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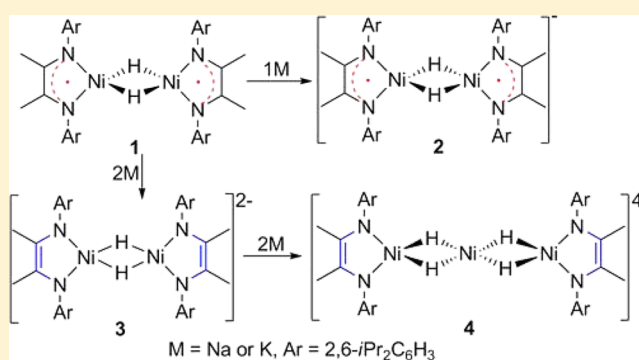
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Synthesis and Reactivity of Nickel Hydride Complexes of an α -Diimine LigandQingsong Dong,^{†,§} Yanxia Zhao,^{†,§} Yuanting Su,^{†,§} Ji-Hu Su,[‡] Biao Wu,[†] and Xiao-Juan Yang^{*,†}[†]State Key Laboratory for Oxo Synthesis & Selective Oxidation, Lanzhou Institute of Chemical Physics, CAS, Lanzhou 730000, China[‡]Hefei National Laboratory for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei 230026, China[§]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information

ABSTRACT: Reaction of L^0NiBr_2 with 2 equiv of NaH yielded the Ni^{II} hydride complex $[(L^{\bullet-})Ni(\mu-H)_2Ni(L^{\bullet-})]$ (**1**) ($L = [(2,6-iPr_2C_6H_3)NC(Me)]_2$; L^0 represents the neutral ligand, $L^{\bullet-}$ is its radical-anionic form, and L^{2-} denotes the dianion) in good yield. Stepwise reduction of complex **1** led to a series of nickel hydrides. Reduction of **1** with 1 equiv of sodium metal afforded a singly reduced species $[Na(DME)_3]-(L^{\bullet-})Ni(\mu-H)_2Ni(L^{\bullet-})$ (**2a**) ($DME = 1,2$ -dimethoxyethane), which contains a mixed-valent core $[Ni(\mu-H)_2Ni]^+$. With 2 equiv of Na a doubly reduced species $[Na(DME)_2]_2[L^{2-}Ni(\mu-H)_2NiL^{2-}]$ (**3a**) was obtained, in which each monoanion ($L^{\bullet-}$) in the precursor **1** has been reduced to L^{2-} . By using potassium as the reducing agent, two analogous species $[K(DME)_4][(L^{\bullet-})Ni(\mu-H)_2Ni(L^{\bullet-})]$ (**2b**) and $[K(DME)_2]_2[L^{2-}Ni(\mu-H)_2NiL^{2-}]$ (**3b**) were obtained. Further treatment of **3b** with 2 equiv of K led to a trinuclear complex $[K(DME)(THF)]_2K_2[L^{2-}Ni(\mu-H)_2Ni(\mu-H)_2NiL^{2-}]$ (**4**), which contains one Ni^{II} and two Ni^I centers with a triplet ground state. When **1** and **3a** were warmed in toluene or benzene, respectively, three reverse-sandwich dinickel complexes, $[(L^{\bullet-})Ni(\mu-\eta^3:\eta^3-C_7H_8)Ni(L^{\bullet-})]$ (**5**) and $[Na(DME)_2]_2[L^{2-}Ni(\mu-\eta^3:\eta^3-C_6H_5R)NiL^{2-}]$ (**6**; $R = CH_3$; **7**: $R = H$), were isolated. Reaction of **1** with Me_3SiN_3 gave the N_3 -bridged complex $[(L^{\bullet-})Ni(\mu-\eta^1-N_3)_2Ni(L^{\bullet-})]$ (**8**). The crystal structures of complexes **1**–**8** have been determined by X-ray diffraction, and their electronic structures have been fully studied by EPR/NMR spectroscopy.



INTRODUCTION

Metallo-organic compounds containing M–H bonds have been widely used in many bond transformations.¹ As typical metal hydride complexes, the nickel hydrides have been known for a long time, and a number of such species have been synthesized, which can serve as models for many catalytic reactions, such as hydrogenation and olefin polymerization.^{2,3} Moreover, the Ni–H interaction also plays important roles in biological functions. For example, a bridging hydride ligand between the Ni and Fe centers has been verified in the $[NiFe]$ -hydrogenase, and the nickel portion was proposed to be the active sites in the catalytic cycle.⁴ Therefore, much attention has been focused on the study of bridging hydride derivatives of nickel, which are less explored compared to the abundant terminal hydride nickel complexes.⁵ Recently, Limberg et al.⁶ reported some bridging hydride nickel complexes stabilized by β -diketiminate ligands, while Suzuki and Ogo et al.⁷ prepared a nickel dihydride, $[Ni_2(Me_2tpa)_2(\mu-H)_2](BF_4)_2$ ($Me_2tpa = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine$), to mimic the hydride active form of $[NiFe]H_2ase$.

α -Diimine derivatives are well-known ligands for both main-group and transition metals. Since Brookhart reported that

nickel(II) α -diimine complexes are highly active in olefin polymerization,⁸ this class of catalysts stirred up great interest, and many analogous complexes have been successively synthesized.⁹ However, metal hydrides with α -diimine ligands are very rare,¹⁰ which is in contrast to the relatively rich metal hydride complexes with β -diketimines.¹¹ Furthermore, to the best of our knowledge, neither terminal nor bridging hydride nickel derivatives with α -diimine ligands have been known.¹² Our team has been exploring the use of bulky α -diimine ligands in the synthesis of low-coordinate binuclear (metal–metal bonded) and mononuclear metal compounds.¹³ Because of their low-lying antibonding π^* orbital, α -diimine ligands can readily accept one or two electrons to form the monoanion ($L^{\bullet-}$) or dianion (L^{2-}),¹⁴ which have been found to be able to stabilize many low-valent, low-coordinate metal complexes.^{13a–f,15} By virtue of this special redox behavior of α -diimine ligands and the fascinating chemistry of bridging hydride nickel species, we extended our research to the nickel hydride complexes with α -diimine ligands. Herein, we report the

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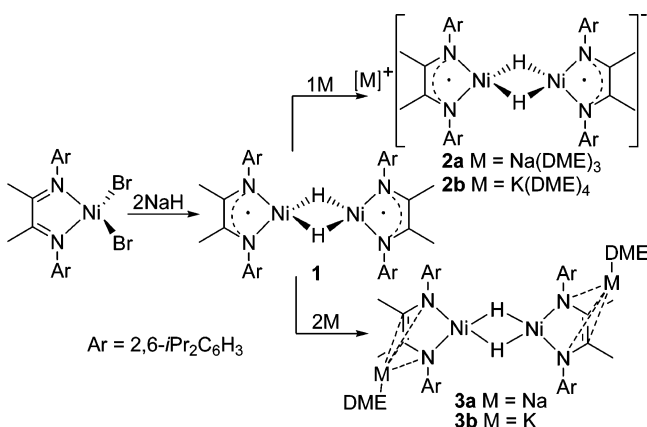
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synthesis and structures of dinickel and trinickel hydride species (1–4) stabilized by different oxidation states of ligand L ($L = [(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2]$), their electronic structures and redox properties, as well as their reactivity. Three toluene- or benzene-bridged products (5–7) were obtained from 1 and 3 via reductive elimination of H_2 , and one N_3 -bridged complex (8) was isolated from the reaction of 1 with Me_3SiN_3 .

