Abstract: Geminal phosphorus/aluminum-based frustrated Lewis pairs (FLPs) are easily obtained by hydroalumination of alkynylphosphines. These FLPs can activate terminal acetylenes by two competitive pathways, which were analyzed by DFT calculations, and they can bind carbon dioxide reversibly. Therefore, alongside polyfluorinated boranes, alanes are also ideal Lewis acids for FLP chemistry.

NOTE: The work described in this chapter results from a collaboration with the group of Prof. Werner Uhl (University of Münster). All the experimental work described herein, which was the basis for the computational analysis, was performed in Münster by PhD student Christian Appelt and will be reported in his PhD thesis. The computational work was entirely performed by the author of this thesis.

3.1. Introduction

Frustrated Lewis pairs (FLPs)\(^1\) bearing donor and acceptor sites in close proximity are of considerable interest for the dipolar activation of small molecules, such as hydrogen, alkynes, and the greenhouse gases carbon dioxide and nitrous oxide. So far, phosphines, amines, thioethers, and carbenes have been applied as Lewis base, while polyfluorinated boranes are the common Lewis acid in FLP chemistry. Surprisingly, alanes have only been used a few times, while generally these are the better Lewis acids that can circumvent the need for decorating the acceptor site with electron-withdrawing fluorinated substituents. Here we report on a simple one-step synthesis of geminal phosphorus/aluminum-based FLPs by hydroalumination of readily available alkynylphosphines, as well as on their propensity to activate small molecules.

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

\[ \text{Mes}_2\text{PC}≡\text{P} \longrightarrow \text{Mes}_2\text{PC}≡\text{CHR}^\text{R}^2 \]

3.2. Results and Discussion

To illustrate the diversity of our general method, Mes\(_2\)P=CC\(_6\)H\(_5\) (1) was treated with di(neopentyl)aluminum hydride and Mes\(_2\)P=CC\(_6\)H\(_5\) (2) 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 (\(\delta_{31P} = -32.0\) ppm, \(3\)J\(_{HP} = 37.9\) Hz) and 4 (\(\delta_{31P} = -14.2\) ppm, \(3\)J\(_{HP} = 17.7\) Hz) both have distinct \(3\)J\(_{HP}\) 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), which showed that 3 represents the expected cis hydroalumination adduct with a Z configured C=\(\text{C}\) bond, while a cis/trans isomerization occurred in the case of E-4. Such an isomerization requires intermolecular activation, 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 \(\alpha\)-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. In addition, both heteroatoms are perfectly oriented for small molecule activation.

**Figure 1.** Molecular structures of 3 and 4 (30% probability); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°], average values of 3: Al−C(vinyl) 1.980, P−C(vinyl) 1.830, C=C 1.336, Al−P 3.153, Al−C−P 111.0. 4: Al−C(vinyl) 1.992, P−C(vinyl) 1.822, C=C 1.343, Al−P 3.287, Al−C−P 119.1.

In order to investigate the reactivity of our new FLPs, we decided to examine the reaction of 4 with terminal acetylenes, CO₂ and H₂ and to analyze the reaction profiles computationally. Treating FLP 4 with phenylacetylene in toluene at room temperature gave a 3:1 mixture of 5a (δ₃¹P = –5.1 ppm) and 6a (δ₃¹P = 24.2 ppm, 3J₃₁P = 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 1J₃₁P coupling of 503.5 Hz is characteristic for a P–H species, indicating that it is formed via C–H activation of the alkyne.[3a] This hypothesis was confirmed by the reaction of 4 with tert-butylacetylene at 40 °C (2 h) that afforded only 5b (92%); δ₃¹P = –5.2 ppm, 1J₃₁P = 507.5 Hz), which could be characterized crystallographically (Figure 2). The molecular structure of 5b reveals a phosphonium alkynylaluminate with typical Al−C and CEC bond lengths of 1.987 and 1.203 Å, respectively.
Scheme 2. Reaction of FLP 4 with terminal acetylenes.

