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ARTICLE

Stabilization of β-diketiminato nickel(I) with alkaline metal halide entities for small molecule activation

Patrick Holze,[a] Beatrice Braun-Cula,[a] Stefan Mebs[b] and Christian Limberg*[a]

Dedicated to Professor Peter Comba on occasion of his 65th birthday

Abstract: The reduction of the β-diketiminato nickel(II) halide complex [L^{tBu}Ni^{II}Br] (L^{tBu} = CH(C*t*BuNdipp)$_2^-$, dipp = 2,6-Di-*iso*-propylphenyl) with potassium sources proceeds via the initial formation of [(L^{tBu}Ni^{I})$_x$(μ-Br)$_x$K$_x$] aggregates which could be isolated and characterized for X = ∞ and 6. The KBr equivalents readily give way to external donors or substrates to be activated at the nickel(I) centers. To test, in how far the steric bulk induced by the residues at [L^{tBu}]$^-$ influences the formation of the KBr adducts β-diketiminato ligands with less sterical congestion, namely L^{Me6} and L^{Me7} (L^{Me6} = CH(CMeNdmp)$_2^-$, L^{Me7} = CMe(CMeNdmp)$_2^-$, dmp = 2,6-dimethylphenyl) were employed. Through deprotonation of HL^{Me6} with *n*BuLi followed by treatment with NiBr$_2$(dme) the nickel(II) precursor compound [L^{Me6}Ni^{II}(μ-Br)$_2$Li(THF)$_2$] was prepared and shown to enter an equilibrium with [(L^{Me6}Ni^{II}Br)$_2$] and LiBr in solution; [(L^{Me6}Ni^{II}Br)$_2$] could be accessed also independently. Syntheses of the complexes [L^{Me7}Ni^{II}(μ-Br)$_2$Li(THF)$_2$] and [(L^{Me7}Ni^{II}Br)$_2$] could be achieved analogously. To test the potential of nickel complexes with the L^{Me6} and L^{Me7} ligands for the activation of N$_2$ the thf-free [(L$^{Me6/7}$Ni^{II}Br)$_2$] complexes were reduced with potassium in an N$_2$ atmosphere. This led neither to a KBr adduct nor to an N$_2$ complex but to the dimer [(L^{Me6}Ni^{I})$_2$], as the smaller ligands allow an efficient interaction of the nickel centres with the aryl rings.

Introduction

β-diketiminato nickel(I) complexes have demonstrated unique potential in the area of small molecule activation.[1] They have been shown to react, for instance, with the group 16 elements, dinitrogen,[2-4] phosphorous,[5] but also with SF$_6$,[6] CO$_2$,[7] and dihydrogen,[4,8] weakening bonds through transfer of electron density or even cleaving them reductively. However, the co-ligand saturating the residual coordination sphere of the nickel(I) center is also decisive. Obviously, LNi^{I}-D complexes (L = β-diketiminate, D = donor) show the highest reactivity when D corresponds to a weakly coordinating ligand or a good leaving unit. Here we take a closer look at the formation and behavior of LNi^{I}-D in dependence on the nature of D with a special focus on representatives where D corresponds to an alkali metal halide entity.

Results and Discussion

As there are no suitable nickel(I) halide precursors, which could form LNi^{I}-D complexes in course of a salt metathesis reaction with deprotonated β-diketimines, such complexes are typically prepared through the reduction of a nickel(II) complex LNi^{II}-X (X = halide) with alkali metals.[2,3,9,10] Hence, LNi^{II}-X are important precursors, and the bromide [L^{tBu}Ni^{II}Br], **1**, (L^{tBu} = CH(C*t*BuNdipp)$_2^-$, dipp = 2,6-Di-*iso*-propylphenyl) has been accessed by us originally via refluxing of LiL^{tBu} with Ni^{II}Br$_2$(dme) for 16 h followed by filtration and crystallization. The maximum yield of pure **1** reached by this procedure was 47%.[3] In the meantime we have found, that better yields can be obtained via an alternative procedure, developed along the lines of a method reported for the synthesis of [L^{Me2}Fe^{II}Cl]$_2$ (L^{Me2} = HC(CMeNdipp)$_2$):[11] after performing the reaction as before and removal of all volatiles the resulting residue was heated under reduced pressure for 12 h to 90°C. Afterwards adequate work-up involving extraction, crystallization and washing provides **1** in yields of 74%. The compound has been characterized previously, but we have now in addition recorded the ^{1}H NMR and the ^{1}H^{1}H COSY NMR spectrum of this paramagnetic compound and assigned the signals.

Setting out from **1**, nickel(I)-donor complexes can be obtained via reaction with K or KC$_8$ in the presence of the chosen donor; naturally the strongest donor available will coordinate. Hence, isolation of the labile N$_2$ complex [(L^{tBu}Ni^{I})$_2$(μ-η^1-η^1-N$_2$)], **2**, required hexane as the solvent.[3] As the N$_2$ ligand is bound only very weakly, **2** in turn proved an excellent precursor for the activation of other small molecules.[6,7,9] Based on the results of our investigations and those obtained by Holland and co-workers for the formation of [(L^{tBu}Fe^{I})$_2$(μ-η^1-η^1-N$_2$)] the following mechanism may be postulated for the formation of **2**:[12,13] After reduction with KC$_8$ in a non-coordinating solvent like hexane a di-, oligo- or even polymeric nickel(I) complex [(L^{tBu}Ni^{I})$_x$(μ-Br)$_x$K$_x$], **(3)$_x$** (x = 1, 2…n), is formed, where KBr units are saturating the coordination spheres of the nickel centers. This hypothesis is fueled by the fact that a dinuclear compound of that type, namely [(L^{Me2}Ni^{I})$_2$(μ_3-Br)$_2$Li$_2$(THF)] – with LiBr units and the smaller ligand [L^{Me2}]$^-$ – has been isolated before (the Li$^+$ cations were not derived from the reductant though), and this complex reacted even with N$_2$, which replaced the LiBr.[3] Donor molecules are expected to

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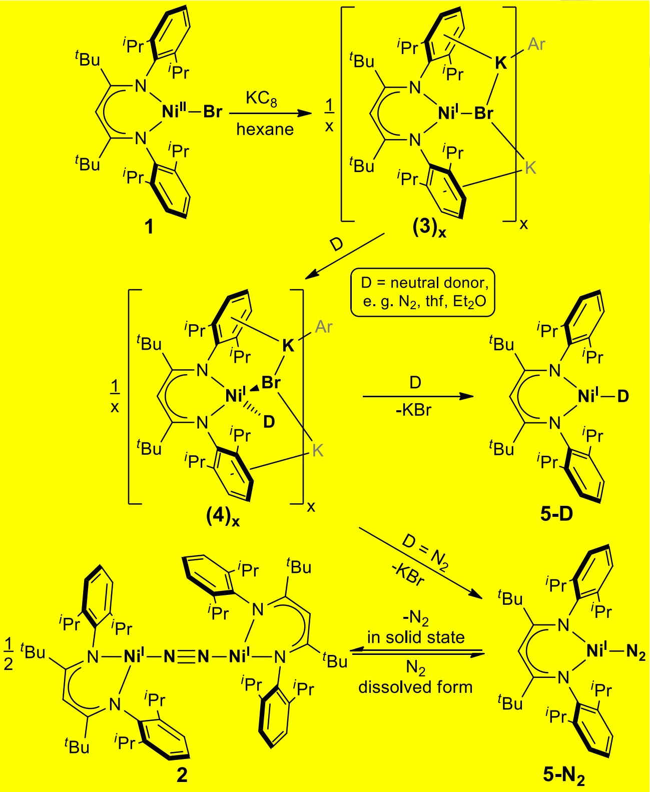
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) first of all coordinate to the Ni centers in **(3)$_x$** to give $[(L^{tBu}Ni^I)_x(D)_x(\mu\text{-}Br)_xK_x]$, **(4)$_x$** (D = donor molecule), before the elimination of KBr leads to the corresponding mononuclear adduct $[L^{tBu}Ni^I\text{-}D]$, **5-D** (Scheme 1).

