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N_2 Activation

A Dinuclear Nickel(I) Dinitrogen Complex and its Reduction in Single-Electron Steps**

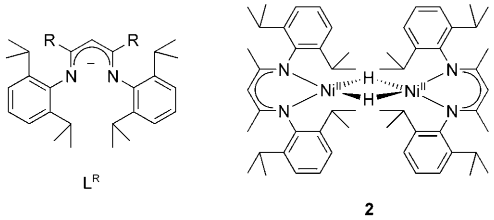
Stefan Pfirrmann, Christian Limberg, Christian Herwig, Reinhard Stößer, and Burkhard Ziemer*

Dedicated to Professor Michael Linscheid on the occasion of his 60th birthday

N_2—a small and readily accessible molecule—is known to be notoriously unreactive and eludes coordination unless certain conditions are fulfilled. Hence, the activation of dinitrogen has been a challenge for a long time, and a lot of effort has been spent to synthesize dinitrogen complexes, especially in the context of structural or functional modeling of biological nitrogen fixation.[1] The last decades have led to tremendous progress in understanding the binding modes and reactivity patterns of N_2 in transition-metal complexes, culminating in the first catalytic cycle for conversion of N_2 into ammonia.[2]

N_2 complexes can be subdivided into weakly, moderately, strongly, and highly activated systems, according to the degree of elongation of the N–N bond and the decrease of the ν_{NN} frequency.[3] Usually, complexes with terminal N_2 coordination show weak or moderate activation, while N_2 bridging two transition metals in an end-on mode can be weakly, moderately, or strongly activated.[4] More recently, the coordination of dinitrogen to highly reduced transition-metal ions bearing sterically hindered ligands has proven to be a very successful synthetic route to complexes with activated N_2 ligands. Pioneering work was performed by Holland and co-workers employing β-diketiminato ligands L^R ($L^R = [HC(CRNC_6H_3(iPr)_2)_2]^-$, Scheme 1) with R = *t*Bu.[5] Reduction of a corresponding Fe^{II} complex as precursor in the presence of dinitrogen led to the compound $[L^{tBu}Fe(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)FeL^{tBu}]$ (**1**) in which each iron site donates significant electron density into the π* orbitals of dinitrogen, resulting in a configuration best described as two high-spin Fe^{II} ions bridged by a triplet N_2^{2-} ion. It further proved possible to doubly reduce this unit.[5] Studies with other bulky ligands and low-coordinate metals followed,[6,7] and in three of these, β-diketiminates (L^{Me}) were again employed, in combination with the elements Ti, Ir, and Cr.[7]

Literature concerning Ni/N_2 compounds is rather scarce, and the few reported examples mainly contain phosphines as coligands. Early work from the 1970s included the Ni^0 compound $[(Cy_3P)_2NiN_2Ni(PCy_3)_2]$[8] (Cy = cyclohexyl) and π-bonded N_2 in Ni/Li salts.[9] It took 30 years before the only other known Ni-N_2 complex was isolated in 2005,[10] with N_2 bound to Ni^0 in an end-on fashion.[11] We recently reported the synthesis and reactivity of the compound $[L^{Me}Ni(\mu\text{-}H)_2NiL^{Me}]$ (**2**, Scheme 1).[12] Attempts to synthesize a mononuclear version of this complex by changing the ligand to L^{tBu} and treating the corresponding precursor with a hydride source in a dinitrogen atmosphere has now led us to the first Ni^I dinitrogen complex.



Scheme 1. Ligand L^R and $[L^{Me}Ni(\mu\text{-}H)_2NiL^{Me}]$ (**2**).

Compound **2** can be prepared by treating $[L^{Me}Ni(\mu\text{-}Br)_2Li(thf)_2]$ with $KBEt_3H$, and according to spectroscopic investigations it does not enter into an equilibrium in solution with the monomer $[L^{Me}NiH]$.[12] Hence, the question arose as to whether such a monomer $[L^RNiH]$, by analogy to the corresponding iron chemistry, can be forced to form if the steric bulk at the ligand is increased by replacing the methyl residues in L^{Me} by *tert*-butyl residues.[13] This alteration pushes the aryl rings at the nitrogen atoms further in front of the coordinated metal, and hence the bromide precursor, for instance, does not form an ate complex (see above) but can be isolated as $[L^{tBu}NiBr]$ with three-coordinate Ni^{II} ions. $[L^{tBu}NiBr]$ was thus treated 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 **2**, with L^{tBu} a red-brown solution was obtained. Crystallization of the product and X-ray diffraction analysis revealed it to be $[L^{tBu}Ni(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)NiL^{tBu}]$ (**3**, Scheme 2).[14] Its molecular structure is displayed in Figure 1.

