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Reduction and Hydrogenation of a Diazene by a (β-Diketiminato)nickel Hydrazide

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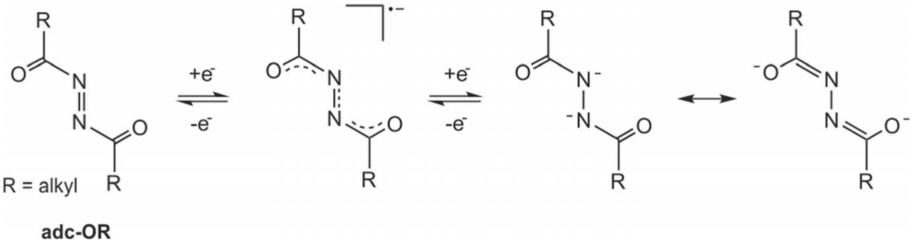
A (β-diketiminato)nickel(II) hydrazido(1–) complex [L^{tBu}Ni(η^2-N_2H_3)], {**1**, L^{tBu} = [HC(CtBuNC$_6$H$_3${iPr}$_2$)$_2$]$^-$} has been obtained by treatment of [L^{tBu}NiBr] with hydrazine. In a reaction of **1** with two equivalents of the azo compound diisopropyl azodicarboxylic ester (adc–O*i*Pr) the Ni(N_2H_3) entity acts as both a hydrogenating and a reducing agent: diisopropyl hydrazidodicarboxylate (hdc–O*i*Pr) is formed, and more adc–O*i*Pr is reduced by two electrons. The resulting (adc–O*i*Pr)$^{2-}$ is found as a ligand in the ultimate nickel product complex, the trinuclear nickel(II) compound [L^{tBu}Ni(μ-adc–O*i*Pr)Ni(μ-adc–O*i*Pr)NiL^{tBu}] (**2**), in which two $L^{tBu}Ni^+$ units are linked by a [Ni^{II}(adc–O*i*Pr)$_2$]$^{2-}$ moiety. The hypothesis that $L^{tBu}Ni^I$ species are acting as intermediates was supported by the independent finding that **2** can also be obtained by reaction of [L^{tBu}Ni(OEt$_2$)] with adc–O*i*Pr.

Introduction

The bonding and activation of hydrazine and diazene compounds at transition metal complexes is of fundamental interest in chemistry as the latter are postulated as intermediates in the conversion of N_2 to NH_3.[1–3] In this context bulky β-diketiminates have proved to be valuable spectator ligands. For instance, Holland and co-workers have investigated the reactivity of low-coordinate β-diketiminato iron complexes towards N_2 as well as various N_xH_y substrates, and the cleavage of NN π as well as σ bonds has been observed; in one case N_2 has been even cleaved completely.[4–9] We have shown that N_2 and hydrazine derivatives can also be activated by β-diketiminato complexes of nickel; the difference in character of this late transition metal from that of iron yielded interesting differences.[10–13] For instance, reduction of a dinuclear nickel(I) dinitrogen complex in single-electron steps has been achieved.[11] Recently, we reported the reductive deprotonation and dehydrogenation of phenylhydrazine at a nickel center to give a nickel diazenido complex.[13] These results encouraged us to expand our studies to the reduction/hydrogenation of N=N double bonds in azo compounds, specifically, in azodicarboxylic esters. Azodicarboxylic esters (adc–OR) are strong electron acceptors and can thus represent the starting point of a two-step redox system (adc–OR)$^{0/\cdot-/2-}$ with strong π conjugation and a resonance-stabilized dianionic state (Scheme 1).[14]



Scheme 1. Two-step redox behavior of azodicarboxyl ligands (adc–OR) with a radical intermediate.

Various transition metal complexes containing azodicarboxyl ligands have been prepared and characterized.[15–25] The ability of the adc–OR$^{0/\cdot-/2-}$ system to act as a bridging ligand has been demonstrated for diruthenium,[16,17] diosmium,[18] and dicopper(I)[19–22] complexes. For example, the complex {(μ-adc–O*t*Bu)[Cu(dppf)]$_2$}(PF$_6$) contains two heterodinuclear 1,10-bis(diphenylphosphanylferrocene)copper(I) moieties, bridged by the radical anion of di-*tert*-butyl azodicarboxylic ester (adc–O*t*Bu).[22] Recently, neutral diruthenium(III) complexes, [(acac)$_2$Ru(μ-