An interesting question concerns the nuclearity of **(3)$_x$**, in particular considering the findings of Holland and co-workers that more than one iron(I) center is required for the activation of N_2[13] and that the degree of activation increases with increasing number of cooperating iron(I) centers.[14] Initial indications on the existence of **(3)$_x$** were obtained investigating the reaction between **1** and KC_8 in hexane solution. An orange colored solid was isolated, which, however, could not be separated from the graphite generated simultaneously, so that it could not be characterized adequately. **(3)$_x$** thus generated readily reacted with N_2 to give **2** after work-up, which does not cause an EPR signal as a solid. Investigation of a hexane solution of **2** showed a characteristic signal for LNi^I, though, from which it could be derived that mononuclear $[LNi^I\text{-}N_2]$ exists in solution as part of an equilibrium.[3]

To obtain more information on **(3)$_x$** the synthetic procedure was modified, avoiding KC_8. Instead, elemental potassium was used that had been sublimed into the reaction vessel before a hexane or heptane solution of **1** was added. Simple stirring of the mixture led to the precipitation of **(3)$_x$** as an amorphous powder within one day, which again posed problems with regards to a separation from the reductant. Hence the mixture was heated to 68 °C (hexane) or 98 °C (heptane), respectively, for 2 h – thus increasing the reaction rate and keeping the product dissolved – before the temperature was lowered to 60°C to allow for the aggregation and solidification of the potassium (m.p. = 63°C). Afterwards the solution containing **(3)$_x$** could be easily transferred through a pre-warmed cannula into a pre-warmed Schlenk tube, the temperature of which was lowered every 24 h by 20 K (hexane) or 10 K (heptane), respectively (Scheme 1).



Scheme 1. Formation of **(3)$_x$** in course of reduction of **1**, subsequent reaction with donor molecules like dinitrogen.

This procedure also led to the crystallization of **(3)$_x$** in form of orange-red crystals, which were suitable for X-ray diffraction and the result of a corresponding analysis of crystals grown from heptane is shown in Figure 1. The molecular entities of **(3)$_x$**, $[L^{tBu}Ni^I(\mu\text{-}Br)K]$, are arranged in form of chains where $[L^{tBu}Ni^I\text{-}Br]^-$ units are connected by potassium ions, that is, each bromido ligand connects three metals. The potassium ions further undergo electrostatic interactions with two aryl residues of two different β-diketiminato ligands, that primarily involve the closest meta and the para C atoms (K–C 3.016(18) – 3.066(11) Å), so that they may be regarded as η^2-π interactions. While comparable complexes often exhibit T-shaped ligand arrangement, the coordination spheres of the nickel centers in **(3)$_x$** can be described best as trigonal planar as the differences between the larger and the smaller N–Ni–Br angles amount to only 5.3(3) –7.4(2) °. This is probably due to the aggregation of the molecular units to a coordination polymer. Compared to $[(L^{Me2}Ni^I)_2(\mu_3\text{-}Br)_2Li_2(THF)]$ the Ni–Br distances in **(3)$_x$** are enlarged (2.373(2) – 2.3794(15) Å), as one could expect upon the presence of a bulkier β-diketiminato ligand.[4]

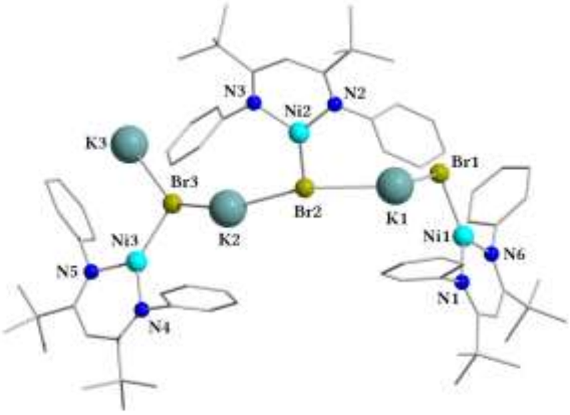


Figure 1. Molecular structure of crystalline **(3)$_x$**. Half a molecule of heptane, hydrogen atoms and i-Propyl groups of the N-Aryl groups are not depicted for clarity. Selected bond lengths (/Å): Ni1–N1 1.904(8), Ni1–N6 1.910(8), Ni2–N2 1.902(7), Ni2–N3 1.918(7), Ni3–N4 1.895(9), Ni3–N5 1.906(7), Ni1–Br1 2.3727(15), Ni2–Br2 2.3746(14), Ni3–Br3 2.3795(15), K1–Br1 3.167(3), K1–Br2 3.174(2), K2–Br2 3.183(2), K2–Br3 3.190(2), K3–Br3 3.180(3), K3–Br1' 3.167(3). Selected atom distances (/Å): Ni1–Ni2 8.337(3), Ni2–Ni3 9.063(2). Selected bond and torsion angles (/°): N1–Ni1–N6 99.8(4), N2–Ni2–N3 99.5(4), N4–Ni3–N5 99.2(3), N1–Ni1–Br1 132.8(4), N6–Ni1–Br1 127.5(3), N2–Ni2–Br2 133.6(3), N3–Ni2–Br2 126.9(2), N4–Ni3–Br3 134.1(2), N5–Ni3–Br3 126.7(2), Br1–K1–Br2 126.27(8), Br2–K2–Br3 152.34(11), Br1'–K3–Br3 122.62(10), N2–N3–N4–N5 -140.3(5), N1–N2–N3–N6 -15.32(9), N1–N4–N5–N6 4.88(13).

Upon dissolution the chains are probably broken up and oligomers are formed. This assumption is corroborated by the fact that a hexamer **(3)$_6$** could be crystallized from hexane, the molecular structure of which is shown in Figure 2; the quality of the data does not allow a discussion of bond lengths and angles, though. An EPR spectrum recorded for solid **(3)$_6$** at 77 K showed a signal of unusually low anisotropy, the simulation of which gave g values of $g_x = 2.277$, $g_y = 2.197$ and $g_z = 2.164$. Observation of this signal indicates only weak coupling of the nickel(I) centers even at these low temperatures. Since the hexamer, once crystallized is only sparingly soluble in hexane or heptane a solution spectrum could not be recorded.

