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Reactions of hydrazones and hydrazides with Lewis acidic boranes†

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The reaction of (diphenylmethylene)hydrazone or 1,4-bis-hydrazone-ylidene(phenylmethyl)benzene with Lewis acidic boranes B(2,4,6-F$_3$C$_6$H$_2$)$_3$ or B(3,4,5-F$_3$C$_6$H$_2$)$_3$ generates the Lewis acid–base adducts. Alternatively, when (9*H*-fluoren-9-ylidene)hydrazone is employed several products were isolated including 1,2-di(9*H*-fluoren-9-ylidene)hydrazone, the 2 : 1 borane adduct of NH$_2$–NH$_2$ and the 1-(diarylboraneyl)-2-(9*H*-fluoren-9-ylidene) hydrazone in which one ArH group has been eliminated. The benzhydrazide starting material also initially gives an adduct when reacted with Lewis acidic boranes which upon heating eliminates ArH generating a CON$_2$B heterocycle.

With over a century since the dawn of the Haber–Bosch process, the activation and subsequent functionalisation of dinitrogen remains a challenge. Typically, metal catalysts, such as those based upon Fe or Mo, have been trialled for the reduction of N_2 to NH_3. The ability of transition metal complexes to bind to N_2 has been attributed to the roles of the metal d-orbitals in bonding and back-bonding interactions with N_2.[1] Recently however, the activation of nitrogen–nitrogen bonds such as azides, diazo-compounds, hydrazones and dinitrogen using boranes has gained momentum.[2,3] Both Szymczak[4] and Simonneau[5] reported the use of B(C$_6$F$_5$)$_3$ to activate M–N$_2$ (M = Fe, Mo, W) complexes (Fig. 1) towards protonation or borylation/silylation. A major advance in this area was to remove the transition metal altogether. While (N$_2$)BF$_3$ has been generated *via* supersonic expansion at 600 Torr and 170 K,[6] it was only last year that the metal-free activation of N_2 was reported using a cyclic (alkyl)(amino)carbene (CAAC) stabilised borylene (Fig. 1).[7] Prior to this, Stephan[3a,8] had shown that the strong Lewis acid B(C$_6$F$_5$)$_3$ can be used to release N_2 from Ph$_2$CN$_2$, and can be used in reactions with Ph$_2$C═NNH$_2$ to form an adduct (Fig. 1). Yamashita[9] has subsequently shown that a highly Lewis acidic diborane can react with azobenzene and pyridazine *via* diboration and, when phthalazine is employed, N═N bond cleavage occurs. At a similar time, we have been investigating the synthesis and comparative reactivity of new boranes bearing fluorinated aryl groups as an alternative to the archetypical B(C$_6$F$_5$)$_3$.[10] In this regard, we were interested in comparing the reactivity of boranes other than B(C$_6$F$_5$)$_3$ with a variety of N–N bonded compounds including hydrazones and hydrazides, which are reported herein (Fig. 1). These may provide alternative reactivity and reaction rates depending upon the borane Lewis

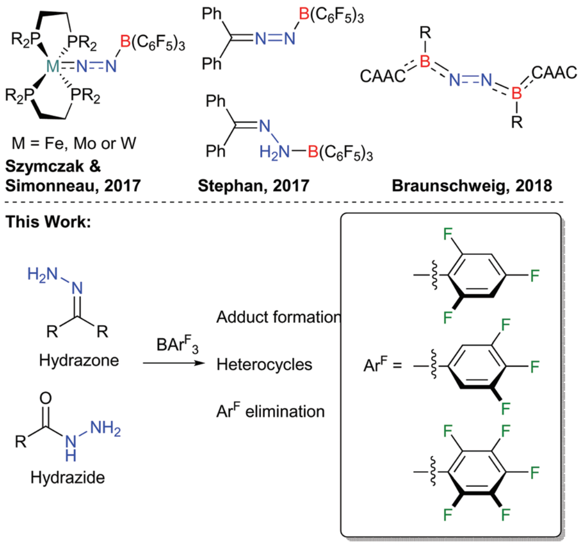

Fig. 1 Previous work on activation of N–N bonds using B(C$_6$F$_5$)$_3$ and borylenes, and outline of the work described in this article.

