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Borohydride reduction of a rhenium-bound acetonitrile: an example of a chelating iminoborane ligand at a low valent metal center

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Abstract

The reduction of acetonitrile by $[Bu_4N]BH_4$ at the rhenium(I) metal center in $ReCl_2(PMe_3)_2(CH_3CN)NO$ to afford $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (**2**) is reported. The coordinated iminoborane moiety is an intermediate in acetonitrile reduction. A mechanism is proposed for its formation. Further reaction with a hydride source ($LiBH_4$, $NaBH_4$, $LiHBEt_3$) results in replacement of chloride with hydride to give $ReH\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (**3**), together with varying proportions of $ReH_2(PMe_3)_3NO$ (**4**). Compounds **2** and **3** have been characterized by NMR and infrared data. The structure of **3** has additionally been elucidated by a single crystal X-ray diffraction study. Crystal data: $C_8H_{26}BN_2OP_2Re$, triclinic, $P\bar{1}$, $a = 8.821(7)$ Å, $b = 12.4062(11)$ Å, $c = 15.5822(12)$ Å, $\alpha = 70.004(9)^\circ$, $\beta = 82.726(9)^\circ$, $Z = 4$, $R = 0.0535$, $R_w = 0.1325$. The H_b/H_t hydrogen exchange process in the iminoborane moiety of **2** and **3** has been studied by NMR spectroscopy and a negative value of $\Delta S^{\#}$ found for this process. The proposed mechanism for this exchange resembles that of β-hydrogen elimination in metal alkyls.

Keywords: Rhenium; Borohydride; Acetonitrile

1. Introduction

The use of borohydride reagents in the reduction of unsaturated organic molecules such as aldehydes and ketones is well established [1]. Nitriles, however, are more difficult to reduce and generally require more powerful reducing agents. Reduction of nitriles to amines either with hydrogen in the presence of a catalyst, or by potent hydride reagents such as $LiAlH_4$, is a well-known reaction [2,3]. The coordination of organonitrile to a metal center, thereby polarizing the CN bond, is a common strategy for activating the CN bond, enabling the use of gentler reaction conditions. A number of examples of metal-mediated nitrile reductions involving bimetallic or cluster complexes has been reported and isolation of intermediates is often possible [4]. The characterization of intermediates in nitrile reduction promoted by metal monomers is, however, less well documented. Creaser and Sargeson first reported in 1975 that the reduction of coordinated acrylonitrile with BH_4^- occurred substantially faster than the same reaction for the uncoordinated nitrile [5]. Other examples are employing a metal in intermediate to high oxidation state, or a cationic metal center, to activate the CN bond to nucleophilic attack. Reduction intermediates have been obtained in some cases [6–10], notably in the elegant study of Feng and Templeton on the stepwise reduction of acetonitrile in the cation $[Tp'W(CO)(PhCCMe)(NCMe)]^+$ ($Tp' = 3,5$-dimethyl-*tris*(pyrazolyl)borate) by sequential hydride and proton addition reactions [9]. Intermediate metal complexes containing coordinated azavinylidene, imine, amide and amine nitrogen donor ligands have been isolated. The iminoacylation reactions of coordinated acetonitriles with a variety of oximes have also recently been reported [11].

The coordination chemistry of nitriles at electron-rich metal sites has not been so extensively explored, despite the interest in some nitriles as nitrogenase substrates [12]. $HBF_4 \cdot Et_2O$ has been used to protonate organonitriles at molybdenum and rhenium centers to give variously imine- [13], azaallylic- [14], azavinylidene-

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and hydrido-containing products [12,15]. Pombeiro has recently reviewed the coordination chemistry of organonitriles at rhenium(I) centers [12,14]. Proposed mechanisms for the protonation step vary. Kinetic studies on the protonation of $[ReCl(NCR)(dppe)_2]$, which affords either the monosubstituted azavinylidene complexes $[ReCl(N{=}CHR)(dppe)_2]BF_4$ or the hydrido derivatives $[ReHCl(NCR)(dppe)_2]^+$ [12,15], indicate that proton addition occurs first at the nitrile ligand and the hydride complexes are derived from methylene intermediates by proton migration to the metal [16]. On the other hand, protonation of the η^2-bonded nitrile in $[Cp_2Mo(MeCN)]$ in acetonitrile solution to form $[Cp_2Mo(NCMe)(NH{=}CHMe)][BF_4]_2$ is proposed to occur via initial protonation at the metal followed by hydrogen shift to the NC triple bond [13]. Further reactivity can occur at an electron-rich metal center with labile ligands. Replacement of N_2 or phosphine in *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with an alkyl- or arylnitrile followed by protonation by $HBF_4{\cdot}Et_2O$ affords amines, ammonia and hydrocarbons [17].

An exception to the general rule that a high valent or cationic metal center leads to nucleophilic attack, and a low valent metal to electrophilic attack at a coordinated nitrile is found with the d^6 tungsten(0) complex $W(PhCCPh)_3(NCMe)$, which reacts with the nucleophiles MeLi, PhLi and $LiHBEt_3$ to afford, respectively, $W(PhCCPh)_3(NH{=}CRMe)$ (R = Me, Ph) and $W(PhCCPh)_3(NH_2Et)$ after hydrolytic workup [18]. Presumably in this case the π-accepting ability of the alkyne ligands is sufficient to prevent extensive π-back-donation to the acetonitrile.

Given the relative paucity of information regarding borohydride reduction mechanisms and intermediate species in such reactions, the isolation of such intermediates is of importance. Here we present the borohydride reduction of acetonitrile at a rhenium(I) center. The initial reduction step is addition of $[H{-}BH_3]^-$ across the CN bond to produce an unusual iminoborane $(H_3BN{=}C(H)Me)^-$ moiety, which chelates to Re to form a four-membered ReHBN ring. 2D-EXSY-NMR studies have been carried out on this ring system and slow exchange of the bridging and terminal borane hydrogens observed above 273 K.

2. Experimental

2.1. Materials

All operations were carried out under nitrogen atmosphere using standard Schlenk line and glovebox techniques unless otherwise stated. Solvents were predried over KOH (THF) or sodium wire (hexane), dried over sodium diphenylketyl (THF, Et_2O, hexane, pentane) and distilled under nitrogen, then either used immediately or stored in a glovebox prior to use. Deuterated solvents used in NMR experiments (C_7D_8, C_6D_6, C_4H_8O) were predried over sodium then dried and stored over sodium/potassium alloy (3:1 Na:K) in ampoules fitted with Teflon stopcocks. For reactions studied by NMR spectroscopy the solids were weighed (±1 mg) into 5 mm NMR tubes inside the glovebox, then tightly fitted into an airtight Swagelock apparatus attached to a Teflon stopcock. Solvent was then vacuum transferred into the tube on a vacuum line and the tube sealed under vacuum. ^{1}H-, ^{13}C-, ^{31}P- and ^{11}B-NMR experiments were carried out on a Varian Mercury 200, a Varian Gemini-300 (operating at 300.1, 75.4, 121.5 and 96.2 MHz, respectively), or a Bruker DRX500 spectrometer (operating at 500.2, 125.8, 202.5 and 160.5 MHz, respectively). Chemical shifts are given in ppm. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 and ^{11}B chemical shifts to $BF_3{\cdot}OEt_2$. Elemental microanalyses were performed by the microanalytical service of the Inorganic Chemistry Institute at the University of Zurich. IR spectra were recorded on a BIO RAD FTS-45 spectrophotometer.