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adc–OR)Ru(acac)$_2$] (acac$^-$ = 2,4-pentanedionato, adc–OR^{2-} = dialkyl azodicarboxylato, R = *tert*-butyl or isopropyl), were obtained from electron transfer reactions between [Ru(acac)$_2$(CH$_3$CN)$_2$] and azodicarboxylic esters (adc–OR).[15] Furthermore, palladium complexes have been synthesized in which azodicarboxylates are coordinated to a mononuclear palladium center in a side-on coordination mode, and the first catalytic cycle for reduction of azo compounds to hydrazines at a single palladium center has been reported.[23]

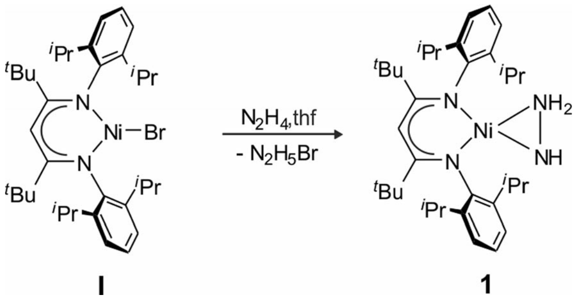
Here we report interconversions within a nickel/hydrazido/azo system that led, inter alia, to a novel trinuclear nickel complex with adc–OR^{2-} ligands.

Results and Discussion

Hydrazine-mediated double-bond reduction has been known for a long time.[26–28] However, the hydrogenation of symmetrical multiple bonds is not performed by hydrazine itself but by diazene, which is generated in situ from hydrazine via oxidation. In recent work, we showed that a phenylhydrazido(1–)nickel(II) complex [L$^{t\text{Bu}}$Ni(η^2-NPhNH$_2$)] {L$^{t\text{Bu}}$ = [HC(C*t*BuNC$_6$H$_3${*i*Pr}$_2$)$_2$]$^-$} hydrogenates adc–O*i*Pr, forming a phenyldiazenidonickel complex, [L$^{t\text{Bu}}$Ni(η^1-NNPh)].[13] Thus the question arose of whether a hydrazido(1–)nickel(II) complex with an unsubstituted hydrazido ligand also stops at the diazenido stage to give [L$^{t\text{Bu}}$Ni(NNH)] or whether it reacts further with adc–O*i*Pr, acting as more than two reducing equivalents. Alternatively, an intermediate diazene species could be formed that should be capable of reducing a further equivalent of an azo compound, with simultaneous hydrogenation of the N–N double bond. To provide an answer, a β-diketiminatohydrazido(1–)nickel(II) complex, [L$^{t\text{Bu}}$Ni(η^2-N$_2$H$_3$)] (**1**), had to be accessed first; however, the synthetic route analogous to the one used for [L$^{t\text{Bu}}$Ni(η^2-NPhNH$_2$)], namely the reaction of [L$^{t\text{Bu}}$Ni(OEt$_2$)] (**II**) with PhNHNH$_2$, did not lead to success.[13] Hence, an alternative approach was pursued.

Synthesis and Characterization of a Mononuclear Hydrazido Complex [L$^{t\text{Bu}}$Ni(η^2-N$_2$H$_3$)] (1)

Reaction of [L$^{t\text{Bu}}$NiBr][11] with an excess of hydrazine in tetrahydrofuran (thf) at room temperature resulted in a color change from dark green to orange and the formation of hydrazinium bromide (N$_2$H$_5$Br), which precipitated as a white solid (Scheme 2).



Scheme 2. Formation of [L$^{t\text{Bu}}$Ni(η^2-N$_2$H$_3$)] (**1**).

After work-up of the reaction mixture, the hydrazine complex [L$^{t\text{Bu}}$Ni(η^2-N$_2$H$_3$)] (**1**) was obtained in 81% yield in the form of orange crystals. The identity of **1** was confirmed by X-ray crystallography, IR and NMR spectroscopy, and elemental analysis. Crystals could be grown by slow evaporation of a thf solution. The solid-state structure of **1**·(thf) is shown in Figure 1. It reveals η^2-coordination of the hydrazido anion at the nickel center; thus the nickel ion is surrounded by four N donor atoms in distorted square-planar fashion. The sum of the angles around the nickel center is 360°. The N3 atom is disordered over two positions with 50% occupancy each. This disorder was satisfactorily modeled and is presumably a result of dynamic behavior of the η^2-N$_2$H$_3$ ligand, as has already been observed for the phenylhydrazido(–1) ligand in [L$^{t\text{Bu}}$Ni(η^2-NPhNH$_2$)].[13] Unfortunately, the NH protons were not located in the Fourier map, but were introduced in their idealized positions and refined as riding.

