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Toggling the Z-Type Interaction Off-On in Nickel-Boron Dihydrogen and Anionic Hydride Complexes

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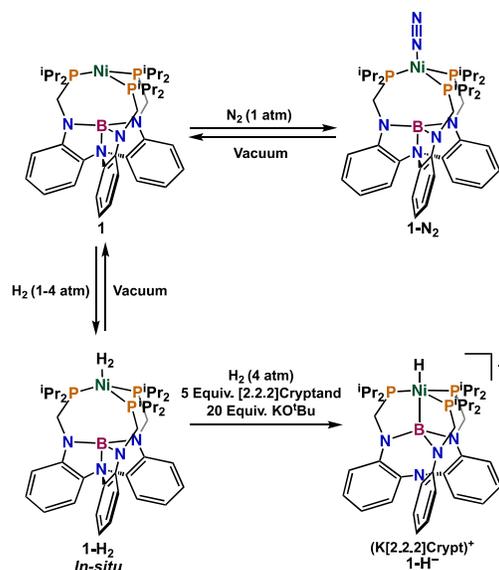
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Completing a series of nickel-group 13 complexes, a coordinatively unsaturated nickel-boron complex and its derivatives with a H₂, N₂, or hydride ligand were synthesized and characterized. The toggling “on” of a Ni(0)-B(III) inverse-dative bond enabled the stabilization of a nickel-bound anionic hydride with a remarkably low thermodynamic hydricity of $\Delta G^{\circ}_{\text{H}^-} = 21.4 \pm 1.0$ kcal/mol in THF. The flexible topology of the boron metalloligand confers both favorable hydrogen binding affinity and strong hydride donicity, albeit at the cost of high H₂ basicity during deprotonation to form the hydride.

Organic hydride donors are ubiquitous in organic transformations and are readily tuned to produce a wide range of hydride donor abilities.¹ However, the lack of regenerable, strongly hydric reagents is a current hurdle that limits catalytic applicability. Transition metal hydrides, on the other hand, are regenerable from H₂ and are widely used in catalysis. However, only a few precious metal hydride complexes are able to match the lowest hydricity values exhibited by the strongest organic hydride donors, such as trialkylborohydrides ($\Delta G^{\circ}_{\text{H}^-} \sim 20$ to 26 kcal/mol in CH₃CN).^{1,2} Frustrated Lewis pairs, where main-group-based Lewis acid-base pairs facilitate H₂ heterolysis, also catalyze difficult hydrogenation reactions and represent another alternative strategy to avoid precious metals.^{1b,3}

Within the last decade the use of a Lewis acidic borane as a supporting moiety⁴ has proven to be an effective strategy in bolstering first-row transition metal-based H₂ and hydride reactivity.⁵ We have found that bonding a heavy group 13 ion (Al, Ga, In) to a *d*¹⁰ nickel atom engenders catalytic hydrogenation reactivity.⁶ Despite precedence in the literature,^{5c,7} the Ni–B pairing has until now remained elusive in our double-decker ligand scaffold, [N((*o*-C₆H₄)NCH₂PⁱPr₂)₃]³⁻

(abbrev. L³⁻).⁸ Herein we report the synthesis of a dinitrogen, dihydrogen, and hydride adduct of a nickel complex with the supporting boron metalloligand, BL. The anionic nickel hydride is the first example of a first-row metal complex with a thermodynamic hydricity lower than HBEt₃⁻, while also deriving its hydride from H₂ heterolysis.



Scheme 1. Interconversions between **1**, **1-N₂**, and **1-H₂**, and the synthesis of **1-H⁻**.

Initially, we pursued the synthesis of BL using similar protocols as those published for the heavier group 13 analogues,⁸ which involved metalation of the ligand with various B(III) precursors. Unfortunately, these reactions showed incomplete substitution and/or formation of side products. An alternative strategy where the nickel atom is first installed in the trisphosphine pocket prior to the metallation of the supporting atom ultimately proved successful.⁹ Heating NiLi₃⁹ with excess B(OMe)₃ yielded a red residue after workup (see ESI for details). Gratifyingly, an X-ray diffraction study of a yellow crystal grown

