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Borane-catalysed dinitrogen borylation by 1,3-B–H bond addition†

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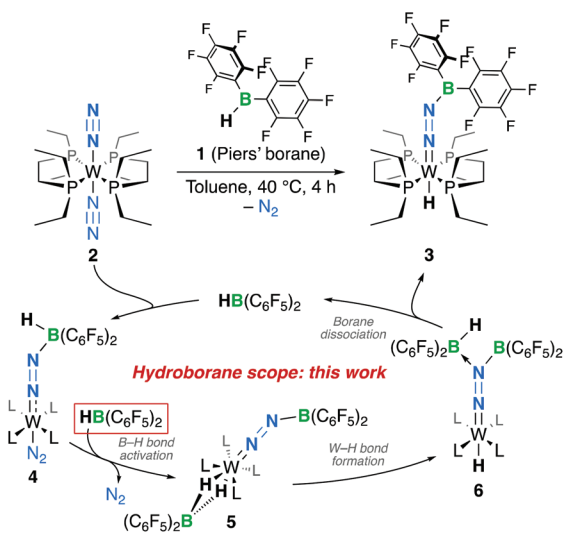
The borylation of ligated dinitrogen by 1,3-B–H bond addition over a W–N≡N unit using various hydroboranes has been examined. In a previous study, we have shown that Piers' borane (**1**) reacted with the tungsten dinitrogen complex **2** to afford a boryldiazenido–hydrido–tungsten species. The ease and mildness of this reaction have encouraged us to extend its scope, with the working hypothesis that **1** could potentially catalyse the 1,3-B–H bond addition of other hydroboranes. Under productive reaction conditions, dicyclohexylborane ($HBCy_2$) and diisopinocampheylborane ($HBIpc_2$) underwent retro-hydroboration to give cyclohexylborane (H_2BCy) or isopinocampheylborane (H_2BIpc), respectively; these monoalkylboranes act as N_2-borylating agents in the presence of a catalytic amount of **1**. Under similar conditions, 9-borabicyclononane (9-BBN) slowly adds over the W–N≡N unit without rearrangement to a monoalkylborane. Catecholborane (HBcat) undergoes the 1,3-B–H bond addition without the need for a catalyst. We were not able to build more than one covalent B–N bond between the terminal N of the N_2 ligand and the boron reagent with this methodology.

Introduction

The chemistry of dinitrogen complexes has attracted important research efforts over almost 60 years.[1] Indeed, they can serve as platforms to transform the inert but abundant N_2 molecules, and since the early 2000s several catalysts for the reduction of dinitrogen into ammonia[2] at ambient temperature and pressure have been devised. This contrasts with the harsh conditions found in the Haber–Bosch plant,[3] where N_2 is converted into ammonia by hydrogenolysis at the industrial level. N_2 complexes can also serve as models for the active sites of nitrogenases,[4] the enzymes responsible for biological nitrogen fixation. Beyond ammonia and hydrazine, the quest for the direct conversion of dinitrogen into more complex nitrogen-containing compounds has fuelled interest towards the construction of N–E bonds (E = C, B, Si, Al, Ga) at ligated dinitrogen.[1a] In this perspective, our team has reported N_2 silylation and borylation methods inspired by the chemistry of frustrated Lewis pairs.[5] We have notably shown that in the presence of Piers' borane [$HB(C_6F_5)_2$, **1**],[6] the compound *trans*-[$W(N_2)_2(depe)_2$] [**2**, depe = 1,2-bis(diethylphosphino)ethane] underwent a formal 1,3-addition of the B–H bond across the W–N≡N unit (**2**→**3**, Scheme 1),[5b] a complementary N_2 borylation method to 1,3-B–X bond addition.[7] The proposed mechanism to account for this transformation, based on experimental observations, involved two molecules of **1**, one being the N_2 borylating agent and the other assuming the role of B–H bond cleavage and hydride shuttling to the metal centre,



Scheme 1 Previously reported[5b] 1,3-B–H bond addition of Piers' borane (**1**) to dinitrogen complex **2** and the proposition of a borane-catalysed mechanism (L = ½ depe).

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thus closing a catalytic cycle (Scheme 1). As a continuation of this work, we wanted to check whether this 1,3-B–H addition can be extended to other hydroboranes and whether Piers' borane would be a competent catalyst for this reaction.[8]

Results

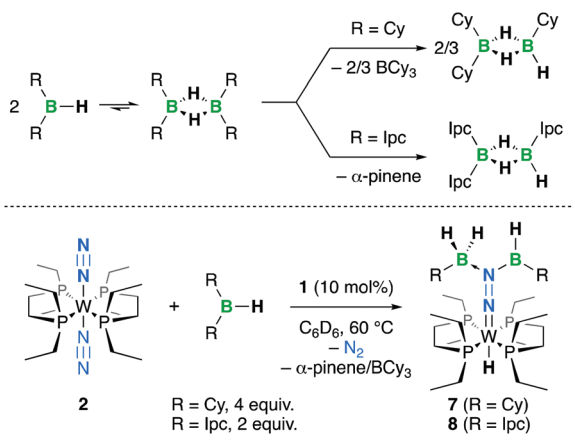
Four different organo-hydroboranes, namely dicyclohexylborane ($HBCy_2$), diisopinocampheylborane ($HBIpc_2$), 9-borabicyclononane (9-BBN) and catecholborane (HBcat), were examined. Three types of reactivities have been observed, as detailed below.

