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Reductive Deprotonation and Dehydrogenation of Phenylhydrazine at a Nickel Center To Give a Nickel Diazenido Complex

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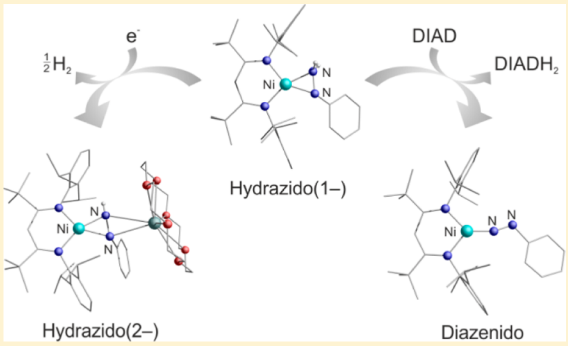
Supporting Information

ABSTRACT: The reaction of $[L^{tBu}Ni(OEt_2)]$ (where L^{tBu} = $[HC(C^tBuNC_6H_3(^iPr)_2)_2]^-$) with phenylhydrazine leads to the phenylhydrazido(1−) complex $[L^{tBu}Ni(\eta^2\text{-}NPhNH_2)]$ (**1**) with concomitant formation of H_2. Treatment of **1** with potassium graphite in the presence of crown ether again leads to H_2 evolution and affords the heterobimetallic complex $[L^{tBu}Ni(\mu\text{-}\eta^2{:}\eta^2\text{-}NPhNH)]K(18\text{-crown-}6)$ containing the doubly deprotonated phenylhydrazido(2−) ligand. **1** can be converted into a phenyldiazenido complex $[L^{tBu}Ni(\eta^1\text{-}NNPh)]$ in the course of a dehydrogenation reaction employing 1,2-diisopropylazo dicarboxylate (DIAD) as the oxidant.



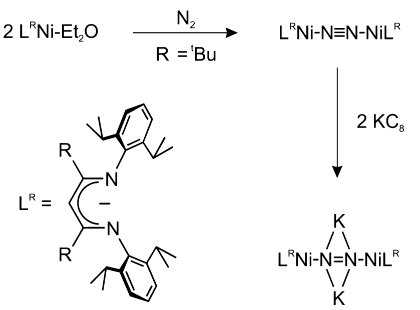
INTRODUCTION

After the pioneering work by Holland,[1] Warren,[2] and Stephan[3] on β-diketiminate complexes featuring mononuclear, three-coordinate Ni^I centers representatives with weakly bound coligands have proved to be versatile precursors for the activation of small molecules,[4] including H_2[5] and N_2.[6,7] The latter represent the reactants for the synthesis of ammonia during the course of the Haber−Bosch process[8] and in nature nitrogenases[9] catalyze the same conversion utilizing protons and electrons instead of intact H2; in both the corresponding reaction mechanisms proceed via N_xH_y intermediates in various reduction and protonation states.

The finding that, after coordination of N_2 at LNi^I moieties, it could be further reduced[6,7] (Scheme 1) encouraged an extension of these studies to important intermediates en route from N_2 to ammonia.

Among those are hydrazine and diazene,[10] and accordingly, a large variety of metal complexes containing substituted and unsubstituted diazene, hydrazine, or hydrazido ligands have been reported in the last two decades.[11−18]

Scheme 1. Reaction of a L^RNi^I Complex with N_2 and Subsequent Reduction with Potassium Graphite



Hydrazine represents a 1,2-σ donor ligand and can thus coordinate in various different modes and protonation states, whereas the assessment of the latter can pose problems, when a single-crystal XRD analysis does not unequivocally reveal the position of the H atoms. Because of the low electron density of H atoms, this is quite often the case and then determining how many protons are located at a certain N atom can be difficult.

Only few nickel hydrazine complexes are known. The dinuclear complex $[L^*Ni_2(\mu\text{-}N_2H_4)]^{2+}$ (L^* = hexaazodithiophenolate) contains a bridging N_2H_4 ligand.[17] Furthermore, complexes of the type $[Ni(NH_2NHR)_4Cl_2]$ (R = CH_3CH_2, $CF_3{-}CH_2$) are known, where the coordination modes of the organo hydrazine ligands vary with the residues R.[18]

Turning the focus onto β-diketiminato metal hydrazine/hydrazido systems, in particular, work on iron compounds should be mentioned. Treatment of an Fe^{II} dihydridoborate complex ($[L^{Me}Fe(\mu\text{-}H)_2BEt_2]$, L^{Me} = $[HC(C(Me)NC_6H_3(^iPr)_2)_2]^-$, compare Scheme 1 showing L^R) with hydrazine led to the formation of $[L^{Me}Fe(\eta^1\text{-}N_2H_4)(\mu\text{-}H)_2BEt_2]$. At slightly elevated temperatures this complex eliminates H_2 to give the diamido compound $[L^{Me}Fe(\mu\text{-}NH_2)_2BEt_2]$.[19] A 1,2-diphenylhydrazido complex $[L^{tBu}FeN(Ph)NHPh]$ has been obtained during the course of a hydrometallation of azobenzene with $[(L^{tBu}FeH)_2]$.[20] Furthermore, treatment of the sulfide-bridged diiron(II) compound $L^{Me}Fe(\mu\text{-}S)FeL^{Me}$ with 1.5 equiv of phenylhydrazine resulted in the formation of a mixed-valency $Fe^{II}Fe^{III}$ complex $L^{Me}Fe(\mu\text{-}S)(\mu\text{-}NPhNH_2)FeL^{Me}$ containing an anionic, bridging phenylhydrazido ligand; aniline and ammonia were found to be

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produced concomitantly, suggesting that the N−N single bond can be cleaved by the diiron(II) sulfide complex.[21] A dinuclear vanadium(V) complex is the only precedence for an arrangement featuring a bridging and side-on bound ($\mu-\eta^2:\eta^2$) phenylhydrazine(2−) ligand.[22]

In contrast to hydrazine, free diazene and its derivates are unstable species that readily decompose.[23] However, complexation to transition metals increases the stability of substituted diazenes, and it was shown that they can coordinate to transition metals in a number of different binding modes.[13,15,24,25] The most common motif found for aryldiazenes is the end-on (η^1) mode, including singly and doubly bent versions.[15] Only a few examples of side-on (η^2)[13,24] or bridging ($\mu-\eta^1:\eta^1$)[25] aryl-substituted diazene complexes have been reported.

