A Diazabutadiene stabilized Nickel(0) Cyclooctadiene Complex: Synthesis, Characterization and the Reaction with Diphenylacetylene

Thomas Schaub and Udo Radius*

Karlsruhe, Institut für Anorganische Chemie der Universität (TH)

Received October 31st, 2005.

Professor Kurt Dehnicke zum 75. Geburtstag gewidmet

Abstract. The reaction of $[Ni(COD)_2]$ with one equivalent of DAB^{Mes} (DAB^{Mes} = (2,4,6-Me_3C_6H_2)N=C(Me)-C(Me)=N(2,4,6-Me_3C_6H_2)) affords a mixture of the compound $[Ni(DAB^{Mes})_2]$ (2) and starting material $[Ni(COD)_2]$. The crystallographically characterized, diamagnetic complex 2 can be obtained in a stoichiometric reaction of $[Ni(COD)_2]$ and two equivalents of DAB^{Mes}. This reaction can be accelerated by addition of 1-chloro-fluorobenzene or methyl iodide. In the presence of 1-chloro-fluorobenzene, $[Ni(DAB^{Mes})(COD)]$ (3) is available via reaction of $[Ni(COD)_2]$ and

one equivalent of DAB^{Mes}. The crystallographically characterized complex **3** reacts with diphenylacetylene to afford [Ni(DAB^{Mes})-(Ph-C=C-Ph)] (4). A long-wavelength absorption band in the UV-Vis spectrum of this compound has to be assigned to a mixed MLCT/LL'CT transition, as quantum chemical calculations reveal.

Keywords: Diazabutadiene complexes; Nickel; Alkyne complexes; DFT calculations.

Introduction

Because of their high electronic and coordination mode flexibility [1, 2], the coordination chemistry of diazabutadiene ligands (RN=C(Me)-C(Me)=NR; DAB^R) has attracted attention over the last decades. This includes unusual electron-donor and -acceptor properties of these ligands, combining the useful features of N-based donor ligands such as 2,2'-bipyridine or 1,10-phenanthroline and unsaturated acceptor systems such as dienes. Consequently, these ligands are generally compatible with metal atoms in both high and low oxidation states. Especially organometallic nickel complexes with these α -diimine ligands have gained an enormous interest, mainly due to their success as effective catalysts in olefin polymerization or olefin/CO copolymerization [3]. It has been established mainly by Brookhart and co-workers, that nickel(II) organyl complexes with carefully designed diazabutadiene ligands exhibit higher activities than classical Ziegler catalysts combined with a greatly reduced sensibility towards poisoning by polar functions. DAB stabilized nickel complexes date back to the 1960s [1, 2], and especially the groups of Walther and tom Dieck developed the chemistry of such compounds [4]. In their work it has been demonstrated that the DAB ligand

* Priv.-Doz. Dr. Udo Radius Institut für Anorganische Chemie der Universität

Engesserstr., Geb. 30.45 D-76128 Karlsruhe, Germany

Tel: (Int) + 721-608-8097

email: radius@aoc1.uni-karlsruhe.de www.ak-radius.de system is ideally suited to stabilize nickel(0) complexes and that the application of DAB nickel(0) complexes in various fields of catalysis has been established.

We became interested into DAB nickel(0) chemistry during our latest work on C-C and C-F activation using N-heterocyclic carbene stabilized complexes of the type $[Ni_2(Im^{R2})_4(COD)]$ ($Im^{R2} = 1,3$ -di(R)imidazole-2-ylidene) [5]. $[Ni_2(Im^{iPr2})_4(COD)]$ (A) activates the C-F bond of hexafluorobenzene very efficiently and is also an excellent catalyst for the catalytic insertion of diphenyl acetylene into the



2,2'-C-C-bond of biphenylene. As was previously shown for other nickel(0) complexes [6], the reaction of **A** with equimolar amounts of biphenylene at low temperature proceeds under insertion of the nickel(0) biscarbene complex fragment into the strained 2,2'-C-C-bond to give the complex [Ni(Im^{*P*r2})₂(Biphenylene)] (**B**). Theoretical calculations on the reaction path performed on model systems revealed a probable intermediate of the type [NiL₂(η^4 -Biphenylene)] **C** (L = Im^{*P*r2}) [5b], which is located at a local minimum on the energy surface (see Scheme 1).

For the reaction of A with biphenylene, however, there is no evidence so far for the involvement of such an intermediate, since this particular insertion into the strained single bond of biphenylene is very fast on the NMR timescale. Earlier studies of Eisch and co-workers demonstrated a dependence of the insertion rate on the metal basicity of the nickel(0) complex fragment involved in the process, and therefore we aimed at isolating or identifying a η^4 - coordinated biphenylene nickel complex using a different set of ligands L. A comparison of the CO stretching vibrations of different known dicarbonyl complexes of the type $[NiL_2(CO)_2]$ [7] revealed that the complex fragment [Ni(DAB^R)] is much less basic compared to similar fragments with L = NHC, phosphine, and bipyridyl ligands, and hence appropriate for our purposes. Furthermore, cyclobutadiene complexes of the type [Ni(DAB^R)- $(\eta^4 - C_4 R'_4)$] have been reported previously [8], and thus we decided to investigate the reaction of a suitable DAB-Ni⁰ precursor and biphenylene in order to characterize a possible η^4 -coordinated intermediate.

