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Carbene-Based Lewis Pairs for Hydrogen Activation

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A series of Lewis acid–base pairs containing sterically demanding carbenes were investigated for hydrogen activation that could potentially be reversible for use in hydrogen storage applications. When electron-rich boranes are employed as electrophiles, the imidazolium cation is reduced to a 2H-imidazoline (aminal). The aminals were synthesized independently by reduction of imidazolium cations with strong reducing agents. Carbocations were also found to act as electrophiles for hydrogen activation. Preliminary results revealed that it is possible to reduce an alcohol to an alkane using hydrogen gas as a reducing agent in these systems. Finally, it was demonstrated that a transition metal can be used as an electrophile to activate hydrogen through heterolytic cleavage.

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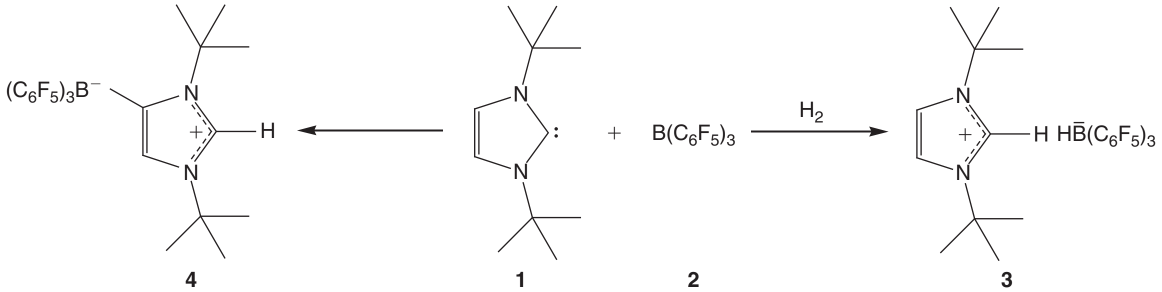
Introduction

The abundance of hydrogen gas (H_2) and the benign byproduct (H_2O) produced when it is used as a fuel make it a promising source of portable energy. Currently, one of the problems with using hydrogen as a fuel is its storage and transportation. The use of large, heavy cylinders is required for the compressed gas and cryogenic containers are required for storage as a liquid. These containment options result in unfavourable costs and difficulty in implementation. Safety is also a concern when transporting high-pressure cylinders of hydrogen or cryogenic materials. Therefore, molecular systems that can activate hydrogen gas and store it in an alternative chemical form are in need of investigation.

Stephan et al. demonstrated that Lewis acid–base pairs containing sterically demanding Lewis bases and electrophilic Lewis acids exhibit unusual reactivity that may offer an approach to chemical hydrogen storage.[1a] When there is a thermodynamic driving force for the formation of a Lewis pair but a large kinetic barrier to this reaction, these non-traditional Lewis pairs are said to be 'frustrated.' In these circumstances, small molecules that can bridge the Lewis acid–base interaction can be heterolytically cleaved (activated). The first reported example of non-metallic hydrogen activation was demonstrated using a Lewis base such as $P(^tBu)_3$ and an electron-poor tris (pentafluorophenyl)borane ($B(Ar_F)_3$) Lewis acid.[1b,c] Carbenes themselves have been proposed as activators and storage sites for dihydrogen.[2] A major benefit compared with transition metal activation is a lower-molecular-weight system for hydrogen activation, which is desired for use in transportation.

Tamm et al. have demonstrated that sterically shielded carbenes such as 1,3-bis-*tert*-butylimidazol-2-ylidene **1** can be used in a 'frustrated' Lewis pair with the fluoroaryl borane **2** to activate hydrogen.[3] In the presence of 0.1 MPa of H_2, heterolytic cleavage occurs, resulting in the formation of imidazolium borohydride **3**, as depicted in Scheme 1. The elimination of hydrogen is not reversible in these systems owing to the poor



Scheme 1. A carbene–borane Lewis pair for hydrogen activation.

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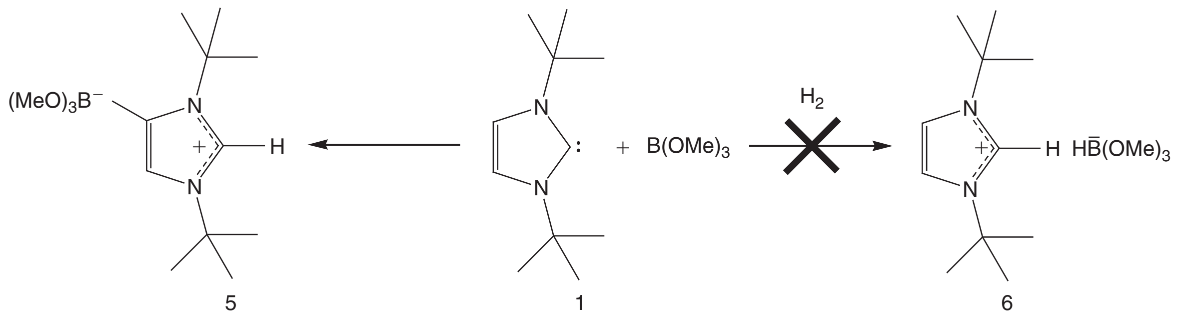
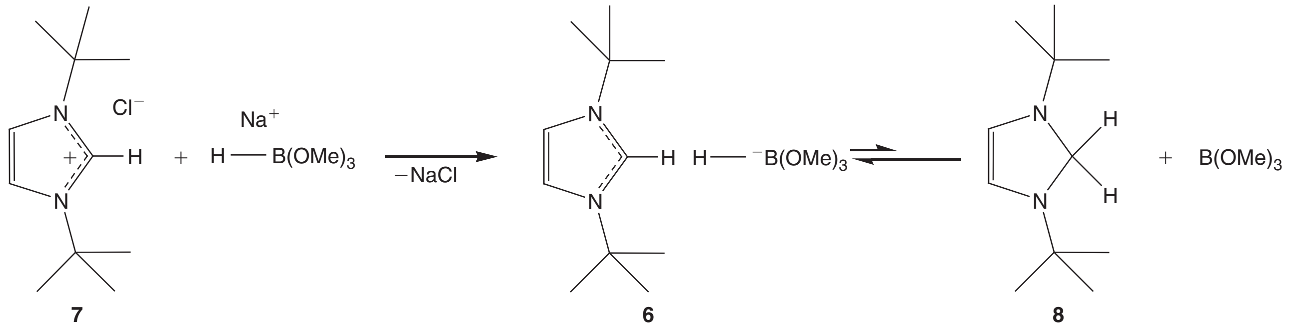


Scheme 2. Trimethoxyborane as a Lewis acid for hydrogen activation.