The N_2 molecule in **3** is coordinated in an end-on mode bridging two three-coordinated Ni centers. Their coordination spheres can be described as T-shaped planar (sum of bond angles 359.45(11)°), which is often found for Ni^I complexes containing β-diketiminato ligands.[12,15] By comparison to data for other L^RNi^I complexes,[12] EPR measurements indicate an oxidation state of +I at the nickel ions, too.

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[*] Dipl.-Chem. S. Pfirrmann, Prof. Dr. C. Limberg, Dr. C. Herwig, Prof. Dr. R. Stößer, Dr. B. Ziemer
Humboldt-Universität zu Berlin, Institut für Chemie
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
Fax: (+49) 30-2093-6966
E-mail: christian.limberg@chemie.hu-berlin.de
Homepage: http://www.chemie.hu-berlin.de/aglimberg

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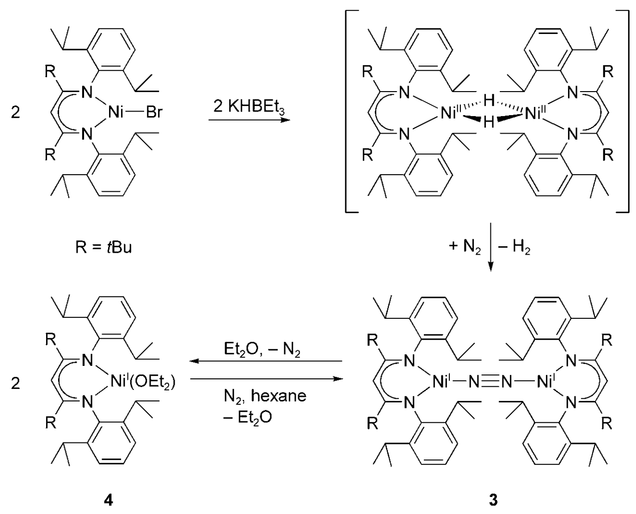


Scheme 2. Formation of **3** via a potential hydride intermediate and reaction of **3** with diethyl ether.

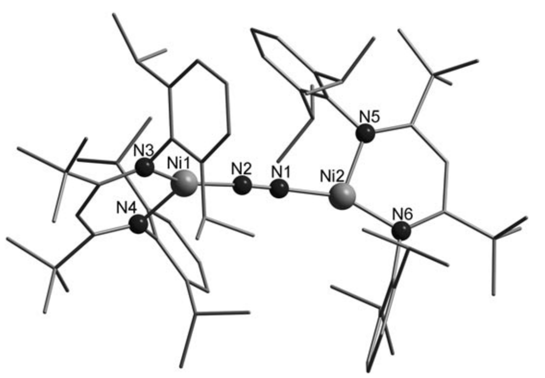
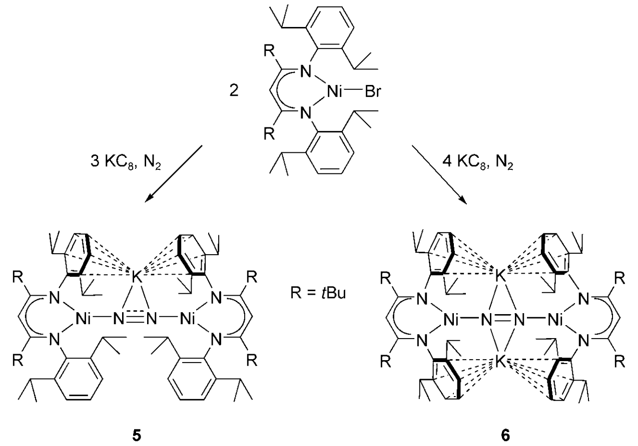


Figure 1. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–N2 1.120(4), Ni1–N2 1.836(3), Ni2–N1 1.830(3), Ni1–N3 1.880(3), Ni1–N4 1.920(3), Ni2–N5 1.927(3), Ni2–N6 1.882(3); N2-Ni1-N3 153.98(12), N2-Ni1-N4 107.75(11), Ni1-N2-N1 174.1(3), N3-Ni1-N4 97.91(11), N1-Ni2-N5 107.51(11), N1-Ni2-N6 153.97(11), N5-Ni2-N6 97.97(11).