RESULTS AND DISCUSSION

Synthesis. The dibromo nickel(II) complex L^0NiBr_2 was prepared by a literature procedure.⁸ As illustrated in Scheme 1,

Scheme 1. Synthesis of the Dinickel Hydride Complexes 1–3



reaction of the precursor L^0NiBr_2 with 2 equiv of NaH in Et_2O afforded purple crystals of $[(\text{L}^{\bullet-})\text{Ni}^{\text{II}}(\mu\text{-H})_2\text{Ni}^{\text{II}}(\text{L}^{\bullet-})]$ (1), in which the original neutral ligand has been reduced to the monoanion but the formal divalent nickel ion remains unchanged. The presence of Ni^{2+} ions and monoanionic ligands ($\text{L}^{\bullet-}$) in complex 1 implies that further reduction is possible, and thus stepwise reduction of 1 was carried out. Treatment of complex 1 with 1 equiv of Na yielded the mixed-valent ($\text{Ni}^{\text{II}}\text{Ni}^{\text{I}}$) species $[\text{Na}(\text{DME})_3][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (2a), while the reaction with more Na (2 equiv) led to a doubly reduced species $[\text{Na}(\text{DME})_2][\text{L}^{2-}\text{Ni}(\mu\text{-H})_2\text{NiL}^{2-}]$ (3a). For comparison, two potassium analogues, $[\text{K}(\text{DME})_4][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (2b) and $[\text{K}(\text{DME})_2][\text{L}^{2-}\text{Ni}(\mu\text{-H})_2\text{NiL}^{2-}]$ (3b), have also been prepared by reduction of complex 1 by 1 or 2 equiv of K metal, respectively. In complexes 3, each ligand has been reduced to a closed shell dianion L^{2-} , but there is a core of $[\text{Ni}(\mu\text{-H})_2\text{Ni}]^{2+}$ which may continue to be reduced. Reaction of 3b with potassium (2 equiv) afforded black brown crystals of the trinuclear nickel hydride $[\text{K}(\text{DME})(\text{THF})]_2\text{K}_2[\text{L}^{2-}\text{Ni}(\mu\text{-H})_2\text{Ni}(\mu\text{-H})_2\text{NiL}^{2-}]$ (4). Complexes 1–4 are highly sensitive to air and moisture, but are thermally quite stable under argon at room temperature. Furthermore, reactions of compounds 1–4 with some small molecules were examined, which gave the products 5–8 (vide infra).

Crystal Structures. $[(\text{L}^{\bullet-})\text{Ni}^{\text{II}}(\mu\text{-H})_2\text{Ni}^{\text{II}}(\text{L}^{\bullet-})]$ (1). Complex 1 is a dimeric structure in the solid state, with two nickel atoms bridged by two hydride ligands which are located in the Fourier difference map (Figure 1). The Ni atoms are four-coordinate in a distorted-square-planar fashion (the N–Ni–N and H–Ni–H planes form dihedral angles of 22.8° or 26.3°) and slightly deviate (by 0.028/0.028 Å) from the C_2N_2 planes of the ligands. As reported in the literature,¹⁶ the oxidation state of α -diimine ligand is readily reflected by the C–N and C–C bond

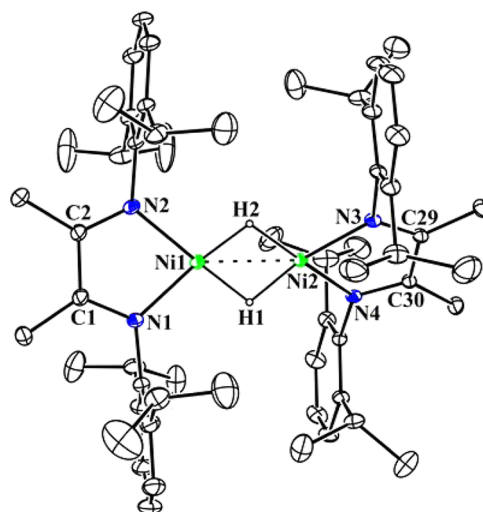


Figure 1. Molecular structure of 1 (thermal ellipsoids are at the 20% probability level). Solvent molecules and hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–H1 1.49(4), Ni1–H2 1.51(3), Ni2–H1 1.59(4), Ni2–H2 1.43(3), Ni1...Ni2 2.3563(9), Ni1–N1 1.915(3), Ni1–N2 1.920(3), Ni2–N3 1.922(3), Ni2–N4 1.919(3), N1–C1 1.318(4), C1–C2 1.438(5), C2–N2 1.313(4), N3–C29 1.327(5), C29–C30 1.421(6), C30–N4 1.323(5), N1–Ni1–N2 81.34(12), N3–Ni2–N4 81.54(13).

lengths of the central C_2N_2 moiety. In complex 1, the C–N (1.313(4)/1.318(4) Å, 1.323(5)/1.327(5) Å) and C–C (1.438(5) and 1.421(6) Å) bond distances indicate that each ligand has accepted one electron to form the monoanionic π radical ($\text{L}^{\bullet-}$). Thus, the nickel centers have the formal oxidation state of +2. The Ni–N bond lengths are between 1.915(3) and 1.922(3) Å, and the N–Ni–N chelating angles are $81.34(12)$ and $81.54(13)^\circ$. The separation of Ni...Ni (2.3563(9) Å) is slightly shorter than that (2.3939(6) Å) in the analogous β -diketiminato compound $[(\text{Nacnac})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{Nacnac})]$ ($\text{Nacnac} = [\text{HC}(\text{CMeNC}_6\text{H}_3(i\text{Pr})_2)_2]^-$),^{6a} but both are much shorter than that of a previously reported octahedral Ni^{II} dihydride complex (2.6105(8) Å).⁷ As in other nickel dihydride complexes,^{6,17} the bridging Ni–H bond lengths of 1 span a quite wide range of 1.43(3) to 1.59(4) Å. The two $\text{C}_2\text{N}_2\text{Ni}$ planes are arranged in a twisted orientation with a dihedral angle of 48.2° , and the substituted N-aryl planes are nearly perpendicular to the $\text{C}_2\text{N}_2\text{Ni}$ metallacycles with an average dihedral angle of 87.2° .

