

Electrophilic Fluorophosphonium Cations in Frustrated Lewis Pair Hydrogen Activation and Catalytic Hydrogenation of Olefins**

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Abstract: The combination of phosphorus(V)-based Lewis acids with diaryl amines and diaryl silylamines promotes reversible activation of dihydrogen and can be further exploited in metal-free catalytic olefin hydrogenation. Combined experimental and density functional theory (DFT) studies suggest a frustrated Lewis pair type activation mechanism.

The catalytic hydrogenation of unsaturated functionalities is one of the most important fundamental tools in modern chemical synthesis.^[1] While the field is still largely dominated by metal-based catalytic systems, the discovery of reversible hydrogen activation by frustrated Lewis pairs (FLPs) in 2006 has paved the way for metal-free catalytic hydrogenation.^[2] Over the past nine years, a number of FLP catalysts have emerged for an increasing scope of substrates. To date, FLP hydrogenation has been used to reduce unsaturated functionalities, including imines,^[3] aziridines,^[3] enamines,^[4] silyl enol ethers,^[5] olefins,^[6] alkynes,^[7] polyaromatics,^[8] and most recently ketones^[9] and aldehydes.^[10] The catalysts used for these reductions have involved boron-based Lewis acids. While the majority of studies employ highly electrophilic boranes such as B(C₆F₅)₃ or related derivatives,^[11] a recent development has been the use of carbene-stabilized boronium-based catalysts.^[12] Another innovation exploits hydroboration of chiral-derived olefins by Piers' borane HB(C₆F₅)₂,^[13] affording a highly efficient catalyst for asymmetric hydrogenations.^[14] In terms of the basic component of the FLP, a variety of sterically demanding phosphines or amine species are most common, although this has been extended to include electronic deficient phosphines, as well as ethers.^[6b,9,15]

Despite the apparent limitation of FLP hydrogenations to largely boron-based Lewis acids, a growing range of Lewis acids including Al, C, Si as well as Ti and Zr derivatives have been investigated in FLP chemistry.^[15,16] The Lewis acidity of

phosphonium centers received lesser attention^[17] although Gabbai and co-workers have used phosphonium centers for enhanced fluoride ion sensing.^[18] On the other hand, we have developed highly electrophilic phosphonium cations (EPCs). These latter compounds proved to be highly Lewis acidic. This arises from a low lying σ* orbital, whereas classical Group 13 Lewis acids derive their Lewis acidity from a vacant p orbital. In an initial study we showed that an electrophilic P center can be used in CO₂ capture,^[19] in manner analogous to that seen for FLPs. Utilizing this acidity we have also shown that EPCs are more Lewis acidic than B(C₆F₅)₃ and effective catalysts for hydrodefluorination of fluoralkanes,^[20] hydrosilylation of olefins, alkynes,^[21] imines, and ketones^[22] and dehydrocoupling of silanes with carboxylic acids, alcohols, thiols, and amines.^[23] Furthermore, concurrent catalytic hydrogenation was achieved upon addition of olefins to these dehydrocoupling reactions.^[23] In these studies of catalysis by the EPC [FP(C₆F₅)₃][B(C₆F₅)₄] **1**, DFT computations inferred intermediates including hydridophosphorane [(C₆F₅)₃PFH] and [Ph₂N(H)SiEt₃]⁺. We recognized that these intermediates could also be generated by the activation of hydrogen between **1** and Ph₂NSiEt₃. Herein, we demonstrate that Lewis acidity of EPCs in combination with sterically encumbered aryl-substituted amines can be exploited as FLPs for H₂ activation and hydrogenation catalysis.

In an initial experiment, an equimolar mixture of *p*-Tol₂NH and **1** was heated under an HD atmosphere. After 24 h at 100 °C the formation of H₂ was observed, indicating reversible hydrogen activation. HD scrambling was subsequently shown to proceed at lower temperatures (60 °C) albeit at lower rates of reaction (see the Supporting Information, Section S3). These observations suggest that the combination of **1** and *p*-Tol₂NH acts as an FLP to effect the heterolytic activation of H₂.