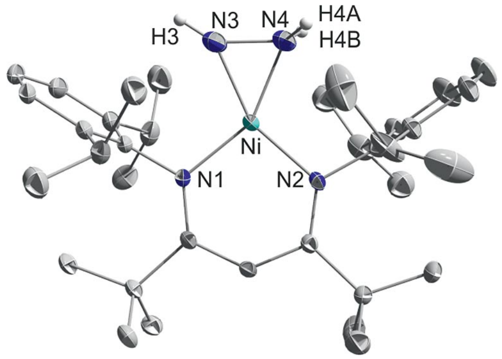
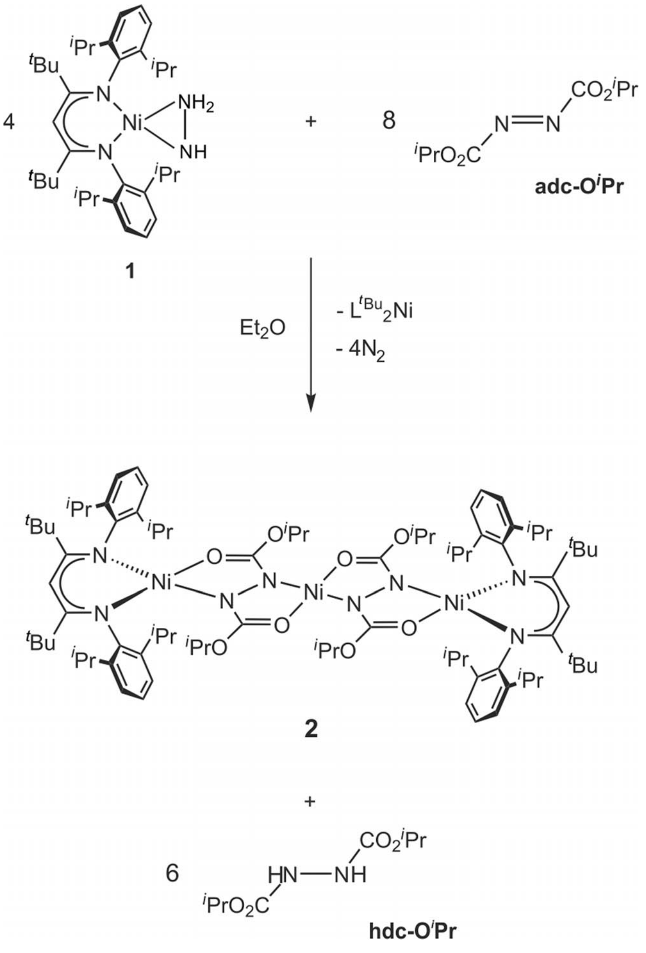


Figure 1. Displacement ellipsoid (30%) representation of the solid-state structure of [L$^{t\text{Bu}}$Ni(N$_2$H$_3$)]·thf, (**1**·thf). Hydrogen atoms (exept those directly coordinated to nitrogen atoms), solvent molecules, and minor components of disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: Ni–N1, 1.867(3); Ni–N2, 1.881(3); Ni–N3, 1.871(11); Ni–N3S, 1.908(9), Ni–N4, 1.871(4); N3–N4, 1.478(19); N3S–N4, 1.419(12); N3–H3, 0.8800; N4–H4A, 0.9200; N4–H4B, 0.9200; N1–Ni–N2, 99.71(12); N1–Ni–N3, 104.7(6); N2–Ni–N4, 109.21(15); N1–Ni–N4, 151.08(16); N3–Ni–N4, 46.5(6).

The N–N bond length of the hydrazido(–1) ligand is 1.419(12)–1.478(19) Å, which agrees well with corresponding distances found previously in mononuclear η^2-hydrazine and η^2-hydrazido complexes[29–42] and is consistent with an N–N single bond. The Ni–N3 bond length is 1.871(11) Å [*d*(Ni–N3S) = 1.908(9) Å] and equal to the Ni–N4 distance of 1.871(4) Å. These in turn are similar to the Ni–N(sp^3) bond length [1.8691(16) Å] observed in the phenylhydrazido(1–) complex [L$^{t\text{Bu}}$Ni(η^2-NPhNH$_2$)].[13] The room-temperature ^{1}H NMR spectrum of **1** dissolved in [D$_8$]toluene displays broad peaks without apparent coupling constants. This again indicates that the η^2-N$_2$H$_3$ ligand changes its configuration very quickly, and this dynamic behavior causes broadening of the signals in the ^{1}H NMR spectrum. Furthermore, it results in a local symmetry at the nickel center if averaged over the NMR timescale, and consequently both *tert*-butyl and all isopropyl residues of L$^{t\text{Bu}}$ are equivalent at room temperature. Consistently, at elevated temperatures (40 °C) the resonances are sharper, but still too broad for a resolution of a fine structure, thus preventing assignment of the NH protons; not even a 2D ^{1}H–^{15}N HMQC experiment allowed the identification of a corresponding signal. Likewise, lowering of the temperature did not lead to a sharpening of the signals sufficient to reveal the NH positions. Nevertheless, IR spectroscopy clearly showed the presence of a NH function through a band belonging to its stretching vibration at 3312 cm^{-1}.

