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Pairwise H₂/D₂ Exchange and H₂ Substitution at a Bimetallic Dinickel(II) Complex Featuring Two Terminal Hydrides

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ABSTRACT: A compartmental ligand scaffold HL with two β -diketiminato binding sites spanned by a pyrazolate bridge gave a series of dinuclear nickel(II) dihydride complexes M[LNi₂(H)₂], M = Na (Na·2), K (K·2), which were isolated after reacting the precursor complex [LNi₂(μ -Br)] (1) with MHBEt₃ (M = Na and K). Crystallographic characterization showed the two hydride ligands to be directed into the bimetallic pocket, closely interacting with the alkali metal cation. Treatment of K-2 with dibenzo(18crown-6) led to the separated ion pair [LNi₂(H)₂][K(DB18C6)] (2[K(DB18C6)]). Reaction of Na·2 or K·2 with D₂ was investigated by a suite of ¹H and ²H NMR experiments, revealing an unusual pairwise H_2/D_2 exchange process that synchronously involves both Ni-H moieties, without H/D scrambling. A mechanistic picture was provided by DFT calculations which suggested facile recombination of the two terminal hydrides within the bimetallic cleft, with a moderate enthalpic barrier of $\sim 62 \text{ kJ/mol}$, to give H₂ and an antiferromagnetically coupled $[LNi_2]^{-}$ species. This was confirmed by SQUID monitoring during H₂ release from solid 2[K(DB18C6)]. Interaction with the Lewis acid cation (Na⁺ or K⁺) significantly stabilizes the dihydride core. Kinetic data for the for the M[L(Ni-H)₂] \rightarrow H₂ transition derived from 2D ¹H EXSY spectra confirmed first order dependence of H₂ release on M·2 concentration and a strong effect of the alkali metal cation M^+ . Treating $[LNi_2(D)_2]^-$ with phenylacetylene led to D_2 and dinickel(II) complex 3⁻ with a twice reduced styrene-1,2-divl bridging unit in the bimetallic pocket. Complexes $[LNi^{II}_{2}(H)_{2}]^{-}$ having two adjacent terminal hydrides thus represent a masked version of a highly reactive dinickel(I) core. Storing two reducing equivalents in adjacent metal hydrides that evolve H₂ upon substrate binding is reminiscent of the proposed N₂ binding step at the FeMo cofactor of nitrogenase, suggesting the use of present bimetallic scaffold for reductive bioinspired activation of a range of inert small molecules.

INTRODUCTION

Transition metal hydride complexes hold an important place in inorganic chemistry, and they represent key intermediates in organometallic catalytic processes involving the transfer of H atoms, protons or hydride to substrates.^{1,2} In recent times, a focus in molecular metal hydride chemistry has been the search for catalysts mediating the reversible interconversion of protons and H₂, spurred by the interest in using H₂ as an energy carrier.³ Bioinorganic chemistry has provided much inspiration for the field, as natural hydrogenase enzymes use earthabundant iron and nickel for H₂ formation and oxidation.⁴ In particular, the mechanistic interrogation of [NiFe] hydrogenase,⁵ and the development of efficient bioinspired H₂ evolution catalysts based on nickel,^{6,7} has led to an impressive progress in nickel hydride chemistry.⁸

Biology is also offering blueprints for the use of metal hydride species in the reductive binding and activation of inert substrates. In this case, reducing equivalents are stored as hydrides, preferably at multimetallic sites, which upon reductive elimination of H₂ unmask the low-valent metal species. This strategy avoids strong reducing agents and may bypass highly unfavorable one-electron reduced substrate intermediates. The prominent metallobiosite exploiting this mechanism is the FeMo cofactor of nitrogenase,⁹ where binding of inert N₂ is preceded by charging of the Fe/S active site with four electrons and four protons, and is accompanied by the obligatory release of one molecule of H_2 .^{10,11} It has recently been shown that photolysis of the charged state, denoted $E_4(4H)$ according to the Lowe-Thorneley kinetic scheme for the nitrogenase mechanism,^{11a} generates an intermediate $E_4(H_2;2H)$ described as an H_2 complex of the doubly reduced Fe/S cluster.¹² It has further been suggested that this H_2 complex may be a thermally populated intermediate on the trajectory of reductive elimination of H_2 from, and reaction of N_2 with, the $E_4(4H)$ state (Scheme 1).¹²



Scheme 1. Cartoon of the proposed H_2 reductive elimination scenario that leads to the doubly reduced FeMoco intermediate prior to N_2 binding.

The nitrogenase background provides a strong impetus for synthetic efforts targeting the use of transition metal hydrides s Environment as masked low-valent complexes capable of reductively activating small molecules.¹³ β -diketiminato ligands have proven extremely valuable in this context, and a particularly rich chemistry has evolved from the iron and nickel type A complexes with $M(\mu-H)_2M$ core mainly developed by the groups of Holland and Limberg, respectively (Figure 1; including variants thereof with other aryl and backbone substituents).^{14,15} These bimetallic hydrides were shown to readily eliminate H₂ when treated with external donors or upon heating, leading to a variety of iron(I) and nickel(I) complexes.^{16,17} A dinucleating scaffold composed of two β -diketiminato subunits bridged by pyridine afforded a hydride-bridged mixed-valent $Ni^{I}(\mu-H)Ni^{II}$ species.¹⁸ Mechanistic studies on the reaction of a β diketiminato supported $Fe(\mu-H)_2Fe$ complex with azobenzene, which leads to N=N bond cleavage, indicated that substrate binding occurs prior to rate limiting H-H bond formation and triggers reductive H₂ release.¹⁹



Figure 1. Selected examples of iron(II) and nickel(II) hydride complexes supported by β -diketiminato ligands.

A cyclophane type scaffold containing three β -diketiminato binding pockets, developed recently by *Murray* and coworkers, gave access to tris(μ -hydrido) trimetallic clusters such as the triiron(II) complex **B** (Figure 1).²⁰ The latter showed COinduced reductive elimination of H₂ to produce a low-valent Fe¹₂Fe^{II} species that reversibly regenerates the trihydride complex under H₂ atmosphere.²¹

Exchange of the hydrides with D_2 in type A diiron(II) dihydrides produced all isotopologues with H/D scrambling, though the mechanism could not be fully elucidated. It was suggested, however, that H_2/D_2 exchange does proceed at the dimeric molecule and not via a transient monomer with a terminal Fe-H.²² It should be noted that hydride complexes that can bind H_2 (or D_2) *cis* to the hydride usually undergo a facile low barrier (~5 kcal·mol⁻¹ or less) ligand exchange.²³ Such effective intramolecular site exchange of H atoms between H₂ ligands and hydride ligands leads to a single hydride resonance in 'H NMR, and to the rapid incorporation of deuterium accompanied by the formation of HD when the protio form of the hydride complex is treated with D₂ gas. Mechanistically the H₂/H exchange can be considered as an oxidative addition/reductive elimination route via a tris-hvdride intermediate, or as a nondissociative single step transfer of a hydrogen atom involving quantum mechanical exchange phenomena (Scheme 2).^{23,24}



Scheme 2. Possible mechanisms of H_2/H exchange for a hydride complex which in case of D_2/H exchange leads to H/D scrambling and formation of HD.^{23,24}

Here we present a new ligand scaffold that provides two β diketiminate binding pockets spanned by a pyrazolate bridge. This system was designed to feature two terminal M-H units in close proximity within a bimetallic pocket, potentially prone to H₂ elimination and two-electron reductive activation of substrates while capitalizing on metal-metal cooperativity. In contrast to type A, B, and related systems, however, any bridging hydrides, μ -H, should be prevented because of the larger metal---metal separation enforced by the pyrazolate bridge. We report a family of dinickel(II) dihydride complexes of that new ligand, their unusual H_2/D_2 exchange reactivity that proceeds without any scrambling and synchronously exchanges both terminal Ni-H, the effect of Lewis acids on hydride stability and reactivity, and we demonstrate that the dinickel(II) dihydride indeed serves as a masked dinickel(I) synthon capable of reductive substrate binding.