Here, we report the reaction of a $L^{tBu}Ni^I$ precursor (L^{tBu} = $[HC(C(^tBu)NC_6H_3(^iPr)_2)_2]^-$) with phenylhydrazine, yielding a Ni^{II} phenylhydrazido(1−) complex (**1**), which can be converted to a heterobimetallic Ni^{II} phenylhydrazido(2−) complex (**2**) and oxidized to a diazenido complex (**3**).

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out in a glovebox, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer (^1H 300.1 MHz, ^{13}C 75.5 MHz, MHz) with C_6D_6 as solvent at 20 °C. The ^1H NMR spectra were calibrated against the residual proton, the ^{13}C NMR spectra against natural abundance ^{13}C resonances of the deuterated solvents (^1H 300.13 MHz; ^2H 61.42 MHz; ^{13}C 100.63 MHz). Chemical shifts are reported in ppm, relative to residual proton signals and natural-abundance ^{13}C resonances of C_6D_6 at 7.15 ppm and 128.02 ppm, respectively. Microanalyses were performed on a Leco CHNS-932 elemental analyzer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S spectrometer. UV−vis data were recorded on a Cary 100 (Varian) spectrometer using quartz cuvettes.

Materials. Solvents were purified, dried, degassed, and stored over molecular sieves prior to use.

$[L^{tBu}Ni(Et_2O)]$ (**I**) was prepared by reduction of $[L^{tBu}NiBr]$[6] with KC_8 in a diethyl ether solution. The analytical data were identical to those published previously.[6]

Synthesis of $[L^{tBu}Ni(\eta^2\text{-}NPhNH_2)]$ (1). Phenylhydrazine (47 μL, 0.47 mmol) was added to a solution of $[L^{tBu}Ni(OEt_2)]$ (**I**) (300 mg, 0.47 mmol) in 20 mL of diethyl ether at room temperature. During the reaction, gas development was observed, and a color change to red-brown occurred immediately. The mixture was stirred for 16 h and the solvent was removed in vacuo. The residue was extracted with hexane (15 mL). After filtration, hexane was removed in vacuo to yield dark red $[L^{tBu}Ni(\eta^2\text{-}NPhNH_2)]$ (**1**) (246 mg, 0.37 mmol, 78%). Recrystallization of the crude product from hexane at −30 °C yielded analytically pure red crystals.

Elemental analysis (%) calc. for $C_{41}H_{60}N_4Ni$ (667.64 g mol^{-1}): C 73.76, H 9.06, N 8.39; found: C 74.10, H 9.23, N 8.16; UV−vis (Et_2O) (λ_{max} (ε in mM^{-1} cm^{-1})): 278 (21), 390 (18), 531 (2); ^1H NMR (benzene-d$_6$, 300 MHz): δ 7.04 (1H, m, **Ph *p*-H**), 6.96 (2H, m, **Ar *p*-H**), 6.86 (4H, m, **Ar *m*-H**), 6.72 (2H, m, **Ph *m*-H**) 5.38 (1H, s, $C\mathbf{H}CC(CH_3)_3$), 5.05 (2H, d, $^2J_{H,H}$ = 7.6 Hz, **Ph *o*-H**), 4.14 (2H, m, $C\mathbf{H}(CH_3)_2$), 3.82 (2H, m, $C\mathbf{H}(CH_3)_2$), 2.01 (6H, d, $^2J_{H,H}$ = 6.4 Hz, $CH(C\mathbf{H}_3)_2$), 1.68 (2H, s, $N\mathbf{H}_2$), 1.55 (6H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.38 (6H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.27 (6H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.08 (18H, s, $C(C\mathbf{H}_3)_3$) ppm; ^{13}C NMR (benzene-d$_6$, 300 MHz): δ 167.8 ($N\mathbf{C}C(CH_3)_3$), 165.8 ($N\mathbf{C}C(CH_3)_3$), 154.1 (**Ph *i*-C**), 152.8 (**Ar *o*-C**), 149.3 (**Ar *o*-C**), 142.6 (**Ar *i*-C**), 140.1 (**Ar *i*-C**), 129.5 (**Ph *p*-C**), 124.6 (**Ar *p*-C**), 124.4 (**Ar *p*-C**), 123.7 (**Ar *m*-C**), 123.1 (**Ar *m*-C**), 118.4 (**Ph *m*-C**), 114.3 (**Ph *o*-C**), 98.6 ($\mathbf{C}HCC(CH_3)_3$), 42.2 ($\mathbf{C}(CH_3)_3$), 33.3 ($C(\mathbf{C}H_3)_3$), 28.5 ($\mathbf{C}H(CH_3)_2$), 24.8 ($CH(\mathbf{C}H_3)_2$), 24.4 ($CH(\mathbf{C}H_3)_2$), 23.8 ($CH(\mathbf{C}H_3)_2$), 23.4 ($CH(\mathbf{C}H_3)_2$). IR (KBr): 3329(w), 3249(vw), 3163(vw), 2957(vs), 2867(s), 1592(m), 1533(m), 1513(s), 1483(m), 1461(m), 1432(m), 1404(vs), 1363(s), 1319(s), 1251(s), 1218(m), 1186(m), 1161(m), 1098(w), 1054(w), 1035(m), 933(w), 803(w), 783(m), 754(m), 692(m), 526(w) cm^{-1}.