Reactions of 2 with dicyclohexylborane ($HBCy_2$) and diisopinocampheylborane ($HBIpc_2$)

We reacted *trans*-[$W(N_2)_2(depe)_2$] **2** with one equivalent of dicyclohexylborane ($HBCy_2$) at room temperature in C_6D_6. NMR spectroscopy analysis revealed the absence of new tungsten species, and raising the temperature to 80 °C overnight did not change this outcome. This contrasts with the reaction of **2** with the electrophilic hydroborane **1**, occurring under milder conditions and during which the Lewis acid–base adduct thereof (**4**, Scheme 1) could be detected.[5b] ^{11}B NMR analysis revealed the presence of tricyclohexyldiborane and BCy_3 (see Fig. S1†). This substituent scrambling presumably arose from a retro-hydroboration, a reaction known for thexyl- and isopinocampheyl-substituted boranes that readily occurs in the absence of **2** (Scheme 2, top, and Fig. S1†).[9] To verify whether $HB(C_6F_5)_2$ (**1**) could catalyse 1,3-B–H bond addition of $HBCy_2$ (or *in situ*-formed H_2BCy), we repeated the experiment in the presence of 10 mol% of **1** at 60 °C in C_6D_6. After a day, NMR analysis revealed again the presence of BCy_3 as well as tricyclohexyldiborane. We also noticed the formation of two new metal complexes according to $^{31}P\{^1H\}$ NMR with singlets at δ 45.2 and 41.7 ppm and **2** remaining the major product of the mixture. Hoping to achieve higher conversion, we increased the amount of $HBCy_2$. ^{31}P NMR analysis of the reaction mixture run with four equivalents thereof for 2 hours at 60 °C revealed the conversion to compound **7** (Scheme 2, bottom). The ^1H NMR spectrum of the crude reaction mixture showed a hydride quintet coupling to four magnetically equivalent phosphorus nuclei (δ −3.38, quintet, $^2J_{HP}$ = 30 Hz). Diagnostic signals for a four-coordinated boron species carrying 2 hydrogens were observed in the ^1H and ^{11}B NMR spectra (^1H: δ 3.29, broad singlet; $^1H\{^{11}B\}$: δ 3.29, singlet; ^{11}B: δ −30.0, triplet, J_{BH} = 91 Hz). Layering a concentrated toluene solution with pentane afforded a crystalline material (76% yield) suitable for an X-ray diffraction study. This allowed us to confirm that the targeted formal 1,3-B–H bond addition had been achieved, with H_2BCy being the actual borylating agent (Fig. 1), thus explaining the need for an excess of $HBCy_2$ to achieve the full conversion of **2**.

In the molecular structure, a second tetracoordinated boron moiety is found. Its presence is explained by the capture of another equivalent of H_2BCy, forming a Lewis pair with the distal Lewis basic nitrogen of the boryldiazenido moiety [N2–B2 1.618(6) Å]. The latter could not be observed in the ^{11}B NMR spectrum and is characterised by a B–N linkage having a double bond character [N2–B1 1.405(6) Å].[10] The distal N atom adopts a trigonal planar geometry ($\sum_{angles}$ = 360°), yet the wide B–N–B angle (126°), presumably originating from steric repulsions between the boron substituents, deviates it from ideality. The N–N bond length [1.346(3) Å] lies halfway between those of double (*ca.* 1.25 Å) and single (*ca.* 1.45 Å) N–N bonds. This noticeable elongation (d_{N-N} 1.1233(17) Å in **2**) results from the formal two-electron reduction of the N_2 ligand upon functionalisation, as well as the effect of H_2BCy complexation pulling the electron density from the metal into the antibonding orbitals of the boryldiazenido ligand.[11] The W–N bond is 1.789(2) Å long, indicative of a double bond character,[12] and the W centre lies in a distorted octahedron (all P–W–N angles >90° and up to 106°). Likewise, the W–N–N unit deviates from linearity [W1–N1–N2 170°]. These deviations from ideal geometries are, again, probably of steric origin. Overall, these structural features compare well with those of the previously reported compound **6** (Scheme 1).[5b]

In comparison with $HBCy_2$, diisopinocampheylborane ($HBIpc_2$) did not react with **2** even under forcing conditions. At room temperature and in C_6D_6, $HBIpc_2$ also underwent a substituent rearrangement (Scheme 2, top). Indeed, its dimer evolves into triisopinocampheyldiborane and α-pinene (see Fig. S6†).[9a] Having established from the above-discussed reaction involving $HBCy_2$ that dihydroboranes seem to add more easily to the W–N_2 unit than monohydroboranes, we adjusted the number of equivalents of $HBIpc_2$ in order to generate the right amount of H_2BIpc in the reaction mixture, and added a catalytic amount (10 mol%) of **1**. With two equivalents of $HBIpc_2$, full and selective conversion of **2** to compound **8** was achieved after 15 min at 60 °C (Scheme 2, bottom). Although the newly formed compound **8** could not be crystallised, its NMR characterisation is very similar to that of compound **7**: the ^1H NMR spectrum showed a hydride signal coupling to the



Scheme 2 Generation of monoalkylboranes from HBR_2 (top) and reactions of *trans*-[$W(N_2)_2(depe)_2$] (**2**) in the presence of dicyclohexyl- or diisopinocampheylborane catalysed by **1** (bottom).