To probe the interactions of **1** and *p*-Tol₂NH, stoichiometric combination of the Lewis acid and base were monitored by ¹H NMR spectroscopy. The normally sharp resonances for the amine are broadened dramatically. A very broad resonance is observed at 7.10 ppm while the resonances attributable to the *p*-Me fragment is not seen. A low-temperature NMR study was also undertaken, however [FP(C₆F₅)₂Ph][B(C₆F₅)₄] **2** was used for solubility reasons. At -90 °C the peaks arising from the *p*-Tol₂NH began to resolve (Supporting Information, Section S3), although a limiting spectrum was observed. These experimental data support the postulate of the generation of an encounter complex analogous to that computed for the Lewis acid-base combination of *t*Bu₃P and B(C₆F₅)₃.^[24]

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In further probing the FLP character of the present system, DFT calculations at WB97XD/def2TZV level of theory^[25] were performed on the Lewis acidic cation $[(C_6F_5)_3P]^+$ and the Lewis base Ph_2NH . Interestingly, the optimized structure shows an approach of the donor to the acceptor but no direct covalent interaction between P and N centers. The resulting $P\cdots N$ distance is 3.52 Å. π -Stacking interactions^[26] between two of the electron poor C_6F_5 rings of the fluorophosphonium with the electron-rich phenyl rings of the amine is observed with ring separations of approximately 3.20 Å (Figure 1). The highest occupied molecular orbital

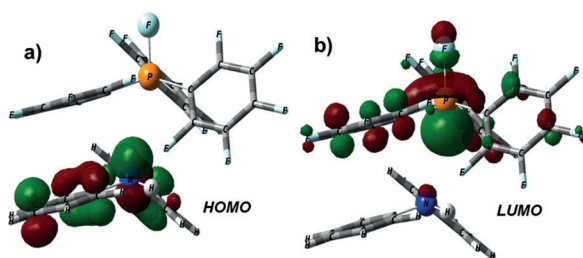


Figure 1. a) HOMO and b) LUMO of the $[(C_6F_5)_3P]^+/Ph_2NH$ encounter complex (isovalue = 0.05).

(HOMO) and lowest unoccupied molecular orbital (LUMO) of this encounter complex were mainly concentrated on the nitrogen atom and the phosphorus atom respectively. While these orbitals are oriented towards each other, the steric conflicts and π -stacking preclude a dative interaction. The formation of the π -stacking-stabilized encounter complex is exergonic ($\Delta G = -6.3$ kcal mol⁻¹) and exothermic ($\Delta H = -23.4$ kcal mol⁻¹; Figure 2).

Calculation of the subsequent barrier for H_2 activation found to be relatively low ($\Delta G^\ddagger = 12.9$ kcal mol⁻¹ and $\Delta H^\ddagger = 6.1$ kcal mol⁻¹) while the overall process of the heterolytic H_2 cleavage is energetically favorable ($\Delta G = -22.6$ kcal mol⁻¹ and $\Delta H = -31.8$ kcal mol⁻¹; Figure 2). This generates an