Reduction and Hydrogenation of adc–O*i*Pr by a β-Diketiminato Nickel(II) Hydrazido Complex

Having prepared and characterized **1**, we could investigate its hydrogenation properties. Reaction of **1** with an excess of adc–O*i*Pr in diethyl ether resulted in a color change, the formation of diisopropyl hydrazidodicarboxylate (hdc–O*i*Pr), and the precipitation of a green solid (Scheme 3). After work-up the latter was identified as the trinuclear nickel azodicarboxyl complex [L^{tBu}Ni(μ-adc–O*i*Pr)Ni(μ-adc–O*i*Pr)NiL^{tBu}] (**2**) by means of X-ray crystallography, IR and NMR spectroscopy, and elemental analysis.



Scheme 3. Formation of **2** with concomitant reduction and hydrogenation of adc–O*i*Pr by **1**.

Crystals of **2** could be obtained by slow evaporation of the solvent from a dichloromethane solution; the structure as revealed by X-ray diffraction is depicted in Figure 2.

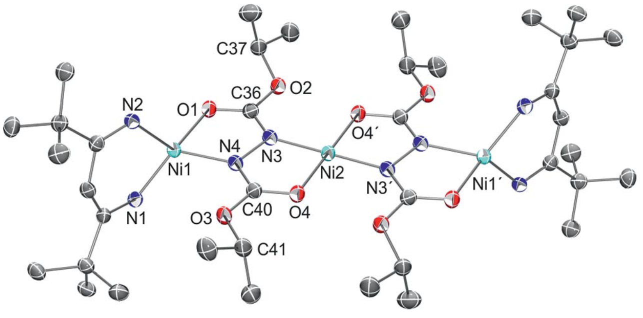
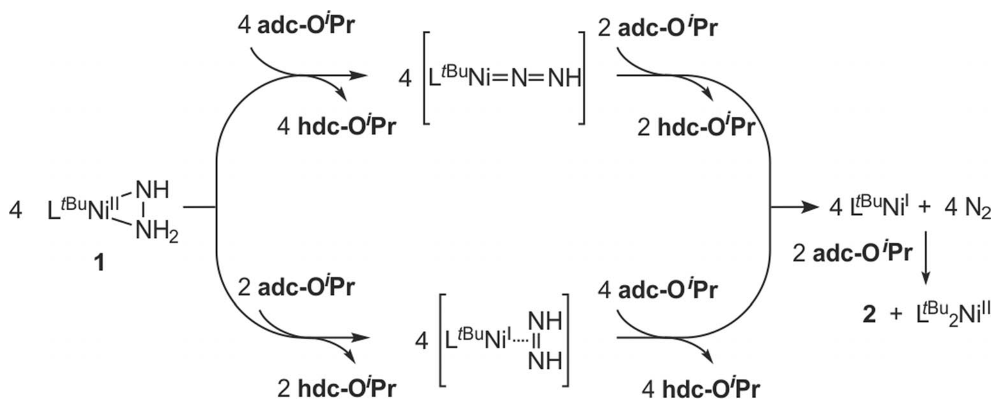


Figure 2. Molecular structure of **2**. Thermal ellipsoids at 50 % level; hydrogen atoms and the aryl groups of the β-diketiminato ligand have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Ni1, 1.9247(14); N2–Ni1, 1.9485(14); N3–N4, 1.428(2); N3–Ni2, 1.8893(14); N4–Ni1, 1.9481(14); Ni1–O1, 1.9824(12); Ni2–O4, 1.8522(12); C36–O1, 1.268(2); C36–N3, 1.320(2); C36–O2, 1.339(2), C37–O2, 1.459(2), N4–C40, 1.310(2); C40–O4, 1.269(2); C40–O3, 1.335(2); N2–Ni1–N1, 96.06(6); O1–Ni1–N4, 79.04(5), O1–C36–N3, 123.63(15); O4–C40–N4, 123.76(15); N3–Ni2–O4, 84.28(5); O4–Ni2–N3′, 95.72(5), N3–Ni2–N3′, 180.00(5), O4–Ni2–O4′, 180.0.