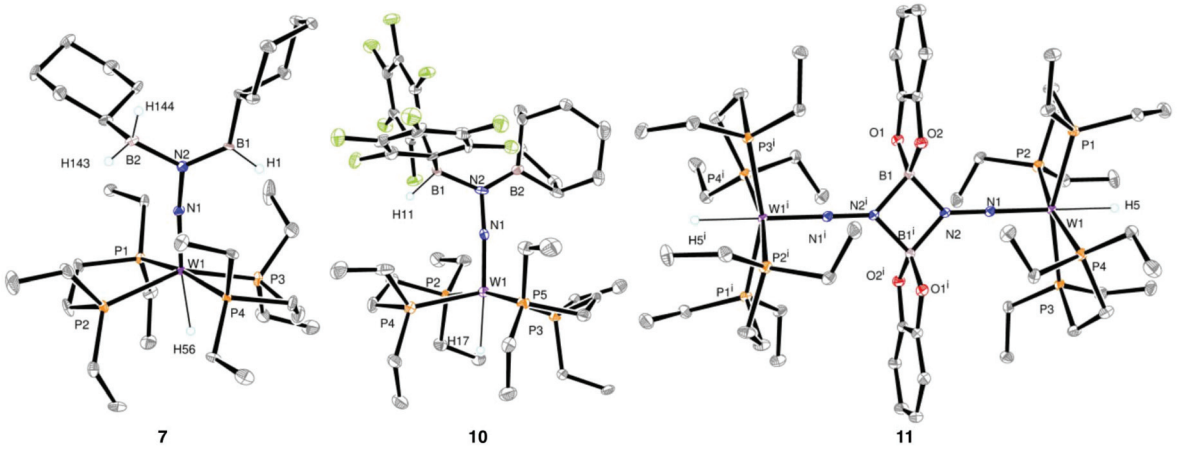
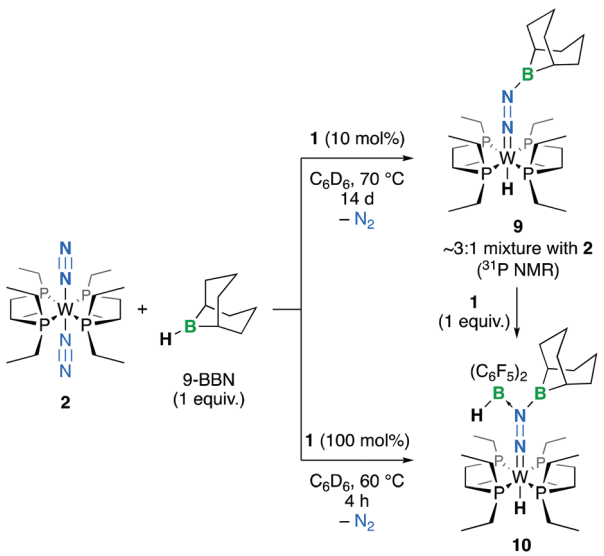


Fig. 1 Solid-state molecular structures of compounds **7**, **10** and **11**, with ellipsoids drawn at the 50% level of probability. All hydrogens have been omitted for clarity except those bound to B or W. Selected distances (Å) and angles (°) for **7**: W1–N1, 1.789(2); N1–N2, 1.346(3); N2–B1, 1.405(6); N2–B2, 1.618(6); W1–H56, 1.77(6); W1–N1–N2, 170.3(3); B1–N2–B2, 126.4(3). **10**: W1–N1, 1.783(6); N1–N2, 1.383(9); N2–B1, 1.56(1); N2–B2, 1.41(1); W1–H17, 1.82; W1–N1–N2, 175.2(5); B1–N2–B2, 129.3(7). **11**: W1–N1, 1.807(3); N1–N2, 1.295(4); N2–B1, 1.545(6); N2–B1^{i}, 1.536(6); W1–H5, 1.87(5); W1–N1–N2, 178.6(3); B1–N2–B1, 94.1(3); N2–B1–N2, 85.9(3).

four phosphorus (δ −3.33, quintet, $^{2}J_{HP}$ = 30.6 Hz), and the ^{11}B NMR spectrum featured a triplet at −30.0 ppm, leaving little doubt on the identity of **8**.

Reactions with 9-borabicyclo[3.3.1]nonane (9-BBN)

The reactivity of *trans*-[W(N$_2$)$_2$(depe)$_2$] **2** with one equivalent of 9-borabicyclo[3.3.1]nonane (9-BBN) at room temperature in C_6D_6 was also examined. Likewise, no reaction occurred even under forcing conditions (2 d, 80 °C). Hence, we added 10 mol% of hydroborane **1** to an equimolar solution of **2** and 9-BBN. ^{31}P{^{1}H} NMR monitoring of the reaction after a few days at 60 °C revealed that two new products **9** and **10** started to form (δ 45.0 and 40.7 ppm, respectively), both showing a corresponding hydride quintet in ^{1}H NMR (δ −3.33 and −4.10 ppm, respectively). Upon prolonged heating, compound **9** formed predominantly, reaching *ca.* 70% of the mixture according to ^{31}P NMR integration after 14 days at 70 °C, and on the basis of NMR spectroscopy, it was assigned to be the product of 1,3-B–H bond addition (Scheme 3). The other tungsten-containing components of the reaction mixture were **2** and unidentified minor impurities (see Fig. S12†), while several unidentified boron species seemed to be present (Fig. S13†). The slow rate of this B–H bond addition incited us to perform the stoichiometric reaction between complex **2**, **1** and 9-BBN. The analysis of the reaction mixture by ^{31}P NMR showed full and selective conversion to compound **10** (Scheme 3) after 4 h at 60 °C. Traces of **10** were also observed in the ^{31}P and ^{19}F NMR spectra acquired at the end of the catalytic reaction (see Fig. S14†). The analysis of the ^{19}F and ^{11}B NMR spectra of **10** suggested, in accordance with previous results,[5b] that it is formed by the Lewis acid–base interaction of **1** with the boryldiazenido moiety of **9**. The reaction of **9** with **1** to give **10** brought convincing evidence supporting the latter assumption, as well as the identity of **9**, for which we could not ascertain the structure with X-ray diffraction.



Scheme 3 Reactions of *trans*-[W(N$_2$)$_2$(depe)$_2$] (**2**) with 9-BBN and catalytic or stoichiometric amounts of HB(C$_6$F$_5$)$_2$ (**1**).

An X-ray diffraction study on single crystals allowed us to confirm the proposed structure of **10** (Fig. 1), with the covalent *vs.* dative bonding between the boron atoms and the terminal N being confirmed by comparison of B–N bond lengths [N2–B1, 1.405(6) Å *vs.* N2–B2, 1.617(6) Å]. The structure of **10** resembles that of **7**, with a tungsten centre in a distorted octahedron and the W–N–N unit deviating from linearity (W1–N1–N2, 175°). While W–N bond lengths are similar in **7** and **10**, the N–N bond in **10** is slightly longer (+0.03 Å), probably as a result of the higher electrophilicity of Piers' borane than that of H$_2$BCy.

