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Hydride Activation

A Phosphorus/Aluminum-Based Frustrated Lewis Pair as an Ion Pair Receptor: Alkali Metal Hydride Adducts and Phase-Transfer Catalysis[**]

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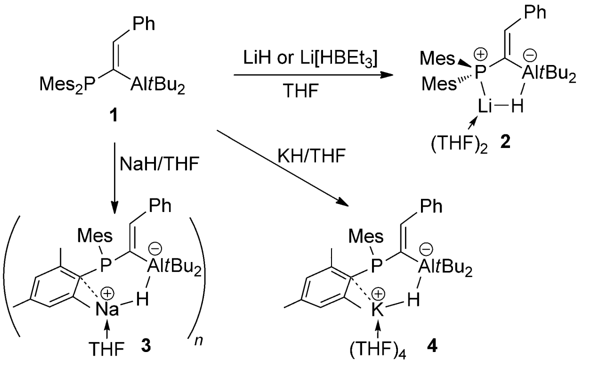
Frustrated Lewis pairs (FLPs) based on main-group elements have been the subject of enormous interest in recent years owing to their metal-free dipolar activation of a multitude of small molecules.[1] Yet, despite all of this progress, the development of catalytic transformations based on FLPs is still in its infancy. So far, only borane-based FLPs bearing electron-withdrawing pentafluorophenyl substituents enable the catalytic hydrogenation of unsaturated substrates.[2] The most notable application for FLPs is in the catalytic tandem hydride transfer/deoxygenative hydrosilylation of carbon dioxide to methane.[3] In this reaction, the second reduction step depends on Lewis acid-catalyzed activation of silanes by $B(C_6F_5)_3$ and a consecutive silyl transfer to the Lewis basic carbonyl oxygen.[4]

The discovery of FLP catalysis with covalent H−H and Si−H[5] bonds inspired us to explore catalysis with ionic hydrides, as these have not yet been used in conjunction with FLPs, to the best of our knowledge. Herein, we wish to report on the propensity of FLPs to solubilize[6] and activate[7] the alkali metal hydrides (LiH, NaH, KH).[8,9] These species are important reducing agents, but with limited applicability owing to their relatively high lattice energies,[10] poor solubility in organic solvents, and the poor purity of commercially available material.[11] To this end, we selected our recently reported, promising, and readily accessible geminal P/Al-based FLP **1** (Scheme 1), which does not require fluorinated substituents to enhance the Lewis acidity of the acceptor site.[12]



Scheme 1. Synthesis of molecular alkali metal hydrides **2**–**4**. Mes = 2,4,6-$Me_3C_6H_2$.

Treatment of FLP **1** with solid lithium hydride and THF (2 equiv) in toluene at room temperature for 15 h afforded, after workup and crystallization, LiH adduct **2** (40 % yield, $\delta^{31}P = -7.9$ ppm; Scheme 1). A direct interaction of the lithium cation with the donor site of FLP **1** is indicated by the large $^1J(Li,P)$ coupling constant of 39.8 Hz[13] ($\delta^7Li = -0.3$ ppm, $^1J(Li,H) = 14.8$ Hz). The hydride resides on the acceptor site, as can be deduced from the broad resonance at $\delta^1H = 2.91$ ppm.[14] The molecular structure of **2**, obtained by a single-crystal X-ray structure determination (Figure 1, top left),[15] shows a Li-H-Al three-center two-electron bond (Li1–H1 191(2), Al1–H1 164(2) pm) with the Li atom connected to the phosphorus atom (Li1–P1 271.1(3) pm)[13,16] and two molecules of THF. This compound is the first structurally characterized monomeric lithium hydride complex.[17] Interestingly, **2** is also obtained in 92 % yield upon treatment of **1** with super hydride $Li[HBEt_3]$, by displacement of triethylborane.