The following reagents were purchased from commercial suppliers and used without further purification: $[Bu_4N]BH_4$, $NaBH_4$, $LiBH_4$, $NaBD_4$, $LiHBEt_3$ (Aldrich). $ReCl_2(PMe_3)_2(MeCN)NO$ was prepared according to the literature procedure [19].

2.2. Preparation of $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (2)

In a typical reaction, $ReCl_2(PMe_3)_2(MeCN)NO$ (100 mg, 0.208 mmol) and $[Bu_4N]BH_4$ (115 mg, 0.43 mmol, 2.1 equivalents) were mixed in a Schlenk and THF (ca. 15 ml) added to give a yellow–orange solution. This solution was stirred for 5 h, during which time it became slightly darker. After removing solvent in vacuo, the resulting yellow oily solid was extracted into Et_2O (4 × 25 ml). Removal of Et_2O afforded an orange oily solid. This solid was washed several times with hexane to afford an orange powder (**2**, 30 mg, 31%) and an orange solution. Evaporation of hexane from the washings afforded a further 45 mg of orange oily solid, which also contained **2** as major species, plus several other phosphorus containing species, as evidenced by ^{31}P-NMR spectroscopy. Some of these additional products could be removed by vacuum sublimation onto a cold finger. Anal. Calc. for $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO{\cdot}(C_4H_8O)_{0.25}(C_4H_{10}O)_{0.5}$: $C_{11}H_{32}N_2O_{1.75}BP_2ClRe$; C 25.66, H 6.27, N 5.44. Found: C 25.48, H 5.99, N 5.53%. IR (KBr pellet, cm^{-1}): 2428, 2388 (ν_{B-Ht}); 1773 (w) (ν_{B-Hb}); 1675 (s) (ν_{NO}); 1174 (s) (δBH_2). ^{1}H (300 MHz, C_7D_8, 293 K): δ 7.33 (br q, $^3J_{HH} \approx 5$ Hz, 1H, $N{=}C(CH_3)H$); 3.53 (br,

THF); 3.15 (q, $J = 7$ Hz, $(CH_3CH_2)_2O$); 1.98 (d, $J = 5$ Hz, 3H, $(CH_3)HC{=}N$); 1.81 (br, THF); 1.15 (t, $J = 7$ Hz, $(CH_3CH_2)_2O$); 0.99 ('t', $J = 4$ Hz, 18H, $P(CH_3)_3$); −3.5 (br d, 1H, B–(μ-*H*)–Re). $^{13}C\{^1H\}$ (75.4 MHz, C_6D_6, 293 K): δ 153.89 (s, $(CH_3)HC{=}N$); 21.90 (s, $(CH_3)HC{=}N$) 11.38 (t, $^1J_{CP} = 16$ Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ (121.47 MHz, C_6D_6, 293 K): δ −26.28 (s, $P(CH_3)_3$). $^{11}B\{^1H\}$ (96.272 MHz, C_6D_6, 293 K): δ −26.57 (br s, BH_3N). ^{11}B (96.272 MHz, C_6D_6, 293 K): δ −26.51 (br t,d $^1J_{BHt} = 125$ Hz (triplet), $^1J_{BHb} = 30$ Hz (doublet), BH_3N).

2.3. Preparation of $ReH\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ (3)

In a typical reaction, $Re(MeCN)(NO)Cl_2(PMe_3)_2$ (300 mg, 0.63 mmol) and $LiBH_4$ (70 mg, 0.32 mmol, four equivalents) were mixed in a Schlenk and THF (30 ml) added at room temperature (r.t.). The reaction was followed by $^{31}P\{^1H\}$-NMR spectroscopy, monitoring the disappearance of starting material. After 21 h stirring at r.t. the THF was removed in vacuo and the resulting yellow oil redissolved in toluene and filtered over Celite. After removal of toluene the yellow oil was further extracted into hexane to afford 50 mg of a mixture of **3** (approximate yield of **3**, 15%, based on starting material, by $^{31}P\{^1H\}$-NMR spectroscopy) and $Re(PMe_3)_3(H)_2NO$. IR (KBr pellet, cm^{-1}): 2479 (sh), 2389 (s, br) (ν_{B-Ht}); 1858 (w, br) (ν_{Re-Ht}); 1750 (w) (ν_{B-Hb}); 1648 (s) (ν_{NO}); 1098 (s), 1022 (s) (δ_{BH2}). ^1H (300 MHz, C_6D_6, 293 K): δ 7.92 (br s, 1H, $(CH_3)HC{=}N$); 2.04 (br d, $J = 5$ Hz, 5H, $(CH_3)HC{=}N$); 1.52 ('t', 4H, ax-(PCH_3) in **4**); 1.40 (d, 2H, eq-(PCH_3) in **4**); 1.21 ('t', $^2J_{PH} = 4$ Hz, 18H, $P(CH_3)_3$ in **3**); −1.12 (t, $J = 20$ Hz, Re–*H*); −6.5 (br, B–*H*–Re); −1.45 (m, Re-$H_2(PMe_3)_3NO$); −3.94 (m, $ReH_2(PMe_3)_3NO$). $^{31}P\{^1H\}$ (121.47 MHz, C_6D_6, 293 K): δ −31.72 (s, '80%', $P(CH_3)_3$ in **3**); −36.01 (d, $J = 13$ Hz, ax-(PCH_3) in **4**); −43.74 (t, $J = 13$ Hz, eq-(PCH_3) in **4**) (total 13% of **4**). $^{13}C\{^1H\}$ (75.4 MHz, C_6D_6, 293 K): δ 153.89 (s, $(CH_3)HC{=}N$); 25.30 (t,d, $J_t = 16.4$ Hz, $J_d = 2.1$ Hz, ax-(PCH_3) in **4**); 24.98 (d,t, $J_d = 27$ Hz, $J_t = 2$ Hz, eq-(PCH_3) in **4**); 24.69 (s, $(CH_3)HC{=}N$); 16.75 (t, $^1J_{CP} = 16$ Hz, $P(CH_3)_3$ in **3**). $^{11}B\{^1H\}$ (96.272 MHz, C_6D_6, 293 K): δ −29.31 (br s, BH_3N). ^{11}B (96.272 MHz, C_6D_6, 293 K): δ −29.31 (br 't,d' $^1J_{BHt} = 115$ Hz (triplet), $^1J_{BHb} = 43$ Hz (doublet), BH_3N).