Scheme 3. Salt metathesis reaction to form imidazolium borohydride **6**.

hydridic nature of the resulting borohydride. A crystal structure of **3** indicates that the hydride and acidic imidazolium proton are not oriented towards each other, indicating no solid-state intermolecular proton–hydride interaction. In the absence of hydrogen, a non-traditional Lewis pair forms where 'abnormal'[4a–c] coordination to the carbene backbone is observed, as in the zwitterion **4**. Functionalities such as aliphatic C–H groups have been shown to undergo molecular activation with this system as well.[5]

Results and Discussion

With literature precedence suggesting that tris(pentafluorophenyl)borane **2** is a sufficiently electrophilic Lewis acid for heterolytic H_2 cleavage to occur, a wide variety of weaker electrophiles were explored for carbene-based activation systems in our laboratory. With a knowledge of the range of reactivities, it may be possible to design a conveniently reversible system.

Boron Electrophiles for Lewis Pairs

Reaction of the electron-rich trimethyl borate with carbene **1** was found not to be electrophilic enough for hydrogen cleavage under 0.3 MPa of H_2 for up to 6 days (Scheme 2). It was found that the carbene–borane reaction in the absence of H_2 is slow and takes hours before the abnormal coordination, **5**, is observed, followed by further decomposition. The imidazolium borohydride, **6**, was synthesized by a salt metathesis reaction of imidazolium salt **7** with sodium trimethoxyborohydride to explore the conditions under which hydrogen elimination may occur (Scheme 3). A reduction of **7** to aminal **8** occurs on addition of $NaHB(OMe)_3$. There is an equilibrium between **6** and **8**, which is identified by the upfield shift of the C2-methylene group (δ 4.08 ppm (^1H) and δ 67.47 ppm (^{13}C)). The equilibrium is solvent- and temperature-dependent, with more polar solvents and lower temperatures favouring **6**. Both $B(OMe)_3$ (s, δ 19) and $HB(OMe)_3^-$ (br, δ 3.1 ppm, $^1J_{B–H}$ unresolved) along with traces of

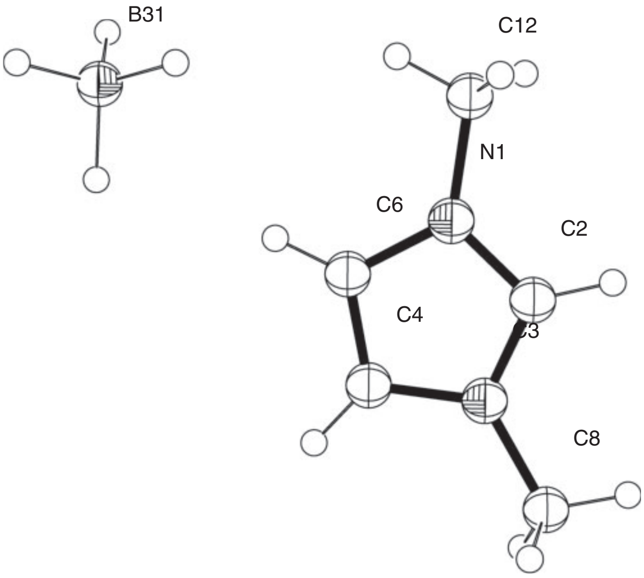
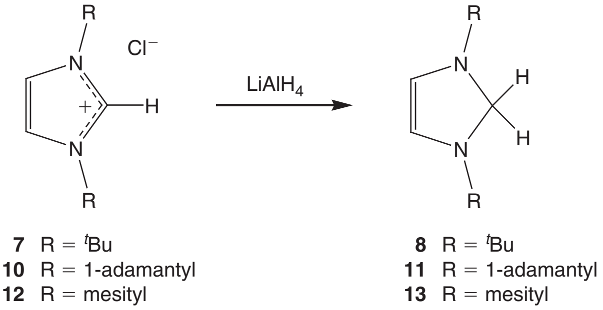


Fig. 1. Crystal structure 1,3-dimethylimidazolium borohydride **9**. Thermal ellipsoids are drawn at the 50 % probability level.



Scheme 4. Reduction of imidazolium salts to imidazole aminals.

