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β-Diketiminato Nickel(I) Complexes with Very Weak Ligation Allowing for H_2 and N_2 Activation

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Reaction of [L^{tBu}NiBr] (L^{tBu} = $[HC(C(CMe_3)NC_6H_3(i\mathrm{Pr})_2)_2]^-$) with KC_8 in toluene solution yields the complex [L^{tBu}Ni(toluene)], **1**, where toluene is bound in a η^2 mode via a C=C unit of the aromatic ring, as revealed by single-crystal X-ray crystallography and DFT calculations (B3LYP/6-31G*). Performing the same reaction in hexane as the solvent did not lead to a traceable product, so that the *β*-diketiminato ligand system was changed from L^{tBu} to the less bulky L^{Me} (L^{Me} = $[HC(CMeNC_6H_3(i\mathrm{Pr})_2)_2]^-$). Reduction of $[L^{Me}NiBr]_2$ with KC_8 in diethyl ether led to $[L^{Me}Ni]_2$, **2**, with intramolecular Ni–aryl interactions, while employment of [$L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2$] as a precursor for a reaction with KC_8 in OEt_2 led to the complex $[L^{Me}Ni(\mu\text{-}Br)Li(thf)_2]_2$, **3**. Both complexes **2** and **3** could be fully characterized, also with the aid of XRD, and their reactivity with respect to H_2 and N_2 was examined. It turned out that they oxidatively add H_2 to give the known compound $[L^{Me}Ni(\mu\text{-}H)]_2$, **I**, while the reaction with N_2 provides the dinitrogen complex $[(L^{Me}Ni)_2(N_2)]$, **4**.

Introduction

Nickel hydride units play decisive roles in many catalytic processes applied in industrial or academic laboratories and in nature.[1,3g] For instance the central intermediate within the catalytic cycle of the [NiFe]-hydrogenase is assumed to contain a bridging hydride ligand between the Ni and the Fe centers.[2] Altogether this has led to an increased interest in Ni–H coordination compounds.[3] Recently we have reported our results concerning the synthesis and reactivity of the compound $[(L^{Me}Ni)_2(\mu\text{-}H)_2]$, **I** (see Scheme 1), which can be prepared by treating [$L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2$] with $KBEt_3H$.[4] On dissolution, **I** does not enter into an equilibrium with a monomer [L^{Me}NiH] according to the results of spectroscopic investigations, and hence, the question arose whether a mononuclear version of this complex can be forced to form by analogy with the corresponding iron chemistry,[5] if the steric bulk at the ligand is further increased by replacing the methyl residues in L^{Me} by *tert*-butyl residues. This pushes the aryl rings at the N atoms further in front of the coordinated metal, and consequently three-coordination is preferred. The precursor [L^{tBu}NiBr] was thus reacted with $KBEt_3H$ under a dinitrogen atmosphere in hexane as the solvent. While similar conditions in the case of L^{Me} had led to a green solution of **I**, with L^{tBu} a red-brown solution was obtained, from which the first Ni^I dinitrogen complex $[(L^{tBu}Ni)_2(\mu\text{-}N_2)]$, **II**, could be isolated (Scheme 1).[6]

Complex **II** can alternatively be prepared via reduction of [L^{tBu}NiBr] by KC_8 in the presence of N_2. Looking at Scheme 1 of course the question arises whether the N_2 triggers the H_2 elimination, and what happens in a hexane solution if it is not there. Likewise, it seems interesting to investigate the reaction of precursors [L^RNiBr] with KC_8 under varying conditions: with R = Me in toluene solution the dinuclear complex $[(L^{Me}Ni)_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_6H_5Me)]$, **III**,[7] is

