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Competing H₂ versus Intramolecular C-H Activation at a Dinuclear Nickel Complex via Metal-Metal Cooperative Oxidative Addition

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KEYWORDS Nickel, Hydride Complexes, Bimetallic Complexes, Metal-Metal Cooperativity, C-H Activation.

ABSTRACT: Nickel(I) metalloradicals bear great potential for the reductive activation of challenging substrates but are often too unstable to be isolated. Similar chemistry may be enabled by nickel(II) hydrides that store the reducing equivalents in hydride bonds and reductively eliminate H₂ upon substrate binding. Here we present a pyrazolate-based bis(β -diketiminato) ligand [L^{Ph}]³⁻ with bulky *m*-terphenyl substituents that can host two Ni-H units in close proximity. Complexes [L^{Ph}(Ni^{II}-H)₂]⁻ (**3**) are prone to intramolecular reductive H₂ elimination, and an equilibrium between **3** and orthometallated dinickel(II) monohydride complexes **2** is evidenced. **2** is shown to form via intramolecular metal-metal cooperative phenyl group C(sp²)-H oxidative addition to the dinickel(I) intermediate [L^{Ph}Ni^I₂]⁻ (**4**); while Ni^I species have been implicated in catalytic C-H functionalization, discrete activation of C-H bonds at Ni^I complexes has rarely been described. The reversible H₂ and C-H reductive elimination/oxidative addition equilibrium smoothly unmasks the powerful 2-electron reductant **4** from either **2** or **3**, which is demonstrated by reaction with benzaldehyde. A dramatic cation effect is observed for the rate of interconversion of **2** and **3**, and also for subsequent thermally driven formation of a twice orthometallated dinickel(II) complex **6**. X-ray crystallographic and NMR titration studies indicate distinct interaction of the Lewis acidic cation with **2** and **3**. The present system allows for unmasking of a highly reactive [L^{Ph}Ni^I₂]⁻ intermediate **4** either via elimination of H₂ from dihydride **3** or via reductive C-H elimination from monohydride **2**. The latter does not release any H₂ byproduct and adds a distinct platform for metal-metal cooperative two-electron substrate reductions while circumventing the isolation of any unstable superreduced form of the bimetallic scaffold.

INTRODUCTION

Molecular nickel hydride complexes are currently receiving much attention because of their ability to transfer hydrides, hydrogen atoms or protons during reactions with substrate molecules.¹ While much of the recent interest is fueled by the relevance of a Ni-H unit in the catalytic cycle of the natural metalloenzyme [NiFe] hydrogenase and in bioinspired complexes for H₂ generation,^{2–8} nickel hydrides are considered as key intermediates also in a variety of other Ni-catalyzed processes.¹ Treatment of nickel(II) halide complexes with borohydride reagents or oxidative addition of H₂ or C-H bonds to nickel(0) precursors are among the various methods to generate the Ni-H moieties.¹

Many nickel hydrides show a propensity to lose their metal-bound hydrogen, mostly in a reductive fashion giving H₂. While this is a major cause of instability of nickel hydride complexes,¹ the resulting low-valent nickel species may give rise to interesting subsequent reactivity. Nickel(I) metalloradicals are quite strong one-electron reductants whose isolation often is challenging, and that bear great potential for, e.g., the activation of small molecules.^{9,10} This is increasingly being exploited for the reductive transformation of unsaturated substrates with double or triple bonds,¹¹ or for cross-coupling chemistry.^{12,13} Though monovalent nickel has also been implicated in catalytic C-H bond functionalization, however, activation of C-H bonds at Ni^I has rarely been evidenced.¹⁴⁻¹⁶ Similar to the oxidative addition of H₂ to give two Ni-H units, many of the above reactions involve two Ni^I entities to enable two-electron chemistry. As an example, Scheme 1 shows the synthesis of nickel(II) hydride complex I from the nickel(I) precursor II and H_2 ,¹⁷ and the thermal loss of H_2 from 55 I to give dinickel complex III which has been described as a 56 toluene-masked Ni^I species.^{18,19} 57

Scheme 1. Selected Transformations of β-Diketiminato-Ligated Ni^I (II, III) and Ni^{II} Hydride (I) Complexes.¹⁷⁻¹⁹



N-aryl substituted β -diketiminato (nacnac) ligands such as the ones shown in Scheme 1 have been extensively used for supporting reactive metal complexes in a variety of oxidation states.^{20–23} Finetuning of the ligand scaffold via modification of the peripheral bulky aryl groups or the backbone substituents allows for stabilizing reactive intermediates,²² which has been favorably exploited in Ni¹ chemistry.^{21,24,25} Dinucleating scaffolds composed of two β -diketiminato have been developed for enabling metalmetal cooperativity, such as a pyridine-based ligand that afforded a hydride-bridged mixed-valent Ni¹(μ -H)Ni^{II} species **IV** (Scheme

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2).²⁶ Recently we introduced a trianionic dinucleating ligand $[L^{iPr}]^{3-}$ that has two β -diketiminato compartments appended to a central pyrazolate bridge.²⁷ In its dinickel(II) dihydride complex V (Scheme 2) the two terminal hydrides are directed into the bimetallic cleft, and experimental as well as computational studies indicated low barriers for intramolecular reductive H₂ elimination that depend on the cation present, viz. Na⁺, K⁺ or [K(DB18C6]⁺ (DB18C6 = dibenzo[18]crown-6). Hence V can be viewed as a masked form of the dinickel(I) species VI, and indeed V was found to undergo pairwise H_2/D_2 exchange and to reductively activate a variety of small molecule substrates within the bimetallic pocket concomitant with H₂ release (Scheme 2; XY is, e.g., HCCPh, O₂, NO or PhNO).²⁷⁻³⁰ Storing reducing equivalents in two adjacent metal hydrides and unmasking the highly reactive intermediate via H₂ elimination upon substrate binding is an attractive option for circumventing the direct formation and isolation of potentially unstable intermediates with reduced metal ions (such as a dinickel(I) species). In fact, such scenario is reminiscent of the operating mode of the metalloenzyme nitrogenase whose FeMo cofactor first accommodates protons and electrons to form metal hydrides and then couples N₂ reduction to the elimination of H₂.

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Scheme 2. Bimetallic ligand scaffolds containing *N*-aryl substituted β -diketiminato sidearms and their nickel hydrido complexes^{26,27}



In the present contribution we now report a modified pyrazolatebased compartmental ligand $[L^{Ph}]^{3-}$ in which the peripheral 2,6diisopropyl substituents of $[L^{iPr}]^{3-}$ are replaced by bulky *m*terphenyl groups, and we evidence that this new ligand system can mask its reactive dinickel(I) species either via H₂ addition to give a dinickel(II) dihydride or via an unusual reversible intramolecular C-H oxidative addition across the bimetallic core. Dramatic counteraction effects are also demonstrated. This offers new prospects for the metal-metal cooperative two-electron activation of challenging substrates within a bimetallic cleft, complementing bimetallic nickel chemistry that exploits metal-metal bonds and/or redox active ligands for storing multiple redox equivalents.^{31–33}

RESULTS AND DISCUSSION

Dinickel Potassium Monohydride and Dihydride Complexes. Drawing on the synthesis of the pyrazole-based dinucleating ligand H_3L^{iPr} used in V (Scheme 2) a multistep route towards the new proligand H_3L^{Ph} was developed, using 2,6-diphenylaniline³⁴ instead of 2,6-di-isopropylaniline; details of the synthetic protocols and characterization data for H_3L^{Ph} are provided in the Supporting Information. Threefold deprotonation of H_3L with *n*-butyllithium and subsequent addition of (dme)NiBr₂ (dme = dimethoxyethane) yields the dinuclear complex $L^{Ph}Ni_2Br$ (1) after several washings with acetone. 1 was obtained in high purity and 56% yield (Scheme 3).

Scheme 3. Preparation of precursor complex 1 and its transformation to the dinickel monohydride complex 2-K and dihydride complex 3-K.



