Thermodynamic and kinetic studies of H₂ and N₂ binding to bimetallic nickel-group 13 complexes and neutron structure of a Ni(η²-H₂) adduct†

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Understanding H₂ binding and activation is important in the context of designing transition metal catalysts for many processes, including hydrogenation and the interconversion of H₂ with protons and electrons. This work reports the first thermodynamic and kinetic H₂ binding studies for an isosstructural series of first-row metal complexes: NiML, where M = Al (1), Ga (2), and L = [Ni(η-o-(NCH₂P₂Ph₂)C₆H₄)H]³−. Thermodynamic free energies (∆G°) and free energies of activation (∆G‡) for binding equilibria were obtained via variable-temperature ³¹P NMR studies and lineshape analysis. The supporting metal exerts a large influence on the thermodynamic favorability of both H₂ and N₂ binding to Ni, with ∆G° values for H₂ binding found to span nearly the entire range of previous reports. The non-classical H₂ adduct, (η²-H₂)Ni(L₃−H₂), was structurally characterized by single-crystal neutron diffraction—the first such study for a Ni(η²-H₂) complex or any d¹⁰ M(η²-H₂) complex. UV-Vis studies and TD-DFT calculations identified specific electronic structure perturbations of the supporting metal which poise NiML complexes for small-molecule binding. ETS-NOCV calculations indicate that H₂ binding primarily occurs via H−H σ-donation to the Ni 4p₂-based LUMO, which is proposed to become energetically accessible as the Ni(0)−M(II) dative interaction increases for the larger M(II) ions. Linear free-energy relationships are discussed, with the activation barrier for H₂ binding (∆G‡) found to decrease proportionally for more thermodynamically favorable equilibria. The ∆G° values for H₂ and N₂ binding to NiML complexes were also found to be more exergonic for the larger M(II) ions.

Introduction

Developing homogeneous base metal catalysts which can activate H₂ and selectively mediate catalytic hydrogenation, H₂ oxidation, and proton reduction have been active areas of research in recent years.¹–³ In such processes, the strength of H₂ binding, the interplay between σ-donation (H₂ σ → M) and π-back-donation (M → H₂ σ*), the resulting extent of H−H activation, and the ease of generating reactive M−H species all can play a critical role in determining catalytic activity and selectivity. H₂ activation is typically initiated by side-on binding of H₂ to form a M(η²-H₂) adduct, which precedes the generation of reactive M−H species via subsequent oxidative addition or deprotonation events.⁴–⁸ Despite the ubiquity of H₂ binding as a key fundamental reaction step in catalysis,⁹ limited experimental data has been reported regarding the thermodynamic and kinetic favorability of H₂ binding to transition metals, especially for the first-row transition metal complexes: Cr(PC₅)$_2$(CO)$_{10–11}$, [Mn(CO)(dppe)$_2$]$_2$,$^{12}$ [Fe(P₃N₂)]$_2$,$^{13}$ and Co(TPB)$_2$,$^{14}$ where dppe is bis(diphenylphosphino)ethane, P₃N₂ is a tetraphosphine with two pendant amines, and TBP is tris(σ-disopropylphosphino)borane. Moreover, without a series of similar M(η²-H₂) adducts with which to compare...
thermodynamic data, the understanding gained by quantifying H₂ binding to a single metal complex is relatively limited. Recently, the double-decker ligand, [Ni(o-N(CH₂)₂PPr₃)₂C₆H₄]⁺ (abbreviated as L), was used to prepare bimetallic (η²-H₂)Ni₃ complexes in which group 13 Lewis acidic supporting metal ions (M₃) induce H₂ binding at Ni(0) and Co(−1) metal centers (M₃).¹⁵,¹⁶ Figueroa and Gabbaï have independently shown that appending a Lewis acidic σ-acceptor to a d¹⁰ transition metal induces binding of a Lewis base donor trans to the σ-acceptor.¹⁷–¹⁹ We and others have used a tethered σ-acceptor to promote activity at the transition metal for catalytic CO₂ functionalization.²⁰–²² Here, we report the first thermodynamic and kinetic studies of H₂ binding to a Ni center in an isostructural series, where M₃ = Al, Ga, and In. In the case of the In(III) supporting ion, strong H₂ binding allowed for structural elucidation via single-crystal neutron diffraction. Significant modulation of the thermodynamic favorability of both H₂ and N₂ binding to Ni was enabled by introducing and varying the group 13 supporting metal ion, with H₂ binding free energies (∆G°) found to span nearly the entire range of previously reported values. The [(η²-H₂)NiML complexes also exhibit different extents of H–H activation and kinetic rates of H₂ binding and loss. Through a combination of experimental and theoretical studies on binding and electronic structure, we present a comprehensive understanding of how a supporting group 13 metal ion poises a proximal transition metal for catalytic CO₂ functionalization.

Results & discussion

Part I. Neutron diffraction study of (η²-H₂)Ni₃L and NMR characterization of (η²-H₂)Ni₃Al.

We have previously reported a series of bimetallic NiML complexes featuring Ni(0)→M(m) dative bonds (M = Al (1), Ga (2), and In (3)), where larger group 13 ions, Ga and In, promote H₂ binding to formally d¹⁰ Ni centers.¹⁶ The resulting nonclassical H₂ adducts, (η²-H₂)NiGaL (2-H₂) and (η²-H₂)NiInL (3-H₂), were characterized by ¹H NMR spectroscopy techniques. In addition, the remarkable stability of 3-H₂ allowed for its molecular structure to be determined by single-crystal X-ray diffraction at 123 K.¹⁶ We currently report a single-crystal neutron diffraction study of 3-H₂ at 100 K (Fig. 1) and the corresponding X-ray structure at 100 K. To our knowledge, 3-H₂ is the first H₂ adduct of Ni, or of any d¹⁰ metal, to be structurally characterized by neutron diffraction. To date, only two other Ni(0) H₂-adducts have been reported, [O(SiH₄)(η²-Pr₃PC₆H₄)]_2 [Ni(η²-H₂)] and [PhH(η²-Pr₃PC₆H₄)]_2[Ni(η²-H₂)], both of which were characterized in situ at low T.²³,²⁴

![Chemical structure of (η²-H₂)Ni₃Al](image)

Table 1 displays selected structural parameters for 3-H₂. Of note, the bond distances for non-hydrogen atoms in the X-ray and neutron structures of 3-H₂ are essentially identical within experimental error (Table S4†). The Ni–H distances between the two structures are also within error, though the H–H bond length differs by 0.12 Å. The neutron structure, which is more reliable for placement of H atoms, validates an intact H₂ molecule that is bound in side-on fashion to the Ni center. Upon H₂ coordination, the Ni–In bond distance increases slightly from 2.457(1) Å in 3 to 2.4789(2) Å in 3-H₂. The H–H bond length of 0.80(2) Å is slightly elongated relative to that in free H₂ (0.74 Å), but shorter than the solution-state distance of 0.91 Å that was determined based on the J_HD coupling constant of 3-H₂.¹⁶ This discrepancy can be attributed to rapid librational motion of H₂ in 3-H₂, a phenomenon which typically leads to an average contraction of ~0.07 Å in the apparent solid-state H–H bond distance relative to the solution-state distance determined by NMR studies.⁷,²⁵–²⁷ Consistent with this attribution, fast H₂ rotation in solution relative to molecular tumbling is also supported by the previously reported T₁ (min) value for the coordinated H₂ ligand of 3-H₂.¹⁶

Notably, the Ni–H bond distance is a parameter that neutron diffraction is uniquely able to experimentally evaluate. The two equivalent Ni–H bond lengths of 1.61(2) Å fall on the longer end of the wide range of the Ni–H distances reported for terminal Ni hydrides (cf. 1.32 to 1.65 Å).²⁸ Although direct comparisons are