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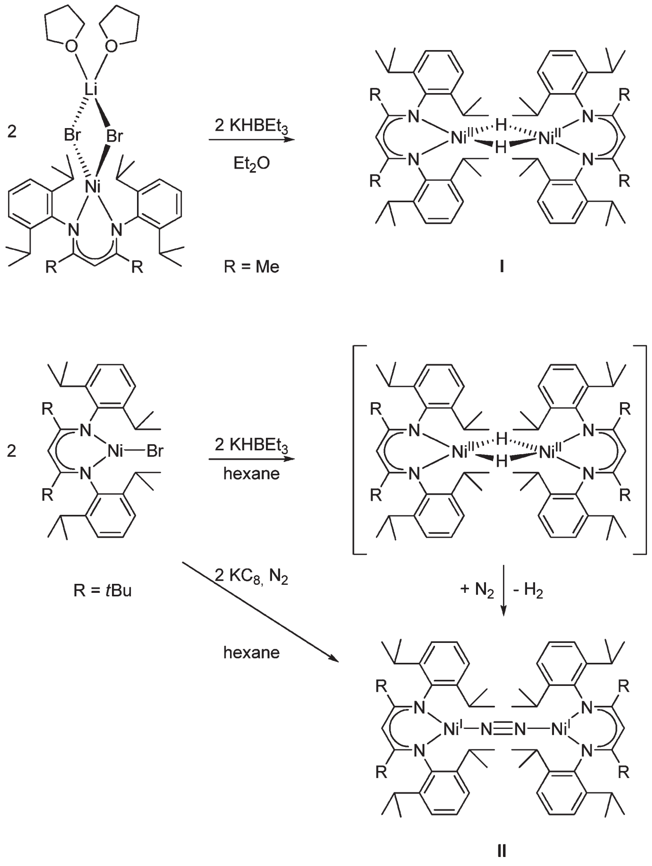
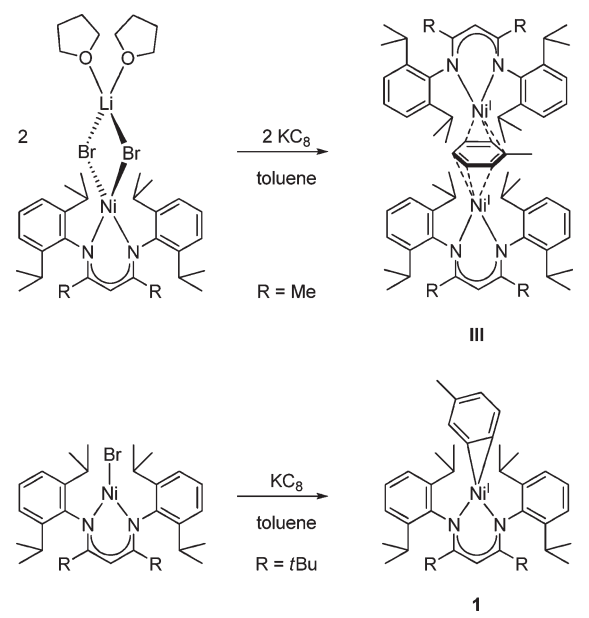
Scheme 1. Synthesis of I by Reaction of [$L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2$] with $KBEt_3H$ and Formation of II via a Potential Hydride as Well as by Reduction of [$L^{tBu}NiBr$] with KC_8



Scheme 2. In Dependence on the Ligand Residue R the Nickel(I) Compounds III or 1 are Obtained by Reduction of the Corresponding Nickel(II) Precursors in the Presence of Toluene



obtained (Scheme 2), but what sort of complex is generated if R corresponds to *tert*-butyl residues, which destabilize the binding of larger ligands at the nickel center and thus a μ-η^3:η^3-coordination mode of toluene? How does the reaction proceed in the complete absence of suitable σ- or π-donors?

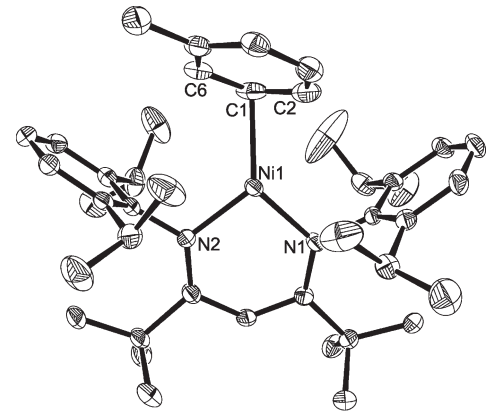


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−N1 1.9281(19), Ni1−N2 1.9121(18), Ni1−C1 2.154(2), Ni1−C2 2.437(3), Ni1−C6 2.8773(27); N1−Ni1−N2 98.61(8), N1−Ni1−C1 129.34(10), N2−Ni1−C1 124.61(10).