Figure 2. Molecular structures of 5b and 6a (30% probability); most hydrogen atoms and toluene (5b) or hexane (6a) are omitted for clarity. Selected bond lengths [Å] and angles [°], average values for 5b: Al1−C5 1.987(3), P1−H1 1.270(2), C5−C6 1.203(3), C1−C2 1.350(3), Al1−C5−C6 171.1(2). 6a: Al1−C5 2.026(3), P1−C6 1.819(3), C1−C2 1.341(4), C5−C6 1.341(4), Al1−C1−P1 106.1(1).

To provide insight into the mode of activation and to establish whether 6a is a primary product or formed via 5a, we resorted to M06-2X/6-31+G(d,p) calculations on the full system. Three van der Waals complexes were found on reacting phenylacetylene with FLP 4 of which the most stable one (vdW, ∆E = –5.7 kcal−mol−1; Figure 3) has the alkyne positioned near the aluminum atom and orthogonal to the P–C–Al plane of 4. Rotating the alkyne into the P–C–Al plane either clockwise or anti-clockwise determines the reaction outcome by rendering the other complexes, 5a-vdW and 6a-vdW (ΔΔE = 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 via initial formation of the Al–C bond and subsequent migration of H to P (ΔΔE‡ = 7.6, ΔΔE = –10.7 kcal−mol−1; Figure 3). In 6a-vdW the CΞC bond is facing both phosphorus and aluminum atoms, facilitating an asynchronous 1,2-addition via Al–C and then P–C bond formation (ΔΔE‡ = 4.5, ΔΔE = –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 to 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 due to steric crowding in the transition state (c.f., TS6a in Figure 3), which precludes the formation of the P–C bond under the reaction conditions.

![Figure 3](image.png)

**Figure 3.** Relative M06-2X/6-31+G(d,p) energies (in kcal·mol⁻¹) for the reaction of FLP 4 with phenylacetylene yielding products 5a and 6a. Selected bond lengths [Å] for vdW: Al1–C35 2.998, Al1–C36 3.531, C35–C36 1.212. 5a-vdW: Al1–C35 3.538, Al1–C36 3.893, C35–C36 1.211. 6a-vdW: Al1–C35 3.593, P1–C36 3.171, C35–C36 1.211. TS5a: Al1–C35 2.149, P1–H47 1.750, C35–H47 1.296. TS6a: Al1–C35 2.835, P1–C36 2.176, C35–C36 1.248. 5a: Al1–C35 2.004, P1–H47 1.393, C35–C36 1.226. 6a: Al1–C35 2.034, P1–C36 1.836, C35–C36 1.348.

The behavior of 4 with terminal alkynes encouraged us to examine the FLP activation of CO₂ of which there are only limited examples.⁴,⁵ CO₂ was bubbled through a solution of 4 in toluene at room temperature for 30 sec., which afforded after crystallization CO₂ adduct 7 in 74% yield (δ₃¹P = 5.6; δ₁₃C (CO₂) = 165.1, ¹JCP = 106.5 Hz). A crystal structure determination confirmed the five-membered heterocycle (Figure 4)⁶ bearing short C–O
(1.280 Å) and C=O (1.206 Å) bonds, but an elongated P–C(O) bond (1.919 Å). This carbon dioxide binding can be reversed as treatment of 7 in the solid state at 135 °C under vacuum for 2 minutes resulted in the complete reformation of FLP 4.

Figure 4. Molecular structure of 7 (30% probability); hydrogen atoms and toluene are omitted for clarity. Selected bond lengths [Å] and angles [°], average values of four independent molecules: Al–C(vinyl) 2.058, Al–O 1.859, P–C(vinyl) 1.788, P–C(O) 1.919, C=C 1.346, C–O 1.280, C=O 1.206, Al–C–P 108.6, O–C–O 126.7.

Analysis of the formation of CO$_2$ adduct 7 at the M06-2X/6-31+G(d,p) level of theory\cite{18} showed the intermediacy of a 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). 7-vdW displays a short contact between the oxygen atom of CO$_2$ and aluminum (2.229 Å), but a rather long P–C distance (2.982 Å) that decreases smoothly upon conversion into 7 via an almost barrier-free transition ($\Delta\Delta E^*=0.07$, $\Delta\Delta E = -16.9$ kcal-mol$^{-1}$).\cite{20} Interestingly, it has been shown computationally that in the case of P/B-based FLPs CO$_2$ interacts first with the Lewis base. 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,\cite{21} which underlines that also alanes are potent Lewis acids for frustrated Lewis pair chemistry.