![Ordered H₂ gas structure](image)

Table 1  Selected structural metrics for 3-H₂ from X-ray and neutron studies at 100 K

<table>
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<th>3-H₂ (neutron)</th>
<th>3-H₂ (X-ray)</th>
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<td>H–H</td>
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<td>0.92(3)</td>
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<td>Ni–H</td>
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<td>1.58(2)</td>
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<td>Ni–In</td>
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<td>2.4789(2)</td>
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<td>Ni–P (avg.)</td>
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<td>2.2618(4)</td>
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<td>In–Namide (avg.)</td>
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<tr>
<td>In to N₃-plane</td>
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*Values in Å (estimated standard deviations in parentheses). See Table 6 for crystallographic details. See Table S4 for a detailed comparison of the X-ray and neutron structures.*
sparse due to the rarity of structurally characterized \(M(\eta^3-H_2)\) complexes, the M–H and H–H distances in 3–H_2 are both similar to those for (\(\eta^2-H_2\)Co(TPB)), which has M–H and H–H distances of 1.66/1.67 Å and 0.83(2) Å, respectively.29 Short contact distances between the H_2 unit and the hydrogen atoms of the ligand isopropyl phosphine groups were observed in both 3–H_2 and (\(\eta^2-H_2\)Co(TPB)), the closest of which were 2.24 Å and 2.10 Å, respectively. These distances are, within error, close to the intermolecular H⋯H van der Waals distance (2.2 Å).28

Previously, no reaction was observed between NiAIL (1) and H_2 (1 atm) at room temperature. Subsequent studies have found that either high H_2 pressure or low \(T\) is needed to observe H_2 binding to 1. At 34 atm H_2 and 232 K, a new species was observed by \(^1\)H NMR spectroscopy that is assigned as (\(\eta^2-H_2\))NiAIL (1–H_2) based on a diagnostic resonance for bound H_2 at \(-1.5\) ppm (Fig. S8 and S9) and a short \(T_1\) (min) value of \(\approx 49(5)\) ms (500 MHz, THF-d_8; Fig. S10†). The \(^1\)H NMR spectrum of the HD isotopomer, (\(\eta^2-HD\))NiAIL (1–HD), which was formed at 213 K under 3.8 atm HD, displayed a characteristic 1:1:1 triplet for the bound HD ligand, with \(J_{\text{HD}} = 34.4\) Hz (Fig. S11†).

With the addition of 1–H_2 to complex the isostrotral trio of Ni(\(\eta^3-H_2\)) complexes, it is apparent that H_2 activation increases as the supporting metal is varied down group 13 from Al to Ga to In, as reflected by the decreasing \(J_{\text{H-H}}\) values (in Hz): 34.4 for 1–HD > 33.2 for 2–HD > 31.7 for 3–HD (at 213 K; Fig. S11†). Thus, the corresponding estimated solution-state H–H bond distances increase as the supporting metal is varied down group 13, from 0.86 Å for 1–H_2, to 0.88 Å for 2–H_2, to 0.91 Å for 3–H_2.33 The relative extents of H–H bond activation for the (\(\eta^2-H_2\))NiML complexes are also in accord with those predicted by DFT calculations (Tables S13, S19 and S20†). That 1–H_2 would have the shortest H–H distance of the trio, and the closest to that of free H_2, is suggestive of the weak and labile nature of H_2 binding to 1 relative to H_2 binding to 2 and 3.6,7,6 We further note that the isosterostronic mononuclear Ni complex, \(\text{NiLH}_2\) (4),28 does not bind H_2 even under forcing conditions (193 K, 34 atm H_2),28 which suggests that the supporting metal plays a pivotal role in inducing H_2 binding and controlling the extent of H_2 activation. Lastly, both 2–H_2 and 3–H_2 exhibit a greater extent of H_2 activation compared to the two other Ni(0) H_2-adducts: [O(SiH(0-Pr_2PC_6H_4)_2)_2]Ni_2(\(\eta^3-H_2\)) \((J_{\text{HD}} = 34.2\) Hz) and [PhB(0-Pr_2PC_6H_4)_2]Ni(\(\eta^3-H_2\)) \((J_{\text{HD}} = 36.5\) Hz).23,24

Part II. H_2 and N_2 binding energies for the NiML triad

Intrigued by the varied propensities for binding and activating H_2 enabled by changing a single atom, we set out to understand how the group 13 supporting metal influences the thermodynamics and kinetics of Ni–H_2 binding equilibria. Previously, (\(\eta^3-H_2\))NiGal (2–H_2) was generated in situ under 1 atm H_2, but reverted to 2 upon exposure to vacuum or Ar.26 Because of its reversible H_2 binding at ambient conditions, 2 was an ideal candidate for initiating binding equilibrium studies. Variable-temperature (VT) \(^31\)P NMR spectra of 2 in toluene-d_8 under 6.8 atm H_2 displayed a single resonance, which shifted downfield from 42.7 to 56.4 ppm as the temperature was decreased from 368 K to 221 K (Fig. 2a). As a control experiment, the VT NMR profile of 2 under Ar showed a minimal change in the \(^31\)P shift (\(\Delta \delta < 0.5\) ppm) over a similar \(T\) range (Fig. S12 and S13†).

Hence, the VT NMR behavior of 2 under an H_2 atmosphere is consistent with an equilibrium between 2 and 2–H_2 that is governed by fast chemical exchange relative to the \(^31\)P NMR timescale (202.4 MHz), where the latter is favored at low \(T\) and both species are three-fold symmetric in solution.

Analogous VT \(^31\)P NMR experiments were also performed for 2 under various H_2 pressures of 1.0, 13.6, and 34 atm (Fig. S1, S14 and S15†). Of note, for all H_2 pressures examined, the same low \(T\) convergence of the \(^31\)P resonance to \(-56.9\) ppm was observed at 193 K, which corresponds to the \(^31\)P chemical shift of 2–H_2 (Fig. 2b). At high \(T\), the observed \(^31\)P chemical shift approaches that of 2, with closer convergence observed at lower H_2 pressures. These observations are consistent with rapid interconversion between 2 and 2–H_2, such that the observed chemical shift (\(^31\)P \(\delta\)) is the population-weighted average of the chemical shifts of these exchanging species.32 Thus, the

\[ \delta_{\text{obs}} = \sum_{i=1}^{2} f_i \delta_i \]

where \(f_i\) and \(\delta_i\) are the populations and chemical shifts of the exchanging species, respectively. The data are best fit by the model \(\delta_{\text{obs}} = \delta_1 f_1 + \delta_2 f_2\), with \(f_1 = 0.75\) and \(f_2 = 0.25\) at 221 K, and \(f_1 = 0.35\) and \(f_2 = 0.65\) at 368 K (Fig. 2c). This indicates that the exchange between 2 and 2–H_2 is fast on the NMR timescale at low \(T\), but slow at high \(T\), consistent with activated exchange.