Suitable crystals for X-ray diffraction analysis were obtained by slow evaporation of a saturated dichloromethane solution of 1. The molecular structure is shown in Figure 1 (top), and selected metric parameters are listed in Table 1; further bond lengths and angles can be found in the Supporting Information. 1 features the expected bimetallic core that has the two nickel(II) ions hosted in the ligand's tridentate $\{N_3\}$ compartments and bridged by the pyrazolate unit, with a Ni…Ni separation of 3.781(5) Å. The exogenous bromido ligand is found within the bimetallic cleft, which gives rise to a distorted square-planar coordination environment of the two metal ions. The overall structure is very similar to that of the corresponding complex L^{iPr}Ni₂Br,²⁷ though the shielding of the dinickel core and of the central bromide is even more pronounced than in previously reported L^{iPr}Ni₂Br (Figure 1, bottom). NMR spectroscopy confirms that 1 is a diamagnetic compound in accordance with low-spin Ni^{II} ions, and that it has apparent C_{2y} symmetry in solution.



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Figure 1. Top: Molecular structure (30% probability thermal ellipsoids) of **1**. Solvent molecules and hydrogen atoms are omitted for clarity. Bottom: Space filling models of the new L^{Ph}Ni₂Br (1; left) and previously reported L^{iPr}Ni₂Br (right).²⁷

The dinickel dihydride complex V was obtained via the reaction of L^{iPr}Ni₂Br with KHBEt₃ or NaHBEt₃.²⁷ Applying the same protocol to 1, viz. adding a THF solution of 2.5 equivalents of KHBEt₃ to a suspension of 1 in THF, resulted in a similar dark red colored solution within 40 mins. However, ¹H NMR spectroscopy after workup indicated the formation of a product of lower symmetry. Red tabular crystals of the product 2-K were obtained by vapor diffusion of pentane into the THF solution at room temperature. The molecular structure determined by X-ray diffraction analysis is shown in Figure 2 and reveals that orthometallation at one of the winglet aryl group has occurred, giving a monohydride complex with a Ni-Caryl bond at the adjacent second subunit. The Ni-H subunit exhibits the same square planar environment previously seen in V, which is typical for low-spin nickel(II). In contrast, at the orthometallated site the metal ion environment is drastically distorted from square planar because of the geometric constraints imposed by the chelate arrangement. Here, the two diketiminato Ndonors are in plane with the pyrazole-N and the Ni center, while the Ni-bound phenyl-C is bent out of that plane by $21.4(9)^{\circ}$. As a consequence of this distortion, the Npz-Ni-C angle is widened to 98.58(16)° and the Ni…Ni distance is elongated to 4.266(7) Å. The potassium cation is found above the pyrazole ring close to the pyrazole-N atoms35 and is additionally involved in an intermolecular cation- π interaction with a phenyl moiety of a nearby molecule $(d(K^+\cdots C) = 2.78-3.28 \text{ Å})$, which results in a chain-like 1D arrangement in the crystal (Figure 2, bottom). Selected bond lengths and angles for 2-K are included in Table 1.





Figure 2. Top: Molecular structure (30% probability thermal ellipsoids) of the anion of 2-K. Bottom: 1D arrangement in the crystal lattice showing interactions with the K⁺ cation. Solvent molecules and hydrogen atoms are omitted for clarity, except for the Ni-H.

¹H- and ¹³C-NMR spectra of **2-K** in THF-d₈ reflect the C_1 symmetry of the complex (Figures S16 and S17), confirming that its molecular structure is retained in solution. Specifically, the four diastereotopic methylene protons (4.41, 4.15, 4.09 and 3.97 ppm) show a distinct pattern in the ¹H-NMR spectrum typical of two AB-spin systems. A second indicator for the orthometallation of one phenyl group is the two high-field shifted triplet signals at 6.29 and 6.38 ppm for the protons in *meta*- and *para*-position with respect to the Ni-bound C atom. The Ni-H shows a sharp discrete signal at -26.12 ppm, consistent with typical chemical shifts for Ni-hydride species reported in the literature;¹ the K⁺ salt of dihydride complex V showed a singlet at -24.16 ppm in THF-d₈.

To explore a possible reversibility of the C-H activation, a degassed THF-d₈ solution of 2-K was treated with an atmosphere of dihydrogen (~1 atm.). In the ¹H-NMR spectrum the hydride signal at -26.12 ppm vanishes while a new downfield signal at -23.80 ppm arises, with doubled intensity. Furthermore, the diastereotopic proton signals for the two CH₂ groups of 2-K in the range 4.41 -3.97 ppm converge to a singlet at 4.04 ppm for the product complex **3-K**, and the two triplets at 6.29 and 6.38 ppm shift downfield into in the region typical for aryl signals. The absolute number of signals decreases, indicative of C_{2v} symmetry of the product **3-K**. The combined NMR data imply formation of the dihydride species 3-K upon reaction of 2-K with dihydrogen (Scheme 3). Further characterization of 3-K was hampered by its instability, because it loses H₂ and transforms back to 2-K when the H₂ atmosphere is removed. However, when 2-K was treated with [2,2,2]cryptand before exposure to H₂ and crystallization was performed under an H₂ atmosphere, single crystals of **3-K(crypt)** grew from the THF solution at room temperature and could be analyzed by X-ray diffraction. The molecular structure of the anion is depicted in Figure 3 and confirms formation of the dihydride complex [L^{Ph}(Ni- H_{2}^{-} ; selected bond lengths and angles are included in Table 1. Each subunit of **3-K(crypt)** is similar to the Ni-H part of **2-K**, and the overall structure is similar to that of dihydride complex V. Both metal ions are found in close to square planar donor environment with angles close to the expected 180° (\angle (N_{trans}-Ni-N_{pz}) = 177.67(7) and 178.71(7)°). The Ni…Ni distance is 4.0478(8) Å, i.e., significantly shorter than in 2-K and also slightly shorter than in the $[K(DB18C6)]^+$ or K^+ or Na^+ salts of V, which were found in the range 4.0636(7) - 4.1636(7) Å.²⁷ This suggests that release of H₂ from 3-K(crypt) (or 3-K) via intramolecular reductive elimination akin to the scenario for V shown in Scheme 2 should be facile.



Figure 3. Molecular structure (30% probability thermal ellipsoids) of the anion of **3-K(crypt)**; solvent molecules, the [K([2,2,2]cryptand)]⁺ cation and hydrogen atoms except for the Ni-H are omitted for clarity.

The variable temperature (VT) ¹H-NMR spectrum of **3-K(crypt)** in THF-d₈ under H_2 atmosphere is shown in Figure 4. At low H_2 pressures (1 atm.), both 3-K(crypt) and 2-K(crypt) are present, reflected by the hydride signals at -23.66 ppm and -26.28 ppm at 243 K. The ratio shifts towards 2-K(crypt) with increasing temperature, in accordance with entropically favored loss of H₂. At room temperature, the signals for the pyrazole-H⁴ of **3-K(crypt)** (5.30 ppm), free dihydrogen (4.56 ppm) and Ni-bound hydride (-23.66 ppm) are broadened beyond detection. Such behavior has also been observed for V, due to dynamic exchange of free dihydrogen with the dihydride species via the dinickel(I) intermediate VI (Scheme 2). Dynamic H₂/Ni-H exchange is also consistent with ESXY NMR measurements for 3-K(crypt) at 243 K that show a clear correlation between the signals for free dihydrogen and the Ni-bound hydrides of 3-K(crypt) (Figure 4, right). In contrast, no EXSY correlation is observed between the hydride signals of 2-K(crypt) and 3-K(crypt).



Figure 4. Left: VT ¹H-NMR spectra of **3-K(crypt)** in THF-d₈ under H₂ atmosphere from 303 – 203 K; only the N-H region is shown. Right: part the EXSY spectrum of **3-K(crypt)** in THF-d₈ showing exchange between the Ni-H of **3-K(crypt)** and free H₂.