Results and Discussuion

Following our work on NHC stabilized complexes, we intended to synthesize complexes of the type [Ni(D- AB^{R} (COD)] as a valuable precursor for the [Ni⁰(DAB^{R})] complex fragment. Previous work done in the groups of tom Dieck and Walther [4d, e, f] demonstrated that diazadiene stabilized Ni⁰ complexes are accessible via reduction of nickel(II) precursors in the presence of diazadiene or from the reaction of [Ni(COD)₂] and a corresponding diazadiene. In the latter case usually the substitution of a second DAB ligand of an intermediate [Ni(DAB^R)(COD)] usually proceeds much faster compared to the first substitution of COD. The reactions of [Ni(COD)₂] and two equivalents of diazadiene led to persubstituted complexes of the type [Ni(DAB)₂] with some exceptions for diazadienes with sterically very demanding groups substituted at the nitrogen atom. For the sterically very demanding DAB^{Dip} (Dip = 2,6 di(isopropyl)phenyl) ligand, tom Dieck et al. reported the formation of metallic nickel during the reaction of [Ni(COD)₂] with one or two equivalents of the diazadiene [4g], respectively, and only traces of the complex [Ni(DAB^{Dip})-(COD)] using an excess of the ligand. For other aryl substituted ligand systems, however, compounds of the type [Ni(DAB^{Ar})₂] are known [4g]. Therefore, we decided to use the sterically less demanding mesityl substituted DAB^{Mes} ligand 1. This diazabutadiene was synthesized according to a procedure reported by *tom Dieck* and co-worker [4g] for other aryl-substituted diazadienes, i.e. via the acid catalyzed condensation reaction of 2,4,6-trimethyl aniline and 2,3-butanedione. The molecular structure of 1 (see Figure 1) reveals a *trans*-alignment of the nitrogen atoms in the solid state with a C(1)=N-double bond (bond length 1.278(2) Å) and a C(1)-C(1)' single bond (1.500(2) Å) in the diazadiene unit. The C=N stretching vibration in the infrared spectrum of 1 was observed as a strong band at 1638 cm⁻¹.



Figure 1 ORTEP diagram of the molecular structure of DAB^{Mes} (1) in the solid state (ellipsoids set at 40 % probability level). H atoms have been omitted for clarity.

Selected bond lengths/Å and angles/°: C(1)-C(1)': 1.500(2), C(1)-C(2): 1.497(3), N-C(1) 1.278(2), N-C(3): 1.427(2), N-C(1)-C(1)': 116.23(15), N-C(1)-C(2): 125.75(19), C(1)-N-C(3): 119.79(15).

In order to synthesize a useful precursor of the [Ni(DAB^{Mes})] complex fragment, the nickel bis(cyclooctadiene) complex was reacted with one equivalent of the diazadiene, which resulted in a mixture of purple [Ni(DAB^{Mes})₂] (2) and starting material. The pure diamagnetic compound 2 can be synthesized from the reaction of [Ni(COD)₂] and two equivalents diazadiene in good yield. This reaction can be accelerated by addition of 1-chlorofluorobenzene or methyl iodide. In the proton NMR spectrum of 2, a set of singlets for the methyl groups of the backbone (-1.43 ppm), the methyl groups of the arene rings (2.22 ppm, 2.43 ppm) and for the arene hydrogen atoms (6.80 ppm) were detected. The mass spectrum of the isolated purple powder reveals a signal for the molecular ion, which fragmented under cleavage of the diazadiene ligand. The UV-Vis spectrum of a 10^{-4} M solution of 2 in hexane shows a main absorption at $\lambda = 508$ nm ($\varepsilon_{max} =$ 2449 1mol⁻¹cm⁻¹) and a absorption of lower intensity at $\lambda = 762 \text{ nm} (\epsilon_{max} = 876 \text{ 1mol}^{-1} \text{cm}^{-1})$ in the visible region. The presence of two absorption bands in the UV-Vis spectra of bis(diaazadiene) nickel complexes is characteristic for compounds with a significant distortion from tetrahedral to square planar (see below) and are - according to theoretical calculations – due to charge transfer excitations [9].

Crystals suitable for X-ray diffraction have been obtained from saturated hexane solutions. Complex **2** crystallizes in the orthorhombic space group Fdd2 with half of the molecule in the asymmetric unit. The molecular structure of $[Ni(DAB^{Mes})_2]$ (**2**) along with selected bond lengths and angles is shown in Figure 2.



Figure 2 ORTEP diagram of the molecular structure of [Ni(DAB^{Mes})₂] (2) in the solid state (ellipsoids set at 40 % probability level). H atoms have been omitted for clarity.

Selected bond lengths/Å and angles/°: Ni-N(1): 1.943(6), Ni-N(2): 1.953(5), N(1)-C(1): 1.316(9), N(1)-C(3): 1.459(7), N(2)-C(12): 1.356(9), N(2)-C(14): 1.432(6), C(1)-C(12): 1.416(6), C(1)-C(2): 1.484(11), C(12)-C(13): 1.501(10), N(1)-Ni-N(2): 148.44(13), N(1)-Ni-N(1)': 108.8(3), N(2)-Ni-N(2)': 107.8(3), N(1)-Ni-N(2): 80.45(19).