Single-point DFT calculations (B3LYP/6-31G*) based on the molecular structure of **3** including consideration of broken-symmetry states predict a triplet ground state (see the Supporting Information). Room-temperature magnetic measurements found $\mu_{\text{eff}} = 2.40\mu_B$ (Evans method in C_5D_{12}; hardly any change was observed on cooling to 203 K; the spin-only value $\mu_{\text{s.o.}}$ expected for two uncoupled Ni^{I} ions is $2.45\mu_B$). These results are in line with two uncoupled or very weakly coupled metal centers of spin $^1/_2$. Because the two {L^{tBu}Ni} units are twisted with respect to each other in the solid state, the structure does not contain a center of inversion, thus allowing for IR spectroscopic investigation of the ν_{NN} stretching mode. The corresponding band was identified at 2164 cm^{-1}, and it shifted to 2093 cm^{-1} when $^{15}N_2$ was used, which points to a weakening of the N–N bond (ν_{NN} for free $^{14}N_2$ 2331 cm^{-1} and for $^{15}N_2$ 2254 cm^{-1}, see the Supporting Information),[16] in agreement with a N–N bond that is only slightly elongated ($\Delta(d_{NN})$ 0.022 Å) in comparison to the free N_2 molecule. Hence, the transfer of electron density from the Ni atoms to the N_2 molecule is far less pronounced than in case of the iron compound **1** (ν_{NN} 1778 cm^{-1}, $\Delta(d_{NN})$ 0.084 Å),[5a] which is also consistent with the formulation of **3** as a Ni^{I} complex. However, the degree of N_2 activation in **3** is comparable to that found for the Ni complexes mentioned above.

Formation of **3** can be explained by assuming that [{L^{tBu}NiH}$_2$] is formed initially, but its increased steric demand makes it even more reactive than **2**, and even contact with N_2 triggers H_2 elimination (H_2 elimination from **2** occurs only on addition of stronger neutral donors)[12] to yield **3**, in which the strain is released, as the Ni centers are only three-coordinate and the bridging unit is larger. As observed for other N_2 complexes,[5b,7,8] the N_2 ligand is readily displaced by other ligands, including by exogenous N_2 molecules. When the ^{15}N isotopologue [L^{tBu}Ni^{15}N^{15}NNiL^{tBu}] is stirred in a $^{14}N_2$ atmosphere, complete exchange occurs within 10 min. In contact with diethyl ether, [L^{tBu}Ni(OEt$_2$)] (**4**) is formed with concomitant N_2 evolution. Compound **4** in turn reacts to give **3** after dissolution in N_2-saturated hexane. Accordingly, **3** might serve as a suitable Ni^{I} source that could replace [(L^{Me}Ni)$_2$(μ-η^3:η^3-C_6H_5Me)][17] if toluene is undesirable in subsequent reactions.[17b] Alternatively, **3** can also be prepared by reduction of [L^{tBu}NiBr] by KC_8 in the presence of N_2.

Complex **3**—isolated or prepared in situ—can be further reduced by KC_8, and remarkably, it is possible to achieve this conversion in single-electron steps. Treatment of [L^{tBu}NiBr] with 1.65 equivalents KC_8 reproducibly leads to a red-purple compound that was identified as K[L^{tBu}Ni(μ-η^1:η^1-N_2)NiL^{tBu}] (**5**, Scheme 3) by single crystal X-ray diffraction analysis.[14]



Scheme 3. Synthesis of **5** and **6** by reaction of [L^{tBu}NiBr] with KC_8 in a dinitrogen atmosphere.