The existence of the ligands as radical anions was also proved by the EPR spectrum of 1 recorded in Et_2O at room-temperature (Figure 2), which shows a 10-lined signal originating from the superimposition of overlapping quintets (due to two equivalent ^{14}N nuclei, $I = 1$) and septets (due to six equivalent ^1H nuclei of two methyl groups, $I = 1/2$). The g value (2.007) and coupling pattern indicate ligand-centered radicals delocalized on the NCCN atoms of the α -diimine ligands. The experimental results are in good agreement with the simulated spectrum (Supporting Information, Figure S1) and compare well with literature reports on related compounds containing radical diimine ligands.^{13c,18}

$[\text{M}(\text{DME})_n][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ ($\text{M} = \text{Na}$, $n = 3$, 2a; $\text{M} = \text{K}$, $n = 4$, 2b). Treatment of complex 1 with 1 equiv of Na or K in the mixed solvent ($\text{Et}_2\text{O}/\text{DME}$) afforded the products $[\text{Na}(\text{DME})_3][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (2a) and $[\text{K}(\text{DME})_4][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (2b), respectively. Complex 2a

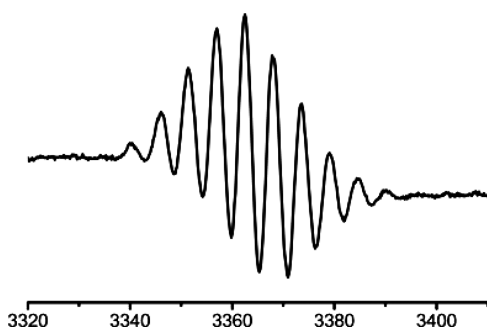


Figure 2. EPR spectrum of $[(L^{\bullet-})Ni(\mu-H)_2Ni(L^{\bullet-})]$ (**1**) in Et_2O at room temperature.

crystallizes in the monoclinic space group $P2_1/c$ without crystal-imposed symmetry on the molecule (Figure 3), while in **2b** a

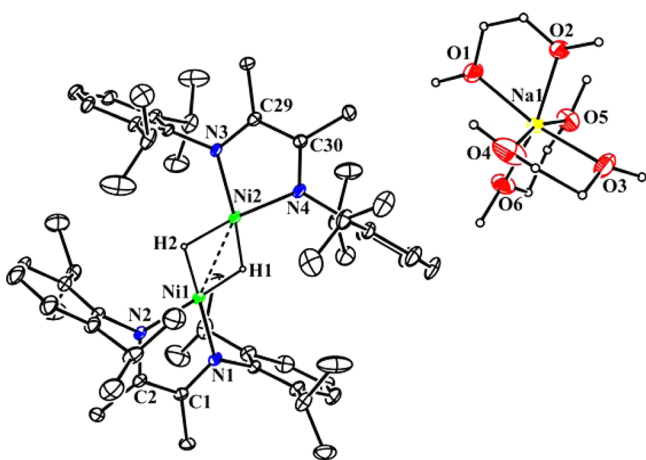


Figure 3. Molecular structure of **2a** (thermal ellipsoids are at the 20% probability level). Solvent molecules and carbon–hydrogen atoms are omitted, and the carbon atoms of DME molecules are drawn as small spheres for clarity. Selected bond lengths (Å) and angles (deg): Ni1–H1 1.661(13), Ni1–H2 1.713(17), Ni2–H1 1.661(13), Ni2–H2 1.673(16), Ni1...Ni2 2.4066(11), Ni1–N1 1.927(3), Ni1–N2 1.905(3), Ni2–N3 1.916(3), Ni2–N4 1.920(3), N1–C1 1.340(5), C1–C2 1.410(6), C2–N2 1.343(5), N3–C29 1.345(5), C29–C30 1.410(6), C30–N4 1.347(5), Na1–O1 2.407(4), Na1–O6 2.327(4), N1–Ni1–N2 81.50(14), N3–Ni2–N4 81.88(14).

C_2 axis is found to bisect the molecule (Supporting Information, Figure S2). The two isostructural complexes show the presence of an anionic $[(L^{\bullet-})Ni(\mu-H)_2Ni(L^{\bullet-})]^-$ unit and a solvated $[Na(DME)_3]^+$ (**2a**) or $[K(DME)_4]^+$ cation (**2b**). Each ligand retains the monoanionic form ($L^{\bullet-}$) as reflected by the C–N (ca. 1.34 Å for **2a**, 1.34 Å for **2b**) and C–C (ca. 1.41 Å for **2a**, 1.39 Å for **2b**) bond lengths, which are between the corresponding values of the neutral and dianionic ligand.¹⁶ The $[Ni(\mu-H)_2Ni]^{2+}$ core in the precursor **1**, however, has been reduced by one electron to $[Ni(\mu-H)_2Ni]^+$. Notably, although the complexes contain the mixed-valent core $[Ni(\mu-H)_2Ni]^+$, the two Ni atoms are essentially indistinguishable and their corresponding bond parameters are very close (in **2a**) or identical (in **2b**, symmetry-related).

In the dinickel fragment, each Ni atom is four-coordinate in a distorted-square-planar fashion. As in **1**, the Ni atoms are bridged by two hydride ligands. The Ni...Ni distance (2.4066(11) Å in **2a**, 2.4040(10) Å in **2b**) is longer than that in **1** containing two Ni^{II} centers, but is slightly shorter than that

(2.433(1) Å) of a previously reported Ni^I dihydride stabilized by bulky phosphane ligands.¹⁹ The average bond lengths of Ni–N (1.917 Å in **2a**, 1.923 Å in **2b**) are very close to that in complex **1** (1.919 Å). However, the dihedral angles between the two C_2N_2Ni planes (29.9° in **2a** and 29.7° in **2b**) are smaller than that in **1** (48.2°). In the countercation fragment, the Na^+ ion is solvated by three dimethoxyethane (DME) molecules in an octahedral geometry in **2a**, while the larger K^+ is chelated by four DME molecules in an irregular octa-coordinate geometry in **2b**.

The EPR spectrum of **2a** in the solid state at 77 K shows three components (Supporting Information, Figure S3a). The $g_{||}$ component appears at 2.298 and the g_{\perp} at 2.148, and the third one at 2.008 which is attributable to the organic radical ($L^{\bullet-}$). The second component is partly overlapped by a somewhat broad, structureless signal at $g = 2.196$, which may be due to the interaction between the metal atom and the bridging hydrides. These features clearly establish the presence of one unpaired electron on the $[Ni(\mu-H)_2Ni]^+$ core. The organic radical ($L^{\bullet-}$) was further supported by the room temperature electron paramagnetic resonance (EPR) in DME showing multi lines with $g = 2.005$, which is consistent with the highly delocalized radical ($L^{\bullet-}$) state of the ligands, and in addition the broad signal is attributable to the nickel centers (Supporting Information, Figure S3b).

$[M(DME)]_2[L^2-Ni(\mu-H)_2NiL^{2-}]$ ($M = Na$, **3a**; $M = K$, **3b**). When the nickel dihydride **1** was reduced by 2 equiv of Na or K, dark-purple species $[Na(DME)]_2[L^2-Ni(\mu-H)_2NiL^{2-}]$ (**3a**) and $[K(DME)]_2[L^2-Ni(\mu-H)_2NiL^{2-}]$ (**3b**) were obtained, which are isomorphous and show close cell parameters (see Supporting Information, Table S1). Complexes **3a** (Figure 4) and **3b** (Supporting Information, Figure S4) feature a centrosymmetric dimeric structure with a $[Ni(\mu-H)_2Ni]^{2+}$ core similar to complex **1**. Each Ni atom is four-coordinated by one chelating ligand and two bridging hydride ligands in a square-planar geometry. The Ni...Ni separation of 2.4237(7) Å