Molecular structures of complexes [Ni(DAB^R)₂] reported earlier have shown that dialkyl-substituted derivatives adopt a distorted tetrahedral coordination (D_{2d}) in which the planes of the chelates are orthogonal with respect to each other, whereas this angle significantly deviates from 90° for aryl-substituted derivatives to adopt (pseudo) D₂ symmetry [4f, g, 10]. This deviation presumably reflects the excellent π accepting properties especially of the aryl substituted ligand system and a partial oxidation of the nickel(0) atom takes place, which is connected with a distortion of the coordination sphere from tetrahedral towards square planar. In 2, the chelates intersect each other under an angle of $75.0(6)^{\circ}$, which is much larger (i.e. towards a tetrahedral coordination) compared to the corresponding dihedral angles found for $[Ni(DAB^{DMP})_2]$ (44.5°, DMP = 2,6-Me₂C₆H₃) and $[Ni(DAB^{DIP})_2]$ (51°). It is also interesting to note that for the isoelectronic tetraazadiene complex [Ni{(3,5- $Me_2C_6H_3)_2N_4$ [2] this dihedral angle is 90° [11]. Since tetraazadiene ligands are considered as even better π -electron acceptors than diazabutadiene ligands other factors may also be operative. The planes through the aryl rings intersect the C₂N₂ cores of the ligands under an angle of approximately 50° (49.6(9)°). This tilting might be expected for sterical reasons, but also diminishes delocalization throughout the coordinated ligand system. Within the DAB core, the C-N bond lengths of the ligand are slightly increased (N(1)-C(1) of 1.316(9) Å and N(2)-C(12) of 1.356(9) Å vs. 1.278(2) Å in 1) and the C-C bonds decreased (C(1)-C(12) of 1.416(6) vs. 1.500(2) A in 1) compared to the uncoordinated ligand, which also reflects significant charge transfer from the nickel(0) atom to the ligand.

Since all attempts to synthesize $[Ni(DAB^{Mes})(COD)]$ (3) starting from DAB^{Mes} and $[Ni(COD)_2]$ failed in first experiments due to a fast second substitution of the COD ligand in 3, we were interested in a procedure both to differentiate and to labilize the COD substituents in $[Ni(COD)_2]$. This concept was realized by an addition of equimolar amounts of methyl iodide or 1-fluoro-chlorobenzene to $[Ni(COD)_2]$ and a subsequent addition of one equivalent of the DAB^{Mes} ligand. Following this procedure, $[Ni(DAB^{Mes})(COD)]$ (3) was synthesized in 72 % isolated yield as a dark purple compound. The ¹H and ¹³C NMR spectra of 3 show the signals typically found for coordinated DAB^{Mes} and COD ligands and the signal for the molecular ion in the EI-MS spectrum of complex 3 was detected. The UV/Vis spectrum of a 10^{-4} M solution of 3 in hexane shows absorptions at $\lambda =$ 280 nm ($\varepsilon_{max} = 10348$ 1mol⁻¹cm⁻¹) and at $\lambda = 496$ nm ($\varepsilon_{max} = 3892$ 1mol⁻¹cm⁻¹).

Crystals of 3 suitable for X-ray diffraction were grown from saturated toluene solutions at -40 °C (see Figure 3). Complex 3 crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The nickel atom is distorted tetrahedrally coordinated with two nitrogen atoms of the DAB^{Mes} ligand and two alkene entities of the COD ligand. The Ni-N and Ni-C distances are unexceptional. The C=N distances of the diazadiene ligand of 1.348(11) and 1.332(12) as well as the C-C distances of 1.404(15) differ significantly from the corresponding bond lengths in uncoordinated 1 and also from those observed for the molecular structure of 2. A shorter C-C distance and an elongated C-N bond of the diazadiene ligand is a result of a more pronounced backbonding to the diazadiene π^* orbital in 3 compared to the bis(diazadiene) complex 2, which clearly indicates that the metal atom in the [Ni(COD)] complex fragment is more basic than the metal atom in [Ni(DAB^{Mes})].



Figure 3 ORTEP diagram of the molecular structure of [Ni(DAB^{Mes})-(COD)] (3) in the solid state (ellipsoids set at 40 % probability level). H atoms have been omitted for clarity.

Selected bond lengths/Å and angles/°: Ni-N(1): 1.942(8); Ni-N(2): 1.938(7); Ni-C(23): 2.075(10); Ni-C(26): 2.077(11); Ni-C(27): 2.077(12); Ni-C(30): 2.076(10); N(1)-C(1): 1.348(11); N(2)-C(2): 1.332(12); C(1)-C(2) 1.404(15); C(27)-C(26): 1.382(16); C(30)-C(23): 1.367(15); N(1)-Ni-N(2): 81.6(3), N(1)-Ni-C(23): 120.6(4), N(2)-Ni-C(23): 116.8(4), N(1)-Ni-C(30): 99.8(4), N(2)-Ni-C(30): 151.4(4), N(1)-Ni-C(27): 115.6(4), N(2)-Ni-C(30): 99.8(4), N(2)-Ni-C(30): 38.5(4), C(23)-Ni-C(27): 102.0(4), C(27)-Ni-C(30): 84.5(4), N(1)-Ni-C(26): 150.7(4), N(2)-Ni-C(26): 100.2(4), C(23)-Ni-C(26): 85.0(4), C(26)-Ni-C(30): 92.3(4), C(26)-Ni-C(27): 38.8(4), C(1)-N(1)-C(5): 117.9(7), Ni-N(1)-C(1): 113.7(6), Ni-N(1)-C(5): 128.1(5), C(2)-N(2)-C(14): 118.1(7), Ni-N(2)-C(2): 114.7(7), Ni-N(2)-C(14): 126.7(6), N(1)-C(1)-C(2) 115.2(8), N(2)-C(2)-C(1) 114.6(8).