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from pentane under N_2 at $-25\text{ }^\circ\text{C}$ revealed the complex to be the end-on N_2 adduct, $(N_2)NiBL$, or $1-N_2$ (Scheme 1). A notable feature in the structure of $1-N_2$ is the lack of any Ni–B interaction (Fig. 1a), as the Ni–B distance of $3.735(2)\text{ \AA}$ greatly exceeds the sum of the elements' atomic radii (2.36 \AA).¹⁰ The interaction of the B with the triarylamine base forms three fused five-membered rings. With the B positioned slightly below the triamido-plane, the three ligand arms are canted significantly outward. An unexpected consequence is the preclusion of a planar $Ni(P_3)$ unit, and instead, Ni is positioned $0.7280(5)\text{ \AA}$ above the P_3 -plane. Such a geometric distortion is in stark contrast to that of $Ni(LH_3)$ and the heavier group 13 bimetallic congeners, $NiAlL$ (**2**), $NiGaL$ (**3**), and $(N_2)NiInL$ (**4-N₂**), which all have a nearly planar $Ni(P_3)$ unit and shorter Ni– P_3 -plane distances (0.03 to 0.38 \AA).^{8b, 11} With N_2 in the apical pocket, the Ni center in $1-N_2$ has an ideal tetrahedral geometry ($\tau_4 = 0.98$).¹² The N–N bond length of $1.116(6)\text{ \AA}$ and the corresponding stretching frequency of 2065 cm^{-1} are indicative of a weakly activated N_2 ligand.¹³ Of note, the N_2 ligand is more activated in $1-N_2$ than in the analogous Ni–In complex (*c.f.* 2144 cm^{-1}), which is consistent with the Ni center being more electron-rich in the absence of a Z-type interaction.^{6a, 14}

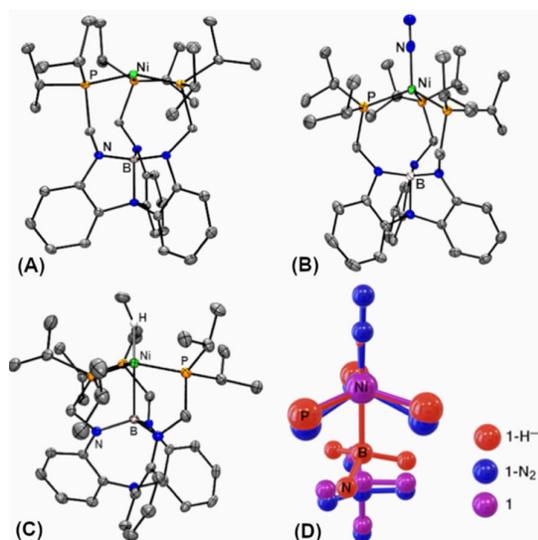


Fig. 1 Molecular structures of (A) **1**, (B) **1-N₂**, and (C) $K(\text{crypt-222})[1-H]$ plotted at 50% probability. Ligand hydrogen atoms and solvent molecules omitted for clarity. (D) Overlay of the first-coordination spheres for **1** (in purple), **1-N₂** (in blue), and **1-H⁻** (in red).

Solutions of $1-N_2$ exposed to vacuum or handled under argon allowed for the isolation of the coordinatively unsaturated $NiBL$, **1**. The $^{31}\text{P}\{^1\text{H}\}$ NMR shift of 23.9 ppm for $1-N_2$ shifted upfield to 17.1 ppm after freeze-pump-thaw cycles, alongside a color change from yellow to bright red. An X-ray diffraction study of a crystal of **1** grown from a concentrated pentane solution at $-35\text{ }^\circ\text{C}$ revealed a long Ni–B distance of $3.380(4)\text{ \AA}$, which is consistent with an absence of a direct bonding interaction. The Ni sits closer to the P_3 -plane at 0.358 \AA and has a pseudo trigonal pyramidal geometry ($\sum(\angle P-Ni-P = .351.8^\circ)$). No significant structural changes occurred at B, which

is consistent with the observation of the same broad ^{11}B NMR peak at 17 ppm for both **1** and $1-N_2$.