Results and Discussion

After suspension of [$L^{tBu}NiBr$] in toluene the reaction with KC_8 leads to a color change from green to yellow-brown. Appropriate workup allowed for the isolation of the reaction product as a yellow-brown solid in 70% yield. Crystals could be obtained via slow evaporation of the volatiles from toluene solutions at room temperature, and an X-ray crystal structure analysis revealed the product constitution as [$(L^{tBu}Ni)(\eta^2\text{-}C_6H_5Me)$] (Scheme 2), **1**. Figure 1 shows the molecular structure of **1**.

The Ni−N distances of 1.9281(19) and 1.9121(18) Å in **1** are in the range of the bond lengths found in other nickel(I) complexes containing that β-diketiminato ligand.[6] In contrast to the system [$L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2$]/$KC_8$/toluene, which leads to compound **III**, **1** does not react with a further $L^{tBu}Ni$ species to generate a dinuclear complex. Its nickel center binds asymmetrically to the toluene unit, forming two short bonds of 2.154(2) (Ni1−C1) and 2.437(3) Å (Ni1−C2) and one longer bond of 2.8773(27) Å (Ni1−C6) to the toluene carbon atoms. The nickel−carbon distances in **III** containing the sterically less demanding ligand L^{Me} are shorter in general and show a smaller variance (1.980(5)−2.209(5) Å). From this point of view the coordination mode of the arene unit in **1** would be described best as η^2. However, as hydrogen atoms cannot be localized unambiguously by means of X-ray crystallography, there remained the possibility of a σ-interaction of the metal center with a C−H bond, especially with that belonging to C1. To analyze the bonding situation in detail density functional theory (DFT) calculations (B3LYP/6-31G*) were carried out, using the molecular structure of **1** as starting geometry (see Supporting Information). The optimized structure is shown in Figure 2. As expected, calculations predict a doublet ground state with the unpaired electron located at the Ni center. A detailed natural bond orbital (NBO) analysis revealed a significant stabilization of the $L^{tBu}Ni$ molecule (183 kJ/mol) by a donor−acceptor interaction between an occupied Ni(d) orbital and the empty π^* orbital of the C1−C2 bond. Further stabilization (106 kJ/mol) is achieved by a back-donation from the occupied π orbital of the C1−C2 bond to the empty Ni(4s) orbital. Since other

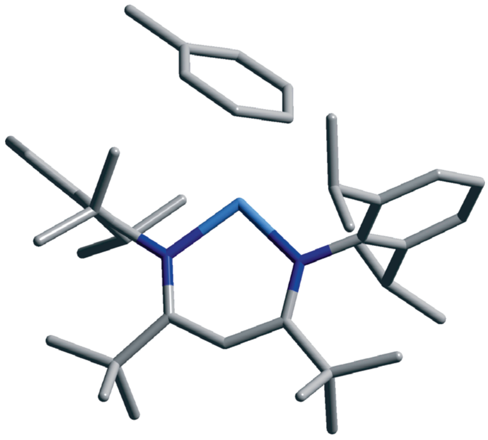


Figure 2. Optimized structure of **1** according to DFT calculations (B3LYP/6-31G*, doublet state). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Ni−C1 2.065, Ni−C2 2.141, Ni−C6 3.009; C1−Ni−C2 39.58.

donor−acceptor interactions involving the Ni atom are much weaker, this makes clear that the coordination of the toluene molecule indeed occurs in a η^2 mode.

The magnetic moment of 2.06 μ_B displayed by **1** in the solid state at room temperature is only slightly higher than the expected spin-only value of 1.73 μ_B for one unpaired electron and thus points to the oxidation state of +I at the nickel center, in agreement with the theoretical data. The EPR spectrum of **1** (see Supporting Information) in the solid state at 77 K shows a rhombic signal ($g_x = 2.468$, $g_y = 2.152$, $g_z = 2.072$), which further supports the formulation of **1** as a nickel(I) complex, by comparison with the results found for other β-diketiminato nickel(I) complexes.[4,7,8]