Alternatively the reaction could be carried out following the same procedure utilizing five equivalents of $NaBH_4$ and stirring in THF at r.t. for 4 weeks, then working up as before to afford 30 mg of orange oily solid containing 90% of **3** (by $^{31}P\{^1H\}$-NMR spectroscopy), equivalent to 27 mg, 60% yield based on starting material.

2.4. Alternative synthesis of 3: reaction of 2 + $LiHBEt_3$

A 5 mm NMR tube fitted with a Young's tap was charged under nitrogen with $LiHBEt_3$ (0.05 ml of a 1 M solution in THF, 0.05 mmol) and the THF removed in vacuo. Compound **2** (10 mg, 0.02 mmol) was added as a solid in the drybox. The tube was then reconnected to a vacuum line and THF-d_8 vacuum-transferred into the tube. Warming the tube to r.t. gave a yellow–orange solution. The progress of the reaction was monitored by NMR spectroscopy, with ca. 40% of **2** used up after 20 min. The conversion of **2** to **3** appeared complete after 3–4 h. The solvent was removed in vacuo and the resulting yellow–brown oil extracted into CH_2Cl_2 and filtered over Celite, then solvent removed to afford 7 mg of brown oily solid which contained **3** as ca. 70% of phosphorus-containing species by $^{31}P\{^1H\}$-NMR spectroscopy, equivalent to 47% yield (based on **2**).

2.5. Preparation of $ReD\{(\mu\text{-}D)B(D)_2N{=}C(D)Me\}(PMe_3)_2NO$ (3′)

Compound **3′** was prepared in analogous fashion to **3**, utilizing five equivalents of $NaBD_4$ and stirring in THF at r.t. for 5 weeks, then working up as for **3** to afford 40 mg of brown oil containing 71% of **3′** relative to other phosphorus-containing species (by $^{31}P\{^1H\}$-NMR spectroscopy). Approximately 10% of **2′** and 5% of **4′** were also identified in the oil, together with a fourth, unidentified species. IR (KBr pellet, cm^{-1}): 1750 (ν_{B-Dt}); 1637 (s) (ν_{NO}); 1336 (w, br) (ν_{Re-Dt}); 1302 (w) (ν_{B-Db}); 777 (s) (δ_{BD2}).

2.6. X-ray structure analysis

A yellow–orange plate of **3**, covered with hydrocarbon oil, was cut to a suitable size for the X-ray experiment. It was mounted on top of a glass fiber and immediately transferred to the goniometer of a STOE IPDS diffractometer where it was cooled to 183(2) K using an Oxford Cryo System. Collection of diffraction intensities and data processing was performed using the STOE IPDS software [20]. A numerical absorption correction [21], based on 12 crystal faces, was applied with FACEitVIDEO and XRED [20]. The structure was solved by Patterson methods using the program system SHELXS-97 [22]. Two independent molecules could be determined in the asymmetric unit of the triclinic unit cell. No higher symmetry was found using the program MISSYM [23]. All heavy atoms were refined using anisotropic displacement parameters. Positions of H-atoms were calculated after each refinement cycle (riding model), except for the two hydride atoms H_1, H_{1c}, H_2, H_{2c} at each of Re_1 and Re_2. These were located from difference electron density maps and their positions fixed during the refinement. Crystal drawings

were generated by ORTEP [24]. Further crystallographic data and refinement results are given in Table 4.

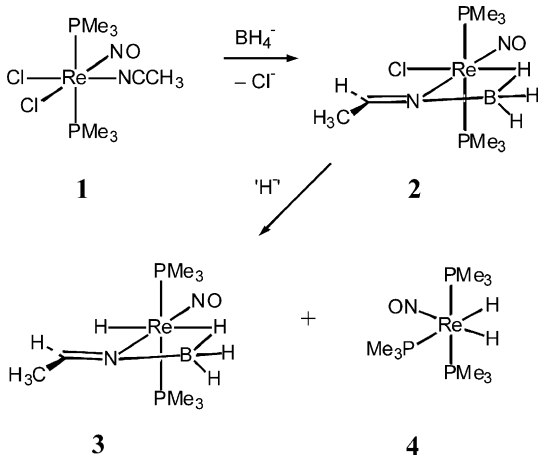
3. Results and discussion

3.1. Synthesis and characterization of $ReX\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$ ($X = Cl$, **2**; H, **3**)

It was hoped that replacement of the carbonyl ligand in $ReCl_2(PMe_3)_2(CO)(NO)$ by a potentially more labile acetonitrile group in $ReCl_2(PMe_3)_2(CH_3CN)NO$ [19] (**1**) would enable the facile substitution of the acetonitrile by other ligands. This substitution has been shown to proceed in good yield with a number of neutral σ-donor ligands such as phosphines, phosphites and amines [19b]. Reaction with borohydride, however, rather than giving the desired hydride borohydride complex $Re(\eta^2\text{-}BH_4)H(PMe_3)_2NO$ via replacement of the acetonitrile and the two chlorides in **1**, results in either reduction of the acetonitrile CN triple bond, or formation of the tris(phosphine)-dihydride $Re(H)_2(PMe_3)_3NO$, apparently depending on the reaction conditions (Scheme 1).

Thus, reaction of **1** with $[Bu_4N]BH_4$ in THF affords an orange oil which, after washing with hexanes, gives poor yields of an orange powder (**2**). It has not been possible to obtain satisfactory elemental microanalytical data for **2** owing to the presence of small amounts of solvent (Et_2O, THF) which cannot be removed by placing the sample under dynamic vacuum for several hours. The data of the elemental analysis allows to formulate the compound as '$ReCl(BH_4)(PMe_3)_2(CH_3CN)NO(Et_2O)_{0.5}(THF)_{0.25}$'. The presence of low amounts of ether and THF is also indicated by ^{1}H-NMR spectroscopy. Removal of solvent from the hexane washings, followed by vacuum sublimation of impurities onto a cold finger affords a further quantity of **2**, although this is not a satisfactory purification method as it is not possible to obtain **2** entirely pure in this way. The $^{31}P\{^1H\}$-NMR spectrum of **2** displays a singlet at δ −26.28 ppm and the $^{11}B\{^1H\}$-NMR spectrum a singlet at δ −26.51 ppm which is resolved in the proton-coupled ^{11}B spectrum as a triplet of doublets ($J_{triplet} = 125$ Hz, $J_{doublet} = 30$ Hz). The ^{11}B chemical shift is in the range expected for tetracoordinate boron and the coupling constants observed correspond to $^1J_{BHterminal}$ and $^1J_{BHbridging}$, compared with values of 135 and 45 Hz, respectively, in diborane [25]. The CH_3CN signals at δ 1.7 (CH_3) and 134.0 (CN) ppm in the $^{13}C\{^1H\}$-NMR spectrum of the starting material **1** are considerably shifted to δ 21.9 and 153.9 ppm, respectively, in **2**, indicative of the reduction of the nitrile CN triple bond to a C=N double bond. The ^{1}H-NMR spectrum of **2** in toluene-d_8 displays a broad, poorly resolved quartet ($^3J_{HH} \approx 5$ Hz) centered at δ 7.3 ppm in the aromatic region and a broad doublet ($^3J_{HH} = 5$ Hz) at δ 1.98 ppm, consistent with reduction of CH_3CN to $(CH_3(H)C{=}N)^-$, as well as a pseudo-triplet ($J_{second\ order} = 4$ Hz) at 0.99 ppm for the *trans*-phosphines and a broad signal centered around −3.6 ppm assigned to the $B{-}H_b{-}Re$ bridging hydrogen. The $^1H\{^{11}B\}$ spectrum exhibits an additional resonance at δ 1.95 ppm, assigned to the $B{-}H_t$ terminal hydrogens on the basis of the ^{11}B, ^1H correlation spectrum and the broad resonance at δ −3.6 ppm is resolved into a multiplet with coupling constant of ca. 9 Hz at low temperature (250–280 K). No sharpening of the other signals is observed on decoupling from ^{11}B. The broadness of the imine methyl and methine proton resonances is, therefore, attributed to fast relaxation owing to the neighboring quadrupolar nitrogen atom. On the basis of the spectroscopic and elemental microanalytical data, **2** has been assigned the composition $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$.