RESULTS AND DISCUSSION

Synthesis and characterization of dinickel dihydride complexes. A multi-step synthetic route starting from readily available 3,5-disubstituted pyrazole derivatives was developed to afford the new proligand H₃L in good yields and gram quantities; details of the reaction sequence and experimental protocols are provided in the Supporting Information (SI). Deprotonation of H₃L with *n*-BuLi and subsequent addition of $NiBr_2(dme)$ (dme = dimethoxyethane) at room temperature, all in THF solution, gave the beige bromido-bridged complex $[LNi_2(\mu-Br)]$ (1) (Scheme 3). 1 is a diamagnetic compound with apparent C_{2v} symmetry according to NMR spectroscopy. Single crystals were obtained from CH₂Cl₂ or CHCl₃ solutions, and the molecular structure of 1 determined by X-ray diffraction confirmed that the two nickel(II) ions are hosted in the two $\{N_3\}$ -tridentate binding sites of the trianionic ligand scaffold, bridged by the pyrazolate and an exogenous bromide (Figure 2). The metal ions are found in roughly square-planar coordination environment with $d(Ni \cdot Ni) = 3.8066(5)$ Å. However, the bromide appears to be a bit small for the bimetallic pocket and is thus pulled into the cleft, which is reflected by the angles N3-Ni1-Br and N5-Ni2-Br (~168°) which deviate significantly from linearity.





Scheme 3. Preparation of complexes $[LNi_2(\mu-Br)]$ (1), K $[LNi_2(H)_2]$ (K·2), Na $[LNi_2(H)_2]$ (Na·2), and $[LNi_2(H)_2]$ [K(DB18C6)] (2[K(DB18C6)]).



Figure 2. Molecular structure (30% probability thermal ellipsoids) of **1**. Solvent molecules and hydrogen atoms omitted for clarity).

Treatment of $[LNi_2(\mu-Br)]$ with 2.5 equivalents of MHBEt₃ (M = Na and K) in THF smoothly gave the dihydride complexes $M[LNi_2(H)_2]$ (K·2 for M = K, Na·2 for M = Na). Crystals

suitable for X-ray diffractometry for both compounds were obtained by slow diffusion of pentane into THF solutions at room temperature. The molecular structures of K-2 and Na-2 are shown in Figure 3 (the asymmetric unit of K-2 contains two crystallographically independent but very similar molecules; only one is shown). The two hydride ligands in each complex are directed into the bimetallic pocket, as anticipated, and the coordination spheres of all nickel ions are only slightly distorted from square-planar. In both cases, the alkali metal cation is closely associated with the anionic $[LNi_2(H)_2]^-$ core, but the location of Na^+ and K^+ is distinct. In K·2, the K^+ ion is hold between the two aryl rings of the DIPP substituents via cation- π interactions and is located within the plane defined by the pyrazolate-bridged dinickel dihydride core, presumably supported by attractive K^+ ...hydride interactions ($d(K^+$...H) = 2.45(3) - 2.53(3) Å). A related situation has been observed in a trinuclear Ni₃H₄ complex capped by β-diketiminato ligands, where K⁺ ions sandwiched between aryl rings were located close to two bridging hydrides (2.47(3) Å).²⁵ The distance between K^+ and the centroid of the DIPP aryl rings in K-2 is 2.84 Å, which lies in the typical range for cation- π bonding of K^{+} to aromatic systems.²⁶ In Na·2, the smaller Na⁺ ion is situated above the pyrazolate-bridged dinickel dihydride core and outside of the DIPP cleft, with close contacts to the two hydrides, the two pyrazolate-N, and coordinated by two addi-Ni…Ni tional THF ligands. distances for K•2 (4.1584(7)/4.1636(7) Å) and Na·2 (4.1049(5) Å) are similar, suggesting that the alkali metal cation does not exert any major structural influence on the dinickel dihydride core, and that the arrangement of the two DIPP aryl rings is favorably suited for accommodating a K^+ cation.



Figure 3. Molecular structures (30% probability thermal ellipsoids) of $K[LNi_2(H)_2]$ (K·2; top; only one of two independent molecules shown) and Na[LNi_2(H)_2] (Na·2; bottom). Hydrogen atoms except the Ni-bound hydride omitted for clarity.

	1	K-2	Na•2	2 [K(DB18C6)]	K-3
Ni–N	1.843(2) - 1.897(2)	1.878(2) - 1.911(2)	1.866(2) - 1.921(2)	1.862 (2) - 1.920(2)	1.850(2) - 1.949(2)
Ni–Br	2.3812(4) / 2.3978(4)	-	-	-	-
Ni–H	-	1.32(2) - 1.38(3)	1.37(2) / 1.40(2)	1.44(3) / 1.46(3)	-
Ni–C	-	-	-	-	1.896(3) - 1.928(2)
K–C	-	3.098(2) - 3.239 (2)	-	-	3.005(2) - 3.112(2)
K–H	-	2.45(3) - 2.53(3)	-	-	-
K–N	-	-	-	-	2.875(2) - 3.138(2)
Na–N	-	-	2.567(2) / 2.705(2)	-	-
Na–H	-	-	2.26(2) / 2.50(3)	-	-
Ni⋯Ni	3.8066(5)	4.1584(7) / 4.1636(7)	4.1049(5)	4.0636(7) / 4.1152(7)	3.876(1) / 3.890(1)
Ni⋯K	-	3.7807(5) - 3.8307(5)	-	-	3.454(6) - 3.786(7)
Ni⋯Na	-	-	2.8468(8) / 3.0084 (8)	-	-
N–Ni–N	175.98(9) / 178.02(9)	176.55(7) - 178.66(7)	176.93(7) / 178.19(7)	177.22(8) / 177.25(8)	162.04(8) - 173.60(9)
(opposite)					
N–Ni–Br	167.91(7) / 168.20(6)	-	-	-	-
(opposite)					
N–Ni–H	-	172.5(12) - 174.7(10)	172.7(9) / 173.4(10)	171.0(13)/172.4(13)	-
(opposite)					
N–Ni–C	-	-	-	-	153.62(9) - 167.12(9)
(opposite)					

To further assess the effect of the alkali metal cations and to prepare dinickel dihydride complex with a vacant cleft, K-2 was treated with [2,2,2]cryptand or dibenzo(18-crown-6) (DB18C6) to separate the K^+ cation from the $[LNi_2(H)_2]^$ complex anion. No obvious color change is associated with these reactions, but the ionic products become poorly soluble in THF; these differences in solubility suggest that the alkali metal cations remain closely associated with the [LNi₂(H)₂] anion and that contact ion pairs are present in THF solutions of K·2 and Na·2. Single crystals of [LNi₂(H)₂][K(DB18C6)] (2[K(DB18C6)]) were obtained from THF/Et₂O solutions and subjected to X-ray diffraction. The asymmetric unit contains two crystallographically independent molecules with crystallographically imposed C_2 symmetry (the idealized point group of the anion is C_{2v} ; one of the two molecules is shown in Figure 4. The core structure of the "naked" [LNi₂(H)₂] complex anion shows no significant differences compared to the neutral compounds K-2 and Na-2. Selected metrical parameters of the three dinickel dihydrido complexes are listed in Tables 1 and 2. 2[K(DB18C6)] appears to feature longer Ni-H bonds and a shorter H1…H1' distance than K·2 and Na·2 (in fact, Ni-H bonds in the range 1.32(2) - 1.40(2) Å determined for K·2 and Na·2 are shorter than most terminal Ni-H bonds reported in literature.^{8,15,27} However, all these data have to be considered with caution because of inherent ambiguities of H atom positions derived from X-ray crystallography. In the absence of neutron diffraction data, NMR and IR signatures (vide infra) can be considered more reliable for assessing differences among the Ni-H moieties in the three compounds.



Figure 4. Molecular structure (30% probability thermal ellipsoids) of the anion of 2[K(DB18C6)] (only one of two independent molecules shown). Most hydrogen atoms omitted for clarity, except for the nickel-bound hydrides. Symmetry transformations used to generate equivalent atoms: (') -x, y, 3/2-z.

Table 2. Selected metrical and spectroscopic data for the three complexes K.2, Na.2 and 2[K(DB18C6)].

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Compound	K-2	Na•2	2 [K(DB18C6)]
Ni…Ni [Å]	4.158/4.164	4.105	4.115 4.064
Ni-H [Å]	1.32(2) 1.38(2)	1.37(2) 1.40(2)	1.46(3) 1.44(3)
NiH…HNi [Å]	2.33(3) /2.33(3)	2.28(4)	2.11(5)/2.14(5)
K…H/Na…H [Å]	2.45(3)/ 2.53(3)/ 2.49(2)/ 2.53(3)	2.26(2) 2.50(3)	-
$\delta(^{1}\text{H})$ (ppm)	-24.16	-23.54	-
$v (cm^{-1})$ (N-H/N-D) ^{<i>a</i>}	1961/1367	1846/1337	1907/-

^a ATR-IR spectra recorded on solid samples.