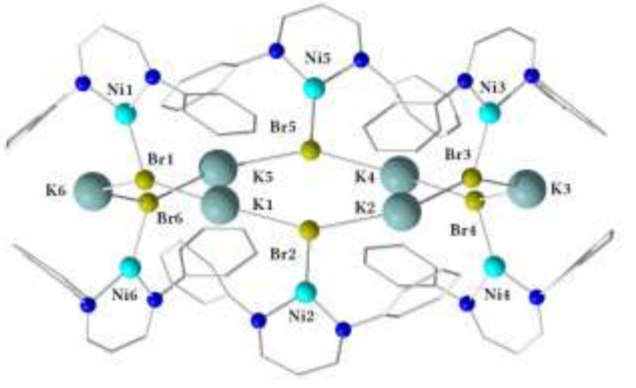
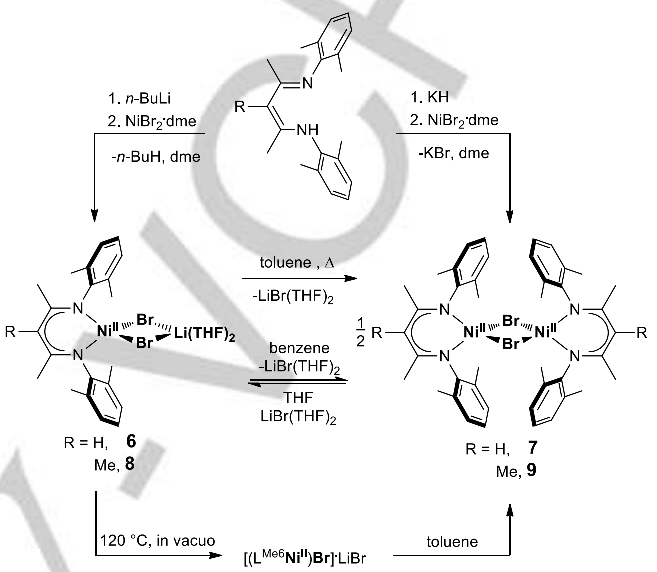


Figure 2. Molecular structure of (3)$_6$. For clarity, hydrogen atoms, i-propyl and t-butyl groups are not depicted. The molecule shown is one of two structural isomers in the unit cell of the crystal. The data quality does not allow for discussion of the bond parameters. Additionally, the cell parameters of the unit cell could not be determined to full certainty which allows for the possibility that the unit cell is half the size featuring only one hexamer.

The structural characterization of **3** in two different levels of aggregation supports the previous proposal that the reduction of **1** with potassium first of all leads to an $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Ni}^{\mathrm{I}}]$ complex, where KBr entities are saturating the coordination spheres of the nickel centers, as depicted in Scheme 1; similar complexes have been proposed by Holland and co-workers to form with iron(I) as the central metal but these could never be isolated.[12,13] Considering that in both molecular structures the nickel centers are separated from each other by more than 8 Å, an added donor like N_2 will interact initially with just one nickel center, and apparently this contact is sufficient to trigger KBr elimination and activation.

The next question was, how this situation changes if the steric bulk induced by the residues at $[\mathrm{L}^{t\mathrm{Bu}}]^-$ is reduced, bearing in mind that in case of iron changing from $\mathrm{L}^{t\mathrm{Bu}}$ to $\mathrm{L}^{\mathrm{Me7}}$ ($\mathrm{L}^{\mathrm{Me7}} = \mathrm{CMe(CMeNdmp)_2}^-$, dmp = 2,6-Dimethylphenyl) finally allowed even for the cleavage of N_2 as four iron(I) centers could approach sufficiently for a cooperative action.[14]

Hence, we have employed β-diketiminato ligands with less sterical congestion, namely $\mathrm{L}^{\mathrm{Me6}}$ and $\mathrm{L}^{\mathrm{Me7}}$ ($\mathrm{L}^{\mathrm{Me6}} = \mathrm{CH(CMeNdmp)_2}^-$, see Scheme 2). $\mathrm{HL}^{\mathrm{Me6}}$ was deprotonated with *n*-BuLi and then treated with $\mathrm{NiBr_2(dme)}$, analogously to reported protocols for $[\mathrm{L}^{\mathrm{Me2}}]$ complexes,[15] which led to the complex $[\mathrm{L}^{\mathrm{Me6}}\mathrm{Ni}^{\mathrm{II}}(\mu\text{-Br})_2\mathrm{Li(THF)_2}]$, **6**, in 87% yield after appropriate work-up. **6** corresponds to an aggregate of the desired $[\mathrm{L}^{\mathrm{Me6}}\mathrm{Ni\text{-}Br}]$ complex and one equivalent of LiBr, which was generated during its synthesis but did not leave the coordination sphere of the nickel center, as it is often observed when less bulky substituents are chosen at the β-diketiminate framework. Upon dissolution of **6** in benzene LiBr is partly eliminated and a mixture between **6** and $[(\mathrm{L}^{\mathrm{Me6}}\mathrm{Ni}^{\mathrm{II}}\mathrm{Br})_2]$, **7**, is formed (ratio 2:1 after 12 h) as revealed by an NMR spectrum (^{1}H NMR, ^{1}H,^{1}H-COSY), where two signal sets became visible. Unequivocal identification of the second signal set as arising from **7** became possible through development of an independent synthesis for **7**: When the deprotonation of $\mathrm{HL}^{\mathrm{Me6}}$ was performed with KH rather than *n*-butyl lithium, **7** was formed and could be isolated in 54% yield. Alternatively, **7** could be generated from **6** through warming to 110 °C in toluene followed by filtration at 80 °C (87% yield) and a third possibility was warming of solid **6** for 3 d to 120 °C under reduced pressure followed by extraction with a non-coordinating solvent (quantitative yield). Previously, Zhang et al. had claimed that **7** can be synthesized in 67% yield through treatment of $\mathrm{HL}^{\mathrm{Me6}}$ with *n*-butyl lithium and then with $\mathrm{NiBr_2(dme)}$.[16] In the ^{1}H NMR spectrum they had found two signal sets of paramagnetically shifted resonances for the β-diketiminate ligand, which they proposed to be due to an equilibrium of **7** with a monomeric species, similarly to $[\mathrm{L}^{\mathrm{Me2}}\mathrm{Ni}^{\mathrm{II}}\mathrm{Cl}]_2$, which has been shown to enter into such an equilibrium by Holland and co-workers.[17] However, our results suggest that the inferences of Zhang et al. are not correct: isolated, pure **7** does not enter into an equilibrium in benzene and just one signal set is observed. The chemical shifts of these signals are rather similar to those assigned to monomeric **7** by Zhang et al., while their second signal set resembles the one we were able to assign to **6**.



Scheme 2. Synthesis of nickel(II) complexes with sterically less congested β-diketiminato ligands.

Cooling of a saturated solution of **7** in hexane to –30 °C led to single crystals that were suitable for an X-ray diffraction analysis and the result is shown in Figure 3. The overall geometry is quite similar to the one found for [L^{Me2}Ni^{II}Cl]$_2$.[17] The nickel centers of **7** are located somewhat more deeply in the binding pockets of L^{Me6}, though.

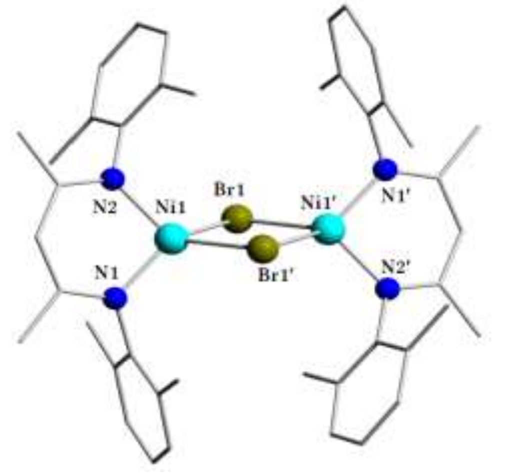


Figure 3. Molecular Structure of **7**. Hydrogen atoms are not depicted. Selected bond lengths (/Å): Ni1-N1 1.924(3), Ni1-N2 1.911(3), Ni1-Br1 2.4210(6), Ni1-Br1′ 2.4265(6). Selected bond angles (/°): N1-Ni1-N2 94.97(13), Ni1-Br1-Ni1′ 88.886(19), Br1-Ni1-Br1′ 91.11(2).

