DOI: 10.1002/ejic.201100779

Experimental and Theoretical Studies of the Potential Interconversion of the Amine–Borane $iPr_2NH{\cdot}BH(C_6F_5)_2$ and the Aminoborane $iPr_2N{=}B(C_6F_5)_2$ Involving Hydrogen Loss and Uptake

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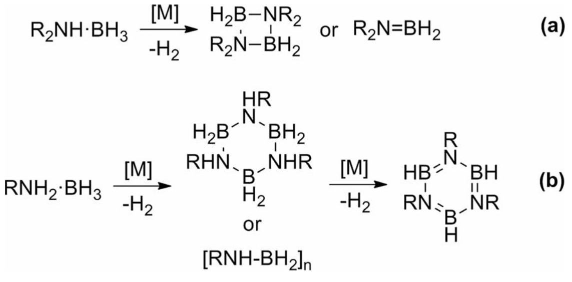
Keywords: Main group elements / Amines / Boranes / Dehydrogenation / Hydrogenation

The amine–borane adduct $iPr_2NH{\cdot}BH(C_6F_5)_2$ (**1**) and the aminoborane $iPr_2N{=}B(C_6F_5)_2$ (**2**) have been prepared and crystallographically characterised. Interconversion between the two compounds has been attempted using thermal and transition-metal-catalysed dehydrogenation and hydrogenation protocols and the overall reaction thermodynamics were probed by computational methods. Thermal dehydrogenation of **1** was found to yield **2**, together with uncharacterised by-products. Treatment of **1** with the carbene 1,3-di-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (**3**) under ambient conditions did not lead to the elimination of hydrogen, but instead to the loss of C_6F_5H to afford $iPr_2N{=}B(H)C_6F_5$ (**4**). Attempts to hydrogenate aminoborane **2** were unsuccessful with no reaction observed either thermally or in the presence of transition-metal catalysts. A computational study of the interconversion between compounds **1** and **2** indicated a thermodynamically unfavourable hydrogenation reaction, which was inverse to that demonstrated for the analogous phosphane–borane/phosphanylborane pair, $iPr_2PH{\cdot}BH(C_6F_5)_2$ (**5**) and $iPr_2P{-}B(C_6F_5)_2$ (**6**). The contrasting reactivity was attributed to the different N–B and P–B π-bond strengths in **2** and **6**, respectively.

Introduction

Lewis base adducts of borane are well-studied compounds, historically finding applications as reducing agents in organic synthesis.[1–3] Of these species, amine–borane adducts, $R_xNH_{3-x}{\cdot}BH_3$, are an interesting subclass that can exhibit unique reactivity due to the presence of both protic and hydridic hydrogen atoms. The elimination of dihydrogen from molecules of this type affords new intra- or intermolecular boron–nitrogen bonds, and a wide range of catalysts have now been reported which can promote such processes under mild conditions (Scheme 1).[3]



Scheme 1. Products of catalytic dehydrogenation of (a) secondary and (b) primary amine–borane adducts.

Initial studies in the area of catalytic amine–borane dehydrogenation focussed primarily upon the use of rhodium complexes as precatalysts, where the mechanism was suggested to occur via reduction of the precatalyst to either colloidal rhodium, Rh_{4-6} clusters or nanoparticles.[4–10] More recently, the range of metal complexes reported to be capable of catalytically dehydrogenating amine–boranes has been significantly expanded. For example, homogeneous systems based on Rh,[11] Ru,[12,13] Re,[14] Ni[15,16] and Ir[17–19] are now known, along with those based on Group 2 and 4 metals,[20–25] and systems based on p-block metals.[26] In addition, photoactivated catalysts of the first-row transition metals have also recently been reported.[27–29] Mechanistic insights into metal-catalysed dehydrocoupling processes have also been provided through various studies demonstrating the coordination of amine- and aminoboranes to metal centres,[11,30–39] with the isolation of species implicated in the catalytic cycle.[40]

Transition-metal-catalysed dehydrocoupling of amine–borane adducts generally affords aminoboranes and borazines, with the products defined by both the choice of substituents on the adduct and the catalyst. These factors have recently been exploited in the preparation of polyaminoboranes, a novel class of inorganic polymers, which can be regarded as the boron–nitrogen analogues of polyolefins.[19,41] A significant driving force behind the development of amine–borane dehydrocoupling processes is the potential application of such adducts for hydrogen storage, with ammonia–borane, $NH_3{\cdot}BH_3$, attracting particular interest due

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100779.

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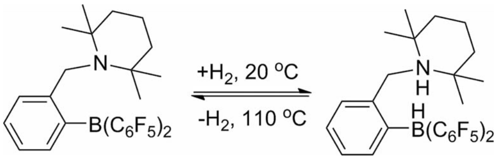
to its high hydrogen content (19.6 wt.-%).[42,43] However, there are no reported examples of the resulting aminoboranes or borazines reacting directly with dihydrogen in the reverse reaction, although chemical regeneration may be achieved by using other reagents.[44–48] The group of Rieger, however, have reported a compound containing tethered amine and borane moieties that is capable of undergoing co-operative hydrogenation in a reversible fashion (Scheme 2).[49] The thermodynamics of hydrogen activation in this system have since been studied computationally by Pápai and co-workers, with ΔG for the hydrogenation in toluene calculated at $-12.5\ \mathrm{kcal\,mol^{-1}}$.[50] It should be noted, however, that in the context of aminoborane regeneration, hydrogen loss and uptake by this particular system does not involve making and breaking B–N bonds.