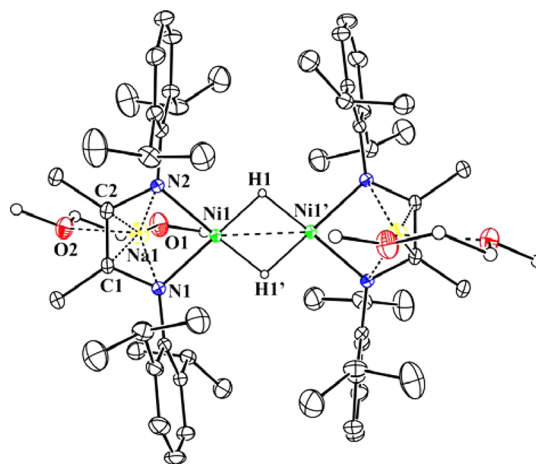


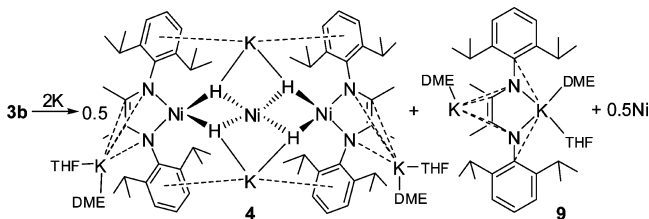
Figure 4. Molecular structure of **3a** (thermal ellipsoids are at the 20% probability level). Solvent molecules and carbon–hydrogen atoms are omitted, and the carbon atoms of DME molecules are drawn as small spheres for clarity. Selected bond lengths (Å) and angles (deg): Ni1–H1 1.59(3), Ni1'–H1 1.58(3), Ni1–N1 1.943(2), Ni1–N2 1.927(2), Ni1...Ni1' 2.4237(7), Ni1...Na1 2.8899(15), Na1–O1 2.336(3), Na1–O2 2.409(3), N1–C1 1.406(3), C1–C2 1.364(4), C2–N2 1.400(3), N1–Ni1–N2 82.71(9), Ni1–Ni1–Na1 124.50(4). Symmetry code: (') 1–x, –y, 1–z.

in **3a** is about 0.02 Å longer than that in **3b** (2.3997(6) Å). The average bond length of Ni–N (1.935 Å) in **3a** is slightly longer than that (1.924 Å) in **3b**, but the Ni–H distances (av. 1.59 Å) in the former are slightly shorter than in the latter (av. 1.62 Å). The two C₂N₂Ni metallacycles adopt a parallel but not coplanar orientation (with vertical distances of 0.145 Å and 0.011 Å, respectively), which is different from the twisted conformations in **1** and **2**.

Interestingly, in complexes **3**, the initial [Ni(μ-H)₂Ni]²⁺ core in the precursor **1** is persistent, but the two monoanionic L^{•−} ligands have been reduced to the dianion L^{2−}, and the negative charges are balanced by solvated Na⁺ or K⁺ ions. This is contrary to the situation in complexes **2**, in which the metal ions rather than the ligands have been reduced. The [Na(DME)]⁺ or [K(DME)]⁺ units sit above or below the five-membered metallacycles, with the Na or K atoms being η⁴-bonded by the N=C=C–N moiety of L^{2−}. The ¹H NMR spectra of complexes **3** display sharp resonances indicative of diamagnetic compounds, which result from the square-planar geometry of Ni centers (low-spin d⁸-Ni^{II}). A signal corresponding to the bridging hydride can be located at δ = −14.37 ppm for **3a** and −14.78 ppm for **3b**, which yet again confirms the presence of the hydride ligands. These chemical shifts are similar to the bridging hydride nickel complex, [(Ni(dippe))₂H₃][BPh₄] (dippe = *i*Pr₂PCH₂–CH₂PiPr₂) (δ = −13.38 ppm),⁵ and the terminal nickel hydride, [Ni(dmpe)₂H](PF₆) (dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂) (δ = −14.02 ppm),²⁰ as well as the carbene nickel hydride (δ = −14.96 ppm) formed by “insertion” of the nickel center into the C–H bond of imidazolium salts.²¹ In the literature, however, it has been reported that the signal of hydride ligands in diamagnetic nickel hydride complexes falls in a rather wide range from −6 to −37 ppm.^{5,6b,19,22}

[K(DME)(THF)]₂K₂[L^{2−}Ni(μ-H)₂Ni(μ-H)₂NiL^{2−}] (**4**). Further reduction of the [Ni(μ-H)₂Ni]²⁺ core in **3b** by 2 equiv of K yielded the trinuclear compound **4** (Scheme 2). This

Scheme 2. Synthesis of the Trinickel Hydride Complex 4



compound crystallizes in the monoclinic space group C2/c with a C₂ axis passing through the central Ni atom (Figure 5). It contains a [Ni(μ-H)₂Ni(μ-H)₂Ni] backbone (the H atoms were located in the Fourier difference map) in a “boat” conformation with the central NiH₄ unit at the bottom and the other two Ni atoms at the stern and head, respectively, and the Ni–Ni–Ni angle (156°) deviates from linearity. A trinuclear nickel hydride complex with a β-diketiminato ligand, K₂[(Nacnac)Ni(μ-H)₂Ni(μ-H)₂Ni(Nacnac)], has recently been reported; however, the three Ni atoms are in a straight line.^{6b} The Ni···Ni separations (2.3956(4) Å) in **4** are significantly shorter than those (2.461(3) Å) observed for the β-diketiminato compound, but are longer than those (2.283(1) Å) reported for a trinickel species with Ni–Ni bonding interaction obtained from one-electron oxidation of Ni₃(dpa)₄Cl₂ (dpa = di-2,2′-pyridylamide).²³

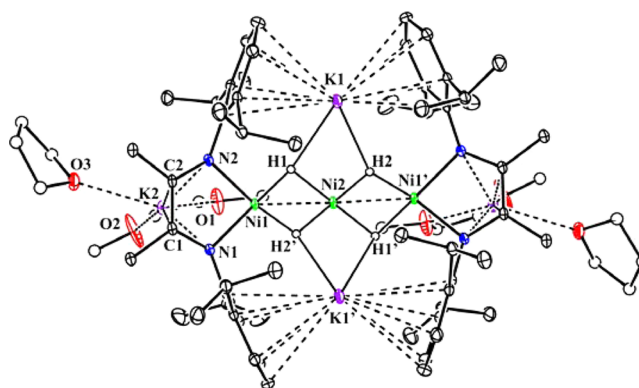


Figure 5. Molecular structure of **4** (thermal ellipsoids are at the 40% probability level). Solvent molecules and carbon–hydrogen atoms are omitted, and the carbon atoms of DME and THF molecules are drawn as small spheres for clarity. Selected bond lengths (Å) and angles (deg): Ni1–H1 1.63(3), Ni1–H2′ 1.59(4), Ni2–H1 1.58(3), Ni2–H2 1.40(4), Ni1···Ni2 2.3956(4), Ni1–N1 1.940(2), Ni1–N2 1.958(2), Ni1···K1 3.7432(8), Ni1···K2 3.1587(7), Ni2···K1 3.1874(7), K1–H1 2.64(3), K1–H2 2.64(4), N1–C1 1.409(3), C1–C2 1.363(3), C2–N2 1.413(3), Ni1–Ni2–Ni1′ 156.57(3), N1–Ni1–N2 83.49(8). Symmetry code: (′) −*x*, *y*, 0.5−*z*.