Syntheses of the complexes [L^{Me7}Ni^{II}(μ-Br)$_2$Li(THF)$_2$], **8**, and [(L^{Me7}Ni^{II}Br)$_2$], **9**, could be achieved analogously to the syntheses of **6** and **7** (see Scheme 2).

To test the potential of nickel complexes with the L^{Me6} and L^{Me7} ligands for the activation of N$_2$ **7** and **9** appeared more suitable than **6** and **8**, as the latter contain Lewis basic thf ligands which can compete with N$_2$ for coordination sites. Upon treatment of **7** dissolved in hexane with KC$_8$ in an N$_2$ atmosphere the original dark blue suspension changed color to intense red. After filtration slow cooling of a concentrated hexane solution to –30 °C yielded single crystals which were subjected to an X-ray diffraction study, and the result is shown in Figure 4. The respective complex represents a dimer [(L^{Me6}Ni^{I})$_2$], **10**, where each nickel ion binds to the β-diketiminate N atoms as well as to an aryl ring of a second [L^{Me6}Ni^{I}] unit of the dimer in a η^2-coordination mode. This constitution becomes possible due to the T-shaped ligand geometry around the nickel ions that is typical for nickel(I) complexes with β-diketiminate ligands: The N1(N4))–Ni–C and N2(N3)–Ni–C angles amount to 105.04(8)-109.37(8) and 144.40(8)-151.47(9)°, respectively, and this asymmetry is also expressed in different Ni–N bond lengths of 1.8812(17)-1.8840(17) and 1.9232(17)-1.9244(17) Å. In consequence the two coordinating arene units are nearly parallel to each other with a dihedral angle of 3.88(10)° between the two aromatic planes, and the distance between the gravity centers is 4.415(13) Å which may indicate extra stabilization due to π-π stacking interactions. The respective aryl rings are not significantly influenced by the nickel contacts: all C–C bonds are very similar and also compare well with those of the uncoordinated aryl rings. For the second independent molecule in the asymmetric unit which lies on the inversion center, the N6–Ni–C and N6–Ni–C angles amount to 103.75(8)- 113.54(9) and 141.67(8)- 154.13(9) and the coordinating arene rings are parallel due to symmetry. The distance between the centers of gravity is 4.441(13). Altogether the structure is similar to the one of [(L^{Me2}Ni^{I})$_2$] which features somewhat longer Ni-C bonds and larger separation of the parallel aryl residues which is not surprising considering the bulkiness of its L^{Me2} ligand.[4]

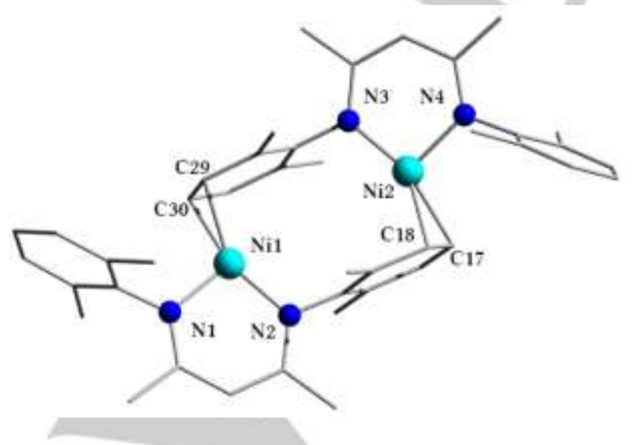


Figure 4. Molecular structure of **10**. The crystal structure contains two independent molecules in the asymmetric unit: one of them lies in general position (above) and the second one in special position. Hydrogen atoms are omitted for clarity. Selected bond lengths for the molecule in general position (/Å): Ni1–N1 1.9244(17), Ni1–N2 1.8812(17), Ni1–C29 2.074(2), Ni1–C30 2.0806(19), Ni2–N3 1.8840(17), Ni2–N4 1.9232(17), Ni2–C17 2.065(2), Ni2–C18 2.0881(19), C29–C30 1.402(3), C17–C18 1.405(3). Selected bond angles (/°): N1–Ni1–N2 97.45(7), N1–Ni1–C29 108.75(8), N1–Ni1–C30 105.88(8), N2–Ni1–C29 145.16(8), N2–Ni1–C30 150.63(8), N3–Ni2–N4 97.55(8), N3–Ni2–C17 151.47(9), N3–Ni2–C18 144.40(8), N4–Ni2–C17 105.04(8), N4–Ni2–C18 109.37(8).

Although, the reduction that had led to **10** and the subsequent crystallization of the product had been generated and crystallized in an N$_2$ atmosphere, as in case of the reduction of **1** that had led to the N$_2$ complex **2**, **10** does not contain N$_2$, and unlike [(L^{Me2}Ni^{I})$_2$] it was not reactive towards N$_2$. To test whether **10** only selectively crystallized from a mixture of compounds, the reduction of the bromide precursor with KC$_8$ was performed again in the presence and absence of N$_2$ and the two raw products were investigated EPR, IR and ^{1}H NMR spectroscopically. As can be seen from Figure 5 both EPR spectra were identical and the same was true for the IR and NMR spectra suggesting that **10** was formed in both cases as the main product.

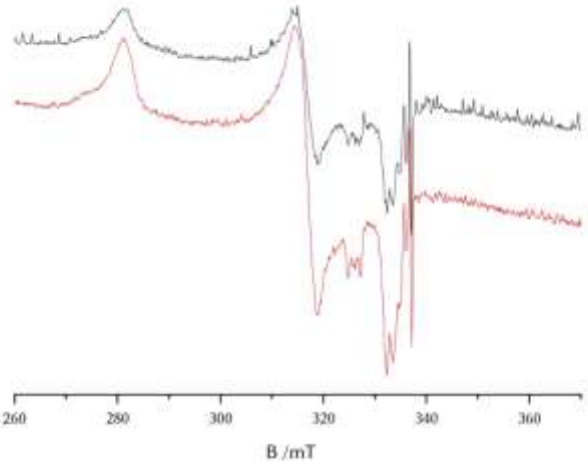


Figure 5. Comparison of EPR spectra (9.45 GHz, 77K) recorded for the frozen crude product solutions in hexane of the reduction of **7** with potassium graphite in an Ar (black) and an N_2 (red) atmosphere, respectively.

That **10** apparently is inert towards N_2 at first sight seems surprising considering that $[(L^{Me2}Ni^{I})_2]$ reacts with N_2 to form $[(L^{Me2}Ni^{I})_2(\mu\text{-}N_2)]$.[4] However, it is plausible that the less sterically demanding methyl groups of the aryl unit allow for a stronger clamping and interaction of the two monomeric $[L^{Me6}Ni^{I}]$ units than the more bulky *iso*-propyl groups of the aryl groups do in $[(L^{Me2}Ni^{I})_2]$, comparing the structural parameters.

Analogous observations as in case of **7** were made investigating the reduction of **9** containing the L^{Me7} ligand, although in this case no crystals were grown.

