

Reversible H₂ 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*-Ph₂PC₆H₄)₂ ([^{Ar}DPB^{Ph}]; Ar = Ph, Mes). The [^{Ar}DPB^{Ph}] framework supports pseudo-tetrahedral nickel complexes featuring η²-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 η²-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 silyl⁴ or borane⁵ 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 center⁶ 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}

As a prototypical two-electron organometallic reaction, H₂ activation provides a suitable test case for this strategy. Heterolysis of the H₂ 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 H₂ addition across an M–B bond for any TM is rare,^{7a,8} it is conceptually related to H₂ 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

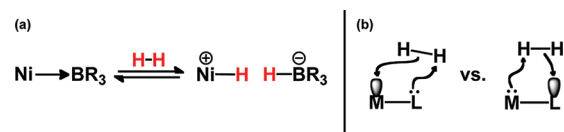
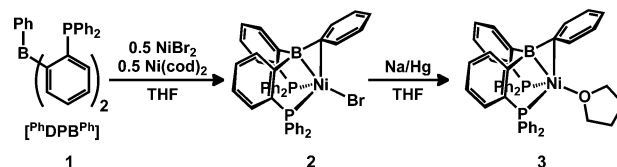


Figure 1. Schematic representation of (a) H₂ activation across a nickel–borane pair and (b) conventional (left) versus polarity-inverted (right) H₂ heterolysis at a TM–ligand pair.

oxidative addition of H₂ and catalyzes the hydrogenation of olefins under mild conditions.

We initially investigated nickel complexes of Bourissou’s phenyl-substituted ligand PhB(*o*-Ph₂C₆H₄)₂ ([^{Ph}DPB^{Ph}], **1**).¹¹ Deep red-orange [^{Ph}DPB^{Ph}]NiBr (**2**) was synthesized by the comproportionation of NiBr₂ and Ni(cod)₂ in the presence of **1** in THF (Scheme 1). Reduction of **2** in THF by Na/Hg

Scheme 1



afforded the diamagnetic pseudo-tetrahedral nickel–THF complex [^{Ph}DPB^{Ph}]Ni(THF) (**3**). Complexes **2** and **3** feature short Ni–(η²-B,C) interactions, as demonstrated by their solid-state structures (Figure 2).¹²

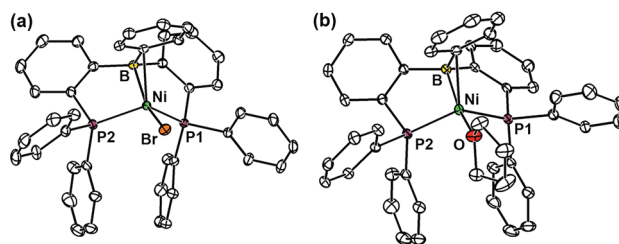


Figure 2. Thermal ellipsoid representations (50%) of (a) [^{Ph}DPB^{Ph}]NiBr (**2**) and (b) [^{Ph}DPB^{Ph}]Ni(THF) (**3**). Hydrogen atoms are omitted for clarity.

Complexes **2** and **3** were found to be highly stable with respect to cleavage of the Ni–(η²-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 $\text{MesB}(\text{o-PPh}_2\text{C}_6\text{H}_4)_2$ ($[\text{MesDPB}^{\text{Ph}}]$, **4**, see SI for details).

Deep maroon $[\text{MesDPB}^{\text{Ph}}]\text{NiBr}$ (**5**) was accessed by comproportionation analogously to **2** (Scheme 2). The solid-

Scheme 2

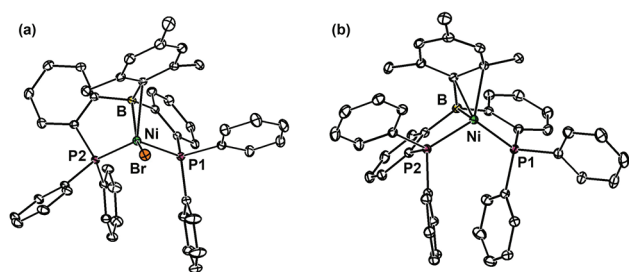
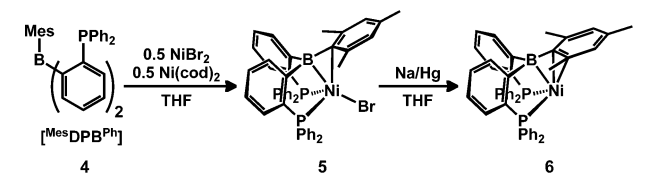


Figure 3. Thermal ellipsoid representations (50%) of (a) $[\text{MesDPB}^{\text{Ph}}]\text{NiBr}$ (**5**) and (b) $[\text{MesDPB}^{\text{Ph}}]\text{Ni}$ (**6**). Hydrogen atoms are omitted for clarity.