When the same reaction was performed in hexane instead of toluene as the solvent, an orange solid precipitated from the reaction mixture. An attempt to separate this solid from the concomitantly produced graphite by using more polar solvents than hexane was unsuccessful, as only the corresponding solvent adducts [$\mathrm{L}^{t\mathrm{Bu}}$Ni(solv)] (with solv = diethyl ether,[6] toluene) could be isolated. When hexane suspensions of this product were allowed to react with dinitrogen, the dinitrogen complex **II** was generated. We therefore assume the orange solid to correspond to a transient nickel(I) species similar to the corresponding iron compound [$\mathrm{L}^{t\mathrm{Bu}}$Fe(KCl)(solv)$_x$] reported by Holland et al.,[9] which is supported by results obtained for the analogous system with L^{Me} (vide infra). Similar observations could be made when [$\mathrm{L}^{t\mathrm{Bu}}$NiBr] suspended in hexane was treated with $\mathrm{KBHEt_3}$ in an argon instead of a $\mathrm{N_2}$ atmosphere: an orange solid precipitated from the reaction mixture, but again all efforts to isolate or to crystallize the compound failed. Hence we have reduced the sterics around the Ni centers somewhat by replacing $\mathrm{L}^{\mathrm{tBu}}$ by L^{Me} and found that depending on the starting materials, different types of Ni^{I} complexes are formed: Reduction of [L^{Me}NiBr]$_2$, which can be obtained from [L^{Me}Ni(μ-Br)$_2$Li(thf)$_2$] by heating it in toluene,[10] with $\mathrm{KC_8}$ in hexane led to a red-brown solution from which [(L^{Me}Ni)$_2$], **2**, could be isolated in 23% crystalline yield (Scheme 3). Its molecular structure as revealed by single-crystal X-ray diffraction analysis is shown in Figure 3.

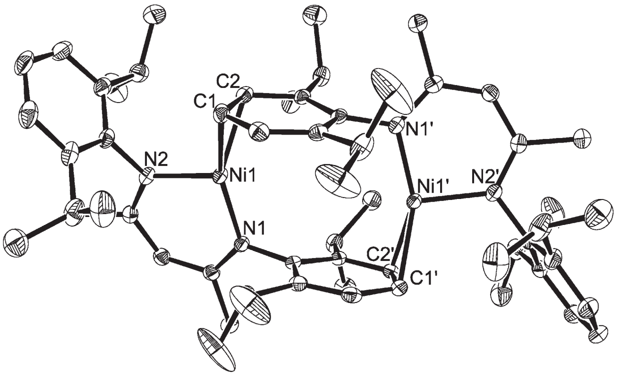
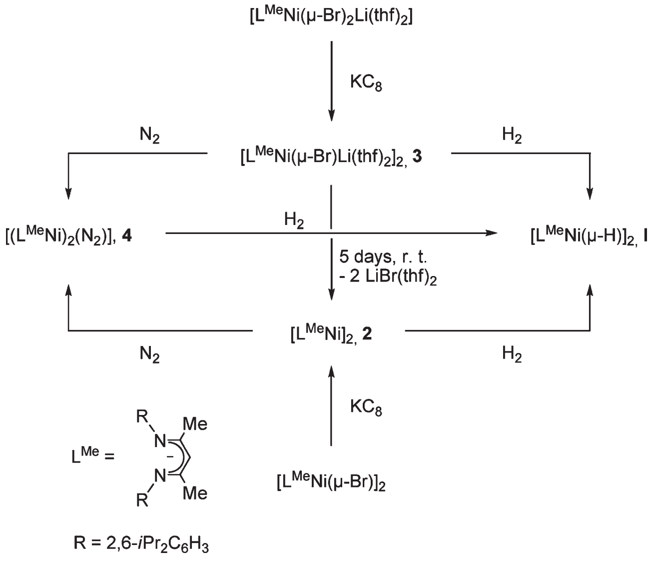


Figure 3. Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−N1 1.9062(13), Ni1−N2 1.9350(14), Ni1−C1 2.1337(15), Ni1−C2 2.0747(15); N1−Ni1−N2 97.30(6), N1−Ni1−C1 149.56(6), N1−Ni1−C2 145.46(6), N2−Ni1−C1 106.45(6), N2−Ni1−C2 109.89(6).