Scheme 2. Reversible H_2 activation by an *ansa*-aminoborane.[49]

Due to the interest in aminoborane regeneration, we have previously studied the thermodynamic parameters for hydrogen loss/uptake from amine–boranes/aminoboranes computationally, primarily in the gas phase.[51] The free energy of dehydrogenation for simple adducts was shown to be small and negative in character, with the entropic contribution due to hydrogen release driving dehydrogenation. The major factor in defining the reaction enthalpy of dehydrogenation/hydrogenation was also demonstrated to be the strength of the B–N bond(s) in the respective reactants and products, generally with aminoborane hydrogenation becoming increasingly favourable with electron-donating groups at nitrogen and electron-withdrawing groups at boron. However, solvent effects were also demonstrated to have a significant influence on the thermodynamics of dehydrogenation. Calculations on this effect indicated variations in ΔG of up to $10\ \mathrm{kcal\,mol^{-1}}$ relative to the gas phase values; a change which in some cases was of sufficient magnitude to reverse the sign of ΔG.[51]

In 2008, Stephan and co-workers reported the irreversible activation of dihydrogen by the phosphanylborane systems, $t\mathrm{Bu_2P\text{-}B(C_6F_5)_2}$ and $\mathrm{Cy_2P\text{-}B(C_6F_5)_2}$ (Scheme 3).[52,53]

$$\mathrm{R_2P\text{-}B(C_6F_5)_2} \xrightarrow[25\ ^{\circ}\mathrm{C}]{4\ \mathrm{bar\ H_2}} \mathrm{R_2PH{\cdot}BH(C_6F_5)_2} \qquad \mathrm{R = Cy}, t\mathrm{Bu}$$

Scheme 3. Hydrogenation of $\mathrm{R_2P\text{-}B(C_6F_5)_2}$.[52,53]

Aminoboranes and phosphanylboranes are formally isoelectronic, although the bonding within these systems is markedly different, with the 3p phosphorus centre leading to poorer orbital overlap with the vacant 2p-orbital at boron, and more significant lone-pair character at phosphorus.[54] The demonstration of hydrogen uptake by phosphanylboranes, coupled with our own computational studies of aminoborane hydrogenation provided the impetus for our current investigation. In this manuscript we report the synthesis and characterisation of the amine–borane adduct $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (**1**) and the corresponding aminoborane $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$ (**2**) and probe their dehydrogenation and hydrogenation chemistry, respectively. These species incorporate electron-donating groups at nitrogen and electron-withdrawing groups at boron to help produce favourable thermodynamics for reversible hydrogenation.[51] DFT studies on the thermodynamics of dehydrogenation/hydrogenation are also presented for the amine- and aminoborane using identical methods to those applied by Stephan and co-workers for phosphane–boranes/phosphanylboranes,[52,53] allowing for a direct comparison between the related systems.

Results and Discussion

(a) Synthesis of $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1)

The synthesis of the amine–borane **1** was carried out by slow addition of neat diisopropylamine to a toluene solution of $\mathrm{HB(C_6F_5)_2{\cdot}SMe_2}$ at –78 °C, in analogous fashion to amine–borane synthesis from $\mathrm{BH_3{\cdot}SMe_2}$ (Scheme 4).[10] Warming to 20 °C and removal of the solvent gave the product as a white solid in 92% yield and high purity, with additional purification possible by recrystallisation from toluene/hexanes.

$$\mathrm{(C_6F_5)_2BH{\cdot}SMe_2} + i\mathrm{Pr_2NH} \longrightarrow \underset{\mathbf{1}}{i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}} + \mathrm{SMe_2}$$

Scheme 4. Synthesis of $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (**1**).

Analysis of the product by ^{11}B NMR spectroscopy in $\mathrm{CDCl_3}$ showed a single peak at δ = –14.8 ppm, which split into a doublet on proton coupling ($^1J_{\mathrm{BH}}$ = 101 Hz). These data are consistent with a tetra-coordinate boron centre with a single hydrogen substituent.[55] ^{1}H NMR spectroscopy similarly showed the expected peaks for two closely related isopropyl groups [δ = 3.51 (2 H), 1.34 (6 H), 1.26 (6 H) ppm for 2 × CH and 4 × $\mathrm{CH_3}$ groups, which were present as a multiplet and doublets, respectively] and single N–H and B–H hydrogen atoms (δ = 4.60 and 3.64 ppm, respectively). ^{13}C NMR spectroscopy again showed two peaks at δ = 51.5 and 19.9 ppm corresponding to resonances of the isopropyl groups. However, no resonances were apparent that corresponded to the carbon atoms of the aromatic rings; a phenomenon which has been observed before for the related $\mathrm{Ph(Me)N{=}B(C_6F_5)_2}$ by Knüppel and co-workers.[56] ^{19}F NMR spectroscopy, however, was consistent with the incorporation of pentafluorophenyl units, with three resonances at δ = –133.1 (singlet), –157.7 (triplet, J_{FF} = 19.7 Hz) and –162.8 (broad singlet) ppm. High-resolution electrospray ionisation mass spectrometry (ESI-MS) confirmed the successful synthesis of the desired compound, $[\mathrm{M-H}]^-$ = 446.1156 Da, with chemical impact ionisation mass spectrometry indicating the presence of the expected fragments.

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Crystals of **1** suitable for single-crystal X-ray diffraction were grown from toluene/hexanes at –40 °C (Figure 1). The compound crystallised as colourless plates in the triclinic space-group $P\bar{1}$ with a single molecule per asymmetric unit. Adjacent molecules within the unit cell were in close proximity to one another, as exemplified by the intermolecular C(10)···F(2) separation of 3.231 Å, and the atom connectivity within each molecule confirmed the formulation based on spectroscopic methods. The angles around B(1) and N(1) summed to 438 and 448°, respectively, which were consistent with the expected tetrahedral geometries at each centre. The B(1)–N(1) bond length of 1.628(3) Å falls within the range observed for both tertiary amine–secondary borane adducts [1.578(8)–1.676(3) Å][57–60] and secondary amine–tris(pentafluorophenyl)borane adducts [1.613(3)–1.653(4) Å],[61–64] and is therefore unremarkable. The C(1)–N(1)–B(1)–C(7) dihedral angle of 179.32° inferred a staggered conformation upon the molecule, as expected on the basis of steric arguments.