A comparison of these results with those reported previously is displayed in Scheme 3.[3,4,18,19] Stephan et al. first characterized the toluene complex $[(L^{Me2}Ni^{II})_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-}C_6H_5Me)]$, **I**, which is inert towards N_2 and H_2.[4,18] However, **I** can be used as nickel(I) synthon for the coordination of stronger electron donating molecules like nitriles and is in fact reactive towards stronger oxidants like N_2O.[19] The comparatively inert behavior of **I** is likely an indication of the stronger electron donation from nickel to the toluene ligand which in fact is best described as being dianionic.[18] **I** is synthesized by the reduction of $[L^{Me2}Ni^{II}(\mu\text{-}Br)_2Li(THF)_2]$, **II**, in presence of toluene. We have previously shown, that in absence of any donating molecules like toluene $[(L^{Me2}Ni^{I})_2(\mu_3\text{-}Br)_2Li_2(THF)]$, **III**, is formed.[4] **III** is reactive towards N_2 and H_2 which can be attributed to the weak electron donating character of the $[LiBr]_2(THF)_2$ core. Although **III** is stable enough for isolation, it is best described to be metastable as upon storage it slowly eliminates LiBr forming the dimer $[(L^{Me2}Ni^{I})_2]$, **IV**. Surprisingly, **IV** remains reactive towards N_2 and H_2 whereas in case of **10**, no N_2 reactivity was observed. The inert character towards N_2 can be ascribed to the decreased sterical demand of L^{Me6} and L^{Me7} as compared to L^{Me2}, which allows for an ideal interaction of the nickel(I) centers with the aryl units and thus a strong entanglement of the two LNi^{I} moieties in **10**. In case of L^{Me2} the core of **IV** cannot reach a similar arrangement, as the *iso*-propyl residues of the aryl units do not permit a sufficiently close approach. Hence, the aryl units can be readily displaced even by weak electron donating molecules like N_2.

Finally, in **(3)$_x$** the aryl rings can hardly compete with the [KBr] unit as the *t*Bu residues push them further towards the nickel bound donors forming a smaller binding pocket so that a dimeric complex $[(L^{tBu}Ni^{I})_2]$ as compared to $[(LNi^{I})_2]$ ($L = L^{Me2}$, L^{Me6}, L^{Me7}) is not stable. Consequently, the [KBr] complexes **(3)$_x$** and **(3)$_6$** are accessible and can even be stored. They remain very reactive towards added donors, though, even if they are weak like N_2, so that they can only be isolated in the absence of any donor molecules.

Conclusions

The results described above show that the reduction of the β-diketiminato nickel(II) halide complex $[L^{tBu}Ni^{II}Br]$ with potassium sources proceeds via the initial formation of $[(L^{tBu}Ni^{I})_x(\mu\text{-}Br)_xK_x]$ aggregates. The KBr entities are readily released in the presence of donors – as has been observed previously also for LiBr adducts – and the fact that even the rather weak donor N_2 replaces the alkali metal halide moieties shows that the latter represent rather labile leaving groups with low donor strength. They are thus suitable as placeholders in complexes that activate small molecules, and this recently has been exploited in nickel(II) chemistry.[20] Furthermore, the presence of stoichiometric amounts of a Lewis acid – namely potassium ions – may influence the activation process or allow for the trapping of intermediates. The findings made varying the substituents in L further show that an undisturbed interaction with the π system of an aryl ring is preferred over N_2 ligation.

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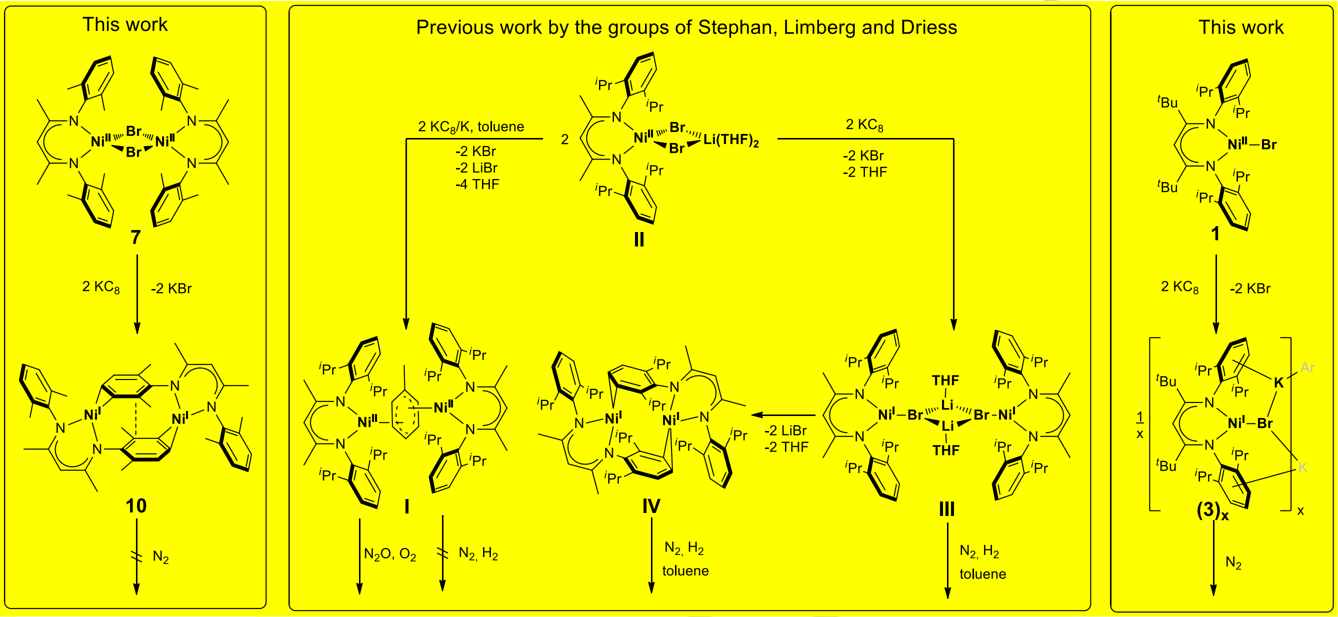

Scheme 3. Comparison of our findings to previously reported work. Upon increased bulkiness of the nacnac ligand, nickel(I) complexes with metal halide entities can be isolated. These prove to be key to the activation of very weak donating molecules like N_2.[3,4,18,19]

Experimental Section

General procedures. All experiments were carried out in a dry argon or dinitrogen atmosphere using standard Schlenk techniques and/or an MBraun glovebox. Solvents were purified using a Solvent Purification System SPS. When necessary, further purification of hexane and heptane was achieved using KC_8. $[L^{tBu}H]$,[21] $[L^{Me6}H]$[22] and $[L^{Me7}H]$[14] were prepared according to known procedures. Deuterated solvents were stored in an MBraun glovebox and further purified by the use of appropriate molecular sieves. NMR samples were prepared in an argon or dinitrogen atmosphere in an MBraun glovebox. The tubes were sealed with a J. YOUNG valve. ^1H spectra were recorded on a Bruker DPX 300 spectrometer (^1H 300.1 MHz) or on a Avance II 400 (^1H 400 MHz) at room temperature (r.t.) without rotating the tube. Paramagnetic samples were measured with a higher number of scans and with a wider sweep area (e. g. ns = 256, o_{1p} = –20 ppm, sw = 140 ppm). Chemical shifts are reported in ppm relative to the residual proton signals. Microanalyses were performed with a HEKA Euro 3000 elemental analyzer. EPR spectra were recorded at an ESR 300 X-Band EPR spectrometer (BRUKER), equipped with a quartz dewar (for measurements at 77 K) in cooperation with Dr. A. Schnegg from Helmholtz-Zentrum Berlin für Materialien und Energie.