Next, H_2 binding to **1** was investigated. Upon exposure to $1\text{ atm } H_2$, a solution of **1** in C_6D_6 changed color from bright red to yellow and the $^{31}\text{P}\{^1\text{H}\}$ NMR peak shifted downfield to 31.7 ppm , while the ^{11}B NMR shift did not change appreciably. In the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, a signal at 0.42 ppm that integrated to $2H$ and has a $T_1(\text{min})$ value of $13(2)\text{ ms}$ at 400 MHz evidences an intact H_2 ligand and the formation of $(\eta^2-H_2)NiBL$, **1-H₂** (ESI, Fig. S23).¹⁵ Exposure of **1** to HD generated **1-HD** *in situ*, for which the J_{H-D} constant of 33 Hz provides an estimated H–D bond length of 0.88 \AA (ESI, Fig. S24).¹⁶ The equilibrium for H_2 binding was then investigated using VT ^{31}P -NMR spectroscopy of **1** in $THF-d_8$ under $1\text{ atm } H_2$ from 25 to $55\text{ }^\circ\text{C}$. The linear regression of the van't Hoff plot yielded the following thermodynamic values:^{6a} $\Delta H^\circ = -9.1(9)\text{ kcal/mol}$, $\Delta S^\circ = -24(3)\text{ cal/mol}\cdot\text{K}$, and $\Delta G^\circ = -1.8(9)\text{ kcal/mol}$, where the standard state is defined as $1\text{ atm } H_2$, $25\text{ }^\circ\text{C}$, and 1 M solutions for **1** and **1-H₂** (ESI Fig. S25).

To compare with the other Ni-group 13 bimetallics, the ΔG° for H_2 binding was also measured in toluene- d_8 (ESI Fig. S27). Ranking all the Ni-group 13 bimetallics in this ligand platform, the ΔG° for H_2 binding becomes increasingly exergonic in the following order (in kcal/mol): Ni–Al, $1.6(2) >$ Ni–Ga, $0.6(2) >$ Ni–B, $-2.4(5) >$ Ni–In, $-3.0(7)$.¹⁷ Previously, our group and others had noted the strong correlation between ΔG° values and the Shannon ionic radius of the group 13 support.¹⁸ In contrast, the Ni–B variant bucks this trend, suggesting an electronic basis that is distinct from the others, for which increasing Ni–M Z-type interactions was proposed to facilitate H_2 binding. For the unique case of Ni–B, we propose that the significantly smaller B ion leads to ligand distortion that forces the $Ni(P_3)$ unit to pyramidalize, which could also favor H_2 binding as a puckered Ni site would be more capable at π -backbonding and require less structural reorganization. The electron-richness of the Ni site in **1** is supported by its more negative oxidation potential ($E_{1/2} = -1.26\text{ V vs. FeCp}_2^{+/0}$, ESI Fig. S28, Table S6) relative to the other Ni-group 13 bimetallic complexes and even $NiLH_3$ (*c.f.* $E_{1/2} = -1.02\text{ V vs. FeCp}_2^{+/0}$).^{6a} A quasi-reversible reduction was also observed for **1** at $-3.00\text{ V vs. FeCp}_2^{+/0}$, which is similarly the most negative in the Ni-group 13 series.

Previously, adding a base to deprotonate the Ni-group 13 H_2 adducts enabled the isolation of rare d^{10} Ni hydride species.¹⁹ Adding the strongly basic phosphazene, $P_4^t\text{Bu}$ ($pK_a^{\text{CH}_3\text{CN}} = 42.7$; $pK_a^{\text{THF}} = 33.9$)²⁰ to **1-H₂** in $THF-d_8$ under $1\text{ atm } H_2$, the anionic hydride complex, $[HNiBL]^-$ (**1-H⁻**), was observed in equilibrium with **1-H₂**, alongside $P_4^t\text{Bu}$ and its conjugate acid (Fig. S29). By varying the base stoichiometry and monitoring the equilibrium for one week, the pK_a value for **1-H₂** was determined to be $36.0(2)$ in THF, with an estimated pK_a of $44.6(2)$ in CH_3CN . The characteristic ^1H NMR signal for the hydride was observed at -8.2 ppm as a broad complex multiplet. Upon applying ^{31}P decoupling the signal simplifies to a 1:1:1:1 quartet ($^2J_{H-B} = 26\text{ Hz}$), showing coupling to the major ^{11}B nucleus. Applying ^{11}B decoupling results in a 1:2:2:1 quartet ($^2J_{H-P} = 44\text{ Hz}$), arising from coupling to the three P donors. Additionally, the sharp doublet ($^2J_{B-H} = 26\text{ Hz}$) in the ^{11}B NMR spectrum at 22.6 ppm collapses to a singlet upon ^1H decoupling. Together, the data

support a direct role of the B support in stabilizing the anionic Ni–H.