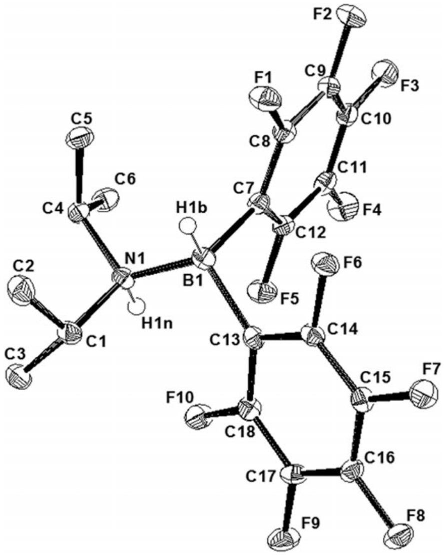

Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: N(1)–B(1) 1.628(3), N(1)–C(1) 1.537(3), N(1)–C(4) 1.536(3), C(7)–B(1) 1.640(4), C(13)–B(1) 1.632(4), H(1N)–N(1)–C(4) 103.2(14), H(1N)–N(1)–C(1) 103.9(14), C(4)–N(1)–C(1) 111.26(18), H(1N)–N(1)–B(1) 107.7(13), C(4)–N(1)–B(1) 117.91(18), C(1)–N(1)–B(1) 111.46(18), H(1B)–B(1)–N(1) 107.1(10), H(1B)–B(1)–C(13) 109.9(11), N(1)–B(1)–C(13) 111.7(2), H(1B)–B(1)–C(7) 108.6(11), N(1)–B(1)–C(7) 111.82(19), C(13)–B(1)–C(7) 107.74(19).

This geometry has obvious implications with regard to the intramolecular elimination of hydrogen from this molecule. Should the solid-state structure persist in solution, direct combination of the proton and hydride would be impossible without rotation around the B–N bond into an energetically disfavoured conformation. It should be noted, however, that thermal elimination of hydrogen from some amine–borane adducts is believed to occur via an intermolecular route followed by rapid dissociation of the dimeric product.[10,65,66]

(b) Synthesis of $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$ (2)

The preparation of the corresponding aminoborane **2** was attempted by reaction of in situ prepared $\mathrm{ClB(C_6F_5)_2{\cdot}SMe_2}$ with Li[N*i*Pr$_2$] in Et$_2$O at –78 °C (Scheme 5). Upon warming to 20 °C the solvent was removed under vacuum and the product then extracted into hexanes and filtered. The solvent was then removed under high vacuum, and the resulting solids recrystallised from the minimum quantity of hexanes to afford **2** as an off-white solid in 77% yield.

$$\mathrm{Li[N}i\mathrm{Pr_2]} + \mathrm{ClB(C_6F_5)_2{\cdot}SMe_2} \longrightarrow \underset{\mathbf{2}}{i\mathrm{Pr_2N{=}B(C_6F_5)_2}} + \mathrm{LiCl}$$

Scheme 5. Synthesis of *i*Pr$_2$N=B(C$_6$F$_5$)$_2$ (**2**).

The ^{11}B NMR spectrum of the product showed a single signal at δ = 33.2 ppm, which remained as a singlet on proton coupling. The shift and multiplicity of this signal are consistent with the postulated trigonal planar boron environment with no hydrogen substituents.[55] ^{1}H NMR spectroscopy of the product showed two peaks at δ = 3.32 and 0.90 ppm, which appeared as a septet and a doublet, respectively, and were consistent with the presence of two chemically equivalent isopropyl groups. The ^{13}C NMR spectrum was also consistent with this assignment with peaks apparent at δ = 51.2 and 23.3 ppm. The equivalence of the two isopropyl groups is also in line with the expected planar molecular structure. As for amine–borane **1**, no resonances were observed for the carbon atoms of the aromatic rings, but ^{19}F NMR spectroscopy confirmed the inclusion of the pentafluorophenyl moieties within the product structure.

Recrystallisation of **2** from hexanes at –40 °C afforded crystals suitable for single-crystal X-ray diffraction, which confirmed the formulation based on spectroscopic data

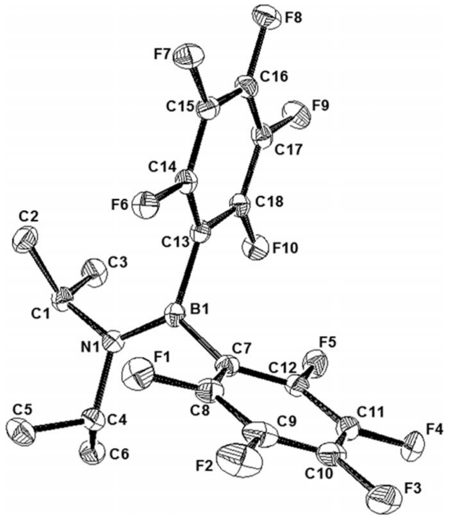

Figure 2. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: N(1)–B(1) 1.376(4), N(1)–C(1) 1.493(4), N(1)–C(4) 1.498(4), C(7)–B(1) 1.603(5), C(13)–B(1) 1.600(5), B(1)–N(1)–C(1) 125.3(3), B(1)–N(1)–C(4) 121.2(3), C(1)–N(1)–C(4) 113.5(2), N(1)–B(1)–C(13) 124.7(3), N(1)–B(1)–C(7) 121.6(3), C(13)–B(1)–C(7) 113.6(3).

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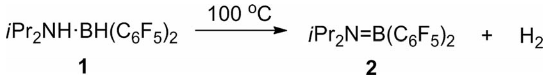
(Figure 2). The compound crystallised as colourless needles in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit.

As observed in the crystals of **1**, adjacent molecules were packed in close proximity to one another, leading to a short intermolecular separation of 2.961 Å between F(5) and F(8). The angles around B(1) and N(1) both summed to 360° and the C(1)–N(1)–B(1)–C(7) dihedral angle was 179.94°, all of which were consistent with the planar C_2BNC_2 core expected for monomeric aminoboranes. Furthermore, the planes defined by the two C_6F_5 groups were tilted with respect to this core (78.39 and 81.25°), which would preclude any substantial orbital overlap between the electron-deficient π-system and the B=N bond. This orientation, however, is what would be expected to minimise steric interactions between the two rings. The presence of bulky substituents on both B and N was also manifested in a narrowing of the C–B–C and C–N–C angles (113.60 and 113.48°, respectively) away from the ideal value (120°). The B=N bond length of 1.376(4) Å is within the range formed by unconstrained aminoboranes containing organic substituents at both B and N [1.365(5)–1.441(2) Å].[67–73] In addition, this represents a significant length contraction of 15% from **1**, which is consistent with an increase in bond order and change in hybridisation state.