Synthesis of $[L^{tBu}Ni(\mu-\eta^2:\eta^2\text{-}NPhNH)]K([18]\text{-}crown\text{-}6)$ (2). $[L^{tBu}Ni(\eta^2\text{-}NPhNH_2)]$ (**1**) (100 mg, 0.15 mmol) and potassium graphite (25 mg, 0.19 mmol, 1.25 equiv) were suspended in 20 mL of diethyl ether in the presence of 18-crown-6 (40 mg, 0.15 mmol) at ambient temperature. Intense gas development was observed, and a color change from brown-red to orange occurred. The mixture was stirred overnight, solid components were filtered off, and the solvent was removed in *vacuo*. The residue was washed with hexane and dissolved in diethyl ether again. Slow evaporation of the solvent led to red crystals of $[L^{tBu}Ni(\mu-\eta^2:\eta^2\text{-}NHNPh)]K([18]\text{-}crown\text{-}6)$ (**2**) (97 mg, 0.10 mmol, 67%). Elemental analysis (%) calc. for $C_{53}H_{83}KN_4NiO_6$ (970.04 g mol^{-1}): C 65.62, H 8.62, N 5.78; found: C 65.60, H 8.72, N 4.83. As mentioned in the text, **2** is very sensitive to air, especially O_2, which replaces the PhN_2H unit. This posed severe problems during sample preparation and may explain the deviation in the N content. UV−vis (Et_2O) (λ_{max} (ε in mM^{-1} cm^{-1})): 301 (25), 395 (7), 470 (2); ^1H NMR (benzene-d$_6$, 300 MHz): δ 7.21 (2H, m, **Ph *m*-H**), 7.06 (4H, m, **Ar *m*-H**), 6.94 (2H, m, **Ar *o*-H**), 6.83 (2H, m, **Ph *o*-H**), 6.96 (1H, t, $^2J_{H,H}$ = 7.6 Hz, **Ph *p*-H**), 5.43 (1H, s, $C\mathbf{H}CC(CH_3)_3$), 4.78 (2H, m, $C\mathbf{H}(CH_3)_2$), 4.30 (1H, m, $C\mathbf{H}(CH_3)_2$), 3.80 (1H, m, $C\mathbf{H}(CH_3)_2$), 2.88 (24H, s, $O\text{-}(C\mathbf{H}_2)_2{-}O$), 2.21 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 2.07 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 2.02 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.70 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.60 (6H, d×d, $CH(C\mathbf{H}_3)_2$), 1.55 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.47 (1H, s, N**H**), 1.40 (3H, d, $^2J_{H,H}$ = 6.8 Hz, $CH(C\mathbf{H}_3)_2$), 1.32 (9H, s, $C(C\mathbf{H}_3)_3$), 1.30 (9H, s, $C(C\mathbf{H}_3)_3$). ^{13}C NMR (benzene-d$_6$, 300 MHz): δ 164.0 ($N\mathbf{C}C(CH_3)_3$), 154.7 (**Ph *i*-C**), 152.2 (**Ar *o*-C**), 151.3 (**Ar *o*-C**), 142.5 (**Ar *i*-C**), 141.7 (**Ar *i*-C**), 141.1 (**Ar *i*-C**), 140.6 (**Ar *i*-C**), 130.8 (**Ph *p*-C**), 123.3 (**Ar *p*-C**), 122.7 (**Ar *p*-C**), 122.3 (**Ar *m*-C**),121.9 (**Ph *m*-C**), 121.3 (**Ar *m*-C**), 114.5 (**Ph *o*-C**), 98.00 ($\mathbf{C}HC(CH_3)_3$), 69.8 ($O{-}(\mathbf{C}H_2)_2{-}O$), 43.0 ($\mathbf{C}(CH_3)_3$), 42.7 ($\mathbf{C}(CH_3)_3$), 33.6 ($C(\mathbf{C}H_3)_3$), 28.8 ($\mathbf{C}H(CH_3)_2$), 28.5 ($\mathbf{C}H(CH_3)_2$), 28.4 ($\mathbf{C}H(CH_3)_2$), 27.8 ($\mathbf{C}H(CH_3)_2$), 25.5 ($CH(\mathbf{C}H_3)_2$), 25.6 ($CH(\mathbf{C}H_3)_2$), 25.1 ($CH(\mathbf{C}H_3)_2$), 24.6 ($CH(\mathbf{C}H_3)_2$), 24.5 ($CH(\mathbf{C}H_3)_2$), 24.0 ($CH(\mathbf{C}H_3)_2$), 23.3 ($CH(\mathbf{C}H_3)_2$), 22.7 ($CH(\mathbf{C}H_3)_2$). IR (KBr): 3309(vw), 3148(vw), 3013(w), 2953(vs), 2886(vs), 2864(vs), 1603(m), 1585(m), 1513(m), 1501(m), 1470(m), 1460(m), 1445(m), 1412(vs), 1352(m), 1321(s), 1251(m), 1220(w), 1194(w), 1113(vs), 1057(w), 1028(w), 963(s), 756(m), 703(w) cm^{-1}.