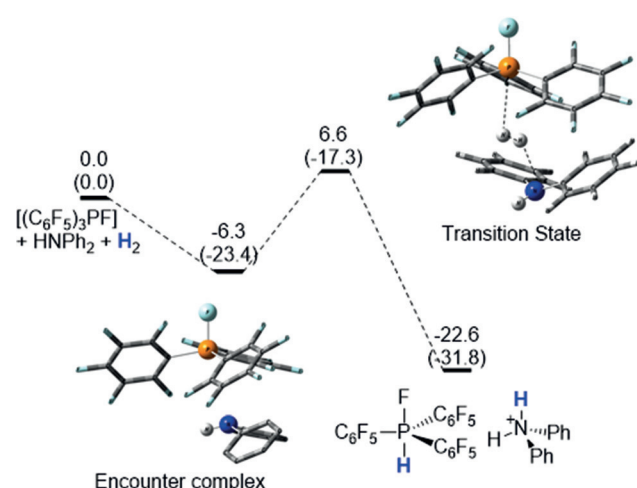


Figure 2. Reaction coordinate of the H_2 activation by $[(C_6F_5)_3P]^+/Ph_2NH$. Gibbs free energy (enthalpy) in kcal mol⁻¹ are given relative to starting materials.

activation barrier of 29.2 kcal mol⁻¹ for the reverse reaction, which is consistent with the requirement of heating to 100 °C for HD scrambling to be observed. The transition state for the activation of H_2 was computed and shows the H_2 molecule oriented between the N and P such that one H atom is 2.46 Å from N and the other is 2.83 Å from P, with an H–H distance of 0.74 Å and N–H–H and P–H–H angles of 119.3° and 102.3°, respectively. This geometry gives rise to a $P\cdots N$ separation of 5.42 Å. This dissymmetric geometry suggests the polarization of the H_2 molecule and is reminiscent of the non-linear transition state computed for the interaction of the FLP $tBu_3P/B(C_6F_5)_3$ with H_2 .^[24]

The ability to activate H_2 suggests the potential for catalytic hydrogenation. To avoid Lewis acid mediated Friedel–Crafts reactions $Ph_2C=CH_2$ was combined with 1 mol % **1** and 20 mol % p -Tol₂NH in C_6D_5Br . This mixture was pressurized under 4 atm of H_2 and heated to 100 °C. This resulted in less than 5 % conversion to Ph_2CHCH_3 (Table 1,

Table 1: Catalytic hydrogenation of $Ph_2C=CH_2$.^[a]

Lewis base (X mol %)		1 (1.0 mol %)			
		C_6D_5Br			
		4 atm H_2 , 100 °C			
	Lewis base	[mol %]	T [°C]	t [h]	Conv. [%]
1	p -Tol ₂ NH	20	100	24	< 5 %
2	p -Tol ₂ NSiEt ₃	20	100	24	98
3	p -Tol ₂ NSiEt ₃	10	100	24	86
4	p -Tol ₂ NSiEt ₃	5	100	24	43
5	p -Tol ₂ NSi(<i>i</i> Pr) ₃	20	100	24	56
6	p -Tol ₂ NSiMe ₂ (<i>t</i> Bu)	20	100	24	54
7	p -Tol ₂ NSiPh ₃	20	100	24	51
8 ^[b]	Et ₃ SiH/ p -Tol ₂ NH	20	100	24	15
9	Et ₃ SiH/ p -Tol ₂ NH	20	100	24	99 (92) ^[c]
10	Et ₃ SiH/ p -Tol ₂ NH	20	100	4	43
11	Et ₃ SiH/ p -Tol ₂ NH	20	100	8	85
12	Et ₃ SiH/ p -Tol ₂ NH	20	75	24	51
13	Et ₃ SiH/ p -Tol ₂ NH	20	50	24	23

[a] Reaction conditions: 0.5 mmol $Ph_2C=CH_2$, 0.005 mmol **1**, 1 mL C_6D_5Br , 4 atm H_2 , 100 °C. Conversion determined by ¹H NMR spectroscopy. [b] Reaction done in absence of H_2 . [c] Yield of isolated product.