(c) Studies of the Interconversion between 1 and 2

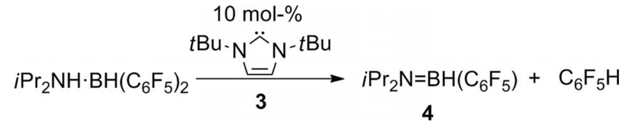
(i) Dehydrogenation of 1: Generally dehydrogenations of amine–borane adducts can be carried out under either thermal or catalytic conditions with the relative kinetics and thermodynamics of the process being influenced by the substitution pattern at nitrogen and boron. Initially, dehydrogenation of **1** was attempted in toluene solution at 50 °C, with no conversion of **1** apparent over 24 h. Heating an identical solution to 100 °C for 70 h was then attempted. Under these conditions the adduct was shown by ^{11}B and ^{19}F NMR analysis to be unstable, partially dehydrogenating to produce the aminoborane **2**, in low yield (23%), along with other unidentified boron-containing products which proved to be inseparable from the desired product (Scheme 6).



Scheme 6. Thermal dehydrogenation of **1**.

Attempts to prepare the aminoborane under milder conditions via the use of transition metal catalysts were unsuccessful, with no dehydrogenative reaction prevailing at 20 °C with $[Rh(\mu\text{-}Cl)(cod)]_2$ (cod = 1,5-cyclooctadiene), colloidal Rh,[10,74] "Cp_2Ti",[23] IrH_2POCOP (POCOP = κ^3-1,3-$(PtBu_2)_2C_6H_3$)[19,75] or the Fagnou catalyst system (KO*t*Bu and $RuCl_2L_2$ [L = $iPr_2PCH_2CH_2NH_2$]).[12] We postulate that this is due to two main factors which prevent the catalysis. Firstly, the adduct is highly sterically encumbered, with large groups at both boron and nitrogen. These are likely to impair coordination to coordinatively unsaturated metal centres, particularly those with their own inherent steric demands, i.e. IrH_2POCOP. Secondly, the presence of highly electron-withdrawing pentafluorophenyl groups at boron is likely to significantly reduce the hydridic character of the hydrogen atoms at boron, certainly making hydrogen loss less favourable, but also possibly making B–H activation at a metal centre less likely. Both factors are likely to result in a high kinetic barrier to dehydrogenation, leading to negligible conversion under ambient conditions, despite the favourable thermodynamics of the desired transformation (vide infra).

Following only moderate success in thermal and metal-catalysed dehydrogenation of amine–borane **1**, alternative approaches were also investigated. Stephan and co-workers previously demonstrated the elimination of pentafluorobenzene from secondary amine adducts of tris(pentafluorophenyl)borane, i.e. $R_2NH{\cdot}B(C_6F_5)_3$ (R = Et, *t*Bu), using a carbene as a catalytic Lewis base.[63] We therefore investigated the employment of the same system with **1**, in which elimination of H_2 might be expected to be feasible and possibly entropically more favourable than elimination of pentafluorobenzene. Using a 10-mol-% loading of 1,3-di-*tert*-butyl-4,5-dihydroimidizol-2-ylidene (**3**), we observed complete consumption of the adduct by ^{11}B NMR spectroscopy over 24 h. This was accompanied by the growth of a new peak at δ = 33.2 ppm, which appeared as a doublet in the proton-coupled spectrum ($^1J_{BH}$ = 129 Hz). The product of this reaction was identified as $iPr_2N{=}BH(C_6F_5)$ (**4**), produced via elimination of pentafluorobenzene, which was also detected in the ^1H NMR spectrum as a complex multiplet centred at 5.7 ppm when the reaction was repeated in C_6D_6 (Scheme 7). ^1H, ^{13}C and ^{19}F NMR spectra of the reaction product, a colourless oil, were also consistent with the assigned structure.



Scheme 7. Reaction of amine–borane adduct **1** with carbene **3**.

Previous work has also demonstrated the use of frustrated Lewis pairs (FLPs)[76] in stoichiometric[77,78] and catalytic[25] quantities in the dehydrogenation of various amine–borane adducts. We therefore attempted the dehydrogenation of amine–borane **1** using the combination of nBu_3SnOTf/TMP (TMP = 2,2,6,6-tetramethylpiperidine) at 20 °C. Over 65 h at this temperature however, no reaction occurred, with only unreacted **1** being observed in the ^{11}B NMR spectrum. Again, in this case it is likely that the lack of reactivity can be attributed to the reduced hydridic character of the hydrogen at boron relative to those found in adducts of BH_3, which would hinder hydride abstraction by the Lewis acid.

(ii) Hydrogenation of 2: Of perhaps greater interest than the dehydrogenation of the amine–borane, **1**, was the potential hydrogenation of aminoborane **2**. Treatment of a toluene solution of **2** with 4 bar of H_2 at 20 °C, conditions

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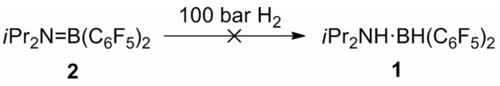
closely related to those employed in the hydrogenation of $t\mathrm{Bu_2P\text{-}B(C_6F_5)_2}$ and $\mathrm{Cy_2P\text{-}B(C_6F_5)_2}$,[79] resulted in no reaction after 24 h. Despite attempted hydrogenations at 20 °C and 100 bar H_2 over 24 h and later 430 h, and at 100 °C over 24 h at the same pressure, there was no evidence for the hydrogenation of **2** by ^{11}B NMR spectroscopy (Scheme 8).



$$i\mathrm{Pr_2N{=}B(C_6F_5)_2}\ \xrightarrow{100\ \mathrm{bar}\ H_2}\ i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$$

2 **1**

Scheme 8. Attempted hydrogenation of aminoborane **2**.