Synthesis of $[L^{tBu}Ni(\mu-\eta^2:\eta^2\text{-}O_2)]K(18\text{-}crown\text{-}6)$ (2a). $[L^{tBu}Ni(\mu-\eta^2:\eta^2\text{-}NPhNH)]K([18]\text{-}crown\text{-}6)$ (**2**) (30 mg, 0.03 mmol) was dissolved in 20 mL of diethyl ether. The argon atmosphere in the flask was exchanged by dioxygen. The color of the solution immediately changed from red to orange. After stirring for 15 min, all volatiles were removed in vacuo and an orange residue of $[L^{tBu}Ni(\mu-\eta^2:\eta^2{-}O_2)]K(18\text{-}crown\text{-}6)$ (**2a**) (26 mg, 0.028 mmol, 93%) could be isolated. Elemental analysis (%) calc. for $C_{47}H_{77}KN_2NiO_8$ (895.91 g mol^{-1}): C 63.01, H 8.66, N 3.13; found: C 63.00, H 8.46, N 3.09. ^1H NMR (benzene-d$_6$, 300 MHz): δ 6.84 (4H, m, **Ar *m*-H**), 6.79 (2H, m, **Ar *o*-H**), 5.24 (1H, s, $C\mathbf{H}CC(CH_3)_3$), 4.47 (5H, sept., $C\mathbf{H}(CH_3)_2$), 3.03 (24H, s, $O{-}(C\mathbf{H}_2)_2{-}O$), 2.15 (12H, d, $^2J_{H,H}$ = 6.6 Hz, $CH(C\mathbf{H}_3)_2$), 1.55 (12H, d, $^2J_{H,H}$ = 6.9 Hz, $CH(C\mathbf{H}_3)_2$), 1.30 (18H, s, $C(C\mathbf{H}_3)_3$). ^{13}C NMR (benzene-d$_6$, 300 MHz): δ 164.3 ($N\mathbf{C}C(CH_3)_3$), 152.4 (**Ar *o*-C**), 141.8 (**Ar *i*-C**), 141.6 (**Ar *i*-C**), 123.1 (**Ar *p*-C**), 122.5 (**Ar *p*-C**), 122.0 (**Ar *m*-C**), 121.5 (**Ar *m*-C**), 98.1 ($\mathbf{C}HC(CH_3)_3$), 69.9 ($O{-}(\mathbf{C}H_2)_2{-}O$), 42.8 ($\mathbf{C}(CH_3)_3$), 42.7 ($\mathbf{C}(CH_3)_3$), 33.4 ($C(\mathbf{C}H_3)_3$), 28.6 ($\mathbf{C}H(CH_3)_2$), 28.3 ($\mathbf{C}H(CH_3)_2$), 25.5 ($CH(\mathbf{C}H_3)_2$), 24.1 ($CH(\mathbf{C}H_3)_2$), 23.9 ($CH(\mathbf{C}H_3)_2$), 23.8 ($CH(\mathbf{C}H_3)_2$). IR (KBr): 2954(vs), 2900(vs), 2866(s), 1527(w), 1513(m), 1460(m), 1445(m), 1412(vs), 1365(w), 1381(w), 1352(m), 1321(m), 1251(m), 1220(w), 1196(vw), 1161(w), 1112(vs), 1056(vw), 1031(w), 961(m), 828(m), 778(w), 768(w), 757(w) cm^{-1}.

Synthesis of [L^{tBu}Ni(η^1-NNPh)] (3). 1,2-Diisopropyl azodicarboxylate (DIAD) (45 μL, 0.22 mmol) was added to a solution of [L^{tBu}Ni(η^2-NPhNH$_2$)] (**1**) (150 mg, 0.22 mmol) in 20 mL acetonitrile at room temperature. After stirring for 16 h a violet solid precipitated which was separated from the solvent by filtration. The residue was extracted with hexane twice (10 mL). Subsequent filtration and removing the solvent from the filtrate in vacuo yielded violet [L^{tBu}Ni(η^1-NNPh)], **3**, (94 mg, 0.14 mmol, 64%). Recrystallization of the crude product from diethyl ether afforded dark violet crystals. Elemental analysis (%) calc. for $C_{41}H_{58}N_4Ni$ (665.64 g mol^{-1}): C 73.98, H 8.78, N 8.42; found: C 73.87, H 8.91, N 7.96; UV–vis (Et$_2$O) (λ_{max} (ε in mM^{-1} cm^{-1})): 274 (14), 349 (11); ^{1}H NMR (benzene-d$_6$, 300 MHz): δ 7.09 (6H, m, **Ar–H**), 6.80 (1H, m, **Ph *p*-H**), 6.41 (2H, m, **Ph *m*-H**), 5.97 (2H, d, $^2J_{H,H}$ = 7.5 Hz, **Ph *o*-H**), 5.02 (1H, s, C**H**CC(CH$_3$)$_3$), 4.31 (4H, sept, C**H**(CH$_3$)$_2$), 1.97 (12H, d, $^2J_{H,H}$ = 6.6 Hz, CH(C**H$_3$**)$_2$), 1.45 (12H, d, $^2J_{H,H}$ = 6.9 Hz, CH(C**H$_3$**)$_2$), 1.10 (18H, s, C(C**H$_3$**)$_3$) ppm; ^{13}C NMR (benzene-d$_6$, 300 MHz): δ 186.4 (**Ph *i*-C**), 167.2 (N**C**C(CH$_3$)$_3$), 142.2 (**Ar *i*-C**), 130.3(**Ph *m*-C**), 127.0 (**Ph *p*-C**), 125.6 (**Ph *o*-C**), 125.1 (**Ar *p*-C**), 122.9 (**Ar *m*-C**), 118.9 (**Ar *o*-C**), 94.6 (**C**HCC(CH$_3$)$_3$), 43.0 (**C**(CH$_3$)$_3$), 33.0 (C(**C**H$_3$)$_3$), 28.8 (**C**H(CH$_3$)$_2$), 25.9 (CH(**C**H$_3$)$_2$), 23.4 (CH(**C**H$_3$)$_2$). IR (KBr): 3063(w), 2957(vs), 2925(s), 2904(s), 2867(m), 1689(vs), 1585(m), 1576(s), 1543(m) 1532(m), 1511(s), 1482(w), 1471(w), 1458(m), 1444(w), 1433 (m), 1388(vs), 1365(vs), 1317(s), 1253(m), 1220(m), 1194(w), 1180(w), 1159(w), 1135(w), 1098(m), 1030(w), 1022(w), 970(w), 933(w), 801(m), 780(s), 768(m), 754(s), 685(m), 613(w), 583(w), 529(w) cm^{-1}.

CRYSTAL STRUCTURE DETERMINATIONS

All data collections were performed at 100 K with a STOE IPDS 2T diffractometer (see Table 1). In all cases, Mo Kα radiation (λ = 0.71073 Å) was used; the radiation source was a sealed tube generator with a graphite monochromator. The structures were solved by direct methods (SHELXS-97)[38] and refined by full-matrix least-squares procedures based on *F*2 with all measured reflections (SHELXL-97).[38] Numerical absorption correction was applied for complexes **1** and **3**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their idealized positions and refined as riding. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 882129 (for **1**) and CCDC 882130 (for **3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Residual electron density for **1** belonging to the solvent of crystallization could not be modeled; squeeze refinement was performed.