The structure analysis of **2** reveals a trinuclear nickel entity with two "S-frame" bridging μ-adc–O*i*Pr ligands[14] each forming two five-membered chelate rings. The assignment of the oxidation state +2 is supported by the coordination geometry at the nickel centers: The Ni1/Ni1′ ions are coordinated in a tetrahedral geometry, whereas the Ni2 ion is surrounded by two N and two O atoms in a distorted square-planar fashion. The sum of the bond angles at Ni2 is 360°. The most revealing structural parameter is the N–N distance of 1.428(2) Å, which indicates a single bond and is similar to the values observed before for doubly reduced adc–OR ligands (1.404–1.463 Å).[15,23–25] This corroborates the complete two-electron reduction of both azo precursor ligands. The nickel coordination is unsymmetrical with shorter (stronger) Ni–N bonds [*d*(Ni1–N4) = 1.9481(14) Å and *d*(Ni2–N3) = 1.8893(14) Å], and longer (weaker) Ni–O bonds [*d*(Ni1–O1) = 1.9824(12) Å and *d*(Ni2–O4) = 1.8522(12) Å], which is consistent with the corresponding bond parameters found for [(acac)$_2$Ru(μ-adc–O*i*Pr)-Ru(acac)$_2$].[15] This hints at a carbonyl character for the CO units, which thus form coordinate bonds. The CO distances do indeed correspond well with those expected for coordinated carbonyl groups [1.268(2) Å and 1.269(2) Å]. The N4–C40 bond length [1.310(2) Å; *d*(N3–C36) = 1.320(2) Å] is close to the typical N–C single-bond value.

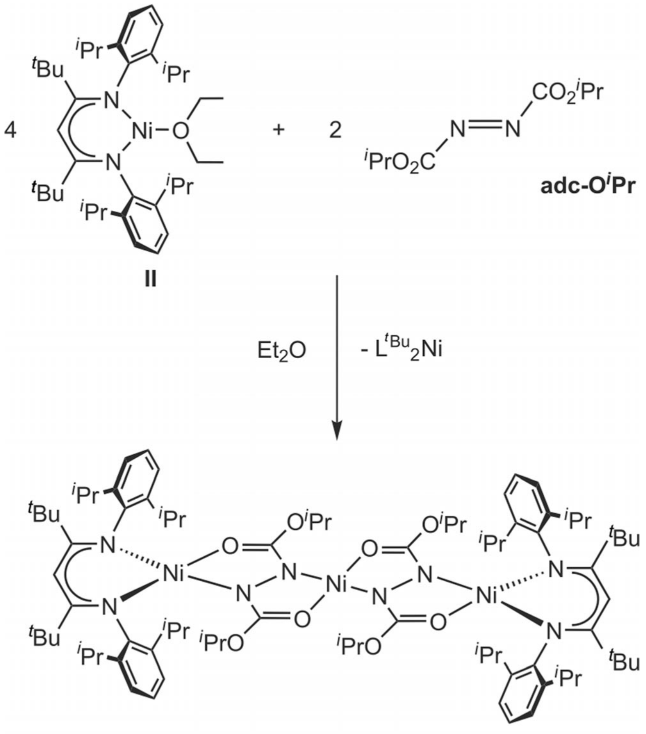
A ^{1}H NMR spectrum recorded for **2** indicated paramagnetism through large shifts and some broadening of the signals belonging to the protons of the β-diketiminato coligand, which is in accordance with the tetrahedral coordination geometry of the two d^8 nickel(II) ions. The IR spectrum of **2** shows the characteristic absorptions of the β-diketiminato unit as well as a very strong band at 1540 cm^{-1}, which is assigned to the C=O stretching vibrations.



Scheme 4. Alternative proposed pathways for the formation of **2**.