state molecular structure of **5** (Figure 3a) is crudely similar to that of the phenyl analogue **2**. The $\text{Ni}-\text{C}_{\text{ipso}}$ distance (2.4329(10) Å) is lengthened by ~ 0.2 Å relative to that in **2**, suggesting some steric disruption of the $\eta^2\text{-B,C}$ interaction by the flanking methyl groups of the mesityl substituent. Reduction of **5** with Na/Hg affords the $[\text{MesDPB}^{\text{Ph}}]\text{Ni}$ 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 $\text{Ni}-\text{B}$ distance as well as close contacts with both the *ipso* and one of the *ortho* carbons of the mesityl unit ($\text{Ni}-\text{C}_{\text{ipso}} = 2.0751(8)$ Å, $\text{Ni}-\text{C}_{\text{ortho}} = 2.1616(8)$ Å). The coordinated aryl ring exhibits bond length alternation consistent with partial dearomatization from the strongly back-donating nickel center.¹²

In sharp contrast to $[\text{PhDPB}^{\text{Ph}}]$ 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 ^1H , ^{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 ^1H NMR spectrum of **7**

Scheme 3

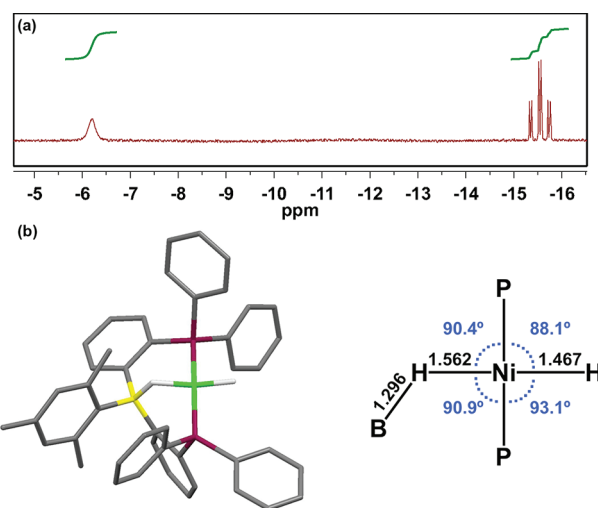
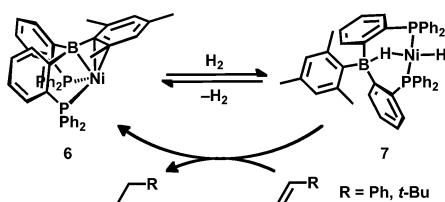


Figure 4. (a) Hydridic region of the ^1H NMR spectrum of **7** in C_6D_6 under 4 atm of H_2 at 298 K. (b) DFT-minimized structure of **7** (B3LYP/6-31G(d)) and selected bond lengths (Å) and angles of the core structure. Hydrogen atoms bound to carbon have been omitted for clarity.

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 ($^2J_{\text{PH}} = 57.8$ Hz, $^2J_{\text{H(B-H)}} = 14.6$ 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 ^1H NMR to the broad ^1H 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 $[\text{MesDPB}^{\text{Ph}}](\mu\text{-H})\text{NiH}$. 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 $\text{Ni}-\text{H}$, and a hydride ligand that bridges between B and Ni. This assignment is supported by the existence of structural analogues $(\text{R}_3\text{P})_2\text{NiH}(\text{BH}_4)$ ($\text{R} = \text{Cy}, \text{i-Pr}$),¹³ which have been characterized by IR and NMR^{13a} and X-ray crystallography.^{13b}

Under 1 atm of H_2 in C_6D_6 at 298 K, **6** and **7** exist in an equilibrium ratio of $\sim 1:5$ (**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 $K_{\text{obs}} \approx 5$. 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 $\text{B}-\text{H}-\text{Ni}$ 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 $\text{Ni}-\text{H}_2$ chemistry; indeed, only a single thermally stable example of an H_2 adduct of Ni is

presently known.^{15,16} Heterolysis of H₂ 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 H₂, 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 C₆D₆ 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 [MesDPB^{Ph}]-Ni(η²-H₂C=CHPh) (**8**) (see SI). After exposure to an atmosphere of H₂ 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 H₂ was observed by ¹H NMR spectroscopy so long as styrene was present. Provided the reaction was agitated sufficiently so as to replenish dissolved H₂, 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 H₂ 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 D₂ 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 H₂ and D₂ (1:1, 1 atm) in C₆D₆ 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 H₂ to realize appreciable activity. Oxidative addition of H₂ is not thought to be relevant in these systems.¹⁸

In conclusion, nickel hydrogenation catalyst **6** mediates the facile activation of H₂ 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 H₂ activation carried out by **6**, the possibility that hydrogenase activity²¹ 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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