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

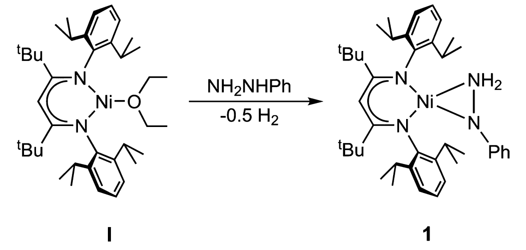
	1	2	3
formula	$C_{41}H_{60}N_4Ni$	$C_{106}H_{166}N_8Ni_2K_2O_{12}$	$C_{41}H_{58}N_4Ni$
weight (g mol^{-1})	667.64	1940.08	665.62
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	18.6151(6)	13.2242(17)	9.8640(10)
b (Å)	12.2221(3)	21.3214(4)	12.3300(13)
c (Å)	19.5038(7)Å	24.3297(4)	16.8483(16)
α (deg)	90	80.963(15)	95.819(8)
β (deg)	90	76.447(12)	96.008(8)
γ (deg)	90	78.705(13)	110.731(8)
V (Å^3)	4055.9(2)	6495.15	1884.7(3)
Z	4	4	2
density (g cm^{-3})	1.093	0.954	1.173
μ(Mo Kα) (mm^{-1})	0.509	0.402	0.547
F(000)	1448		720
goodness of fit, GoF	0.839		1.040
$R_{ind}[I > 2\sigma(I)]$	R_1 = 0.0370		R_1 = 0.0875
	w_{R2} = 0.0818		w_{R2} = 0.2143
R_{ind} (all data)	R_1 = 0.0593		R_1 = 0.1082
	w_{R2} = 0.0855		w_{R2} = 0.2307
$\Delta\rho_{min}/\Delta\rho_{max}$ (eÅ^{-3})	−0.651/0.694		−0.819/2.408

The solution of the X-ray crystal structure of **2** did not allow reliable structural metrics to be obtained.

RESULTS AND DISCUSSION

Treatment of [L^{tBu}Ni(OEt$_2$)][6] with hydrazine dissolved in tetrahydrofuran (THF) led to intractable products, so that phenylhydrazine was employed instead of the parent N_2H_4. During the reaction of [L^{tBu}Ni(OEt$_2$)] with H$_2$NNHPh in a diethyl ether solution, gas evolution was observed and a red-brown solution was obtained. Dark red crystals could be isolated upon slow evaporation of the solvent from a hexane solution. Their characterization by infrared (IR) and multinuclear nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction (XRD) analysis identified the product as [L^{tBu}Ni(η^2-NPhNH$_2$)] (**1**; see Scheme 2).

Scheme 2. Synthesis of [L^{tBu}Ni(η^2-NPhNH$_2$)] (1)



The molecular structure of **1** is shown in Figure 1. **1** contains an anionic phenylhydrazido(1−) ligand binding in a side-on mode, and thus the Ni ion is surrounded by four N donor atoms in a distorted square planar fashion. The N3–N4 bond length of the phenylhydrazido(1−) ligand amounts to 1.405(2) Å and therefore lies within the range that is typical for η^2-organohydrazido(1−) ligands;[11,13] it corresponds to a N–N single bond.

The phenyl ring is bent out of the Ni–N–N plane, as observed previously for the side-on bound phenylhydrazido(1−) ligands in [W(Cp)$_2$(η^2-NH$_2$NPh)]BF$_4$[26] and [Ru(η^2-NH$_2$NPh)(dmpe)$_2$]BPh$_4$,[13] which points to a sp^3 hybridization of the NPh unit. Contrary to the expectation, the Ni–NPh bond (1.9332(15) Å) is slightly longer than the Ni–NH$_2$ bond (1.8691(16) Å). In most of the other known phenylhydrazide complexes, the M–NPh bonds are shorter; however, the situation in **1** resembles that recently reported for [Ru(η^2–

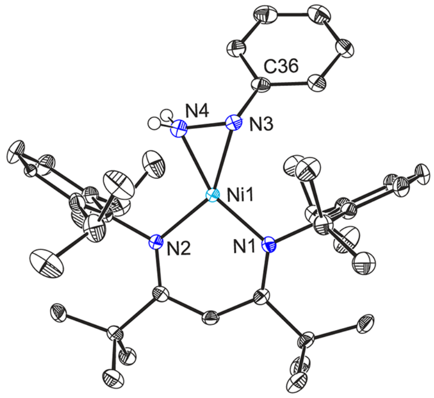


Figure 1. Molecular structure of **1** using 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity, except those binding to N4. Selected bond lengths (Å) and angles (°): Ni−N1, 1.8798(15) Å; Ni−N2, 1.8837(14) Å; Ni−N3, 1.9332(15) Å; Ni−N4, 1.8691(16) Å; N3−N4, 1.405(2) Å; N3−C36, 1.406(2) Å; N1−Ni−N2, 98.27(6)°; N1−Ni−N3, 114.82(6)°; N2−Ni−N4, 103.63(7)°; N1−Ni−N4, 158.08(7)°; N3−Ni−N4, 43.34(7)°; N4−N3−C36, 114.68(15)°.

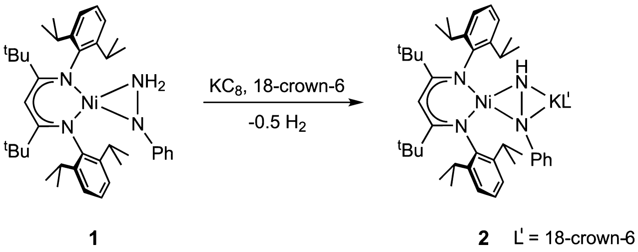
$NH_2NPh)(dmpe)_2]BPh_4$,[13] where the Ru−NPh bond is significantly longer than the Ru−NH_2 bond.