Ni-H stretching vibrations for solid samples of the three complexes are found at 1961 cm⁻¹ (K·2), 1846 cm⁻¹ (Na·2) and 1907 cm⁻¹ (2[K(DB18C6)]), well within the range 1690-

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2000 cm⁻¹ reported in literature for terminal Ni-H stretching bands.⁸ Band assignment has been corroborated by recording spectra for the corresponding Ni-D compounds (*vide infra*) which show the expected isotopic shift of $v(\text{Ni-H})/v(\text{Ni-D}) \approx$ 1.4 (Table 2; spectra are shown in the Supplementary Information). According to a SQUID measurement, solid K·2 is diamagnetic over the temperature range 2 – 295 K (Figure S47), reflecting the low-spin d⁸ configuration of the nickel(II) ions. In contrast, **2**[K(DB18C6)] proved to be highly sensitive and decayed when crystals were dried under reduced pressure or kept at rt for some time. These findings will be discussed in more detail below.

The SQUID results are in agreement with solution properties of the complexes. ¹H NMR spectra of K·2 and Na·2 in THF-d₈ reveal high field shifted resonances at -24.16 (K·2), -23.54 (Na·2) assigned to the Ni-bound hydrides (Figures S8 and S16, respectively; Table 2). These values are within the wide range of chemical shifts reported for terminal nickel hydrides.⁸ The different alkali metal cations in K·2 and Na·2 obviously have only a minor effect on the electronical shielding of the hydrides. 2[K(DB18C6)] appears to be rather unstable in solution and gives rise to broad, paramagnetically shifted resonances (Figure S25).

 H_2/D_2 exchange reaction. Upon addition of D_2 (atmospheric pressure) to degassed solutions of $K \cdot 2$ or $Na \cdot 2$ in THF-d₈, both nickel bound hydrogen atoms are rapidly exchanged to give the deuterated congeners $K[LNi_2(D)_2]$ (K·2-D) and $Na[LNi_2(D)_2]$ (Na·2-D), respectively, and these reactions are reversed upon addition of H₂ to solutions of the deuterated complexes in THF (Scheme 4). The latter reaction from 2-D⁻ to 2^{-} is most conveniently followed via ²H NMR spectroscopy, which shows the disappearance of the signals for Ni-D around -24 ppm (concomitant for the appearance of Ni-H in the ¹H NMR spectrum) and the rise of a signal at 4.57 ppm originating from D_2 (Figure 5). Surprisingly, no HD formation is observed during the initial stages of the reaction: the ²H NMR spectrum after 75 min still shows solely the presence of D_2 , while signals for HD, identified by a doublet at 4.58 ppm with ${}^{1}J_{\text{HD}} = 42.7$ Hz, evolve only slowly after longer reaction times (see spectrum after 7 h in Figure 5). HD formation during later stages of the reaction presumably occurs via secondary processes that may involve trace amounts of Ni-containing decomposition products. These findings indicate that 2⁻ undergoes a pairwise H_2/D_2 exchange process that synchronously involves both Ni-H (or Ni-D, respectively) moieties, clearly distinct from the common monometallic mechanisms sketched in Scheme 4. This process is observed for both compounds, K-2-D and Na-2-D, showing that it does not depend on the type of, and mode of association with, the alkali metal cation.



Scheme 4. Synchronous pairwise H_2/D_2 exchange reaction between $[LNi_2(H)_2]^-$ and $[LNi_2(D)_2]^-$.



Figure 5. ²H NMR spectrum (77 MHz, 298K) of K-2-D in THF (bottom spectrum) and upon treatment with H₂, yielding K-2 and D₂ (middle spectrum). HD is formed only after long reaction times (top spectrum). Residual solvents are marked (*).

To directly monitor the exchange processes and to confirm the synchronous exchange of both hydrides of a single molecule of 2^{-} , the following NMR experiment was designed: a solution of $K[LNi_2(H)_2]$ (K·2) was treated with a small amount of HD, not sufficient for full conversion to K[LNi₂(H)(D)] (K·2-HD) but adjusted to provide roughly equal peaks intensities for the two isotopologues. The reaction mixture then contained K-2, K·2-HD, H₂, and HD, all of which are detectable in the ¹H NMR spectrum. The hydride resonances of K-2 and K-2-HD differ slightly (-24.16 vs. -24.18 ppm at rt; -24.03 vs. -24.05 at 273 K) because of a secondary isotope effect between the two hydrides. Importantly, the two-dimensional ¹H EXSY spectrum of the mixture (Figure 6) revealed correlations only between $K \cdot 2$ and H_2 as well as between $K \cdot 2$ -HD and HD, clearly evidencing a synchronous (i.e., pairwise) exchange of H₂ and HD, respectively, without any scrambling. All possible exchange processes in this scenario are shown in the upper part of Figure 6.



Figure 6. ¹H-¹H EXSY spectrum (400 MHz, 0.5 s mixing, 273 K) of a mixture of K·2, K·2-HD, H₂ and HD in THF-d₈ (bottom) and the possible exchange processes (top).

To provide mechanistic insight for the H_2/D_2 exchange process and to explain the effect of the alkali metal ions on the stability of (and H_2 release from) the dihydride complex, density functional theory computations were performed.

DFT Calculations. Possible pathways for H_2/D_2 exchange were probed through DFT calculations. For ease of discussion, we will consider 2^- as the reactant, D_2 as the entering molecule and $2-D^-+H_2$ as the products. The alkali metal cation was removed in this initial set of calculations to allow for more flexibility in the exchange paths.

The first question addressed the potential binding of D_2 to the complex. Although η^2 -H₂ coordination to transition metals is well known, no stable minimum for such structure could be found in the present case. Indeed, Ni^{II} dihydrogen complexes are very rare.^{28,29} All attempts for side-on D_2 binding to the Ni^{II} ions in 2⁻ resulted in a weak end-on interaction with one of the metal ($d(H \cdot \cdot \cdot Ni) \approx 2.6$ Å)). We carried out an extensive search of minima, placing the entering molecule close to the Ni ions in different orientations (see SI for details), but other structures were less stable than the one with end-on bound D_2 . All concerted pathways for insertion of D₂ starting from these minima were particularly high in energy. The lowest connected path for insertion was through an early H₂ recombination in the pocket, but such path yields a lower bound for the electronic energy barrier of 136 kJ/mol. This would be much too high in energy, so that we excluded the possibility of a concerted mechanism in which the incoming D₂ forms Ni-D bonds at the same time as the Ni-H bonds are broken.

An alternative to the substitution mechanism is a nonconcerted but stepwise pathway, with H_2 leaving the pocket and subsequent D_2 coordination at the vacant Ni¹ sites. This would also be consistent with the pairwise non-scrambling exchange of H_2/D_2 . To explore this potential mechanism, two sets of constrained optimizations were performed, fixing the distance between the two hydrides in K-2 and 2^- . Figure 7 shows the results at the level of theory used for the optimizations (BP86-D3/SVP), and also energies for the meta-GGA M06L functional with a larger basis, but using the same geometries. For each point in the curve the singlet, the triplet and the broken symmetry state (with the two lone electrons at the Ni¹ centers) were computed. Down to d(H-H) = 0.95 Å the pure singlet state is the most stable. At even shorter H-H distances, the broken symmetry state is found to be lowest, with the triplet still lying higher above in energy. The energetic order of the states was further confirmed with the B3LYP and PBE0 functionals at d(H-H) = 0.8 Å, providing the same qualitative picture. All results reported (including the optimized structures) correspond to the lowest electronic state found at each point.



Figure 7. Potential energy surface plots for the recombination of the Ni-bound H atoms in 2^{-} and K·2. Relaxed scans were computed along the H-H distance at the BP86-D3/def2-SVP level. The dotted vertical line represents the bond distance in the H₂ molecule at the same level of theory (0.767 Å). The reference point is provided by the most stable geometry, in both cases a distance of 2.1 Å.