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).\cite{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 (see Computational Section for additional details).
Figure 5. Relative M06-2X/6-31+G(d,p) energies (in kcal·mol⁻¹) for the reaction of FLP 4 with CO₂ yielding 7. Selected bond lengths [Å] and angles [°] for 7-vdW: Al₁–O₁ 2.229, P₁–C₃₅ 2.982, C₃₅–O₁ 1.176, C₃₅–O₂ 1.156; O₁–C₃₅–O₂ 171.0. 7: Al₁–O₁ 1.879, P₁–C₃₅ 1.934, C₃₅–O₁ 1.278, C₃₅–O₂ 1.208; O₁–C₃₅–O₂ 129.1.

3.3. Conclusions

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 explored in our laboratories.
3.4. Computational Section

**General.** The theoretical study which complements the experimental work was performed using Gaussian 09 suite of programs. All DFT calculations were conducted using the dispersion-corrected functional M06-2X and 6-31+G(d,p) basis set. In this work, frequency calculations on the computed structures could not be performed due to the too demanding computational cost. Consequently, the computed energies reported in this chapter are not ZPE-corrected.

3.4.1. Gas Phase Calculations and Solvent Effect

The calculations described in this chapter refer to the molecules in the gas phase. We have considered the possibility that even a low-polar solvent as toluene, which is the solvent used for the reactions, may influence significantly the relative energies of the computed structures. Therefore, we performed single point energy calculations on all the optimized structures for the reactions of 4 with phenylacetylene and carbon dioxide, using PCM as solvation model (solvent=toluene), with the default settings as it is implemented in Gaussian 09. We can conclude that considering the solvent effect doesn’t lead to significant changes in our conclusions. The computed solvation energies are all in the range of -0.9 to -4.4 kcal·mol⁻¹, with the higher values for the zwitterionic molecules, as expected. The energies of the computed minima and transition states in the gas phase and in toluene and the solvation energies are reported in Tables 2-4.

3.4.2. NBO Calculations and cis-trans Isomerization

NBO calculations were performed to rationalize the highly selective attack of the positively charged aluminum atom at the α-carbon of the alkynylphosphines 1 and 2. Such calculations showed, as expected, that the α-carbon of 1 and 2 is negatively charged, while the charges on the β-carbon atom are near to neutral for both 1 and 2. The computed SCF energies of alkynylphosphines 1 and 2 and the natural charges for the α- and β-carbon atoms of 1 and 2 are reported in Table 1.

Hydroalumination of alkynylphosphines is expected to result in the cis addition product as in the case of 3, which possesses Z configuration at the double bond, while the trans addition product E-4 is obtained when 2 is reacted with tBu₂AlH. According to our
calculations, the observed *cis*-trans isomerization which has occurred in the case of 4 is energetically favored by 7.9 kcal-mol⁻¹ (Table 2).

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**Table 1.** M06-2X/6-31+G(d,p) energies (given in a.u. and kcal·mol⁻¹) and NBO values for 1 and 2.

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<th></th>
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**Table 2.** M06-2X/6-31+G(d,p) energies (a.u.) and relative energies (kcal·mol⁻¹) in the gas phase and in toluene, and solvation energies (kcal·mol⁻¹) for E-4 and Z-4.

### 3.4.3. Reaction of 4 with Phenylacetylene

The computed structures, selected bond distances and angles, and energy profiles for the reaction of 4 with phenylacetylene are shown in Figure 3 (par. 3.2). The electronic energies for the computed structures in the gas phase and in toluene are reported in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>E_{(gas phase)}</th>
<th>ΔE_{(gas phase)}</th>
<th>E_{(toluene)}</th>
<th>ΔE_{(toluene)}</th>
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**Table 3.** M06-2X/6-31+G(d,p) energies (a.u.) and relative energies (kcal·mol⁻¹; relative to 4 + PhCCH) in the gas phase and in toluene, and solvation energies (kcal·mol⁻¹) for the reaction of 4 with phenylacetylene.
3.4.4. Reaction of 4 with CO$_2$

In our computational analysis aimed to unravel the mechanism for the CO$_2$ uptake by FLP 4 we could locate structures 7-vdW and TS7 as an energy minimum and a transition state on the PES (potential energy surface), respectively. However, the small difference in the computed structures for 7-vdW and TS7 suggested us that such structures may not be true stationary points. Instead, we believe that 7-vdW and TS7 result as stationary points on the PES consequently to the flatness of the PES in this region and to the fact that geometry optimizations are computed on a PES which is not ZPE-corrected. On the ZPE-corrected PES, 7-vdW and TS7 may not exist as stationary points and the reaction is most likely just barrierless.