The diamagnetic complex **1** was formed by oxidation of the Ni center during the course of a reductive deprotonation of phenylhydrazine with a concomitant release of dihydrogen; the formation of H_2 could be detected by hydrogen sensors based on metal insulator semiconductor structures.[27] The resulting phenylhydrazido(1−) ligand undoubtedly is bound as the NH_2−NPh^- tautomer: The two protons were located in the Fourier map and further support came from multinuclear NMR experiments. For the NH protons of the NH_2−NPh unit, a single resonance with an integral of 2 was detected at 1.71 ppm in the ^1H NMR spectrum. The assignment was also confirmed using a 2D ^1H−^{15}N HMQC experiment. Only one ^{15}N correlation with these two protons became evident, suggesting equivalent NH protons, residing at the same N atom. The occurrence of a single NH_2 resonance results from a dynamic behavior of the N−Ph unit.

Apart from the NH_2 resonance, the ^1H NMR spectrum of **1** showed a set of sharp signals for the β-diketiminato unit L^{tBu}. Based on the structure depicted in Figure 1 with the N3−C36 bond sticking out (42.29(12)°) of the plane defined by Ni, N4, and N3, eight doublet signals should be expected for the methyl residues of the isopropyl groups, since, in the absence of a plane of symmetry within **1**, all methyl groups are chemically inequivalent. However, apparently N3 rapidly changes configuration, presumably through an inversion process involving an up−down motion of the aryl ring. On the NMR time scale, this leads to a more symmetric average structure where C36 is located within the N4, N3, Ni plane, and, hence, only four doublets are observed, as the methyl groups above and below this plane become pairwise equivalent. Consistently two of the four methine groups also are different and lead to two multiplets. Remarkably, the *ortho* protons of the phenyl group of the phenylhydrazido(1−) unit resonate at a relatively *high field* (5.06 ppm), which is unusual for protons belonging to an aromatic systems. This may be attributed to the ring current effect of the aryl rings at the β-diketiminato ligand. To see, whether the dynamic process described above can be frozen out, a sample in d_8-toluene was cooled to −80 °C. However, this did not alter the number of methyl signals; that is, the inversion motion is still fast at that temperature. However, rotation of the phenyl ring was slowed sufficiently, so that all CH units became inequivalent.

In order to examine whether it is possible to further activate the N−N bond of the phenylhydrazido(1−) ligand, **1** was treated with 1 equiv of KC_8 in the presence of 18-crown-6 (see Scheme 3), which led to a color change from red-brown to dark red.

Scheme 3. Synthesis of $[L^{tBu}Ni(\mu\text{-}\eta^2\text{:}\eta^2\text{-NPhNH})]K(18\text{-crown-}6)$ (2)



Workup and crystallization from diethylether led to red crystals, which were suitable for single-crystal XRD but always decomposed during the data collection, so that the latter could never be completed. The solution of the X-ray crystal structure did not allow reliable structural metrics to be obtained, but the basic framework and structural arrangement of the system was revealed, as displayed in Figure 2.

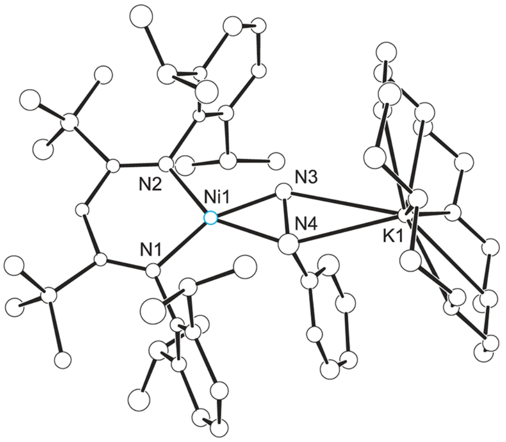


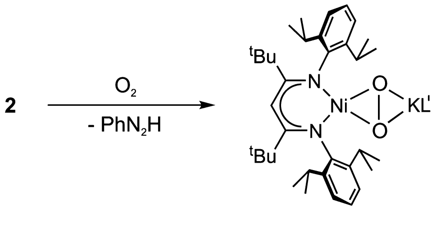
Figure 2. Structural framework of **2**, as revealed by a single crystal X-ray diffraction (XRD) analysis. All H atoms are omitted for the sake of clarity.

It became obvious that, similar to the case of **1**, the product is composed of a L^{tBu}Ni unit, binding a PhN_2H_x entity, whose protonation state did not become clear directly from the diffraction analysis. However, interaction of the $[(18\text{-crown-}6)K]^+$ complex cation with the N_2 unit already suggested that the starting material **1** had been singly deprotonated by KC_8 (with formation of H_2 as a byproduct), leading to the product $[L^{tBu}Ni(\mu\text{−}\eta^2\text{:}\eta^2\text{-NPhNH})K](18\text{-crown-}6)$ (**2**). As mentioned above, there is, hithero, only one report on a complex containing a μ−η^2:η^2-HNNPh(2-) ligand (namely, a divanadium complex),[22] and to our knowledge, **2** is the first heterobimetallic complex binding a phenylhydrazido(2−) ligand in a μ−η^2:η^2 geometry.

To further confirm the identity, an NMR spectroscopic analysis has been performed. As expected, the complex is diamagnetic, and the ^{1}H and ^{13}C NMR spectroscopic data revealed a highly unsymmetric structure. Apparently, the interaction with the K^+ ion freezes the N−Ph motion observed for **1** on the NMR time scale, so that now all eight methyl groups at the aryl rings of L^{tBu} were found to be chemically inequivalent, as one should expect, based on the structure shown in Figure 2. They lead to eight doublets in the ^{1}H NMR spectrum, and, consistently, the four methine groups are inequivalent, also giving rise to four multiplets. Furthermore, the ^{1}H NMR spectrum confirmed deprotonation of the phenylhydrazide(1−) ligand: Only one signal with an integral of 1 is observed for the NH proton of the NPhNH unit.