Scheme 3. Synthesis of the Nickel(I) Complexes 2 and 3 and Their Conversion into the Compounds 4 and I upon Exposure to Dinitrogen and Dihydrogen, Respectively



In **2** the nickel ions bind to the β-diketiminato-N atoms as well as to an aryl ring of a second L^{Me}Ni unit of the dimer in a η^2-coordination mode. This constitution becomes possible due to the T-shaped geometry around the nickel ions that is typical for nickel(I) complexes of β-diketiminato ligands:[4,7,11] The N1−Ni1−C1 and N2−Ni1−C1 angles amount to 149.56(6)° and 106.45(6)°, respectively, and this asymmetry is also expressed in two different Ni−N bond lengths of 1.9062(13) and 1.9350(14) Å. In consequence the two

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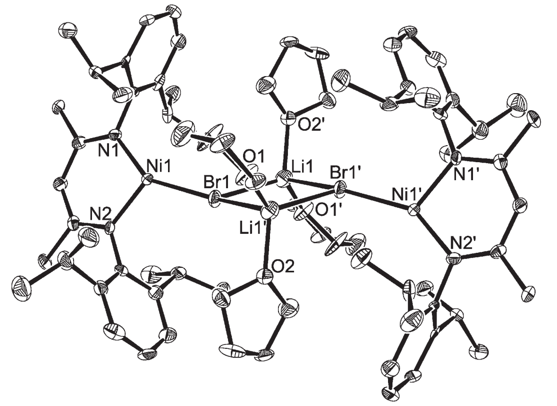

Figure 4. Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−N1 1.910(5), Ni1−N2 1.887(5), Ni1−Br1 2.3652(10), Br1−Li1 2.595(11), Br1−Li1′ 2.465(11); N1−Ni1−N2 98.8(2), N1−Ni1−Br1 114.28(15), N2−Ni1−Br1 146.66(16).

coordinating arene units are nearly parallel to each other with a dihedral angle of 7.177(60)° between the two aromatic planes and distances between the C atoms of one aromatic unit and the plane of the second one ranging from 3.68 to 4.03 Å, which may indicate extra stabilization due to $\pi-\pi$ interactions.[12]

Preliminary measurements concerning the magnetic moments of **2** in the solid state as well as in solution point to two basically uncoupled Ni^I centers at room temperature with spins of $S_1 = S_2 = 1/2$, which is probably due to the thermal energy antagonizing the coupling: single-point DFT calculations (B3LYP/6-31G*) based on the molecular structure of **2** predict an antiferromagnetic coupling between the two metal centers, leading to a broken symmetry singlet ground state (see Supporting Information). The coupling may be mediated by $\pi-\pi$ stacking interactions of the ligand aryl units, similarly to that in a case recently described by Wieghardt et al.,[13] and the diamagnetism of **III** is also due to antiferromagnetic coupling via an aryl unit.[7] Consistently, compound **2** is EPR silent at 77 K in frozen hexane solutions as well as in the solid state.

The same kind of compound is formed if in L^{Me} the isopropyl residues are replaced by ethyl residues (see Supporting Information, complex **2a**).

By contrast, reaction of the "ate-complex" $[L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2]$[7] with KC_8 in diethyl ether led to the isolation of the orange-red complex $[L^{Me}Ni(\mu\text{-}Br)Li(thf)_2]_2$, **3**, in 29% yield, as revealed by X-ray diffraction analysis (Scheme 3). The molecular structure of **3** is shown in Figure 4. Two $L^{Me}Ni^I$ moieties are coordinated to a Li_2Br_2 unit, so that, again, a T-shaped coordination sphere results for the Ni centers: The N1−Ni1−Br1 and N2−Ni1−Br1 angles amount to 114.28(15)° and 146.66(16)°, respectively. The lithium ions are additionally coordinated by two thf molecules, thus yielding a distorted tetrahedral coordination geometry around lithium. Hence, the structure of **3** is similar to the one displayed by the iron compound $[L^{tBu}Fe(KCl)(18\text{-}crown\text{-}6)]$[5a] and represents—to our knowledge—the first example of a complex where an alkali metal halide segment is coordinated to a Ni^I center. If **3** is dissolved in toluene, the complex $[(L^{Me}Ni)_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_6H_5Me)]$, **III**, is formed immediately, as confirmed by ^1H NMR spectroscopy. Consequently it appears plausible that **3** represents an intermediate species in the formation of **III** from $[L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2]$ and KC_8. Additionally, **3** seems to be only metastabile and readily eliminates LiBr to give $[(L^{Me}Ni)_2]$, **2**: If concentrated solutions of **3** in hexane are stored at room temperature for several days, the precipitation of a white solid, which presumably corresponds to $Li(thf)_2Br$, and the formation of crystalline $[(L^{Me}Ni)_2]$, **2**, can be observed.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 1, 2, and 3

