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Reversible H_2 Addition across a Nickel–Borane Unit as a Promising Strategy for Catalysis

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Supporting Information

ABSTRACT: We report the synthesis and characterization of a series of nickel complexes of the chelating diphosphine-borane ligands ArB(*o*-$Ph_2PC_6H_4)_2$ ([^{Ar}DPB^{Ph}]; Ar = Ph, Mes). The [^{Ar}DPB^{Ph}] framework supports pseudo-tetrahedral nickel complexes featuring η^2-B,C coordination from the ligand backbone. For the *B*-phenyl derivative, the THF adduct [^{Ph}DPB^{Ph}]Ni(THF) has been characterized by X-ray diffraction and features a very short interaction between nickel and the η^2-B,C ligand. For the *B*-mesityl derivative, the reduced nickel complex [^{Mes}DPB^{Ph}]Ni is isolated as a pseudo-three-coordinate "naked" species that undergoes reversible, nearly thermoneutral oxidative addition of dihydrogen to give a borohydrido-hydride complex of nickel(II) which has been characterized in solution by multinuclear NMR. Furthermore, [^{Mes}DPB^{Ph}]Ni is an efficient catalyst for the hydrogenation of olefin substrates under mild conditions.

The noble metals are prominent in organometallic catalysis owing to their predisposition for controlled multielectron reactivity (e.g., oxidative addition).[1] Of late, increased focus has been given to developing catalyst systems using more abundant first-row transition metals (TMs).[2] This task entails special challenges given the propensity of the late 3d metals to undergo single-electron processes. Redox active ligands have emerged as one strategy to overcome this issue.[3]

We have recently explored the reactivity of first-row TM complexes featuring a silyl[4] or borane[5] moiety in the supporting ligand scaffold. In principle, the Lewis acidic functionality can serve to accommodate lower oxidation states via direct interaction with the metal center[6] and/or to operate in tandem with the TM to activate a small-molecule substrate.[7] The latter arrangement can be thought of as a minimal heterobimetallic system, wherein the main-group atom mimics a second metal and is preinstalled in the ligand framework.[7c]

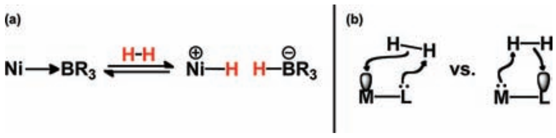
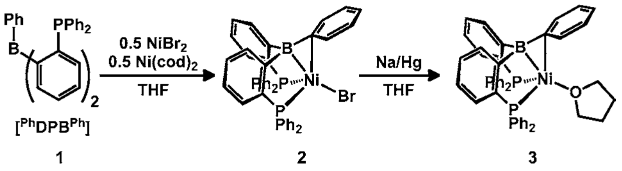


Figure 1. Schematic representation of (a) H_2 activation across a nickel–borane pair and (b) conventional (left) versus polarity-inverted (right) H_2 heterolysis at a TM–ligand pair.

As a prototypical two-electron organometallic reaction, H_2 activation provides a suitable test case for this strategy. Heterolysis of the H_2 bond across a low-valent TM–borane interaction would provide a metal hydride/borohydride pair that could ideally be intercepted by substrate to achieve catalysis (Figure 1). Although H_2 addition across an M–B bond for any TM is rare,[7a,8] it is conceptually related to H_2 activation by frustrated Lewis pairs (FLPs)[9,10] and constitutes an attractive approach to extend to the base metals. We herein disclose an organometallic nickel complex supported by a diphosphine-borane ligand that undergoes facile, reversible oxidative addition of H_2 and catalyzes the hydrogenation of olefins under mild conditions.