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† Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra and details of the X-ray analyses of compounds **2a–c**, **4–5**, **6a,b**, **7**. CCDC 1897205–1897211 and 1903201. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt01359h

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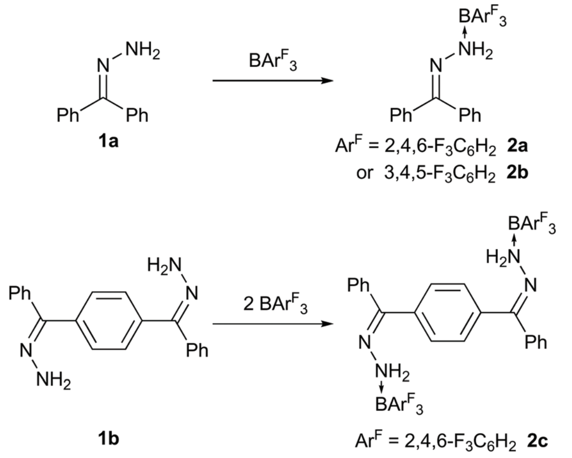
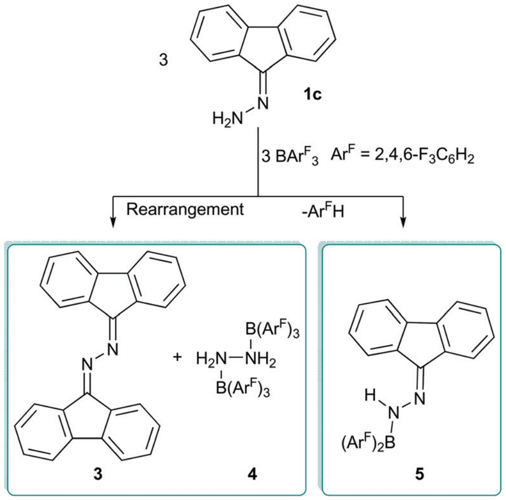


Scheme 1 Reactions of hydrazones with Lewis acidic boranes.



Scheme 2 Reactions of **1c** with B(2,4,6-$F_3C_6H_2$)$_3$.

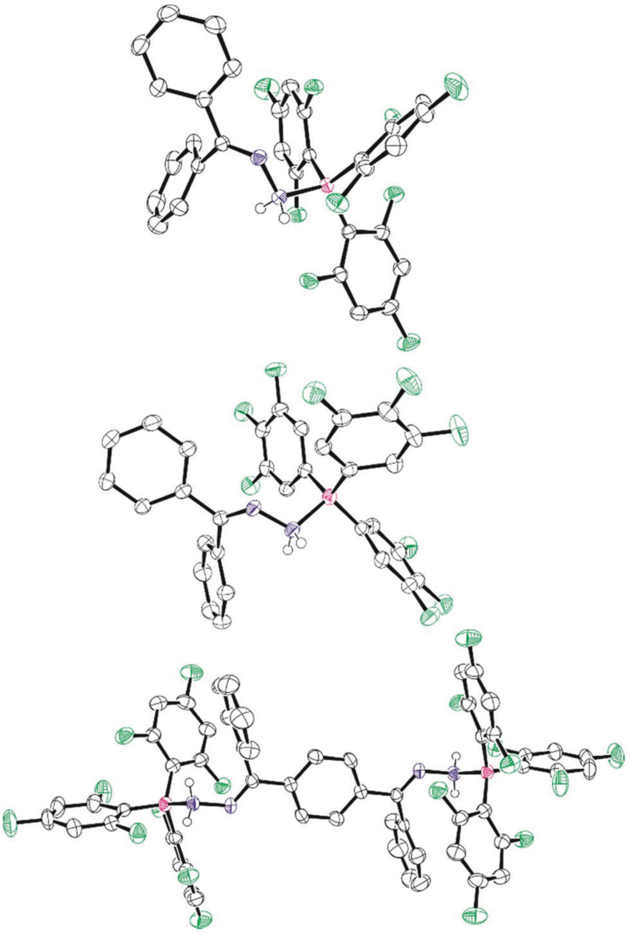


Fig. 2 Solid-state structures of **2a** (top), **2b** (middle) and **2c** (bottom). C: black, N: blue, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. H atoms except N–H omitted for clarity.

