DOI: 10.1002/anie.201203362

Frustrated Lewis Pairs

H_2 Activation and Hydride Transfer to Olefins by $Al(C_6F_5)_3$-Based Frustrated Lewis Pairs**

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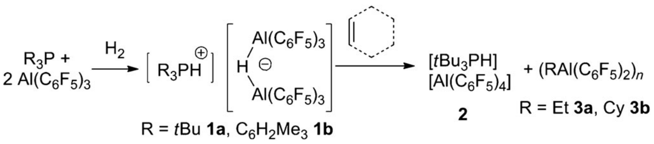
The homogeneous reduction of olefins has been deemed to be the purview of transition metal catalysis since the seminal work of Wilkinson on Rh[1] and Ru[2] species, some 50 years ago. Since then, numerous advances have resulted in the evolution of such metal-based technologies to include Nobel prize-winning work on asymmetric hydrogenations.[3] More recent developments have produced Ru-based olefin-specific reduction catalysts,[4] as well as remarkably active hydrogenation catalysts based on Fe[5] and Co.[6] An alternative strategy that is garnering attention is based on non-transition-metal systems. As far back as the 1970s, it was reported that strong Brønsted acids, such as $HBr{\cdot}AlBr_3$, could mediate the reduction of some aromatics to alkanes; however, changes to the C–C framework of the arenes were often observed.[7] More recently, main group systems, such as cyclic (alkyl)(amino)carbenes[8] or heavier group 14 alkene analogues[9] have been shown by the research groups of Bertrand and Power to effect H_2 activation. In very recent work, the research groups of Harder[10] and Okuda[11] have developed Ca-based species capable of reducing the activated olefin, 1,1-diphenylethene. Our own efforts have involved exploring frustrated Lewis pairs (FLPs), the combination of main group Lewis acids and bases that are sterically inhibited from forming classical adducts. Such systems have been shown to activate small molecules[12] and, in particular, H_2.[13] The latter finding has led to the development of boron-based hydrogenation catalysts for the reduction of polar unsaturated bonds, such as imines,[14] nitriles,[14a,b] aziridines,[14a,b] enamines,[14c] and silylenolethers.[15] Most recently, we have demonstrated the ability of FLPs to effect the stoichiometric reductions of anilines to cyclohexylammonium derivatives.[16] Nonetheless, the delivery of H_2 to simple, unactivated olefins by any main group system has not been reported. In targeting FLP systems that could effect such reductions, we[17] and others[18] have begun to explore the use of aluminum-based FLPs. Herein, we present an aluminum-based FLP system capable of activating H_2 that reacts stoichiometrically with the unactivated olefins ethylene and cyclohexene, to give alkylalanes. A plausible mechanism is considered and is thought to involve aluminum-activation of the olefin. This view is supported by the characterization of the first simple intermolecular aluminum-olefin adduct. The implications for the future development of an aluminum-based FLP hydrogenation catalyst for unactivated olefins is considered.

Combining tBu_3P and $Al(C_6F_5)_3{\cdot}$toluene in a 1:2 ratio in fluorobenzene under 4 atm of H_2 at 25 °C resulted in product **1a**, which was isolated in 88 % yield. The ^1H NMR spectrum of **1a** showed a broad signal at 4.30 ppm and doublets at 4.09 and 0.94 ppm. The corresponding $^{31}P\{^1H\}$ NMR resonance was seen at 60.0 ppm, but the ^{27}Al NMR spectrum showed no discernible resonance. The $^{19}F\{^1H\}$ NMR spectrum showed signals at −120.5, −153.1 and −161.8 ppm. These data, together with elemental analysis, were consistent with the formulation of **1a** as $[tBu_3PH][(\mu\text{-}H)\{Al(C_6F_5)_3\}_2]$ (Scheme 1).



Scheme 1. Synthesis of **1**–**3**.