Fig. 2  (a) VT \(^31\)P NMR spectra of 2 under 6.8 atm H_2 in toluene-d_8 from 368 to 221 K. (b) Plots of \(\delta_{\text{obs}}\) vs. \(T\) obtained for various H_2 pressures. Data are shown as points, and solid traces represent the best–fit curves obtained by varying \(\Delta H^\circ\) and \(\Delta S^\circ\) as parameters (see ESI†). (c) Representative van’t Hoff plot of ln(\(K_{\text{H}}\)) vs. \(1/T\) at 6.8 atm H_2. The thermodynamic binding parameters shown in Table 2 were determined from van’t Hoff plots for data sets collected at 6.8 and 13.6 atm H_2, which exhibit fast chemical exchange.
observed $^{31}$P $\delta$ can be converted into the equilibrium concentration ratio of 2 and 2-H$_2$ (see ESI†). The equilibrium constant for H$_2$ binding, $K_{H_2}$, was determined according to eqn (1), where $P_{H_2}$ is the H$_2$ pressure:

$$K_{H_2} = \frac{[(\eta^2-H_2)\text{NiML}]}{[\text{NiML}] \times P_{H_2}}$$

(1)

Next, the thermodynamic parameters for H$_2$ binding, $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$, were determined using two complementary methods: (1) non-linear fitting of the $^{31}$P $\delta$ vs. $T$ plot in Fig. 2b; and (2) linear regression of the van’ Hoff plot of ln($K_{H_2}$) vs. 1/$T$, as shown in Fig. 2c. The analyses were performed using the 6.8 and 13.6 atm datasets, where chemical exchange was rigorously fast relative to the $^{31}$P NMR timescale and the variability of $^{31}$P $\delta$ with $T$ was significant enough to reflect the sampling of an adequate portion of the binding equilibrium. The van’ Hoff plot gives $\Delta H^\circ = -6.3(2)$ kcal mol$^{-1}$, $\Delta S^\circ = -23.0(7)$ cal (mol K)$^{-1}$, and $\Delta G^\circ = +0.6(3)$ kcal mol$^{-1}$ for H$_2$ binding to 2, where the standard state conditions are defined as 298 K, 1 atm H$_2$, and 1 M concentrations of all other species in toluene-d$_8$. Non-linear fitting of the $^{31}$P $\delta$ vs. $T$ plot yields the same thermodynamic values within experimental error (Fig. S16, S17 and Table S2†).

The H$_2$ binding equilibria for the other NiML complexes, 1 (M = Al) and 3 (M = In), were also investigated by VT $^{31}$P NMR spectroscopy. For H$_2$ binding to 1, the VT $^{31}$P NMR spectra in toluene-d$_8$ [363 to 210 K, 34 atm H$_2$] show a single $^{31}$P resonance shifting downfield relative to that of 1 (30.7 ppm) with decreasing $T$, and ultimately converging to a chemical shift of $\sim$44.3 ppm for 1-H$_2$ (Fig. S18†). The corresponding van’t Hoff analysis for H$_2$ binding to 1 gives $\Delta H^\circ = -6.3(1)$ kcal mol$^{-1}$, $\Delta S^\circ = -26.4(4)$ cal (mol K)$^{-1}$, and $\Delta G^\circ = +1.6(2)$ kcal mol$^{-1}$ (Fig. S19†). Since 3 binds H$_2$ strongly, sub-ambient H$_2$ pressure was necessary to establish a measurable equilibrium between 3 and 3-H$_2$ (Fig. S20–S22†). Under 1 atm of 10% H$_2$ in Ar, where $P_{H_2} = 0.1$ atm, a single $^{31}$P peak was observed from 299 to 357 K (Fig. S20†). However, the lineshapes of the observed $^{31}$P peaks are noticeably broadened, which indicates that chemical exchange between 3 and 3-H$_2$ falls into the fast-intermediate regime relative to the $^{31}$P NMR timescale. This is problematic because non-Lorentzian lineshapes and exchange broadening may diminish the reliability of the thermodynamic parameters determined under fast-intermediate exchange conditions. Hence, we caution that the thermodynamic values for H$_2$ binding to 3, $\Delta H^\circ = -14.8(6)$ kcal mol$^{-1}$, $\Delta S^\circ = -37(2)$ cal mol$^{-1}$ K$^{-1}$, and $\Delta G^\circ = -3.7(7)$ kcal mol$^{-1}$ (Fig. S23† and Table 2), should be treated as estimates.

To assess the reliability of this estimated $\Delta G^\circ$ value, a control experiment was performed on 2 under identical conditions with 0.1 atm H$_2$, which showed similarly broad $^{31}$P peaks due to fast-intermediate chemical exchange (Fig. S24 and S25†). Comparing the binding parameters obtained for 2 under 0.1 atm H$_2$ to those obtained under rigorously fast exchange conditions (6.8 and 13.6 atm H$_2$), we find that the thermodynamic favorability of H$_2$ binding was overestimated by 0.7 kcal mol$^{-1}$ using the 0.1 atm H$_2$ dataset. Thus, by applying this 0.7 kcal mol$^{-1}$ empirical correction, we propose that a better $\Delta G^\circ$ estimate for H$_2$ binding to 3 is $\sim$3.0(7) kcal mol$^{-1}$. In support, lineshape simulations of VT $^{31}$P NMR spectra of 3 under 1 atm H$_2$ independently gives $\Delta G^\circ = -2.3(2)$ kcal mol$^{-1}$, which is within experimental error of the corrected value of $\sim$3.0(7) kcal mol$^{-1}$ (Fig. S26†).

Next, we sought to investigate the related equilibria of N$_2$ binding to the NiML complexes using VT $^{31}$P NMR experiments. The equilibrium between 2 and 2-N$_2$ was monitored at 1 atm N$_2$ and low T (226 to 193 K). Distinct $^{31}$P resonances were observed for both 2 and 2-N$_2$ (Fig. S30†), which is characteristic of slow chemical exchange relative to the $^{31}$P NMR timescale (161.9 MHz). Quantitative integration of the $^{31}$P NMR peaks for 2 and 2-N$_2$ allowed for a straightforward determination of $K_{N_2}$ using eqn (2), where $P_{N_2}$ is the N$_2$ pressure:

$$K_{N_2} = \frac{[(N_2)\text{NiML}]}{[\text{NiML}] \times P_{N_2}}$$

(2)

Conversely, the interconversion of 3 and 3-N$_2$ is fast relative to the $^{31}$P NMR timescale (161.9 MHz) at 1 atm N$_2$ and T > 288 K (Fig. S6 and S31†). As such, the observed chemical shift of the single $^{31}$P NMR resonance represents the population-weighted average of the chemical shifts of 3 and 3-N$_2$, and the VT NMR data were analyzed as previously described for H$_2$ binding to 2 (Fig. S31 and S32†). Lastly, the observed equilibrium between 1 and 1-N$_2$ at 51 atm N$_2$ switches from slow exchange at low T (210 K) to fast exchange at higher T (243 K) (Fig. S33†). Thus, $K_{N_2}$ was evaluated based on the distinct $^{31}$P NMR peak integrations for 1 and 1-N$_2$ at low T, and based on the observed $^{31}$P chemical shift at high T. The thermodynamic binding parameters for the H$_2$ and N$_2$ binding equilibria of the NiML complexes are compiled in Tables 2 and 3. Additionally, DFT calculations using the M06-L/6-311G* method correctly predict the experimental trends in both the H$_2$ and N$_2$ binding free energies for the trio of NiML complexes (Tables 2 and 3).