Two mechanisms are conceivable for the interconversion of orthometallated **2-K** and dihydride **3-K**. In scenario **A** implying metal-metal-cooperativity (Scheme 4), reductive C-H elimination from **2-K** or reductive H₂ elimination from **3-K** generates a dinickel(I) intermediate **4-K** that can undergo either bimetallic C-H or H₂ oxidative addition. Scenario **B** proceeds via σ -metathesis

type direct hydrogenation of the Ni-C bond and involves only one subunit of the dinickel core (alternative monometallic oxidative addition/reductive elimination pathways via a formal Ni^{IV} intermediate seem unlikely). The ESXY NMR results that show a correlation between the signals for free H₂ and the Ni-H of **3-K**, but not between the Ni-H signals of 3-K and 2-K, are in line with scenario A. To further probe the mechanism, the reaction of 2-K with D₂ was studied by both ¹H and ²H NMR spectroscopies (Figure 5). The ¹H NMR spectrum of the product does not show any signal for a Ni-H unit that would be expected for 3^{HD}-K (Figure 5, middle) while Ni-D formation is evidenced by the singlet at -23.77 ppm in the ²H-NMR spectrum (cf. the Ni-H resonance at -23.62 ppm in the ¹H-NMR spectrum of dihydride complex **3-K**). Furthermore, deuteration of a phenyl ring is not observed, based on the absence of any signal in the typical range 6.5 - 8.5 ppm in the ²H-NMR spectrum (Figure 5, bottom). All these findings strongly suggest that 3^{D2}-K is formed and that mechanism A is operative. At moderate D₂ pressures, trace amounts of 2-K (with a single Ni-H unit resonating at -26.12 ppm) are present besides 3^{D2}-K, providing further support for mechanistic pathway A.

Scheme 4. Possible pathways for D₂ activation by 2-K. Left: reductive elimination. Right: Ni-C bond hydrogenation.



The conclusion that **2-K** forms from the Ni¹Ni¹ intermediate **4-K** via bimetallic intramolecular C-H oxidative addition suggested an alternative synthesis of **2-K** that does not involve hydride reagents such as KHBEt₃. The cyclic voltammogram of the precursor complex **1** shows a quasireversible reduction with $E^{p,c} = -2.85 \text{ V vs.}$ Fc^{0/+} in THF (Supporting Information), indicating that **4-K** might be accessible from **1** when using strong reductants. Upon treatment of **1** in THF with 2.2 eq. of KC₈ at rt, the green suspension turned into a red solution over 6 hours, and analysis of the crude material by ¹H NMR spectroscopy showed formation of **2-K** as the major product. Crystallization *via* layering of hexane resulted in red tabular crystals of **2-K** in a yield of 72 % (Scheme 3). This synthetic route provides further indirect evidence that **2-K** forms via a Ni¹Ni¹ intermediate; the same method was also utilized for the selective synthesis of the sodium derivative **2-Na** (*vide infra*).

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Figure 5. Top: ¹H-NMR spectrum of **3-K** under H_2 atmosphere in THF-d₈. Middle: ¹H-NMR of **3^{D2}-K** under D_2 atmosphere in THF-d₈. Bottom: ²H-NMR of **3^{D2}-K** under D_2 atmosphere in THF. The asterisks indicate THF signals.

Since the Ni¹Ni¹ intermediate **4-K** could not be isolated but was assumed to form via the equilibrium with **2-K**, a trapping experiment with an unsaturated substrate featuring a double bond was pursued, anticipating twofold substrate reduction akin to the reactivity of the dinickel(I) complex VI (Scheme 2).^{27–30} Upon addition of benzaldehyde to **2-K** in THF the color of the solution changed from red to brown, and brown crystals of the new product **5-K** could be isolated in 68% yield (Scheme 5).

Scheme 5. Reactivity of 2-K, shown by trapping of the Ni¹Ni¹ intermediate 4-K with benzaldehyde.



The molecular structure of **5-K** determined by X-day diffraction (Figure 6) reveals that the aldehyde substrate is hosted in C,Obridging mode within the bimetallic pocket, the Ni···Ni distance (3.9594(4) Å) being similar to the one in the dihydride complex **3-K(crypt)** (4.0478(8) Å). The K⁺ is located above the central sixmembered ring of **5-K** and is additionally ligated by two THF molecules, complemented by two K⁺···arene contacts. Selected bond lengths and angles for **5-K** are included in Table 1. Importantly, the C-O bond of the bound substrate is substantially elongated to $d_{C-O} = 1.388(3)$ Å, much longer than in free benzaldehyde (1.212(3) Å)³⁶ and closer to the C-O bond length of benzyl alcohol (1.424(6) Å).³⁷ Furthermore, the angle Ca^{ar}-C-O of 114.58(19)° is significantly smaller than in benzaldehyde (123.6(4)°)³⁶ and approaches the tetrahedral angle found for benzyl alcohol (108.9(3)°).³⁷ These geometric changes confirm that the benzaldehyde substrate is twofold reduced in 5-K. In view of the redox balance (Scheme 5) and the roughly square planar coordination environment of the two nickel ions (\angle (N_{trans}-Ni-O) = $168.50(8)^{\circ}$ and $\angle(N_{trans}-Ni-C) = 168.43(9)^{\circ})$ **5-K** appears to be best described as a low-spin dinickel(II) complex with a doubly deprotonated benzyl alcohol species in the bimetallic cleft. This assumption is supported by NMR data for 5-K in C₆D₆ (Supporting Information) which show that the ¹H and ¹³C NMR signals of the "aldehyde-CH" are dramatically shifted to higher field and are found at 2.03 ppm and 86.10 ppm, respectively. The findings corroborate that **2-K** serves as a masked dinickel(I) species and as a powerful two-electron reductant, operating via intramolecular C-H reductive elimination and intermediate 4-K. However, no evidence for oxidative addition of external substrates C6D6 or toluene-d₈ has been obtained when these were added in excess to a solution of 2-K in THF-d₈ at rt or 60°C, likely reflecting that the high local concentration of the ligand phenyl groups favors an intramolecular reaction. Further experiments with external substrates having lower C-H bond dissociation energies (BDEs) are in progress.



Figure 6. Molecular structure (30% probability thermal ellipsoids) of **5-K**. Solvent molecules and hydrogen atoms (except for the one bound to C52) omitted for clarity.

Dinickel Sodium Monohydride and Dihydride Complexes. In case of dihydride complex V, the cation (either K⁺ or Na⁺ or [K(DB18C6]⁺) and its specific interaction with the pyrazolatebridged dinickel dihydride core was found to play a major role regarding the stability of the dihydride and the release of H₂.²⁷ Therefore, the effect of the cation was also probed for the present system by using Na⁺ instead of K⁺. Reaction of 1 with 2.5 eq. of NaHBEt₃ resulted in a mixture of two species according to ¹H NMR spectroscopy, which were identified as the monohydride **2-Na** and dihydride complex **3-Na** (Scheme 6). Increasing the amount of NaHBEt₃ up to 100 equiv. or longer reaction times resulted in only minor changes in the product ratio. Similar to **2-K**, however, the Na⁺ salt **2-Na** could be selectively synthesized in high yields (95%) by direct reduction of **1**, using the strong reductant sodium naphtalide in this case ($E^0 = -3.10$ V vs Fc^{0/+}).³⁸

Scheme 6. Synthetic transformations for the Na⁺ salts of the mono- and dihydride dinickel complexes



Single crystals were obtained by vapor diffusion of pentane into a THF solution of **2-Na**. Overall, the molecular structure of **2-Na** in solid state (Figure 7) is very similar to the one of **2-K**, featuring orthometallation at a winglet aryl group at one side of the bimetallic core and a Ni-H unit on the other side. Again, the alkali metal cation is found above the pyrazole ring close to the pyrazole-N atoms with close contacts to the Ni-H unit and nearby aryl rings, but in **2-Na** the Na⁺ is additionally bound to a THF and thus lacks any intermolecular M⁺···arene interactions as found for **2-K**. In the ATR-IR spectrum of solid **2-Na** the nickel-bound hydride gives rise to a broad band for the Ni-H stretch at $\tilde{v} = 1897$ cm⁻¹.



Figure 7. Molecular structure (30% probability thermal ellipsoids) of **2-Na**. Solvent molecules and hydrogen atoms omitted for clarity, except for the Ni-H.