The crystallographic data were collected at 100 K on a BRUKER D8 VENTURE area detector for **(3)$_x$** and **(3)$_6$** and STOE IPDS-2T diffractometer for **7** and **10** and, Mo Kα radiation (λ = 0.71073 Å). Multiscan absorption correction[25] was applied to the data. The structures **(3)$_x$** and **(3)$_6$** were solved by the intrinsic phasing method (SHELXT-2013)[26] the structures **7** and **10** were solved by direct methods (SHELXS-2013)[26]. All structures were refined by full-matrix least-squares procedures based on F2 with all measured reflections (SHELXL-2017)[27] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. The structure of **(3)$_x$** suffers of disorder. Some atoms involved in disorder could only be refined isotropically. **(3)$_x$** and **(3)$_6$** are heptane and hexane solvates, respectively. Part of the solvent could be refined. Smeared low remaining electron density, which could not be properly refined, was squeezed out. Additionally, for **(3)$_6$** a twin refinement has been performed. CCDC 1830051- 1830053 contains 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.

Complex (3)$_x$, Formula: $C_{231}H_{364}Br_6K_6N_{12}Ni_6$, molecular mass 4375.64 g/mol , crystal system monoclinic, Space group *Cc*, Z= 2, *a*= 32.946(4) Å, *b*= 23.350(4) Å, *c*= 23.219(4) Å, *β*= 130.678(7)°, *V*= 13546(4) Å^3, size/color/habit: 0.12x0.28x0.32/ orange/ fragment. Density (calc.) 1.073 g/cm^3, F000= 4652, R_{int} = 0.0500, total nr. of refl. 265744, indep. refl. 24222, Parameters 1210, R_1= 0.0613 (0.0711 all data), wR_2= 0.1590 (0.1631 all data), *GooF*= 1.108 (1.110 all data), data completeness 99%, largest diff. peak / hole [e/Å^3] 1.04/ -0.50. CCDC 1830053

Complex 7: Formula: $C_{42}H_{50}Br_2N_4Ni_2$, molecular mass 888.10 g/mol , crystal system monoclinic, Space group *P* 2_1/n, Z= 2, *a*= 12.7814(4) Å, *b*= 9.0306(3) Å, *c*= 17.4435(6) Å, *β*= 103.469(3)°, *V*= 1958.02(11) Å^3, size/color/habit: 0.11x0.25x0.39/ brown/ plate. Density (calc.) 1.506 g/cm^3, F000= 912, R_{int} = 0.0216, total nr. of refl. 5221, Parameters 232, R_1=

10.1002/zaac.201800100

0.0600 (0.0693 all data), wR_2= 0.1638 (0.1756 all data), *GooF*= 1.032 (1.032 all data), data completeness 99%, largest diff. peak / hole [e/Å^3] 1.70/ -2.04. CCDC 1830052

Complex 10: Formula: $C_{21}H_{25}N_2Ni$, molecular mass 364.14 g/mol , crystal system monoclinic, Space group *P* -1, Z= 6, *a*= 9.5181(3) Å, *b*= 9.5181(3) Å, *c*= 18.7375(6) Å, α= 80.597(3)°, β= 103.469(3)°, γ= 74.782(3)°, *V*= 2673.42(16) Å^3, size/color/habit: 0.09x0.19x0.29/ red/ plate. Density (calc.) 1.357 g/cm^3, F000= 1158, R_{int} = 0.0560, total nr. of refl. 47800, indep. refl. 14932, parameters 667, R_1= 0.0436 (0.0687 all data), wR_2= 0.0927 (0.0999 all data), *GooF*= 1.026 (1.026 all data), data completeness 99%, largest diff. peak / hole [e/Å^3] 0.88/ -1.04. CCDC 1830051

Improved synthesis of [$L^{tBu}Ni^{II}Br$], **1**,[3] (L^{tBu} = CH(C*t*BuNdipp)$_2^-$, dipp = 2,6-Di-*iso*-propylphenyl). 6.9 g (13.7 mmol) [$L^{tBu}H$] were dissolved in 40 mL THF. At -78 °C 6.0 mL (15.0 mmol, 1.1 eq) of a solution of a *n*-butyl lithium solution in hexanes (2,5 M) were slowly added. After 10 minutes the pale yellow solution was allowed to warm to room temperature and after another two hours, the yellow solution was added to a violet suspension of 4.2 g (13.7 mmol, 1 eq) $NiBr_2$·dme in 60 mL thf and the resulting dark suspension was heated to 66 °C for 16 hours. The resulting dark green suspension was filtered at room temperature. The filtration residue was extracted with thf until the extract was colorless. All volatiles of the combined thf solutions were removed in vacuo and the remaining residue was solidified by freeze-drying. The green powder was heated to 90 °C in a dynamic vacuo for 12 hours and subsequently it was extracted three times with 30 mL dichloromethane. The combined extracts were concentrated to 20 mL at 35 °C under reduced pressure and carefully layered with 30 mL diethyl ether followed by storage at -30 °C overnight. Black block-shaped crystals (4.30 g) grew over night and were isolated by filtration, washed with 15 mL hexanes and 15 mL diethyl ether. The collected filtrate was combined with the diethyl ether wash liquid and all volatiles were removed in vacuo. The green powder was dissolved in 20 mL dichloromethane. The solution was concentrated to 5 mL and layered with 10 mL diethyl ether. After storing the solution overnight at -30 °C, another 2.20 g of crystalline material was isolated by filtration, washed with 5 mL hexanes and 5 mL diethyl ether. 6.50 g (10.1 mmol, 74%) of crystalline **1** was isolated. The collected analytical data was identical to the previously published data. Additionally, the ^1H NMR spectrum of paramagnetic **1** was recorded and the signals assigned: δ (400.1 MHz, C_6D_6 /ppm) = 32.9 (brm, 4 H, *m*-Ar*H*), 22.1 (brs, 4 H, C*H*Me$_2$), 6.4 (d, 12 H, *Me*$_2$CH), 5.7 (d, 12 H, *Me*$_2$CH), 2.4 (s, 18 H, *t-Bu*), –18.5 (brm, 2 H, *p*-Ar*H*), –140.8 (brm, 1 H, *α-H*C(C(*t*-Bu)NAr)$_2$). δ (300.1 MHz, CD_2Cl_2 /ppm) = 24.7 (brm, 4 H, *m*-Ar*H*), 16.4 (brs, 4 H, C*H*Me$_2$), 4.8 (d, 12 H, *Me*$_2$CH), 4.5 (d, 12 H, *Me*$_2$CH), 2.1 (s, 18 H, *t-Bu*), –10.6 (brm, 2 H, *p*-Ar*H*), –98.8 (brm, 1 H, *α-H*C(C(*t*-Bu)NAr)$_2$). $^1H^1H$ COSY cross peaks: δ_1/δ_2 (400.1 MHz, C_6D_6 /ppm/ppm) = 32.9/-18.5 (*m*-Ar*H*/*p*-Ar*H*), 22.1/6.4 (C*H*Me$_2$/*Me*$_2$CH), 22.1/5.7 (C*H*Me$_2$/*Me*$_2$CH).