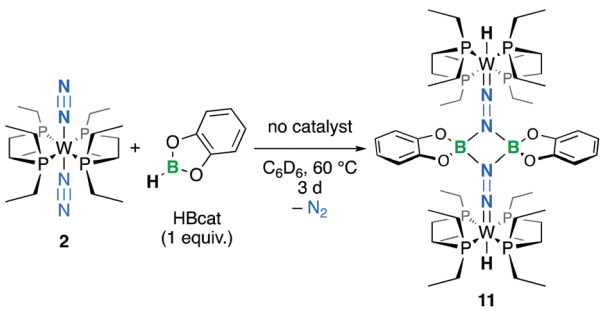
Reaction with catecholborane (HBcat)

Next, we checked the reactivity of *trans*-[W(N$_2$)$_2$(depe)$_2$] **2** with one equivalent of catecholborane (HBcat) at room temperature in C_6D_6 (Scheme 4). Quite contrastingly, NMR analysis revealed that a reaction occurred in a selective manner. Indeed, we observed a new diamagnetic compound **11** having a singlet resonance at δ 43.8 ppm in $^{31}P\{^1H\}$ NMR with a corresponding hydride quintet at −3.6 ppm in ^1H NMR after a few minutes at room temperature. Almost full conversion was obtained after 3 days at 60 °C (>90% according to ^{31}P NMR). Compared to the previous examples, Piers' borane **1** was not necessary to perform the targeted formal 1,3-B–H bond addition.

Layering the reaction mixture with pentane allowed us to grow single crystals of **11** (33% yield) suitable for X-ray diffraction analysis, which revealed a dimeric solid-state structure of D_{2h} symmetry for **7** (Fig. 1): two boryl groups are bridging two W–N$_2$ units in an almost square BNBN arrangement (N–B bond lengths *ca.* 1.54 Å, B–N–B angles 94°, and N–B–N angles 86°). Compared to the structures of **3** and **6**, the octahedron formed by the W ligands is less distorted, and the W–N–N arrangement is linear (W1–N1–N2, 179°). The N–N bond is also shorter [1.295(4) Å]. Similar dimeric structures have been obtained from the reactions of group 13 chlorides with end-on dinitrogen complexes.[13] The dimeric nature of **11** in the solid, which contrasts with that of **7** or **9** (as suggested by diffusion-ordered NMR spectroscopy, see Fig. S15†), is likely to result from the diminished steric hindrance of the flat Bcat group.

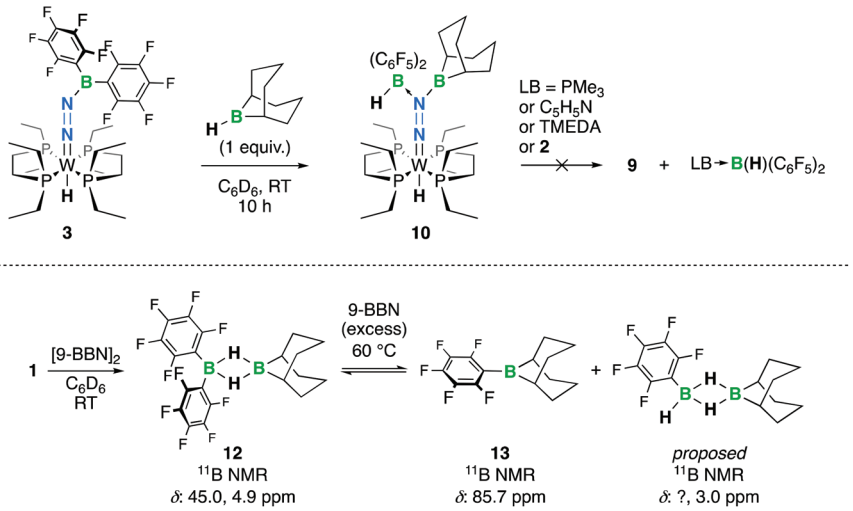
Discussion

The above-described experiments have confirmed the possibility to use Piers' borane as a catalyst for the borylation of N$_2$ bound to a group 6 metal centre by 1,3-B–H bond addition when using dialkylhydroboranes (HBCy$_2$, HBIpc$_2$ and 9-BBN). Within this family of compounds, two different behaviours have been observed depending on the propensity of the dialkylhydroborane to undergo retro-hydroboration under the reaction conditions to give a monoalkylborane. The latter is the active borylating agent, and in the case of HBCy$_2$ and HBIpc$_2$, only the products of the 1,3-B–H bond addition of H$_2$BCy and H$_2$BIpc over the W–N–N unit were observed. The reason is most probably of kinetic origin, since monoalkylboranes are less sterically hindered than their disubstituted parents, making the interaction with the N$_2$ complex as well as the B–H bond activation by **1** easier. 9-BBN, which does not undergo retro-hydroboration, reacts much slower and also needs catalytic amounts of **1**. Interestingly, when the reaction of 9-BBN with the dinitrogen complex is conducted in the presence of an equimolar amount of **1**, the B–H bond addition proceeds very rapidly and selectively. Indeed, the 1,3-B–H bond addition product of Piers' borane[5b] (**3**, Scheme 1) is not observed. The following experiment allowed us to shed light on this fact: when product **3** was treated with an equimolar amount of 9-BBN at RT, **10** was obtained quantitatively in a few hours (Scheme 5). This result suggests that in the catalytic 1,3-B–H bond addition mechanism with H$_2$BCy, H$_2$BIpc or 9-BBN, the addition of Piers' borane to give **3** may precede the interaction of the alkylhydroborane with the M–N≡N unit. After complexation of the latter with the thus-formed C_6F_5-substituted boryldiazenido moiety in **3**, boron-to-boron hydride transfer then affords a Piers' borane-complexed 1,3-B–H bond addition compound such as **10**. The dissociation of **1** followed by reaction with dinitrogen complex **2** would then close the catalytic sequence. However, further experimental work cast doubts on this conjecture, at least in the case of 9-BBN. Attempts to dissociate **1** in compound **10** in the presence of various Lewis bases such as PMe$_3$, pyridine, tetramethylethylenediamine (TMEDA) or **2** at elevated temperatures for several hours proved unsuccessful (Scheme 5, top).[14] We have checked the integrity of Piers' borane (**1**) in the presence of a 10-fold excess of 9-BBN: at RT, a new species forms in C_6D_6 within a few hours, which we believe is the mixed diborane **12** (Scheme 5, bottom). Upon heating to a temperature relevant to the above-described experiments, the putative dimer seems to get involved in an equilibrated substituent rearrangement process with two other compounds, one being 9-C_6F_5-BBN[15] (**13**), while the second one is presumably a mixed diborane composed of 9-BBN and *in situ*-formed H$_2$BC_6F_5 (see Fig. S22–23† and Scheme 5). The ^{19}F NMR spectrum recorded at the end of the reaction affording **9** does not feature the spectral signature of **1**, but unambiguously shows the presence of **10** along with another unidentified compound (see Fig. S13 and S14†). These data suggest that **1** is a precatalyst in the reaction involving 9-BBN, but the presence of **10** at the end of the reaction also implies that this species might be a catalyst resting state.