NaH and KH also reacted with FLP **1** at room temperature, but required longer reaction times to break up the solid metal hydride material to afford soluble adducts **3** (7 days, 40 % yield) and **4** (2 days, 45 % yield; Scheme 1). Both **3** ($\delta^{31}P = 0.9$ ppm) and **4** ($\delta^{31}P = 1.0$ ppm) display very broad resonances in the ^{31}P NMR spectrum, indicating a dynamic interaction of the alkali metal cations with the P atom. Single-crystal X-ray analysis unequivocally established that the bonding of **2** differs from that of both **3** and **4**. In contrast to **2**, the softer Lewis acidic alkali metals Na and K display no interactions with the phosphorus atom in the solid state (**3**: Na1–P1 359.8, **4**: K1–P1 378.2 pm; Figure 1),[15,18] but instead have short contacts with the P–mesityl ring (**3**: Na1–C61 281.3(2), **4**: K1–C71 329.2(3) pm).[19] The coordination sphere of the potassium ion in **4** is completed with four THF molecules, whereas only one THF molecule coordinates to the sodium atom in **3**, creating a one-dimensional chain that is held together by additional contacts between the Na cation and the phenyl-ring of a neighboring molecule (Na1–C35 277.2(2), Na1–C36 302.2(2) pm; Figure 1).

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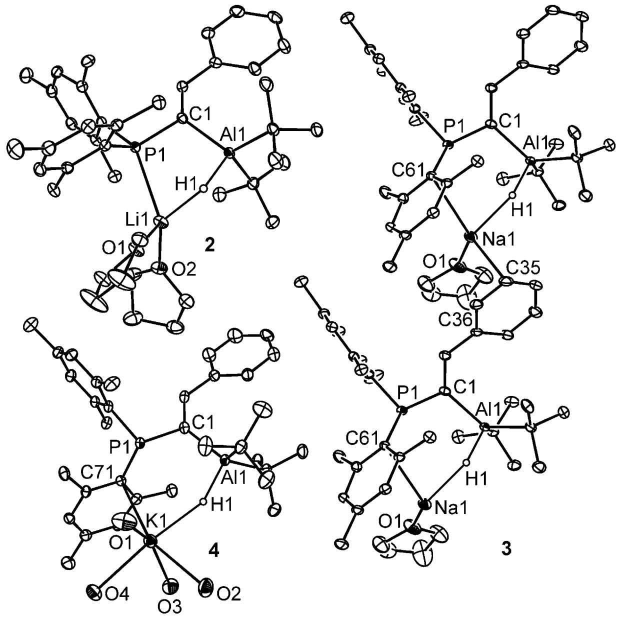
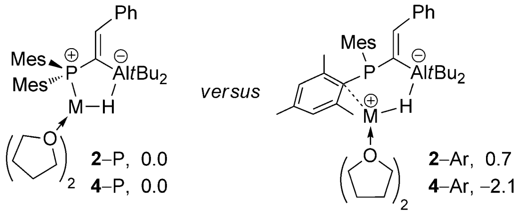


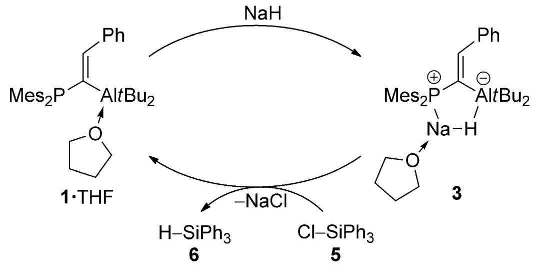
Figure 1. Molecular structures of **2** and **4**, and polymeric structure of **3** (two units shown). Ellipsoids set at 30% probability; hydrogen atoms (except H1), and CH_2 groups of the THF molecules of **4** are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **2**: P1–C1 184.2(2), C1–Al1 205.7(2), Al1–H1 164(2), H1–Li1 191(2), Li1–P1 271.1(3); P1-C1-Al1 109.7(8), Al1-H1-Li1 128.5. **3**: P1–C1 183.1(2), C1–Al1 205.1(2), Al1–H1 154(2), H1–Na1 220(2), Na1–C61 281.3(2), Na1–C35 277.2(2), Na1–C36 302.2(2), C61–P1 185.4(2); P1-C1-Al1 109.36(9), Al1-H1-Na1 155.7. **4**: P1–C1 184.9(3), C1–Al1 206.8(3), Al1–H1 174(5), H1–K1 257(5), K1–C71 329.2(3); P1-C1-Al1 109.2(1), Al1-H1-K1 146.8.