The molecular structure of **5** is shown in Figure 2. The N–N bond is lengthened from 1.120(4) Å in **3** to 1.143(8) Å, and ν_{NN} could be detected at 1825 cm^{-1} in the Raman spectrum (1765 cm^{-1} for the ^{15}N isotopologue, Figure 4). The coordination spheres of the Ni centers can now be described as trigonal planar (sum of bond angles 359.9(3)°), and the alkali-metal cation produced in the reduction process interacts with the N_2 fragment as well as with the aryl rings of the ligand.

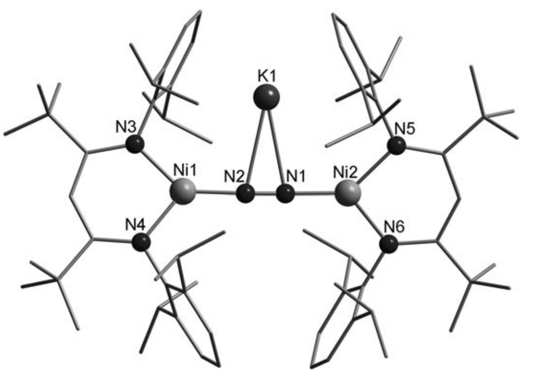


Figure 2. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–N2 1.143(8), Ni1–N2 1.770(7), Ni2–N1 1.770(7), Ni1–N3 1.917(6), Ni1–N4 1.908(7), Ni2–N5 1.928(7), Ni2–N6 1.918(6), K1–N1 2.764(8), K1–N2 2.773(8); N2-Ni1-N3 135.1(3), N2-Ni1-N4 127.6(3), N3-Ni1-N4 97.2(3), N1-Ni2-N5 134.0(3), N1-Ni2-N6 128.5(3), N1-N2-Ni1 174.1(8), N5-Ni2-N6 97.4(3), N1-K1-N2 23.82(17).

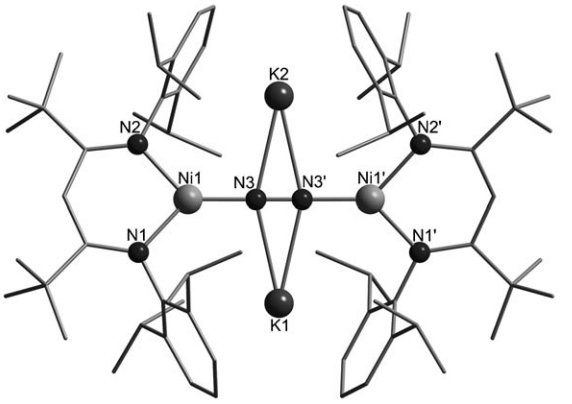


Figure 3. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N3–N3′ 1.185(8), Ni1–N1 1.931(5), Ni1–N2 1.933(4), Ni1–N3 1.747(4), K1–N3 2.719(6), K2–N3 2.714(6); N2-Ni1-N3 130.8(2), N1-Ni1-N3 132.5(2), N1-Ni1-N2 96.68(18), Ni1-N3-N3′ 178.8(7), N3-K1-N3′ 25.17(18), N3-K2-N3’ 25.21(18).

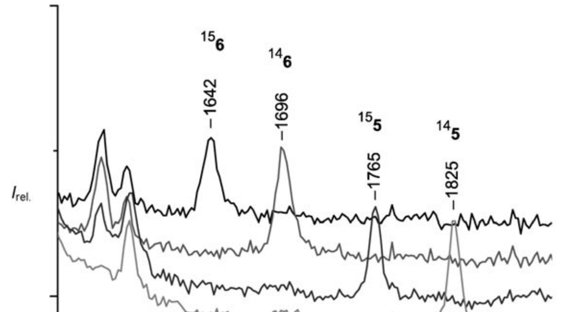


Figure 4. Raman spectra of ^{15}**6**, ^{14}**6**, ^{15}**5**, and ^{14}**5** in the region from 1525 to 1900 cm^{-1}. The spectra were recorded in hexane at room temperature employing an Ar$^+$ ion laser with a wavelength of 514.5 nm and a power of 100 mW (^{15}**5** and ^{14}**5**) or 20 mW (^{15}**6** and ^{14}**6**).