In addition to the initial hydrogenation experiments, it was also of interest to investigate the potential catalytic hydrogenation of aminoborane **2**. Although no literature precedent for such hydrogenations exists, examples are of course abundant for alkenes, the formally isoelectronic C=C analogues. Transition-metal-catalysed olefin hydrogenation is an exceptionally well-developed field within which various metals have now been shown to be effective,[80] with the recent focus mainly on enantioselective hydrogenations.[81,82] With a view to probing the catalytic hydrogenation of **2** we selected representative examples of homo- and heterogeneous rhodium catalysts, $\mathrm{Rh(PPh_3)_3Cl}$ (Wilkinson's catalyst),[83] and $\mathrm{Rh/Al_2O_3}$, for initial investigation. Catalytic alkene hydrogenation can often be achieved at room temperature under 1 bar or less of H_2,[83,84] but in our own system, no reaction prevailed using 3 mol-% of either catalyst at 20 °C over 24 h under 1 or 100 bar of H_2 according to analysis by ^{11}B NMR spectroscopy.

(d) DFT Calculations

With a view to understanding the experimentally observed behaviour of **1** and **2** towards dehydrogenation and hydrogenation, respectively, we performed DFT calculations on this system. We have previously reported related data for these compounds as part of a larger study aimed at correlating the substituents at boron and nitrogen with the thermodynamic reversibility of amine–borane dehydrogenation.[51] In order to permit a direct comparison with the phosphane–borane systems described by Stephan and co-workers (Scheme 3) and thereby to promote understanding of the markedly different thermodynamic behaviour of the two systems, we performed the DFT calculations reported here using the same method, and at the same level of theory.[52,53] In instances where particular data has not been reported for the phosphorus-containing compounds, it has been calculated for the direct analogues of **1** and **2**, namely $i\mathrm{Pr_2PH{\cdot}BH(C_6F_5)_2}$ (**5**) and $i\mathrm{Pr_2P\text{-}B(C_6F_5)_2}$ (**6**).

The structures of both **1** and **2** were optimised at the MPW1K level of theory and all pertinent bond lengths and angles were in good agreement with those obtained by X-ray crystallographic methods (see Supporting Information, section 6). This was exemplified by the B–N bond lengths (1.626 and 1.384 Å for **1** and **2**, respectively) and gross geometries, as expressed by the calculated H–N–B–H and C–B–N–C dihedral angles. The former agree to within 3σ of those determined experimentally, and the latter (175.3 and 179.9° for **1** and **2**, respectively) are also in good agreement (<4% deviation).

Calculations on the dehydrogenation thermodynamics of **1** to yield **2** indicate that this process is favoured under standard conditions with ΔG = –5.6 kcal mol^{-1} (Table 1). Furthermore, this value would be expected to become more negative with increasing temperature, due to the positive ΔS term that results from the liberation of H_2. In this sense, the calculations are broadly in line with the observed results, although at elevated temperatures alternative reaction pathways clearly compete with dehydrogenation of **1**.[85]

Table 1. Thermodynamics of hydrogen release from **1** and **5**.[a]

	$\mathbf{1} \to \mathbf{2} + H_2$	$\mathbf{5} \to \mathbf{6} + H_2$
$\Delta E_{\mathrm{reaction}}$	2.7	31.0
$\Delta H_{\mathrm{reaction}}$	4.9	33.1
$\Delta G_{\mathrm{reaction}}$	–5.6	22.7
ΔH formation π-bond	–29.7	–16.6

[a] All energies are in kcal mol^{-1}, gas phase at 1 bar. ΔG was calculated at 298.15 K. ΔE is the zero-point-corrected electronic energy, and was calculated at 0 K.

The data for **1** should be contrasted with that calculated for the dehydrogenation of **5** to afford **6**, which is unfavourable with ΔG = 22.7 kcal mol^{-1}. Consistent with this result is the reported reverse reaction for $t\mathrm{Bu_2P\text{-}B(C_6F_5)_2}$, to yield $t\mathrm{Bu_2PH{\cdot}BH(C_6F_5)_2}$, which occurs over 2 d at 60 °C.[52] Although no free energy value was reported for this process, the enthalpy change was calculated (ΔH = –41.4 kcal mol^{-1})[53] and found to be broadly in agreement with that for the *i*Pr analogue (ΔH = –33.1 kcal mol^{-1}).

The key to understanding the contrasting thermodynamics of these amine and phosphane–borane dehydrogenation reactions lies in the relative strengths of the σ-bonds in the starting materials and the π-bonds of the dehydrogenated products. While the σ-bonds are of similar strength for both adducts (ΔH_σ = –29.0 kcal mol^{-1} for **1**, and –32.0 kcal mol^{-1} for **5**), (Table 2), the π-bond[86] of the phosphanylborane **6** is much weaker (ΔH_π = –16.6 kcal mol^{-1}),[87] leading to an overall relative stabilisation of the phosphane–borane **5**. This is not the case for the aminoborane, where the strength of the π-bond (29.7 kcal mol^{-1}) is almost the same as that of the σ-bond in the amine–borane. The reduced bond energy for the P–B π-bond, when compared to that for N–B, may be explained by a combination of poorer overlap of the 3p-orbital on phosphorus, relative to the 2p-orbital on nitrogen, with the 2p-orbital on boron [see Supporting Information, Figure SI1; for comparison of molecular orbitals (MOs) comprising the π-bonds in **2** and **6**], and the large

Table 2. Thermodynamics of σ-bond formation in **1** and **5**.[a]

	1	**5**
ΔH formation σ-bond	–29.0	–32.0

[a] All energies in kcal mol^{-1}, gas phase.

barrier to inversion at phosphorus. Both factors result in an increased lone pair character at phosphorus, and also therefore, reduced P–B π-bonding.[54]

Stephan and co-workers note that, based on their own calculations, the π-bond is very much polarised towards the phosphorus atom in $t\mathrm{Bu_2P{-}B(C_6F_5)_2}$ and a similar finding has previously been reported for $t\mathrm{Bu_2P{-}B(CF_3)_2}$.[52,88] The limited participation of the boron 2p-orbital in this MO suggests that it would dominate the corresponding antibonding orbital, enabling coordination of H_2 to boron. Indeed, the authors calculated the activation energy for a hydrogenation that proceeded in this manner and stated that it was in reasonable agreement with the observed rate.[52] It is noteworthy that such an interaction is less likely in aminoboranes, as the greater participation of the boron 2p-orbital in B=N π-bonding would destabilise H_2 binding in the transition state.