entry 1). In contrast, employing 1 mol % **1** and 20 mol % p -Tol₂NSiEt₃ to generate the FLP catalyst resulted in the efficient hydrogenation of $Ph_2C=CH_2$, affording Ph_2CHCH_3 after 24 h (Table 1, entry 2). Lowering the catalyst loading gave the correspondingly lower conversion (Table 1, entries 3, 4). Employing 20 mol % of the amino silanes p -Tol₂NSi(*i*Pr)₃, p -Tol₂NSiMe₂(*t*Bu), and p -Tol₂NSiPh₃ also promoted the catalytic hydrogenation of $Ph_2C=CH_2$, yielding Ph_2CHCH_3 after 24 h in yields ranging from 51–56 % (Table 1, entries 5–7). The reduced conversions of these latter catalyst systems in comparison to that generated from **1**/ p -Tol₂NSiEt₃ suggest that increased steric encumbrance of the N-base lowers the catalytic efficiency, presumably by impeding formation of the appropriate encounter complex geometry.

The above experiments demonstrate that p -Tol₂NSiEt₃ is the best of the bases tested. We have previously reported the

synthesis of this species by catalyzing the dehydrocoupling of *p*-Tol₂NH and HSiEt₃ using **1** as the catalyst.^[23] Thus, treatment of Ph₂C=CH₂ with 20 mol % of *p*-Tol₂NH and HSiEt₃ using **1** as the catalyst but in absence of hydrogen gave only 15 % reduction via the reported transfer hydrogenation pathway (Table 1, entry 8).^[23] However, this process did show that the silylamine *p*-Tol₂NSiEt₃ could be conveniently generated in situ (Supporting Information, Figure S82). Thus, 20 mol % of Et₃SiH and *p*-Tol₂NH was added to a solution of **1** in the presence of Ph₂C=CH₂ under H₂ (4 atm). Heating to 100 °C for 24 h afforded near quantitative conversion to the hydrogenated olefin which was isolated in 92 % yield (Table 1, entry 9). Reduction of the time to 4 or 8 h, or reduction of the temperature to 50 or 75 °C lead to diminished reduction conversion (Table 1, entries 10–13). The observed difference in reactivity of *p*-Tol₂NH (Table 1, entry 1) and *p*-Tol₂NSiEt₃ (Table 1, entry 4) suggests a beneficial effect of silyl moiety on the catalytic hydrogenation (see mechanistic discussion below).

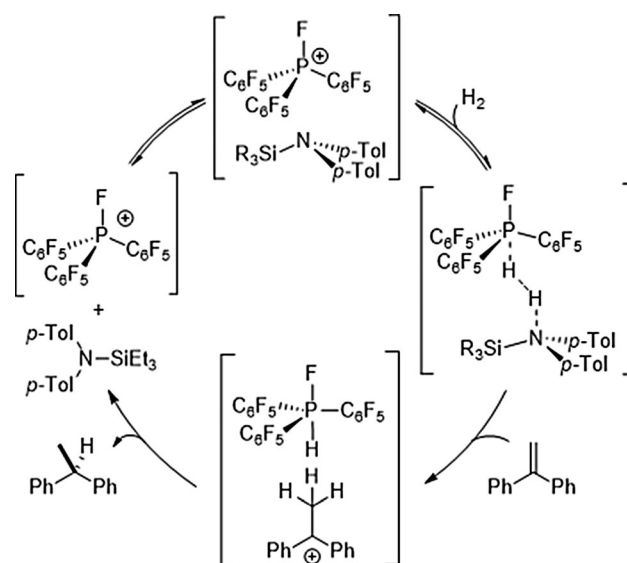
With these optimized conditions, the scope of substrates for these reductions were assessed. Thus, treatment of Ph(3,4-Me₂(C₆H₃))C=CH₂ with 20 mol % of *p*-Tol₂NH and HSiEt₃ using **1** as the catalyst for 24 h at 100 °C and 4 atm of H₂ resulted in full hydrogenation in 99 % and 92 % yield (Table 2, entry 1). The corresponding reaction of Ph(2-MeC₆H₄))C=CH₂ was quite sluggish, ultimately requiring 96 h to achieve 18 % conversion (Table 2, entries 2, 3). This retarded reaction is attributable to the steric congestion about the olefinic bond. In contrast, Ph(4-Br-C₆H₄))C=CH₂, Ph(4-F-C₆H₄))C=CH₂, and Ph(4-Me₃SiO-C₆H₄))C=CH₂ were hydrogenated efficiently (Table 2, entries 4–6). On the other hand the *meta* substitution in Ph(3-Br-C₆H₄))C=CH₂ reduced the susceptibility to hydrogenation (Table 2, entry 7). Anthracene derivatives were reduced with increased catalyst loadings and reaction times (Table 2, entries 8 and 9). While methyl stilbene Ph(Me)C=CPh could be reduced in 45 % yield, phenyl-substituted Ph₂C=CHPh was essentially unreactive (Table 2, entries 10 and 11). This further supports the previous observation that bulky olefins represent challenging substrates. On the other hand, styrene derivative Ph(Me)C=CH₂ gave mostly the dimerized olefin (Table 2, entry 12).