In an analogous fashion, the species $[(C_6H_2Me_3)_3PH][(\mu\text{-}H)\{Al(C_6F_5)_3\}_2]$ (**1b**) was prepared. This was subsequently confirmed by X-ray crystallography (Figure 1).[19] While the metric parameters of the cation are unexceptional, a single H atom bridges the two pseudo-tetrahedral Al centers with Al–H distances of 1.818 Å and an Al-H-Al angle of 138.0°. The formation of this bridging hydride anion stands in contrast to the analogous borane chemistry,[13a] although the anionic fragment of **1a** is reminiscent of the anion

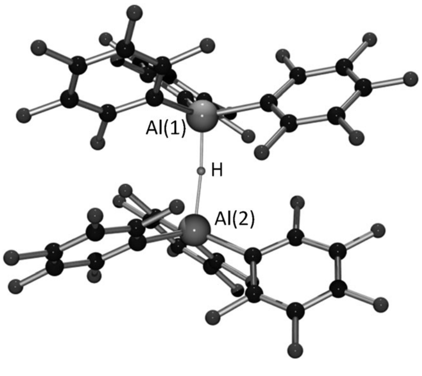


Figure 1. POV-Ray depiction of the anion of **1a**.

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[**] D.W.S. gratefully acknowledges the financial support of the NSERC of Canada and the award of a Canada Research Chair. G.M. is grateful for the support of NSERC and Walter C. Sumner Fellowships.

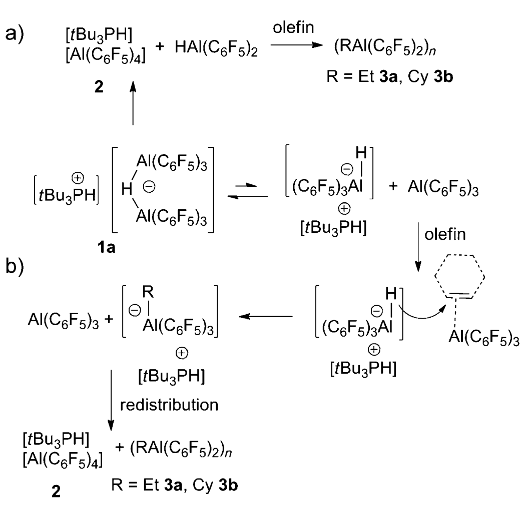
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203362.

$[(\mu\text{-Me})\{Al(C_6F_5)_3\}_2]^-$, previously reported by Chen and Abboud[20] and the hydride-bridged species $[Me_2Si(Indenyl)_2Zr(\mu\text{-H})(AlR_2H)_2]$,[21] $[\{(C_3HR_2N_2)Al\textit{i}Bu_2\}_2(\mu\text{-H})]$,[22] and $[\{(C_3HMe_2N_2)Al\textit{t}Bu_2\}_2(\mu\text{-H})]$.[23] This is consistent with our previous results, which demonstrated that using a 1:2 ratio of phosphine/alane was optimal for small-molecule activation.[17a,b,d] Similar to the salt $[tBu_3PH][HB(C_6F_5)_3]$, salt **1a** shows no evidence of H_2 loss when heated under vacuum. Nonetheless, all efforts to prepare the related 1:1 species $[tBu_3PH][HAl(C_6F_5)_3]$ resulted only in reduced yields of the isolated 1:2 species, **1a**. This observation is consistent with both the presumed nucleophilicity of the anion, $[HAl(C_6F_5)_3]^-$, and the Lewis acidity of $Al(C_6F_5)_3$.

Exposure of **1a** to an atmosphere of ethylene at 60 °C for 2 h results in the consumption of **1a** and the formation of two products, **2** and **3a**.[19] Compound **2** was easily identified as the previously reported salt $[tBu_3PH][Al(C_6F_5)_4]$, based on its spectroscopic signature.[17d] Compound **3a** gave a triplet and a broad quartet at 1.15 and 0.57 ppm, respectively, in the ^1H NMR spectrum, inferring the presence of an ethyl fragment. The ^{19}F NMR signals were found to be at −120.5, −150.9, and −160.2 ppm, similar to those previously reported for alkylalanes of the general formula $RAl(C_6F_5)_2$.[24] In this report, compound **3a** was independently generated by the redistribution reaction of $AlEt_3$ and $B(C_6F_5)_3$ in a 3:2 ratio.[24] The corresponding reaction of **1a** with cyclohexene generates **2** and the cyclohexylalane derivative **3b**. By analogy to the previously reported alane $[MeAl(C_6F_5)_2]_2$,[24] the compounds **3** are thought to be dimers of the form $[RAl(C_6F_5)_2]_2$ (Scheme 1), although this was not unambiguously confirmed.