The use of $LiBH_4$ as nucleophile in THF also results in initial formation of **2**, as observed by following the evolution of the ^{31}P-NMR signals either in an NMR tube reaction in THF-d_8, or by monitoring the progress of a preparative scale reaction in protio-THF. Only small amounts of **2** are observed, however, and the reaction continues to afford a second product **3** with a ^{31}P-NMR signal at δ −31.7 ppm, accompanied by formation of 10–30% of $Re(H)_2(PMe_3)_3NO$ (**4**) and small amounts of other unidentified compounds. $Re(H)_2(PMe_3)_3NO$ has been prepared previously by an alternative route, reacting **1** with a small excess of PMe_3 to obtain $ReCl_2(PMe_3)_3NO$, followed by short reflux of $ReCl_2(PMe_3)_3NO$ with $NaBH_4$ in butanol and appropriate workup [19b]. Relevant spectroscopic data for **4** is given here. Removal of THF from a preparative scale reaction solution, followed by extraction into toluene and filtration over Celite then removal of toluene, affords a yellow oil which is identified as a mixture of **3** and **4** together with some further phosphorus-contain-



Scheme 1.

ing compounds. The smaller quantities of impurities can be removed by extraction into hexane or pentane, to leave a 'clean' mixture of ca. 70–90% **3** and 30–10% **4**. Separation of **3** from **4** has proved difficult. Both are soluble in pentane and sublime at 30–40 °C under vacuum. Column chromatography results in decomposition, affording a mixture of several intractable products and recrystallization affords only very poor yields of **3**. Compounds **3** and **4** do not appear to interact with each other, however, and although accurate elemental analysis data could not be obtained, it has been possible to obtain spectroscopic data on **3** in the presence of **4**. The ^{11}B-NMR spectrum of **3** exhibits a triplet of doublets as for **2**, at δ −29.3 ppm ($J_t = 115$ Hz, $J_d = 43$ Hz). The $^{13}C\{^1H\}$-NMR spectrum of **3** in C_6D_6 is similar to that obtained for **2**, as is the ^{1}H-NMR spectrum, with the exception of the high field region which displays a triplet for a rhenium hydride ($^2J_{HP} = 20$ Hz) at δ −1.12, and the H_{bridge} resonance as a broad doublet centered at δ −6.8 ppm. In the ^{11}B-decoupled spectrum at 300 K this H_b resonance resolves into a multiplet in which the major component is a triplet ($^2J_{HP} = 9$ Hz), with additional coupling believed to be to ^{10}B. The signal for the $H_{terminal}$ hydrogens, a broad pseudo-quartet ($J = 9$ Hz) owing to coupling of similar magnitude to H_b and ^{31}P, at δ 1.57 ppm, was located by subtraction of the ^{1}H from the $^1H\{^{11}B\}$-NMR spectrum. The ^{1}H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR data for complexes **1**, **2**, **3** and **4** are given in Tables 1 and 2.

Reaction of **1** with $NaBH_4$ over 3–4 weeks at room temperature affords a slightly higher ratio of compound **3** to **4** after the same workup procedure as for the reaction with $LiBH_4$ and with smaller quantities of minor impurities. This route has also been employed to prepare the analogous deuterated complex **3′**, employing $NaBD_4$.

Infrared spectroscopy is a valuable tool in the identification of different bonding modes of borohydride ligands [26]. In addition the complexes reported here possess infrared-active CN and NO stretches. The infrared data for **1**, **2**, **3**, **3′** and **4** are listed in Table 3. The solid state (KBr) infrared spectrum of **2** exhibits a strong doublet for ν_{B-Ht} at 2428, 2388 cm^{-1}, a single ν_{B-Hb} peak at 1773 cm^{-1}, and ν_{NO} at 1675 cm^{-1}. A BH_2 deformation band has also been identified at 1174 cm^{-1}. The solid state (KBr) infrared spectrum of **3** displays bands at 2479 (shoulder), 2389 (ν_{B-Ht}), 1750 (ν_{B-Hb}) and 1648 (ν_{NO}) cm^{-1} and a further broad band at 1858 cm^{-1}, attributed to ν_{Re-H}. The BH_2 deformation mode is split into a doublet, occurring at 1098, 1022 cm^{-1}. The bands for **4**, which occur at 1838 and 1752 cm^{-1} (Re–H) in THF solution, presumably overlap with the Re–H and B–H–Re bands at similar wavenumbers for complex **3**, contributing to broadening of these signals. It has not been possible to identify C=N stretching modes. This is unsurprising, since the C=N in other azavinylidene ligands is usually reported at 1600–1680 cm^{-1}, in the same range as the nitrosyl ligand [27,9a,11c,11e]. A shoulder on the NO band for **3**, at 1609 cm^{-1}, could be attributed to a C=N stretch, although this could also arise from the NO band for **4**, at 1596 cm^{-1} in THF solution. Assignment of the B–H and Re–H bands for **3** was assisted by comparison with those for **3′**.

Although it was not possible to separate **3** from the byproduct **4** by sublimation, slow evaporation of a hexane solution of the oily mixture over several weeks afforded several small orange platelets, one of which was suitable for X-ray diffraction studies.