We initially investigated nickel complexes of Bourissou's phenyl-substituted ligand PhB(*o*-$PPh_2C_6H_4)_2$ ([^{Ph}DPB^{Ph}], **1**).[11] Deep red-orange [^{Ph}DPB^{Ph}]NiBr (**2**) was synthesized by the comproportionation of $NiBr_2$ and $Ni(cod)_2$ in the presence of **1** in THF (Scheme 1). Reduction of **2** in THF by Na/Hg afforded the diamagnetic pseudo-tetrahedral nickel–THF complex [^{Ph}DPB^{Ph}]Ni(THF) (**3**). Complexes **2** and **3** feature short Ni–(η^2-B,C) interactions, as demonstrated by their solid-state structures (Figure 2).[12]

Scheme 1



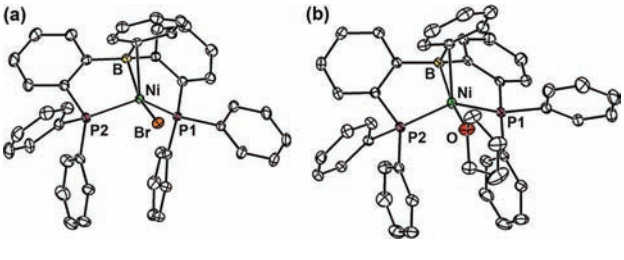


Figure 2. Thermal ellipsoid representations (50%) of (a) [^{Ph}DPB^{Ph}]NiBr (**2**) and (b) [^{Ph}DPB^{Ph}]Ni(THF) (**3**). Hydrogen atoms are omitted for clarity.

Complexes **2** and **3** were found to be highly stable with respect to cleavage of the Ni–(η^2-B,C) interaction. In

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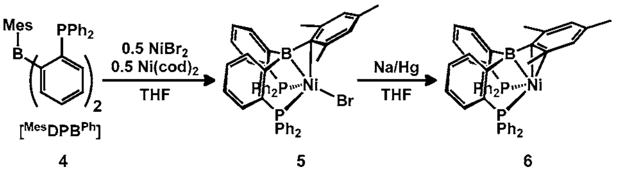
particular, **3** fails to react with H_2 after days at 60 °C. To facilitate the desired bifunctional reactivity, we therefore installed a bulky mesityl substituent in the place of phenyl at boron to give MesB(o-$PPh_2C_6H_4$)$_2$ ([^{Mes}DPB^{Ph}], **4**, see SI for details).

Deep maroon [^{Mes}DPB^{Ph}]NiBr (**5**) was accessed by comproportionation analogously to **2** (Scheme 2). The solid-state molecular structure of **5** (Figure 3a) is crudely similar to that of the phenyl analogue **2**. The Ni−C$_{ipso}$ distance (2.4329(10) Å) is lengthened by ~0.2 Å relative to that in **2**, suggesting some steric disruption of the η^2-B,C interaction by the flanking methyl groups of the mesityl substituent. Reduction of **5** with Na/Hg affords the [^{Mes}DPB^{Ph}]Ni complex (**6**), as confirmed by single-crystal X-ray diffraction (Figure 3b). Noteworthy is the absence of a solvent ligand. The coordination sphere features a shortened Ni−B distance as well as close contacts with both the *ipso* and one of the *ortho* carbons of the mesityl unit (Ni−C$_{ipso}$ = 2.0751(8) Å, Ni−C$_{ortho}$ = 2.1616(8) Å). The coordinated aryl ring exhibits bond length alternation consistent with partial dearomatization from the strongly back-donating nickel center.[12]

Scheme 2



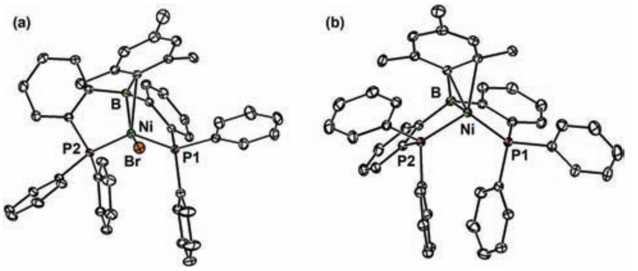
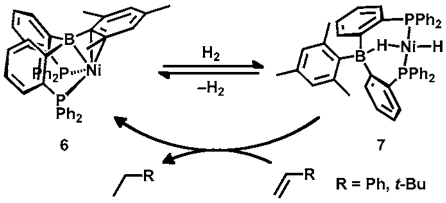


Figure 3. Thermal ellipsoid representations (50%) of (a) [^{Mes}DPB^{Ph}]-NiBr (**5**) and (b) [^{Mes}DPB^{Ph}]Ni (**6**). Hydrogen atoms are omitted for clarity.