Across the NiML series, $\Delta G^\circ$ for both H$_2$ and N$_2$ binding was modulated by $\sim$5 kcal mol$^{-1}$, with increasing thermodynamic favorability for both H$_2$ and N$_2$ binding observed as the
A similar trend was reported for \([\text{Fe}(\text{P}4\text{N}2)]^+\) and \([\text{Cr}(\text{CO})3(\text{PCy}_3)2]\), also striking that both \(\text{H}_2\) and \(\text{N}_2\) binding to for \(\text{N}_2\) binding than for \(\text{H}_2\) binding; this trend can be explained whereas \(\text{H}_2\) binds H2 even more favorably, with \(4.8(1.3)\) kcal mol\(^{-1}\) unfavorable H2 binding free energies, with acceptor with a d\(^{10}\) transition metal enhances donor-binding at the trans position.\(^{17-19}\) Calculations predict that supporting metal was varied down group 13 (Tables 2 and 3). Notably, \(\Delta G^0\) values for \(\text{H}_2\) binding to the NiML complexes nearly span the entire range of previously reported values (from \(-2\) to \(+3\) kcal mol\(^{-1}\); Tables S6 and S7). This is remarkable considering that the full range of literature \(\Delta G^0\) values encompasses \(\text{H}_2\) binding to various transition metals (e.g. Cr, Mo, W, Re, Fe, Ru, Co, and Ir) in diverse ligand environments.\(^{10,11,13,14,39-45}\) In contrast, the NiML trio features an iso-structural Ni site within the same ligand framework, where the primary difference is the identity of the group 13 metal. We hypothesize that the strength of the Ni(0)\(\rightarrow\)M(III) dative interaction directly tunes the binding at Ni in the position \(\text{trans}\) to M(m), where greater Ni(0)\(\rightarrow\)M(m) interactions lead to smaller strong-molecule binding. This hypothesis is generally consistent with other literature examples wherein the interaction of a σ-acceptor with a d\(^{10}\) transition metal enhances donor-binding at the trans position.\(^{17-19}\) Good agreement was generally achieved between the experimental and simulated spectra, as illustrated in Fig. 3a for the VT \(^{31}\text{P}\) NMR study of \(1\) under 1 atm \(\text{H}_2\). Similar lineshape analyses were performed for each NiML complex, which allowed exchange rates to be determined at seven or more different temperatures between 213 K and 344 K (Fig. S42–S44†). Notably, the exchange rate decreases by a factor of \(~6\) at 298 K upon varying the supporting metal from Al to In (Table 4). Exchange rates at 298 K were found to correlate strongly with both \(\text{H}_2\) binding free energies \(\left(R^2 = 0.996, \text{Fig. S47}\right)\) and H–H bond distances in \((\eta^2\text{-H}_2)\text{NiML}\) complexes \(\left(R^2 = 0.958, \text{Fig. S48}\right)\), with slower kinetic rates of \(\text{H}_2\) exchange for more thermodynamically favorable binding equilibria where \(\text{H}_2\) is more activated. The \(\text{H}_2\) binding equilibrium for complex 1 is especially dynamic, with interconversion between 1 and \(\text{H}_2\) occurring over 28 000 times per second at 298 K and 1 atm \(\text{H}_2\) (Fig. 3a and Table 4).

We propose a self-exchange mechanism comprised of \(\text{H}_2\) loss from \((\eta^1\text{-H}_2)\text{NiML}\) to generate NiML and free \(\text{H}_2\), and \(\text{H}_2\) binding to another NiML complex to form \((\eta^2\text{-H}_2)\text{NiML}\) (Fig. 3c). The rate constants for \(\text{H}_2\) loss from \((\eta^2\text{-H}_2)\text{NiML}\), \(k_{\text{loss}}\), were determined at each \(T\) both on the exchange rates and the known equilibrium concentrations of \((\eta^2\text{-H}_2)\text{NiML}\) (see ESIT). Eyring analyses for \(k_{\text{loss}}\) allowed for the determination of activation barriers for \(\text{H}_2\) loss from \((\eta^2\text{-H}_2)\text{NiML}\) complexes, as shown in Fig. 3b for 1–\(\text{H}_2\). Eyring plots for \(\text{H}_2\) loss from 2–\(\text{H}_2\) and 3–\(\text{H}_2\) are shown in Fig. S49 and S50†, respectively. The free energy barriers for \(\text{H}_2\) loss \(\Delta G^\ddagger_{\text{loss}}\) were found to be similar for all complexes (9.1 to 9.4 kcal mol\(^{-1}\)), with \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) values ranging from 9.3 to 11.3 kcal mol\(^{-1}\) and from \(-0.3\) to \(+7.5\) cal (mol K\(^{-1}\)) (Table 4). The fact that \(\Delta S^\ddagger\) values are positive or close to zero in all cases is consistent with the expected gain in \(\text{H}_2\) freedom of motion, while positive \(\Delta H^\ddagger\) values suggest that partial Ni–\(\text{H}_2\) bond breaking is the dominant process involved in reaching the transition state for \(\text{H}_2\) loss. Interestingly, both \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) values for the \((\eta^2\text{-H}_2)\)NiML complexes decrease as the supporting metal is varied down group 13 (Al > Ga > In; Table 4).

### Table 3: Experimental and DFT-calculated \(\text{N}_2\) thermodynamic binding parameters for 1, 2, and 3

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</table>

\(^a\)Same as Table 2 footnote a. \(^b\)Same as Table 2 footnote c.
Furthermore, Δ$G$\text{loss} values (~0 or >0) are consistent with unimolecular H$_2$ loss from (η$_2$-H$_2$)NiML, as opposed to H$_2$ self-exchange via an intermolecular LMNi...H$_2$...NiML transition state. Such a transition state also seems unlikely because of the sterically close between the diisopropyl ligand groups surrounding each Ni site. Using the proposed reaction coordinate diagram, one can further extract the free energy barrier for H$_2$ binding (∆$G$\text{bind}) by using the thermodynamic relationship: ∆$G$\text{loss} = ∆$G$\text{bind} - ∆$G$\text{M}. Of note, ∆$G$\text{M} is the free energy of H$_2$ binding after converting the H$_2$ standard state from 1 atm to 1 M (as given in Table 2) to 1 M. Hence, the ∆$G$\text{bind} values for 1, 2, and 3 are 7.2(3), 6.2(5), and ~2.9(8) kcal mol$^{-1}$, respectively, where the activation barriers for H$_2$ binding are lower for more thermodynamically favorable binding equilibria (Table 4).