2 is very sensitive to air (in particular, to O_2). Remarkably, directed experiments unraveled that O_2 replaces the PhN_2H unit in **2** to give the heterobimetallic Ni^{II} peroxo complex $[L^{tBu}Ni(\mu-\eta^2:\eta^2-O_2)]K(18\text{-crown-}6)$ (**2a**) (see Scheme 4). A corresponding complex with the methyl-substituted β-diketiminate ligand L^{Me} had been described already[28] and the L^{tBu} derivative has been identified as such by means of IR and NMR spectroscopy, as well as elemental analysis.

Scheme 4. Formation of $[L^{tBu}Ni(\mu\text{-}\eta^2:\eta^2-O_2)]K(18\text{-crown-}6)$ (2a)



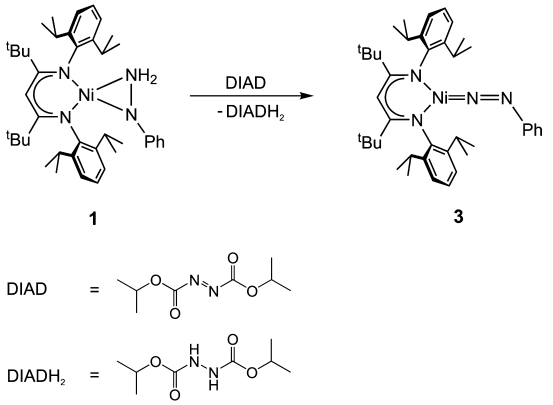
2a L' = 18-crown-6

Since in the formation of **2** KC_8 formally "only" acted as a deprotonation reagent, naturally experiments with nonredox active bases offered itself. However, reactions with reagents like, for instance, KO^tBu proceeded differently and did not lead to tractable products. This might indicate that the successful formation of **2** requires an initial electron transfer from a reductant to the Ni^{II} center, which then reduces the NHPh unit.

In order to gather further information cyclo voltammetric measurements were performed. A cyclic voltammogram of **1** in THF did not show a reduction wave. Only after an irreversible oxidation at −0.05 V vs Fc^+/Fc a reduction event is observed. This indicated that, for a successful reduction of **1**, not only the electron is needed but also the K^+ cation produced in cause of reduction with potassium, which stabilizes the anion formed by coordination (formation of ion pairs). Consistently, all attempts to separate the K^+ ion from the peroxide oxygen atoms in the isoelectronic complex $[L^{Me}Ni(\mu-\eta^2:\eta^2-O_2)K(18\text{-crown-}6)]$ had been unsuccessful, not even the powerful [2,2,2] cryptand was capable of cleaving the $K\cdots O_2$ contact.[28] Hence, cyclic voltammetry (CV) experiments with **1** were repeated in the presence of an excess of KBr (see the Supporting Information), and remarkably an irreversible reduction could be observed then at −2.82 V vs Fc^+/Fc (irreversibility can be rationalized by simultaneous dihydrogen formation).

To further exploit the redox chemistry of **1**, it was treated with 1,2-diisopropyl azodicarboxylate (DIAD, see Scheme 5), as the ethyl derivative, which is far more toxic and sensitive, had already been employed successfully for the dehydrogenation of $CpTiCl_2(NHNHR)$ to yield the diazenido complexes $CpTiCl_2(NNR)$ (R = Ph, ^{t}Bu).[29]

Scheme 5. Synthesis of $[L^{tBu}Ni(\eta^1\text{-NNPh})]$ (3)



Reaction of **1** with DIAD led to a color change from red-brown to violet within 1 day, and workup yielded a violet powder that could be recrystallized from diethyl ether. Investigation of a single crystal by X-ray diffraction revealed the molecular structure shown in Figure 3. A NNPh ligand is coordinated to nickel through only one N atom, and the NN bond length of 1.273(9) Å suggests a double bond between these atoms, as it is comparable to the NN distances in diazene (HN=NH, d_{NN} = 1.247−1.266 Å),[30] dimethyldiazene ($H_3CN{=}NCH_3$, d_{NN} = 1.245 Å),[31] and diphenyldiazene (PhN=NPh, d_{NN} = 1.173−1.259 Å).[32] This interpretation is further corroborated by the occurrence of a strong band at 1689 cm^{-1} in the IR spectrum, which can be assigned to the ν_{N_2} vibration of the phenyldiazenido ligand, based on a comparison with the corresponding absorptions of other aryl diazene compounds (1730−1660 cm^{-1}).[15] These findings clearly indicate a reaction as anticipated to give the envisaged product $[L^{tBu}Ni(\eta^1\text{-NNPh})]$ (**3**). Because of the local symmetry around the Ni center in **3**, all isopropyl residues are equivalent, so that

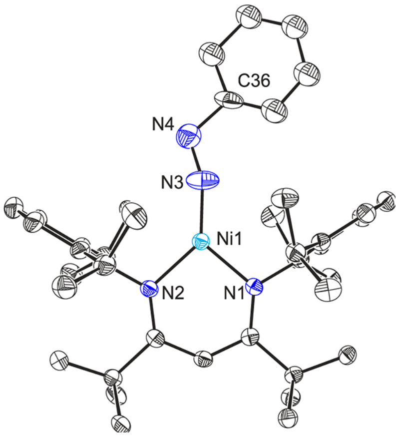
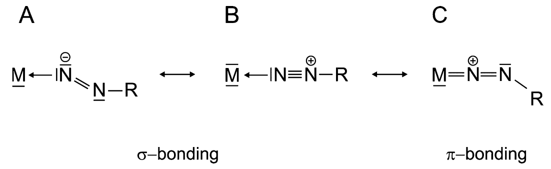


Figure 3. Molecular structure of **3** using 50% thermal ellipsoids. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths and angles (°): Ni−N1, 1.874(4); Ni−N2, 1.872(4) Å; Ni−N3, 1.631(6) Å; N3−N4, 1.273(9) Å; N4−C36, 1.489(10) Å; N1−Ni−N2, 97.90(19)°; N1−Ni−N3, 133.6(3)°; N2−Ni−N3, 128.4(3)°; Ni−N3−N4, 158.9(7)°; N3−N4−C36, 115.1(7)°.

just one methine signal and two methyl signals are observed in the ^{1}H NMR spectrum.