Both BP86 and M06L agree in that H₂ recombination is much more facile when the K⁺ cation is not present. We start by discussing the latter curves. An estimate to the barrier for removal of H₂ is provided at distances slightly above the optimal H-H bond value for free H₂ (0.767 Å) In the case of **2**⁻, both methods agree in a barrier of about 50 kJ/mol. Carrying out a linear interpolation of the M06-L/TZVP energy curve, the barrier can be approximated by the energy value at the H₂ equilibrium bond distance, which is 62.5 kJ/mol. Differences between the results using the two functionals are foremost in the shape of the curve. In the case of BP86, we found a shallow minimum, which we were able to fully optimize and characterize at d(H-H) = 1.16 Å; this feature is not visible in the M06L curve. The electronic structure of this minimum is similar to the hydride complex, still keeping the Ni-H bonds.

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59 60 Due to the flatness of the potential in this region it was not possible to converge the transition state to the lower neighboring minimum. The impact of the zero-point vibrational energy correction on the energies cited above should be very small since the Ni-H harmonic vibrational frequency is roughly half of the H-H stretching frequency in the hydrogen molecule.

In the case of K-2, the estimated activation barrier for removal of H_2 would lie between 80-105 kJ/mol (102.2 kJ/mol in the case of M06-L/TZVP). Along the relaxed surface scan the K⁺ remained relatively fixed in its position between the two aryl rings, approximately in plane with the leaving H_2 and thereby raising the energy. It is likely that the reported values correspond to an upper estimate. The cation could potentially change its position along the faces of the aryl rings, lowering the energy barrier for H_2 formation.

The electronic structure calculations carried out quite clearly go against any concerted (associative or associate interchange) mechanism for substrate substitution. Instead, in a first step, the two Ni-bound hydrides should recombine to H_2 , then exit the pocket and leave two Ni(I) centers with a vacant bimetallic cleft. The barrier for H_2 formation is quite low in the absence of K⁺ (about 50 kJ/mol), but could also be lowered in the presence of cations due to binding equilibria ins solution, viz. if there is dynamic exchange with the solvent or the cation is readily displaced. The calculations have not included quantum tunneling effects which would further lower the effective barrier.

H₂ loss from the "naked" dinickel dihydride. The experimentally observed instability of 2[K(DB18C6)] in combination with the above DFT results suggested that H₂ release from the dinickel dihydride core 2^{-} should be facile in the absence of a stabilizing alkali metal ion within the dihydride cleft. Keeping a sample of freshly prepared crystalline 2[K(DB18C6)] in a closed flask under N₂ at rt for 6 hours and monitoring the headspace by GC-MS indeed shows the gradual formation of H₂. Reductive elimination of H₂ from 2^- can be expected to yield a {LNi¹₂} species, and therefore a series of challenging SOUID measurements were performed (Figure 8; see SI for details). A sample of crystalline material of 2[K(DB18C6)] that was quickly removed from the mother liquor without drying and kept under residual solvent in a sealed tube showed the expected diamagnetism in the temperature range 2–295 K. When crystals of 2[K(DB18C6)] were dried in glove-box atmosphere for 1 h (mother liquor evaporated without applying vacuum), however, a paramagnetic contribution arises that amounts to 0.32 cm³·mol⁻¹·K (corresponding to 1.6 μ_B) at 295 K. SQUID data for a sample of crystalline 2[K(DB18C6)] that has been thoroughly dried under vacuum for 15 h (resulting in a powder sample) shows a magnetic moment of 0.5 cm³·mol⁻¹·K (corresponding to 2.0 $\mu_{\rm B}$) at 295 K, not too far from the value expected for two S = $\frac{1}{2}$ ions (2.45 $\mu_{\rm B}$ for g = 2.0). The decrease of $\mu_{\rm B}$ upon lowering the temperature (shown as $\chi_{\rm M}T$ vs. T plot in Figure 8) indicates significant antiferromagnetic coupling. These experiments provide experimental evidence for the idea that the dinickel(II) dihydride core 2^{-} , in the absence of any alkali metal ion within the dihydride cleft, is prone to facile loss of H_2 and can be viewed as a masked dinickel(I) species. The presence of K^{+} (or Na⁺) obviously stabilizes the dinickel(II) dihydride complex and prevents H₂ loss, in line with the DFT results.

The proposed scenario of H_2 release from 2^- is reminiscent of the oxidatively induced bimolecular H_2 reductive elimination

reported for some porphyrin ruthenium monohydride complexes, proposed to proceed via an intermolecularly bridging dihydrogen intermediate.³⁰ Using a dimeric system with two cofacial porphyrin subunits it was then possible to detect the bridged dihydrogen complex, for which NMR evidence suggested that the H₂ ligand is bound with the H-H axis perpendicular to the Ru···Ru axis.³¹ Steric constraints of the present pyrazolate-based ligand scaffold clearly enforce a different geometric situation in 2^- .



Figure 8. $\chi_M T$ vs. *T* measurements in the temperature range of 2 – 295 K at 0.5 T for a solid sample of **2**[K(DB18C6)] after different sample preparations: (i) pristine crystals kept under residual mother liquor in a sealed tube (red data points); (ii) after drying in glove-box atmosphere for 1 h (blue data points); and (iii) after prolonged drying under vacuum for 15 hours. The solid red line represents the best fit for two coupled $S = \frac{1}{2}$ spin centers with J = -69.5 cm⁻¹ and g = 1.79 ($\hat{H} = -2J\hat{S}_1\hat{S}_2$ Hamiltonian; see SI for details); the unreasonably low *g* value reflects incomplete conversion of **2**[K(DB18C6)] to the dinickel(I) species.

Kinetics of the H₂/D₂ exchange. ¹H-¹H EXSY spectra of mixtures containing $K \cdot 2$ (or Na $\cdot 2$) and H_2 , recorded in the temperature range from 253 to 278 K (in steps of 5 K), showed exchange between H₂ and the Ni-bound hydrides. While a full EXSYCALC analysis was hampered by partial peak overlap that introduced large errors, it was possible to use two EXSY peaks to obtain pseudo-first order rate constants for the transition $[L(Ni-H)_2]^- \rightarrow H_2$ in the initial build up regime ($k_{ex}\tau_{mix} < 0.15$), which is in the temperature range from 253 to 278 K (spectra recorded in steps of 5 K; Table S1 in the SI). Samples with different concentrations of K-2 yielded essentially the same pseudo-first-order rate constants (Figure 9), in agreement with the reaction being first order in [L(Ni-H)2]-. Arrhenius plotting (Figure 9) gives an apparent activation energy $E_a = (74 \pm 5) \text{ kJ mol}^{-1}$ for K·2, attributed to the rate determining loss of H₂ from the dinickel(II) dihydride core (Eyring analysis gives $\Delta H^{\dagger} = (72 \pm 5) \text{ kJ mol}^{-1}$, see SI; the limited temperature range does not allow to derive a reliable value for ΔS^{\dagger}). Pseudo-first order rate constants for the transition $[L(Ni-H)_2]^- \rightarrow H_2$ in case of Na·2 were found to be significantly different (Figure 9; $E_a = (39 \pm 3)$ kJ mol⁻¹ for Na·2), which reveals a strong dependence on the alkali metal cation in qualitative agreement with the computational results (vide supra). This furthermore indicates that H₂ exchange is likely affected by the solution dissociation equilibria between M·2 and solvated $2^{-} + M^{+}$. More detailed kinetic studies considering those equilibria will thus be required for deriving a comprehensive mechanistic picture and reliable activation parameters. A similar hydride exchange between K-2-D and D₂ was observed in ${}^{2}\text{H}{-}^{2}\text{H}$ EXSY spectra (Figure S12) but not quantitatively analyzed due to the much lower sensitivity of ${}^{2}\text{H}{-}$.



Figure 9. Arrhenius plot for the M[L(Ni-H)₂] \rightarrow H₂ exchange for K·2 (0.1, 0.2, 0.3 and 0.4 M) and Na·2 (0.2 M) with data points determined in 5 K steps between 278 K and 253 K. Rate constants k/s^{-1} were extracted from the integral ratios of exchange and diagonal peaks in 2D ¹H EXSY spectra at the various temperatures.