The mechanism of these hydrogenations is thought to proceed via initial H₂ activation analogous to that described above between **1** and *p*-Tol₂NH. In the present case, the generation of the transient hydridophosphorane [FP(C₆F₅)₃H] and ammonium salt [*p*-Tol₂N(H)SiEt₃]⁺ is postulated (Scheme 1). This view is also supported by experimental H₂ and HD activation studies (Supporting Information, Sections S5 and S3.2)^[27] as well as DFT calculations at WB97XD/def2TZV^[25] level of theory (Supporting Information, Section S6), in which the activation of H₂ by [FP-

Table 2: Catalytic hydrogenation of olefins.^[a]

	Substrate	1 [mol %]	Base [mol %]	<i>t</i> [h]	Conv. ^[b] [%]
1	Ph(3,4-Me ₂ (C ₆ H ₃))C=CH ₂	1.5	Et ₃ SiH/ <i>p</i> -Tol ₂ NH (20)	24	99 (91)
2	Ph(2-MeC ₆ H ₄))C=CH ₂	2	Et ₃ SiH/ <i>p</i> -Tol ₂ NH (20)	24	14
3	Ph(2-MeC ₆ H ₄))C=CH ₂	2	<i>p</i> -Tol ₂ NSiEt ₃ (20)	96	18
4	Ph(4-F-C ₆ H ₄))C=CH ₂	2	Et ₃ SiH/ <i>p</i> -Tol ₂ NH (20)	24	85
5	Ph(4-Et ₃ SiO-C ₆ H ₄))C=CH ₂	1	<i>p</i> -Tol ₂ NSiEt ₃ (20)	24	99 (90)
6	Ph(4-Br-C ₆ H ₄))C=CH ₂	2	Et ₃ SiH/ <i>p</i> -Tol ₂ NH (20)	24	50
7 ^[c]	Ph(3-Br-C ₆ H ₄))C=CH ₂	5	<i>p</i> -Tol ₂ NSiEt ₃ (20)	24	22
8 ^[c]	C ₁₄ H ₁₀	5	<i>p</i> -Tol ₂ NSi(<i>i</i> Pr) ₃ (20)	72	65
9 ^[c]	MeC ₁₄ H ₉	5	<i>p</i> -Tol ₂ NSi(<i>i</i> Pr) ₃ (20)	72	43
10 ^[c]	Ph(Me)C=CHPh	10	<i>p</i> -Tol ₂ NSi(<i>i</i> Pr) ₃ (40)	96	45
11 ^[c]	Ph ₂ C=CHPh	10	<i>p</i> -Tol ₂ NSi(<i>i</i> Pr) ₃ (40)	240	8
12 ^[c]	Ph(Me)C=CH ₂	1	<i>p</i> -Tol ₂ NSiEt ₃ (40)	24	99 ^[d]

[a] Reactions conditions: 0.5 mmol olefin, 1 mL C₆D₅Br, 4 atm H₂ pressure. Conversions determined by ¹H NMR integration. [b] Yields of isolated product in brackets. [c] 0.1 mmol olefin, 0.75 mL C₆D₅Br. [d] 1,3-dimethyl-1-phenyl-2,3-dihydro-1*H*-indene is the major product.