	1	**2**	**3**
formula	$C_{42}H_{61}N_2Ni$	$C_{58}H_{82}N_4Ni_2$	$C_{74}H_{114}Br_2$-$Li_2N_4Ni_2O_4$
weight, g mol^{-1}	652.64	952.70	1414.81
temp, K	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/c$
a, Å	9.9120(4)	17.0249(8)	21.8673(6)
b, Å	16.9945(5)	18.1902(9)	19.8655(5)
c, Å	22.2217(9)	16.8559(7)	17.5029(5)
α, deg	90	90	90
β, deg	96.818(3)	90.302(4)	91.549(2)
γ, deg	90	90	90
V, Å^3	3716.8(2)	5220.0(4)	7600.6(4)
Z	4	4	4
density, g cm^{-3}	1.166	1.212	1.236
μ(Mo Kα), mm^{-1}	0.552	0.761	1.593
F(000)	1420	2056	3000
GoF	0.830	0.913	0.819
R_1 [$I > 2\sigma(I)$]	0.0402	0.0282	0.0685
wR_2 [all data]	0.0760	0.0654	0.1241
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	0.539/−0.472	0.494/−0.338	0.880/−0.577

At room temperature complex **3** exhibits a magnetic moment in solution of $\mu_{eff} = 2.58\ \mu_B$ (Evans' method,[14] pentane-d_{12}), which points to the presence of two uncoupled spins of $S_1 = S_2 = 1/2$ (the spin-only value expected for two uncoupled Ni^I ions amounts to 2.45 μ_B). The EPR spectrum of **3** at 77 K in the solid state shows a rhombic signal (g_x = 2.441, g_y = 2.237, g_z = 2.085), which further supports that formulation (see Supporting Information).

Having learned that in the absence of donors **I** is thermodynamically stable in hexane solution at room temperature, naturally the question occurred, whether **2** or **3** can be reacted with H_2 to give **I** in a binuclear oxidative addition. For this purpose a hexane solution of **3** was stirred under an atmosphere of hydrogen. In the course of 16 h a color change from red to green could be observed with concomitant precipitation of a white solid ($Li(thf)_2Br$). Filtration and removal of the solvent afforded the hydride **I** in good yields (53%). In the case of **2** an immediate color change from brown to red-orange could be observed when a hexane solution was exposed to a dihydrogen atmosphere. Subsequently, this reaction mixture turns to green within 1 h, and from such solutions again **I** could be isolated in 86% yield. The initial color change is suggestive of an intermediate species between **2** and **I**, but so far all attempts to isolate that intermediate were unsuccessful. Reactions of **2** and **3** with H_2 are possible only due to their strained structures and weak ligation. **III**, for instance, seems to be far more stable (although the toluene ligand is also readily displaced by

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stronger donors)[7,8c,15] and remains unchanged in contact with H_2 (16 h stirring of a hexane suspension under an H_2 atmosphere). **III** is also stable in a dinitrogen atmosphere, while, consistently, **2** and **3** react instantaneously: If hexane solutions of **2** and **3** are exposed to N_2, the immediate precipitation of the dinitrogen complex $[(L^{Me}Ni)_2(N_2)]$, **4** (the L^{Me} derivative of **III**, see Scheme 1), which is poorly soluble in this solvent, can be observed. In turn, the reaction of **4** with dihydrogen also results in the formation of **I**. This finding is in contrast to the analogous iron chemistry where the corresponding dinitrogen complex $[(L^{tBu}Fe)_2(N_2)]$ does not react with dihydrogen,[16,17] probably due to the stronger activation of the N_2 unit within the iron compound as compared to that within **4**. However, treatment of a mixture of $[L^{tBu}FeCl]$ and KC_8 in diethyl ether with dihydrogen yielded the hydride complex $[L^{tBu}Fe(\mu\text{-}H)]_2$.[16]

An overview of the various synthetic routes to **4** as well as **I** starting from different nickel(I) complexes is given in Scheme 3.