Given the favourable thermodynamics for the dehydrogenation of **1** to give **2**, unfavourable kinetics clearly play a significant role in the experimentally observed chemistry. It would be expected that either inter- or intramolecular pathways would be hindered by the bulky substituents at N and B, which prevent close approach between molecules, or rotation about the B–N bond so as to bring both hydrogen atoms into close proximity.

Conclusions

The amine–borane adduct, $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (**1**) and the aminoborane $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$ (**2**) were prepared, with both species isolated in high yields. Dehydrogenation of the amine–borane to the corresponding aminoborane was found to be possible at 100 °C, although this also resulted in the formation of other unidentified products. Despite screening common dehydrocoupling catalysts, this transformation could not be achieved in a catalytic manner. We attribute the sluggish reactivity to a combination of the high steric bulk of the adduct itself, which may impair coordination to catalytic centres, and also to deactivation of the hydrides at boron due to the electron-withdrawing effect of the pentafluorophenyl groups. Hydrogenation of the aminoborane **2** was also attempted without success under a variety of thermal and catalytic conditions.

A theoretical study of the amine–borane/aminoborane system revealed a thermodynamically unfavourable hydrogenation reaction, the opposite to the situation found for the analogous phosphane–borane/phosphanylborane system. The calculations indicated that the lack of reactivity of the aminoborane under conditions where analogous phosphanylboranes are hydrogenated can be attributed primarily to the different relative strengths of the N–B and P–B π-bonds in aminoborane **2** and phosphanylborane **6**.

Experimental Section

General: All manipulations were carried out under an atmosphere of nitrogen gas using standard vacuum line and Schlenk techniques, or under an atmosphere of argon within an MBraun glovebox. All solvents were dried via a Grubbs-type solvent purification system. Deuterated solvents were purchased from Sigma Aldrich and distilled from potassium (C_6D_6) or CaH_2 ($CDCl_3$). Diisopropylamine was purchased from Sigma Aldrich and distilled from CaH_2 prior to use. $\mathrm{[Rh(\mu\text{-}Cl)(cod)]_2}$, $\mathrm{Cp_2TiCl_2}$ and dichlorobis[2-(diisopropylphosphanyl)ethylamine]ruthenium were purchased from Sigma Aldrich and used without further purification. Dihydrogen was purchased from BOC in 99.995% purity and used as received. $\mathrm{IrH_2POCOP}$[75] and $\mathrm{HB(C_6F_5)_2{\cdot}SMe_2}$[89] were synthesised via literature methods. $\mathrm{B(C_6F_5)_3}$ was synthesised via the method of Lancaster and co-workers and sublimed at 100 °C at 2×10^{-2} mbar prior to use.[90] 1,3-Di-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (**3**) was synthesised via deprotonation of the corresponding imidazolium $\mathrm{BF_4^-}$ salt with a stoichiometric quantity of KO*t*Bu in THF, before extracting into toluene and removing the solvent.

NMR spectra were recorded with JEOL JNM-ECP300/400 or JNM-LA300 spectrometers. Chemical shifts were reported relative to residual solvent peaks (^{1}H and ^{13}C) or to external standards: $\mathrm{CFCl_3}$ (^{19}F); $\mathrm{BF_3{\cdot}Et_2O}$ (^{11}B). Elemental analysis was performed with a Eurovector EA 3000 Elemental Analyser by Desmond Davis of the University of Bristol Microanalysis Laboratory. ESI mass spectra were recorded with a Bruker Daltonics Apex IV Fourier-transform Ion Cyclotron resonance mass spectrometer and EI and CI mass spectrometry were carried out with a VG Analytical AutoSpec mass spectrometer, all at the University of Bristol.

X-ray Structural Characterisation: Diffraction data were collected with a Bruker-Nonius KappaCCD using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were integrated and scaled using the Denzo-SMN package.[91] The structures were solved and refined with the SHELXTL-PC V6.1 software package.[92] Refinement was by full-matrix least-squares on F_o^2 using all data (negative intensities included). Molecular structures are presented with thermal ellipsoids at a 30% probability level and all hydrogen atoms attached to carbon are omitted for clarity. In all structures, hydrogen atoms bonded to carbon were included in calculated positions and treated as riding atoms, whereas those attached to boron or nitrogen were located and refined with isotropic thermal parameters.

$i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1): To a solution of $\mathrm{HB(C_6F_5)_2{\cdot}SMe_2}$ (1.00 g, 2.45 mmol) in toluene (30 mL) at –78 °C was added dropwise neat $i\mathrm{Pr_2NH}$ (0.25 g, 2.45 mmol). The mixture was stirred at –78 °C for 30 min before warming to 20 °C and stirring for a further 1 h. The solvent was then removed under high vacuum to yield the product as an off-white solid. X-ray quality crystals of **1** were attained by recrystallisation from toluene/hexane at –40 °C. Yield: 1.00 g, 92%. ^{11}B NMR (96 MHz, $CDCl_3$): δ = –14.8 [d, $^1J_{BH}$ = 101 Hz, $\mathrm{BH(C_6F_5)_2}$] ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.60 (br. s, 1 H, N-H), 3.51 (multiplet, 2 H, C-H), 1.34 (d, $^3J_{HH}$ = 6.61 Hz, 6 H, CH_3), 1.26 (d, $^3J_{HH}$ = 6.97 Hz, 6 H, CH_3) ppm. ^{1}H {^{11}B} NMR (300 MHz, $CDCl_3$): δ = 4.60 (br. s, 1 H, N-H), 3.64 (s, 1 H, BH), 3.51 (sept, $^3J_{HH}$ = 6.79 Hz, 2 H, C-H), 1.34 (d, $^3J_{HH}$ = 6.61 Hz, 6 H, CH_3), 1.26 (d, $^3J_{HH}$ = 6.97 Hz, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.5 (s, CH), 19.9 (s, CH_3) ppm. ^{19}F NMR (283 MHz, $CDCl_3$): δ = –133.1 (s, C_6F_5), –157.7 (t, J_{FF} = 19.7 Hz, C_6F_5), –162.8 (br. s, C_6F_5) ppm. MS (ESI$^-$): *m*/*z* (%) = 446.1156 (5) $[M - H]^-$. MS (CI$^+$): *m*/*z* (%) = 345.0 (10) $[M - i\mathrm{Pr_2NH} - H]^+$, 169.0 (47) $[\mathrm{H_2C_6F_5}]^+$, 102.1 (97) $[i\mathrm{Pr_2NH_2}]^+$, 86.1 (100) $[i\mathrm{Pr_2NH} - \mathrm{CH_3}]^+$. $\mathrm{C_{18}H_{16}BF_{10}N}$ (447.12): calcd. C 48.35, H 3.61, N 3.13; found C 49.31, H 3.52, N 3.07.