Following our work on nickel carbene complexes, we studied the reaction behavior of complex **3** towards diphenylacetylene and biphenylene as well as mixtures thereof.

Unfortunately, complex 3 does not react with biphenylene at all, even if the reaction is carried out in refluxing toluene for more than a week. There was also no evidence for a possible nickel complex with an n⁴-coordinated biphenylene ligand. In contrast to the nickel precursors described earlier [5], in which COD acts as a monodentate, bridging ligand, the COD ligand in 3 chelates the metal atom and can not readily be replaced by biphenylene. Reaction mixtures of biphenylene and diphenylacetylene, however, react smoothly to afford a blue green material, which turned out to be the alkyne complex $[Ni(DAB^{Mes})(Ph-C=C-Ph)]$ (4). Compound 4 was synthesized separately either from the reaction of 3 with an equimolar amount of diphenylacetylene or from the reaction of [Ni(COD)₂] with one equivalent of DAB^{Mes} and one equivalent of diphenylacetylene. Complex 4 shows a simple proton and carbon NMR spectrum, which is in accordance with a monomeric complex of C_{2v} symmetry. The EI mass spectrum of 4 reveals a signal for the molecular ion. In the UV-Vis spectrum of 4, an absorbtion at 666 nm ($\varepsilon_{max} = 2424 \text{ 1mol}^{-1}\text{cm}^{-1}$) was observed which can be assigned to a metal to ligand and/or ligand to ligand charge transfer (see below).

Crystals suitable for X-ray diffraction have been obtained from saturated diethyl ether solutions at -40 °C (see Figure 4). The nickel atom of **4** is essentially planar coordinated with both the DAB ligand nitrogen atoms and the carbon atoms of the alkyne entity. The C-C-vector (C(23)-C(24)) of the alkyne is aligned within the plane defined by the nickel atom and the nitrogen atoms of the DAB^{Mes} ligand. The average Ni-C separation of 1.852 Å is comparable with Ni-C σ -bonds involving sp²-hybridized carbon centers. The C-C separation of 1.297(8) Å is indicates the presence of a C=C rather than a C=C bond. Furthermore, complex **4** displays a sharp absorption at 1752 cm⁻¹ in its infrared spectrum, shifted substantially to lower frequencies



Figure 4 ORTEP diagram of the molecular structure of $[Ni(DAB^{Mes})-(Ph-C=C-Ph)]$ (4) in the solid state (ellipsoids set at 40 % probability level). H atoms have been omitted for clarity.

Selected bond lengths/Å and angles/°: Ni-N(1): 1.916(4), Ni-N(2): 1.911(5), Ni-C(23): 1.849(5), Ni-C(24): 1.854(5), N(1)-C(1): 1.323(7), N(2)-C(2): 1.313(6), N(1)-C(14): 1.448(6), N(2)-C(5): 1.460(6), C(1)-C(2): 1.444(7), C(23)-C(24): 1.297(8), N(1)-Ni-N(2): 81.37(19), C(23)-Ni-C(24): 41.0(2), N(1)-Ni-C(23): 160.4(2), N(1)-Ni-C(24): 119.4(2), N(2)-Ni-C(23): 118.2(2), N(2)-Ni-C(24): 159.2(2), C(1)-N(1)-Ni: 115.7(4), C(14)-N(1)-Ni: 123.4(3), C(2)-Ni(2)-Ni: 115.8(3), C(5)-N(2)-Ni: 123.6(3), N(1)-C(1)-C(2): 113.0(5), N(2)-C(2)-C(1): 113.9(5), C(23)-C(24)-C(31): 141.5(5), C(24)-C(23)-C(25): 145.7(5).

than the C=C stretching vibration of unsymmetrically substituted acetylenes. The molecular structure of **4** is in much closer agreement with a C=C bond stretching vibration of unconjugated disubstituted *cis*-alkenes. Hence, a nickelacyclopropene (or nickelirene) structure with a nickel(ll) oxidation state seems to be a more important resonance structure contributor than a resonance structure where the nickel center is viewed as in a Ni⁰ oxidation state. A similar situation was observed in other nickel diphenyl acetylene complexes [5, 12].