acidity.[11] Initially, the hydrazone compounds **1a–c** (Schemes 1 and 2) were prepared from the condensation reaction of the corresponding ketone with hydrazine monohydrate. Upon reaction of **1a** with B(2,4,6-$F_3C_6H_2$)$_3$ or B(3,4,5-$F_3C_6H_2$)$_3$ the corresponding N → B adducts **2a** and **2b** were formed in which the –NH_2 group of the hydrazone coordinated to the Lewis acidic boron atom analogous to that reported by Stephan when **1a** was combined with B(C_6F_5)$_3$.[8] Similarly, when bis-hydrazone **1b** was reacted with B(2,4,6-$F_3C_6H_2$)$_3$ in a 1 : 2 stoichiometric ratio a 1 : 2 adduct (**2c**) was formed. Compounds **2a**, **2b** and **2c** were isolated in 61%, 65% and 56% yield respectively. Adducts **2a–c** all displayed a broad peak ranging between −2.6 and −6.2 ppm in the ^{11}B NMR spectrum. Recrystallisation of the reaction mixtures from a CH_2Cl_2/pentane solution resulted in single crystals of the adducts whose structures were determined by single crystal X-ray diffraction (Fig. 2). In these structures the boron atom adopted a tetrahedral arrangement with B–N bond lengths ranging from 1.646(5)–1.696(4) Å, similar to those observed in previous reports (1.631(7) Å).[7] The single N–N bond lengths (range 1.438(4)–1.449(2) Å) were also similar to those reported previously.[8] Likewise, the C═N bond lengths of 1.287(3)–1.294(5) Å are typical of C═N double bonds.[12] In all cases, heating adducts **2** resulted in an unidentifiable mixture of compounds and no elimination of Ar^{F}H was observed, in contrast with previous reports where B(C_6F_5)$_3$ was employed as the Lewis acid.[8] Alternatively, if the compound **1c** was used in the reactions with boranes BAr$^F_3$ (Ar^F = 3,4,5-$F_3C_6H_2$, C_6F_5), the reaction gave a complex and inseparable mixture of products. However, if **1c** is reacted with the less Lewis acidic borane B(2,4,6-$F_3C_6H_2$) several products could be selectively crystallised from the reaction mixture to shed light on this reactivity. These could be structurally identified by single crystal X-ray diffraction as the previously reported 1,2-di(9*H*-fluoren-9-ylidene)hydrazone (**3**),[13] the bis borane adduct of hydrazone, NH_2NH_2 (**4**) and the 1-(diarylboraneyl)-2-(9*H*-fluoren-9-ylidene)hydrazone (**5**) (Scheme 2 and Fig. 3). It is unclear how the three products are formed from the reaction, but it is likely that initially an adduct is formed between **1c** and the borane. Indeed, *in situ* NMR studies showed that when **1c** is added to the borane in toluene then a

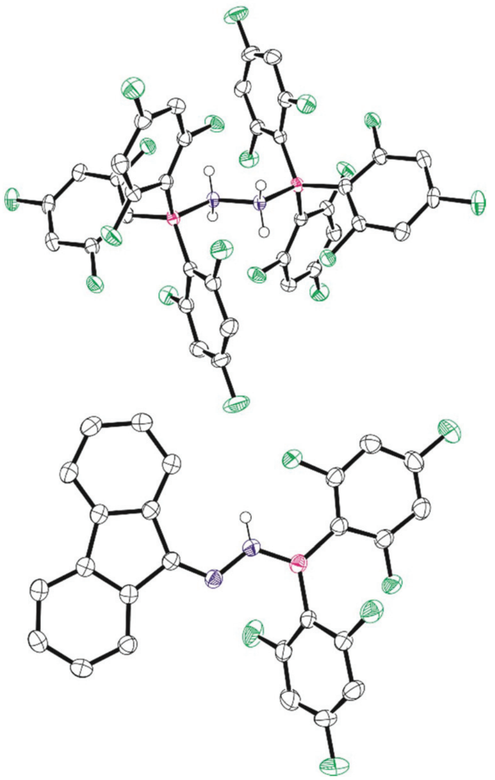
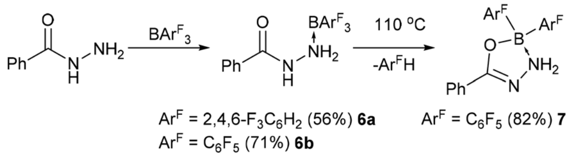