One conceivable mechanism for the formation of **2** might proceed as follows. Hydrazido(–1) complex **1** is first converted to an intermediate nickel(I) diazenido species by hydrogenation of adc–O*i*Pr, leading to the formation of hdc–O*i*Pr, which has been detected by means of NMR and IR spectroscopy (Scheme 4). This type of reactivity has already been observed in the dehydrogenation of a phenylhydrazido(1–) ligand in [L^{tBu}Ni(η^2-NPhNH$_2$)] to yield the diazenido complex [L^{tBu}Ni(η^1-NNPh)].[13]

Alternatively, one equivalent of adc–O*i*Pr could convert two equivalents of **1** to a diazene complex first. The diazene generated in situ is an unstable intermediate and hydrogenates another adc–O*i*Pr N–N double bond while itself being oxidized to dinitrogen (note that the stereospecific *cis*-hydrogenation of symmetrical multiple bonds is a typical reaction of diazene and in fact the only way to detect it in solution[26,27,43,44]).



2

Scheme 5. Synthesis of [L^{tBu}Ni(μ-adc–O*i*Pr)Ni(μ-adc–O*i*Pr)NiL^{tBu}] (**2**).

Both of the routes depicted in Scheme 4 lead to a nickel(I) species that reacts with two further equivalents of adc–O*i*Pr to give compound **2** through a four-electron redox process (two equivalents of adc–O*i*Pr were reduced to [adc–O*i*Pr]$^{2-}$). Three nickel(II) ions are found in **2**, so that formally a homoleptic nickel(II) complex containing two β-diketiminato ligands[45] has to be formed as a by-product.

To verify the mechanism, the reactivity of a nickel(I) precursor towards adc–O*i*Pr was examined. Reaction of [L^{tBu}Ni(OEt$_2$)][11] with an excess of diisopropyl azodicarboxylate in diethyl ether at room temperature resulted in a color change and the immediate formation of a green precipitate (Scheme 5). After work-up of the reaction mixture, **2** was indeed obtained in 69 % yield as dark green crystals.

Treatment of a solution of **2** in CDCl$_3$ with an excess of acetic acid in a ^{1}H NMR spectroscopic experiment led to a clean reaction and an immediate color change to pale tur-

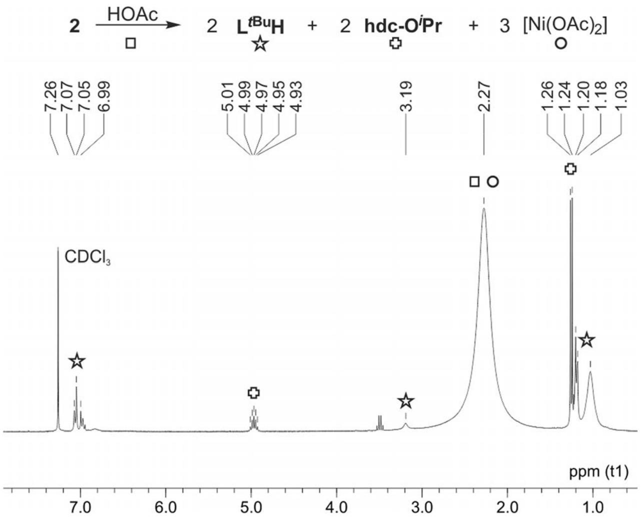


Figure 3. Protonolysis of **2** with an excess of acetic acid and the corresponding ^{1}H NMR spectrum.

quoise. Subsequently, the products diisopropyl hydrazidodicarboxylate (hdc–O*i*Pr), nickel acetate [Ni(OAc)$_2$], and protonated β-diketiminato ligand L$^{t\mathrm{Bu}}$H could be identified by NMR spectroscopy (Figure 3).

Conclusions

The β-diketiminate nickel(II) hydrazido(–1) complex [L$^{t\mathrm{Bu}}$Ni(η^2-N$_2$H$_3$)] (**1**) is capable of transferring its *N*-bound H atoms onto the azo compound adc–O*i*Pr. Concomitantly, the L$^{t\mathrm{Bu}}$Ni unit is reduced, and the resulting L$^{t\mathrm{Bu}}$Ni$^{\mathrm{I}}$ species reduces excess adc–O*i*Pr by two electrons to yield (adc–OR)$^{2-}$. In principle, this could have led to a complex of the type [L$^{t\mathrm{Bu}}$Ni(μ-adc–O*i*Pr)NiL$^{t\mathrm{Bu}}$]; however, apparently the trinuclear nickel(II) compound **2** is much more stable, perhaps as the [Ni$^{\mathrm{II}}$(adc–O*i*Pr)$_2$]$^{2-}$ moiety separates the two L$^{t\mathrm{Bu}}$Ni units. Hence, two L$^{t\mathrm{Bu}}$Ni fragments are sacrificed to yield L$^{t\mathrm{Bu}}{}_2$Ni and the Ni$^{\mathrm{II}}$ ion needed for **2**. Independently, it has been shown that L$^{t\mathrm{Bu}}$Ni$^{\mathrm{I}}$ indeed activates adc–O*i*Pr through reduction: **2** is formed and yields the corresponding hydrazine via protonation.