The DAB stabilized nickel complexes reported here are brightly colored, ranging from purple to blue green in the solid as well as in solution. The absorption spectra are dominated by two broad bands of medium intensity in the visible region and an intense band in the UV region. In agreement with earlier work by Stufkens et al. [9] we can assign two long-wavelength bands to charge-transfer transitions (CT) to the π^* orbitals of the diazadiene ligands and the UV bands to ligand-centred π - π * transitions. Additionally, the occurrence of mixed MLCT/LL'CT (ligandto-ligand charge transfer) transitions instead of pure MLCT transitions have to be discussed for the alkyne complex due to contributions of the co-ligands to the frontier orbitals of the complex [13]. To investigate the electronic structure of the alkyne complex in more detail, DFT calculations have been performed on the full compound $[Ni(DAB^{Mes})(Ph-C=C-Ph)]$ (4) as well as on a significantly reduced model of this complex, [Ni(^HDAB^H)(H-C≡C-H)] (4') ($^{H}DAB^{H} = HN = C(H) - C(H) = NH$). The molecular structures were calculated on the RIDFT/BP/SVP level of theory using the TURBOMOLE set of programs. For compound 4, the HOMO has almost exclusively d-Orbital character, whereas the HOMO-1 shows significant admixture of the alkyne π_{\perp} -orbital and of one of the DAB π^* -Orbitals (see Figure 5).



Figure 5 The orbitals HOMO-1 and LUMO of $[Ni(DAB^{Mes})-(Ph-C=C-Ph)]$ 4 (left side) and the MO scheme of $[Ni(^{H}DAB^{H})-(H-C=C-H)]$ 4'.

To gain more insight into the nature of the electronic transitions, the lowest singlet excitation energies have been calculated. For complex **4** we obtain a transition at 649 nm,

which is close to the experimentally observed transition at 666 nm. The calculated singlet excitation predominantly consists of a transition from HOMO-1 to the LUMO of complex 4 (see Figure 5, left side). The ground state oneelectron energies and percentage composition of selected highest occupied and lowest unoccupied molecular orbitals have also been calculated for the reduced model system under C_{2v} symmetry and a similar ¹A₁ transition can be assigned, albeit at significantly higher energies ($\lambda = 435 \text{ nm}$) due to the modified ligand system. The dominant contributions to this band are transitions from orbital 5b₂ (89.0%) to the LUMO $6b_2$, which is predominately DAB π^* in character (see Figure 5, right side). Therefore, these transitions have mixed character, in which the contribution from the alkyne ligand cannot be neglected for the full as well as for the model system and the corresponding transitions should be assigned as mixtures of MLCT/L'LCT transitions. In the investigated systems the character of the LUMO is only moderately influenced by the variation of the alkyne coligand. More substantial changes are observed in the composition of the unoccupied orbitals at higher energy levels, which have larger contributions of the alkyne coligand.

In conclusion, we have synthesized a novel diazabutadiene nickel(0) cyclooctadiene complex, which might be a useful precursor for further studies on the reactivity of diazadiene stabilized nickel complexes. First investigations have shown that this compound does not react with biphenylene under ambient conditions, but that the COD ligand is readily displaced by good donating ligands such as diphenylacetylene. Quantum chemical calculations on the resulting alkyne complexes reveal a low energy band of the alkyne complex in the UV-Vis spectrum, that has to be assigned to a mixed MLCT/LL'CT transition instead of pure MLCT transitions.

Experimental Section

General methods and instrumentation All air/moisture sensitive manipulations were performed using standard Schlenk-line and drybox (N₂) techniques. Solvents were predried and distilled from sodium (toluene), potassium (thf), sodium-potassium alloy (1:3 w/w) (diethyl ether) and lithium aluminium hydride (hexane) under N₂. Solvents were distilled at atmospheric pressure prior to use. Deuterated solvents were dried over potassium (C₆D₆) under N₂.

¹H- and ¹³C{¹H}-NMR spectra were recorded on a Bruker AMX 300 or AV 400 spectrometer. Spectra are referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0.00$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. IR spectra were recorded on a Bruker IFS28 spectrometer as KBr pellets. All data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded on a Varian MAT 3830 spectrometer and the data are quoted as their mass/charge (*m*/*z*) ratios. UV-VIS spectra were recorded on a Perkin Elmer Lambda 900 as 10⁻⁴ M solutions in hexane; ε is quoted in mol⁻¹cm⁻¹. Elemental analyses were carried out by the analytical laboratory at the University of Karlsruhe (TH).

Synthesis of DAB^{Mes} (1). Formic acid (2 ml) was added to a solution of 2,4,6-trimethyl aniline (43.6 ml, 0.30 mol) in 90 ml methanol. Under stirring, 2,3-butanedione (13.2 ml, 0.15 mol) was added slowly at room temperature and the product starts to precipitate. The reaction mixture was stirred over night and the product was filtered off and washed twice with small portions of methanol. Yield 68.0 g (75 %); yellow powder. Crystals suitable for X ray diffraction were grown from saturated toluene solutions at -40 °C.

IR (KBr/cm⁻¹: 2971 m, 2910 m, 2849 m, 2727 w, 1737 w, 1638 s, 1477 s, 1363 s, 1211 s, 1119 s, 853 s, 292 m, 540 m. – ¹H-NMR (C_6D_6): $\delta = 1.99$ (s, 12 H, Ar-CH₃), 2.07 (s, 6 H, N=C-CH₃), 2.25 (s, 6 H, Ar-CH₃), 6.85 (s, 4 H, Ar-H). – ¹³C-NMR (C_6D_6): $\delta = 16.5$ (N=CCH₃), 18.7 (Aryl-*o*-CH₃), 21.6 (Aryl-*p*-CH₃), 125.3 (Aryl-*o*-C), 129.9 (Aryl-*m*-C), 133.1 (Aryl-*p*-C), 147.5 (Aryl-*i*-C), 169.2 (N=C).