In complex **4**, the central Ni atom shows the formal oxidation state of +2 and is coordinated in a square-planar fashion with short Ni–H bond lengths of 1.40(4) and 1.58(3) Å, while the C₂-related stern and head nickel atoms (in the oxidation state of +1) adopt a slightly distorted-square-planar coordination environment with slightly longer Ni–H distances, at 1.63(3) and 1.59(4) Å. Another interesting structural feature of **4** is that there are two coordination modes for the potassium ions (K1 and K2) in the molecule. One K atom (K1) interacts with hydride ligands (K1–H distances: 2.64(3) and 2.64(4) Å) and with the flanking aryl rings in the η⁶/η⁶ fashion (K1···C(aryl) contacts range from 3.218(3) to 3.277(3) Å), which compare with previously reported examples of aryl sandwiched potassium ions.²⁴ The second (K2) atom is η⁴-bonded by the five-membered metallacycle and solvated by DME and tetrahydrofuran (THF) molecules. The two [K(DME)(THF)]⁺ units are situated on the same side of the five-membered metallacycles, which is different from the oppositely arranged alkali metal ions in the dinuclear complexes **3**.

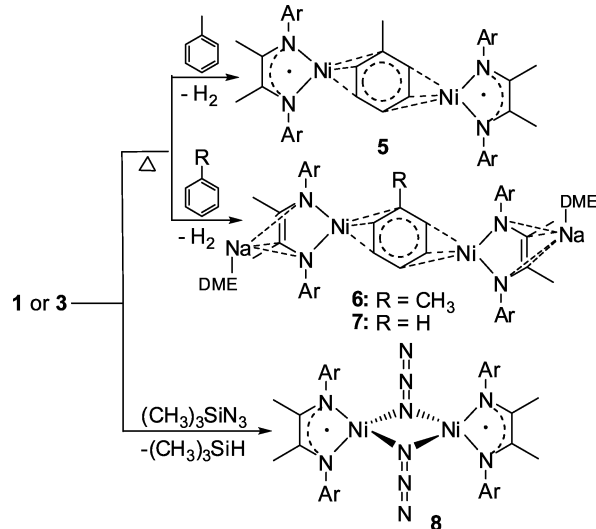
The formation of compound **4** may proceed through a disproportionation process involving some nickel(I) intermediate, which is supported by the isolation of the potassium salt of the ligand, [K(DME)][L^{2−}–K(DME)(THF)] (**9**) (Supporting Information, Figure S5), from the same reaction and the observation of Ni metal, as illustrated in Scheme 2. Reduction of metal(II) hydrides destroying metal–hydride bonds to form the metal(I) hydrides has been reported in other metal hydride complexes.^{11f,25} However, the related compound K₂[(Nacnac)Ni(μ-H)₂Ni(μ-H)₂Ni(Nacnac)] obtained from the reaction of nickel(II) hydrides with 2 equiv of KC₈ was considered to result from elimination of H₂ to give nickel(0) species followed by readdition of H₂.^{6b} Although the electronic structure of **4** is similar to the diamagnetic K₂[(Nacnac)Ni(μ-H)₂Ni(μ-H)₂Ni(Nacnac)], the ¹H NMR spectrum of **4** shows broad signals and provides little information. In contrast, the X-band EPR measurement in the solid state at 110 K confirmed the presence of a paramagnetic species with two components. The *g*_{||} component appears at 2.564 and the *g*_⊥ at 2.108, implying the presence of d⁹-Ni^I centers (*S* = 1/2) with localized

valences. Furthermore, the interaction with the bridging hydrogen was also observed by the weak signals (Supporting Information, Figure S6).

In the nickel hydrides 1–4, upon stepwise reduction, the ligands exist either as monoanionic π radical $L^{\bullet-}$ (in 1 and 2) or as dianion L^{2-} (in 3 and 4), and the oxidation state of the nickel centers varies from +2 (in 1 and 3) to +1.5 (in 2) and to +1 (in 4, except for the central Ni^{II}). The Ni...Ni separations are very close to each other except for 1 which shows a slightly shorter Ni...Ni distance and might be due to the smaller radius of nickel(II) in 1. The average Ni–N bond length in 1 (1.919 Å) is very similar to that in 2 (1.917 Å in 2a, 1.923 Å in 2b) and 3 (1.935 Å in 3a, 1.924 Å in 3b), while they are all shorter than that in 4 (1.949 Å). The elongation of Ni–N bond lengths in 4 can be explained in terms of the increase of the Lewis basicity for the lower oxidation state Ni^I .

Reactivity of Compounds 1–4. For metallo-organic hydrides, evidence for the existence of hydrogen is essential. 1H NMR spectrum is the most common way to diagnose the hydride hydrogen in diamagnetic metal hydrides.^{5,6b,19–22,26} Reactions with potential π -ligands may be another way,²⁷ but some metallo-organic hydrides are stable in contact with such ligands.^{6a} On addition of stronger neutral donors such as N_2 , CO, and pyridine, reductive elimination of H_2 has been reported for dinickel hydrides^{6a,28} and iron analogues.²⁹ Next, the reactivity of compounds 1–4 was studied (Scheme 3), which provides further evidence for the bridging hydride ligands.

Scheme 3. Synthesis of Complexes 5–8



$[(L^{\bullet-})Ni(\mu-\eta^3:\eta^3-C_7H_8)Ni(L^{\bullet-})]$ (5) and $[Na(DME)]_2[L^{2-}Ni(\mu-\eta^3:\eta^3-C_6H_5R)NiL^{2-}]$ (6: $R = CH_3$; 7: $R = H$). The reactions of 1–4 with aromatic molecules were examined. Compounds 1–4 were warmed to 80 °C in toluene or benzene, and three dinickel complexes (5, 6, and 7) were isolated from 1 and 3 upon reductive elimination of H_2 . Unfortunately, the products from heating compounds 2 and 4 in toluene or benzene could not be isolated.

The reverse-sandwich complex 5 contains two “ $(L^{\bullet-})Ni$ ” units bridged by a toluene molecule in an $\eta^3:\eta^3$ binding manner (Figure 6). The two five-membered C_2N_2Ni planes are almost coplanar (dihedral angle 7.6°), in contrast to the twisted situation of the precursor 1. The ligand retains $L^{\bullet-}$, and the

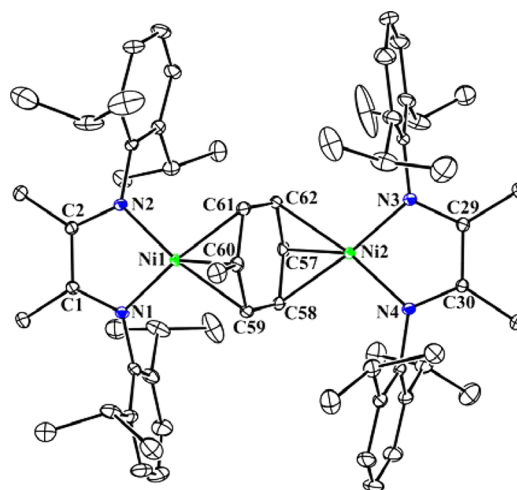


Figure 6. Molecular structure of 5 (thermal ellipsoids are at the 30% probability level). Selected bond lengths (Å) and angles (deg): Ni1–N1 1.9064(19), Ni1–N2 1.8956(19), Ni2–N3 1.9057(19), Ni2–N4 1.8963(19), Ni1–C60 1.925(2), Ni1–C61 2.093(2), Ni1–C59 2.096(2), Ni2–C57 1.951(2), Ni2–C62 2.069(2), Ni2–C58 2.089(2), C58–C59 1.452(4), C61–C62 1.448(4), N1–C1 1.346(3), C1–C2 1.407(3), C2–N2 1.343(3), N3–C29 1.343(3), C29–C30 1.414(3), C30–N4 1.340(3), N1–Ni1–N2 83.60(8), N3–Ni2–N4 84.04(8).