Conclusions

Three novel complexes are reported that contain $L^{R}Ni^{I}$ complex metal fragments (R = Me, *t*Bu): In **1** the coordination sphere of $L^{tBu}Ni$ is saturated by a toluene ligand binding in a η^2-coordination mode, while the aryl rings of L^{Me} are serving as intramolecular donors in the dimer $[L^{Me}Ni]_2$, **2**. $[L^{Me}Ni(\mu\text{-}Br)Li(thf)_2]$, **3**, contains a Li_2Br_2 diamond core unit between two $L^{Me}Ni$ units, which is bound only very loosely, considering that it is eliminated continuously on storing of complex solutions at room temperature with concomitant formation of **3**. **2** and **3** are therefore very reactive sources of transient $L^{Me}Ni^{I}$: They even react with H_2 and N_2 to give $[L^{Me}Ni(\mu\text{-}H)]_2$ and $[(L^{Me}Ni)_2(N_2)]$, respectively, while the known $L^{Me}Ni^{I}$ precursor $[(L^{Me}Ni)_2(\text{toluene})]$, **III**, is inert. These compounds are thus the most reactive representatives of this substance class, and future research will now further exploit its chemistry.

Experimental Section

General Procedures. All experiments were carried out in a dry nitrogen/argon atmosphere using a glovebox and/or standard Schlenk techniques. Solvents were purified employing an MBraun SPS solvent purification system. IR spectra were recorded on solid samples prepared as KBr pellets with a Shimadzu FTIR-8400S spectrometer. Microanalyses were performed on a Leco CHNS-932 elemental analyzer. Magnetic measurements of the solids were performed with an Alfa magnetic susceptibility balance at RT. Solution magnetic susceptibilities were determined by the Evans method with a Bruker AV 400 NMR spectrometer (^{1}H 400.13 MHz).[14] EPR spectra were recorded at the X-band spectrometer ERS 300 (ZWG/Magnettech Berlin/Adlershof, Germany) equipped with a fused quartz Dewar for measurements at liquid nitrogen temperature. The *g*-factors were calculated with respect to a Cr^{3+}/MgO reference (g = 1.9796).

Materials. The complexes $[L^{tBu}NiBr]$,[6] $[L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2]$,[7] and $[L^{Me}Ni(\mu\text{-}Br)]_2$[10] were prepared according to the literature methods.

Syntheses. $[(L^{tBu}Ni)(\eta^2\text{-}C_6H_5Me)]$ (1). $[L^{tBu}NiBr]$ (600 mg, 0.94 mmol) and KC_8 (165 mg, 1.22 mmol, 1.3 equiv) were suspended in 20 mL of toluene, and the reaction mixture was stirred for 12 h at room temperature. After filtration from the graphite the solvent was removed under vacuum. The resulting yellow-brown residue was extracted with 10 mL of hexane, and the solvent was removed again, affording **1** (430 mg, 0.66 mmol, 70%) as a brown solid. Crystals suitable for X-ray crystallography could be obtained by slow evaporation of a toluene solution at room temperature. Anal. (%) Calcd for $C_{42}H_{61}N_2Ni$ (652.64 g mol^{-1}): C 77.29, H 9.42, N 4.29. Found: C 75.67, H 9.55, N 4.65 (consistently low C analyses may result from formation of NiC upon combustion); μ_{eff} = 2.06 μ_B (295 K, $\mu_{s.o.}$ = 1.73 μ_B);

$[L^{Me}Ni]_2$ (2). $[L^{Me}NiBr]_2$ (232 mg, 0.42 mmol) and KC_8 (85 mg, 0.63 mmol, 1.5 equiv) were suspended in 20 mL of diethyl ether, and the reaction mixture was stirred for 16 h. The solvent was removed under vacuum, and the brown residue was extracted with 8 mL of hexane. Cooling of the brown solution to −30 °C afforded **2** as brown crystals (47 mg, 0.05 mmol, 23%). Anal. (%) Calcd for $C_{58}H_{82}N_4Ni_2$ (952.69 g mol^{-1}): C 73.12, H 8.68, N 5.88. Found: C 72.42, H 8.87, N 5.58 (consistently low C analyses may result from formation of NiC upon combustion).