The computed structures, selected bond distances and angles, and energy profiles for the reaction of 4 with carbon dioxide are shown in Figure 5 (Section 3.2). The electronic energies for the computed structures in the gas phase and in toluene are reported in Table 4.

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Table 4. M06-2X/6-31+G(d,p) energies (a.u.) and relative energies (kcal·mol$^{-1}$; relative to 4 + CO$_2$) in the gas phase and in toluene, and solvation energies (kcal·mol$^{-1}$) for the reaction of 4 with CO$_2$.

3.4.5. Reaction with H$_2$

Since their discovery, FLPs gained great attention for their ability to activate H$_2$. FLP 4 does not react with H$_2$, however, we wished to address this point computationally and consequently we performed preliminary calculations which predicted the reaction of 4 with H$_2$ to be only slightly endothermic by 5.9 kcal·mol$^{-1}$. Nevertheless, in this study we have applied mesityl substituents on phosphorus and tert-butyl substituents on aluminum that by far do not yield the most Lewis basic and acidic sites. Our computational analysis revealed that the reaction of model systems A and B with H$_2$ is predicted to be exothermic by -2.3 and -7.3 kcal·mol$^{-1}$ respectively. Hence, replacing electron withdrawing mesityl substituents on phosphorus with electron donating tert-butyl substituents, enhances the reactivity of the FLP enough to render the H$_2$ uptake energetically favored, as shown in the
case of A. Replacing the tert-butyl substituents on aluminum with electron withdrawing substituents such as phenyl substituents, further increases the reactivity of such geminal P/Al-based Lewis pairs, as illustrated by model system B.

![Diagram of A and B](image)

Consequently, we can conclude that increasing the Lewis acidity of the acceptor site (e.g. with phenyl substituents) and concomitant increase of the basicity of the donor site (e.g. with tert-butyl substituents) will increase the potential of reacting with H$_2$. This should be synthetically feasible, since the concept of hydroaluminating a P-alkyne was designed to be able to tune the Lewis acidity of the acceptor site and the Lewis basicity of the donor site by simply using differently substituted P-alkynes and aluminum hydrides. The computed energies for the reaction of 4 and model systems A and B with H$_2$ are reported in Tables 5-7.

<table>
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Table 5. M06-2X/6-31+G(d,p) energies (a.u.) and relative energy (kcal·mol$^{-1}$) for the reaction of 4 with H$_2$.

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Table 6. M06-2X/6-31+G(d,p) energies (a.u.) and relative energy (kcal·mol$^{-1}$) for the reaction of A with H$_2$.

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<td>B + H$_2$</td>
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Table 7. M06-2X/6-31+G(d,p) energies (a.u.) and relative energy (kcal·mol$^{-1}$) for the reaction of B with H$_2$. 
3.5. Experimental Section

**General.** All manipulations were carried out under argon in dried solvents.

**Synthesis of 1:** n-Butyllithium (1.6 M in n-hexane, 4.4 mL, 7.00 mmol) was added dropwise to a solution of 3,3-dimethyl-1-butyne (0.86 mL, 0.574 g, 7.00 mmol) in diethyl ether (50 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. After cooling to -78 °C, a solution of Mes$_2$PX (Mes = mesityl, 0.6:1.0 mixture of X = Cl and Br)$^{23}$ (2.13 g, 6.4 mmol) in diethyl ether (25 mL) was added slowly. The mixture was stirred at -78 °C for 30 min and for 14 h at room temperature. Water was added and this layer was extracted three times with diethyl ether (25 mL). The combined organic layers were dried over MgSO$_4$, and all volatiles were removed in vacuo.