To provide insight into the stability of the different coordination modes, we optimized the geometries of monomers **2** and **4** with two molecules of THF at the M06-2X/6-31G(d) level of theory (**2**,**4**–P vs. **2**,**4**–Ar; Scheme 2).[20] In accord with the molecular structures, **2**–P, which has a lithium–phosphorus interaction, was found to be more stable than **2**–Ar ($\Delta E = 0.7$ kcal mol^{-1}); whereas the bigger potassium ion favors coordination to the arene ring (**4**–Ar, $\Delta E = -2.1$ kcal mol^{-1}).[19]



Scheme 2. Relative M06-2X/6-31G(d) energies (in kcal mol^{-1}) for the two different coordination modes (M–P vs. M–Ar) of **2**,**4**·2THF.

So far, we have demonstrated that FLP **1** can solubilize metal hydrides (LiH, NaH, KH), but do the resulting molecular hydrides also display enhanced reactivity? To address this question, we selected the least solvated alkali metal hydride adduct **3** and studied its ability to convert chlorotriphenylsilane (**5**) to triphenylsilane (**6**).[21] Treatment of **3** with chlorosilane **5** (1 equiv) in THF at room temperature for 48 h quantitatively afforded silane **6** together with precipitated sodium chloride and the THF adduct of FLP **1** (**1**·THF; Scheme 3). For comparison, sodium hydride alone proved to be unreactive under the same reaction conditions. The fact that **1** was regenerated, suggested the feasibility of catalytically converting chlorosilane **5**. Indeed, treating a suspension of **5** with commercially available NaH (1.5 equiv) in THF using **1** (10 mol%) under reflux conditions for 48 h resulted in full conversion according to ^{1}H NMR spectroscopy, affording **6** in 76% yield after a vacuum distillation workup (Scheme 3). As expected, the same reaction without the FLP phase-transfer catalyst proved to be much less effective[22] and even the use of Al*t*Bu$_3$ as a Lewis acid (29 mol%) only resulted in a 30% conversion of **5** to **6** under similar conditions, which underscores the cooperative action[23,24] of the donor and acceptor sites of FLP **1** in the reaction.



Scheme 3. Phase-transfer catalysis with FLP **1** by NaH adduct **3**.

To gain insight into the underlying mechanism of the catalytic transformation, we resorted to M06-2X/6-31G(d) calculations[20] on model structures where the phenyl substituent and all the Me groups of **1**·THF were replaced by H atoms (model species labeled with ′). We found the substitution reaction to be exothermic by 24.5 kcal mol^{-1} (Figure 2). First, after break-up of the polymer chain, monomer **3′** and chlorosilane **5** form reactant complex **7′** ($\Delta E = -18.2$ kcal mol^{-1}), which undergoes a frontside nucleophilic substitution at silicon (S$_N$2-f@Si)[25] affording product complex **8′** ($\Delta\Delta E^{\pm} = 17.7$, $\Delta\Delta E = -0.9$ kcal mol^{-1}). In the pentacoordinate transition species (**TS7′**–**8′**) the hydride attacks the silicon center at an angle of 77.6° (H1-Si1-Cl1) to the leaving chloride, in contrast to the 180° common for backside S$_N$2 substitutions. Subsequently, **8′** rearranges to the more stable **9′** ($\Delta\Delta E = -23.2$ kcal mol^{-1}; Figure 2),[26] which is a van der Waals complex of **10′** (the NaCl adduct of **1′**) and triphenylsilane **6**. Finally, dissociation of **6** ($\Delta\Delta E = 18.0$, $\Delta E = -24.5$ kcal mol^{-1}) and precipitation of NaCl generates FLP **1′**, which then reenters the catalytic cycle. This FLP-mediated nucleophilic substitution at silicon proceeds with retention of configuration[25] and holds promise for the development of S$_N$2-f@Si reactions for silicon-stereogenic silanes with conservation of stereochemistry.