$[L^{Me}Ni(\mu\text{-}Br)Li(thf)_2]_2$ (3). $[L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2]$ (1.5 g, 1.90 mmol) and KC_8 (320 mg, 2.38 mmol, 1.25 equiv) were suspended in 20 mL of diethyl ether, and the reaction mixture was stirred for 16 h. The solvent was removed under vacuum, and the red solid was extracted with 5 mL of hexane. Cooling of the solution to −30 °C afforded **3** as dark red crystals (387 mg, 0.27 mmol, 29%). Anal. (%) Calcd for $C_{74}H_{114}Br_2Li_2N_4Ni_2O_4$ (1414.80 g mol^{-1}): C 62.82, H 8.12, N 3.96, Br 11.30. Found: C 62.35, H 8.15, N 4.06, Br 11.65 (consistently low C analyses may result from formation of NiC upon combustion); μ_{eff} = 2.58 μ_B (Evans method, pentane-d_{12}, 297 K, $\mu_{s.o.}$ = 2.45 μ_B).

$[(L^{Me}Ni)_2(N_2)]$ (4). Method A, starting from **2**: A solution of **2** (50 mg, 0.05 mmol) in 5 mL of hexane was stirred for 12 h in a dinitrogen atmosphere, during which the precipitation of a brown solid occurred. Removal of the solvent under vacuum afforded **4** as a brown solid (41 mg, 0.04 mmol, 80%). Method B, starting from **3**: A solution of **3** (50 mg, 0.04 mmol) in 5 mL of hexane was stirred in a dinitrogen atmosphere for 12 h, during which the precipitation of a brown solid occurred. Filtration and exhaustive extraction with hexane (approximately 100 mL) and removal of the solvent under vacuum afforded **4** as a brown solid (31 mg, 0.03 mmol, 89%). Anal. (%) Calcd for $C_{58}H_{82}N_6Ni_2$ (978.53 g mol^{-1}): C 71.03, H 8.43, N 8.57. Found: C 69.64, H 8.49, N 7.58 (due to the rather high reactivity and sensitivity of **4**, elemental analyses always showed deviations higher than commonly accepted). IR (KBr): 2170 (vw, ν_{NN}) cm^{-1}.

$[L^{Me}Ni(\mu\text{-}H)]_2$ (I). (alternative route starting from 3). A solution of **3** (50 mg, 0.07 mmol) in hexane (7 mL) was stirred in a hydrogen atmosphere for 14 h. The resulting green solution was filtered off from the white precipitate, and the solvent was removed under vacuum to afford **I** (18 mg, 0.04 mmol, 53%) as a dark green solid. The synthesis of **I** starting from **2** and **4** was performed in an identical fashion (86% and 75% yield, respectively).

Crystal Structure Determinations. The crystal data were collected on a Stoe IPDS 2T diffractometer using Mo Kα radiation, λ = 0.71073 Å. In all cases, the structures were solved by direct methods (SHELXS-97)[18] and refined versus F^2 (SHELXL-97)[19]

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[15] (a) Yao, S.; Bill, E.; Milsmann, C.; Wieghardt, K.; Driess, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7110. (b) Yao, S.; Milsmann, C.; Bill, E.; Wieghardt, K.; Driess, M. *J. Am. Chem. Soc.* **2008**, *130*, 13536. (c) Yao, S.; Xiong, Y.; Zhang, X.; Schlangen, M.; Schwarz, H.; Milsmann, C.; Driess, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4551.

[16] Dugan, T. R.; Holland, P. L. *J. Organomet. Chem.* **2009**, *694*, 2825.

[17] Whether $[(L^{Me}Fe)_2(N_2)]$ also is inert toward dihydrogen was not reported. However, its reactivity should be higher than that of $[(L^{tBu}Fe)_2(N_2)]$.

[18] Sheldrick, G. M. *SHELXS-97*, Program for Crystal Structure Solution; University of Göttingen, 1997.

[19] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen, 1997.

with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. Relevant crystallographic data are collected in Table 1.

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Supporting Information Available: CIF file containing full details of the structural analysis of complexes **1**, **2**, **2a**, and **3**, experimental procedure for **2a**, crystal structure of **2a** (Figure S1), EPR spectra of **1** and **3**, text describing the DFT method including a full citation of the Gaussian 03 program. This material is available free of charge via the Internet at http://pubs.acs.org.