The effect of the alkali metal ion is most evident in the ¹H-NMR spectra of **2-Na** and **2-K** recorded in THF-d₈, with $\delta_{hydride} = -25.81$ ppm for **2-Na** and -26.12 ppm for **2-K** at rt (Figure 8). Addition of 1 equiv. of KOTf to the solution of **2-Na** in THF-d₈, or addition of 1 equiv. of NaOTf to the solution of **2-K**, gives rise to a single resonance at -26.10 ppm, very close to the signal for **2-K** (Figures 8 and S55). This indicates that interaction of K⁺ with the bimetallic complex is much favored. Titrating further equivalents of NaOTf into the solution of **2-K** in THF-d₈ gradually shifts the hydride signal to lower field, towards the one expected for **2-Na**, but beyond 10 equiv. of NaOTf the trend reverses and the hydride

signal shifts back to higher fields (Figure 8). We assume that interactions between **2-Na** and additional Na⁺ play a role and become dominant at higher Na⁺ concentrations. These conclusions are consistent with trends for the pyrazole-H⁴ signal where the same chemical shifts are found for **2-Na** and **2-K** (5.70 ppm at 298 K) but a clear shift to higher field is observed upon addition of >10 equiv. NaOTf ($\delta_{H4} = 5.55$ ppm after addition of 100 equiv. NaOTf; see Figure S54).



Figure 8. High-field range of the ¹H-NMR spectra of **2-K** (top) and **2-Na** (bottom) in THF-d₈ at rt and effect of titration of NaOTf into the solution of **2-K** (second from top to second from bottom).

Upon reaction with H₂ (~1 atm), **2-Na** converts fully to the dihydride complex **3-Na**; crystals suitable for X-ray diffraction analysis could be obtained from THF/diethyl ether solutions. Compared to **3-K**, complex **3-Na** is less prone to H₂ loss and orthometallation but is stable under dinitrogen atmosphere for several days. The molecular structure of **3-Na** is similar to that of **3-K(crypt)**, with very similar metric parameters. The Na⁺ is positioned above the pyrazolato-bridged dinickel core and appears to interact with both hydrides and one of the ligand's wingtip phenyl groups; additionally it has two bound THF molecules (Figure 9).



Figure 9. Molecular structure (30% probability thermal ellipsoids) of **3-Na**. Solvent molecules and hydrogen atoms omitted for clarity, except for the Ni-H.

Addition of D_2 (1 atm.) to **2-Na** in THF results in the formation of **3^{D2}-Na** as evidenced by the characteristic signal at -23.58 ppm in the ²H-NMR spectrum (Figure 10, top). After replacing the D_2 atmosphere by H_2 (to give **3-Na**; see ¹H NMR spectra in Figure

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S59), free D_2 is observed at 4.57 ppm while no signal for HD is detected (Figure 10, bottom). This finding is in accordance with pairwise exchange of the two hydrides (or deuterides, respectively) and with scenario A shown in Scheme 4.



Figure 10. ²H-NMR spectrum of 3^{D2} -Na in THF (prepared from exposing the solution of **2-Na** to an atmosphere of D₂) (top) and ²H-NMR spectrum after replacing the D₂ atmosphere with H₂ (bottom); corresponding ¹H-NMR spectra are shown in Figure S59. The asterisks indicate THF signals.

Twofold orthometallation at the dinickel core. To study the conversion of **3-Na** to **2-Na** and to probe further reactivity of **2-Na**, a mixture of **2-Na** and **3-Na** was heated at 60°C in THF-d₈ and changes were monitored by ¹H NMR spectroscopy (Scheme 6, Figure 11). While the ratio between **2-Na** and **3-Na** remained nearly constant, both compounds gradually disappeared and formation of a new species **6-Na** was observed, evident from a new characteristic signal for the pyrazole-H⁴ and two new signals in the aromatic region of the ¹H NMR spectrum (Figure 10). **6-Na** does not show any hydride signal, but the methylene groups in 3- and 5-positions of the pyrazolate backbone are diastereotopically split into two doublets characteristic for an AB spin system. The overall ¹H NMR spectrum indicates C_2 symmetry of the new species **6-Na** in solution.



Figure 11. ¹H NMR spectra in THF-d₈ of a mixture of **2-Na** and **3-Na** at rt (top) and after heating to 60° C for 24 hours (middle) and 48 hours (bottom).

After heating to 60°C for 48 hours and slow vapor diffusion of pentane into the dark red THF solution at rt, single crystals suitable for X-ray crystallography were obtained. The molecular structure of **6-Na** (Figure 12) shows that wingtip phenyl groups at both subunits have undergone C-H activation to furnish two Ni-C bonds. Steric congestion and distortion of the two nickel coordination planes away from square planar is substantial, and the orthometallated phenyl rings are constrained to lie above and below the plane defined by the pyrazolato-bridged dinickel core with the Ni-C bonds forming an angle of $26.503(15)^{\circ}$ and $26.859(24)^{\circ}$ with the respective {NiN₃} plane. The Na⁺ is located above one of the orthometallated phenyl rings (distance between Na⁺ and the phenyl plane ~2.66 Å) and is additionally bound to three THF molecules.



Figure 12. Molecular structure of 6-Na; hydrogen atoms omitted for clarity.

When **2-K** in THF-d⁸ was subjected to the same reaction conditions and heated to 60°C, the second C-H activation to give **6-K** is also observed but the reaction takes much longer than in case of **2-Na/3-Na**; full conversion is not reached even after 2 weeks at 70°C and multiple degassing processes. To further study the effect of the cation, DB18C6 was added to the mixture of **2-Na** and **3-Na** in THF-d₈ before heating the dark red solution to 60°C for multiple days. Interestingly, almost no conversion to **6-Na(DB18C6)** was observed even after 3 days at 70°C (Supporting Information). This indicates that the cation has a dramatic effect on the second orthometallation reaction, and that Na⁺ promotes the C-H activation to enable formation of **6-Na**.



Figure 13. ²H NMR spectrum of the reaction of **6-Na** with D_2 (1 atm.) in THF-d₈ after heating to 65°C for 10 d.

To investigate the reversibility of the second orthometallation, which obviously cannot proceed via a dinickel(I) intermediate as proposed for the first orthometallation, **6-Na** was treated with H_2 and the reaction progress was monitored by ¹H NMR spectroscopy over a period of several days (Figure S57). The reaction back to dihydride complex **3-Na** is fairly slow, requires elevated temperatures (65°C), and full conversion to **3-Na** was not observed. Interestingly, only very small amounts of the monohydride complex **2-Na** with H_2 to give **3-Na** is much faster that the reaction of **6-Na** with H_2 , and suggesting different mechanisms for the two steps. Even at higher H_2 pressures (3 atm.) the conversion of **6-Na** to **3-Na** is incomplete and requires heating to 65°C. These observation are in line with challenging direct hydrogenation of the first Ni-C bond in **6-Na** akin to mechanism **B** shown in Scheme 4, in contrast to facile C-H reductive elimination followed by bimetallic H₂ oxidative addition for the second step, viz. conversion of monohydride **2-Na** to dihydride **3-Na** according to mechanism **A** (Scheme 4). Apparently, the activation energy for the direct Ni-C hydrogenation via heterolytic H₂ splitting is significantly higher. The mechanistic scenario is supported by a deuteration experiment: heating **6-Na** with D₂ for prolonged times not only gave rise to the characteristic signals for the Ni-D unit of the dideuteride (major) and monodeuteride (minor) complexes, but also a new set of signals in the aromatic region of the ²H-NMR spectrum, indicative of D incorporation in the phenyl groups (Figures 13 and S58).

Table 1. Selected atom distances and bond angles of 1, 2-K, 2-Na, 3-K(crypt), 3-Na, 5-K and 6-Na.