Activation barriers and rate constants for H$_2$ binding and loss have seldom been reported despite their relevance for many catalytic processes. ∆$H$\text{loss} values for (η$_2$-H$_2$)NiML (9.3 to 11.3 kcal mol$^{-1}$) are comparable to those reported (in kcal mol$^{-1}$) for [Ru(η$_2$-H$_2$)H$_2$(PCy$_3$)$_2$] (8.8),$^{31}$ Cr(η$_2$-H$_2$)(CO)$_3$(PCy$_3$)$_2$ (12.1),$^{18}$ Ir(η$_2$-H$_2$)(H)$_2$X(PBu$_3$)$_2$ (9.4 to 11.3 for X = Cl, Br, I),$^{30}$ and Ir(η$_2$-H$_2$)(H)$_2$X(PPr$_3$)$_2$ (10.1 to 11.4 for X = Cl, Br, I),$^{30}$ and are significantly lower than those reported for W(η$_2$-H)$_2$(CO)$_3$(PCy$_3$)$_2$ (16.9)$^{4}$ and Ru(η$_2$-H$_2$)(H)$_2$X(PPh$_3$)$_2$ (17.9)$^{31}$ Perhaps the most thoroughly studied H$_2$ binding equilibrium is that of W(η$_2$-H)$_2$(CO)$_3$(PCy$_3$)$_2$, for which rate constants for both H$_2$ binding (k$_{\text{bind}}$) and loss (k$_{\text{loss}}$) have been directly measured to be ~2 × 10$^{14}$ M$^{-1}$ s$^{-1}$ and 469 s$^{-1}$ at 298 K, respectively.$^{44,45}$ In comparison, the k$_{\text{loss}}$ values for (η$_2$-H$_2$)NiML complexes are 3 to 5 orders of magnitude greater than that for W(η$_2$-H)$_2$(CO)$_3$(PCy$_3$)$_2$ (Table 4). This can be rationalized by the fact that H$_2$ is much more active in W(η$_2$-H)$_2$(CO)$_3$(PCy$_3$)$_2$, which co-exists with its dihydride species at 298 K ($K$ < 0.25).$^{4,44}$ In contrast, HNi(μ-H)ML dihydride species, which have some precedent in the literature,$^{24,53,54}$ have not been observed.$^{44,55}$ DFT calculations predict such a species to be unstable relative to (η$_2$-H$_2$)NiML by 12 to 19 kcal mol$^{-1}$ under 1 atm H$_2$ (Table S25, S26 and Fig. S55).
To better understand chemical bonding between H_2 and Ni in the (n^2-H_2)NiML complexes, we conducted energy decomposition analysis (EDA). EDA allows for the total interaction energy (\(\Delta E_{\text{int}}\)) between the H_2 and NiML fragments to be partitioned into the following terms: electrostatic energy (\(\Delta E_{\text{elstat}}\)), Pauli repulsive interaction (\(\Delta E_{\text{Pauli}}\)), dispersion (\(\Delta E_{\text{disp}}\)), and covalent interaction (\(\Delta E_{\text{orb}}\)). The \(\Delta E_{\text{orb}}\) term can be further divided into individual energy contributions associated with specific orbital interactions, and thereby allows for differentiation of \(\sigma\), \(\pi\), and \(\delta\) bonding interactions. The extended transition-state method coupled with natural orbitals for chemical valence theory (EVT-NOCV\(^\text{p}\)) was then utilized to analyze the bonding interactions between Ni and H_2. Fig. 4 illustrates the two most important NOCV pairs for the Ni–H_2 interaction in 3-H_2, in which chemical bonding is indicated by deformation in the electron densities (\(\Delta \rho\)). Overall, two orbital interactions are important: (1) \(\sigma\)-donation from the H_2 \(\sigma\)-bond to the empty Ni 4p_\(z\) orbital, which accounts for 56% of \(\Delta E_{\text{orb}}\) and is comprised of \(\Delta \rho_1\) (38%; Fig. 4) and \(\Delta \rho_2\) (18%; Fig. S53); and (2) \(\pi\)-back-donation from a Ni 3d_\(z\) orbital to the empty H_2 \(\sigma^*\) orbital, which accounts for 35% of \(\Delta E_{\text{orb}}\). Similarly, greater contributions of \(\sigma\)-donation (57–59% of \(\Delta E_{\text{orb}}\)) compared to \(\pi\)-back-donation (34–35% of \(\Delta E_{\text{orb}}\)) were also observed for Ni–H_2 orbital interactions in 1-H_2 and 2-H_2 (Table S22).

The total interaction energy (\(\Delta E_{\text{int}}\)) between the H_2 and Ni fragments becomes increasingly favorable in the order, (n^2-H_2) NiLiH_3 < 1-H_2 < 2-H_2 < 3-H_2 (Table S21). Of interest, the less favorable \(\Delta E_{\text{elstat}}\) predicted for (n^2-H_2)NiLiH_3 arises from a large, unfavorable \(\Delta E_{\text{Pauli}}\) term, which is the repulsive interaction energy between like spins in the H_2 and NiLiH_3 fragments. This makes sense as NiLiH_3 lacks a Ni–M interaction that would result in attenuation of Ni electron density. Within the (n^2-H_2) NiML series, both the \(\Delta E_{\text{elstat}}\) and \(\Delta E_{\text{orb}}\) terms become more favorable as M is varied down the group 13 triad (Table S21). Furthermore, the greater relative importance of \(\sigma\)-donation to H_2 binding than \(\pi\)-back-donation is consistent with the trend that H_2 binding favorability increases as the Ni center becomes more electron-deficient, as judged by the Ni(I/0) redox potentials (Fig. S71 and Table S39). Hence, we propose that increased electron-withdrawal via Ni–M dative bonding as M is varied down group 13 induces stronger electrostatic and covalent interactions between H_2 and NiML, with a concomitant decrease in unfavorable Pauli repulsion between the two fragments.

Given the rarity of H_2 and N_2 binding to a Ni(0) metal center, we next sought to understand the specific electronic perturbations of the supporting group 13 metal ion that poise NiML to bind small molecules. To lend insight, UV-Vis spectroscopy studies in conjunction with time-dependent density functional theory (TD-DFT) calculations were conducted to investigate the electronic structure of complexes 1–4 and their H_2 and N_2 adducts. The UV-Vis spectra of NiLiH_3 and 1–3 are shown in Fig. 5a (THF, 298 K), along with the corresponding TD-DFT predicted spectra, where M06-D3/bs4 showed the best agreement with experiment (Fig. 5b and Table S29). We also sought to understand how the binding of H_2 and N_2 to the NiML complexes further impacts electronic structure. In this regard, it is notable that small-molecule binding to NiML often manifests in vibrant color changes. For example, exposure of a THF solution of 3 under Ar to an N_2 or H_2 atmosphere resulted in a color change from a deep red-purple color to a lighter red (3-N_2) or yellow-brown (3-H_2), respectively (Fig. 5c).

The UV-Vis spectra of 1–3 share the same pattern of three peaks between 400 and 800 nm, which are marked with asterisks in Fig. 5a and listed in Table 5 as peaks I, II, and III. These peaks all red-shift upon varying the supporting metal from Al to Ga to In. The TD-DFT calculated transition energies for 1–3 agree reasonably well with experiment, with the predicted excitations generally blue-shifted by 0.04 to 0.3 eV for peaks I to III (Table 5). The TD-DFT results also correctly predicted the red-shift of all peaks for 2 relative to 1, but the subtle spectral differences between 2 and 3 were not discerned by TD-DFT despite testing several methods (Table S29, Fig. S57 and S58). For NiLiH_3, a broad absorption feature is observed at ~500 nm, which was fit with two overlapping peaks with maxima at 491 and 533 nm, along with a low-intensity shoulder at 663 nm (Table S27, Fig. S56).

UV-Vis peaks I–III for NiLiH_3 and 1–3 were assigned based on the TD-DFT results (Table 5). Each peak corresponds to an electronic excitation from either a Ni 3d orbital or a ligand-based molecular orbital (MO) to the lowest unoccupied molecular orbital (LUMO), the latter of which is highly similar for all complexes. For NiLiH_3, the LUMO has both Ni 4p and P 4p character, whereas the LUMO for complexes 1–3 also has additional contributions from Ni (3d, 4s) and M (s, p) atomic orbitals (Fig. S59 and Table S31). For all complexes, peaks I and II arise from electronic excitations to the LUMO from the Ni d_{xy} and d_{xz}/d_{yz} orbitals, respectively. Peak III for NiLiH_3 is a transition from a pure d_{z^2} orbital to the LUMO, while peak III for 1–3 is a more complex transition from a mixed ligand-based aren \(\pi^*\) MO with partial Ni d_{z^2} character to the LUMO (Table S28).

Based on these transition assignments, semi-quantitative MO diagrams for NiLiH_3 and 1–3 can be constructed (Fig. 6).
For NiLH₃, the d-orbital manifold is consistent with that expected for a trigonal-planar metal center with three σ-donors: the degenerate dₓz/dᵧz orbitals are the most destabilized, followed by dₓ²−ᵧ², and then the dₓz/dᵧz set. For 1–3, the presence of the supporting group 13 metal ion results in the stabilization of the Ni 3dₓz orbital via Ni→M(pₓ/s) dative bonding, which is consistent with the blue shift in the predicted pure 3dₓz → LUMO transitions in the bimetallic NiML complexes (363 to 385 nm; Table S30†) relative to NiLH₃ (443 nm). The Ni dₓz/dᵧz orbitals, on the other hand, are destabilized upon the introduction of the supporting metal and its variation down group 13. Presumably, the π-back-bonding interaction, Ni dₓz/dᵧz → P–C σ*, becomes weaker as the Ni center becomes more electron-deficient due to stronger electron withdrawal by the supporting metal (In > Ga > Al > no support). In support, both the Ni–P bonds elongate and the ³¹P NMR signal shifts downfield from NiLH₃ to 1 to 2 to 3.