Synthesis of [Ni(DAB^{Mes})₂] (2). DAB^{Mes} (640 mg, 2.00 mmol) and [Ni(COD)₂] (270 mg, 1 mmol) were dissolved in 40 ml THF and methyl iodide (0.062 ml, 1.00 mmol) was added at room temperature. The reaction mixture was stirred over night and filtered over a pad of celite afterwards. All volatiles were removed *in vacuo*, the solid residue was suspended in 20 ml hexane and the purple product was filtered off and dried *in vacuo*. A second fraction of the product was obtained by cooling the mother liquor to $-40 \,^{\circ}\text{C}$ over 12 h. Combined yield: 415 mg (0.59 mmol, 59 %), purple powder. Crystals suitable for X ray diffraction were grown from saturated hexane solutions at $-40 \,^{\circ}\text{C}$. C₃₆H₃₈N₂Ni [698.6 g/mol]. – Calcd. (found): C 75.54 (75.44), H 8.07 (8.02), N 8.01 (8.12) %. EI-MS m/z (%): 698 (16) [M]⁺; 378 (19) [M-DAB^{Mes}]⁺.

IR (KBr/cm⁻¹): 2993 (s), 2943 (s), 2906 (s), 2854 (s), 2725 (w), 1777 (w), 1746 (w), 1720 (w), 1692 (w), 1656 (w), 1642 (w), 1573 (w), 1555 (w), 1473 (vs), 1384 (s), 1354 (s), 1302 (vs), 1212 (s), 1163 (m), 1147 (w), 1121 (w), 1105 (w), 1033 (w), 1009 (w), 988 (m), 873 (m), 859 (m), 843 (m), 721 (w), 633 (m), 611 (m), 389 (w). - ¹H-NMR (C₆D₆): δ = -1.43 (s, 12H, N=CCH₃), 2.22 (s, 24 H, Ar-CH₃), 2.43 (s, 12H, Ar-CH₃), 6.80 (s, 8 H, Ar-H). - ¹³C-NMR (C₆D₆): δ = 19.38 (Aryl-*o*-CH₃), 21.61 (DAB-CH₃), 22.71 (Aryl-*p*-CH₃), 129.52 (Aryl-*m*-C), 129.85 (Aryl-*o*-Cm), 133.69 (Aryl-*p*-C), 140.46 (Aryl-*i*-*c*), 156.68 (DAB-N=C). - UV-Vis: λ_{max} (ε)/nm: 277 (9786), 508 (2449), 762 (876).

Synthesis of [Ni(DAB^{Mes})(COD)] (3). DAB^{Mes} (3.20 g, 10.0 mmol) and [Ni(COD)₂] (2.70 g, (10.0 mmol) were dissolved in 100 ml toluene and 1-chloro-fluorobenzene (0.74 ml, 10.0 mmol) was added at room temperature. The reaction mixture was stirred over night and all volatiles were removed *in vacuo* afterwards. The resulting solid was suspended in hexane and the product was filtered off and dried *in vacuo*. A second fraction of the product was obtained by cooling the mother liquor to -40 °C for several days. Combined yield: 3.50 g (7.20 mmol; 72 %), dark purple powder. Crystals suitable for X ray diffraction were grown from saturated toluene solutions at -40 °C. - EI-MS m/z (%): 486 (45) [M-H]⁺; 378 (100) [M-COD]⁺.

IR (KBr/cm⁻¹): 2915 (s), 2856 (m), 1644 (m), 1576 (m), 1472 (s), 1352 (s), 1232 (s), 1105 (m), 985 (m), 843 (m); 567 (m). - ¹**H-NMR** (C₆D₆): δ = -0.47 (s, 6 H, N=C-CH₃), 1.58 (m, 4 H, COD-CH₂), 2.10 (s, 12 H, Ar-CH₃), 2.36 (s, 6H, Ar-CH₃), 2.38 (m, 4 H, COD-CH₂), 3.81 (s, 4 H, COD-CH), 7.00 (s, 4 H, Ar-H). - ¹³C-NMR (C₆D₆): δ = 18.75 (Aryl-o-CH₃), 19.371 (DAB-CH₃), 21.98 (Aryl-p-CH₃), 31.59 (COD-CH₂), 86.63 (COD-CH), 128.35 (Aryl-m-C), 129.77 (Aryl-o-Cm), 133.35 (Aryl-p-C), 146.36 (Aryl-i-C), 152.79 (DAB-N=C). - **UV-Vis**: λ_{max} (ε)/mm: 280 (10348), 496 (3892).

Synthesis of [Ni(DAB^{Mes})(Ph-C=C-Ph)] 4. A solution of diphenylacetylene (1.60 g, 8.97 mmol) in 20 ml toluene was added at room temperature to a solution of [Ni(COD)₂] (2.47 g, 8.97 mmol) and DAB^{Mes} (2.87 g, 8.97 mmol) in 30 ml toluene. The resulting bluegreen reaction mixture was stirred for an hour at room temperature and afterwards all volatile material was removed *in vacuo*. The remaining solid was suspended in 30 ml hexane, the product was filtered off, washed with 5 ml hexane and dried in vacuum. Yield:

Literature preparations Ni(COD)₂ [14].