average distance of Ni–N bonds (1.901 Å) is slightly shorter than that in 1 (1.919 Å). In the structure of 5, the bridging toluene ligand is significantly distorted from planar, and its C–C distances (ranging from 1.413(4) to 1.452(4) Å) indicate a partial loss of aromaticity. Thus, upon reductive elimination of H_2 , two electrons may be transferred to toluene to give the dianionic form, and the metal ions remain their +2 state. Similar toluene-bridged structures have also been reported for $[(Nacnac)Ni(\mu-\eta^3:\eta^3-C_7H_8)Ni(Nacnac)]$, obtained by treating $(Nacnac)Ni(\mu-Br)_2Li(THF)_2$ with Na/K alloy in toluene,³⁰ and for the complex $[Ni(Priso)]_2(\mu-\eta^3:\eta^3-C_7H_8)$ (Priso = $[(C_6H_3iPr_2-2,6)N]_2CN(iPr)_2$) arising from the reaction of $[Ni(Priso)(\mu-Br)]_2$ with K in toluene.³¹ The EPR spectrum (Figure S7, Supporting Information) of 5 in toluene solution at room temperature shows a multilined signal ($g = 2.006$), suggesting that the unpaired electrons are delocalized over the ligands.

Compounds 6 and 7 are very closely related to each other and to 5, possessing two $[Na(DME)][L^{2-}Ni]$ units (as in 3) bridged by a reduced toluene (Figure 7) or benzene (Supporting Information, Figure S8) molecule, which is significantly distorted from planarity (the dihedral angle between C57–C58–C59 (C60–C61–C62) and C57–C62–C60–C59 least-squares planes: 18.3° (22.6°) in 6; the C29–C30–C31 and the C29–C31–C29′–C31′ least-squares planes: 20.9° in 7), in an $\eta^3:\eta^3$ manner. As in the parent compound 3a, the nickel ions display the formal oxidation state of +2, while the ligands exist as the dianionic form. The 1H NMR spectra of 6 and 7 show sharp resonances indicative of diamagnetic compounds.

$[(L^{\bullet-})Ni(\mu-\eta^1-N_3)_2Ni(L^{\bullet-})]$ (8). Reaction of the dinickel dihydride 1 with Me_3SiN_3 afforded the product 8 with a Ni_2N_2 four-membered ring (Scheme 3). The compound is dimeric, with symmetrically bridging azide ligands and tetrahedrally coordinated nickel atoms (Figure 8), which is different from that (planar coordination geometry) of a

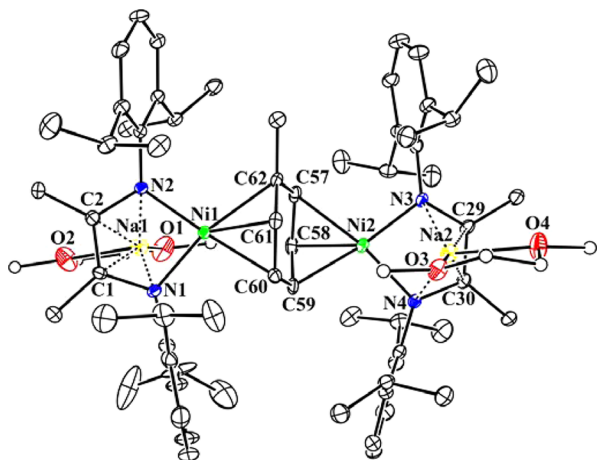


Figure 7. Molecular structure of **6** (thermal ellipsoids are at the 30% probability level). Solvent molecules and carbon–hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–N1 1.925(4), Ni1–N2 1.893(4), Ni2–N3 1.934(4), Ni2–N4 1.896(4), Ni1–C62 2.138(5), Ni1–C61 1.895(5), Ni1–C60 2.060(5), Ni2–C57 2.204(5), Ni2–C58 1.939(5), Ni1–C59 2.049(5), C57–C62 1.446(8), C59–C60 1.458(7), Na1⋯Ni1 2.917(2), Na2⋯Ni2 2.932(2), N1–C1 1.415(6), C1–C2 1.371(8), C2–N2 1.388(6), N3–C29 1.410(6), C29–C30 1.355(7), C30–N4 1.407(6), N1–Ni1–N2 83.96(17), N3–Ni2–N4 83.85(17).

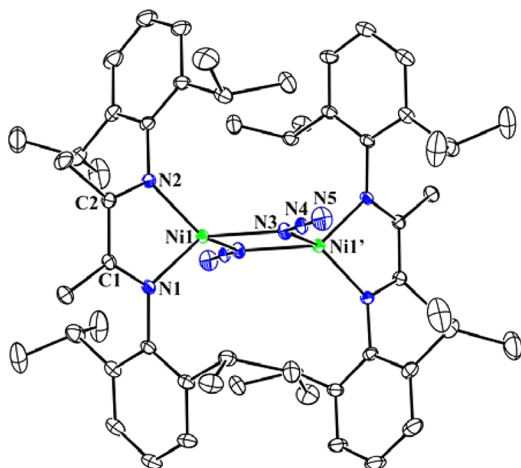


Figure 8. Molecular structure of **8** (thermal ellipsoids are at the 30% probability level). Solvent molecules and carbon–hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–N1 1.923(3), Ni1–N2 1.923(3), Ni1–N3 2.032(4), Ni1'–N3 2.079(4), N3–N4 1.057(5), N4–N5 1.233(6), N1–C1 1.314(5), C1–C2 1.439(6), C2–N2 1.329(5), N3–N4–N5 178.8(6), Ni–N3–Ni' 97.76(19), N1–Ni–N2 81.27(13). Symmetry code: (') 1.5–*x*, 0.5–*y*, 1–*z*.

previously reported four-membered ring of the nickel(II) azide complex $[\{\text{Ni}(\text{Priso})(\mu\text{-N}_3)\}_2]$ obtained from the reaction of $[\{\text{Ni}(\text{Priso})\}_2](\mu\text{-}\eta^3\text{-}\eta^3\text{-C}_7\text{H}_8)$ with Me_3SiN_3 .³¹ The similar reaction of Me_3SiN_3 with a low-coordinate iron(II) hydride complex has also been reported. However, the product features an eight-membered ring $(\text{FeN}_3)_2$, in which the azide ligands are in a $\mu\text{-}\eta^1\text{:}\eta^1$ bridging fashion.²⁹ The IR spectrum of **8** shows a strong absorption at 2083 cm^{-1} , consistent with the presence of bridging azide ligands. Its EPR spectrum in solid state at 77 K (Figure 9) displays a rhombic signal with a significantly smaller g anisotropy: $g_1 = 2.023$, $g_2 = 2.008$, and $g_3 = 1.989$, indicative of