Synthesis of **3** as hexamer (method 1) or polymer (method 2). Method 1: 150 mg (0.23 mmol) **1** and 100 mg (2.56 mmol, 10.9 eq) elemental potassium were heated to 68 °C in freshly dried hexanes. After 2 hours, the temperature was cooled to 60 °C and the suspension was gently stirred to allow for aggregation of the remaining elemental potassium. 75% of the solution was transferred quickly into a preheated vessel at 60 °C. Subsequently, the solution was concentrated to 30 mL while remaining at 60 °C. Afterwards, the solution was stored at 60 °C. After 24 hours the temperature was decreased to 40 °C. After another 24 hours, the solution was allowed to cool to room temperature. After one week, crystals were formed which were isolated by filtration and washed with 5 mL hexanes. 37 mg (54 µmol, 22%) **(3)$_6$** were isolated as orange prisms. Method 2: 100 mg (0.16 mmol) **1** and 100 mg (2.56 mmol, 16.4 eq) elemental potassium were refluxed in 150 mL freshly dried heptane at 99 °C. Aftler two hours the temperature was reduced to 60 °C. It was stirred gently to ensure a complete agglomeration of the potassium in large agglomerates. 75% of the solution was transferred quickly into a preheated vessel at 60 °C. Subsequently, the solution was heated to 90 °C and concentrated to 30 mL while remaining at 90 °C. Afterwards, the solution was stored at 90 °C for 24 hours. Every 24 hours the temperature was reduced by 10 K until room temperature was reached. During the process, large orange crystals were formed which were isolated by filtration and washed with 5 mL hexanes. 40 mg (59 µmol based on one LNi entity, 37%) **(3)$_6$** were isolated. EPR (powder, 77 K, 9.46 GHz): $g_x = 2.277$, $g_y = 2.197$, $g_\perp = g_z = 2.164$. Elemental analysis (%) calculated for polymeric $(3)_6$·heptane[23] (4177.23 g·mol^{-1}): C 62.39, H 8.06, N 4.02; found: C 62.01, H 7.92, N 3.98.

The synthesis [$L^{Me6}Li(THF)$] was performed according to a protocol for [$L^{Me6}Li(OEt_2)$] developed by Roesky and co-workers.[24] At -90 °C 4 mL of an *n*-butyl lithium solution in hexane (10 mmol, 1.1 eq, 2.5 M) were added carefully to 2.79 g (9.09 mmol, 1 eq) $L^{Me6}H$ in 30 mL THF. After the addition, the pale yellow solution was allowed to warm to room temperature. After one hour, all volatile components were removed under reduced pressure and the yellow residue was extracted three times with 30 mL hexane. The combined extract was concentrated to 30 mL and stored for three days at -30 °C. The suspension was filtered and the filtrate was concentrated to 5 mL and stored at -30 °C for two weeks resulting in the precipitation of a powder which was isolated by filtration and washed at -30 °C using 5 mL cold hexane. 2.76 g (7.2 mmol, 79%) [$L^{Me6}Li(THF)$] were recovered as pale yellow polycrystalline powder. δ (400.1 MHz, C_6D_6 /ppm) = 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, *m*-Ar*H*), 6.93 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, *p*-Ar*H*), 4.98 (s, 1 H, *α-H*C(CMeNAr)$_2$), 2.84 (m, 4 H, *α*-C*H*$_2$ (THF)), 2.23 (s, 12 H, *o-Me*Ar), 1.82 (s, 6 H, *Me*CNAr), 0.86 (m, 4 H, *β*-C*H*$_2$ (THF)).

Synthesis of [$L^{Me6}Ni^{II}(\mu\text{-}Br)_2Li(THF)_2$], **6**. A solution of 2.46 g (6.42 mmol) [$L^{Me6}Li(THF)$] in 30 mL THF was added to a solution of 1.98 g (6.42 mmol, 1 eq) $NiBr_2$·dme in 30 mL THF and refluxed at 66 °C. After 22 hours the suspension was allowed to cool to room temperature while removing all volatile components under reduced pressure. The blue solid material was extracted three times with 20 mL dcm. All volatile components of the combined extracts were removed under reduced pressure and the solid was washed with 5 mL hexane and 5 mL THF. 3.8 g (5.6 mmol, 87%) of **6** were isolated as blue powder. δ (400.1 MHz, C_6D_6 /ppm) = 50.6 (s, 12 H, *o-Me*Ar), 47.0 (brm, 4 H, *m*-Ar*H*), 0.83 (brm, 8 H, *THF*), –0.51 (brm, 8 H, *THF*), –24.9 (brm, 2 H, *p*-Ar*H*), –67.8 (s, 6 H, *Me*CNAr), –191.0 (brs, 1 H, *α-H*C(CMeNAr)$_2$). Note: in C_6D_6, **6** enters into an equilibrium with the dinuclear nickel complex **8** and LiBr. Analytical data for **8** are listed below. Elemental analysis (%) calculated for $C_{29}H_{39}Br_2LiN_2NiO_2$ (M = 673.09 g·mol^{-1}): C 51.75, H: 5.84, N: 4.16; found: C: 52.08, H: 5.94, N: 4.02.

Synthesis of [$L^{Me7}Ni^{II}(\mu\text{-}Br)_2Li(THF)_2$], **7**. At –78 °C 2 mL of a solution of *n*-butyl lithium in hexane (2.5 M, 5 mmol, 1.05 eq) was carefully added to a solution of 1.53 g (4.77 mmol) [$L^{Me7}H$] in 30 mL THF. After complete addition the pale yellow solution was allowed to warm to room temperature and added to a suspension of 1.47 g (4.77 mmol, 1 eq) $NiBr_2$·dme in 40 mL THF after one hour. Subsequent to refluxing for 22 hours at 66 °C, the blue suspension was filtrated and the solid residue extracted with thf until the extract was colorless. Subsequently, all volatile components of the combined blue solutions were removed in vacuo and the residue was washed with 10 mL hexanes and 5 mL THF. 2.07 g (3.01 mmol, 63%) **7** were isolated as blue powder. δ (300.1 MHz, C_6D_6 /ppm) = 170.9 (brs, 3 H, *α-Me*C(CMeNAr)$_2$), 52.2 (s, 12 H, *o-Me*Ar), 48.4 (s, 4 H, *m*-Ar*H*), 0.7 (m, 8 H, *THF*), –0.5 (m, 8 H, *THF*), –30.3 (s, 2 H, *p*-Ar*H*), –73.2 (s, 6 H, *Me*CNAr). Note: in C_6D_6, **7** enters into an equilibrium with the binuclear nickel complex **9** and LiBr. δ (300.1 MHz, THF-d_8 /ppm) = 160.7 (brs, 3 H, *α-Me*C(CMeNAr)$_2$), 50.7 (s, 12 H, *o-Me*Ar), 47.6 (s, 4 H, *m*-Ar*H*), 3.5 (*THF*), –1.7 (*THF*), –28.7 (s, 2 H, *p*-Ar*H*), –69.5 (s, 6 H, *Me*CNAr). In THF-d_8 the resonances of the THF molecules bound to LiBr could not be integrated due to the exchange equilibrium of bound THF with THF-d_8. Elemental analysis (%) calculated for $C_{42}H_{50}Br_2N_4Ni_2$ (M = 687.10 g·mol^{-1}): C 52.44, H: 6.01, N: 4.08; found: C: 52.34, H: 6.21, N: 4.23. $\tilde{\nu}$ (KBr, cm^{-1}) = 3432 (s), 3062 (w), 3015 (m), 2975 (s), 2916 (s), 2873 (s), 2731 (vw), 1653 (m), 1528 (s), 1462 (s), 1443 (s), 1368 (s), 1326 (vs), 1305 (vs), 1293 (s), 1253 (w), 1192 (vs), 1161 (w), 1136 (w), 1096 (m), 1083 (w), 1045 (vs), 996 (s), 911 (m), 893 (m), 868 (s), 804 (m), 766 (vs), 761 (vs), 705 (w), 668 (w), 650 (w), 620 (vw), 497 (w).