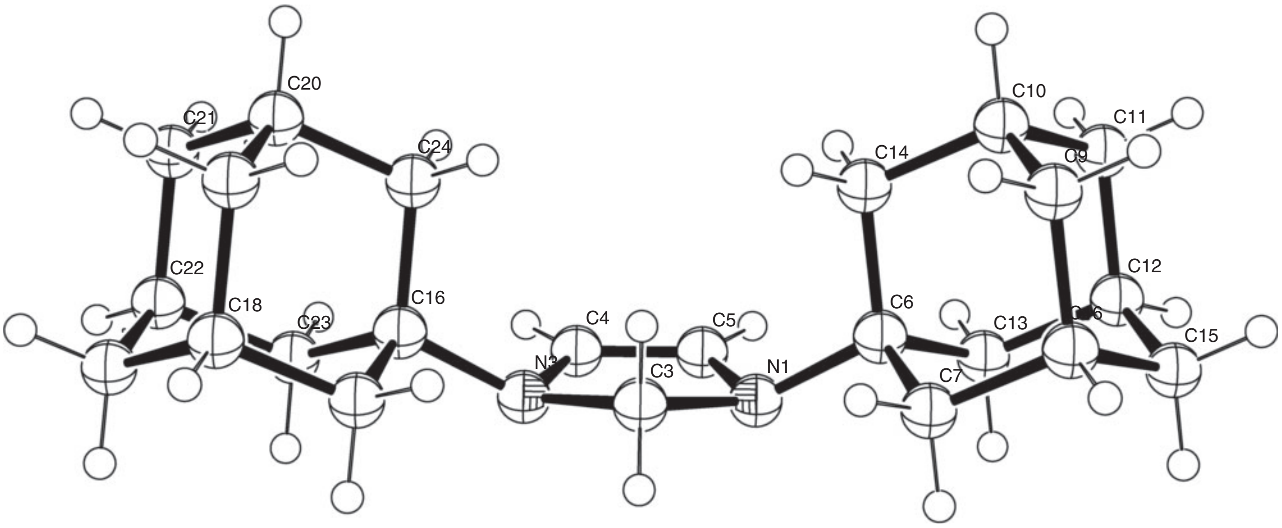
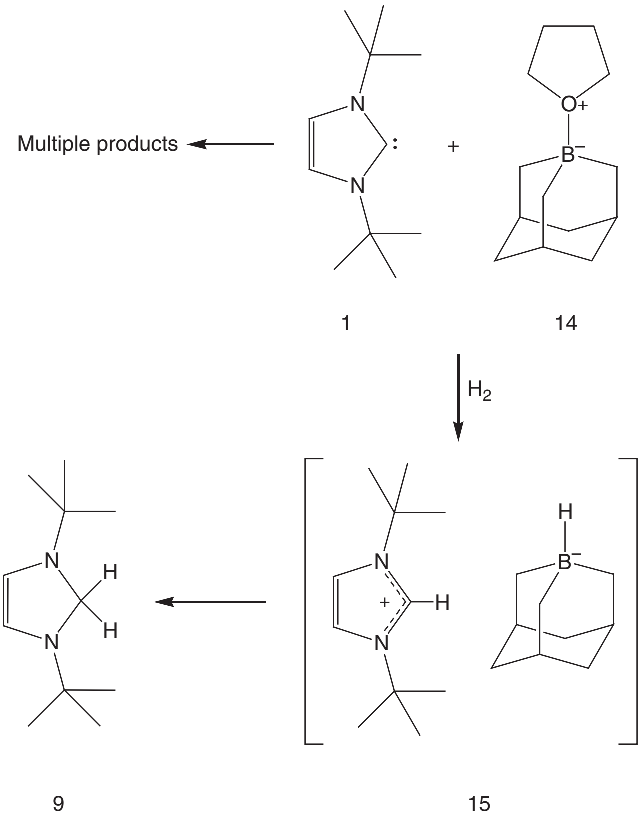


Fig. 2. Crystal structure of the imidazole aminal **11**. Thermal ellipsoids are drawn at the 50 % probability level.

BH_4^- (quintet, δ −38 ppm, $^1J_{B-H}$ 82 Hz) are observed in the ^{11}B NMR spectrum. It has been demonstrated that weaker reducing agents such as $NaBH_4$ undergo anion exchange without reduction to form stable imidazolium borohydrides, as seen in **9**.[6] However, unlike **3**, the crystal structure of **9** (Fig. 1) reveals weak H–H interactions between the borohydride anion and the imidazolium protons at positions 2 and 4(5). Such anionic hydrogen bonding to imidazolium cations has been previously reported.[7] Stronger reducing agents such as $LiAlH_4$ completely reduce **7** to **8**; however, X-ray-quality crystals could not be grown owing to the low melting point of **8**. The reduction of imidazolium salts **10** and **12** with $LiAlH_4$ results in aminals **11** and **13**, seen in Scheme 4, and a crystal structure could be obtained in the case of the adamantyl-substituted imidazole. The crystal structure of **11** (Fig. 2) shows that the nitrogen atoms pyramidalize in contrast to planar (delocalized) structures observed for the imidazolium salt **10** and its carbene. The likely cause for this distortion is a combination of the introduction of an sp^3 centre at C2, and the π-electron repulsion in the electron-rich ene-1,2-diamine fragment.

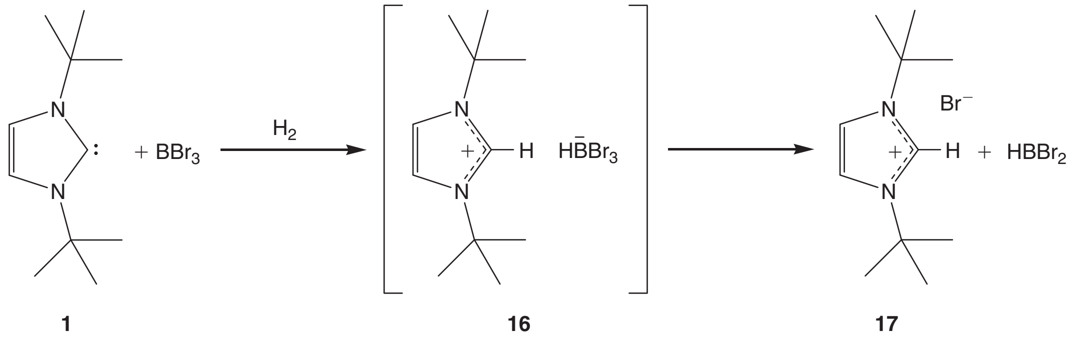
Alkylboranes are not as highly electrophilic as the fluoroaryl boranes mentioned above; however, 1-boraadamantane · THF (**14**) was of interest owing to the unusual electrophilicity of the borane centre that results in the geometric constraints in the system. The boron atom is fixed in a trigonal pyramidal geometry due to the fused adamantane ring system. This geometry causes the vacant boron valance orbital to retain substantial s orbital character and thus strong electrophilicity. The electrophilicity of **14** is so extreme that it is always observed as a base-complexed adduct and suffers decomposition when in the absence of a stabilizing base.[8a,b] Addition of carbene **1** to 1-boraadamantane results in a mixture of by-products that likely occur from ring-opening reactions and 'abnormal' coordination to the carbene. In the presence of 0.3 MPa of hydrogen gas, addition of carbene **1** to **14** results in the formation of aminal **9** (Scheme 5).

The 1-boraadamantane **14** activates hydrogen gas, followed by heterolytic cleavage to form the intermediate imidazolium borohydride **15**. Like the reaction with $HB(OMe)_3^-$, however, the borohydride **15** acts as a reducing agent to produce the aminal **8**. As THF is lost from **14** on hydrogen activation, the borane subsequently decomposes owing to the lack of base for stabilization.