H₂/**D**₂ **substitution by substrate.** Removal of H₂ from 2⁻ (or D₂ from 2-D⁻) formally leaves two reducing equivalents on the {LNi¹₂} core available for reductive substrate binding. To probe whether the synchronous replacement of H₂ from 2⁻ (or D₂ from 2-D⁻) occurs with substrates other than D₂ (or H₂, respectively), reactions with phenylacetylene have been studied. These experiments also provided further evidence that substrate binding indeed proceeds via formation of H₂ (or D₂) without scrambling. Treatment of a THF solution of 2⁻ or 2-D⁻ (either K·2-D or Na·2-D) with one equivalent of phenylacetylene gives in a clean reaction the product [LNi₂(μ - η ¹: η ¹-CHCPh)]⁻ (3⁻) (Scheme 5). When starting from K·2, the product K·3 could be isolated in crystalline form and analyzed by X-ray diffraction (Figure 10).



Scheme 5. Preparation of K[LNi₂(μ - η ¹: η ¹-CHCPh)].



Figure 10. Molecular structure (30% probability thermal ellipsoids) of one of the two crystallographically independent molecules of $K \cdot 3$; most hydrogen atoms and disorder omitted for clarity.

The molecular structure of K-3 shows the phenylacetylene substrate bound within the bimetallic pocket, having replaced the two hydrides. The two nickel ions are again found in distorted square-planar coordination environment, suggesting they are in the +II oxidation state in accordance with the diamagnetic nature of $K \cdot 3$. In line with this, the length of the central C-C bond (C41-C42) of 1.358(3) Å is indicative of a double bond, consistent with twofold reduction of the phenylacetylene substrate. The bridging unit thus is best described as a dianionic styrene-1,2-diyl group. The potassium cation in K-3 is associated with the π -system of the bridging C=C unit and is further ligated by three THF molecules. The Ni...Ni separation in $K \cdot 3$ is in the common range (3.88 Å), but because of the steric requirements of the substrate phenyl group, the bimetallic scaffold is significantly more distorted and the DIPP substituent on the Ni2 side is bent out of the plane of the pyrazolate-based dinickel core. The resulting C_1 symmetry of the entire complex is reflected in the NMR spectra, which could be fully assigned (see SI for details). Furthermore, temperature-dependent NMR spectra revealed hindered rotation of the phenyl group around the C42-C43 bond. Lineshape analysis yielded activation parameters $\Delta H^{\dagger} = (52 \pm 1) \text{ kJ mol}^{-1}, \Delta S^{\dagger} =$ (-18 ± 4) J mol⁻¹ K⁻¹, and $\Delta G_{298}^{\dagger} = (57 \pm 1)$ kJ mol⁻¹ (see SI for details), which is in the range of the rotational barriers measured for some phenylallyl alkali metal salts (Figures S27-29 and Tables S3 and S4).³²

When K-2-D was treated with phenylacetylene and the reaction monitored by ²H NMR spectroscopy, the formation of D_2 was clearly detected (Figure 11). No evidence could be found for the formation of HD, and no D incorporation into the styrene-1,2-diyl bridge was observed, neither at the vinylic C-H group nor at the phenyl group. This indicates that alkenyl or vinylidene intermediates are not involved, and it is in agreement with intramolecular D_2 formation prior to binding of the incoming phenylacetylene substrate, akin to the H₂ (or D₂) formation from the two adjacent terminal Ni-H (Ni-D) as described above.

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Figure 11. ²H NMR spectrum (77 MHz, 298 K) of K·2 in THF (bottom) and after reaction with phenylacetylene, showing formation of D_2 from the two Ni-D (top). Residual solvent signals are marked (*).

SUMMARY AND CONCLUSIONS

In this contribution we present a new dinucleating ligand scaffold comprising two nacnac compartments spanned by a central pyrazolate-bridge. Dinickel complexes of this ligand scaffold having bulky substituents at the peripheral nacnac-N (DIPP substituents in the present case) create a bimetallic cleft into which the remaining accessible coordination sites are directed; these sites are available for binding exogenous ligands or substrates within the clamp of the two metal ions. This way we have prepared a series of dinickel(II) dihydride complexes in which the two Ni-H units are oriented such that the hydrides are located in rather close proximity in the bimetallic pocket. H₂/D₂ exchange was found to proceed via an unprecedented pairwise H₂/D₂ exchange that synchronously involves both Ni-H units of [LNi^{II}₂(H)₂]⁻, without H/D scrambling. DFT calculations provided a mechanistic picture of this process and revealed that the exchange mechanism should not be concerted, meaning that both Ni-H bonds are broken and H₂ is formed in a late transition state scenario before the incoming D₂ forms new Ni-D bonds. In a first step, H₂ can form within the cleft with a moderate, mostly enthalpic activation barrier of around 62 kJ/mol and will then exit the complex, which formally leaves two reducing equivalents on the {LNi2} core for substrate binding, such as the bimetallic, homolytic splitting of D₂. The $[LNi_{2}^{II}(H)_{2}]^{-}$ complex (2⁻) can thus be viewed as a masked form of a reactive, antiferromagnetically coupled [LNi¹₂]⁻ species. In the present work this concept, demonstrated for the H₂/D₂ exchange reaction, has been further exploited for the reaction of $[LNi^{II}_2(H)_2]^-$ or $[LNi^{II}_2(D)_2]^-$ with phenylacetylene. Treating [LNi^{II}₂(D)₂]⁻ with phenylacetylene leads to D_2 formation and twofold reduction of the substrate, giving a product complex with unusual styrene-1,2-diyl bridging unit in the bimetallic pocket (3^{-}) . Alkali metal ions Na⁺ and K⁺ were found to be closely associated with the dinickel dihydride core in 2^- and also with the olefinic C=C bond in the case of 3^- (shown for K+). While these interactions have only a minor influence on the structural and spectroscopic properties of the $[LNi^{II}_{2}(H)_{2}]^{-}$ core, the alkali metal ions significantly stabilizes the dihydride complex against H₂ release. This points to a potentially important effect of Lewis acids on metal-hydride reactivity, which will be further explored in future work.

Storing two reducing equivalents in adjacent metal hydrides that evolve H_2 upon substrate binding is reminiscent of the proposed N_2 binding step at the FeMo cofactor of nitrogenase. However, recent electro catalytic and DFT studies have shown that the rate-limiting step for H_2 formation in the FeMo protein involves proton transfer from sulfur to a bridging iron hydride, highlighting the important role of the sulfide ligands in FeMoco³³ Appreciating the possibility of different mechanistic trajectories for reductive H_2 release, using metal hydrides is increasingly recognized as a means of avoiding unstable lowvalent metal species or thermodynamically unfavorable oneelectron reduced intermediates during the reductive activation of small molecules. The present bimetallic system based on the new pyrazolate-bridged bis(nacnac) ligand appears particularly well suited for exploiting this concept. We are currently studying the activation and transformation of a range of rather inert substrates using the new dinickel dihydride complex.

EXPERIMENTAL SECTION

Materials and methods. Manipulations involving air- and moisture sensitive compounds were conducted under an atmosphere of dried (phosphorous pentoxide on solid support [Sicapent®, Merck]) dinitrogen or argon using standard Schlenk techniques, or in a glovebox ($O_2 < 0.5$ ppm and H_2O < 0.5 ppm) filled with dinitrogen atmosphere. THF, THF-d₈, *n*-hexane and pentane were dried over sodium in the presence of benzophenone. Hydrogen gas was purchased from Messer and deuterium gas from Linde. Chemicals used were either present in the working group or were purchased from commercial sources, or their synthesis is described below or in the supporting information. NMR samples for the H₂/D₂ exchange reactions were prepared under an inert atmosphere. $M[LNi_2(H)_2]$ (M = Na, K) was dissolved in THF-d₈ and transferred into a J. Young NMR tube. The solution was degassed by means of pump-freeze-thaw procedure with liquid N₂. The process was repeated three times. Because the dihydride complexes are extremely sensitive to traces of moisture (ultimately giving the hydroxido-bridged dinickel(II) complex $[LNi^{II}_{2}(\mu -$ OH)]), gases HD, D₂ and H₂ were rigorously dried by storing them over conc. H₂SO₄ for around 1 d; this method proved superior over transfer through cooling traps (liquid N₂) followed by passage over phosphorus pentoxide (Sicapent).