$i\mathrm{Pr_2N{=}B(C_6F_5)_2}$ (2): To a solution of $\mathrm{HB(C_6F_5)_2{\cdot}SMe_2}$ (1.00 g, 2.45 mmol) in Et_2O (5 mL) was added dropwise a 2 M solution of

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HCl in Et_2O (1.22 mL, 2.45 mmol) at 0 °C. The mixture was then stirred for 1 h before warming to 20 °C and stirring for 16 h. All volatiles were then removed under vacuum, with a view to removing any residual HCl, yielding a colourless oil which was immediately redissolved in Et_2O (5 mL). A solution of lithium diisopropylamide (2.44 mmol) in Et_2O (5 mL) was prepared and added dropwise to the mixture at –78 °C. The reaction mixture was stirred for 30 min before warming to 20 °C and stirring for a further 2 h. The reaction was then monitored by ^{11}B NMR spectroscopy, indicating complete consumption of the starting material, and 84% conversion to $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$. The solvent was removed under high vacuum to yield an off-white solid, which was extracted with hexanes (50 mL), and filtered through glass-fibre filter paper, before the solvent was once again removed yielding the desired product as a white solid. The product was recrystallised from the minimum volume of hexanes at –40 °C, which produced crystals suitable for X-ray diffraction. Yield: 0.84 g, 77%. ^{11}B NMR (96 MHz, C_6D_6): δ = 33.2 [s, $B(C_6F_5)_2$] ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 3.32 (sept, $^3J_{HH}$ = 6.79 Hz, 2 H, C-H), 0.90 (d, $^3J_{HH}$ = 6.79 Hz, 12 H, CH_3) ppm. ^1H {^{11}B} NMR (300 MHz, C_6D_6): δ = 3.32 (sept, $^3J_{HH}$ = 6.79 Hz, 2 H, C-H), 0.90 (d, $^3J_{HH}$ = 6.79 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 51.2 (s, CH), 23.3 (s, CH_3) ppm. ^{19}F NMR (283 MHz, C_6D_6): δ = –130.3 (s, C_6F_5), –153.0 (t, J_{FF} = 20.56 Hz, C_6F_5), –161.1 (br. s, C_6F_5) ppm. MS (CI^+): m/z (%) = 446.1140 (4) $[M + H]^+$, 430.2 (43) $[M – Me]^+$, 278.2 (32) $[M – C_6F_5]^+$, 93.1 (100) [Toluene (Solvent)]. $C_{18}H_{14}BF_{10}N$ (445.11): calcd. C 48.57, H 3.17, N 3.15; found C 49.04, H 3.63, N 3.59.

Attempted Thermal Dehydrogenation of $i\mathbf{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1): A solution of $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (0.05 g, 0.11 mmol) in toluene (3 mL) was heated to 50 °C for 24 h before analysis by ^{11}B NMR spectroscopy, which indicated that no reaction had ocurred. The solution was then heated to 100 °C for 70 h, before further analysis by ^{11}B NMR spectroscopy. ^{11}B NMR (96 MHz, Toluene): δ = 32.5 [br. s, $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$, 23%], 19.3 (br. s, 52%), –0.57 (br. s, 24%) and –25.6 (s, 1%) ppm.

^{19}F NMR spectroscopy also confirmed the presence of the desired aminoborane **2** as a component of the reaction mixture: ^{19}F NMR (283 MHz, Toluene): δ = –130.3 (s, C_6F_5), –153.0 (t, J_{FF} = 20.56 Hz, C_6F_5), –161.1 (br. s, C_6F_5) ppm.

Reaction of $i\mathbf{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1) with 1,3-Di-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (3): To a solution of $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (0.5 g, 1.12 mmol) in toluene at 20 °C was added 10 mol-% 1,3-di-*tert*-butyl-4,5-dihydroimidizol-2-ylidene (0.02 g, 0.11 mmol). The mixture was then stirred at 20 °C for 24 h, leading to complete consumption of the starting material, and the appearance of a new peak at δ = 33.2 ppm in the ^{11}B NMR spectrum. The solvent was then removed under high vacuum to yield the product, $i\mathrm{Pr_2N{=}BH(C_6F_5)}$, **4**, as a clear oily liquid. Yield: 0.20 g, 65%. ^{11}B NMR (96 MHz, C_6D_6): δ = 33.2 [d $^1J_{BH}$ = 129 Hz, $B(C_6F_5)H$]. ^1H (300 MHz, C_6D_6): δ = 5.11 (br. q, 1 H, BH), 3.52 (sept, $^3J_{HH}$ = 6.79 Hz, 1 H, CH), 2.97 (sept, $^3J_{HH}$ = 6.79 Hz, 1 H, CH), 1.13 (d, $^3J_{HH}$ = 6.79 Hz, 6 H, CH_3), 0.86 (d, $^3J_{HH}$ = 6.79 Hz, 6 H, CH_3) ppm. ^1H {^{11}B} (300 MHz, C_6D_6): δ = 5.11 (s, 1 H, BH), 3.52 (sept, $^3J_{HH}$ = 6.79 Hz, 1 H, CH), 2.97 (sept, $^3J_{HH}$ = 6.79 Hz, 1 H, CH), 1.13 (d, $^3J_{HH}$ = 6.79 Hz, 6 H, CH_3), 0.86 (d, $^3J_{HH}$ = 6.79 Hz, 6 H, CH_3). ^{19}F NMR (283 MHz, C_6D_6): δ –132.9 (m, C_6F_5), –155.2 (t, J_{FF} = 19.48, C_6F_5), –162.4 (td, J_{FF} = 22.61, J_{FF} = 10.02 Hz, C_6F_5) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 52.8 (s, CH), 46.0 (s, CH), 27.4 (s, CH_3), 22.0 (s, CH_3) ppm. MS (CI^+): m/z (%) = 278.1 (6) $[M – H]^+$, 169.0 (60) $[C_6F_5H_2]^+$, 102.1 (73) $[i\mathrm{Pr_2NH_2}]^+$, 86.1 (100) $[i\mathrm{Pr_2NH} – \mathrm{CH_3}]^+$.