3.2. Crystal structure of $ReH\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. Both exhibit the same structure, which is shown for one molecule in Fig. 1. Hydrogen atoms $H_{1(2)}$ and $H_{1c(2c)}$ were located in the difference Fourier map and their positions fixed in final refinement cycles. Terminal B–H hydrogens H_{1a} and H_{1b} could not be located and their positions were fixed at 1 Å from the boron atom. The crystal chosen for study was not of high quality and the

Table 1
$^1H\{^{11}B\}$-NMR data for compounds **1** [c], **2** [b], **3** [b] and **4** [c] (δ in ppm, J in Hz)

Compound	$P(CH_3)_3$	$CH_3(R)CN$ [a]	$CH_3(H)CN$	B–H_b	B–H_t	Re–H
1[19]	1.43 ('t', $J = 4$)	1.22 (s)				
2	0.99 ('t', $J = 4$)	1.98 (br d, $^3J_{HH} = 5$)	7.33 (br q, $^3J_{HH} = 5$)	−3.6 (br d)	1.95 (br s)	
3	1.21 ('t', $J = 4$)	2.04 (br d, $^3J_{HH} = 5$)	7.92 (br s)	−6.84 (br d)	1.57 (br q, $J = 9$)	−1.12 (t, $^2J_{HP} = 20$)
4[19]	1.52 (t, $J_{PH} = 5$, ax-PMe_3) 1.40 (d, $J_{PH} = 5$, eq-PMe_3)					−1.45 (m), −3.94 (m)

[a] R = no substituent (**1**); H (**2**, **3**).
[b] In C_7D_8.
[c] In C_6D_6.

Table 2
$^{31}P\{^{1}H\}$- and $^{13}C\{^{1}H\}$-NMR data for compounds **1** [c], **2** [b], **3** [b] and **4** [c] (δ in ppm, J in Hz)

Compound	$^{31}P\{^{1}H\}$ (ppm)	$^{13}C\{^{1}H\}$ (ppm)		
	$P(CH_3)_3$	$P(CH_3)_3$	$CH_3(R)CN$ [a]	$CH_3(R)CN$ [a]
1[19]	−30.1 (s)	12.4 ('t' $^{1}J_{CP} = 15$)	1.7 (s)	134.0 (s)
2	−26.51 (s)	11.38 (t, $^{1}J_{CP} = 16$)	21.90 (s)	153.89 (s)
3	−31.72 (s)	16.75 (t, $^{1}J_{CP} = 16$)	24.69 (s)	153.89 (s)
4[19]	−36.01 (d, ax-PMe_3); −43.74 (t, eq-PMe_3)	26.00 (t,d, $J_t = 16$, $J_d = 2$, ax-PMe_3) 25.30 (d,t, $J_d = 26$, eq-PMe_3)		

[a] R = no substituent (**1**); H (**2**, **3**).
[b] In C_7D_8.
[c] In C_6D_6.

Table 3
Selected IR data for compounds **1** [19], **2**, **3** and **4** [19] (cm^{-1})

1	2019 [a] (w)(ν_{CN}); 1671 [a] (s), 1678 [b] (s) (ν_{N-O})
2 [a]	2428 (s), 2388 (s) (ν_{B-Ht}); 1773 (ν_{B-Hb}) (w); 1675 (s) (ν_{N-O}); 1174 (s) (δ_{BH2})
3 [a]	2479 (sh), 2389 (s) (ν_{B-Ht}); 1858 (w, br) (ν_{Re-Ht}); 1750 (w) (ν_{B-Hb}); 1648 (s) (ν_{N-O}); 1098 (s), 1022 (s) (δ_{BH2})
3′ [a]	1750 (w) (ν_{B-Dt}); 1637 (s) (ν_{N-O}); 1336 (w) (ν_{Re-Dt}); 1302 (w) (ν_{B-Db}); 777(s) (δ_{B-D2})
4 [b]	1752 (w), 1838 (w) (ν_{Re-Ht}); 1596 (s) (ν_{N-O})

[a] KBr pellet.
[b] THF solution.

Table 4
Experimental data for the X-ray study of compound **3**

Compound	ReH{(μ-H)B(H)$_2$N=C(H)Me}(P-Me$_3$)$_2$NO
Empirical formula	$C_8H_{26}BN_2OP_2Re$
Fw	425.26
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Space group	$P\bar{1}$
a (Å)	8.8821(7)
b (Å)	12.4062(11)
c (Å)	15.5822(12)
α (°)	70.004(9)
β (°)	82.726(9)
γ (°)	89.860(10)
V (Å^3)	1599.0(2)
Z	4
ρ_{calc} (g cm^{-3})	1.766
μ (Mo–K$_\alpha$) (cm^{-1})	77.81
Crystal size (mm)	0.51 × 0.23 × 0.16
θ Range (°)	2.75–30.28
Index ranges	$-12 \le h \le 11$, $-16 \le k \le 17$, $0 \le l \le 22$
Reflections collected	20 805
Number of unique total data	8714 [$R_{int} = 0.0733$]
Max. and min. transmission	0.3691 and 0.1094
Goodness-of-fit on F^2	1.015
R_1	0.0535 [$I > 2\sigma(I)$]
wR_2	0.1325 [$I > 2\sigma(I)$]
wR_2 (all data)	0.1498

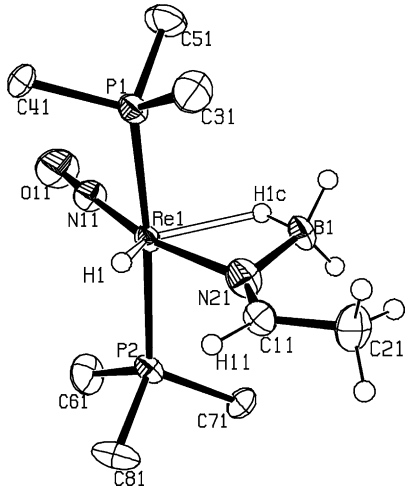


Fig. 1. Molecular structure of ReH{(μ-H)B(H)$_2$N=C(H)Me}(P-Me$_3$)$_2$NO (**3**) shown with 50% ellipsoids, with the atom-numbering scheme.

standard deviations (S.D.) are relatively large. Selected bond distances and angles for both independent molecules are found in Table 5. The bond distances and angles for the two independent molecules are similar and only molecule 1 will be discussed, unless otherwise stated.

Although the rhenium center is six-coordinate, an octahedral coordination geometry fits the data poorly and the coordination geometry about the central rhenium atom is better described as capped trigonal bipyramidal (Fig. 2). In the trigonal bipyramidal structure the two phosphorus atoms occupy apical positions and the equator is defined by the NO nitrogen and the two hydrogen atoms, one terminal and one bridging to boron. The imine nitrogen atom caps the P_2–H–H face very close to the H–H edge.