D [Å] / ∠ [°]	1	2-К	2-Na	3-K(crypt)	3-Na	5-K	6-Na
Ni…Ni	3.7813(7)	4.266(8)	4.345(5)	4.0478(8)	4.057(6)	3.9594(4)	4.1840(8)
Ni-H	-	1.291(3)	1.336(3)	1.39(2) 1.42(2)	1.403(2) 1.454(5)	-	-
Ni-N _{pz}	1.841(2) 1.836(2)	1.878(3) 1.936(4)	1.881(2) 1.925(2)	1.8651(16) 1.8672(17)	1.859(2) 1.914(3)	1.8526(18) 1.8919(18)	1.8963(18) 1.9046(16)
Ni-N _{nac}	1.877(2)- 1.892(2)	1.877(4)- 1.936(4)	1.8810(15)- 1.9178(15)	1.8645(17)- 1.9179(17)	1.859(3)- 1.914(2)	1.8813(18)- 1.9709(18)	1.8630(18)- 1.9310(18)
Ni-C	-	1.901(5)	1.901(5)	-	-	2.015(2)	1.8854(18) 1.900(2)
Ni-O	-	-	-	-	-	1.8299(15)	-
M ⁺ -H	-	2.226(6)	2.227(3)	-	2.354(3) 2.449(4)	-	-
N _{trans} -Ni-N _{pz}	177.90(10) 178.75(10)	167.15(14) 177.22(15)	164.96(7) 176.70(8)	177.67(7) 178.71(7)	175.91(11) 178.19(11)	172.90(8) 178.36(8)	166.14(7) 166.55(6)
N _{trans} -Ni-C	-	158.55(17)	153.94(8)	-	-	168.43(9)	153.14(7) 153.50(8)
N _{trans} -Ni-O	-	-	-	-	-	168.50(8)	-
Ni-C _{ald} -O	-	-	-	-	-	114.58(19)	-

CONCLUSIONS

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The new compartmental pyrazolato-bridged bis(nacnac) ligand with bulky peripheral *m*-terphenyl substituents $[L^{Ph}]^{3-}$ is shown to form a dinickel(II) dihydride complex $[L^{Ph}(Ni-H)_2]^-$ (3) in which the two hydride ligands are in rather close proximity within the bimetallic pocket and are prone to facile pairwise reductive H₂ elimination. However, the putative dinickel(I) intermediate $[L^{Ph}Ni_2]^-$ (4) is not observed, in contrast to previously reported $[L^{iPr}Ni_{2}]^{-}$ (VI)²⁷ equipped with peripheral 2,6-diisopropylphenyl substituents, because of rapid intramolecular Caryl-H oxidative addition that gives the orthometallated monohydride complex 2. While Ni^I species have been implicated in catalytic C-H bond functionalization, discrete activation of C-H bonds at Ni^I complexes has rarely been described in literature.14,16 In the present reversible 2-electron Caryl-H system the reductive elimination/oxidative addition chemistry is enabled by metal-metal cooperativity of the highly preorganized dinickel core. Dihydride complex 3 and orthometallated monohydride complex 2 are in fast equilibrium via the intermediate dinickel(I) species 4, the amount of **3** depending on the applied H_2 pressure. Hence, in accordance with the proposed mechanism, addition of D2 rapidly gives [LPh(Ni- D_{2}^{-} (3^{D2}) as the sole product, without H/D scrambling.

The reversible H₂ and C-H reductive elimination/oxidative addition equilibrium allows to smoothly unmask the reactive dinickel(I) intermediate 4 in the presence of added substrate, with 4 serving as a powerful 2-electron reductant. As a first example presented in this work, addition of benzaldehyde to a solution of 2 rapidly gives complex 5 with a twice reduced benzaldehyde, viz. a doubly deprotonated benzyl alcohol, as C,O-bridging ligand within the bimetallic pocket. While the analogous [L^{iPr}(Ni-H)₂]⁻ (V) operates only via reductive H₂ elimination to access the dinickel(I) species $[L^{iPr}Ni_{2}]^{-}$ (VI),²⁷ the present system now offers both elimination of H₂ from **3** or reductive C-H elimination from **2** for unmasking $[L^{Ph}Ni_{2}]^{-}$ (4). The former process is known from the FeMo cofactor of nitrogenase that stores redox equivalents in two adjacent metal hydrides, and for which exothermic H₂ release contributes significantly to providing the driving force for N₂ reduction.³⁹ In contrast, reductive C-H elimination from 2 does not release any byproduct (such as H₂), and hence it adds a distinct platform (likely with a different thermochemistry) for providing reducing equivalents via the dinickel(I) intermediate while circumventing the isolation of any unstable superreduced form of the bimetallic complex. Studies towards exploiting this scenario for the activation of challenging substrates are in progress in our laboratory.

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An interesting aspect is the pronounced cation effect on the interconversion between **2** and **3**, and also on the formation of the twice orthometallated **6**. E.g., the dihydride complex **3-K(crypt)** loses H₂ if not kept under H₂ atmosphere, while **3-Na** loses H₂ only slowly and is stable under N₂ atmosphere for several days. This may reflect differences in ground state stabilization of the individual complexes **2** or **3** by interaction with Na⁺, K⁺ (or the lack of such interaction in case of [K(crypt)]⁺), or an influence of the Lewis acidic cation on reaction trajectories. The roles that Lewis acids can play in transition-metal hydride reactivity are currently receiving much attention.⁴⁰ It will be particularly interesting to investigate how different Lewis acids can work in concert with this $\{L^{Ph}Ni_2\}$ platform to impart selectivity during substrate transformations.

EXPERIMENTAL SECTION

14 Materials and Methods. Manipulations involving air- and 15 moisture-sensitive compounds were conducted under an 16 atmosphere of dried (phosphorous pentoxide on solid support 17 [Sicapent, Merck]) dinitrogen or argon using standard Schlenk 18 techniques, or in a glovebox ($O_2 < 0.5$ ppm and $H_2O < 0.5$ ppm) 19 filled with dinitrogen atmosphere. THF, THF-d₈, diethyl ether and pentane were dried over sodium or sodium/potassium in the 20 presence of benzophenone. Triethylamine and dichloromethane 21 were dried over calcium hydride (ABCR) and freshly distilled 22 before use. Hydrogen gas was purchased from Messer and 23 deuterium gas from Sigma-Aldrich. 2,6-Diphenylaniline³⁴ and 24 sodium naphtalide⁴¹ were synthesized according to known 25 literature procedures. All other chemicals used were either present in the working group or purchased from commercial sources, or 26 their synthesis is described in the Supporting Information. 27

NMR samples for H₂ experiments were prepared under an inert 28 atmosphere. Reactants were dissolved in THF-d₈ and transferred 29 into a J. Young NMR tube. The solution was degassed by means of 30 a pump-freeze-thaw procedure using liquid nitrogen, which was 31 repeated three times before H₂ was added. Because all new 32 compounds except [L^{Ph}Ni₂(µ-Br)] are extremely sensitive to 33 moisture (ultimately giving the hydroxido-bridged dinickel(II) complex $[L^{Ph}Ni^{II}(\mu-OH)]$, gases such as H₂ and D₂ were dried with 34 a cooling trap, cooled with liquid dinitrogen, or stirred above 35 concentrated sulfuric acid before use. 36

Instrumentation. ¹H-, ²H- and ¹³C-NMR spectra were recorded on 37 Bruker Avance spectrometers (300 and 500 MHz for ¹H) at room 38 temperature unless otherwise noted. Chemical shifts are reported in 39 parts per million relative to residual proton and carbon signals of 40 the solvent.⁴² Electron ionization (EI) and electrospray ionization 41 (ESI) mass spectra were collected on a Bruker HCTultra 42 instrument. Moisture- or oxygen-sensitive samples were prepared in a glovebox (MBRAUN UNIlab) under a dinitrogen atmosphere 43 and injected into the Bruker HCTultra instrument via a direct PEEK 44 tubing connection. Elemental analyses were carried out with an 45 Elementar 4.1 vario EL 3 instrument by the Analytical Laboratory 46 of the Department of Chemistry at the Georg-August-University. 47 IR spectra of solid samples were measured with a Cary 630 FTIR 48 spectrometer equipped with a DialPath and Diamond ATR accessory (Agilent) placed in a glovebox. IR bands were labeled 49 according to their relative intensities with vs (very strong), s 50 (strong), m (medium), w (weak), and very weak (vw). 51

52 H_3L^{Ph} . 2-[(2,6-Diphenylphenyl)imido]-pent-2-en-4-one V (3.3 g,5310 mmol, 2.0 eq.) was dissolved in dichloromethane (30 mL) to54give a slight yellow solution. To this solution triethyloxonium55tetrafluoroborate (3.1 g, 16 mmol, 3.2 eq.) was added and the56yellow solution was then added dropwise to a suspension of57bis(3,5-aminomethyl)pyrazole hydrochloride III (1.0 g, 5.1 mmol,