Like NO, the diazenido group is a versatile ligand and it can behave in different ways: It may be regarded as a deprotonated diazene, which consequently carries a negative charge and, after metal coordination, leads to doubly bent structures (Scheme 6, A). However, a two-electron transfer to the metal center leads to a RNN^+ ligand resembling NO^+ (B) and back-donation from the metal leads to the resonance structure C (corresponding complexes show a singly bent MNNR geometry). In the context of NO comparison, it is noteworthy that a β-diketiminato-nickel-nitrosyl complex has already been reported;[33] however, the nature of the NiNO unit has not been discussed. It is linear but this should not be taken as evidence for an NO^+ ligand in the compound as outlined by Bergman, DeBeer, Toste, and Wieghardt et al.[34] Applying spectroscopic and correlated ab initio computational investigations for a Tp*NiNO complex (Tp* = hydrotris(3,5-dimethylpyrazolyl)-borate), they have deduced an electronic situation, where a high-spin nickel(II) center is antiferromagnetically coupled to a triplet $(NO)^-$ ligand (both $S = 1 \rightarrow$ singlet ground state for the molecule). This discussion is also interesting with regard to the electronic structure of **3**, because it points out the limitations of valence bond descriptions in certain cases and problems that may be encountered in such compounds trying to apply commonly established oxidation state formalisms. Nevertheless, analyzing the bonding situation in **3**, we set out with the formulas shown in Scheme 6.

Scheme 6. Valence Structures of (A) Doubly Bent, (B) Linear, and (C) Singly Bent M−N−N−R Structural Skeletons



Considering these valence bond structures, in principle, it should be possible to elucidate the nature of **3** and the most relevant mesomeric structure through the analysis of the M−N−N angle: In case A, it should amount to ~120°; in cases B and C, the unit should be linear. In turn, cases B and C can be distinguished by the NNR angle. However, note that such considerations must be treated with caution, as crystal packing forces could have a serious impact, too. Within the structure of **3**, the Ni−N3−N4 angle amounts to 158.9(7)° and the N3−N4−C36 angle is found to be 115.1(7)°, suggesting an electronic situation where the resonance structure C outweighs the other ones. Remarkably, corresponding Ni−N3−N4 angles observed for most other phenyldiazendio complexes amount to 172°−179°,[15] so that they can be assigned to case C more clearly. However, an angle comparable to that of **3** has been found for an iron compound $[Fe(ArN_2)\{P(OEt)_3\}_4]^+$ (Ar = $4-CH_3C_6H_4$) (166.6(9)°),[35] whose diazenido unit has been discussed as $ArNN^+$. The attribution of a bonding situation within **3** that can mainly be described as C is supported by the Ni−N3 bond length (1.631(6) Å), which is much shorter than expected for a Ni−N single bond (e.g., 0.238 Å shorter than the Ni−N4 bond length in **1**) and is more comparable to Ni−N distances observed for nickel imides (1.657(5)−1.703(4) Å).[2,36] It clearly indicates that binding of the diazenido ligand involves π-overlap with a d orbital of the Ni, as one should expect for the resonance structure C. Within the oxidation state formalism, assigning the electrons in the π-bond purely to the metal results in a d^{10} configuration, while an assignment to the diazenido ligand produces a d^8 configuration, and the fact that the Ni−N bond lengths belonging to the β-diketiminato ligand compare well with those within **1** and other β-diketiminato-nickel(II) complexes suggests the latter, i.e., the presence of an "imido-like" ligand.

To further analyze the electronic structure of **3**, DFT calculations were performed (B3LYP Def2-TZVPD/Def2-SVP).[37] A geometry optimization was carried out, setting out with the structure shown in Figure 3. The ground state turned out to be a closed-shell singlet state. Considering the above-mentioned results obtained in the analysis of the complex Tp*Ni(NO),[34] also a thorough search for wave functions with broken symmetry (e.g., Ni^{2+} ($S = 1$) antiferromagnetically coupled to $PhNN^-$ ($S = 1$)) was performed. However, no stable broken symmetry solution was found, optimizations resulted only in an additional singlet solution with some spin polarization and almost the same geometry and energy as the closed-shell singlet state (energy difference of 0.90 kJ/mol; see the Supporting Information). The calculated ground-state structure compares well with the experimental structure (see the Supporting Information); only the Ni−N═N-Ph unit is somewhat closer to linearity in the calculated structure, which probably indicates that the corresponding angles in **3** are indeed influenced by packing forces. A subsequent NBO analysis revealed two π bonds, Ni−N3 and N3−N4, which yet again strongly supports bonding situation C. A N3−N4 σ bond was found, too, but instead of a Ni−N3 σ bond, a strong stabilizing donor−acceptor interaction of the N3 lone pair with the Ni 4s orbital was revealed (see Figure S2 in the Supporting Information). The NBO charge distribution provides further evidence for bonding situation C, since the N3 and N4 atoms are much less negative (−0.3 and −0.2) than N1 and N2 (both −0.7).

■ CONCLUSIONS

$L^{tBu}Ni^{I}$ species react with H_2NNHPh via electron transfer followed by H_2 evolution to yield a H_2NNPh^- ligand. Reduction of the resulting Ni^{II} complex again leads to H_2 formation and deprotonation, so that a phenylhydrazido(2−) complex is produced. On the other hand, the $Ni^{II}(NH_2NPh)$ unit can be dehydrogenated by means of 1,2-diisopropyl azodicarboxylate (DIAD), which results in a nickel diazenido moiety. Further work will explore the redox chemistry of hydrazido complexes including bimetallic activation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cyclic voltammogram of **1**, DFT calculations of **3**, and X-ray crystallographic data 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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