In **5** the $[NiNNNi]^{2+}$ core of **3** is reduced by one electron. Starting from two unpaired electrons in **3**, this reduction can lead to a quartet or a doublet ground state. The magnetic moment of $\mu_{eff} = 1.66\,\mu_B$ found for **5** in the solid state points to the latter ($\mu_{s.o.} = 1.73\,\mu_B$ for one unpaired electron), and again an EPR spectrum typical for L^RNi^I complexes is observed. Evidently, the additional electron couples very strongly antiferromagnetically to one of the original unpaired Ni^I electrons, and the question arises as to whether it has been added to a d orbital (→Ni^0) or to an N-based orbital. The results of preliminary single-point DFT investigations and a natural bond orbital analysis reveal that the positive charge at the potassium ion is compensated mainly by an increased negative charge at the N_2 unit, suggesting that the additional electron is located mainly at the N_2 ligand. Considering the electronic structure of the unreduced complex **3**, calculations indicate that the two unoccupied spin orbitals of lowest energies have N–N π* antibonding character (see the Supporting Information). Population of these orbitals is expected to weaken the N–N bond, as observed experimentally for the reduced compound **5**. Consistently, DFT predicts a doublet ground state for **5** and a spin-density distribution corresponding to one spin-up electron at each nickel atom and one spin-down electron in an N–N π* orbital between the Ni atoms.

Addition of 2.3 equivalents KC_8 to $[L^{tBu}NiBr]$ leads to doubly reduced **3** as a deep purple solid. The molecular structure of the product $K_2[L^{tBu}Ni(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)NiL^{tBu}]$ (**6**, Scheme 3) as revealed by single crystal X-ray diffraction analysis is shown in Figure 3.[14] The trigonal-planar coordination around the nickel centers found for **5** is maintained in **6** (sum of bond angles 359.98(18)°). The second potassium ion is positioned opposite to the first one, and it, too, interacts with the N_2 unit as well as with the two remaining aromatic residues of the β-diketiminato ligands. The additional electron leads to a further lengthening of the N–N bond to 1.185(8) Å,[18] while the distances between the dinitrogen N atoms and the nickel centers in **6** (1.747(4) Å) become significantly shorter than those in the less reduced compounds (1.836(3) and 1.830(3) Å in **3** and 1.770(7) Å in **5**). The Ni–N(dinitrogen) distances of both **5** and **6** lie between the bond lengths reported for β-diketiminato nickel amido complexes ($[L^{Me}NiN(SiMe_3)_2]$ 1.873(2) Å)[19] and those found for β-diketiminato nickel imido complexes ($[L^*Ni{=}NAd]$ 1.662(2) Å, $L^* = [HC(CMeNC_6H_3(Me)_2)_2]^-$, Ad = adamantyl).[15b] Hence, the N_2 unit in **6** has diazene character. In keeping with this assessment, the ν_{NN} band of **6** appears at 1696 cm^{-1} and is shifted further to 1642 cm^{-1} upon ^{15}N enrichment (Figure 4). Calculations predict a singlet ground state for **6**, and indeed **6** shows diamagnetic behavior, giving rise to sharp signals in its NMR spectra (see the Supporting Information). Further experiments showed that it is possible to perform comproportionation reactions with **6** and $[L^{tBu}NiBr]$ (3:2) or **3** (1:1) as alternative routes to **5**.

In summary, we have prepared and fully characterized the first Ni^I dinitrogen complex **3** displaying an activated N_2 ligand coordinated by two Ni^I centers in an end-on bridging mode. Complex **3** can be further reduced in single-electron steps, resulting in singly reduced **5** and doubly reduced **6**, in which the extent of N–N bond activation is more pronounced. The contribution of each electron to activation could be monitored by Raman spectroscopy and single crystal X-ray diffraction. Current research now focuses on a more detailed investigation and understanding of the electronic structures of **3**, **5**, and **6**. Moreover, it will be interesting to study the behavior of **6** in reactions with reducible small molecules.

Experimental Section

All experiments were carried out in a dry nitrogen or argon atmosphere using a glove box or standard Schlenk techniques. The preparation of [L$^{t\mathrm{Bu}}$NiBr] and [L$^{t\mathrm{Bu}}$Ni(OEt$_2$)] is described in the Supporting Information.