Scheme 4 Reaction of *trans*-[W(N$_2$)$_2$(depe)$_2$] (**2**) with catecholborane (HBcat).

HBcat stands out against the 3 other boranes examined. This boron reagent is known to be a much milder hydroboration reagent than HBCy$_2$ or HBIpc$_2$ due to its quenched Lewis acidity.[16] As such, HBcat is also a weak hydride donor compared to 9-BBN on the basis of the calculated hydride donor abilities [ΔG_{H^-}(298 K) = 159.2 *vs.* 99.0 kcal mol^{-1}, respectively], but this trend reverses upon Lewis base [for example, NHC-HBcat, ΔG_{H^-}(298 K) = 44.8 kcal mol^{-1} and NHC-9-BBN, ΔG_{H^-}(298 K) = 47.0 kcal mol^{-1} with NHC = 1,3-di(isopropyl) imidazole-2-ylidene] or hydride coordination {[H$_2$Bcat]$^-$, ΔG_{H^-}(298 K) = 26.3 kcal mol^{-1} and [9-H$_2$BBN]$^-$, ΔG_{H^-}(298 K) =



Scheme 5 Reaction of **3** with 9-BBN and attempts to dissociate **1** from **10** with various Lewis bases (top) and reaction of **1** with 9-BBN in the absence of a dinitrogen complex (bottom).

32.8 kcal mol^{-1}}.[17] Although the flatness of HBcat and its monomeric nature in non-coordinating solvents also offer a kinetic advantage, we believe the peculiarity of HBcat reactivity lies in its electronic properties. We propose a similar mechanism for the 1,3-B–H bond addition of HBcat to that with Piers' borane (Scheme 1): Lewis acid–base adduct formation of HBcat with **2** increases the polarisation of the B–H bond to an extent that a second equivalent of HBcat is now able to abstract the hydride, generating the $[H_2Bcat]^-$ anion. The latter is a competent hydride donor (*vide supra*), especially when compared to $[H_2B(C_6F_5)_2]^-$ [ΔG_{H^-}(298 K) = 61.5 kcal mol^{-1}], which also bears a steric penalty due to its C_6F_5 substituents. This may explain why in the reactions with HBcat we were not able to detect a species resembling **5** (Scheme 1), the W–H bond formation event being probably too fast under the experimental conditions. In the case of Piers' borane, we surmise that an important factor for W–H bond formation (**5→6**, Scheme 1) is the nature of the *trans* ligand, $NNB(C_6F_5)_2$, whose electron-withdrawing properties might counter-balance the weak hydride donor ability of $[H_2B(C_6F_5)_2]^-$.[18]

Conclusions

In the present article, we expand the scope of 1,3-B–H bond addition over a W–N_2 unit. This mild method for N_2 borylation, which complements 1,3-B–X bond addition,[7] can be attractive for who seeks to synthesise nitrogen–boron compounds directly from dinitrogen. Having this goal in mind, we have examined the reactivity of 4 different boranes. Only HBcat reacts spontaneously with the dinitrogen complex **2**, affording the 1,3-B–H bond addition product **11**. Hydroboranes $HBCy_2$, $HBIpc_2$ and 9-BBN required catalytic amounts of Piers' borane (**1**) to react with **2**. In the case of $HBCy_2$ and $HBIpc_2$, monoalkylboranes H_2BCy and H_2BIpc formed *in situ* are the actual borylating agents. None of the boranes examined have allowed building more than one covalent N–B bond. According to the experimental observations, we believe that the mechanism of these catalytic reactions starts with the 1,3-B–H bond addition of **1** to give **3**, followed by complexation of the alkylhydroborane to the terminal N of the resulting W-ligated boryldiazenido ligand and a boron-to-boron hydride transfer ensues. While it is reasonable to think that the dissociation of **1** should close the catalytic cycle, such an elementary step could not be validated in the case of 9-BBN because **1** is likely to be a pre-catalyst in this specific reaction. This urges us to explore in detail the reactivity of $H_2BC_6F_5$ but also L·BH_3 (L = THF, SMe_2, *etc.*) or diborane (B_2H_6) with zero-valent group 6 dinitrogen complexes. We will share the results of this future work in due time.

Experimental section

General considerations

All reactions were performed in flame- or oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen filled Jacomex glovebox (O_2 < 1 ppm, H_2O < 1 ppm). Solvents used were pre-dried (toluene and *n*-pentane by passing through a PureSolv MD 7 solvent purification machine; *n*-hexane and hexamethyldisiloxane (HMDSO) by distillation over CaH_2), degassed by freeze–pump–thaw cycles, dried over molecular sieves and stored in a glovebox. C_6D_6 (purchased from Eurisotop) was degassed by freeze–pump–thaw cycles, dried over molecular sieves and stored in a glovebox. HB$(C_6F_5)_2$ (**1**),[6a] $HBCy_2$ [19] and $HBIPc_2$ [20] were synthesized according to reported procedures and stored in a glovebox. 9-BBN and HBcat were purchased from Sigma-Aldrich and used as received in a glovebox. ^{1}H, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded in C_6D_6 or toluene-d_8 using NMR tubes equipped

with J. Young valves on a Bruker Avance III 400 spectrometer. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard (C_6HD_5: δ reported = 7.16 ppm; C_7HD_7: δ reported = 2.08 ppm for ^{1}H NMR). ^{11}B, ^{19}F, ^{29}Si and ^{31}P NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as the primary reference.[21] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, m_c = centrosymmetric multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded in a glovebox on an Agilent Cary 630 FT-IR spectrophotometer equipped with ATR or transmission modules and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed on samples sealed in tin capsules under N_2 by the analytical service of the Laboratoire de Chimie de Coordination; results are the average of two independent measurements.