Fig. 3 Solid-state structures of **4** (top) and **5** (bottom). C: black, N: blue, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. H atoms except N–H omitted for clarity.

characteristic broad shift at $\delta = -5.1$ ppm in the ^{11}B NMR spectrum was observed. Two divergent pathways then operate to generate either **3** and **4**, or compound **5**. Elimination of Ar^{F}H generates **5** which is similar to observations made by Stephan for hydrazone $Ph_2C{=}NNH_2$ with $B(C_6F_5)_3$.[8] The trigonal planar boron atom in **5** can be observed in the solid-state structure with N–B–C bond angles of 117.8(1)° and 119.7(1)°, and a C–B–C bond angle of 122.5(1)°. The B–N bond length of 1.397(2) Å was also significantly shorter than observed in the adducts **2** indicating some π-donation from N → B generating a *trans*-diene structure in which the CN_2B atoms lie in the same plane. If the reaction of **1c** with $B(2,4,6\text{-}F_3C_6H_2)_3$ is performed at low temperatures (0 °C) in toluene then compound **5** is formed selectively in 46% yield.

Alternatively, another reaction can take place when **1c** is reacted with $B(2,4,6\text{-}F_3C_6H_2)_3$. Here a hydrazone metathesis reaction occurs to yield the azine (**3**) and borane adduct of hydrazone (**4**). This reaction is more predominant when the reaction is performed at elevated temperatures (*e.g.* r.t. to 50 °C). N–N-linked diimines (azines) are an important class of compounds isoelectronic to 1,3-butadiene. These compounds have a variety of uses including applications as chromophores in optoelectronic devices.[14] Previously, **3** has been reported to have been synthesised by the decomposition of diazo compounds catalysed by $Pt(C_2H_4)(PPh_3)_2$.[15] Similar reactions which generate a diazine from hydrazones have been reported and involve harsh conditions and long time periods *e.g.* refluxing in ethanolic hydrogen chloride for several hours.[16] More interesting is that, in our case, the borane adduct of hydrazone **4** is also generated in the reaction. Previously, the hydrazine bisborane $N_2H_4(BH_3)_2$ has been postulated as a good hydrogen storage material containing 16.9 wt% hydrogen. Additionally, coordinated hydrazine has been identified as a potential intermediate in nitrogen fixation reactions.[17–19] While $N_2H_4(BH_3)_2$ is easily prepared from the reaction of hydrazine sulfate with sodium borohydride, other borane adducts are more challenging to synthesise and a search of the literature reveals that generally intramolecular bis boranes are employed. Previously, Gabbaï[20] and Szymczak[17] have reported that intramolecular bisboranes can react with hydrazine monohydrate ($N_2H_4{\cdot}H_2O$). In these reactions, the use of a bisborane appears key to trapping and activating the hydrazone unit. We attempted to generate **4** independently from the reaction $BAr^F{}_3$ (Ar = 2,4,6-$F_3C_6H_2$) and hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) in a 2 : 1 ratio with the use of molecular sieves to trap the water by-product. Pleasingly, this led to the formation of compound **4** as observed by *in situ* multinuclear NMR spectroscopy. The structure of **4** displays a B–N bond length of 1.673(2) Å which is longer than that in hydrazine bisborane (1.609 Å)[21] and slightly shorter than that reported by Gabbaï (1.688(2) Å) and Szymczak (1.697(2) Å and 1.698(2) Å) for the chelating bisborane complexes.[17,20] The N–N distance of 1.461(2) Å is similar to that reported for other hydrazine bisborane complexes (range 1.356(2) Å–1.469(2) Å).[17,20,22]