The remaining solid was thoroughly dried in vacuo and afterwards dissolved in CH$_2$Cl$_2$ (5 mL). The crude product precipitated at -45 °C as a colorless powder, which was then recrystallized from a mixture of n-pentane (5 mL) and diethyl ether (5 mL) at -45 °C to afford 1 as a colorless solid in 78% yield (based on Mes$_2$PX; 1.75 g). Mp. (argon, sealed capillary): 94 °C (dec.).

$^1$H NMR (C$_6$D$_6$, 400 MHz): δ = 6.69 (d, $^3$J$_{HP} = 3.5$ Hz, 4H; m-MesH), 2.54 (s, 12H; o-CH$_3$-Mes), 2.06 (s, 6H; p-CH$_3$-Mes), 1.07 (s, 9H; C(CH$_3$)$_3$). $^{13}$C($^1$H) NMR (C$_6$D$_6$, 100 MHz): δ = 142.2 (d, $^2$J$_{CP} = 15.6$ Hz; o-Mes), 138.1 (s; p-Mes), 131.4 (d, $^1$J$_{CP} = 13.6$ Hz; ipso-Mes), 130.4 (d, $^3$J$_{CP} = 3.5$ Hz; m-Mes), 116.0 (d, $^2$J$_{CP} = 6.8$ Hz; PCEC), 76.8 (d, $^3$J$_{CP} = 3.8$ Hz; PCEC), 30.3 (s; C(CH$_3$)$_3$), 29.1 (s; C(CH$_3$)$_3$), 23.3 (d, $^3$J$_{CP} = 14.9$ Hz; o-CH$_3$-Mes), 20.9 (s; p-CH$_3$-Mes). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 162 MHz): δ = -55.6. MS (EI, 20 eV, 298 K): 350 (55%, M$^+$), 335 (46%, M$^+$ - CH$_3$).

**Synthesis of 2:** n-Butyllithium (1.6 M in n-hexane, 5.7 mL, 9.12 mmol) was added dropwise to a solution of phenylacetylene (1.00 mL, 0.93 g, 9.12 mmol) in diethyl ether (50 mL) at -78 °C. The mixture was stirred for 1 h at this temperature, and was subsequently allowed to warm to room temperature and stirred for an additional hour. After cooling of the suspension to -78 °C, a solution of Mes$_2$PX (Mes = mesityl, 0.6:1.0 mixture of X = Cl and Br)$^{11}$ (3.03 g, 9.12 mmol) in diethyl ether (20 mL) was added slowly. The mixture was stirred at -78 °C for 1 h and for 14 h at room temperature. Water was added and this layer was extracted three times with diethyl ether (20 mL). The combined organic layers were dried over MgSO$_4$, and all volatiles were removed in vacuo. The remaining solid was thoroughly dried in vacuo and afterwards dissolved in CH$_2$Cl$_2$ (5 mL). The product (2) precipitated at -45 °C as a colorless powder, which was isolated in 49% yield (1.66 g). Mp. (argon, sealed capillary): 119 °C (dec.). $^1$H NMR (C$_6$D$_6$, 400 MHz): δ =
Synthesis of 3: Np₂AlH (0.115 g, 0.68 mmol) was dissolved in n-hexane (10 mL) and added to a solution of Mes₂PĊCCCCBu (0.231 g, 0.66 mmol) in n-hexane (10 mL) at room temperature. The mixture was stirred for 38 h after which all volatiles were removed in vacuo. The residue was dissolved in 1,2-difluorobenzene and upon cooling to -45 °C 3 was obtained as a crystalline yellow solid in 45% yield (0.156 g). Mp. (argon, sealed capillary): 91 °C. ¹H NMR (Ç₆D₆, 400 MHz): δ = 6.70 (4H, m-MesH), 6.48 (4H, o-MesH), 2.53 (s, 12H; o-CH₂-Mes), 1.82 (s, 12H; o-CH₂-Mes). ¹³C{¹H} NMR (Ç₆D₆, 100 MHz): δ = 142.3 (d, JCP = 15.5 Hz; o-Mes), 138.4 (s; p-Mes), 131.4 (d, JCP = 1.9 Hz; o-Ph), 130.5 (d, JCP = 3.6 Hz; m-Mes), 130.5 (d, JCP = 12.5 Hz; ipso-Mes), 128.5 (s; m-Ph), 128.3 (s; p-Ph), 124.2 (d, JCP = 1.0 Hz; ipso-Ph), 107.4 (d, JCP = 8.4 Hz; PĊCCCC), 88.8 (d, JCP = 7.7 Hz; PĊCCCC), 23.3 (d, JCP = 14.5 Hz; o-CH₃-Mes), 20.9 (s; p-CH₂-Mes). ³¹P{¹H} NMR (Ç₆D₆, 162 MHz): δ = -55.7. Analysis: Calc. C 84.4, H 7.3; found C 83.7, H 7.3.