Synthesis of $[(L^{Me6}Ni^{II})_2(\mu\text{-}Br)_2]$, **8**. The previously reported[16] synthesis of **8** did not lead to **8** but to a mixture of two compounds. According to our findings, **8** can be obtained via 3 different methods. Method 1: 1.00 g (1.49 mmol) $[L^{Me6}Ni^{II}(\mu\text{-}Br)_2Li(THF)_2]$ (**6**) were suspended in 25 mL toluene and refluxed at 111 °C for one hour. After filtration at 100 °C all volatile components of the blue filtrate were removed under reduced pressure. 571 mg (0.64 mmol, 87%) **8** were isolated as blue green solid. Method 2: A solution of 2.00 g (6.53 mmol) $[L^{Me6}H]$ in 30 mL THF was added to a suspension of 262 mg (6.53 mmol, 1 eq) potassium hydride in 20 mL THF and refluxed at 66 °C for 1 day. After cooling to room temperature, 2.02 g (6.53 mmol) $NiBr_2$·dme and 50 mL THF were added and subsequently refluxed at 66 °C. After 22 h the suspension was filtrated and the solid residue was extracted with THF until the extract was colorless. All volatile components of the combined solutions were removed in vacuo. The green blue residue was solidified by freeze-drying and further dried in high vacuum at 80 °C for 3 hours. The solid was extracted three times with 30 mL toluene at 60 °C. After evaporation of all volatile components in vacuo, 1.57 g (1.77 mmol, 54%) **8** were isolated as blue green powder. Method 3: 1.00 g (1.49 mmol) **6** in form of a fluffy powder was dried for 3 days at 120 °C in high vacuum and subsequently extracted with toluene until the extract was colorless. After evaporation of all volatile components in vacuo, 647 mg (0.73 mmol, 98%) of **8** were isolated as a blue green solid. δ (400.1 MHz, C_6D_6 /ppm) = 46.2 (brm, 8 H, *m*-Ar*H*), 42.5 (s, 24 H, *o-Me*Ar), –24.9 (brm, 4 H, *p*-Ar*H*), –80.6 (s, 12 H, *Me*CNAr), –216.8 (brs, 2 H, *α-H*C(CMeNAr)$_2$). Elemental analysis (%) calculated for $C_{42}H_{50}Br_2N_4Ni_2$ (M = 888.07 g·mol^{-1}): C 56.80, H: 5.67, N: 6.31; found: C: 56.82, H: 5.70, N: 6.20. Single crystals of **8** that were suitable for X-ray diffraction analysis were grown by storing a saturated hexane solution of 8 at -30 °C for 1 week.

Synthesis of $[(L^{Me7}Ni^{II})_2(\mu\text{-}Br)_2]$, **9**. **9** can be obtained following 2 different protocols. Method 1: A suspension of 1.00 g (1.46 mmol) **7** in 25 mL toluene was refluxed at 111 °C for 3 hours and filtrated at 100 °C. After evaporation of all volatile components of the green filtrate 615 mg (0.67 mmol, 92%) **9** was isolated as dark blue solid. Method 2: A suspension of 1.53 g (4.77 mmol) $[L^{Me7}H]$ and 201 mg (5 mmol, 1.05 eq) potassium hydride in 60 mL THF was refluxed at 66 °C. After 20 hours the suspension was cooled to room temperature and 1.47 g (4.77 mmol, 1 eq) $NiBr_2$·dme were added. After refluxing at 66 °C for 20 hours, all volatile components of green suspension were removed under reduced pressure. The residue was solidified by freeze-drying and further dried in high vacuum at 100 °C for 3 hours. Subsequently, the blue residue was extracted with a total of 150 mL hexane. All volatile components of the extract were removed in vacuo and 1.62 g (1.77 mmol, 74%) **9** was isolated as a blue solid. δ (300.1 MHz, C_6D_6 /ppm) = 200.9 (brs, 3 H, *α-Me*C(CMeNAr)$_2$), 47.4 (s, 4 H, *m*-Ar*H*), 43.0 (s, 12 H, *o-Me*Ar), –43.3 (s, 2 H, *p*-Ar*H*), –86.9 (s, 6 H, *Me*CNAr). Elemental analysis calculated for $C_{44}H_{54}Br_2N_4Ni_2$ (M = 916.12 g·mol^{-1}): C 57.69, H: 5.94, N: 6.12; found: C: 58.21, H: 6.38, N: 5.76.

Synthesis of $[(L^{Me6}Ni^{I})_2]$, **10**. A suspension of 200 mg (225 μmol) **8** and 183 mg (1.35 mmol, 6 eq) KC_8 in 40 mL hexane were reacted for 36 hours. The orange red suspension was filtrated and the solid residue was extracted with hexane until the extract was colorless. The combined solutions were concentrated to 10 mL at 50 °C under reduced pressure and slowly (over the course of several hours) allowed to cool to room temperature. After storing for 2 weeks at room temperature and subsequent filtration 68 mg (93 μmol, 42%) **10** were isolated as red crystals that were suitable for X-ray diffraction analysis. δ (400.1 MHz, C_6D_6, /ppm) = 26 – 23 (brs), 2 – 1 (brs), 0.5 – –0.5 (brs). Elemental analysis calculated for $C_{42}H_{50}N_4Ni_2$ (M = 728.26 g·mol^{-1}): C 69.27, H: 6.92, N: 7.69; gef.: C: 68.61, H: 6.90, N: 7.46.

Reduction of **9** in N_2/Ar. 30 mg (32.7 µmol) **9** und 10 mg (72.0 µmol, 2.2 eq) KC_8 in hexane were reacted for 22 hours. After subsequent filtration all volatile components of the orange red filtrate were removed under reduced pressure and the red brown polycrystalline material was analyzed. In absence and presence of N_2 identical analytical data were obtained. δ (300.1 MHz, C_6D_6 /ppm) = 30 – 20 (brs), 19 – 17 (brs), 2.8 – 1.5 (brm), –15 – –18 (brs). $\tilde{\nu}$ (KBr, cm^{-1}) = 3026 (vw), 3031 (w), 3009 (w), 2962 (s), 2913 (s), 2853 (m), 2724 (vw), 1651 (m), 1591 (w), 1557 (w), 1530 (vs), 1468 (m), 1461 (m), 1450 (m), 1447 (m), 1440 (m), 1395 (w), 1368 (vs), 1356 (vs), 1314 (w), 1200 (vs), 1087 (vs), 1057 (s), 1021 (vs), 998 (s), 871 (w), 788 (s), 762 (vs), 698 (vw), 689 (vw), 498 (vw).

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Keywords: nickel(I) • small molecule activation • low-coordination • weak ligands • alkali metals • dinitrogen activation

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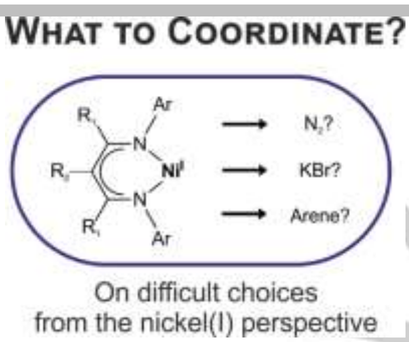
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

KBr entities formed in the course of reduction of nickel(II) halides in the ligand sphere of resulting nickel(I) complexes are readily released in the presence of donors as they represent rather labile leaving groups with low donor strength. They are thus suitable as placeholders in complexes that activate small molecules.



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Page No. – Page No.

Stabilization of β-diketiminato nickel(I) with alkaline metal halide entities for small molecule activation

ARTICLE

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