Another notable MO trend involves the energy difference between the Ni dₓz/dᵧz orbitals and the LUMO, as reflected in the peak II energies, which decrease upon the introduction and variation of the supporting metal down group 13. This particular energy gap is important because the LUMO and the Ni dₓz/dᵧz orbitals are the frontier Ni-based MOs that participate in small-molecule binding, with the Ni-based LUMO accepting σ-donation from either the H₂ or N₂ lone pair, and the Ni dₓz/dᵧz orbitals participating in π-back-bonding to either the H₂ σ*- or N₂ π*-LUMOs. Overall, the Ni dₓz/dᵧz → LUMO excitation energy decreases by ~0.2 eV across the NiML complexes, from 2.53 eV in 1 to 2.44 eV in 2 to 2.34 eV in 3 (Table S28†). Thus, it is reasonable to propose that varying the supporting metal from Al to Ga to In results in the destabilization of the Ni dₓz/dᵧz orbital set and the stabilization of the Ni-based LUMO, such that both become more energetically accessible to interact with small-molecule substrates.

The involvement of the LUMO in small-molecule binding is further supported by examining the changes in the UV-Vis spectra for 3 upon binding H₂ and N₂ (Fig. 5c). Notably, both the experimental and theoretical spectra of 3-H₂ and 3-N₂ lack any intense features between 400 and 700 nm. Instead, the lowest energy transitions for 3-H₂ and 3-N₂ are predicted at 375 and 391 nm, respectively. The shift to higher energy excitations for the H₂ and N₂ adducts can be qualitatively explained by the nature of their acceptor MOs, which we define as the lowest-energy unoccupied MO with significant Ni character, rather

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**Table 5** UV-Vis peaks (nm) for NiLH₃ and 1–3, with TD-DFT data (in parentheses) and transition assignments

<table>
<thead>
<tr>
<th>Peak</th>
<th>Transition</th>
<th>NiLH₃</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>dₓz/dᵧz   → LUMO</td>
<td>663</td>
<td>600</td>
<td>638</td>
<td>699</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(490)</td>
<td>(573)</td>
<td>(650)</td>
<td>(642)</td>
</tr>
<tr>
<td>II</td>
<td>dₓz/dᵧz   → LUMO</td>
<td>491</td>
<td>490</td>
<td>508</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(413)</td>
<td>(437)</td>
<td>(478)</td>
<td>(475)</td>
</tr>
<tr>
<td>III</td>
<td>π-ligand + dₓz → LUMO</td>
<td>533</td>
<td>430</td>
<td>464</td>
<td>488</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(443)</td>
<td>(410)</td>
<td>(448)</td>
<td>(449)</td>
</tr>
</tbody>
</table>

*a* Pure Ni dₓz → LUMO transition.
than those that are ligand based (Fig. S60–S63 and Tables S33–S38†). For both 3-H₂ and 3-N₂, the acceptor MO appears to be an anti-bonding combination of the LUMO in 3 and the donor MO of the small molecule (Fig. S64†). Thus, upon small-molecule binding via the dominant s-donation interaction with the LUMO of NiML, the resulting acceptor orbitals in (L₀NiML) adducts (L₀ = H₂, N₂) to which electrons can be excited are of higher energy relative to the Ni 3d manifold, and thereby give rise to higher energy electronic transitions.

**Part V. Linear free-energy relationships**

We examined linear free-energy relationships across the NiML series to quantify the effect of the supporting group 13 metal on the thermodynamics and kinetics of small-molecule binding. For H₂ binding, an excellent correlation was observed between the thermodynamic free energies (ΔG₁M) and the free energies of activation (ΔG_bind), where more exergonic binding equilibria have smaller activation barriers (R² = 0.999, Fig. 7a). The slope of +0.93 in the ΔG_bind versus ΔG₁M plot indicates that a decrease of ~1 kcal mol⁻¹ in ΔG₁M for H₂ binding corresponds to a commensurate lowering of the free energy barrier. Reasonably strong correlations were also found between the Ni 3dₓz/dᵧz/LUMO excitation energy and ΔG.createElement(“sub”) for H₂ (R² = 0.924) and N₂ (R² = 0.963) binding (Fig. 7b). This correlation makes sense since the Ni 3dₓz/dᵧz orbitals and the LUMO are the Ni-based frontier orbitals that participate in small-molecule binding (vide supra). The slopes of the plots of ΔG for H₂ and N₂ binding versus the Ni 3dₓz/dᵧz → LUMO excitation energy (in kcal mol⁻¹) are close to unity, where a decrease of 1 kcal mol⁻¹ in the Ni 3dₓz/dᵧz → LUMO excitation energy is associated with a nearly equivalent increase in the favorability of H₂/N₂ binding.

The isostructural nature of the (η²-H₂)NiML series allows us to further interrogate which intrinsic properties of the group 13 metal (Ga, In, or Al) most strongly influence small-molecule binding through these linear free-energy relationships.
support (M) dictate the favorability of H₂ and N₂ binding. A strong negative correlation was found between the size of the supporting metal, as represented by Shannon’s M(III) ionic radii, and ΔG° for both H₂ (R² = 0.988) and N₂ (R² = 0.999) binding (Fig. 7c), where larger supporting ions induce more exergonic binding. The finding that larger supporting metals better poise Ni for small-molecule binding is likely a composite effect of both electronic and steric factors. Larger group 13 supporting metals show stronger Ni → M bonding interactions (Table S24†) and shift the Ni(0/1) oxidation to more positive potentials, both of which should lower the Pauli repulsion associated with binding a donor (Fig. S71†). Also, larger group 13 ions force Ni to move further above the P₃-plane which should minimize the structural reorganization energy associated with small-molecule binding (Fig. S72†).

The confluence of steric and electronic effects is also supported by the fact that neither effect can solely account for the observed trends. For example, the position of Ni above the P₃-plane is identical for both Al and Ga (0.13 Å), despite their distinct differences in ΔG° for H₂/N₂ binding. Also, correlations between ΔG° for H₂/N₂ binding and Ni redox potentials are comparatively poor, whether one considers the Ni(0/1) oxidation or the Ni(−1/0) reduction potentials (R² = 0.726 to 0.891, Fig. S68 and S69†). Typically Lewis acidity is expected to correlate with σ-accepting ability, yet no linear relationship exists between ΔG° for H₂/N₂ binding and the relative Lewis acidities of group 13 metals, as given by the pK values of the corresponding M(H₂O)₆ complexes (R² = 0.02–0.05, Fig. S66†). It is plausible that the Lewis acidity scale based on M–OH₂ bonds, where H₂O is the Lewis base, is an inappropriate benchmark for a Ni(0) Lewis base. You and Gabbaï have recently proposed that the double-decker ligand framework, which imposes spatial constraints, may “accentuate” the influence of the group 13 ion’s size. It is noteworthy that ΔG° values for H₂ (R² = 0.945) and N₂ (R² = 0.977) binding correlate reasonably well with the degree of Ni → M dative bonding, as quantified by the ratio of the solid-state Ni–M bond distance to the sum of the covalent radii of Ni and M (Fig. S67†). This finding is consistent with the hypothesis that group 13 metals can significantly tune the reactivity of a proximal Ni center via a direct Ni(0) → M(III) dative interaction.