Instrumentation. ¹H NMR, ²H NMR and ¹³C NMR spectra were recorded on Bruker Avance spectrometers (300 MHz, 400 MHz, 500 MHz for ¹H) at room temperature unless otherwise noted. Chemical shifts are reported in parts per million relative to residual proton and carbon signals of the solvent $(\text{CDCl}_3, \delta_H = 7.26, \delta_C = 77.16 \text{ ppm}; \text{THF-d}_8, \delta_H = 1.73 \text{ and}$ 3.59; $\delta_{\rm C} = 25.31$ and 67.21). ¹H-¹H NOESY/EXSY spectra were recorded at 400 MHz using a mixing time of 0.5 s. Electron ionization (EI) and electrospray ionization (ESI) mass spectra were collected on an Applied Biosystems API 2000 device or on a Bruker HCTultra instrument. Moisture or oxygen sensitive samples were prepared in a glovebox (MBRAUN UNIlab) under an N2 atmosphere and injected into the Bruker HTCultra instrument via a direct Peek[™] tubing connection. Elemental analyses were carried out with an Elementar 4.1 vario EL 3 instrument. IR spectra of solid samples were measured with a Cary 630 FTIR spectrometer equipped with a DialPath and Diamond ATR accessory (Agilent) placed in a glovebox (MBRAUN UNIlab, argon atmosphere). IR bands were labeled according to their relative intensities with vs (very strong), s (strong), m (medium), w (weak) and very weak (vw). The detection of molecular hydrogen was carried out by gas chromatography using a GC-2014 gas chromatrography with ShimAdzu, Shincarbon column (4.0 m × 2.00 mm, oven temperature 100°C, carrier gas Ar, 180 KPa). Temperature-dependent magnetic susceptibilities were measured using a Quantum-Design MPMS XL-5 SQUID magnetometer equipped.

Single-Crystal X-Ray structure determinations. Crystal data and details of the data collections are given in Table S5.

X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-K α radiation, $\lambda = 0.71073$ Å) by use of scans at -140 °C. The structures were solved by SHELXT,³⁴ and refined on F^2 using all reflections with SHELXL-2013/14/16.35 Non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.2/1.5 $U_{eq}(C)$. The nickel bound hydrogen atoms in K·2 and Na-2 were refined freely. In case of 2[K(DB18C6)] a fixed isotropic displacement parameter of 0.08 Å² was applied. Two disordered 'Pr groups in K·2 (occupancy factors = 0.766(14)/ 0.234(14) and 0.731(5)/0.269(5)) have been refined using SIMU, DELU, ISOR, BUMP, SAME and SADI restraints and EADP constraints. Disordered potassium coordinating solvents (thf (only C atoms): occupancy factors = 0.616(9) / 0.384(9); thf/Et₂O: occupancy factors = 0.712(7) / 0.288(7)) and non-coordinating Et₂O (occupancy factors = 0.504(11) / 0.496(11)) in 2[K(DB18C6)] have been refined using SIMU, DELU, ISOR, DFIX, SAME and SADI restraints and EADP constraints. In case of the coordinating solvents thf and Et₂O occupy the same coordination site of the potassium atom. In $K \cdot 3$ one carbon atom of a coordinating thf was found to be disordered about 2 positions (occupancy factors = 0.55(2) / 0.45(2)) and was refined using SADI restraints and EADP constraints. Face-indexed absorption corrections were performed numerically with the program X-RED.³⁶

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DFT calculations. Geometry optimizations and frequency calculations were carried out with the BP86 functional³⁷ and the def2-SVP basis set,³⁸ referred in the text as SVP. Dispersion corrections were included as proposed by Grimme and coworkers, with a Becke-Johnson type damping.³⁹ All results were computed at this level of theroy unless otherwise noted. The nature of all stationary points mentioned in the text was confirmed through vibrational frequency analysis. The refinement of electronic energies for the approximate reaction pathway of hydrogen abstraction was carried out with the M06L functional⁴⁰ and the def2-TZVP orbital basis set, referred in the text as TZVP. The default def2 Coulomb fitting basis were used.⁴¹ All calculations were carried out with the Orca 4.0 program package.⁴²

H₃L. 2-[(2,6-diisopropylphenyl)imido]-pent-2-en-4-one (16.4 g, 63 mmol, 2 equiv.) was dissolved in dry dichloromethane (100 mL) to give a colorless solution. To this solution triethyloxonium tetrafluoroborate (12.7 g, 67 mmo, 2.1 equiv.), dissolved in dry dichloromethane (20 mL) was added slowly and the mixture stirred under inert atmosphere over night at room temperature. Triethylamine (9.3 mL) was added to the yellowish reaction mixture resulting in a color change to red after 20 minutes. This solution was then slowly added to a suspension of bis(3,5-aminomethyl)pyrazole (4.0 g, 32 mmol, 1 equiv) in dry triethylamine. The mixture was stirred for 3 days under inert atmosphere at room temperature. After removal of the solvents under reduced pressure the orange residue was extracted with toluene. The solvent was removed and the crude material purified by Kugelrohr distillation (10⁻⁵ mbar, 110 °C). After recrystallization from ethanol the ligand was obtained as yellow solid material (9.7 g, 16 mmol, 43 %). ¹H NMR (300 MHz, CDCl₃) = 7.11-7.02 (m, 6 H, CH^{Ar}), 6.02 (s, 1 H, CH^{Pz}), 4.73 (s, 2 H, CH), 4.40 (s, 4 H, CH₂), 2.90-2.85 (sept, 4 H, CH^{iPr}), 1.95 (s, 6 H, CH₃), 1.65 (s, 6 H, CH₃), 1.15 (d, 12 H, CH₃^{iPr}), 1.06 (d, 12 H, CH₃^{iPr}). ¹³C NMR (75 MHz, $CDCl_3$ = 166.22 (3.5- C^{pz}), 155.58(CH^{Ar}), 146.28(CH^{Ar}),

138.10(*C*H^{Ar}), 122.80 (*C*H^{Ar}), 101.20 (*C*H^{Pz}), 94.52 (*C*H), 40.06 (*C*H₂), 28.08 (*C*H^{iPr}), 23.76 (*C*H₃^{iPr}), 22.77 (*C*H₃^{iPr}), 21.62 (*C*H₃), 19.17 (*C*H₃). MS (ESI(+), MeCN) m/z: $[M+H]^+$ 609.36. IR: 3190(br)(NH), 3130 (NH), 3104 (NH), 3060 (w), 3020 (w), 2960(m), 2923 (w), 2867 (w), 1621 (vs), 1551 (vs), 1501 (w), 1454 (m), 1432 (m), 1377 (m), 1361 (m), 1292 (m), 1284 (m), 1268 (m), 1226 (m), 1179 (m), 1159 (m), 1090 (m), 1049 (m), 1020 (m), 1005 (w), 934 (w), 919 (w), 879 (w), 819 (w), 804 (w), 784 (s), 758 (s), 728 (s), 695 (m), 664 (w), 626 (w), 607 (w), 582 (w), 519 (w), 497 (w). Elemental analysis (%) calc. for C₃₉H₅₆N₆·(C₄H₈O) (681.00 g/mol) = C 72.84 H 9.47 N 12.34; Found C 72.92 H 9.20 N 12.48.