Finally, we turned our attention to other N–N bonded substrates, namely hydrazides (Scheme 3). When commercially available benzhydrazide was reacted with $BAr^F{}_3$ an adduct was formed initially between the NH_2 group and the borane. In the case of the boranes where Ar = 2,4,6-$F_3C_6H_2$ or C_6F_5 the adducts **6a–b** could be isolated in 56% and 71% yield, respectively. Recrystallisation of the solutions afforded crystals of the adducts which could be structurally determined (Fig. 4 and ESI†). The ^{11}B NMR spectra showed a broad peak at $\delta = -6.1$ ppm (**6a**) and −6.2 ppm (**6b**) similar to that observed with the hydrazone borane adducts. In the case of **6b** *in situ* heating of the $BAr^F{}_3$ adduct of benzhydrazide to 110 °C in toluene led to loss of Ar^{F}H and generation of a CON_2B heterocycle (**7**). Recrystallisation of the reaction mixture afforded pink crystals of the product in 82% yield. Compound **7** crystallised in the $P\bar{1}$ space group with two molecules in the asymmetric unit. The N–H hydrogen atoms were identified in the difference map. X-ray diffraction analysis revealed the CON_2B rings to be planar with r.m.s.d. of 0.010 Å and 0.023 Å. The B–N bond



Scheme 3 Reaction of hydrazides with $BAr^F{}_3$.

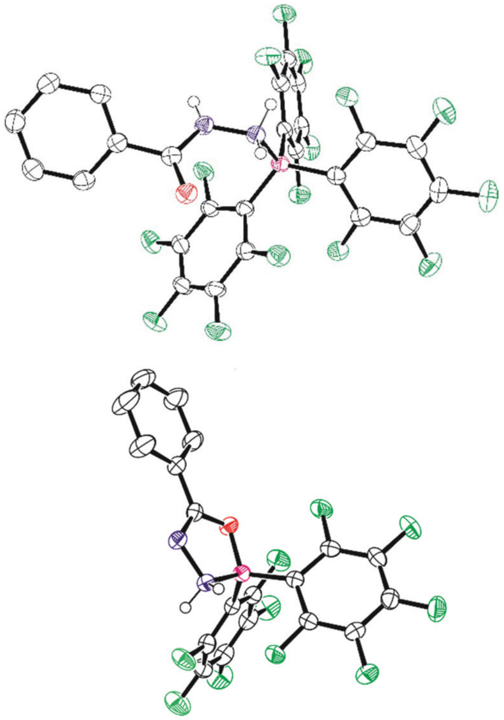


Fig. 4 Solid-state structures of **6b** (top) and **7** (bottom). C: black, N: blue, O: red, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. Non-essential H atoms omitted for clarity.

lengths of 1.621(2) Å and 1.608(3) Å are slightly shorter than that in the adduct **6a–b** (1.635(3) Å and 1.643(2) Å respectively) presumably due to the formation of a 5-membered intramolecular chelate. Conversely, the N–N bond in **7** is slightly longer at 1.468(2) Å and 1.464(3) Å compared to 1.429(3) Å and 1.426(2) Å in **6a–b**.

Preliminary computational studies (DFT B3LYP-D3/6-31G(d,p)) to probe these elimination reactions (Scheme 3) focused on the model compound $MeCONHNH_2 \rightarrow BPh_3$. Calculations revealed 1,4-elimination of C_6H_6 (implementing the NH_2 proton) appears to be the thermodynamically favoured process and forms acyclic MeCON(H)N(H)BPh_2, whereas 1,5-elimination (using the amide-NH) is a near energetically neutral process leading to formation of a 3-membered BN_2 heterocycle as the initial elimination product (see ESI†).

Conclusions

In conclusion we have prepared a series of hydrazone and hydrazide adducts of Lewis acidic boranes to investigate the interactions of Lewis acidic boranes with nitrogen containing compounds which may be of interest to those working in the area of metal-free dinitrogen activation and conversion. Initially adducts are formed which upon heating lead to loss of Ar^FH to generate novel covalent N–N–B systems including the chain compound **5** and heterocyclic compound **7**. Of particular interest is the reaction to generate the bisborane hydrazine dimer **4** from a hydrazone metathesis reaction. Subsequent studies to explore the independent synthesis and reactivity of **4** in hydrogen release are ongoing within our group.

Conflicts of interest

There are no conflicts to declare.

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