3.90 g (78 %), green powder. Crystals suitable for X ray diffraction were grown from saturated diethyl ether solutions at -40 °C. C₃₆H₃₈N₂Ni [557.4 g/mol]. - Calcd. (found): C 77.57 (77.59), H 6.87 (6.77), N 5.03 (4.91) %. - EI-MS m/z (%):556.1 (18) [M-H]⁺; 378.1 (53) [M-Ph-C=C-Ph]⁺.

IR (KBr/cm⁻¹): 3063 (m), 2903 (m), 2842 (m), 1752 (m) v(C≡C), 1592 (m), 1538 (m), 1447 (s), 1378 (s), 1333 (s), 1226 (s), 967 (s), 837 (s), 753 (s), 693 (s), 235 (s). $^{-1}$ H-NMR (C₆D₆): δ = -0.03 (s, 6 H, N=C-CH₃), 2.22 (s, 12 H, Ar-CH₃), 2.41 (s, 6 H, Ar-CH₃), 7.00 (m, 4 H, Ar-H), 7.15 (m, 10 H, Ar-H). $^{-13}$ C-NMR (C₆D₆): δ = 19.18 (DAB-Aryl-*o*-CH₃), 19.56 (DAB-CH₃), 21.92 (DAB-*p*-CH₃), 126.11 (Alkyne-*i*-C), 126.99 (DAB-*o*-C), 128.51 (Alkyne-*p*-C), 128.71 (Alkyne-*o*-C), 130.13 (DAB-*m*-C), 130.28 (Alkyne-*m*-C), 131.40 (Alkyne-*C*), 134.77 (DAB-*p*-C), 152.58 (DAB-*i*-C), 159.51 (DAB-N=C). $^{-1}$ U-V-Vis: λ_{max} (ε)/nm: 280 (12652), 296 (9599), 374 (1258), 666 (2424).

Computational details

All calculations were carried out with the DFT implementation of the TURBOMOLE program package [15]. For the DFT calculations we used the BP86 functional [16], SVP basis sets and the RI-J approximation [17–19]. The equilibrium structures of the complexes were optimized at the RIDFT level using a SVP basis. Analytic second derivatives were calculated with theprogram AOFORCE [20] using the RI-J approximation. The DFT-BP86 calculations for the excitation energies were performed with the ESCF program [21].

Details on the crystal structure determinations of DAB^{Mes} (1), $[Ni(DAB^{Mes})_2]$ (2), $[Ni(DAB^{Mes})(COD)]$ (3), and $[Ni(DAB^{Mes})(Ph-C=C-Ph)]$ (4)

CCDC-287384 to CCDC-287387 contain the supplementary crystallographic data for the structures of compounds **1–4**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS diffractometer (Ag-K_{α} radiation; compounds **1**, **2**, **3**) or a STOE-STADI4-CCD (Mo-K α radiation, compounds **4**), equipped with a FTS AirJet low

temperature device. Data were collected at 203 K. The images were processed with the Stoe software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97 [22].

Acknowledgments. This work was financially supported by the University Karlsruhe (TH), the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We thank Professor D. Fenske for his continuing support and interest in our work.

References

- [1] G. Van Koten, K. Vrieze, Adv. Organomet. Chem. 1982, 21, 151.
- [2] K. Vrieze, J. Organomet. Chem. 1986, 300, 307.
- [3] (a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, Angew. Chem.
 1999, 111, 448; Angew. Chem. Int. Ed. 1999, 38, 428; (b) S. D. Ittel, L. K. Johnson, M. Brookhart, Chem. Rev. 2000, 100, 1169; (c) S. Mecking, Angew. Chem. 2001, 113, 550; Angew. Chem. Int. Ed. 2001, 40, 534; (d) A. Michalak, T. Ziegler, Organometallics 2001, 20, 1521.
- [4] for DAB stabilized Ni⁰ complexes see for example: (a) H. Bock, H. tom Dieck, Angew. Chem. 1966, 78, 549; Angew. Chem. Int. Ed. 1966, 5, 520; (b) A. L. Balch, R. H. Holm, J. Am. Chem. Soc. 1966, 88, 5201; (c) D. Walther, Z. Anorg. Allg. Chem. 1974, 405, 8; (d) D. Walther, Z. Anorg. Allg. Chem. 1977, 431, 17; (e) H. tom Dieck, M. Svoboda, J. Kopf, Z. Naturforsch. 1978, 33b, 1381; (f) M. Svoboda, H. tom Dieck, C. Krüger, Y. H. Tsay, Z. Naturforsch. 1981, 36b, 814; (g) H. tom Dieck, M. Svoboda, T. Greiser, Z. Naturforsch. 1981, 36b, 823; (h) R. Diercks, L. Stamp, H. tom Dieck, Chem. Ber. 1984, 117, 1913; (i) R. Diercks, H. tom Dieck, Chem. Ber. 1985, 118, 428; (j) T. Schleis, T. P. Spaniol, J. Okuda, J. Heinemann, R. Mülhaupt, J. Organomet. Chem. 1998, 569, 159; (k) J. W. Strauch, G. Erker, G. Kehr, R. Fröhlich, Angew. Chem. 2002, 114, 2662; Angew. Chem. Int. Ed. 2002, 41, 2543.
- [5] (a) T. Schaub, U. Radius, *Chem. Eur J.* 2005, *11*, 5024; (b) T.
 Schaub, U. Radius, *Tetrahedron Lett.* 2005, *46*, 8195; (c) T.
 Schaub, U. Radius, unpublished.