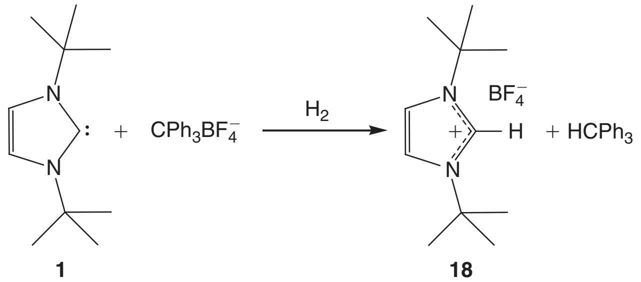


Scheme 5. 1-Boraadamantane as a Lewis acid for hydrogen activation.

Boron tribromide was also tested as a Lewis acid for hydrogen activation reactions, as depicted in Scheme 6. The molecule contains electronegative halogens, which are large enough to form a 'frustrated' acid–base system. The imidazolium bromide **17** was isolated from the reaction from the addition of carbene **1** to BBr_3 in the presence of H_2 (0.3 MPa) at −60°C. The imidazolium cation was easily identified by the characteristic downfield ^1H resonance (δ 9.06 ppm) for the C2 proton with no other observable hydrogen or boron atoms.[9] This suggests that the initial hydrogen activation by BBr_3 to form **16** was successful, but bromide is eliminated from this intermediate as the borane is reduced and appears in products as various disproportionates.



Scheme 6. Boron tribromide as a Lewis acid for hydrogen activation.

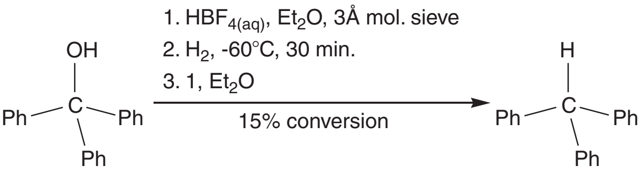


Scheme 7. Trityltetrafluoroborate as a Lewis acid for hydrogen activation.

Carbon Electrophiles for Lewis Pairs

Because of undesired decomposition and reduction reactions following hydrogen activation with simple carbene–borane pairs, carbocations were investigated as Lewis acids to determine if they are sufficiently electrophilic to activate hydrogen. It was expected that, in general, carbocations would be stronger electrophiles than boranes for hydrogen activation. An additional challenge with these electrophiles includes the solubility of the carbocations (salts) in a relatively polar, non-coordinating solvent. An electron-poor non-coordinating anion is important so that coordination does compete with hydrogen coordination. The relatively stable, easy to handle trityl tetrafluoroborate was selected as a candidate electrophile. Direct addition of the carbene **1** to trityl tetrafluoroborate in the absence of H_2 provided evidence that there are many possible side reactions, some of which occur through redox pathways, as suggested by the many colour changes and multiple products observed by ^{1}H NMR spectroscopy. In the presence of H_2 at −60°C, the imidazolium tetrafluoroborate salt **18** is formed, along with triphenylmethane, which can be easily identified by signals in the ^{1}H and ^{13}C NMR spectra (Scheme 7). Although trityl tetrafluorborate can successfully activate H_2, the system is not reversible even at temperatures up to 100°C.

Because using carbocations to activate H_2 in an acid–base pair with nucleophilic singlet carbenes is a unique approach to this problem, we sought to determine if carbocations could be generated in situ to allow the direct reduction of alcohols to alkanes using H_2 as a reducing agent, seen in Scheme 8. Treatment of dry Ph_3COH in Et_2O with aqueous HBF_4 in the presence of 3-Å molecular sieves and 0.1 MPa of H_2 at −60°C led to the formation trityl tetrafluoroborate, as indicated by a light-yellow precipitate. Addition of carbene **1** under a slight pressure of H_2 results in the formation of tan solids, which were identified to be the imidazolium tetrafluoroborate **18** and triphenylmethane. Although a low conversion of 15 % was obtained, optimization of the reaction conditions by using anhydrous acid and higher pressures of H_2 may be possible. Triphenylcarbenium ions are ideal carbocations because of their stability and ease of preparation, but these results could have implications in the reduction of other carbocations in a one-pot reaction as well.



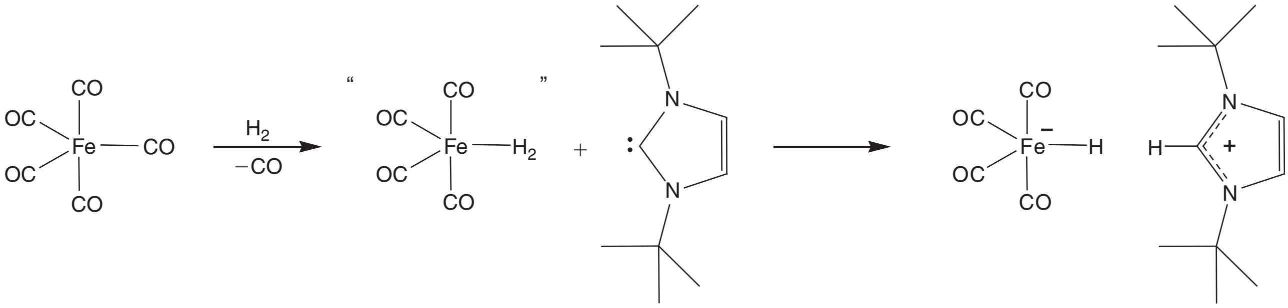
Scheme 8. Reduction of Ph_3COH to Ph_3CH with hydrogen gas.

Transition Metal Electrophiles for Lewis Pairs

Although transition metals have been shown to undergo homolytic cleavage of hydrogen through oxidative addition, they have not been used as electrophiles in acid–base pairs to heterolytically cleave hydrogen gas. Metal carbonyls are electron-deficient complexes owing to the π-acidity of the carbonyl groups and are typically used as catalysts in hydrogenations, hydroformylations and the water-gas shift reaction.[10a,b] It was anticipated that if hydrogen gas undergoes a ligand substitution with CO, the hydrogen could be activated for attack by a carbene base, shown in Scheme 9. The resulting metal complex would be imidazolium metal hydride **19**.