3: [L$^{t\mathrm{Bu}}$NiBr] (300 mg, 0.47 mmol) and KC$_8$ (70 mg, 0.52 mmol, 1.1 equiv) were suspended in hexane, and the reaction mixture was stirred for 12 h in a dinitrogen atmosphere. Filtration of the red-brown solution and evaporation of the solvent afforded red-brown crystals of **3** (102 mg, 0.09 mmol, 38 %); elemental analysis (%) calcd for $C_{70}H_{106}N_6Ni_2$ (1149.02 g mol^{-1}): C 73.17, H 9.30, N 7.31; found: C 72.66, H 9.26, N 6.95; $\mu_{\mathrm{eff}}=2.40\mu_{\mathrm{B}}$ (296 K, $\mu_{\mathrm{s.o.}}=2.45\mu_{\mathrm{B}}$); *g* values as determined by spectral simulation (77 K): $g_x=2.2750$, $g_y=2.1250$, $g_z=2.0415$ ($A_{xx}=1.0$, $A_{yy}=1.0$, $A_{zz}=1.34$ mT).

5: [L$^{t\mathrm{Bu}}$NiBr] (300 mg, 0.47 mmol) and KC$_8$ (105 mg, 0.78 mmol, 1.65 equiv) were suspended in hexane, and the reaction mixture was stirred for 12 h in a dinitrogen atmosphere. Filtration of the red-purple solution and evaporation of the solvent afforded red-brown crystals of **5** (86 mg, 0.07 mmol, 31 %); elemental analysis (%) calcd for $C_{70}H_{106}KN_6Ni_2$ (1188.12 g mol^{-1}): C 70.76, H 8.99, N 7.07; found: C 69.73, H 9.23, N 5.94 (owing to the rather high reactivity and sensitivity of **5** and **6**, elemental analyses always showed deviations higher than commonly accepted); $\mu_{\mathrm{eff}}=1.66\mu_{\mathrm{B}}$ (296 K, $\mu_{\mathrm{s.o.}}=1.73\mu_{\mathrm{B}}$); *g* values as determined by spectral simulation: $g_x=2.439$, $g_y=2.127$, $g_z=2.105$.

6: [L$^{t\mathrm{Bu}}$NiBr] (300 mg, 0.47 mmol) and KC$_8$ (146 mg, 1.08 mmol, 2.3 equiv) were suspended in hexane, and the reaction mixture was stirred for 12 h in a dinitrogen atmosphere. Filtration of the dark purple solution and removal of the solvent afforded dark purple **6** (68 mg, 0.06 mmol, 12 %); elemental analysis (%) calcd for $C_{70}H_{106}K_2N_6Ni_2$ (1227.21 g mol^{-1}): C 68.51, H 8.71, N 6.85; found: C 67.05, H 9.12, N 5.27; ^{1}H NMR (400.13 MHz, C$_6$D$_6$, RT): $\delta=6.76$ (12 H, Ar-*H*), 5.05 (2 H, C*H*C(CH$_3$)$_3$), 3.72 (8 H, C*H*(CH$_3$)$_2$), 1.49 (24 H, CH(C*H*$_3$)$_2$), 1.29 (24 H, CH(C*H*$_3$)$_2$), 1.16 ppm (36 H, C(C*H*$_3$)$_3$); ^{13}C{H} NMR (100.63 MHz, C$_6$D$_6$, RT): $\delta=163.3$ (N*C*C(CH$_3$)$_3$), 152.1 (Ar-*iC*), 140.8, 138.5 (Ar-*oC*), 123.0 (Ar-*mC*), 119.1 (Ar-*pC*), 95.9 (*C*HC(CH$_3$)$_3$), 43.8 (*C*(CH$_3$)$_3$), 33.5 (C(*C*H$_3$)$_3$), 28.1 (*C*H(CH$_3$)$_2$), 24.4, 22.4 ppm (CH(*C*H$_3$)$_2$).

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[1] a) *Molybdenum Enzymes, Cofactors and Model Systems* (Eds.: E. Stiefel, D. Coucouvanis, W. E. Newton), American Chemical Society, Washington, DC, **1993**, chapters 20–23; b) B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385 – 402.