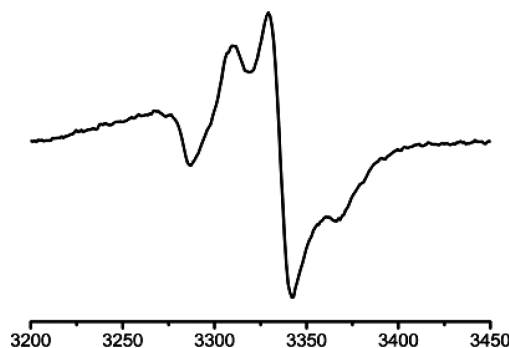


Figure 9. EPR spectrum of $[(\text{L}^{\bullet-})\text{Ni}(\mu\text{-}\eta^1\text{-N}_3)_2\text{Ni}(\text{L}^{\bullet-})]$ (**8**) in solid at 77 K.

a delocalized ligand radical and a diamagnetic $[\text{Ni}(\mu\text{-}\eta^1\text{-N}_3)_2\text{Ni}]^{2+}$ core,³² which can be described as that the two high-spin nickel centers are antiferromagnetically coupled through the bridging azide ligands. In addition, the broad signal at about $g = 2.048$ may be due to contamination by an organic radical whose signal is broadened by interaction with metal.³³

CONCLUSIONS

The bulky α -diimine ligand **L** ($\text{L} = [(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2]_2$) has proven to be very efficient in the stabilization of bridging nickel hydride complexes, which have attracted much interest in the context of structural and functional mimicking of $[\text{NiFe}]$ -hydrogenases. The nickel hydrides **1–4**, synthesized by stepwise reduction of the dibromo precursor L^0NiBr_2 , represent very rare examples of α -diimine-ligated nickel hydride species, demonstrating the promising potential of diimine ligands in the development of metal hydrides. In addition, this work also shows that the bridging nickel hydride complexes with bulky α -diimine ligands are fairly reactive toward some small molecules. Further investigations on the reactivity of these nickel hydride complexes are on the way.

EXPERIMENTAL SECTION

General Considerations. All experiments concerning air- and moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and/or glovebox techniques. The solvents (DME, toluene, THF, and Et_2O) were dried using appropriate methods and were distilled under argon prior to use. Benzene- d_6 was dried over Na/K alloy. Compounds $(\text{DME})\text{NiBr}_2$,³⁴ L^0 ,³⁵ and L^0NiBr_2 ⁸ were prepared according to published procedures. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene- d_6 . EPR spectra of the paramagnetic compounds were recorded on a Bruker EMX-10/12 spectrometer in solution or solid state. IR spectra were recorded (thin film on KBr plate) using a Nicolet AVATAR 360 FT-IR spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument.

Synthesis of $[(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (1**).** The gray power of NaH (0.027 g, 1.13 mmol) was added to a stirred suspension of L^0NiBr_2 (0.310 g, 0.50 mmol) in diethyl ether (25 mL). The mixture was stirred for 24 h at room temperature. All volatiles were then removed in vacuo, and the residue was extracted with toluene. The extract was filtered, concentrated to about 6 mL and stored at room temperature for several days to yield purple crystals of **1**-toluene (0.109 g, 43%). EPR (Et_2O , r.t.): $g = 2.007$. Anal. Calcd for $\text{C}_{63}\text{H}_{90}\text{N}_4\text{Ni}_2$ (1020.80): C 74.13, H 8.88, N 5.49. Found: C 73.66, H 8.91, N 5.54. IR (KBr, ν/cm^{-1}): 1636, 1583, 1437, 1378, 1318, 1249, 1213, 1174, 1097, 970, 834, 786, 732, 694.

Synthesis of $[\text{Na}(\text{DME})_3][(\text{L}^{\bullet-})\text{Ni}(\mu\text{-H})_2\text{Ni}(\text{L}^{\bullet-})]$ (2a**).** Sodium (0.006 g, 0.28 mmol) was added to a purple solution of **1** (0.255 g, 0.25

mmol) in the mixed solvents (20 mL, Et₂O/DME = 3:1), and the reaction mixture was stirred for 24 h at room temperature. After filtration and concentration of the filtrate to about 8 mL, the solution was stored at room temperature for several days to yield **2a**·THF (0.122 g, 38%). EPR (DME, r.t.): $g = 2.005$, the broad signal ($g = 2.033$) is the metal signal; (solid state, 77 K): $g_{\parallel} = 2.298$, $g_{\perp} = 2.148$, and $g = 2.008$. Anal. Calcd for C₇₂H₁₂₀N₄O₇NaNi₂ (1294.10): C 66.82, H 9.35, N 4.33. Found: C 66.01, H 9.53, N 4.71 (the low C content may result from the formation of NiC upon combustion). IR (KBr, ν/cm^{-1}): 1641, 1565, 1438, 1378, 1321, 1250, 1188, 1109, 1030, 974, 853, 787, 733, 681.

Synthesis of $[K(DME)_2][L^{\bullet-}Ni(\mu-H)_2Ni(L^{\bullet-})]$ (2b**).** In a similar manner to the synthesis of **2a** but employing potassium (0.011 g, 0.28 mmol), deep-purple crystals of **2b**·THF (0.142 g, 41%) were isolated. EPR (DME, r.t.): $g = 2.005$, the broad signal ($g = 2.030$) is from the nickel centers. Anal. Calcd for C₇₆H₁₃₀N₄O₉KNi₂ (1400.33): C 65.18, H 9.35, N 4.00. Found: C 64.23, H 9.56, N 3.91 (the low C content may result from the formation of NiC upon combustion). IR (KBr, ν/cm^{-1}): 1640, 1571, 1435, 1378, 1323, 1250, 1192, 1109, 1030, 973, 872, 786, 733, 679.

Synthesis of $[Na(DME)_2][L^2-Ni(\mu-H)_2NiL^{2-}]$ (3a**).** Complex **3a** was synthesized by the same procedure as for **2a** but by employing 2 equiv of sodium (0.012 g, 0.56 mmol) and storing at room temperature. Dark-purple crystals of **3a**·toluene (0.096 g, 31%) were isolated after 2 weeks. ¹H NMR (400 MHz, benzene-*d*₆, 25 °C, TMS): $\delta = -14.37$ (s, 2H, Ni–H), 1.08 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 1.16 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 2.10 (s, 12H, N–CCH₃), 2.14 (s, 3H, Ph–CH₃), 3.03 (m, 8H, CH(CH₃)₂), 3.12 (DME), 3.33 (DME), 6.53–7.16 ppm (m, 17H, Ar–H). Anal. Calcd for C₇₁H₁₁₀N₄O₄Na₂Ni₂ (1247.00): C 68.38, H 8.89, N 4.49. Found: C 67.19, H 8.96, N 5.06 (the low C content may result from the formation of NiC upon combustion). IR (KBr, ν/cm^{-1}): 1664, 1584, 1438, 1379, 1319, 1250, 1176, 1098, 1058, 972, 888, 859, 828, 785, 734, 697.

Synthesis of $[K(DME)_2][L^2-Ni(\mu-H)_2NiL^{2-}]$ (3b**).** Complex **3b** was synthesized by the same procedure as for **2a** but by employing potassium (0.022 g, 0.56 mmol). Dark-purple crystals of **3b**·toluene (0.108 g, 34%) were isolated after 2 weeks. ¹H NMR (400 MHz, benzene-*d*₆, 25 °C, TMS): $\delta = -14.78$ (s, 2H, Ni–H), 1.11 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 1.18 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 2.10 (s, 12H, N–CCH₃), 2.15 (s, 3H, Ph–CH₃), 3.03 (m, 8H, CH(CH₃)₂), 3.11 (DME), 3.33 (DME), 6.32–7.16 ppm (m, 17H, Ar–H). Anal. Calcd for C₇₁H₁₁₀N₄O₄K₂Ni₂ (1279.22): C 66.66, H 8.67, N 4.38. Found: C 66.05, H 8.54, N 4.52. IR (KBr, ν/cm^{-1}): 1661, 1588, 1438, 1380, 1320, 1253, 1136, 1097, 1063, 967, 936, 859, 828, 788, 734, 693.