1.0 eq.) in triethylamine (10 mL). The resulting suspension was stirred for 19 h at 40°C. After removal of the solvent under reduced pressure, the crude solid was extracted multiple times with toluene (2 x 30 mL). After another removal of the solvent the crude material was suspended in ethanol, cooled down to -20°C and filtered. After multiple washings with pentane, H₃L^{Ph} was obtained as a pale yellow solid (2.1 g, 2.8 mmol, 59 %). ¹H-NMR (400 MHz, THF d_8 = 10.79 (s, 1H, NH^{nacnac}), 7.38 (d, J_{H-H} = 8 Hz, 8H, Ph), 7.24 (d, $J_{\text{H-H}} = 8$ Hz, 4H, Ph), 7.19 (d, $J_{\text{H-H}} = 8$ Hz, 8H, Ph), 7.12 – 7.07 (m, 6H, Ph), 5.85 (s, 1H, CH^{pz}), 4.33 (s, 2H, CHCNCH₃), 4.22 (s, 4H, CH₂Pz), 1.81 (s, 6H, CH₂N=CMe). 1.23 (s, 6H, ArN=CMe) ppm. 13 C-NMR(101 MHz, THF) = 166.41 (ArN=C), 156.41 (CH₂N=C), 148.13 (CAr), 147.70 (3,5-Pz), 140.20 (CHAr), 132.66 (CHAr), 128.22 (CHAr), 126.67 (CHAr), 125.21 (CHAr), 121.82 (CHAr), 99.96 (CHPz), 93.70 (CHCNCH₃), 38.84 (CH₂), 21.36 (CH₃), 18.07 (CH₃) ppm. MS (ESI(+), MeCN) *m/z*: calcd. [M+H]⁺ 745.40 exp. $[M+H]^+$ 745.93. Anal. Calcd. for C₅₁H₄₈N₆ (744.39 g/mol) = C 82.25, H 6.57, N 11.17; Found C 82.21, H 6.50, N 11.28.

Complex 1. H₃L^{Ph} (0.75 g, 1.0 mmol, 1.0 eq.) was dissolved in THF (4 mL) and the clear yellow solution cooled to -78°C. n-Butyl lithium (2.6 M in hexane, 1.2 mL, 3.2 mmol, 3.2 eq.) 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 solution. (dme)NiBr₂ (512 mg, 1.8 mmol, 2.0 eq.) was then added. The resulting dark-brown mixture was stirred overnight at 50°C. The suspension was separated by a centrifuge and the THF phase discarded. The solid material was washed several times with acetone until the solvent remained colorless. After removing residual solvent under reduced pressure, 1 was obtained as a green fine powder. (0.53 mg, 0.56 mmol, 56 %). Slow evaporation of a concentrated dichloromethane solution vielded cube-shaped crystals of 1, suitable for XRD analysis. ¹H-NMR (400 MHz, CD_2Cl_2) = 7.92 (d, J_{H-H} = 8 Hz, 8H, Ph), 7.45 – 7.37 (m, 12H, Ph), 7.09 (s, 6H, Ph),), 5.46 (s, 1H, CH^{pz}), 4.49 (s, 2H, CHCNCH₃), 3.93 (s, 4H, CH₂Pz), 1.84 (s, 6H, CH₂N=CMe). 1.36 (s, 6H, ArN=CMe) ppm. ¹³C-NMR(101 MHz, THF) = 160.82 (CH₂N=C), 159.30 (ArN=C), 154.02 (C^{pz}), 148.58 (C^{Ar}), 141.73 (C^{Ar}), 137.92 (C^{Ar}), 131.02 (CH^{Ar}), 130.51 (CH^{Ar}), 128.16 (CH^{Ar}), 127.16 (CH^{Ar}), 126.98 (CH^{Ar}), 97.50 (CHCNCH₃), 92.39 (CH^{Pz}), 54.99 (CH₂), 24.22 (CH₃^{pz}), 21.68 (CH₃^{Ar}) ppm. IR (ATR) v/cm⁻¹ = 3025 (w), 2922 (m), 1898 (w), 1597 (w), 1549 (m), 1529 (s), 1496(w), 1456 (w), 1428 (w), 1392 (s), 1314 (w), 1280 (w), 1261 (w), 1206 (w), 1179 (w), 1085 (w), 1072 (w), 1029 (w) 1016 (m), 957 (w), 946 (w), 912 (w), 872 (w), 802 (m), 752 (s), 732 (m), 695 (vs), 611 (m), 589 (m), 539 (w), 504 (w). Anal. Calcd. for $C_{51}H_{45}N_6Ni_2Br \cdot 4CH_2Cl_2$ (1278.0 g/mol) = C 51.65, H 4.18, N 6.57; Found C 51.89, H 4.20, N 6.61.

Complex **2-K**. The green suspension of **1** (0.10 g, 0.11 mmol, 1.0 eq.) in THF (2 mL) was treated with potassium triethyl borohydride in THF (1 M, 0.30 mL, 0.30 mmol, 3.0 eq.). After stirring for 1 hour the suspension changed to a dark red color. The solution was filtered, and the solvent was removed under reduced pressure. The remaining solid was washed several times with hexane (3 x 10 mL) and the remaining solvent was removed. Red tabular crystals of **2-K** (69 mg, 0.064 mmol, 64%) were obtained by vapor diffusion of pentane into a prepared THF solution.

Alternative Synthesis: The green suspension of **1** (100 mg, 0.11 mmol, 1.0 eq.) in THF (2 mL) was treated with KC₈ (32 mg, 0.24 mmol, 2.2 eq.). The reaction mixture was stirred for 6 hours at room temperature. After removal of the solvent, the crude product was washed with hexane (3 x 4 mL) and dried in vacuo. Crystallization by layering a THF solution with hexane, resulted in red tabular crystals of **2-K** (71 mg, 0.080 mmol, 72%). ¹H-NMR (400 MHz, THF-d₈) = 8.55 (d, 2H, J_{H-H} = 8 Hz, Ar), 7.75 (d, 2H, J_{H-H} = 8 Hz, Ar), 7.67 (d, 1H, J_{H-H} = 8 Hz, Ar), 7.47 (d, 2H, J_{H-H} =

8 Hz, Ar), 7.32 - 6.96 (m, 16H, Ar), 6.37 (t, 1H, $J_{H-H} = 8$ Hz, Ar), 6.29 (t, 2H, $J_{\text{H-H}}$ = 8 Hz, Ar), 5.70 (s, 1H, CH^{pz}), 4.48 (s, 1H, CHCNCH₃), 4.43 (d, J_{H-H} = 24 Hz, 1H, CH₂Pz), 4.24 (s, 1H, CHCNCH₃), 4.21 (d, $J_{\text{H-H}}$ = 24 Hz, 1H, CH₂Pz), 4.06 (d, $J_{\text{H-H}}$ = 24 Hz, 1H, CH₂Pz), 3.99 (d, , J_{H-H} = 24 Hz, 1H, CH₂Pz), 1.92 (s, 3H, Me), 1.05 (s, 6H, 2xllMe), -26.12 (s, 1H, Ni-H) ppm. ¹³C-NMR(101 MHz, THF-d₈) = 160.72 (Cq-Me), 159.57 ($\overline{C^{pz}}$) 159.34 (Cq-Me), 158.90 (Cq-Me), 157.14 (Cq-Me), 157.04 (Cpz), 156.46 (CAr), 154.69 (CAr), 143.26 (CAr), 143.21 (CAr), 142.97 (CAr), 142.20 (CAr), 141.75 (CAr), 140.07 (CAr), 137.31 (CAr), 136.85 (CAr), 135.87 (CAr), 132.46 (CAr), 131.19 (CAr), 131.05 (CAr), 130.14 (CAr), 130.09 (CAr), 129.88 (CAr), 128.80 (CAr), 128.58 (C^{Ar}), 128.38 (C^{Ar}), 128.26 (C^{Ar}), 127.78 (C^{Ar}), 126.84 (C^{Ar}), 126.74 (CAr), 126.43 (CAr), 126.29 (CAr), 125.70 (CAr), 125.37 (C^{Ar}), 124.33 (C^{Ar}), 123.45 (C^{Ar}), 123.02 (C^{Ar}), 120.88 (C^{Ar}), 103.80 (CHCNCH₃), 97.74 (CHCNCH₃), 92.97 (CH^{pz}), 52.65 (CH₂), 52.22 (CH₂), 23.49 (Me), 23.19 (Me), 20.98 (Me), 20.21 (CH₃) ppm. IR (ATR) ν /cm⁻¹ = 3051 (w), 3023 (w), 2984 (w), 2908 (w), 2858 (w), 2821 (w), 1561 (m), 1511 (s), 1422 (s), 1387 (vs), 1306 (m), 1267 (s), 1248 (s), 1204 (s), 1156 (m), 1091 (m), 1068 (m), 1022 (s), 996 (m), 906 (m), 853 (m), 799 (m), 745 (vs), 692 (vs), 605 (s), 541 (s). Anal. Calcd. for 2-K · THF C₅₅H₅₃KN₆Ni₂O (970.50 g/mol) = C 68.06, H 5.50, N 8.66; Found C 67.97, H 5.47, N 8.69.