Synthesis of 4: TBuAlH (0.146 g, 1.03 mmol) was dissolved in toluene (10 mL) and added to a solution of Mes₂PĊCCCCPh (0.380 g, 1.03 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 6 h after which all volatiles were removed in vacuo. The residue was dissolved in toluene and upon cooling to -25 °C 4 was obtained as a yellow crystalline solid in 77% yield (0.409 g). Mp. (argon, sealed capillary): 153 °C. ¹H NMR (Ç₆D₆, 400 MHz): δ = 7.37 (4H, o-MesH), 6.93 (pseudo-t, 2H; o-PhH), 6.88 (pseudo-t, 1H; p-PhH), 6.78 (4H, m-MesH), 2.51 (s, 12H; o-CH₂-Mes), 2.10 (s, 6H; p-CH₂-Mes), 0.96 (s, 18H; AlC(CH₃)₃). ¹³C{¹H} NMR (Ç₆D₆, 100 MHz): δ = 157.5 (d, JCP = 58.1 Hz; PC=CH), 148.4 (d, JCP = 13.3 Hz; ipso-Ph), 144.0 (PC=CH), 143.6 (d, JCP = 14.4 Hz; o-Mes), 134.4 (s; p-Mes), 132.2 (s; m-Ph), 131.3 (d, JCP = 22.3 Hz; ipso-Mes), 130.3 (d, JCP = 3.1 Hz; m-Mes), 127.9 (s; p-Ph), 122.4 (d, JCP = 2.4 Hz; o-Ph), 30.0 (d, JCP = 2.3 Hz; AlC(CH₃)₃), 24.0 (d, JCP = 13.2 Hz; o-CH₃-Mes), 20.9 (s; p-CH₂-Mes), 19.4 (s; AlC(CH₃)₃). ³¹P{¹H} NMR (Ç₆D₆, 162 MHz):
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**Reaction of 4 with phenylacetylene, synthesis of 5a and 6a:** Phenylacetylene (0.06 mL, 0.50 mmol) was added to a solution of 4 (0.255 g, 0.50 mmol) in toluene (8 mL) at room temperature, which resulted in a 3:1 ratio of 5a:6a from which the NMR data of 5a could be obtained. \(^1\)H NMR \((C_6D_6, 400 MHz)\): \(\delta = 9.75 \text{ (d, } \int_{HP} = 503.5 \text{ Hz, 1H; P} C=CH), 7.95 \text{ (d, 2H; o-PhH), 7.33 \text{ (m, 3H, PhH) 6.50 \text{ (s, 4H; } m-\text{MesH}), 2.28 \text{ (s, 12H; o-C}_3\text{H}_3\text{-Mes), 2.11 \text{ (s, 6H; p-C}_3\text{H}_3\text{-Mes), 1.50 \text{ (s, 18H; AlC(C}_3\text{H}_3)_3).} \)