Several possibilities arise in considering the mechanism of the reaction of **1** with olefins. One pathway (Scheme 2a) could involve the redistribution of **1** to generate **2** and $HAl(C_6F_5)_2$. Subsequent reaction of the latter alane with an olefin would afford **3**. However, variable temperature NMR studies on a salt of the anion of **1** (compound **7**, see below) at 25–120 °C in C_6D_5Br did not show any appreciable changes in the ^{19}F NMR spectra, suggesting that redistribution to generate $HAl(C_6F_5)_2$ is unlikely.

A possible alternative mechanism (Scheme 2b) involves olefin interception by $Al(C_6F_5)_3$ from **1a**. The olefin–$Al(C_6F_5)_3$ would then be significantly activated and susceptible to attack by the anion $[HAl(C_6F_5)_3]^-$, leading to the formation of the alkylaluminate anion, $[RAl(C_6F_5)_3]^-$, and free $Al(C_6F_5)_3$. A subsequent redistribution reaction affords **2** and **3**. This possibility is supported by the reaction of **1a** with Lewis bases, such as Et_2O or PMe_3, which results in the rapid loss of H_2 and the formation of the Lewis base adducts $L\cdot Al(C_6F_5)_3$ ($L = Et_2O$, PMe_3). In this case, the donor acts to sequester $Al(C_6F_5)_3$ from **1a**, generating the salt $[tBu_3PH][HAl(C_6F_5)_3]$, which is unstable with respect to H_2 loss in the absence of other electrophiles.



Scheme 2. Possible mechanisms of the reaction of **1** with olefins.

Support for the notion of an olefin–$Al(C_6F_5)_3$ interaction was obtained from the following reaction: cooling a solution of $Al(C_6F_5)_3\cdot$toluene in neat cyclohexene produced crystals of complex **4**, which were isolated in 85 % yield. While elemental analysis confirmed the formulation of the crystals to be $[Al(C_6F_5)_3\cdot(C_6H_{10})]$, the strength of the aluminum–olefin interaction appears to be rather weak, as ^1H NMR analysis of a solution of **4** in bromobenzene showed the signature of free cyclohexene. Nonetheless, crystallographic analysis of **4** showed that the aluminum center is pseudo tetrahedral with an η^2 coordination of the olefinic unit to the aluminum center (Figure 2).[19] The Al–C_{olefin} distances were found to be 2.471(2) and 2.540(2) Å, while the C=C bond is 1.340(3) Å.

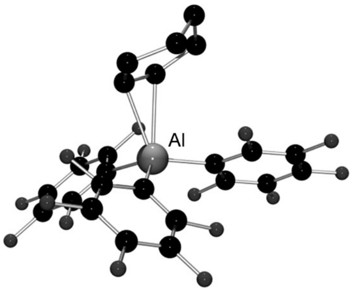


Figure 2. POV-Ray depiction of **4**. H atoms are omitted for clarity.

We[17d] and others[25] have previously described NMR spectroscopic evidence supporting the interaction of pendant olefins to Lewis acidic aluminum[17d,25] or boron[26] centers, and Schnökel and co-workers have reported the tetrametallic dimer derived from 1,4-dialumina-2,5-cyclohexadiene, which has Al–C_{olefin} distances of 2.355 Å.[27] Compound **4** is, to the best of our knowledge, the first crystallographically characterized species derived from the interaction of a simple free olefin with Al.