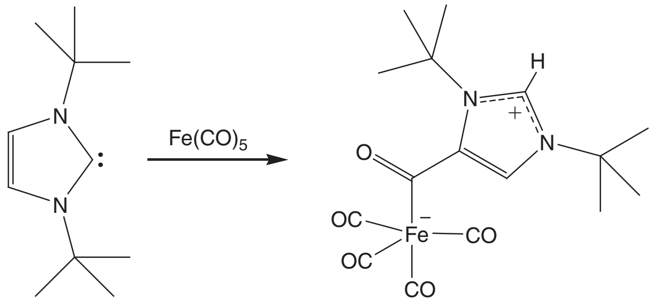
As literature precedence exists for stable iron hydrides and their complexes,[11a–c] $Fe(CO)_5$ was used as an electrophilic partner for the activation system. In the absence of hydrogen gas, direct addition of the carbene to $Fe(CO)_5$ results in ‘abnormal’ carbene coordination. Surprisingly, no CO is eliminated and a carbon–carbon bond is formed between the carbene backbone and the carbonyl group in the same manner as for **4** (Scheme 10). The corresponding imidazolium acyl ferrate (**20**) that forms is a yellow air-sensitive solid. The crystal structure of **20**, depicted in Fig. 3, reveals that the iron centre retains a trigonal pyramidal geometry. The presence of the cationic imidazolium moiety requires that the compound is zwitterionic, with a balancing negative charge on the acyl ferrate group.

It was found that the concentration of hydrogen gas in solution has a direct effect on the amount of imidazolium hydride **19** that is formed when using $Fe(CO)_5$ as an electrophile. Treatment of $Fe(CO)_5$ with carbene **1** in the presence of 0.3 MPa of H_2 results in mainly the imidazolium acyl ferrate **20**. Increasing the pressure of H_2 to above 1.8 MPa results in a darker solid, which is due to the formation of the red-brown imidazolium iron hydride **19** (Scheme 11). Even though the system is subjected to higher pressures of H_2, there is only a



1 19

Scheme 9. Activation and heterolytic cleavage of hydrogen gas using a Fe(CO)$_5$ Lewis acid.



1 20

Scheme 10. Abnormal coordination occurs from direct addition of the carbene **1** to Fe(CO)$_5$.

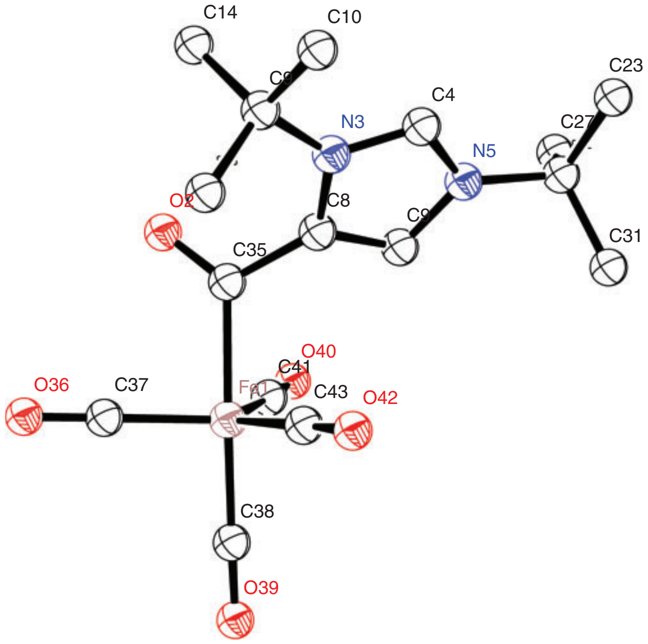


Fig. 3. *ORTEP* drawing of the crystal structure of imidazolium acyl ferrate **20**. Thermal ellipsoids are drawn at the 50 % probability level.

conversion ratio of 1:6 of the desired iron hydride **19** to imidazolium acyl ferrate **20**.

Although the forward reaction to form the iron hydride **19** was promising, questions remained as to whether hydrogen could be eliminated from the iron hydride through deprotonation of the imidazolium proton. The direct synthesis of imidazolium hydride **19** from salt metathesis of the imidazolium chloride **7** with potassium hydridoferrate was conducted.[12]

The resulting red-brown solid can be identified by the characteristic hydride signal, which has an upfield shift of δ −9.0 in the ^{1}H NMR along with the usual imidazolium cation resonances. The imidazolium protons in **19** have signals that are shifted slightly upfield from those of **7**. The solid melts at 75–80°C and discolours at 140–155°C; however, no gas evolution is observed at these temperatures in the solid state and no decomposition is observed by variable-temperature NMR spectroscopy in [D6]DMSO. This result stands in contrast to the cases of the 1,4-dimethyltetrazolium hydridoferrate[13] and 1,3-dimethylimidazolium hydridoferrate,[14] both of which decompose with the elimination of dihydrogen to form the corresponding [azolylidene]irontetracarbonyl complexes.

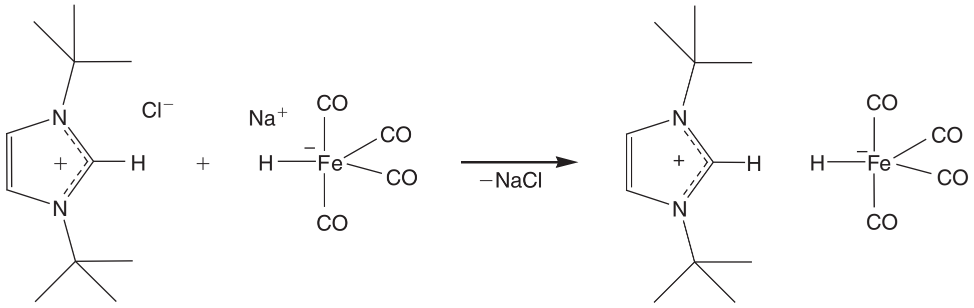
Conclusions

Broadening the scope of electrophiles useful in acid–base activation developed by Stephans et al.[1] and expanded by Tamm et al.[3] has yielded promising results. It has been shown that relatively electron-rich boranes are capable of activating hydrogen in the presence of nucleophilic singlet carbenes. The strong reducing ability of the electron-rich borohydrides provides direct access to 2H-imidazolines (aminals) by reduction of the imidazolium cation at C2. Other electrophiles, such as carbocations and metal carbonyls, proved also to activate hydrogen gas. Higher pressures of H_2 are required for activation to occur when using metal carbonyls such as Fe(CO)$_5$. It was found in all Lewis acid systems that hydrogen storage was not thermally reversible, but the range of reactivities leaves open the possibility that a reversible system may be found. This acid–base-pair activation chemistry could be useful in areas such as direct reduction of organic functional groups using hydrogen gas. Acid–base-pair activation systems can still show some acid–base reactivity in the absence of dihydrogen, which suggests that systems need not be fully ‘frustrated’, but rather merely need a kinetic balance that favours dihydrogen activation over the direct acid–base reaction. The range of reactivities exhibited herein and in earlier works suggests that the design of a reversible dihydrogen activation system remains a possibility.