**Reaction of 4 with phenylacetylene, synthesis of 6a:** Phenylacetylene (0.055 mL, 0.051 g, 0.497 mmol) was added to a warm (50 °C) solution of 4 (0.255 g, 0.497 mmol) in toluene (8 mL), which resulted in a 1:1 mixture of 5a and 6a. The solution was heated to 70 °C for 1 h after which all volatiles were removed in vacuo. The residue was dissolved in n-hexane. Crystallization at room temperature afforded 6a as yellow crystals in 91% yield (0.28 g). Mp. (argon, sealed capillary): 196 °C. \(^1\)H NMR \((C_6D_6, 400 MHz)\): \(\delta = 9.52 \text{ (d, } \int_{HP} = 60.1 \text{ Hz, 1H; P} C=CH), 7.60 \text{ (d, } \int_{HP} = 38.4 \text{ Hz, 1H; C=CH-Al}), 7.41 \text{ (pseudo-d, 2H; C=C[}o\text{Ph}), 7.22 \text{ (pseudo-t, 2H; C=C[}o\text{Ph}), 7.09 \text{ (pseudo-t, 2H; C=C[}o\text{Ph}), 6.88 \text{ (pseudo-t, 1H; C=C[}o\text{Ph}), 6.57 \text{ (d, } \int_{HP} = 3.5 \text{ Hz, 4H; } m\text{-MesH}), 2.26 \text{ (s, 12H; o-C}_3\text{H}_3\text{-Mes), 1.91 \text{ (s, 6H; p-C}_3\text{H}_3\text{-Mes), 1.18 \text{ (s, 18H; AlC(C}_3\text{H}_3)_3).} \)

\(^{31}\)P\(^{1}\)H NMR \((C_6D_6, 162 MHz)\): \(\delta = -5.1. \)

**Reaction of 4 with tert-butylacetylene, synthesis of 5b:** A suspension of 4 (0.247 g, 0.48 mmol) and tert-butylacetylene (4.0 mL, 32.5 mmol) was heated at 40 °C under reflux for two hours. Toluene was added to the suspension at room temperature until a clear solution was obtained. Cooling to +5 °C afforded 5b as yellow, X-ray diffraction suitable crystals in 92% yield (0.264 g). Mp. (argon, sealed capillary): 128 °C. \(^1\)H NMR

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\[ \delta = -14.2. \text{ MS (EI, 20 eV, 365 K): 557 (100\%, M^+)}. \text{ Analysis: Calc. C 82.1, H 8.5; found C 81.9, H 8.8.} \]

**Reaction of 4 with tert-butylacetylene, synthesis of 5b:** A suspension of 4 (0.247 g, 0.48 mmol) and tert-butylacetylene (4.0 mL, 32.5 mmol) was heated at 40 °C under reflux for two hours. Toluene was added to the suspension at room temperature until a clear solution was obtained. Cooling to +5 °C afforded 5b as yellow, X-ray diffraction suitable crystals in 92% yield (0.264 g). Mp. (argon, sealed capillary): 128 °C. \(^1\)H NMR
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(200 MHz, 298 K, C6D6): δ = 9.85 (d, 3Jipso = 507.5 Hz, 1H; Ph), 7.94 (d, 3Jipso = 50.6 Hz, 1H; PC=CH), 7.64 (m, 2H; o-PhH), 7.18 (m, 2H; m-PhH), 7.06 (m, 1H; p-PhH), 6.55 (d, 3Jipso = 3.2 Hz, 4H; m-MesH), 2.34 (s, 12H; o-CH3-Mes), 1.93 (s, 6H; p-CH3-Mes), 1.44 (s, 18H; AlC(CH3)3), 1.27 (s, 9H; AlC2CC(CH3)3). 13C NMR (101 MHz, 298 K, C6D6): δ = 162.6 (d, 3JCP = 4.2 Hz; PC=CH), 143.9 (d, 3JCP = 8.7 Hz; o-Mes), 143.4 (d, 3JCP = 2.5 Hz; p-Mes), 141.0 (d, 3JCP = 38.1 Hz; ipso-Ph), 140.0 (d, 3JCP = 27.1 Hz; PC=CH), 131.3 (d, 3JCP = 9.8 Hz; m-Mes), 129.9 (s; p-Ph), 129.2 (d, 3JCP = 1.3 Hz; o-Ph), 128.9 (s; m-Ph), 119.5 (s; AlC2CC(CH3)3), 118.2 (d, 3JCP = 70.0 Hz; ipso-Mes), 100.6 (s; AlC2CC(CH3)3), 33.5 (s; AlC(CH3)3), 32.3 (s; AlC2CC(CH3)3), 28.7 (s; AlC2CC(CH3)3), 25.1 (s; o-CH3-Mes), 21.0 (s; p-CH3-Mes), 17.0 (s; AlC(CH3)3). 31P(1H) NMR (162 MHz, 298 K, C6D6): δ = -5.2. MS (EI, 20 eV, 395 K): 512 (2%, M+ - BuC=C), IR (cm⁻¹, Paraffin, CsI-plates): 3298 vw, 3159 w, 2965 - 2814 vs (Paraffin), 2745 s, 2727 s, 2716 s, 2679 s, 2629 m, 2452 w, 2398 vw, 2156 vw, 2102 w, 1948 vw, 1701 vw, 1605 m, 1555 vw, 1443 vs (Paraffin), 1414 vw, 1375 vs (Paraffin), 1292 m, 1271 vw, 1246 m, 1202 w, 1165 w, 1155 w, 1067 w, 1030 w, 978 w, 943 vw, 930 w, 881 w, 849 m, 841 w, 810 m, 797 w, 727 vs (Paraffin), 694 m, 669 vw, 644 m, 617 vw, 592 w, 569 w, 542 vw, 523 w, 513 vw, 494 w, 475 vw, 465 w, 447 w, 428 vw, 401 s. Analysis: Calc. C 80.8, H 9.5; found C 80.8, H 9.0.