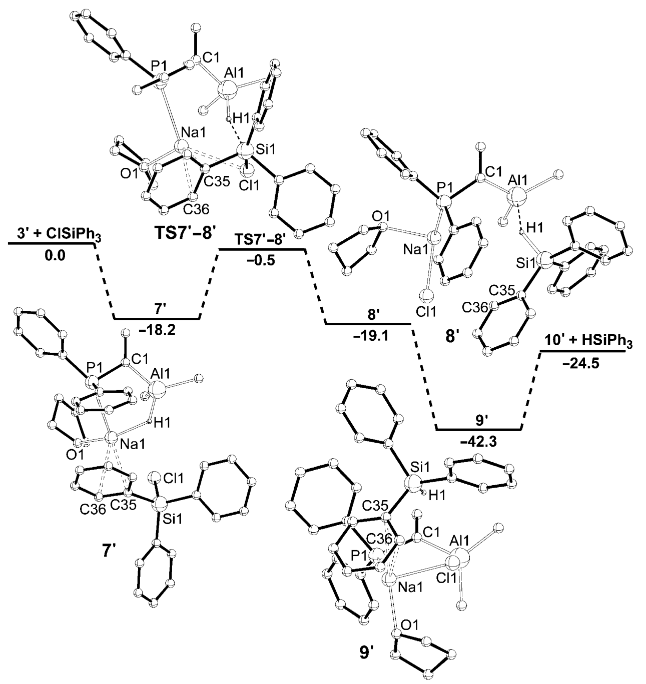


Figure 2. Relative M06-2X/6-31G(d) energies (zero-point energy corrected, in kcal mol^{-1}) for the conversion of **3′** and ClSiPh$_3$ into **10′** and HSiPh$_3$ via reactant complex **7′** and product complexes **8′** and **9′**. Hydrogen atoms (except H1) are omitted for clarity. Selected average bond lengths [pm] and angles [°] for **7′**: Al1–H1 167.0, H1–Na1 212.9, Na1–P1 303.4, Na1–C35 285.3, Na1–C36 284.1, Si1–Cl1 210.9. **TS7′-8′**: Al1–H1 180.0, H1–Si1 175.6, Si1–Cl1 228.4, Na1–P1 299.3, Na1–Cl1 293.0, Na1–C35 266.7, Na1–C36 274.9; H1-Si1-Cl1 77.6. **8′**: Al1–H1 194.4, H1–Si1 152.3, Na1–P1 184.8, Na1–Cl1 247.7. **9′**: Al1–Cl1 231.2, Cl1–Na1 262.2, Na1–P1 285.8, Na1–C35 285.6, Na1–C36 284.7, Si1–H1 148.3.

In summary, FLP **1** is an effective ion pair receptor for converting alkali metal hydrides (LiH, NaH, KH) into soluble, molecular hydrides with enhanced reactivity. We demonstrated their potential as FLP catalysts in the catalytic transformation of chlorotriphenylsilane into the corresponding hydride, which proceeds by a frontside S_N2-f@Si pathway.

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[26] **TS8′ – 9′** could not be found, presumably due to the flat potential energy surface in the region of the transition state.

Hydride Activation

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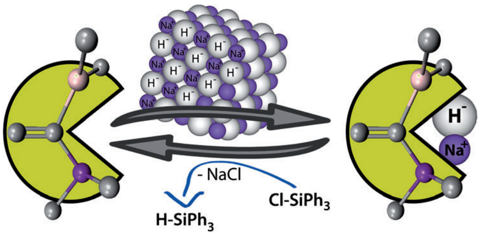
A Phosphorus/Aluminum-Based Frustrated Lewis Pair as an Ion Pair Receptor: Alkali Metal Hydride Adducts and Phase-Transfer Catalysis



Helpful frustration: The geminal phosphorus/aluminum-based frustrated Lewis pair $(Mes_2P)(tBu_2Al)C{=}C(H)Ph$ ($Mes = 2,4,6\text{-}Me_3C_6H_2$) forms stable adducts with alkali metal hydrides (LiH, NaH, KH). These molecular hydride complexes display enhanced reactivity, which was demonstrated by the catalytic transformation of chlorotriphenylsilane to the corresponding hydride through a frontside S_N2-f@Si pathway.