Experimental

General Methods

All moisture- and air-sensitive reactions and manipulations were carried out in oven-dried glassware under a dry nitrogen atmosphere, either in a Vacuum Atmosphere® dry-box or by using standard Schlenk techniques. Unless otherwise



7 **19**

Scheme 11. Direct synthesis of imidazolium hydride **19**.

noted, reagents were used as obtained from commercial sources. Dried solvents were obtained by standard procedures.[15] Tetrahydrofuran was dried over calcium hydride, then distilled from sodium/benzophenone and stored in a dry-box. Methylene chloride, hexane, toluene and acetonitrile were distilled from calcium hydride and stored in a dry-box. Anhydrous dimethylsulfoxide was obtained from Aldrich or Fisher Scientific. Evaporation of solvents was performed using a Büchi rotary evaporator at water aspirator pressure (15–30 mm Hg) or under vacuum using a mechanical vacuum pump. All solvents used for extraction and chromatography (unless otherwise specified) were reagent-grade. Thin-layer chromatography (TLC) was performed using Whatman flexible-backed silica plates (0.25 mm layer thickness) precoated with a fluorescent indicator. Development of TLC plates was accomplished with iodine vapour.

Melting points were obtained using a Laboratory Device MEL-TEMP® II apparatus and are uncorrected. Proton NMR spectra were obtained on a Bruker AM-500-MHz spectrometer. Proton NMR chemical shifts are reported in parts per million (ppm) using residual solvent protons as the internal standard: [D6]DMSO (δ 2.52 ppm), [D6]benzene (δ 7.16 ppm), [D3] acetonitrile (δ 1.94 ppm), [D8]THF (δ 3.58 ppm and 1.73 ppm) are reported as referenced to tetramethylsilane. Proton NMR spectral data are listed as follows: chemical shift (multiplicity, relative number of hydrogen atoms, coupling constant). Multiplicities are denoted as follows: s (singlet), d (doublet), dd (doublets of doublets), t (triplet), q (quartet), m (multiplet), br (broad), brs (broad singlet), quin (quintet). Carbon-13 NMR spectra were recorded at 125 MHz and chemical shifts are reported in ppm relative to tetramethylsilane (δ scale) using an internal standard from the solvents as follows: [D]chloroform (77.23 ppm), [D6]DMSO (39.5 ppm), [D6]benzene (128.39 ppm), [D3]acetonitrile (1.39, 118.69 ppm), [D8]THF (65.57 and 25.37 ppm). Boron-11 NMR (δ scale) spectra were obtained at 160.0 MHz on a 360-MHz Bruker AM spectrometer and referenced to $BF_3 \cdot Et_2O$ as an external standard. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA, and are reported as relative percentage of each element analyzed. X-ray structural analyses were performed at the DuPont Corporate Center for Analytical Science.

General Method for Carbene Dihydrogen Activation

Within the dry-box, the electrophile was dissolved in solvent in a Schlenk flask equipped with a septum and stir bar. In a separate Schlenk flask equipped with a stir bar and septum, carbene **1** was dissolved in solvent. Both flasks were removed from the dry-box. A cannula was used to connect the two flasks under a nitrogen atmosphere. The side-arm of the flask containing the carbene was attached to a hydrogen tank using high-pressure tubing. The side-arm of the flask containing the electrophile was connected to a Schlenk line. All tubing and connections, especially the septa, were secured using metal clamps. With the cannula exposed only to a nitrogen atmosphere above the reaction solutions, both flasks were then cooled to −60°C for 15 min. Next, the system was purged with hydrogen gas. The connection to the Schlenk line was then closed and the pressure of the system was increased to 25 psi for 30 min. To transfer the carbene solution to the electrophile solution, one end of the cannula was placed into the carbene solution and the pressure of hydrogen was increased to 0.3 MPa in the latter flask. Once transferred, the reaction mixture was left to stir at −60°C for 30 min before warming to room temperature. A white precipitate began to form on warming. The flask was purged with nitrogen and transferred into a dry-box where the solvent was removed under vacuum to provide crude reaction products.

Hydrogen Activation using $B(OMe)_3$

Carbene **1** (0.500 g, 2.77 mmol) in THF (6 mL) was added to $B(OMe)_3$ (0.32 mL, 2.8 mmol) in THF (6 mL) under pressure of hydrogen following the *General Method* above. After a period of 6 days at room temperature under 0.3 MPa of H_2, the solution began to turn yellow with a small amount of precipitate. ^1H and ^{13}C NMR indicated a mixture of asymmetric imidazolium species were formed, suggesting ‘abnormal’ carbene reactions with the electrophile.

Hydrogen Activation using 1-Adamantylborane · THF

Following the *General Method* above, carbene **1** (0.087 g, 0.49 mmol) in hexane (4 mL) was added to 1-adamantylborane · THF (**14**)[8a,b] (0.100 g, 0.485 mmol) in hexane (4 mL) under pressure of hydrogen. Proton NMR confirms the formation of aminal **8** as described below with decomposition of borane. δ_H (500 MHz, [D6]DMSO) 5.49 (s, 2H), 4.09 (s, 2H), 1.02 (s, 18H).