Experimental Section

General: All operations with air-sensitive compounds were carried out in a glovebox or by means of Schlenk techniques under a dry argon atmosphere. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 NMR or a Bruker AV 400 NMR spectrometer with [D$_6$]benzene, [D]chloroform or [D$_8$]toluene as solvents at 20 °C if not otherwise stated. The ^{1}H NMR spectra were calibrated against the residual proton, the ^{13}C NMR spectra against natural abundance ^{13}C resonances of the deuterated solvents. Microanalyses were performed with a HEKA Euro 3000 elemental analyzer. IR spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S spectrometer.

Materials: Solvents were purified, dried, degassed, and stored over molecular sieves before use. [L$^{t\mathrm{Bu}}$Ni(OEt$_2$)]$^{[11]}$ and [L$^{t\mathrm{Bu}}$NiBr]$^{[11]}$ were prepared according to literature procedures. Diisopropyl azodicarboxylate and a solution of hydrazine (1 M in thf) were obtained from Sigma–Aldrich.

Crystal Structure Determination: All data were collected at 100 K with a STOE IPDS 2T diffractometer. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer. In all cases Mo-K_α 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)$^{[46]}$ and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).$^{[46]}$ Numerical absorption correction was applied for complex **1**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their idealized positions and refined as riding. Complex **1** is disordered over two sides. A disorder model involving the hydrazido ligand as well as the metal has been developed. The solvent of crystallization, thf, is also disordered and only isotropic refinement was carried out for this molecule. The crystallographic data for **1** and **2** are summarized in Table 1.

Table 1. Crystallographic data and structure refinement for **1**·(thf) and **2**.

	1·(thf)	**2**
Formula	C$_{39}$H$_{64}$N$_4$NiO	C$_{86}$H$_{134}$N$_8$Ni$_3$O$_8$
M_r /g mol^{-1}	663.65	1584.14
Crystal system	monoclinic	triclinic
Space group	$P\,2_1/n$	$P\bar{1}$
a /Å	12.2637(4)	9.9806(3)
b /Å	16.9866(3)	12.5951(3)
c /Å	18.4783(6)	19.0742(5)
α /°	90	79.375(2)
β /°	96.248(2)	88.782(2)
γ /°	90	66.488(2)
V /Å^3	3826.51(19)	2157.35(10)
Z	4	1
Density/g cm^{-3}	1.152	1.219
F(000)	1448	854
GoF	1.027	1.037
R_1	0.0746	0.0360
wR_2	0.1856	0.0921
R_1 (all data)	0.0835	0.0417
wR_2 (all data)	0.1917	0.0949
R_{int}	0.0673	0.1126
$\Delta\rho_{\min}/\Delta\rho_{\max}$ /e Å^{-3}	–1.408/1.992	–0.484/0.427

CCDC-919921 (for **1**) and -919922 (for **2**) 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.

Synthesis of [L$^{t\mathrm{Bu}}$Ni(η^2-NHNH$_2$)] (1): A solution of hydrazine in thf (1 mL, 1 M) was added to a solution of [L$^{t\mathrm{Bu}}$NiBr] (**I**; 200 mg, 0.31 mmol) in thf (30 mL) at room temperature. A color change from dark green to orange occurred immediately, and a white solid precipitated. The mixture was stirred for 1 h, and the solid was filtered off. All volatiles were removed under reduced pressure, and the resulting solid was washed with hexane (10 mL). Recrystallization of the crude product in thf yielded analytically pure orange crystals of [L$^{t\mathrm{Bu}}$Ni(η^2-NHNH$_2$)] (**1**; 158 mg, 0.27 mmol, 86 %). Elemental analysis (%) calcd. for C$_{35}$H$_{56}$N$_4$Ni (591.54 g mol^{-1}): C 71.06, H 9.54, N 9.47; found C 71.32, H 9.56, N 9.07. ^{1}H NMR ([D$_8$]toluene, 300 MHz, 40 °C): δ = 6.77 (m, 6 H, Ar-H), 5.19 [s, 1 H, C*H*CC(CH$_3$)$_3$], 3.85 [sept., $^2J_{\mathrm{HH}}$ = 6.6 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.69 [d, $^2J_{\mathrm{HH}}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.29 [s, $^2J_{\mathrm{HH}}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.07 [s, 18 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR ([D$_8$]toluene, 500 MHz, 40 °C): δ = 123.8 (Ar-*p*C), 122.9 (Ar-*m*C), 122.6, 97.0 [*C*HCC(CH$_3$)$_3$], 42.3 [*C*(CH$_3$)$_3$], 33.8 [C(*C*H$_3$)$_3$], 28.2 [*C*H(CH$_3$)$_2$], 25.7 [CH(*C*H$_3$)$_2$], 23.7 [CH(*C*H$_3$)$_2$] ppm. IR (KBr): ṽ = 3312 (w), 3062 (w), 3016 (w), 2957 (vs), 2926 (s), 2865 (s), 1543 (s), 1528 (m), 1515 (s), 1461 (m), 1445 (m), 1433 (m), 1409 (vs), 1382 (m), 1365 (m), 1320 (m), 1255 (w), 1220 (w), 1194 (vw), 1181 (wv), 1116 (w), 1098 (s), 1052 (m), 1030 (m), 973 (w), 934 (m), 878 (m), 803 (s), 773 (s), 759 (s) cm^{-1}.