Conducting the identical reaction in C_6D_6 allowed us to obtain the ^1H NMR spectrum of the crude mixture, wherein after 24 h a peak at 5.7 ppm, a complex multiplet, was apparent and assigned as pentafluorobenzene [authentic sample purchased from Sigma Aldrich, ^1H NMR shift (C_6D_6): 5.85 ppm]. The ^{19}F NMR spectrum was also consistent with the stoichiometric formation of pentafluorobenzene.

Attempted Catalytic Dehydrogenation of $i\mathbf{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1): Dehydrogenation experiments were carried out according to previously published literature which was appropriate for the catalyst in use. The reactions are summarised below (Table 3).

Table 3. Experimental conditions used in the attempted catalytic dehydrogenation of **1**.

Catalyst	Loading [mol-%]	Solvent	Time [h]	Temp. [°C]
IrH_2POCOP	1	THF	18	25
Rh colloids	5	toluene	18	45
$[Rh(\mu\text{-}Cl)(cod)]_2$	5	toluene	70	25
Fagnou's catalyst[a]	10	Et_2O	18	25
$[Cp_2Ti]$	100	toluene	70	25

[a] $RuCl_2L_2$ [L = $i\mathrm{Pr_2PCH_2CH_2NH_2}$] and 30 equiv. KO*t*Bu.

In all cases, analysis of the crude product mixtures by $^{11}B/^{19}F$ NMR spectroscopy indicated no formation of aminoborane **2** over the time scales indicated.

Reaction of $i\mathbf{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (1) with $n\mathbf{Bu_3SnOTf}$/2,2,6,6-Tetramethylpiperidine: To a solution of $i\mathrm{Pr_2NH{\cdot}BH(C_6F_5)_2}$ (100 mg, 0.22 mmol) in toluene (1.25 mL) was added a mixture of $n\mathrm{Bu_3SnOTf}$ (97 mg, 0.22 mmol) and 2,2,6,6-tetramethylpiperidine (31.6 mg 0.22 mmol) at 20 °C, and the mixture was then stirred for 70 h in a glovebox. The crude mixture was then analysed by ^{11}B NMR spectroscopy, indicating the presence of only unreacted starting material in solution.

Attempted Hydrogenation of $i\mathbf{Pr_2N{=}B(C_6F_5)_2}$ (2): All attempted hydrogenations were performed according to the following general procedure. A solution of $i\mathrm{Pr_2N{=}B(C_6F_5)_2}$ (50 mg, 0.11 mmol) in toluene (3 mL) was prepared and placed into a stainless steel autoclave (200 mL). The system was then pressurised with 100 bar of hydrogen, and stirred at 20 °C for 24 h. The pressure was then vented before transfer of the autoclave to the glovebox prior to sample analysis by ^{11}B NMR spectroscopy.

In the case of the catalytic experiments, the catalysts were added in the solid phase to the toluene solutions within the glovebox immediately prior to sealing the autoclave.

For the reactions performed above ambient temperature, the vessel was pressurised at 20 °C to a value that would ultimately afford the desired pressure at the final temperature.

Table 4. Experimental conditions used in the attempted hydrogenation of **2**.

Temp. [°C]	Catalyst	Loading [mol-%]	Time [h]	H_2, pressure [bar]
25	none	N/A	24	1
25	none	N/A	24	100
25	none	N/A	430	100
100	none	N/A	24	100
25	$Rh(PPh_3)_3Cl$	3	24	1
25	Rh/Al_2O_3	3	24	1
25	$Rh(PPh_3)_3Cl$	3	24	100
25	Rh/Al_2O_3	3	24	100
45	Rh colloids	5	24	100

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The following reactions were performed using the same experimental setup (Table 4).

In all cases, analysis of the crude product mixtures by ^{11}B/^{19}F NMR spectroscopy indicated no formation of amine–borane adduct **1** over the time scales indicated.

Computational Methods: All calculations were performed with the Gaussian (G03) programme.[93] All structures were fully optimised without constraints at the DFT MPW1K/BS0 model, generated using the mPWPW91 model[94] and IOp keywords. The BS0 basis set uses the 6-31+G(d) basis set on non-hydrogen atoms and the 3-21G basis set on hydrogen atoms. Analytical frequency analyses of the optimised structures at this level were used to confirm minima (no imaginary frequencies) or transition states (one imaginary frequency for the determination of the strength of the dative π-bond in the product).

Supporting Information (see footnote on the first page of this article): Full citation of the Gaussian program employed in the DFT calculations, along with crystallographic and computational data for relevant structures discussed within the main text.

Acknowledgments

A. P. M. R. and A. S. acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for funding. I. M. thanks the EPSRC for financial support, the European Union for a Marie Curie Chair and the Royal Society of Chemistry (RSC) for a Wolfson Research Merit Award.

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Received: July 26, 2011
Published Online: October 27, 2011