Hydrogen Activation using BBr_3

Following the *General Method* above, carbene **1** (0.500 g, 2.77 mmol) in hexane (6 mL) was added to $BBr_3 \cdot CH_2Cl_2$ (1 M, 2.8 mL, 2.8 mmol) in hexane (6 mL) under pressure of hydrogen at −60°C. The orange-white solid that formed was isolated by filtration and matched the literature spectra[7] of imidazolium bromide salt **17**. δ_H (500 MHz, [D6]DMSO) 9.06 (t, 1H, $^4J_{H–H}$ 1.7), 8.09 (d, 2H, $^4J_{H–H}$ 1.7), 1.61 (s, 18H). δ_C (125.5 MHz, [D6] DMSO) 132.78, 120.92, 60.12, 29.58.

Hydrogen Activation using Ph_3CBF_4

Following the *General Method* above, carbene **1** (0.100 g, 0.555 mmol) in THF (5 mL) was added to Ph_3CBF_4 (0.183 g, 0.555 mmol) in THF (5 mL) under pressure of hydrogen. The solids that were obtained from the reaction were washed three times with toluene (5 mL), which afforded the imidazolium salt **18** (0.075 g, 0.28 mmol, 50 % yield). δ_H (500 MHz, [D6]DMSO) 9.02 (s, 1H), 8.08 (s, 2H), 1.62 (s, 18H). ^{19}F NMR (470 MHz, [D6]DMSO) −148.22 (s). δ_C (125.5 MHz, [D6]DMSO) 132.62, 120.91, 60.10, 29.52. ^{11}B NMR (160 MHz, [D6]DMSO) −1.44 (s). $HCPh_3$ was isolated from the toluene phase and characterized by ^1H and ^{13}C NMR and TLC comparisons against an authentic sample (R_f 0.84 in 60:40 hexane/ethyl acetate).

Measurement of Imidazolium Borohydride 6 Equilibrium

Solid $NaHB(OMe)_3$ (0.030 g, 0.024 mmol) was added portionwise to a solution of imidazolium chloride **7** (0.051 g, 0.024 mmol) in [D3]acetonitrile (0.7 mL) in an NMR tube within the dry-box. After letting the mixture sit for 2 h at room temperature, the NMR was taken for analysis. The resulting mixture contained 8 % aminal **8** in acetonitrile.

Imidazolium Borohydride **6**: δ_H (500 MHz, [D3]acetonitrile) 9.26 (s, 1H), 7.74 (s, 2H), 1.69 (s, 18H), 1.67 (s, 9H), −0.15 (q, 1H, $^1J_{B–H}$ 81.3). δ_C (125 MHz, [D3]acetonitrile) 132.89, 115.66, 60.39, 48.01 (br), 25.95. ^{11}B NMR (160 MHz, [D3] acetonitrile) 3.08 (br, $^1J_{B–H}$ unresolved).

Synthesis of Aminal 8

Solid $LiAlH_4$ (0.524 g, 13.8 mmol) was slowly added portionwise to imidazolium salt **7** (3.000 g, 13.80 mmol) in THF (20 mL) via weigh-paper within the dry-box. The mixture was left to stir at room temperature overnight before it was filtered through Celite under nitrogen. Removal of THF under vacuum resulted in a clear colourless oil and white precipitate. The mixture was extracted with hexane to afford a clear colourless oil (1.755 g, 9.626 mmol, 70 % yield). δ_H (500 MHz, [D6] DMSO) 5.49 (s, 2H), 4.09 (s, 2H), 1.02 (s, 18H). δ_C (125.5 MHz, [D6]DMSO) 116.24, 67.47, 52.59, 26.89.

Synthesis of Imidazolium Borohydride 9

A solution of sodium borohydride (0.143 g, 3.77 mmol) in acetonitrile (10 mL) was added to a stirred suspension of 1,3-dimethylimidazolium chloride (0.5 g, 4 mmol) in acetonitrile (50 mL). A fine white precipitate was observed during addition. After stirring overnight at room temperature, all solids were removed from the solution by filtration and a white solid was collected by the removal of acetonitrile under vacuum. The white solid (0.37 g, 88 %) was recrystallized from a THF/toluene solution at −20°C. X-ray-quality crystals were grown by cooling an acetonitrile solution of **9** layered with toluene to −20°C for 24 h. δ_H (500 MHz, [D6]DMSO) 9.08 (s, 1H), 7.68 (s, 2H), 3.84 (s, 6H), −0.28 (q, 4H, $^1J_{B–H}$ 81.4). δ_H (500 MHz, [D3] acetonitrile) 8.64 (s, 1H), 7.33 (s, 2H), 3.83 (s, 6H), −0.21 (q, 4H, $^1J_{B–H}$ 81.4). δ_C (125.5 MHz, [D3]acetonitrile) 138.2, 124.8, 37.2. ^{11}B NMR (160 MHz, [D6]DMSO) −37.0 (quin, $^1J_{B–H}$ 81.4).

Synthesis of Aminal 11

Imidazolium salt **10** (2.120 g, 6.20 mmol) was added as a solid to $LiAlH_4$ (0.240 g, 6.32 mmol) dissolved in Et_2O. An immediate reaction was observed with the formation of a yellow solution and a precipitate. After letting the mixture stir for 2 h, Et_2O was removed under vacuum and replaced with toluene. The mixture was filtered to remove the precipitate and toluene was removed from the filtrate under vacuum to produce a pale-yellow solid (1.4 g, 4.6 mmol, 74 % yield). Mp 61–65°C. δ_H ([D8]THF) 6.79 (s, 4H), 5.60 (s, 2H), 4.94 (s, 2H), 2.33 (s, 12H), 2.19 (s, 6H). δ_C (125.5 MHz, [D6]DMSO) 140.28, 137.79, 135.74, 130.12, 117.33, 74.24, 20.85, 19.98.