21 Complex 3-K. 2-K was dissolved in minimal amounts of THF. 22 After degassing the dark red solution three times, an atmosphere of dry dihydrogen was applied (~1 atm.). ¹H-NMR (400 MHz, THF-23 d_8 = 7.78 (d, 8H, J_{H-H} = 8 Hz, Ar), 7.20-7.19 (m, 14H, Ar), 7.07 (t, 24 4H, *J*_{H-H} = 8 Hz, Ar), 5.42 (s, 1H, CH^{pz}), 4.24 (s, 2H, CHCNCH₃), 25 4.04 (s, 4H, CH₂Pz), 1.65 (s, 6H, Me), 1.30 (s, 6H, Me), -23.80 (s, 26 2H, Ni-H) ppm. ¹³C-NMR(101 MHz, THF-d₈) = 158.86 (C^q-Me), 27 157.18 (CAr), 156.98 (Cq-Me), 156.64 (Cpz), 143.79 (CAr), 136.71 28 (C^{Ar}), 131.42 (C^{Ar}), 130.99 (C^{Ar}), 130.15 (C^{Ar}), 128.26 (C^{Ar}), 128.21 (CAr), 126.31 (CAr), 125.71 (CAr), 124.12 (CAr), 97.82 29 (CHCNCH₃), , 92.31 (CH^{Pz}), 53.42 (CH₂), 23.54 (CH₃), 20.61 30 (CH₃) ppm. Crystallization attempts of **3-K** even in a dihydrogen 31 saturated solution always yielded a mixture of 2-K and 3-K. 32 However, crystals of 3-K(crypt) could be obtained as follows: 2-33 K (5.0 mg, 5.6 µmol, 1.0 eq.) was dissolved in minimal amounts of 34 THF-d₈ (0.5 mL). [2.2.2]Cryptand (2.1 mg, 5.6 µmol, 1.0 eq.) was 35 added as a solid and the resulting solution was stirred for 5 mins. After degassing the dark red solution three times, an atmosphere of 36 dry dihydrogen was applied (~1 atm.). The product **3-K(crypt)** was 37 used in situ for further NMR investigations, due to the instability in 38 solution over a longer period of time. Single crystals were obtained 39 after cooling the solution to -30°C.

40 Complex 2-Na. and $Na[LNi_2(H)_2]$ (3-Na). The green suspension of 41 1 (0.10 g, 0.11 mmol, 1.0 eq.) in THF (2 mL) was treated with 42 sodium triethyl borohydride in THF (1 M, 0.30 mL, 0.30 mmol, 3.0 eq.). After stirring for 1 hour the suspension changed to a dark red 43 color. The solution was filtered, and the solvent was removed under 44 reduced pressure. The remaining solid was washed several times 45 with hexane (3 x 10 mL) and the residual solvent was removed. Red 46 tabular crystal mixture of 2-Na and 3-Na were obtained by vapor 47 diffusion of pentane into a THF solution.

48 Alternative Synthesis for 2-Na: The green suspension of 1 (0.20 g, 49 0.21 mmol, 1.0 eq.) in THF (4 mL) was treated with a 1 M solution 50 of sodium naphtalide in THF (0.50 mL, 0.50 mmol, 2.4 eq.). After 51 2 hours, the red solution was filtered, and the solvent was evaporated. After washing with hexane (3 x 5 mL) 2-Na was 52 isolated as a red solid (0.18 g, 0.20 mmol, 95 %). 2-Na: ¹H-NMR 53 (400 MHz, THF-d₈) = 8.58 (d, , $J_{\text{H-H}}$ = 8 Hz, 2H, Ar), 7.85 (d, $J_{\text{H-H}}$ 54 $_{\rm H}$ = 8 Hz 1H, Ar), 7.49 (d, $, J_{\rm H-H}$ = 8 Hz, 2H, Ar), 7.43 (d, $, J_{\rm H-H}$ = 8 55 Hz, 1H, Ar), 7.16-7.07 (m, 17H, Ar), 6.38 (t, , J_{H-H} = 8 Hz, 1H, Ar), 56 6.27 (t, $J_{H-H} = 8$ Hz, 1H, Ar), 5.69 (s, 1H, CH^{pz}), 4.49 (s, 1H, 57 CHCNCH₃), 4.41 (d, J_{H-H} = 18 Hz, 1H, CH₂Pz), 4.32 (s, 1H,

CHCNCH₃), 4.18-3.94 (m, 3H, CH₂Pz), 1.92 (s, 3H, Me), 1.74 (s, 3H, Me), 1.23 (s, 3H, Me), 1.06 (s, 3H, Me), -25.81 (s, 1H, Ni-H) ppm. 13 C-NMR(75 MHz, THF-d₈) = 160.59 (C^q-Me), 160.16 (C^q-Me) 159.43 (Cq-Me), 158.89 (Cq-Me), 157.96 (CAr), 157.72 (CAr), 157.71 (CAr), 155.84 (CAr), 155.82 (CAr), 151.30 (CAr), 144.17 (CAr), 143.56 (CAr), 143.53 (CAr), 142.91 (CAr), 142.61 (CAr), 139.20 (CAr), 137.77 (CAr), 137.02 (CAr), 136.66 (CAr), 134.04 (C^{Ar}), 131.83 (C^{Ar}), 130.81 (C^{Ar}), 130.24 (C^{Ar}), 130.15 (C^{Ar}), 128.93 (CAr), 128.58 (CAr), 128.30 (CAr), 128.01 (CAr), 127.42 (CAr), 126.58 (CAr), 126.54 (CAr), 126.33 (CAr), 125.02 (CAr), 124.39 (CAr), 124.29 (CAr), 123.32 (CAr), 120.85 (CAr), 103.90 (CHCNCH₃), 98.01 (CHCNCH₃), 93.55 (CH^{pz}), 52.41 (CH₂), 52.07 (CH₂), 23.72 (Me), 23.10 (Me), 21.02 (Me), 20.03 (Me) ppm. IR (ATR) $v/cm^{-1} = 3049$ (w), 2952 (w), 2918 (w), 2858 (w), 1897 (w), 1557 (m), 1519 (s), 1496 (m), 1450 (m), 1425 (s), 1386 (vs), 1355 (m), 1314 (m), 1274 (s), 1250 (m), 1208 (m), 1181 (w), 1156 (w), 1107 (w), 1090 (w), 1073 (w), 1046 (w), 1021 (m), 965 (w), 916 (w), 869 (w), 803 (w). Anal. Calcd. for C₅₁H₄₅N₆NaNi₂·2THF (1026.55 g/mol) = C 69.42, H 5.99, N 8.19; Found C 68.64, H 5.84, N 8.36.