Reaction of 2 with $HBCy_2$ catalysed by 1

In a glovebox, *trans*-$[W(N_2)_2(depe)_2]$ (**2**, 52 mg, 80 μmol, 1 equiv.), $HBCy_2$ (57 mg, 32 μmol, 4 equiv.) and $HB(C_6F_5)_2$ (**1**, 3 mg, 8 μmol, 0.1 equiv.) were weighed in a 4 mL vial. After addition of C_6D_6 (0.6 mL), the orange-red solution was heated for 2 hours at 60 °C. The resulting orange solution was concentrated to *ca.* 0.3 mL under reduced pressure and layered with pentane before storage at −40 °C. After a week, orange crystals of **7** were recovered by decantation and dried under vacuum (50 mg, 61 μmol, 76% yield). Single crystals suitable for an X-ray diffraction study were obtained from the same crop.

7: **^{1}H NMR** (400 MHz, C_6D_6) δ: 3.29 (br s, 2H), 2.21–2.02 (m_c, 8H), 2.06 (t, J = 11.6 Hz, 8H), 1.94 (s, 2H), 1.82–1.63 (m, 5H), 1.63–1.38 (m, 14H), 1.39–1.18 (m, 10H), 1.14 (quint, J = 7.6 Hz, 12H), 0.73 (p, J = 7.4 Hz, 12H), −3.38 (quint, J_{HW} = 15.8 Hz, J_{HP} = 30.4 Hz, 1H). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ: 41.7 (J_{PW} = 282 Hz). **^{11}B NMR** (128 MHz, C_6D_6) δ: −30.0 (t, J_{BH} = 91.0 Hz).

IR (ATR) ν/cm^{-1} = 2958, 2900, 2783, 1603, 1503, 1456, 1362, 1335, 1274, 1188, 1163, 1124, 1095, 1081, 1029, 982, 867, 802, 755, 732, 710, 693, 686, 662.

Elem. anal. calcd for $C_{32}H_{74}B_2N_2P_4W$: C, 47.08; H, 9.14; N, 3.43. Found: C, 47.10; H, 8.90; N, 3.26.

Reaction of 2 with $HBIpc_2$ catalysed by 1

In a glovebox, *trans*-$[W(N_2)_2(depe)_2]$ (**2**, 13 mg, 20 μmol, 1 equiv.), $HBIpc_2$ (12 mg, 40 μmol, 2 equiv.) and $HB(C_6F_5)_2$ (**1**, 0.7 mg, 2.0 μmol, 0.1 equiv.) were weighed in a 4 mL vial. After the addition of C_6D_6 (0.6 mL), the orange-red solution was heated at 60 °C for 15 minutes, the time after which the full conversion of **2** into **8** was ascertained by NMR analysis. After evaporation to dryness in a glovebox, the oily residue was triturated in pentane. The supernatant was discarded, and the oily residue was dried under vacuum. Compound **8** could not be isolated otherwise than as a C_6D_6-containing clathrate.

8: **^{1}H NMR** (400 MHz, C_6D_6) δ: 3.38 (br s, 3H), 2.59–2.50 (m, 2H), 2.43–2.34 (m, 4H), 2.27–2.13 (m, 12H), 2.06–1.97 (m, 3H), 1.82 (m, 2H), 1.74–1.65 (m, 3H), 1.48 (d, J = 7.2 Hz, 8H), 1.45 (s, 6H), 1.37 (s, 6H), 1.20–1.10 (m, 16H), 0.80–0.68 (m, 20H), −3.33 (quint, J_{HW} = 13.4 Hz, J_{HP} = 30.7 Hz, 1H). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ: 41.2 (m_c, J_{WP} = 282 Hz, second order pattern). **^{31}P NMR** (162 MHz, C_6D_6) δ: 41.2 (m_c, second order pattern). **^{11}B NMR** (128 MHz, C_6D_6) δ: −3.32 (br s), −30.0 (t, J_{BH} = 88.9 Hz).

IR (ATR) ν/cm^{-1} = 2962, 2936, 2878, 2357, 2081, 1634, 1501, 1453, 1416, 1293, 1104, 1074, 1027, 961, 869, 806, 751, 735, 683.

Elem. anal. calcd for $C_{40}H_{86}B_2N_2P_4W{\cdot}0.55C_6D_6$: C, 53.58; H, 8.93; N, 2.89. Found: C, 54.09; H, 9.55; N, 2.56.

Reaction of 2 with 9-BBN catalysed by 1

In a glovebox, *trans*-$[W(N_2)_2(depe)_2]$ (**2**, 26 mg, 40 μmol, 1 equiv.), 9-BBN (4.9 mg, 40 μmol, 1 equiv.) and $HB(C_6F_5)_2$ (**1**, 1.4 mg, 4.0 μmol, 0.1 equiv.) were weighed in a 4 mL vial. After addition of C_6D_6 (0.5 mL), the dark orange solution was heated at 70 °C for 14 days, the time after which compound **9** became the main component of the reaction mixture (*ca.* 70% according to ^{31}P NMR) that still contained **2** and other unidentified boron species. Attempts to isolate **9** in an analytically pure form have failed.

9: **^{1}H NMR** (400 MHz, C_6D_6) δ: 2.08–1.99 (m, 12H), 1.89–1.85 (m, 3H), 1.80–1.71 (m, 6H), 1.68–1.62 (m, 3H), 1.51 (s, 2H), 1.47–1.34 (m, 12H), 1.17 (dt, J = 14.8, 7.6 Hz, 12H), 0.87 (dt, J = 13.6, 7.5 Hz, 12H), −3.33 (quint, J_{HW} = 26.1 Hz, J_{HP} = 26.3 Hz, 1H). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ: 45.03 (J_{WP} = 282 Hz). **^{11}B NMR** (128 MHz, C_6D_6) δ: 45.9.