[LNi₂(*µ*-Br)] (1). H₃L (505 mg, 0.83 mmol, 1.0 equiv) was dissolved in dry THF (4 mL) and the clear yellow solution cooled to -78 °C. n-BuLi (2.6 M in toluene) was added slowly via a syringe to give a clear orange solution. Under stirring the reaction mixture was warmed to room temperature over 15 minutes to yield a dark red, clear solution. NiBr₂(DME) (512 mg, 1.66 mmol, 2.0 equiv) was then slowly added. The resulting dark-brown mixture was stirred overnight at room temperature. The suspension was separated by a centrifugal device and the dark brown THF solution discarded. The solid material was washed with acetone for several times until the solvent remained colorless. After removing residual solvent under reduced pressure, a beige colored fine powder was obtained (506 mg, 0.63 mmol, 76 %). Slow evaporation of a concentrated solution in CH₂Cl₂ or CHCl₃ yielded small green-brown, cube-shaped crystals of 1. ¹H NMR (300 MHz, $CDCl_3$) = 6.91-6.80 (m, 2 H, CH^{Ar}), 6.73-6.75 (d, J_{H-H} = 6 Hz, 4 H, CH^{Ar}),5.46 (s, 1 H, CH^{Pz}), 4.68 (s, 2 H, CH), 4.07 (s, 4 H, CH₂), 3.30-3.20 (sept, 4 H, CH^{iPr}), 1.95 (s, 6 H, CH₃), 1.39 (d, $J_{\text{H-H}} = 6$ Hz, 12 H, CH_3^{iPr}), 1.26 (s, 6 H, CH_3), 0.95 (d, $J_{\text{H-H}} = 6$ Hz, 12 H, CH_3^{iPr}). ¹H NMR (300 MHz, THF-d₈): = 6.79 - 6.95 (m, 6H, CH^{Ar}), 5.53 (s, 1 H, CH^{Pz}), 4.77(s, 2 H, CH), 4.15(s, 4 H, CH_2), 3.33 - 3.40 (sept, 4 H, CH^{Pr}), 2.01 (s, 6 H, CH_3), 1.47 (d, $J_{H-H} = 6$ Hz, 12 H, CH_3^{Pr}), 1.30 (s, 6 H, CH_3), 1.02 (d, J_{H-H} = 6 Hz, 12 H, CH_3^{iPr}). ¹³C NMR (75 MHz, CDCl₃) = 159.74 $(C^{q}-Me)$, 153.24 $(C^{q}-Me)$, 147.66 (C^{Pz}) , 141.50 (C^{Ar}) 125.43 (CH^{Ar}), 123.30 (CH^{Ar}), 97.24 (CH), 91.51 (CH^{Pz}), 54.44 (CH₂) 28.13 (CH₃^{iPr}), 24.84 (CH₃^{iPr}), 24.12 (CH₃^{iPr}), 23.37 (CH₃), 21.53 (CH₃). HRMS (ESI(+), MeOH/DCM) m/z: calc $[M+H]^+$ 803.2273; exp $[M+H]^+$ 803.2258. IR (ATR) ν / cm⁻¹ = 3058 (w), 2959 (m), 2923 (m), 2862 (m), 1555 (m), 1532 (vs), 1462 (vs), 1435 (s), 1399 (s), 1381 (s), 1369 (vs), 1313 (s), 1279 (s), 1252 (s), 1236 (m), 1186 (m), 1175 (s), 1093 (s), 1052 (s), 1032 (m), 1012 (m), 957 (m), 935 (m), 795 (vs), 759 (vs), 745 (vs), 542 (m). Elemental analysis (%) calc. for $C_{39}H_{53}N_6Ni_2Br \cdot (CH_2Cl_2)_{1.5}$ (926.15 g/mol) = C 52.48 H 6.10 N 9.07; Found C 52.77 H 6.45 N 9.33.

K[LNi₂(H)₂] (K·2). [LNi₂(μ -Br)] (300 mg, 0.37 mmol, 1.0 equiv) was suspended in dry THF (4 mL). After slow addition of a 1 M solution of KHBEt₃ in THF (0.93 ml, 0.93 mmol, 2.5 equiv) to the beige suspension, the mixture was stirred at room temperature under inert conditions for 30 minutes. The formed dark brownish suspension was filtered over a filter medium to yield a clear dark yellow-brownish solutuion. A slow diffusion of pentane vapors into the filtrate yielded the product as large, cube-, rod- or needle shaped crystals (191 mg, 0.25 mmol, 67 %) that were washed with pentane. ¹H NMR (300 MHz, THF-d₈) = 6.77-6.88 (m, 6 H, CH^{Ar}), 5.56 (s, 1 H, CH^{Pz}), 4.56 (s, 2 H, CH), 4.23 (s, 4 H, CH₂), 3.48-3.43 (sept, 4 H, C CH^{IPr}), 1.83 (s, 6 H, CH₃), 1.22 (s, 6 H, CH₃), 1.12 (d, J_{H-H} = 6 Hz, 12 H, CH₃^{IPr}), -24.17 (s, 2 H,

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59 60 Ni*H*). ¹³C NMR (100 MHz, THF-d₈) = 158.64 (*C*^q-Me), 157.57 (*C*^q-Me), 157.13 (*C*^q-Me), 156.60 (*C*^q-Me), 140.34 (*C*^{Pz}), 123.91 (*C*^{Ar}), 123.18 (*C*^{Ar}), 97.03 (*C*H), 92.25 (*C*H^{Pz}), 53.34 (*C*H₂), 28.33 (*C*H₃^{iPr}), 24.46 (*C*H₃^{iPr}), 23.89 (*C*H₃^{iPr}), 22.66 (*C*H₃). MS (ESI(+), THF/MeCN) m/z: $[M+H]^+$ 764.41. IR (ATR) ν / cm⁻¹ = 3054 (w), 2955 (m), 2858 (m), 1961 (Ni-H) (m), 1562 (s), 1518 (vs), 1461 (s), 1431 (vs), 1398 (vs), 1355 (m), 1315 (s), 1272 (s), 1254 (m), 1230 (m), 1196 (m), 1159 (m), 1097 (m), 1057 (w), 1028 (m), 935 (w), 861 (m), 804 (m), 773 (m), 731 (m), 720 (m), 644 (m), 546 (m), 516 (m), 458 (m), 422 (m). Elemental Analysis calculated for C₃₉H₅₅KN₆Ni₂ (%): C 61.28, H 7.25, N 10.99. Found: C 60.73, H 6.95, N 10.84.

K[LNi₂(**D**)₂] (**K**·2-**D**). In a Young tube, a solution of K[LNi₂(H)₂] in THF (0.5 mL) was freeze-thaw degassed under vacuum three times. Then dry D_2 (*ca.* 1 atm) was introduced to the head space of the flask at room temperature.

K[LNi₂(**H**)(**D**)] (**K**·2-**HD**). In a Young tube, a solution of K[LNi₂(H)₂] in THF (0.5 mL) was freeze-thaw degassed under vacuum three times. Then dry HD (*ca.* 1 atm) was introduced to the head space of the flask at room temperature.

Na[LNi₂(H)₂] (Na·2). A solution of NaHBEt₃ in THF (1.0 M) (0.75 mL, 0.75 mmol, 3 equiv) was added dropwise to a stirred brown solution of $[LNi_2(\mu-Br)]$ (200 mg, 0.25 mmol, 1 equiv) in THF (2 mL) at room temperature. After stirring the resulting red-brown solution for 2 hours and filter, all volatiles were removed in vacuo. The red-brown residue was washed twice with hexane (40 mL). After concentration in vacuo the product was obtained as a red powder (130 mg, 0.17 mmol, 68 %). Recrystallization from pentane diffusion into THF at room temperature yielded orange block crystals of Na[LNi₂(H)₂]. ¹H NMR (400 MHz, THF- d_8) = 6.75-6.86 (m, 6 H, CH^{Ar}), 5.61 (s, 1 H, CH^{Pz}), 4.58 (s, 2 H, CHCCH₃), 4.27 (s, 4 H, CH₂Pz), 3.41 - 3.49 (m, 4 H, (CH₃)₂CHPh), 1.86 (s, 6 H, CH₃CCH), 1.23 (s, 6 H, CH₃CCH), 1.04 (dd, 24 H, J_{H-H} = 6 Hz, (CH₃)₂CHPh), -23.54 (s, 2 H. Ni-H). ¹³C NMR (100 MHz, THF-d₈) = 157.91 $(C^{q}-Me)$, 156.99 $(C^{q}-Me)$, 155.16 (CH^{Ar}) , 139.26 (CH^{Ar}) , 123.15(CH^{Ar}), 122.21 (CH^{Ar}), 95.95 (CH^{Pz}), 91.91 (CH_{2}), 51.35 (CH₂), 27.25 (CH₃^{iPr}), 25.39 (CH₃^{iPr}), 23.51 (CH₃^{iPr}), 22.94 (CH₃^{iPr}), 21.53 (CH₃), 19.61 (CH₃). IR (ATR) ν / cm⁻¹ = 3052 (w), 2953 (m), 2962 (m), 1846 (Ni-H) (m), 1554 (m), 1521 (s), 1511 (s), 1459 (vs), 1373 (vs), 1396 (s), 1313 (m), 1271 (m), 1251 (m), 1231 (m), 1189 (m), 1100 (m), 1049 (m), 933 (m), 891 (m), 796 (m), 756 (m), 725 (m), 716 (m), 644 (m), 575 (m), 544 (w). Elemental analysis (%) calc. for $C_{39}H_{55}N_6NiNa (C_4H_8O)_2 (892.50 \text{ g/mol}) = C 63.34 \text{ H } 8.04 \text{ N}$ 9.44; Found C 63.47 H 8.37 N 9.17.