The X-ray structure determined for the starting complex $ReCl_2NO(PMe_3)_2(MeCN)$ contained two independent molecules in the asymmetric unit, of which only two could be refined without disorder [19a]. Any comparisons with **1**, therefore, refer to these two molecules. The Re–P distances in **3** (average 2.403 Å)

Table 5
Selected bond distances (Å) and angles (°) for ReH(NO)(PMe_3)$_2$(μ-HB(H)$_2$N=C(H)CH_3) (values for molecule 2 in parentheses)

Bond distances			
Re–P	2.402(3), 2.403(3) (2.396(3), 2.408(3))	N–O	1.201(13) (1.168(14))
Re–N_{11}	1.773(10) (1.790(10))	B–N	1.55(15) (1.507(15))
Re–N_{21}	2.094(8) (2.086(9))	B–$H_{1c(2c)}$	0.998 (0.986)
Re–$H_{1(2)}$	1.956 (1.944)	N–$C_{11(12)}$	1.273(13) (1.291(14))
Re–$H_{1c(2c)}$	1.960 (1.974)	$C_{11(12)}$–$C_{21(22)}$	1.494(16) (1.487(15))
Re–B	2.532(12) (2.545(12))		
Bond angles			
Re–N_{11}–O	176.3(11) (176.9(10))	Re–$N_{21(22)}$–B	87.3(6) (88.7(7))
P–Re–P	171.23(9) (171.10(9)	Re–N–$C_{11(12)}$	142.6(8) (143.1(8))
N–Re–N	166.5(4) (165.4(4))	N–$C_{11(12)}$–$C_{21(22)}$	123.4(10) (124.1(11))
H–Re–H	113.1 (144.7)		

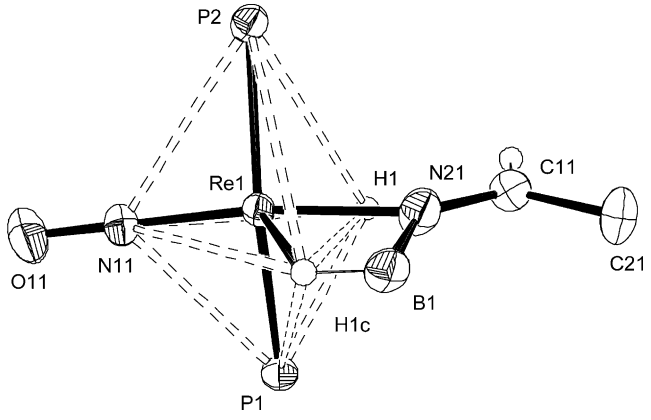


Fig. 2. Trigonal bipyramidal geometry at Re in ReH{(μ-H)B(H)$_2$N=C(H)Me}(PMe_3)$_2$NO (**3**).

are not significantly different from those in **1** (average 2.423 Å), also lying in the same range as for the related six-coordinate Re(I) complexes Re(H)(η^2-BH_4)(NO)(PR_3)$_2$ (R = ^{i}Pr, Ph) [28] and ReClH(CO)NO(PMe_3)$_2$ [29]. The Re–NO distance of 1.773(10) Å is comparable to those observed in the five-coordinate dinitrosyl Re(I) complex ReH(NO)$_2$(P^iPr_3)$_2$ (1.775(5), 1.749(5) Å), and in six-coordinate Re^IClH(CO)NO(P{OMe}$_3$)$_2$ (1.78(1) Å), but shorter than that reported for ReClH(CO)NO(PMe_3)$_2$ (1.921(8) Å). It is also shorter than the bond to the imine nitrogen, presumably owing to the more pronounced ability of the NO group to accept metal electron density, resulting in decreased Re–N and increased N–O distances. The N–O bond length of 1.201(13) (1.168(14)) Å is comparable to those in Re(H)(η^2-BH_4)(NO)(PR_3)$_2$ (R = ^{i}Pr, 1.17(1); Ph, 1.18(2) Å), and shorter than the NO–BF_3 N–O distance (1.304(7) Å) in the BF_3 adduct ReH(NO)(NO-BF_3)(P^iPr_3)$_2$ [28]. The Re–N–O moiety is effectively linear, indicating that the three-electron donor mode of NO is maintained. The Re–H_1 bond of 1.96 Å is quite long compared with the Re–H bond in Re(H_2BEt_2)(*racemic*-tetraphos) (1.685(52) Å), (tetraphos = Ph_2PCH_2-$CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$) [30] but comparable to those in six-coordinate ReClH(NO)(PMe_3)$_3$ (1.97(6) Å) [19] and in the seven-coordinate dihydride ReH_2(hq)(PPh_3)$_2$($PHPh_2$) (1.90(6) Å) (hq = the monocation of 2-hydroxyquinoline) [31]. The overall quality of the data set together with the difficulties inherent in the accurate location of hydrogen atoms in proximity to heavy metal atoms make detailed discussion of these values in terms of electronic or steric factors inappropriate. Further evidence for the position of the Re–H hydride hydrogen atom (although not the Re–H bond length) has, however, been obtained from 2D-NMR spectroscopic methods (vide infra).

The η^1-coordinated azavinylidene moiety Re–N–C (Re–N_{21}–C_{11} 142.6(8)°) is considerably distorted from the linear geometry often associated with such complexes which arises from a large M=N double bond component [32,27b,27c,27d,27e,8]. The Re–N bond in this moiety is also a little long to postulate any double bond character and is somewhat longer than the bond to the nitrosyl ligand (2.094(8) (2.086(9)) compared with 1.773(10) Å) (vide supra). Indeed, it is very close to the Re–NCMe bond distance in **1** (average 2.064 Å). The planar environment at N_{21} and the short N–C bond length of 1.273(13) Å are consistent with sp^2 hybridization at N and a N=C double bond. The C_{11}–C_{21} bond distance is in the single bond range [33].

The most unusual part of the structure is the four-membered cycle Re–H–B–N (Fig. 1), which to our knowledge has not previously been observed for a low-valent metal, nor with a simple (non-substituted) borane unit.

A search of the crystallographic database revealed only a few examples of M–H–B–N rings, most of which contain another boron atom (M=B) [27a,34], although examples with Ti [35] and Zr [36] are also known. The B–H_{1c} bond in **3**, at 1.00 Å, is shorter than those reported for Cp_2ZrCl–N(^{t}Bu)–B(H)NR_2 (NR_2 = tetramethylpiperidene) (B–H = 1.25(2) Å) [36] although comparable (within three S.D.) with those in [{Ti(salen)(BH_4)$_2$}$_2$]·2THF (salen = N,N′-ethylenebis(salicylideneimate)) (B–H = 1.23(12), 1.42(12) Å) [35].

The B–N bond in **3**, at 1.525(15) Å, is comparable to those observed in [{Ti(salen)$(BH_4)_2$}$_2$]·2THF (1.52(4), 1.56(4) Å) and longer than that in Cp_2ZrCl–N(^{t}Bu)–B(H)NR_2 (1.360(3) Å), and is consistent with B–N single bond character. The Re···B distance of 2.532(12) Å compares with that of 2.340(7) Å in Re(H_2BEt_2)(*racemic*-tetraphos) [30], corresponds to the range reported for M(η^2-BH_4) complexes [37] and is shorter than expected for a singly-bridged M–H–B unit [37a,37c,38] presumably owing to the constraints of the ring and the resulting small Re–N–B angle (87.3(6)°).