[2] D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76 – 78.

[3] a) F. Studt, F. Tuczek, *J. Comput. Chem.* **2006**, *27*, 1278 – 1291; b) J. D. Cohen, M. Mylvaganam, M. D. Fryzuk, T. M. Loehr, *J. Am. Chem. Soc.* **1994**, *116*, 9529 – 9534.

[4] F. Tuczek, *Nachr. Chem.* **2006**, *54*, 1190 – 1194.

[5] a) J. M. Smith, R. J. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers, P. L. Holland, *J. Am. Chem. Soc.* **2001**, *123*, 9222 – 9223; b) J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela, P. L. Holland, *J. Am. Chem. Soc.* **2006**, *128*, 756 – 769; c) S. A. Stoian, J. Vela, J. M. Smith, A. R. Sadique, P. L. Holland, E. Münck, E. L. Bominaar, *J. Am. Chem. Soc.* **2006**, *128*, 10181 – 10192.

[6] R. P. Rose, C. Jones, C. Schulten, S. Aldridge, A. Stasch, *Chem. Eur. J.* **2008**, *14*, 8477 – 8480.

[7] a) G. Bai, P. Wei, D. W. Stephan, *Organometallics* **2006**, *25*, 2649 – 2655; b) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2004**, 764 – 765; c) W. H. Monillas, G. P. A. Yap, L. A. MacAdams, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 8090 – 8091.

[8] a) P. W. Jolly, K. Jonas, *Angew. Chem.* **1968**, *80*, 705; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 731 – 732; b) P. W. Jolly, K. Jonas, C. Krüger, Y.-H. Tsay, *J. Organomet. Chem.* **1971**, *33*, 109 – 122.

[9] a) C. Krüger, Y.-H. Tsay, *Angew. Chem.* **1973**, *85*, 1051 – 1052; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 998 – 999; b) K. Jonas, D. J. Brauer, C. Krüger, P. J. Roberts, Y.-H. Tsay, *J. Am. Chem. Soc.* **1976**, *98*, 74 – 81.

[10] R. Waterman, G. L. Hillhouse, *Can. J. Chem.* **2005**, *83*, 328 – 331.

[11] For matrix isolation studies, see: a) J. K. Burdett, J. J. Turner, *J. Chem. Soc. D* **1971**, 885 – 886; b) J. K. Burdett, M. A. Graham, J. J. Turner, *J. Chem. Soc. Dalton Trans.* **1972**, 1620 – 1625; c) C. W. DeKock, D. A. VanLeirsburg, *J. Am. Chem. Soc.* **1972**, *94*, 3235 – 3237; d) H. Huber, E. P. Kuendig, M. Moskovits, G. A. Ozin, *J. Am. Chem. Soc.* **1973**, *95*, 332 – 344; e) W. E. Klotzbuecher, G. A. Ozin, *J. Am. Chem. Soc.* **1973**, *95*, 3790 – 3792; f) G. A. Ozin, W. E. Klotzbuecher, *J. Am. Chem. Soc.* **1975**, *97*, 3965 – 3974; g) W. B. Maier, M. Poliakoff, M. B. Simpson, J. J. Turner, *J. Mol. Struct.* **1982**, *80*, 83 – 86; h) J. J. Turner, M. B. Simpson, M. Poliakoff, W. B. Maier II, *J. Am. Chem. Soc.* **1983**, *105*, 3898 – 3904; i) A. J. Bridgeman, O. M. Wilkin, N. A. Young, *Inorg. Chem. Commun.* **2000**, *3*, 681 – 684. For theoretical calculations, see: j) T. Yamabe, K. Hori, T. Minato, K. Fukui, *Inorg. Chem.* **1980**, *19*, 2154 – 2159; k) K. I. Goldberg, D. M. Hoffman, R. Hoffmann, *Inorg. Chem.* **1982**, *21*, 3863 – 3868; l) J. Guan, Q. Li, *J. Phys. Chem. A* **2005**, *109*, 9875 – 9881. One report on a Ni$^{\mathrm{I}}$-N$_2$ complex exists, which, however was only characterized by IR spectroscopy: m) S. C. Srivastava, M. Bigorgne, *J. Organomet. Chem.* **1969**, *18*, P30 – P32.