Na[LNi₂(**D**)₂] (Na·2-D). In a Young tube, a solution of Na[LNi₂(H)₂] in THF (0.5 mL) was freeze-thaw degassed under vacuum three times. Then dry D_2 (*ca.* 1 atm) was then introduced to the head space of the flask at room temperature.

[K(Dibenzo(18-crown-6))][LNi₂(H)₂)] (2**[K(DB18C6)]**). Dibenzo(18-crown-6) (7.2 mg, 0.02 mmol, 1 equiv) was added into a solution of KLNi₂(H)₂ (K·2) (15.2 mg, 0.02 mmol, 1 equiv) in THF (2 mL) at room temperature. After stirring the resulting red solution for 2 hours, all volatiles were removed in vacuo. The red-brown residue was washed twice with hexanes (10 mL). The crude powder was recrystallized from a solvent mixture of hexanes and diethyl ether layered onto the THF solution at -30° C, yielding orange diamond crystals of the product 2**[K(DB18C6)]** (Yield: 90%). IR (ATR) $\nu/$ cm⁻¹ = 3052 (w), 2982 (m), 2955(m), 2924 (m), 2863 (m), 1913 (Ni-H) (m), 1595 (m), 1503 (vs), 1452 (s), 1436 (s), 1426 (s), 1396 (s), 1366 (s), 1356 (m), 1320 (s), 1298 (w), 1270 (w), 1246 (vs), 1211 (vs), 1191 (w), 1118 (vs), 1094 (m), 1055 (s), 1020 (w), 943 (s), 902 (m), 848 (w), 796 (m), 778 (m), 756 (s), 741 (vs), 726 (vs), 715 (vs), 646 (w), 629 (w), 600 (m), 560 (w), 522 (w).

(2[K(DB18C6)]-D). In a Young tube, a solution of $[LNi_2(H)_2)][K(Dibenzo(18-crown-6))]$ (2[K(DB18C6)]) in THF (0.5 mL) was freeze-thaw degassed under vacuum three times. Then dry D_2 (ca. 1 atm) was introduced into the head space of the flask at rt.

K[LNi₂(μ - η^{1} : η^{1} -CHCPh)] (K·3). K[LNi₂(H)₂] (70 mg, 92 µmol, 1.0 equiv) was dissolved in dry THF (3 mL) to give a clear, dark yellow solution. To this solution phenyl acetylene (12 µL, 110 µmol, 1.2 equiv) was added, resulting in a dark green, clear solution which was cooled (-30 °C) and layered with hexanes. Slow diffusion of the solvents at -30 °C yielded the product as dark green, rod shaped crystals suitable for Xray diffraction (Yield: 54%). ¹H NMR (500 MHz, THF-d₈, -35 °C) = 10.14 (d, ${}^{3}J_{\text{HH}}$ = 7.8 Hz, 1 H, CH^{Ph}), 7.01-6.99 (dd, ${}^{3}J_{\text{HH}}$ = 7.7 Hz, ${}^{4}J_{\rm HH}$ = 1.2 Hz, 2 H, CH^{Ph}), 6.97-6.95 (dd, ${}^{3}J_{\rm HH}$ = 7.7 Hz, ${}^{4}J_{\text{HH}} = 1.2$ Hz, 2 H, CH^{Ph}), 6.89-6.85 (dt, ${}^{3}J_{\text{HH}} = 7.7$ Hz, 2 H CH^{Ph}), 6.76-6.72 (dd, ${}^{3}J_{HH} = 7.7$ Hz, 2 H, CH^{Ar}), 6.62 (m, 2 H CH^Ar), 6.24 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 1 H, CH^{Ph}), 5.63 (s, 1 H, CH^{Pz}), 4.87 (s, 1 H, CH^{vinyl}), 4.62 (s, 1 H, CH), 4.63 (s, 1 H, CH), 4.33-3.91 (d, ${}^{2}J_{\text{HH}} = 17.5$ Hz, 2 H, CH₂), 4.264,07 (d, 2 H, CH₂), 3.76-3.65 (sept, ${}^{3}J_{HH} = 7.1$ Hz, 1 H, CH^{iPr}), 3.58-3.48 (sept, ${}^{3}J_{HH} = 7.1$ Hz, 1 H, CH^{iPr}), 3.29-3.19 (sept, ${}^{3}J_{HH} =$ 7.0 Hz, 1 H, CH^{iPr}), 1.92 (s, 3 H, CH₃), 1.84 (s, 3 H, CH₃), 1.79 (d, ${}^{3}J_{\text{HH}} = 6.5$ Hz, 3 H, CH_{3}^{iPr}), 1.39-1.29 (sept, ${}^{3}J_{\text{HH}} = 7.1$ Hz, 1 H, CH^{iPr}), 1.18 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 1.59-1.29 (sept. ${}^{iPr}J_{HH} = 7.1$ Hz, 1 H, CH^{iPr}), 1.18 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 1.02 (d, ${}^{3}J_{HH} = 6.5$ Hz, 3 H, CH_{3}^{iPr}), 0.93 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 0.91 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 0.79 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 0.79 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 0.79 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3 H, CH_{3}^{iPr}), 0.23 (d, ${}^{3}J_{HH} = 6.5$ Hz, 3 H, CH_{3}^{iPr}). ${}^{13}C{}^{1}H$ NMR (126 MHz, THF-d₈, 25.00) 2.00 + 2 -35 °C): δ / ppm = 160.95 (C^q-Me), 159.19 (C^q-Me), 158.46 (CH^{vinyl}) , 158.36 C^{q} -Me), 157.40 $(C^{q}$ -Me), 155.15 (C^{Pz}) , 155.14 (C^{Pz}), 152.19 (C^{Ar}), 150.56 (C^{Ar}), 150.17 (C^{Ar}), 144.43 $(C^{Ar}), 143.34, (C^{Ar}), 143.14, (C^{Ar}), 142.47, (C^{vinyl}), 140.14, (C^{Vinyl}), 140$ $(C^{\ell}$ 128.34 (CH^{Ph}), 127.18 (CH^{Ph}), 126.15 (CH^{Ph}), 125.89 (CH^{Ar}), 124.92 (CH^{Ar}), 124.38 (CH^{Ar}), 124.10 (CH^{Ar}), 123.81 (CH^{Ar}), 123.35 (CH^{Ph}), 121.63 (CH^{Ph}, CH^{Ar}), 98.55 (CH), 96.43 (CH), 92.73 (CH^{Pz}), 52.76 (CH₂), 51.58 (CH₂), 29.71 (CH₃^{iPr}), 28.50 (CH^{iPr}), 28.14 (CH^{iPr}), 27.96 (\(CH^{iPr}), 26.76 (CH^{iPr}), 26.59 (CH₃^{iPr}), 25.93 (CH₃), 24.78 (CH₃^{iPr}), 24.76 (CH₃^{iPr}), 24.33 (CH_3^{iPr}) , 24.27 (CH_3^{iPr}) , 24.14 (CH_3^{iPr}) , 23.72 (CH_3) , 23.03 (CH₃^{iPr}), 21.43 (CH₃), 20.55 (CH₃). MS (ESI(+), THF/MeCN) m/z: $[M+H]^+$ 823.42. IR (ATR) ν / cm⁻¹ = 3278 (vw), 3119 (vw), 3051 (w), 2955 (m), 2923 (m), 2863 (m), 1553 (m), 1521 (s), 1503 (m), 1430 (s), 1397 (vs), 1314 (m), 1306 (m), 1271 (m), 1250 (m), 1229 (w), 1190 (w), 1175 (m), 1091 (m), 1054 (s), 1028 (m), 1017 (m), 892 (m), 799 (m), 752 (s), 726 (m), 704 (s), 645 (w), 624 (w), 595 (w), 554 (w), 545 (w), 523 (w), 447 (w), 417 (m).

ASSOCIATED CONTENT

Supporting Information.

Detailed synthetic procedures, crystallographic information, NMR, and IR spectra; DFT calculations; The Supporting Information is available free of charge on the ACS Publications website at xxx.

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Notes

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The authors declare no competing financial interest.

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