To probe the transient role of the mono-Al hydride species $[HAl(C_6F_5)_3]^-$, the known salt $K[HAl(C_6F_5)_3]$[28] was prepared; however, its solubility in bromobenzene proved extremely poor and consequently the attempted cation exchange was very sluggish. An alternative synthetic approach involved the initial preparation of $[Et_4N][ClAl(C_6F_5)_3]$ (**5**) in 92 % yield by the combination of $[Et_4N]Cl$ and $Al(C_6F_5)_3\cdot$toluene. Subsequent treatment of **5** with $LiAlH_4$ at 25 °C followed by filtration resulted in the isolation of the pyrophoric salt **6**. The ^1H NMR spectrum of **6** showed a hydride signal at 4.79 ppm, somewhat shifted downfield compared to **1** (4.30 ppm). The X-ray structure of **6** confirmed the formulation of the salt as $[Et_4N][HAl(C_6F_5)_3]$.[19] The metric parameters were generally unexceptional, although the Al–H bond lengths in the two independent molecules of the asymmetric unit averaged 1.51(1) Å, which is comparable to that seen in $K[HAl(C_6F_5)_3]$ (1.59(5) Å)[28] and significantly shorter than those seen in **1**. Compound **6** alone does not react with an added olefin, even upon heating to 60 °C for 12 h. This observation is consistent with the known inability of $LiAlH_4$ to react with isolated olefins.[29] However, the addition of one equivalent of $Al(C_6F_5)_3$ to **6** in C_6D_5Br produced the poorly soluble salt $[Et_4N][H\{Al(C_6F_5)_3\}_2]$ (**7**), as evidenced by ^{19}F and ^{1}H NMR spectroscopy. Heating **6**/$Al(C_6F_5)_3$, or alternatively the isolated salt **7**, under an atmosphere of ethylene at 60 °C for 12 h did result in complete conversion to **3a** and the salt $[Et_4N][Al(C_6F_5)_4]$, as evidenced by NMR spectroscopy. These observations further support the notion that thermal/substrate-induced dissociation of $Al(C_6F_5)_3$ from the anion of **1a** facilitates both the activation of the olefin and the hydride transfer. This is similar to our previously reported hydride delivery from $[HB(C_6F_5)_3]^-$ to the borane-activated olefin fragment of $[(C_6F_5)_2B(CH_2)_4CH{=}CH_2]$ and $[(C_6F_5)_2BOC(CF_3)_2(CH_2)CH{=}CH_2]$.[30]

In the final step of the pathway, a redistribution reaction is proposed to give **2** and **3**. To model this, the salt $[Et_4N][EtAl(C_6F_5)_3]$ (**8**) was prepared in 79 % yield by treating the precursor **5** with EtMgBr. The solid state structure of **8** was confirmed crystallographically.[19] The ^{1}H NMR signals arising from the Al–Et fragment in **8** are observed at 1.40 and 0.75 ppm, considerably shifted downfield relative to those in **3** (1.15, 0.57 ppm). Similarly, the ^{19}F resonances attributable to the *para* and *meta*-F atoms are shifted to −159 and −164 ppm, respectively, from −151 and −160 ppm for the corresponding fragments in **3**. Reaction of **8** with one equivalent of $Al(C_6F_5)_3$·toluene in C_6D_5Br leads to rapid redistribution, thus affording **3a** and the salt $[Et_4N][Al(C_6F_5)_4]$. This observation stands in contrast to the analogous reaction of the anion $[MeAl(C_6F_5)_3]^-$, where the bridging methyl analogue $[(\mu\text{-Me})\{Al(C_6F_5)_3\}_2]^-$[20] is isolated. We recently reported a similar redistribution following ethylene addition to the allyl-bridged species $[tBu_3PH][\{(C_6F_5)_3Al\}_2\{(CH_2)_2CMe\}]$ affording $[tBu_3PH][Al(C_6F_5)_4]$ and $[CH_2{=}C(Me)(CH_2)_3Al(C_6F_5)_2]$.[17d] It appears that such redistribution reactions are driven by steric congestion, as smaller substituents, such as hydride, methyl, or fluoride, do not redistribute.[20,31]

In conclusion, we have presented the facile activation of H_2 using Al-based FLPs and demonstrated subsequent hydride transfer to unactivated olefins. These reactions are thought to involve Al–olefin activation, nucleophilic attack by the anion $[HAl(C_6F_5)_3]^-$, and subsequent redistribution to aluminate and alane. This proposed route is supported by the isolation of the first Al–olefin complex, as well as by parallel reactivity studies. It is interesting to note that, if redistribution could be inhibited, the protic cation derived from FLP activation of H_2 could react with the transient alkylaluminate to provide an entry to a catalytic cycle for hydrogenation. Modification of the aluminum-based FLPs to produce catalysts for the reduction of unactivated olefins is under intense study in our laboratory.

Received: May 2, 2012

Keywords: alkylaluminum · frustrated lewis pairs · hydride delivery · hydrogen · olefins

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[19] CCDC 889612 – 889615 (**1a**, **4**, **6**, and **8**) 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.

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