Reaction of 2 with 9-BBN and 1

In a glovebox, *trans*-$[W(N_2)_2(depe)_2]$ (**2**, 20 mg, 30 μmol, 1 equiv.), 9-BBN (3.8 mg, 30 μmol, 1 equiv.) and $HB(C_6F_5)_2$ (**1**, 10 mg, 30 μmol, 1 equiv.) were weighed in a 4 mL vial. After addition of C_6D_6 (0.6 mL), the dark orange solution was heated at 60 °C for 4 hours. The resulting orange solution was concentrated under vacuum and pentane (2 mL) was added before storage at −40 °C. After one day, orange crystals of **10** were recovered by decantation and dried under vacuum (23 mg, 21 μmol, 70% yield). Single crystals suitable for X-ray diffraction crystallography were obtained from the same crop.

10: **^{1}H NMR** (400 MHz, C_6D_6) δ: 3.98 (d, J = 107.1 Hz, 1H), 2.15–1.98 (m, 4H), 1.97–1.85 (m, 4H), 1.85–1.77 (m, 2H), 1.72 (q, J = 4.7, 4.2 Hz, 4H), 1.65–1.44 (m, 10H), 1.39–1.26 (m, 6H), 1.22–1.07 (m, 8H), 1.00 (quint, J = 7.4 Hz, 12H), 0.62 (quint, J_{HW} = 9.8 Hz, J_{HP} = 7.4 Hz, 12H), −4.10 (quint, J_{HP} = 34.1 Hz, 1H). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ: 40.7 (J_{PW} = 287 Hz). **^{11}B NMR** (128 MHz, C_6D_6) δ: −10.9 (s); the boron shift of the tricoordinated boryl group could not be detected. **^{19}F NMR** (377 MHz, C_6D_6) δ: −132.7 (dd, J_{FF} = 25.5, 9.3 Hz, $4F_{ortho}$), −162.5 (t, J_{FF} = 20.2 Hz, $2F_{para}$), −166.0 to −166.5 (m, $4F_{meta}$).

IR (ATR) ν/cm^{-1} = 2965, 2937, 2917, 2881, 2354, 1639, 1507, 1452, 1375, 1332, 1264, 1228, 1108, 1091, 1075, 1039, 1028, 964, 936, 887, 869, 844, 803, 736, 712, 680, 662.

Elem. anal. calcd for $C_{40}H_{64}B_2F_{10}N_2P_4W$: C, 43.98; H, 5.91; N, 2.65. Found: C, 44.00; H, 6.08; N, 2.48.

Reaction of 2 with HBcat

In a glovebox, *trans*-$[W(N_2)_2(depe)_2]$ (**2**, 52 mg, 80 μmol, 1 equiv.) and HBcat (8.6 μL, 80 μmol, 1.0 equiv.) were weighed in a 4 mL vial. After addition of C_6D_6 (0.6 mL), the orange solution was heated at 60 °C for 3 days. The resulting solution was then concentrated under vacuum before adding hexane (2 mL). The resulting turbid solution was centrifuged, giving a yellow liquid that was stored at −40 °C. After a week, a mixture of crystals and powder of **11** were recovered by filtration and dried under vacuum (26.6 mg, 18 μmol, 45% yield). Single crystals suitable for an X-ray diffraction study were obtained by layering pentane onto a saturated C_6D_6 solution of **11** before storage at −40 °C (33% yield).

11: **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.90–6.86 (m, 4H), 6.83–6.79 (m, 4H), 2.10–1.87 (m, 16H), 1.70 (ddd, J = 11.1, 9.2, 5.5 Hz, 8H), 1.40–1.23 (m, 24H), 1.15 (quint, J = 7.4 Hz, 24H), 0.82–0.70 (m, 24H), −3.60 (quint, J_{HW} = 18.1 Hz, J_{HP} = 29.2 Hz, 2H). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ: 43.8 (J_{PW} = 286 Hz). **^{11}B NMR** (128 MHz, C_6D_6) δ: 5.4 (s).

IR (ATR) ν/cm^{-1} = 2958, 2900, 2839, 2272, 1604, 1503, 1457, 1378, 1362, 1335, 1274, 1188, 1163, 1124, 1095, 1081, 1029, 982, 867, 802, 755, 732, 710, 693, 686, 661.

Elem. anal. calcd for $C_{52}H_{106}B_2N_4O_4P_8W_2$: C, 41.96; H, 7.18; N, 3.76. Found: C, 42.20; H, 7.40; N, 3.70.

Conflicts of interest

The authors declare no conflict of interest.

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Notes and references

1 (*a*) S. Kim, F. Loose and P. J. Chirik, *Chem. Rev.*, 2020, **120**, 5637–5681; (*b*) D. Singh, W. R. Buratto, J. F. Torres and L. J. Murray, *Chem. Rev.*, 2020, **120**, 5517–5581; (*c*) *Transition Metal–Dinitrogen Complexes: Preparation and Reactivity*, ed. Y. Nishibayashi, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2019; (*d*) M. D. Walter, in *Advances in Organometallic Chemistry*, ed. P. J. Pérez, Academic Press, 2016, vol. 65, pp. 261–377; (*e*) B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385–402; (*f*) S. Gambarotta and J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 5298–5308; (*g*) M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115–1133; (*h*) J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589–625.

2 (*a*) M. J. Chalkley, M. W. Drover and J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582–5636; (*b*) S. L. Foster, S. I. P. Bakovic, R. D. Duda, S. Maheshwari, R. D. Milton, S. D. Minteer, M. J. Janik, J. N. Renner and L. F. Greenlee, *Nat. Catal.*, 2018, **1**, 490–500; (*c*) N. Stucke, B. M. Flöser, T. Weyrich and F. Tuczek, *Eur. J. Inorg. Chem.*, 2018, **2018**, 1337–1355; (*d*) Y. Roux, C. Duboc and M. Gennari, *ChemPhysChem*, 2017, **18**, 2606–2617; (*e*) *Nitrogen Fixation*, ed. Y. Nishibayashi, Springer International Publishing AG, Cham, Switzerland, 2017.