In sharp contrast to [^{Ph}DPB^{Ph}] complex **3**, **6** reacts readily with H_2 in C_6D_6 at room temperature (Scheme 3). The product of this reaction has been characterized by a suite of solution NMR techniques. The ^{1}H, ^{31}P, and ^{11}B NMR spectra of the solution resulting from the addition of H_2 to **6** indicate the formation a new diamagnetic product (**7**) in addition to residual **6** and free H_2 (Figure 4). The ^{1}H NMR spectrum of **7** features two signature hydridic resonances that each integrate to one proton: a broad resonance centered at −6.16 ppm and a sharp triplet of doublets at −15.5 ppm ($^2J_{PH}$ = 57.8 Hz, $^2J_{H(B-H)}$ 14.6 Hz). The proton-coupled ^{31}P NMR spectrum confirms that this most upfield hydride peak is coupled to two equivalent ^{31}P nuclei, and the smaller coupling interaction was assigned via two-dimensional ^{1}H NMR to the broad ^{1}H resonance at −6.16 ppm. The ^{11}B resonance of **7** (−5.0 ppm) is shifted upfield versus that of **6** (21.6 ppm), consistent with increased electron density at boron. On the basis of these spectral features, we propose that **7** is the hydrido-borohydrido complex [^{Mes}DPB^{Ph}](μ-H)NiH. Due to the symmetry indicated by the solution NMR data as well as DFT optimization of several potential isomers (Figure 4), we favor a square planar geometry for this species with two *trans*-phosphine donors, a terminal Ni−H, and a hydride ligand that bridges between B and Ni. This assignment is supported by the existence of structural analogues $(R_3P)_2NiH(BH_4)$ (R = Cy, i-Pr),[13] which have been characterized by IR and NMR[13a] and X-ray crystallography.[13b]

Scheme 3



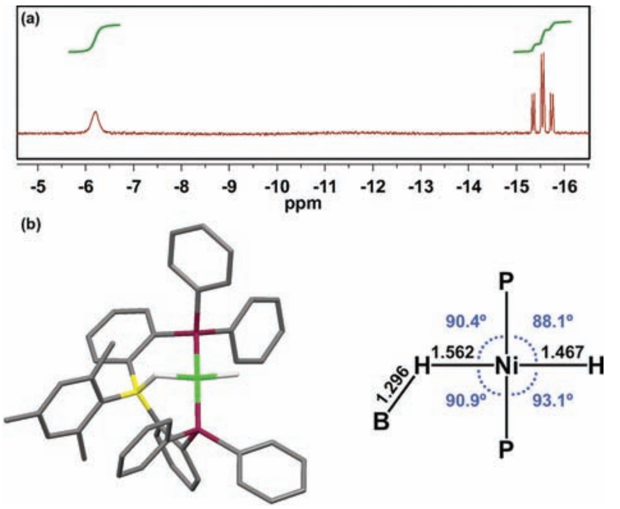


Figure 4. (a) Hydridic region of the ^{1}H NMR spectrum of **7** in C_6D_6 under 4 atm of H_2 at 298 K. (b) DFT-minimized structure of **7** (B3LYP/6-31G(d)) and selected bond lengths (Å) and angles of the core structure. Hydrogen atoms bound to carbon have been omitted for clarity.

Under 1 atm of H_2 in C_6D_6 at 298 K, **6** and **7** exist in an equilibrium ratio of ~1:5 (**6**:**7**). Taking into account the concentration of dissolved H_2, the equilibrium constant for the addition of H_2 to **6** to give **7** is $K_{obs} \approx 5$. This process is reversible, and removal of the H_2 by successive freeze−pump−thaw cycles regenerates **6** quantitatively. Under 4 atm of H_2 in C_6D_6, a solution containing 95% **7** can be obtained. A van't Hoff analysis over a 60 K range (see SI) afforded thermal parameters of $\Delta H = -9.0 \pm 1$ kcal/mol and $\Delta S = -28 \pm 3$ eu.