3.3. ^{1}H-NMR spectroscopic studies

One area of interest in the study of borohydride complexes is the existence and mechanism of bridging/terminal exchange of the boron-attached hydrogens. In this case, since the BH_3 unit is effectively tethered by the B–N bond, it is not clear whether such exchange could occur, or if so, by what mechanism. A dissociative mechanism involving Re–H bond breaking would appear possible, although H_b/H_t exchange has also been found to occur by an associative mechanism involving a M(μ-H)$_3$BH intermediate [39]. Alternatively, 'in place' rotation, as observed for some β-agostic alkyl complexes, offers a further possibility [40].

Variable temperature ^{1}H,^{1}H{^{11}B}-EXSY-NMR spectroscopy on samples of **2** and **3** in toluene-d_8 has demonstrated that the terminal and bridging hydrogens in both are indeed in exchange within the NMR time scale from room temperature up to 363 K. At 273 K (for compound **3**) or 253 K (for compound **2**) this exchange no longer occurs and only NOE signals are observed for **2** and **3** corresponding to dipolar interactions between the bridging (H_b) and terminal (H_t) borohydride hydrogens, between H_b and the phosphine hydrogens, and in **3** between H_b and the terminal Re–H hydrogen. This last interaction corroborates the small H_b–Re–H angle observed in the X-ray diffraction study. The energy barrier for the H_b/H_t exchange process in **2** and **3** appears to be a little higher than in many BH_4 complexes and separate, distinct resonances for H_b and H_t are detectable in the 500 MHz ^{1}H-NMR spectra up to 373 K. This contrasts with the behavior exhibited by agostic β-methyl groups in metal-coordinated vinyl [41] or acyl [42] moieties, which tend to be fluxional with coalescence temperatures lower than 273 K. Variable temperature ^{1}H- and ^{1}H{^{11}B}-NMR experiments in toluene-d_8 suggest that the barrier to exchange is slightly lower in the chloride **2**, consistent with the observation of exchange at lower temperature for **2** than for **3** in the 2D-EXSY experiments. Thus, the signal at δ −3.6 ppm for the bridging hydrogen starts to broaden into the baseline at 333 K and disappears by 373 K on a 300 MHz spectrometer. No emergence of a new coalesced peak is observed in the toluene-d_8 temperature range, however. The hydride **3** displays a similar broadening of the resonance at δ −6.5 ppm into the baseline, although this broad signal is still visible at 373 K (300 MHz). This observation could suggest that the exchange mechanism does not involve Re–H_b bond breaking, since this would be expected to be faster for the Re–H bond *trans* to hydride, which exerts a stronger *trans* influence than chloride and should, therefore, lead to a lower coalescence temperature for **3** than for **2**. However, the severe distortion from linearity of the H–Re–H_b angle should effectively reduce to zero any *trans* influence of the hydride on the Re–H_b bond. This is confirmed by the lack of scalar coupling between the Re-hydride and H_b, with the hydride triplet at δ −1.12 ppm appearing as a sharp singlet in the ^{1}H{^{31}P}-NMR spectrum. On the other hand, the observation of the dipolar interaction between H_b and the Re–H hydrogen allows us to postulate the existence of a hydrogen-bonding interaction which would stabilize the 'static' (on the NMR timescale) configuration.

Kinetic data on the bridging/terminal hydrogen exchange process have been obtained from line shape analysis for a three site exchange over the temperature ranges 273–355 K (hydride **3**) and 260–330 K (chloride **2**). The barrier for H_b/H_t exchange is lower for **2** than for **3** by almost 20 kJ mol^{-1} ($\Delta H^{\#}$(**2**) = 44.9 ± 2.7 kJ mol^{-1}; $\Delta H^{\#}$(**3**) = 63.7 ± 3.7 kJ mol^{-1}). Surprisingly, the entropy values found are negative and larger than expected, ($\Delta S^{\#}$(**2**) = −17 eu ± 9 J mol^{-1} K^{-1}; $\Delta S^{\#}$(**3**) = −6 eu ± 11 J mol^{-1} K^{-1}) implying that the transition state is more ordered than the ground state. The magnitude of $\Delta S^{\#}$ for **2** is larger than that for **3**, which could also suggest that a different mechanism is operating. This is worth noting, since comparison of $\Delta G^{\#}$ values for bridge/terminal exchange in borohydride complexes usually assumes that $\Delta S^{\#}$ for the exchange process is essentially the same for all species, and that exchange proceeds via the same mechanism in all cases [43]. The slightly negative entropy value would appear to disfavor a mechanism involving Re–H bond-breaking. A mechanism involving B–N bond breaking also seems unlikely, given the Lewis acidity of the BH_3 moiety, although this could be compensated by interaction with the electron-rich rhenium center. An associative process would be consistent with the negative entropy values and has some precedent in borohydride complexes [39], although rotation about the M–B vector is precluded here by the observation that the environment of the imine moiety is unaltered. On the other hand, a mechanism invoking initial B–H_b bond breaking to afford an intermediate hydride complex with stabilizing π-donation from N into the empty boron p-orbital, followed by rotation about the B–N bond to align this empty orbital with the hydride hydrogen and reform the BH_3 moiety could provide an alternative

route. This mechanism could be considered as analogous to the β-H elimination process in metal–alkane complexes (Fig. 3). This would also offer a possible pathway for formation of **4**, via loss of 'H_2BN=C(H)Me'. In this case, addition of a coordinating ligand should displace 'H_2BN=C(H)Me' from the metal coordination sphere. Addition of a large excess of acetonitrile to a solution of **3** in benzene-d_6 does not produce any change in the ^{1}H- or ^{31}P-NMR spectra over a period of days at room temperature. On the other hand, addition of ca. eightfold excess of PMe_3 to **3** under the same conditions results in slow formation of the dihydride **4** at room temperature. The conversion of **3** to **4** appears almost complete (by ^{31}P- and ^{1}H-NMR spectroscopy) after ca. 5 weeks. We, therefore, favor the mechanism shown in Fig. 3(a) as the most likely for this exchange process.

Surprisingly, given the strained four-membered ring, compounds **2** and **3** appear to be quite thermally stable, even in solution, and samples sealed under vacuum for variable temperature NMR experiments show only little sign of degradation even after being heated several times, or prolonged periods (weeks) in solution.

3.4. Mechanistic considerations

Transition metal-assisted borohydride reduction of double and triple bonds has been the subject of a mechanistic study [44]. One of the conclusions of this study was that the rate-determining step in the reduction of benzonitrile was hydride (H^-) addition from dissolved uncoordinated $NaBH_4$ (Fig. 4(a)). A hydride may also be introduced indirectly, via a 1,3 metal hydride shift (Fig. 4(b)) [27d].