**Conclusion**

H₂ and N₂ binding is atypical for Ni complexes and facilitating H₂ activation to form reactive Ni[N(η²:H₂)] and/or Ni–H species poses a difficult hurdle for developing homogeneous Ni catalysts for H₂ oxidation, proton reduction, and related processes. Excitingly, we find that supporting Ni with group 13 metals induces the binding of H₂ and N₂ to Ni, with H₂ binding found to be ~2 kcal mol⁻¹ more favorable than N₂ binding in each case. The pivotal role of the supporting metal in promoting binding to the NiML complexes is highlighted by the inability of NiLH₃, a similarly ligated mononuclear Ni center, to bind H₂ or N₂ under any conditions examined. The dramatic tuning effect of the supporting group 13 metal is illustrated by the wide range of ΔG° values for H₂ binding, which span ~8 kcal mol⁻¹ (including NiLH₃) and nearly cover the entire range of previously reported values. H₂ binding to NiNH₃ [3] is more exergonic than any such equilibrium reported, allowing for solid-state characterization of [η²-H₂]NiNH₃ (3-H₂) via neutron diffraction, which is unprecedented for an H₂ adduct of Ni or any d¹⁰ metal.

Theoretical calculations have provided important insights into the role of the supporting metal in promoting small-molecule binding. Specifically, complementary σ-interactions are proposed based on ETS-NOCV calculations, where H₂ → Ni σ-donation to the energetically-accessible Ni(4p₃) based LUMO is the dominant binding interaction, which is likely induced by electron withdrawal from Ni via the dative Ni(0) → M(III) bond. The involvement of the LUMO in small-molecule binding is supported by TD-DFT and UV-Vis studies, along with the strong correlation between ΔG° values for H₂/N₂ binding and the Ni 3dₓz/3dᵧz → LUMO excitation energy. Notably, the size of the supporting M(III) ion correlates best with ΔG° values for H₂ and N₂ binding, with larger group 13 supporting metals inducing more favorable binding by: rendering Ni more electron-deficient, favoring stronger Ni → M interaction, and minimizing the structural reorganization energy. Moreover, thermodynamically favorable H₂ binding equilibria (In > Ga > Al) have proportionally smaller free energies of activation.

Overall, a thorough understanding of H₂ and N₂ binding to NIML complexes, and the integral role of the supporting metal therein, has been presented. Future work will explore the impact of the thermodynamics and kinetics of H₂ binding equilibria on catalytic CO₂ hydrogenation reactivity, where H₂ binding to displace formate has been found to be the rate-determining step in catalysis. Additionally, the generalizability of the strategy of favorably altering base-metal reactivity via interactions with group 13 supporting metals will be assessed, and efforts are currently underway to extend our studies to other ligand frameworks and transition metals.

**Experimental section**

Additional information is provided in the ESI†

**General considerations**

Unless otherwise stated, all manipulations were performed under an Ar or N₂ atmosphere inside a glovebox or using standard Schlenk techniques. Standard solvents were deoxygenated by sparging with N₂ and dried by passing through activated alumina columns of a 5G water solvent purification system. Deuterated solvents and HD gas (97% D content) were purchased from Cambridge Isotope Laboratories, Inc. Deuterated solvents were degassed via freeze–pump–thaw cycles, and either stored over activated 4 Å molecular sieves or stirred with Na–K alloy and distilled. N₂ and H₂ gases were purchased from Matheson Trigas, Inc., and a gas mixture of 10% H₂/90% Ar was purchased from Praxair, Inc. All other reagents were purchased from commercial vendors and used without purification unless otherwise noted. The ligand Ni(o-NHCH₂P₂Pr₂C₆H₄)₃ (abbreviated as LH₃), NiAlL [1], NiGaL [2], NiInL [3], [η²-H₂]NiGaL [2-H₂], [N₃]NiInL [3-N₃], [η²-H₂]NiInL [3-H₂], and NiLH₃ [4] were prepared as described.
synthesized according to the literature.\textsuperscript{16,34,68} \textsuperscript{1}H and \textsuperscript{31}P NMR spectra were recorded on Bruker (400 or 500 MHz) or Varian (500 MHz) spectrometers and referenced to internal residual solvent (or \textsuperscript{1}H\textsubscript{2}PO\textsubscript{4} for \textsuperscript{31}P NMR spectra). For VT NMR experiments, the temperature was calibrated using a methanol (\textless 298 K) or an ethylene glycol (\textgtr 298 K) standard. UV-Vis spectra were collected on a Cary-14 instrument. Cyclic voltammetry experiments were performed using a CHI Instruments 620D potentiostat. The one-cell setup utilized a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgNO\textsubscript{3} reference electrode in CH\textsubscript{3}CN.

**In situ generation of (\textsuperscript{1}H\textsubscript{2})NiAlL (abbreviated as 1-H\textsubscript{2})**

A solution of 1 (15 mg, 19.6 \textmu mol) in THF-d\textsubscript{8} (\textsim 0.30 mL) was added to a PEEK NMR cell and pressurized to 34 atm H\textsubscript{2}. The following NMR data are reported at 34 atm H\textsubscript{2}; an equilibrium between 1 and 1-H\textsubscript{2} can also be observed under 1 atm H\textsubscript{2} at low T. \textsuperscript{1}H(\textsuperscript{31}P) NMR (ppm, THF-d\textsubscript{8}, 232 K, 500 MHz): 7.34 (br, 3H, ArH), 6.87 (br, 3H, ArH), 6.34 (br, 6H, ArH), 3.00 (br, 3H, CH\textsubscript{3}H\textsuperscript{2}), 2.87 (br, 3H, CH\textsubscript{2}H\textsuperscript{2}), 2.10 (m, 6H, CH(CH\textsubscript{3}))\textsubscript{2}, 1.27 to 0.90 (36H, CH(CH\textsubscript{3}))\textsubscript{2}, 1.15 (br, 2H, Ni\textsubscript{2}H\textsubscript{3}N\textsubscript{i}Ni, \textit{T} (min) \textsim 0.49(5) s at 200 K). \textsuperscript{31}P NMR (ppm, 200 K, 202.4 MHz): 44.9 (in THF-d\textsubscript{8}), or 44.3 (in toluene-d\textsubscript{8}). The lability of H\textsubscript{2} precluded elemental analysis from being obtained.

**In situ observation of (N\textsubscript{2})\textsubscript{2}NiAlL (1-N\textsubscript{2}) and (N\textsubscript{2})\textsubscript{2}NiGal (2-N\textsubscript{2})**

A solution of 1 (3.7 mg, 4.8 \textmu mol) in toluene-d\textsubscript{8} (0.30 mL) was added to a PEEK NMR cell and pressurized to 51 atm N\textsubscript{2}. Similarly, a solution of 2 (5.0 mg, 6.2 \textmu mol) in toluene-d\textsubscript{8} (0.41 mL) was added to a J. Young NMR tube under 1 atm N\textsubscript{2}. Neither 1-N\textsubscript{2} nor 2-N\textsubscript{2} was isolable due to lability of the N\textsubscript{2} ligand. Both 1-N\textsubscript{2} and 2-N\textsubscript{2} were observed in the presence of 1 and 2, respectively, which limited \textsuperscript{1}H NMR characterization due to overlapping resonances. For 1-N\textsubscript{2}: \textsuperscript{31}P NMR (ppm, toluene-d\textsubscript{8}, 190 K, 51 atm N\textsubscript{2}, 202.4 MHz): \sim 32.3. For 2-N\textsubscript{2}: \textsuperscript{31}P NMR (ppm, toluene-d\textsubscript{8}, 193 K, 1 atm N\textsubscript{2}, 162 MHz): \sim 43.5.