The equilibrium defined in Scheme 3, whereby reversible oxidative addition occurs at a mononuclear nickel center, is to our knowledge without precedent.[14] Mononuclear dihydrides of nickel are in general not stable and would instead be expected to favor H_2 release by reductive elimination. The presence of the Lewis acidic borane center in the ancillary ligand of **6**, allowing for a B−H−Ni bridge to form in **7** via net H_2 heterolysis (possibly following an OA step at Ni), presumably facilitates the observed equilibrium. H_2 heterolysis reactions are common for Ni−H_2 chemistry; indeed, only a single thermally stable example of an H_2 adduct of Ni is presently known.[15,16] Heterolysis of H_2 at Ni typically involves Ni(II) as a Lewis acid that accepts H^- while an exogenous or internal base accepts H^+.[17] FLPs that incorporate TMs likewise typically exploit the TM as the Lewis acid.[10] The present chemistry invokes an alternative scenario in which a Lewis basic Ni center accepts H^+ and a Lewis acidic borane accepts H^- (Figure 1).

Given the ease with which **6** reversibly activates H_2, we were hopeful that a substrate might intercept **7** to regenerate **6**, providing a turnover step for catalysis (Scheme 3). The addition of 20 equiv of styrene to **6** in C_6D_6 results in a deep maroon solution, the ^1H NMR spectrum of which contains broadened peaks corresponding to free styrene as well as a new diamagnetic nickel complex that we presume to be $[^{Mes}DPB^{Ph}]Ni(\eta^2\text{-}H_2C{=}CHPh)$ (**8**) (see SI). After exposure to an atmosphere of H_2 at room temperature, the formation of ethyl benzene was apparent as soon as a ^1H NMR spectrum could be acquired. During the course of catalysis, the solution remained dark maroon, and the ^1H NMR spectrum exhibited peaks corresponding only to free styrene, ethyl benzene, and **8**. Notably, neither **6**, **7**, nor free H_2 was observed by ^1H NMR spectroscopy so long as styrene was present. Provided the reaction was agitated sufficiently so as to replenish dissolved H_2, catalysis proceeded rapidly, with complete conversion after ca. 1 h. Upon full consumption of styrene, the solution lightened, and the ^1H NMR spectrum revealed an equilibrium mixture of **6**, **7**, and H_2 along with quantitative formation of ethylbenzene. Complete hydrogenation of styrene could be achieved at 1% loadings of **6**. The following observations are also noteworthy: An experiment using D_2 and norbornene as the acceptor substrate confirmed *syn* addition to the *exo* positions. Hydrogenation reactions performed in the presence of metallic Hg were uninhibited. Finally, exposure of **6** to a mixture of H_2 and D_2 (1:1, 1 atm) in C_6D_6 at room temperature resulted in very rapid formation of HD as observed by ^1H NMR spectroscopy.

Taken together, these results establish that hydrogenation catalyst **6** operates in an efficiency regime heretofore unknown for molecular Ni species.[18] Heterogeneous nickel-based materials are widely used in the hydrogenation of olefinic substrates,[19] but few homogeneous nickel catalysts have been reported,[20] and those that are known require uniformly high pressures (50 atm) of H_2 to realize appreciable activity. Oxidative addition of H_2 is not thought to be relevant in these systems.[18]

In conclusion, nickel hydrogenation catalyst **6** mediates the facile activation of H_2 via net oxidative addition across a Ni−B unit. The strategy outlined herein facilitates two-electron reactions at Ni, avoiding one-electron processes that result in thermodynamic traps in other Ni-based systems.[14b] Given the facile H_2 activation carried out by **6**, the possibility that hydrogenase activity[21] may be realized is being explored. Future studies will (i) map the substrate scope of hydrogenation catalyst **6** and (ii) explore the outlined approach in the context of related two-electron organometallic reactions catalyzed by noble metals. The efficient olefin hydrogenation catalysis described herein offers a promising lead toward these goals.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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