Complex 3-Na. The mixture of **2-Na** and **3-Na** after washing with hexane was dissolved in a minimal amount of THF. The red solution was degassed three times before dry dihydrogen gas (~1 atm.) was added. Needle-shaped crystals of **3-Na** for XRD analysis were obtained after layering of diethyl ether on top of the dihydrogen saturated THF solution. Crystals of **3-Na** were only stable under a H₂ atmosphere over a long period of time. ¹H-NMR (400 MHz, THF-d₈) = 7.71-7.69 (d, 8H, J_{H-H} = 8 Hz, Ar), 7.23-7.19 (m, 14H, Ar), 7.11 (t, 4H, J_{H-H} = 8 Hz, Ar), 5.46 (s, 1H, CH^{pz}), 4.29 (s, 2H, CHCNCH₃), 4.06 (s, 4H, CH₂Pz), 1.68 (s, 6H, Me). 1.34 (s, 6H, Me), -23.61 (s, 2H, Ni-H) ppm. ¹³C-NMR(101 MHz, THF-d₈) = 159.25 (C^q-Me), 157.38 (C^{pz}), 157.35 (C^q-Me), 157.20 (C^{Ar}), 143.69 (C^{Ar}), 131.42 (C^{Ar}), 131.38 (C^{Ar}), 131.04 (C^{Ar}), 128.41 (C^{Ar}), 128.18 (C^{Ar}), 126.63 (C^{Ar}), 124.37 (C^{Ar}), 98.04 (CHCNCH₃), 92.94 (CH^{pz}), 53.48 (CH₂), 23.51 (CH₃), 20.64 (CH₃) ppm.

Complex 5-K. 2-K (20 mg, 0.020 mmol, 1.0 eq.) was dissolved in THF. Benzaldehyde (2.2 µL, 2.3 mg, 0.020 mmol, 1.0 eq.) was added to the red solution. After 2 hours of stirring the solution changed to a dark brown color. Crystallization via vapor diffusion into the THF solution, gave 5-K as brown crystals (15 mg, 0.014 mmol, 68%). ¹H-NMR (400 MHz, C_6D_6) $\delta = 8.83$ (d, 2H, J_{H-} $_{\rm H}$ = 8 Hz Ar), 8.03 (d, 2H, $J_{\rm H-H}$ = 8 Hz , Ar), 7.71 (d, 2H, $J_{\rm H-H}$ = 4 Hz, Ar), 7.54 (d, 2H, $J_{\text{H-H}}$ = 8 Hz, Ar), 7.50 (d, 1H, $J_{\text{H-H}}$ = 8 Hz, Ar) 7.31 – 7.21 (m, 6H, Ar), 7.13 – 7.05 (m, 6H, Ar) 6.97 – 6.87 (m, 6H, Ar), 6.78 - 6.69 (m, 4H, , Ar), 5.83 (s, 1H, CHpz), 4.61 (s, 1H, CHCNCH₃), 4.36 (s, 1H, CHCNCH3), 4.13 (d, 1H, J_{H-H} = 16 Hz, CH₂Pz), 4.03 (d, 1H, J_{H-H} = 16 Hz, CH₂Pz), 3.68 (s, 2H, CH₂Pz), 2.03 (s, 1H, PhCHO), 1.61 (s, 3H, Me), 1.56 (s, 3H, Me), 1.36 (s, 3H, Me), 1.22 (s, 3H, Me) ppm. ¹³C-NMR(101 MHz, C6D6) $\delta = 159.92$ (C_a-Me), 159.62 (C_a-Me), 158.68 (C_a-Me), 157.93 (Cq-Me), 156.76 (Cpz), 153.62 (Cpz), 150.38 (CAr), 148.28 (C_{Ar}), 148.14 (C_{Ar}), 146.64 (C_{Ar}), 143.88 (C_{Ar}), 142.92 (C_{Ar}), 140.72 (C_{Ar}), 140.68 (C_{Ar}), 140.44 (C_{Ar}), 138.52 (C_{Ar}), 135.24 (CAr), 134.34 (CAr), 132.07 (CAr), 131.23 (CAr), 131.03 (CAr), 130.86 (C_{Ar}), 130.73 (C_{Ar}), 130.03 (C_{Ar}), 129.52 (C_{Ar}), 129.21 (C_{Ph}-CHO), 127.47 (C_{Ar}), 127.22 (C_{Ar}), 126.35 (C_{Ar}), 125.95 (C_{Ar}), 125.59 (CAr), 125.33 (CAr), 125.20 (CAr), 124.39 (CAr), 124.04 (CAr), 97.63 (CHCNCH3), 97.27 (CHCNCH3), 93.15 (4-Pz), 86.70 (CHO), 51.97 (CH₂Pz), 50.09 (CH₂Pz), 27.98 (Me), 24.41 (Me), 22.12 (Me), 21.40 (Me) ppm. IR (ATR) $\nu/cm^{-1} = 3050$ (vw), 3025 (vw) 2973 (vw), 2912 (vw), 2863 (vw), 1560 (m), 1519 (s), 1493 (m), 1446 (m), 1426 (s), 1386 (vs), 1313 (m), 1274 (s), 1212 (m), 1091 (m), 1045 (m), 1023 (s), 915 (w), 893 (w), 834 (w), 802 (w), 741 (vs), 721 (s), 698 (vs), 639 (m), 601 (s), 542 (m), 480 (m), 457

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(m), 417 (w). Anal. Calcd. for C₅₈H₅₁KN₆Ni₂O · 2THF (1092.3 g/mol) = C 69.13, H 5.71, N 7.33; Found C 68.61, H 5.64, N 7.37. Complex 6-Na. 2-Na (0.10 g, 0.11 mmol, 1.0 eq.) was dissolved in a minimal amount of THF (1 mL). The red solution was heated for at least three days at 60 °C in a closed vessel. 6-Na (95 mg, 0.11 mmol, 96%) was isolated after evaporation of the solvent as a red solid. Dark red needles of 6-Na were obtained by layering hexane on top of the THF solution. ¹H-NMR (400 MHz, THF- d_8) = 7.76 (d, 4H, J_{H-H} = 8 Hz Ar), 7.51 (d, 2H, J_{H-H} = 8 Hz , Ar), 7.30 (d, 2H, $J_{\text{H-H}} = 8$ Hz, Ar), 7.09 (t, 2H, $J_{\text{H-H}} = 8$ Hz, Ar), 6.97 – 6.87 (m, 4H, Ar), 6.69 (d, 2H, J_{H-H} = 8 Hz, Ar), 6.29 (t, 2H, J_{H-H} = 8 Hz, Ar), 5.94 (t, 2H, $J_{\text{H-H}}$ = 8 Hz, Ar), 5.70 (s, 1H, CH^{pz}), 4.30 (d, 2H, $J_{\text{H-H}}$ = 10 16 Hz CH₂Pz), 4.23 (s, 2H, CHCNCH₃), 4.12 (d, 2H, J_{H-H} = 16 Hz 11 CH₂Pz), 1.81 (s, 6H, Me). 1.02 (s, 6H, Me) ppm. ¹³C-12 NMR(101 MHz, THF-d₈) = 158.69 (C^q-Me), 158.39 (C^q-Me), 13 156.54 (CAr), 156.27 (Cpz), 144.94 (CAr), 143.55 (CAr), 140.00 14 (CAr), 139.07 (CAr), 137.47 (Ni-CAr), 135.39 (CAr), 130.49 (CAr), 15 127.81 (CAr), 126.65 (CAr), 126.58 (CAr), 125.04 (CAr), 122.68 (C^{Ar}), 121.66 (C^{Ar}), 120.85 (C^{Ar}), 120.38 (C^{Ar}), 101.84 16 (CHCNCH₃), 91.05 (CH^{Pz}), 52.69 (CH₂), 123.72 (CH₃), 24.14 17 (CH_3) , 20.56 (CH_3) ppm. IR $(ATR) v/cm^{-1} = 3050 (vw)$, 3025 (vw)18 2973 (vw), 2912 (vw), 2863 (vw), 1560 (m), 1519 (s), 1493 (m), 19 1446 (m), 1426 (s), 1386 (vs), 1313 (m), 1274 (s), 1212 (m), 1091 20 (m), 1045 (m), 1023 (s), 915 (w), 893 (w), 834 (w), 802 (w), 741 21 (vs), 721 (s), 698 (vs), 639 (m), 601 (s), 542 (m), 480 (m), 457 (m), 22 417 Anal. Calcd. for C51H43N6NaNi2·3THF (w). (1096.64 g/mol) = C 69.00, H 6.16, N 7.66; Found C 68.73, H 23 6.03, N 7.74. 24

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI ???: Synthetic procedures for ligand synthesis, crystallographic information (CIF), CV of 1, NMR and IR spectra.

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