Single crystals of K(crypt-222)[1-H] were grown by combining **1**, excess KO^tBu, and [2.2.2]cryptand in toluene under 4 atm H₂ and layering with pentane. The hydride ligand was located in the Fourier difference map with a Ni–H bond length of 1.56(2) Å (Fig. 1C). The solid-state structure of **1-H**[−] confirms a Z-type interaction between Ni and B with a Ni–B bond length of 2.237(2) Å, which is slightly on the long side when comparing to other Ni(0)-phosphine borane-appended complexes (range: 2.015–2.244 Å).^{5a, 7b, 7c} In a complimentary fashion, the B is positioned above the N₃ plane by 0.455(2) Å while the Ni–P₃ plane distance decreases to 0.3057(4) Å. To accommodate these changes, the ligand backbone contorts



significantly, where the average P–Ni–B–N torsion angle of 34.5° is much greater than that for **1** and **1-N₂** (Fig. 1D, ESI Table S2).¹¹

The thermodynamic hydricity ($\Delta G^\circ_{H^-}$), or hydride donor ability, of **1-H**[−] can be determined from the thermochemical cycles shown in Eqs. 1–5 (Table S6).^{2b, 21} Owing to the high basicity of **1-H₂**, the $\Delta G^\circ_{H^-}$ of **1-H**[−] is extremely low at 21.4 ± 1.0 kcal/mol, which can be converted to 16.7 ± 1.0 kcal/mol in CH₃CN (ESI, Table S9). To the best of our knowledge, this hydricity value is the lowest reported for any transition metal hydride in organic solvents.^{2b, 21} The superior hydride donor ability exceeds that of many precious-metal hydrides and is on par with the estimated hydricity for the excited state of [IrCp⁺bpy(H)]⁺.^{2b, 22} For experimental validation, we tested hydride-transfer reactions between **1** and strong hydride-donor reagents such as KBHET₃, whose $\Delta G^\circ_{H^-}$ is 26 kcal/mol in CH₃CN.^{2a} In line with the greater hydride donor ability of **1-H**[−], no reaction ensued. Even using a stronger hydride donor such as NaHB^tBu₃, (predicted $\Delta G^\circ_{H^-} = 22.9$ kcal/mol, ESI Table S14) did not result in any production of **1-H**[−]. As further confirmation, isostructural [HNiAlL][−] (**2-H**[−], $\Delta G^\circ_{H^-} = 26.2$ kcal/mol in CH₃CN) was also incapable of transferring any hydride to **1**. On the other hand, the reverse reaction of **1-H**[−] and BEt₃ showed complete hydride transfer within minutes to provide **1** and HBET₃[−] (Fig. S37). The closest reactivity in the literature was reported for the anionic H₂ adduct, [Na(THF)_x][P₃[−]Co(H₂)], which transferred hydride to BEt₃ over the course of 20 h in 85% yield.²³ The combination of the $\Delta G^\circ_{H^-}$ of **1-H**[−], the reduction potential of **1**, and $E^\circ_{1/2}$ for the interconversion of a hydride ion and a hydrogen atom permits an estimation of the Ni–H bond dissociation free energy (BDFE) for **1-H**[−] of 64.6 ± 1.0 kcal/mol (Table S9). Hence, **1-H**[−] is significantly more reactive for hydride transfer than H-atom transfer. Lastly, the Ni–H bond stretching frequency at ~1565 cm^{−1} shifted to 1210 cm^{−1} upon deuteration (Figs. S42–43).

Turning to density functional theory (DFT), the Kohn-Sham orbital manifolds of **1-H**[−] and **1** were calculated (see ESI for

details).¹⁹ The highest occupied molecular orbital (HOMO) of **1-H**[−] is a three-centered σ -bonding MO involving primarily the H(1s), Ni(3d_{z²}), and B(2s/p) orbitals (Fig. 2A). Of note, Ni is bonding and antibonding with respect to B and H, respectively. A couple related MOs are a filled low-lying MO where the three atoms (Ni, B, and H) are σ -bonding and an unfilled MO that is fully σ^* -bonding (ESI Fig. S45).