**X-ray and neutron diffraction crystallographic and structure refinement details**

**X-ray diffraction.** A gold block of (\textsuperscript{1}H\textsubscript{2})NiInL (3-H\textsubscript{2}) was placed onto the tip of a MiTeGen Dual-Thickness MicroLoop\textsuperscript{TM} and mounted on a Bruker Photon II CMOS diffractometer for data collection at 100(2) K (Table 6). The data collections were carried out using Mo K\textalpha radiation (graphite monochromator), and the data intensity was corrected for absorption and decay (SADABS).\textsuperscript{40} Final cell constants were obtained from least-squares fits of all measured reflections. The structure was solved using SHELXT-16 and refined using SHELXL-16, which were executed from the ShelXle graphical user interface.\textsuperscript{79} A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters,\textsuperscript{71} with the exception of the apical H\textsubscript{2} ligand in 3-H\textsubscript{2}, for which the H atoms were sufficiently resolved in the Fourier difference map to allow tentative placement. Images were rendered using POV-ray.\textsuperscript{72}

**Neutron diffraction.** Neutron diffraction data were collected using the TOPAZ single-crystal time-of-flight (TOF) Laue diffractometer at the Spallation Neutron Source (SNS), at Oak Ridge National Laboratory (Oak Ridge, TN).\textsuperscript{73} A block-shaped crystal of 3-H\textsubscript{2}, with dimensions of 0.35 \times 0.30 \times 0.30 mm, was grown from a concentrated toluene solution under 1 atm H\textsubscript{2} at \sim 280 K for several weeks. The crystal was mounted on the tip of a polyimide capillary using fluorinated grease and transferred to the TOPAZ goniometer for data collection at 100 K (Table 6). To ensure good coverage and redundancy, data were collected using crystal orientations optimized with CrystalPlan software\textsuperscript{74} for optimal coverage of symmetry-equivalent reflections of the orthorhombic cell. The integrated raw Bragg intensities were obtained using the 3-D ellipsoidal Q-space integration in accordance with previously reported methods.\textsuperscript{75} Data reduction, including neutron TOF spectrum, Lorentz, and detector efficiency corrections, was carried out with the ANVRED3 program.\textsuperscript{76} A spherical absorption correction was applied with \mu = 0.1570 + 0.1306 \times \textup{cm}^{-1}. The reduced data were saved as SHELX HKLF2 format, in which the wavelength is recorded separately for each reflection, and data were not merged. Starting with the X-ray structure at 100 K as an input model (where all the H atoms were placed except for the H\textsubscript{2} ligand), the neutron crystal structure was refined using the SHELXL-14/7 program\textsuperscript{76,77} with RIGU restraints for the H-atoms’ anisotropic displacement parameters.\textsuperscript{77}

**General procedure for H\textsubscript{2}/N\textsubscript{2} binding studies**

A toluene-d\textsubscript{8} solution of NiML (15 mM) was filtered and transferred to either a J. Young NMR tube (\textless 3.8 atm) or a PEEK NMR
cell (≥6.8 atm). For high-pressure studies, the PEEK cell was sealed and connected to a high-pressure line equipped with a vacuum pump and an ISCO syringe pump. The line was purged with H₂ or N₂ gas three times. Next, the headspace was degassed by opening the PEEK cell to static vacuum (3 × 30 s), and H₂ or N₂ gas was then delivered to the cell from an ISCO syringe pump running constantly at the desired pressure (i.e. continuous gas feed). The contents of the PEEK cell were mixed using a vortex mixer for ~15 min prior to NMR data collection to allow for pressure stabilization and equilibration. For low-pressure studies, J. Young NMR tubes were pressurized after freeze–pump–thaw cycles. VT31P NMR spectra were acquired at several different T (193 to 368 K) in all studies, with an adequate number of scans collected (typically 64 to 160 scans) to quantify the observed peak position (for fast chemical exchange) and/or the relative peak integrations (for slow chemical exchange). 31P spectra were typically collected with a recycle delay time of 2 s and an acquisition time of 1.68 s. In cases where quantitative integration of multiple peaks was desired, a longer delay time of 10 s was used.

CAUTION: H₂ is a highly flammable gas. Pressurized vessels must be handled with care using proper personal protective equipment. PEEK cells were employed for the high-pressure NMR studies, as described previously.78–79

**General procedure for kinetic studies of H₂ self-exchange**

A solution of NiML (7.5 mM in 0.70 mL) was prepared in toluene-d₈ and transferred to a J. Young NMR tube. VT31P NMR spectra were typically collected with a recycle delay time of 2 s, an acquisition time of 1.68 s, and an acquisition time of 1.68 s, and with 160 scans.

**Computational methods**

**Density functional theory (DFT).** DFT calculations were performed using the Gaussian 09 program package. Four functionals [M06-L, M06-D3,56,57 PBE0,82 and PBE0-D3 56,83] and five basis sets (denoted as bs0 to bs4, Table S3†) were evaluated. The M06-L/bs1 method (def2-TZVPP for H₂, N₂, Ni, Al, Ga, and In, with the SDD effective core potential84 for In; def2-TZVP basis set for N, P; and def2-SVP for C and H atoms)85 gave the best match to the experimental binding energies, and had been used in related prior studies.87 Geometric structures were optimized in the gas phase at 0 K, using the crystal structure atomic coordinates as the initial geometries when available (1–3, 3-H₃, and 3-N₃). Vibrational frequency analyses were performed with the harmonic approximation to confirm the nature of all species (0 and 1 imaginary frequency for ground-state and transition-state structures, respectively). Unless otherwise noted, Gibbs free energies at 298.15 K and 1 atm were computed by adding zero-point vibrational energies and thermal corrections. Solvation effects were considered by performing single-point calculations for all stationary points using the SMD solvation model. The H₂ and N₂ binding energies for NiML were calculated according to the following equation:

\[
X_{(g)} + \text{NiML(solv)} \rightarrow X\text{-NiML(solv)}
\]

In eqn (3), X(g) is H₂ or N₂, and the standard state is defined as 1 atm for X(g). The overall energy for eqn (3) was determined based on the gas-phase free energies for H₂ or N₂ and the Gibbs free energies with solvation (in toluene) for NiML(solv) and X-NiML(solv).

**Energy decomposition analysis (EDA).** The EDA method was implemented in the Amsterdam Density Functional (ADF 2016) program package to study chemical bonding between H₂ and Ni in the (η²-H₂)NiML complexes. Single-point energy calculations were performed using PBE0-D3/TZ2P on the M06-L/bs1-optimized geometries. Relativistic effects for In were included by applying the zeroth-order regular approximation (ZORA). EDA breaks the total interaction energy (ΔE_int) between the H₂ and NiML fragments into four components, as shown in eqn (4):

\[
\Delta E_{\text{int}} (\text{EDA}) = \Delta E_{\text{stat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}
\]

ΔE.stat is the attractive, quasi-classical electrostatic interaction between the electrons and the nuclei; ΔE.Pauli is the repulsive interaction between the occupied orbitals of the fragments; ΔE.orb is the interaction between the occupied molecular orbitals of one fragment and the unoccupied molecular orbitals of the other fragment; and, ΔE.disp corresponds to the dispersive effects between the two fragments. The extended transition state—natural orbitals for chemical valence (ETS-NOCV) method, in combination with the energy decomposition scheme, was utilized to break down the orbital interaction component (ΔE.orb) into contributions from specific NOCV pairs (see ESI for further details†).

**Time-dependent (TD) DFT calculations.** TD-DFT calculations (M06-D3/bs4, Gaussian 09) with solvent considerations (SMD, THF) were performed to aid in assigning electronic transitions in the absorption spectra of NiLH₃ (M = Al, Ga, In). The basis sets denoted by bs4 were used: LANL2DZ for In and 6-311G(d,p) for all other atoms.

**Conflicts of interest**

The authors declare no competing financial interests.

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