[12] S. Pfirrmann, C. Limberg, B. Ziemer, *Dalton Trans.* **2008**, 6689 – 6991.

[13] J. M. Smith, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2003**, *125*, 15752 – 15753.

[14] Crystallographic data for **3**: $C_{70}H_{106}N_6Ni_2$, $0.56\times0.32\times0.16$ mm,^{3} $M_r=1149.03$, orthorhombic, *Pbca*, $a=24.6700(5)$, $b=18.2320(3)$, $c=28.9460(8)$ Å, $\alpha=\beta=\gamma=90°$, $V=13019.4(5)$ Å^3, $Z=8$, $T=100(2)$ K, $F=4_{000}992$, $\mu=0.622$ mm^{-1}, $\Theta=2.34$–26.50°, collected reflections 97470, unique reflections 13377 [$R_{\mathrm{int}}=0.0952$], GoF = 1.094, $R_1=0.0521$, $wR_2=0.1254$, largest difference peak and hole 0.733/–0.509 e Å^{-3}. Crystallographic data for **5**: $C_{73}H_{113}KN_6Ni_2$, $0.16\times0.12\times0.06$ mm^3, $M_r=1231.21$, triclinic, $P\bar{1}$, $a=12.7651(7)$, $b=13.1334(7)$, $c=23.1951(13)$ Å, $\alpha=88.393(4)$, $\beta=88.824(4)$, $\gamma=64.589(4)°$, $V=3510.9(3)$ Å^3, $Z=2$, $T=180(2)$ K, $F_{000}=1336$, $\mu=0.639$ mm^{-1}, $\Theta=3.21$–25.25°, collected reflections 44913, unique reflections 12689 [$R_{\mathrm{int}}=0.2459$], GoF = 0.926, $R_1=0.1062$, $wR_2=0.1776$, largest difference peak and hole 0.655/–0.561 e Å^{-3}. Crystallographic data for **6**: $C_{76}H_{120}K_2N_6Ni_2$, $0.16\times0.10\times0.08$ mm^3, $M_r=1313.40$, monoclinic, *C*2/*c*, $a=22.3726(12)$, $b=21.3964(12)$, $c=15.4835(8)$ Å, $\alpha=90$, $\beta=99.398(4)$, $\gamma=90°$, $V=7312.4(7)$ Å^3, $Z=4$, $T=100(2)$ K, $F_{000}=2848$, $\mu=0.673$ mm^{-1}, $\Theta=3.28$–25.25°, reflections collected 70723, reflections unique 6634 [$R_{\mathrm{int}}=0.1325$], GoF = 0.897, $R_1=0.0755$, $wR_2=0.1675$, largest

diff. peak and hole 0.677–1.274 e Å^{-3}. The structures were solved by direct methods (SHELXS-97)[20] and refined versus F^2 (SHELXL-97)[21] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. CCDC 710173 (**3**), 710174, (**5**) and 710175 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] a) N. A. Eckert, A. Dinescu, T. R. Cundari, P. L. Holland, *Inorg. Chem.* **2005**, *44*, 7702–7704; b) E. Kogut, H. L. Wiencko, L. Zhang, D. E. Cordeau, T. H. Warren, *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249.

[16] H. P. Wang, J. T. Yates, Jr., *J. Phys. Chem.* **1984**, *88*, 852–856.

[17] a) G. Bai, P. Wei, D. W. Stephan, *Organometallics* **2005**, *24*, 5901–5908; b) S. Yao, E. Bill, C. Milsmann, K. Wieghardt, M. Driess, *Angew. Chem.* **2008**, *120*, 7218–7221; *Angew. Chem. Int. Ed.* **2008**, *47*, 7110–7113; c) S. Yao, C. Milsmann, E. Bill, K. Wieghardt, M. Driess, *J. Am. Chem. Soc.* **2008**, *130*, 13536–13537.

[18] Compare with 1.233(6) Å in $K_2[L^{tBu}FeNNFeL^{tBu}]$.[5a]

[19] N. A. Eckert, E. M. Bones, R. J. Lachicotte, P. L. Holland, *Inorg. Chem.* **2003**, *42*, 1720–1725.

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

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