3 (*a*) G. Ertl, *Angew. Chem., Int. Ed.*, 2008, **47**, 3524–3535; (*b*) R. Schlögl, *Angew. Chem., Int. Ed.*, 2003, **42**, 2004–2008; (*c*) J. R. Jennings, *Catalytic Ammonia Synthesis: Fundamentals and Practice*, Springer, 1991.

4 (*a*) A. J. Jasniewski, C. C. Lee, M. W. Ribbe and Y. Hu, *Chem. Rev.*, 2020, **120**, 5107–5157; (*b*) C. Van Stappen, L. Decamps, G. E. Cutsail, R. Bjornsson, J. T. Henthorn, J. A. Birrell and S. DeBeer, *Chem. Rev.*, 2020, **120**, 5005–5081; (*c*) H. L. Rutledge and F. A. Tezcan, *Chem. Rev.*, 2020, **120**, 5158–5193; (*d*) O. Einsle and D. C. Rees, *Chem. Rev.*, 2020, **120**, 4969–5004; (*e*) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean and L. C. Seefeldt, *Chem. Rev.*, 2014, **114**, 4041–4062.

5 (*a*) A. Simonneau, R. Turrel, L. Vendier and M. Etienne, *Angew. Chem., Int. Ed.*, 2017, **56**, 12268–12272; (*b*) A. Coffinet, D. Specklin, L. Vendier, M. Etienne and A. Simonneau, *Chem. – Eur. J.*, 2019, **25**, 14300–14303.

6 (*a*) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809–811; (*b*) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503.

7 (*a*) A. Rempel, S. K. Mellerup, F. Fantuzzi, A. Herzog, A. Deißenberger, R. Bertermann, B. Engels and H. Braunschweig, *Chem. – Eur. J.*, 2020, **26**, 16019–16027; (*b*) H. Ishino, Y. Ishii and M. Hidai, *Chem. Lett.*, 1998, **27**, 677–678.

8 Hydroboranes are known catalysts for hydroboration reactions: (*a*) M. Hoshi and A. Arase, *Synth. Commun.*, 1997, **27**, 567–572; (*b*) P. Eisenberger, A. M. Bailey and C. M. Crudden, *J. Am. Chem. Soc.*, 2012, **134**, 17384–17387; (*c*) A. Prokofjevs, A. Boussonnière, L. Li, H. Bonin, E. Lacôte, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2012, **134**, 12281–12288; (*d*) M. Fleige, J. Möbus, T. vom Stein, F. Glorius and D. W. Stephan, *Chem. Commun.*, 2016, **52**, 10830–10833; (*e*) Q. Yin, S. Kemper, H. F. T. Klare and M. Oestreich, *Chem. – Eur. J.*, 2016, **22**, 13840–13844; (*f*) R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. – Eur. J.*, 2017, **23**, 10997–11000; (*g*) Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381–2384; (*h*) N. W. J. Ang, C. S. Buettner, S. Docherty, A. Bismuto, J. R. Carney, J. H. Docherty, M. J. Cowley and S. P. Thomas, *Synthesis*, 2018, 803–808; (*i*) E. Nieto-Sepulveda, A. D. Bage, L. A. Evans, T. A. Hunt, A. G. Leach, S. P. Thomas and

G. C. Lloyd-Jones, *J. Am. Chem. Soc.*, 2019, **141**, 18600–18611.

9 (*a*) H. C. Brown, N. R. Ayyangar and G. Zweifel, *J. Am. Chem. Soc.*, 1964, **86**, 397–403; (*b*) H. C. Brown, E. Negishi and J. J. Katz, *J. Am. Chem. Soc.*, 1975, **97**, 2791–2798.

10 S. Berski, Z. Latajka and A. J. Gordon, *New J. Chem.*, 2011, **35**, 89–96.

11 A. Coffinet, A. Simonneau and D. Specklin, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, ed. R. A. Scott, Wiley-VCH Verlag GmbH & Co. KGaA, 2020, pp. 1–25.

12 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770–12779.

13 (*a*) T. Takahashi, T. Kodama, A. Watakabe, Y. Uchida and M. Hidai, *J. Am. Chem. Soc.*, 1983, **105**, 1680–1682; (*b*) H. F. Klein, K. Ellrich and K. Ackermann, *J. Chem. Soc., Chem. Commun.*, 1983, 888–889; (*c*) K. Takagahara, H. Ishino, Y. Ishii and M. Hidai, *Chem. Lett.*, 1998, 897–898.

14 Traces of **3** were detected when monitoring the reaction of **10** and **2** by $^{31}P\{^{1}H\}$ NMR, but no quantitative build-up was obtained; see the ESI.†

15 M. Erdmann, C. Rösener, T. Holtrichter-Rößmann, C. G. Daniliuc, R. Fröhlich, W. Uhl, E.-U. Würthwein, G. Kehr and G. Erker, *Dalton Trans.*, 2013, **42**, 709–718.

16 H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1971, **93**, 1816–1818.

17 Z. M. Heiden and A. P. Lathem, *Organometallics*, 2015, **34**, 1818–1827.

18 An experiment allowed us to highlight the similarities of **1** and HBcat as far as the title reaction is concerned: when an equimolar mixture of **2** and 9-BBN was treated with a catalytic amount of HBcat, **9** slowly formed (*ca.* 30% conversion according to ^{31}P NMR after 10 days at 80 °C), indicating that HBcat (or potentially a borane issued after reaction with excess 9-BBN) can also catalyse the 1,3-B–H bond addition reaction, though less efficiently than **1** (see Fig. S27†).

19 A. Abiko, *Org. Synth.*, 2002, **79**, 103.

20 H. C. Brown and N. N. Joshi, *J. Org. Chem.*, 1988, **53**, 4059–4062.

21 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795–1818.