Scheme 1. Proposed mechanism for hydrogenation of olefins by **1**/*p*-Tol₂NSiEt₃ ([B(C₆F₅)₄][−] anions are not shown).

(C₆F₅)₃]⁺/Ph₂NSiMe₃ was shown to proceed via an encounter complex, similar to that computed for **1** and *p*-Tol₂NH. However, in the present case only one C₆F₅ ring and one phenyl ring participate in π stacking, probably a result of steric congestion. This gives rise to a weaker stabilization of the encounter complex ($\Delta G = -1.8$ kcal mol^{−1}, $\Delta H = -17.1$ kcal mol^{−1}). The ensuing reaction with H₂ forming (C₆F₅)₃P(F)H and [Ph₂N(H)SiMe₃]⁺ is exergonic ($\Delta G = -32.3$ kcal mol^{−1}) and exothermic ($\Delta H = -26.4$ kcal mol^{−1}), which is 17.9 kcal mol^{−1} more exothermic and 16.0 kcal mol^{−1} more exergonic than the activation of H₂ using Ph₂NH (Supporting Information, Schemes S17 and S18). The effective energy barrier for H₂ activation is $\Delta G^\ddagger = 6.0$ kcal mol^{−1}, which is less than half of the corresponding barrier calculated for *p*-Tol₂NH ($\Delta G^\ddagger = 12.9$ kcal mol^{−1}, see Figure 1). This difference in activation energy accounts for the differing reactivity of the two Lewis bases in catalytic hydrogenations

(see Table 1). Reductive cleavage of the N–Si bond of *p*-Tol₂NSiEt₃ with hydrogen is excluded as the FLP *p*-Tol₂NSi(*i*Pr)₃ catalyzes hydrogenation, but *i*Pr₃SiH and *p*-Tol₂NH does not liberate H₂ to give *p*-Tol₂NSi(*i*Pr)₃ in the presence of **1**, even after 3 days at 100 °C (Supporting Information, Section S4.2.7). Likewise, hydrogen activation and transfer promoted by the generated [*p*-Tol₂N(H)SiEt₃][B(C₆F₅)₄] could be excluded in control reactions (Supporting Information, Section S4.2.2).^[28] Once H₂ is heterolytically split, protonation of the olefin and subsequent hydride delivery from the transient hydridophosphorane follows. In line with this hypothesis, it could be shown that the protonated amino silane [*p*-Tol₂N(H)SiEt₃][B(C₆F₅)₄] is able to protonate 1,1-diphenylethylene at room temperature, leading to catalytic dimerization of the olefin.^[29] Furthermore, an alternative pathway of H₂ activation by the transient Lewis acidic carbocation^[30] has been excluded by control experiments (Supporting Information, Section S4.2.2). Moreover, it is noteworthy that hydridic phosphoranes have recently been described.^[17g,h,31] These observations suggest that in contrast to *p*-Tol₂NH, the steric demands of *p*-Tol₂NSiEt₃ appear to strike the right balance allowing the heterolytic cleavage to proceed and favoring subsequent protonation of olefin, thus permitting catalytic hydrogenation to proceed.

In summary, the present work reports the use of electrophilic phosphonium cations in combination with bulky amines in the frustrated Lewis pair activation of H₂ and in the catalytic hydrogenation of olefins. These findings extend the scope of reactivity of EPCs and broaden the range of FLP systems. Future efforts are targeting specifically designed EPCs for FLP hydrogenations, which will provide improved reactivity. Furthermore, the breadth of Lewis acids and bases that are viable for FLP chemistry continues to be of interest to us.

Keywords: frustrated Lewis pairs · hydrogenation · Lewis acids · alkenes · phosphorus

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