In our case it is believed that the most straightforward mechanism is via initial hydride attack at the nitrile α-C, rather than formation of a rhenium hydride followed by migration, although the second mechanism cannot be ruled out. Although the molecule contains a Re(I) metal center, the presence of the strong π-acceptor NO ligand could decrease the amount of back-donation to the nitrile. It is also conceivable that an interaction between

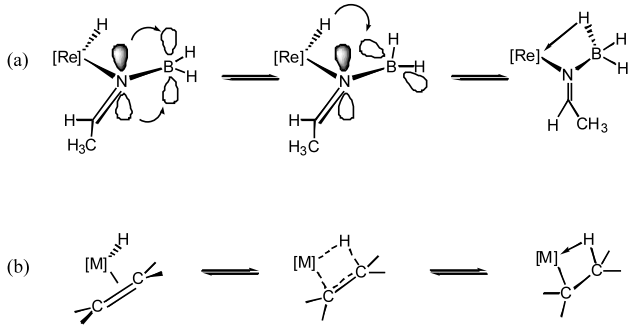


Fig. 3. (a) Proposed mechanism of $B–H_b/B–H_t$ exchange in **2** and **3**; (b) β-H elimination/addition in a metal–alkene complex.

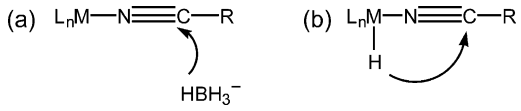
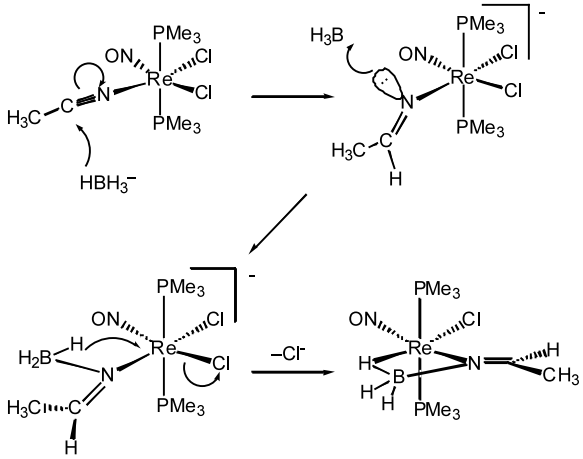


Fig. 4. Mechanisms of hydride attack at nitrile α-carbon.

BH_3 and NO occurs, of the type already observed with BF_3 [28]. Such an interaction would greatly enhance the π-acceptor ability of the nitrosyl, towards the extreme case where the NO adopts a bent, one electron donor configuration. This type of interaction should be observable spectroscopically by infrared methods. Infrared monitoring of the reaction of MeCN with five equivalents of $LiBH_4$ in THF does not reveal an overall shift in the NO stretching frequency. Three new, weak bands are clearly present after a short time, at lower wavenumber (1639, 1580 and 1340 cm^{-1}), increasing slowly in intensity over several hours. The band at 1340 cm^{-1} represents a significant shift of the magnitude observed in the BF_3 adducts $ReH(PR_3)_2(NO)(NOBF_3)$ (R = ^{i}Pr, Cy), with ν_{NOBF3} at 1363 and 1377 cm^{-1}, respectively, compared with ν_{NO} of 1637 and 1646 cm^{-1}, although the relative weakness of all three new bands means that it cannot be concluded with certainty that they result from a $\nu_{NO–BH3}$ interaction.

NMR tube experiments suggest that formation of **3** occurs via a stepwise process, with initial formation of **2** followed by replacement of the remaining chloride by hydride only when a more nucleophilic hydride source ($LiBH_4$) or very long reaction times (3–4 weeks with $NaBH_4$) are used. This observation is also borne out by the alternative preparation of **3** by addition of $LiBHEt_3$ to a solution of **2**. The *trans* addition of BH_4^- across the C–N bond indicates that this is not a concerted process involving a four-membered transition state (the accepted mechanism for hydroboration) but rather two separate processes involving 'H^-' and 'BH_3'. The mechanism of formation of **2** is proposed to occur in two separate steps as shown in Scheme 2.



Scheme 2.

In the first step nucleophilic attack at the CN α-carbon by H^- results in transfer of a pair of CN bonding electrons onto the nitrogen atom to form effectively a lone pair. This pair of σ-electrons might then donate to the rhenium atom to form a linear M–N=C unit with a M=N double bond as has been observed in a number of metal azavinylidene complexes (vide supra). However, the low valent, electron-rich rhenium(I) center is a less attractive target for the electron pair than the electron-deficient boron in BH_3, which is also presumably available in the reaction mixture. Indeed, the BH_3 fragment is an extremely strong Lewis acid, even stronger than BF_3 [45]. Once the B–N bond has been formed, the chelate effect would be expected to drive the formation of the Re–H–B interaction accompanied by expulsion of Cl^-.

Compound **3** is assumed to be formed from **2** by straightforward substitution of the chloride by hydride, thereby also generating additional 'BH_3'.

The mechanism of formation of complex **4** in this system is believed to occur via **2** and **3**. Whilst a straightforward reaction leading from **1** to **4** could be envisaged, namely that in conditions of low BH_4^- concentration (and hence low concentration of phosphine-scavenging 'BH_3'), labile PMe_3 could readily substitute MeCN at rhenium, as already observed on adding PMe_3 to a solution of **1**, this fits uncomfortably with the NMR observations. An alternative route, via complete reduction of MeCN to the weaker donor ligand NH_2Et followed by loss of ethylamine, would leave a vacant coordination site, to be filled by PMe_3. Further reaction with borohydride would then afford complex **4** as already known. Resonances attributed to the ethyl group in ethylamine (δ 1.1 ppm, t, CH_3; 3.3 ppm, q, CH_2) have been observed in the ^{1}H-NMR spectra of the sealed NMR tube reactions after several hours or days, with progressively increasing intensity.

4. Conclusion

We have reported the unexpected borohydride reduction of acetonitrile at a low-valent rhenium(I) metal center, which affords a new type of reduction intermediate, $ReCl\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$, and proposed a mechanism for its formation. This reduction is believed to be facilitated by the π-acceptor properties of the nitrosyl ligand. The use of a more powerful hydride donor allows the replacement of the chloride ligand by a hydride to afford $ReH\{(\mu\text{-}H)B(H)_2N{=}C(H)Me\}(PMe_3)_2NO$, which has been characterized by a single crystal X-ray diffraction study. NMR investigations into the nature of the bidentate iminoborane $H_3BN{=}C(H)Me$ ligand have revealed an exchange process between the bridging and the terminal boron-attached hydrogen atoms, and the activation parameters have been determined by line shape analysis. The negative $\Delta S^{\#}$ values obtained from this analysis provide an insight into the mechanism of the exchange process.

5. Supporting material

Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 151879. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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