminum-based FLPs, which are ideally suited for small-molecule activation. The full potential of these readily available frustrated Lewis pairs for (catalytic) small molecule activation is currently being explored in our laboratories.

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[15] CCDC 796717 (**3**), 796718 (**4**), 797001 (**5b**), 796719 (**6a**), and 796720 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.

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