Synthesis of Aminal 13

Imidazolium salt **12** (1.52 g, 4.07 mmol) was added as a solid portionwise to $LiAlH_4$ (0.174 g, 5.40 mmol) dissolved in Et_2O. An immediate reaction was observed with the formation of a white precipitate. After allowing the mixture stir for 3 h, Et_2O was removed from the filtrate under vacuum and replaced with benzene. The mixture was filtered to remove the precipitate and the toluene was removed under vacuum to produce a white solid (1.2 g, 3.5 mmol, 85 % yield). X-ray-quality crystals were grown by cooling a saturated toluene/hexamethyldisiloxane solution to −25°C. Mp 205–208°C. δ_H ([D8]THF) 5.46 (s, 2H, HC=C), 4.26 (s, 2H, N_2CH_2),2.03 (brs, 6H, C_3CH), 1.68 (brs, 12H, C_2CH_2), 1.67 (br (unresolved ab), 12H, C_2CH_2). δ_H (C_6D_6) 5.60 (s, 2H, HC=C), 4.45 (s, 2H, N_2CH_2), 1.93 (brs, 6H, C_3CH), 1.70 (brs, 12H, C_2CH_2), 1.52 (br (unresolved ab), 12H, C_2CH_2). δ_C (125.5 MHz, [D8]THF) 114.26, 63.58, 53.41, 40.37, 37.72, 30.67. ^{15}N NMR (30.414 MHz, [D8]THF) −293.47. (Anal. calc. for: C 81.60, H 10.12, N 8.28. Found: C 81.72, H 10.01, N 8.23 %.)

Hydrogen Gas Reduction of Triphenylmethanol to Triphenylmethane

Dry Ph_3COH (0.250 g, 0.960 mmol) and 3-Å molecular sieves (3.0 g) in dry Et_2O (2 mL) were placed into a Schlenk flask equipped with a stir bar and septum. Next, $HBF_{4(aq)}$ (48 %, 0.124 mL, 0.960 mmol) was added to the mixture via syringe. The white precipitate turned yellow on addition. The mixture was left to stir for 2 h at room temperature before it was cooled to −70°C. Vacuum was used to remove nitrogen from the system and the atmosphere was replaced with hydrogen via a hydrogen balloon. After stirring the mixture for 30 min, carbene **1** (0.208 g, 1.15 mmol) in dry Et_2O (3 mL) was added to the reaction via syringe. The reaction mixture turned cloudy from the light-brown precipitate that was formed. After stirring for 30 min at −70°C, the reaction was left to warm to room temperature over 2 h before the solids were collected by filtration and dried under vacuum. Proton NMR and comparison with an authentic sample by TLC (40 % ethyl acetate/hexane) confirmed the presence of both Ph_3COH (^1H NMR δ 7.22–7.03 ppm (m, 15H), 2.49 (s, 1H). R_f 0.68) and Ph_3CH (^1H NMR δ 7.52–7.27 (m, 15H), 5.47 (s, 1H). R_f 0.82) in a 6:1 ratio, as well as the imidazolium tetrafluoroborate salt **18**.

High-pressure Hydrogen Activation using $Fe(CO)_5$

Carbene **1** (0.540 g, 3.00 mmol) in THF (0.7 mL) was sealed in a glass ampoule under a nitrogen atmosphere. Within the dry-box, the sealed ampoule was carefully placed in a steel bomb containing $Fe(CO)_5$ (0.710 g, 3.62 mmol) in THF (3 mL) and a loose steel bar that could be used to break the ampoule with agitation once the entire vessel was sealed and pressurized. The bomb was sealed with a needle valve and taken outside the dry-box, where it was connected to a hydrogen cylinder and a Schlenk line using a three-way vacuum adaptor and high-pressure tubing. The bomb was cooled to -40°C and the nitrogen was removed by the vacuum line. Next, 1.8 MPa of H_2 was added to the cylinder. After 30 min at -40°C, the bomb was shaken vigorously in order to break the glass ampoule inside. The reaction was left at -40°C for 30 min with occasional agitation before warming to room temperature over 2 h. The bomb was transferred back into a dry-box where it was opened and the contents removed. The solids were filtered from the mixture and residual solvent removed from the filtrate under vacuum to afford a brown solid. The product mixture contains a 6:1 ratio of imidazolium acyl ferrate **20** to imidazolium hydrido ferrate **19**, which match the spectral properties of the individual components as described in the other procedures herein.

*Synthesis of Imidazolium Iron Hydride **19***

$K^+[HFe(CO)_4]^-$ (0.200 g, 0.962 mmol) was dissolved in THF (8 mL) under nitrogen. Next, imidazolium chloride **7** (0.208 g, 0.962 mmol) was added to the red solution via weighing paper under nitrogen flow. As the white powder began to dissolve, a clear colourless microcrystalline solid began to form on the side of the flask. The reaction was left to stir for 12 h before the mixture was filtered through Celite under nitrogen and the THF removed under vacuum to yield a red-purple solid (0.205 g, 0.585 mmol, 61 % yield). Mp 75–80°C (dec.) δ_H (500 MHz, [D6]DMSO) 9.05 (t, 1H, $^4J_{H-H}$ 1.67), 8.08 (d, 2H, $^4J_{H-H}$ 1.67), 1.62 (s, 18H), -8.96 (s, 1H).

*Synthesis of Imidazolium Acyl Ferrate **20***

Carbene **1** (1.725 g, 9.57 mmol) in THF (6 mL) was added to a 50-mL round-bottom flask containing $Fe(CO)_5$ (2.061 g, 10.5 mmol) in THF (6 mL) within the dry-box. The reaction was left to stir for 15 min, after which point a yellow precipitate formed. After stirring an additional 30 min, hexane (6 mL) was added to the mixture before the yellow precipitate was collected by vacuum filtration under nitrogen. The filtrate was washed with hexane (10 mL) and all residual solvents were removed under vacuum to afford a yellow powder (3.243 g, 8.62 mmol, 90 % yield). Crystals were grown by cooling a saturated acetonitrile solution to -20°C. Mp 120–122°C (dec.). δ_H (500 MHz, [D3]acetonitrile) 8.16 (d, 1H, $^4J_{H-H}$ 2.0), 7.88 (d, 1H, $^4J_{H-H}$ 2.0), 1.70 (s, 18H). δ_C (125 MHz, [D3]acetonitrile) 224.22, 221.08, 219.21, 210.66, 120.15, 117.24, 60.15, 28.72.

Accessory Publication

X-ray diffraction crystallographic data for the structures of **9**, **11** and **20** including *ORTEP* diagrams, fractional coordinates, thermal parameters and tables of bond lengths and angles (24 pages) is available from the publisher. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif (accessed 07/07/11). CCDC 830271, 830272 and 830273 contain the supplementary crystallographic data for this paper.

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