Synthesis of $[K(DME)(THF)]_2K_2[L^2-Ni(\mu-H)_2Ni(\mu-H)_2NiL^{2-}]$ (4**).** Potassium (0.022 g, 0.55 mmol) was added to a dark-purple solution of **3b** (0.319 g, 0.25 mmol) in the mixed solvents (20 mL, Et₂O/DME = 3:1), and the reaction mixture was stirred for 24 h at room temperature. After filtration and concentration of the filtrate to about 9 mL, the solution was stored at room temperature for several days to yield **4**·2Et₂O as black brown crystals (0.093 g, 23%, based on the reaction stoichiometry). EPR (solid state, 110 K): $g_{\parallel} = 2.564$, $g_{\perp} = 2.108$. Anal. Calcd for C₈₀H₁₄₀N₄O₈K₄Ni₃ (1618.43): C 59.37, H 8.73, N 3.46. Found: C 58.17, H 8.79, N 3.17 (the low C content may result from the formation of NiC upon combustion). IR (KBr, ν/cm^{-1}): 1641, 1575, 1462, 1414, 1378, 1320, 1279, 1248, 1163, 1083, 1055, 856, 780, 731, 699.

Synthesis of $[L^{\bullet-}Ni(\mu-\eta^3-C_7H_8)Ni(L^{\bullet-})]$ (5**).** A solution of **1** (0.255 g, 0.25 mmol) in toluene (20 mL) was heated at 80 °C for 12 h. After filtration and concentration of the filtrate to about 6 mL, the solution was stored at room temperature for several days to yield **5** (0.112 g, 44%) as purple crystals. EPR (Et₂O, r.t.): $g = 2.006$. Anal. Calcd for C₆₃H₈₈N₄Ni₂ (1018.75): C 74.27, H 8.71, N 5.50. Found: C 73.32, H 8.89, N 5.31 (the low C content may result from the formation of NiC upon combustion). IR (KBr, ν/cm^{-1}): 1640, 1579, 1528, 1434, 1381, 1321, 1253, 1217, 1176, 1097, 1057, 978, 934, 872, 830, 786, 733, 679.

Synthesis of $[Na(DME)_2][L^2-Ni(\mu-\eta^3-C_7H_8)NiL^{2-}]$ (6**).** Complex **6** was synthesized by the same procedure as described for **5** but by employing **3a** (0.311 g, 0.25 mmol). Black-purple crystals of **6**·toluene

(0.170 g, 51%) were isolated after 2 weeks. ¹H NMR (400 MHz, benzene-*d*₆, 25 °C, TMS): $\delta = 1.08$ (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 1.30 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 2.10 (s, 12H, N–CCH₃), 2.15 (s, 6H, Ph–CH₃), 3.53 (m, 8H, CH(CH₃)₂), 3.12 (DME), 3.33 (DME), 6.88–7.13 ppm (m, 22H, Ar–H). ¹³C{¹H} NMR (benzene-*d*₆, 25 °C): $\delta = 15.4$ (N–CCH₃), 23.5 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 56.9 (DME), 71.8 (DME), 116.0–145.6 (Ar–C), 151.5 (N–CCH₃). Anal. Calcd for C₇₈H₁₁₆N₄O₄Na₂Ni₂ (1337.12): C 70.06, H 8.74, N 4.19. Found: C 69.52, H 8.61, N 3.96. IR (KBr, ν/cm^{-1}): 1636, 1587, 1461, 1438, 1381, 1362, 1322, 1253, 1181, 1119, 1058, 975, 934, 842, 785, 763, 735, 695.

Synthesis of $[Na(DME)_2][L^2-Ni(\mu-\eta^3-C_6H_5)NiL^{2-}]$ (7**).** Complex **7** was synthesized by the same procedure as described for **5** but by heating **3a** in benzene. Black-purple crystals of **7**·benzene (0.134 g, 41%) were isolated after 2 weeks. ¹H NMR (400 MHz, benzene-*d*₆, 25 °C, TMS): $\delta = 1.11$ (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 1.32 (d, 24H, $J = 6.8$ Hz, CH(CH₃)₂), 2.10 (s, 12H, N–CCH₃), 3.43 (m, 8H, CH(CH₃)₂), 3.15 (DME), 3.40 (DME), 6.82–7.16 ppm (m, 24H, Ar–H). ¹³C{¹H} NMR (benzene-*d*₆, 25 °C): $\delta = 15.4$ (N–CCH₃), 22.8 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 55.6 (DME), 69.7 (DME), 122.3–145.2 (Ar–C), 161.5 (N–CCH₃). Anal. Calcd for C₇₆H₁₁₂N₄O₄Na₂Ni₂ (1309.07): C 69.73, H 8.62, N 4.28. Found: C 69.02, H 8.71, N 3.98. IR (KBr, ν/cm^{-1}): 1640, 1584, 1456, 1427, 1380, 1360, 1320, 1253, 1217, 1022, 1058, 975, 934, 842, 792, 761, 731, 677.

Synthesis of $[L^{\bullet-}Ni(\mu-\eta^1-N_3)_2Ni(L^{\bullet-})]$ (8**).** Me₃SiN₃ (0.058 g, 0.50 mmol) was added dropwise to a stirred solution of **1** (0.255 g, 0.25 mmol) in diethyl ether (25 mL), and the solution was stirred for 12 h at room temperature. All volatiles were then removed in vacuo, and the residue extracted with THF. The extract was filtered, concentrated to about 7 mL, and stored at room temperature for several days to yield red-purple crystals of **8**·THF (0.141 g, 52%). EPR (solid, 77 K): $g_1 = 2.023$, $g_2 = 2.008$, $g_3 = 1.989$. Anal. Calcd for C₆₀H₈₈N₁₀ONi₂ (1082.79): C 66.55, H 8.19, N 12.94. Found: C 66.01, H 8.53, N 12.85. IR (KBr, ν/cm^{-1}): 2083, 1640, 1573, 1438, 1378, 1320, 1250, 1217, 1136, 1078, 912, 815, 785, 739, 686.

X-ray Crystal Structure Determinations. Data collections for all complexes were performed on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). SADABS³⁶ absorption correction was applied for all data. The structures were solved by direct methods using the SHELXS program.³⁷ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL.³⁷ The hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The bridging hydrogen atoms in complexes **1**–**4** were found from the difference Fourier map, and after assignment of these positions as hydrogen atoms, the refinement of the positional coordinates and individual isotropic displacement parameters converged. CCDC reference numbers: 887852–887862.

■ ASSOCIATED CONTENT

● Supporting Information

EPR spectra of compounds **1**, **2**, **4**, and **5**, crystal structures of **2b**, **3b**, **7**, and **9**, and detailed information of the X-ray crystal structure analysis of compounds **1**–**9** in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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