Synthesis of [L$^{t\mathrm{Bu}}$Ni(μ-adc–O*i*Pr)Ni(μ-adc–O*i*Pr)NiL$^{t\mathrm{Bu}}$] (2), Route A: Diisopropyl azodicarboxylate (adc–O*i*Pr), (40 µL, 0.200 mmol) was added to a solution of [L$^{t\mathrm{Bu}}$Ni(OEt$_2$)] (**II**, 50 mg, 0.079 mmol) in diethyl ether (30 mL). A green solid precipitated immediately, which was isolated by filtration and washed with hexane (10 mL); yield 22 mg (0.014 mmol, 69 %). Elemental analysis (%) calcd. for C$_{86}$H$_{134}$N$_8$Ni$_3$O$_8$ (1584.11 g mol^{-1}): C 65.20, H 8.53, N 7.07; found C 65.68, H 8.48, N 6.31. ^{1}H NMR (CDCl$_3$, 300 MHz, 20 °C): δ = 34.92, 29.57, 11.92, 5.74, 3.83, 3.25, –0.89, –31.75 ppm. IR (KBr): ṽ = 3154 (vw), 3056 (vw), 2976 (s), 2929 (m), 2908 (m), 2870 (m), 1676 (w), 1603 (m), 1530 (vs), 1501 (m), 1466 (w), 1432 (s), 1382 (vs), 1363 (s), 1316 (s), 1280 (vw), 1217 (w), 1180 (w), 1106 (m), 1068 (m), 1052 (m), 922 (w), 844 (vw), 800 (vw), 781 (w), 757 (w), 721 (m), 715 (vw), 674 (vw) cm^{-1}.

Synthesis of 2, Route B: Diisopropyl azodicarboxylate (adc–O*i*Pr, 34 µL, 0.17 mmol) was added to a solution of $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Ni}(\eta^2\text{-NHNH}_2)]$ (**1**; 40 mg, 0.07 mmol) in diethyl ether (30 mL). Within 24 h, a green solid precipitated. The solvent was removed under reduced pressure. The mixture of **2** and hdc–O*i*Pr was separated by extracting hdc–O*i*Pr with toluene. The insoluble green residue was washed with hexane (10 mL) and dried in vacuo; yield of **2** 15 mg (56%, analytical data see above). All volatiles of the filtrate were removed under reduced pressure, and the resulting white solid was identified as diisopropyl hydrazinedicarboxylate (hdc–O*i*Pr) by means of IR and NMR spectroscopy.[47]

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Diazene Reduction

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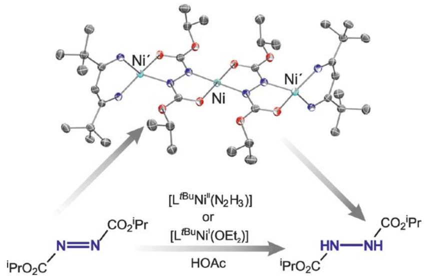
Reduction and Hydrogenation of a Diazene by a (β-Diketiminato)nickel Hydrazide

Keywords: Synthetic methods / Reduction / Azo compounds / Nickel / N ligands



A (β-diketiminato)nickel hydrazido(1–) complex has been synthesized that acts as a four-electron reductant towards a diazene: The corresponding hydrazine is formed, as well as a novel trinuclear complex with bridging hydrazido(2–) ligands, which can also be obtained through activation of the diazene at nickel(I) precursors.