Reaction of 4 with CO2 synthesis of 7: CO2 was bubbled for 30 sec through a solution of 4 (0.802 g, 1.56 mmol) in toluene (10 mL) at room temperature. All volatiles were removed in vacuo and the residue was dissolved in n-hexane. Crystallization at room temperature afforded 7 as yellow crystals in 74% yield (0.639 g). Mp. (argon, sealed capillary): 182 °C. 1H NMR (C6D6, 400 MHz): δ = 7.78 (d, 3Jipso = 40.1 Hz, 1H; PC=CH), 7.48 (pseudo-d, 2H; o-PhH), 7.14 (pseudo-t, 2H; m-PhH), 7.05 (pseudo-t, 1H; p-PhH), 6.54 (m, 4H; m-Mes), 2.34 (s, 12H; o-CH3-Mes), 1.89 (s, 6H; p-CH3-Mes), 1.26 (s, 18H; AlC(CH3)3). 13C(1H) NMR (C6D6, 100 MHz): δ = 165.1 (d, 3JCP = 106.5 Hz; CO2), 160.3 (d, 3JCP = 4.8 Hz; PC=CH), 144.2 (d, 3JCP = 8.9 Hz; o-Mes), 143.4 (d, 3JCP = 2.9 Hz; p-Mes), 141.0 (d, 3JCP = 14.9 Hz; PC=CH), 140.7 (d, 3JCP = 32.2 Hz; ipso-Ph), 132.3 (d, 3JCP = 10.7 Hz; m-Mes), 130.5 (s; p-Ph), 129.3 (s; m-Ph), 128.4 (o-Ph), 118.9 (d, 3JCP = 61.2 Hz; ipso-Mes), 31.9 (s; AlC(CH3)3), 25.1 (d, 3JCP = 4.6 Hz; o-CH3-Mes), 20.8 (s; p-CH3-Mes), 16.7 (s; AlC(CH3)3). 31P(1H) NMR (C6D6, 162 MHz): δ = 5.6. MS (EI, 20 eV, 395 K): 512 (1%, M+ - CO2). Analysis: Calc. C 75.5, H 8.3; found C 75.3, H 8.6.

Regeneration of 4 from 7: Finely dispersed 7 (25 mg, 0.045 mmol) was placed in a NMR-tube and heated at 135 °C under vacuum (1 x 10⁻³ mbar) for about 60 seconds. The
NMR tube was shaken and heated again at 135 °C for about 60 seconds, which afforded FLP 4 in 98% yield (23 mg, 0.044 mmol).
3.6. References


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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 ww.ccdc.cam.ac.uk/data_request/cif. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.

[16] E-4 is more stable than Z-4 by 7.9 kcal/mol at M06-2X/6-31+G(d,p).


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[20] We believe that in fact, structures 7-vdW and TS7 are not true stationary points but that they result from computing geometry optimizations on a non ZPE corrected PES. Consequently, the CO2 uptake should be simply regarded as barrierless. See Computational Section, par. 3.4.4. for additional details.

[21] As observed also for the dimeric P/Al-based Lewis pair described in Chapter 4 of this thesis.