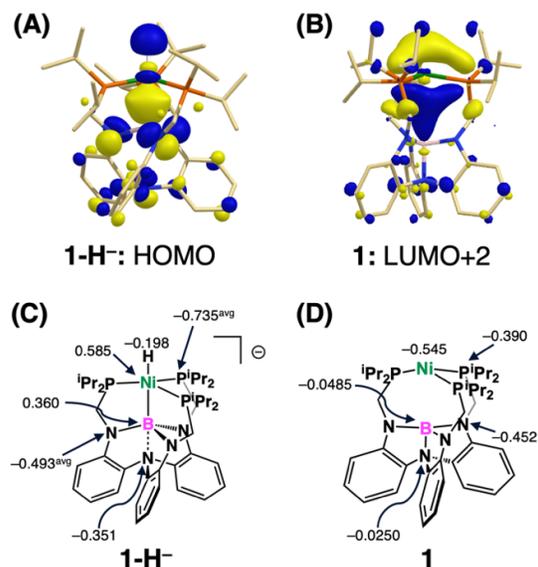


Fig. 2 DFT-calculated Kohn-Sham orbitals corresponding to: (A) the HOMO of **1-H**[−]; and (B) the LUMO+2 of **1**. The Mulliken atomic charges of (C) **1-H**[−] and (D) **1**.

For **1**, a low-lying Ni-based acceptor orbital was found (LUMO+2, Fig. 2b). This MO has sizable contributions from Ni (4p_z, 13.5%) and the three P donors (3p_z, 20.7% total) when compared to the contribution from B (2s, 5.7%). Using the geometry of **1** as a starting point, we calculated a hypothetical anionic hydride congener to **1-H**[−] where the Z-type interaction is absent. The hypothetical hydride species was found to be 18.3 kcal/mol higher in enthalpy than **1-H**[−], highlighting the favorability of stabilizing the hydride via a *trans* Z-type ligand.

The addition of NiBL to the Ni–M series (M = B, Al, Ga, and In) allows us to better examine the effect of the identity of the Group 13 ion on H₂ binding, the pK_a of the H₂ ligand, and hydride donor ability (Table 1). The Ni–B system stands out in the series for having the most basic H₂ adduct and the strongest hydride donor. Although the Ni–B system broke the observed correlation between the size of the Group 13 ion and ΔG° of H₂ binding (vide supra),^{6a} a robust linear relationship was established between hydricity ($\Delta G^\circ_{H^-}$ in THF) and the Shannon ionic radii of the group 13 element ($R^2 = 0.97$, ESI, Table S13). In other words, as the size of the group 13 ion increases, the Ni-hydride donor ability decreases. This trend is reasonable considering that the Ni–M Z-type interaction is intact in all the Ni hydrides in the series, which further underscores the importance of the group 13 identity as a σ -acceptor for stabilizing a *trans* anionic hydride. An inverse linear relationship was found between hydricity and the pK_a of the H₂ adduct ($R^2 =$

0.986, ESI, Fig. S46). This suggests that the ease of deprotonating H₂ in our system depends more significantly on the stability of the hydride product, rather than the ΔG° of H₂ binding or the extent of H₂ activation.²⁴

Table 1 Thermodynamic values for the NiML series such as H₂ binding energies ($\Delta G^\circ_{\text{H}_2}$, kcal/mol), pK_a of H₂ adducts, and thermodynamic hydricity values ($\Delta G^\circ_{\text{H}^-}$, kcal/mol).

NiML	1	2	3	4
M	B	Al	Ga	In
$\Delta G^\circ_{\text{H}_2}$ ^a	-2.4(5)	1.6(2)	0.6(2)	-3.0(7)
pK _a H ₂ in THF	37.4(2)	28.6(1)	27.5(3)	24.1(1)
in CH ₃ CN	44.6(2)	36.7(1)	33.1(3)	31.9(1)
$\Delta G^\circ_{\text{H}^-}$ in THF	21.4±1	31.8±1	34.7±1	39.2±1
in CH ₃ CN	16.7±1	26.2±1	31.3±1	37.5±1

^a in toluene.

With the characterization of **1-H₂** and **1-H⁻**, the hydride chemistry of trivalent group 13 bimetallic nickel complexes in this ligand scaffold has been extended. The Ni-B system further highlights the capability of “adaptable metalloboratrane”^{4b, 25} whereby the Z-type interaction can dynamically change to accommodate diverse reactive ligands at the transition metal. Studies of the application of the metal complexes with this unique binding paradigm are currently underway.

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Conflicts of Interest

There are no conflicts of interest to declare.

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