Table 1 X-ray data collection and processing parameters.

	1	2	3	4
Formula	C ₁₁ H ₁₄ N	C22H28N2Ni0.5	C ₃₀ H ₄₀ N ₂ Ni	C ₃₆ H ₃₈ N ₂ Ni
Formula weight	160.23	349.82	487.35	557.39
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	Pbca	Fdd2	$P2_1/c$	Pna2 ₁
a / Å	16.1438(16)	20.4340(19)	10.6828(4)	21.975(4)
b / Å	7.3948(10)	25.708(4)	30.3688(15)	13.509(3)
c / Å	16.5750(16)	14.6029(13)	8.2622(3)	10.201(2)
β/°	_	_	96.646(5)	_
$V / Å^3$	1978.7(4)	7671.1(15)	2662.44(19)	3028.4(10)
Ζ	8	16	4	4
μ / mm^{-1}	0.041	0.291	0.398	0.667
Tot./Indep. reflns.	4933/1396	4926/2649	10462/4166	16387/4949
Observed reflns. a)	1089	1953	2551	3299
Parameters	113	230	306	360
Final R ^{b)} , wR ₂ ^{c, d}	0.0449, 0.1151	0.0459, 0.0852	0.0826, 0.2166	0.0566, 0.0728

^{*a*)} wReflections with I > 2 $\sigma(I)$; ^{*b*)} R = $\Sigma ||Fo| - |Fc||/\Sigma|Fo|$; ^{*c*} wR₂ = { $\Sigma [w(Fo^2 - Fc^2 - 2)^2]/\Sigma [w(Fo^2 - 2)^2]^{1/2}$; ^{*d*)} For data with I > 2 $\sigma(I)$.

- [6] (a) J. J. Eisch, A. M. Piotrowski, K. I. Han, C. Krüger, Y. H. Tsay, Organometallics 1985, 4, 224; (b) H. Schwager, S. Spyroudis, K. P. C. Vollhardt, J Organomet. Chem. 1990, 382, 191; (c) B. L. Edelbach, D. A. Vicic, W. D. Jones, Organometallics 1998, 17, 4784; (d) B. L. Edelbach, R. J. Lachicotte, W. D. Jones, Organometallics 1999, 18, 4040; (e) B. L. Edelbach, R. J. Lachicotte, W. D. Jones, Organometallics 1999, 18, 4660; (f) C. Müller, R. J. Lachicotte, W. D. Jones, Organometallics 2002, 21, 1975.
- [7] CO stretching vibrations of dicarbonyl complexes of the type $[L_2Ni(CO)_2]$: (a) ref [5]: L = Im^{iPr2}: (1927, 1847 cm⁻¹), (b) J. Chatt, F. A. Hart, J. Chem. Soc. **1960**, 1378: L = bipy (1950, 1861 cm⁻¹); (c) C. A. Tolman, J. Am. Chem. Soc. **1970**, 92, 2956: L = PⁱPr₃ (1984, 1922 cm⁻¹), L = PMe₃ (1990, 1926 cm⁻¹) L = PPh₃ (1994, 1936 cm⁻¹); (d) ref [4a]: L = DAB^{OMe} (2012, 1946 cm⁻¹); (e) ref [4j]: L = DAB^{Dip} (2014 1954 cm⁻¹).
- [8] H. Hoberg, C. Fröhlich, J. Organomet. Chem. 1981, 209, C69.
- [9] (a) P. C. Servaas, D. J. Stufkens, A. Oskam, *Inorg. Chem.* 1989, 28, 1774; (b) P. C. Servaas, D. J. Stufkens, A. Oskam, *Inorg. Chem.* 1989, 28, 1780.
- [10] (a) H. Görls, D. Walther, J. Sieler, *Cryst. Res. Technol.* 1987, 22, 1145; (b) W. Bonrath, K. R. Pörschke, R. Mynott, C. Krüger, *Z. Naturforsch.* 1990, 45b, 1647.
- [11] P. Overbosch, G. van Koten, O. Overbee, *Inorg. Chem.* 1982, 21, 2373.
- [12] (a) J. J. Eisch, X. Ma, J. N. Gitua, C. Krüger, *Eur. J. Inorg. Chem.* 2001, 77; (b) R. Waterman, G. L. Hillhouse, *Organometallics* 2003, *22*, 5182.
- [13] A. Klein, M. P. Feth, H. Bertagnolli, S. Záališ, Eur. J. Inorg. Chem. 2004, 2784.
- [14] W. A. Herrmann, A. Salzer (Eds.), Synthestic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer), Vol. 1, p. 157.

- [15] (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; (b) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104; (c) M. von Arnim, R. Ahlrichs, *J. Comput. Chem.* **1998**, *19*, 1746.
- [16] (a) A. D. Becke, *Phys. Rev. A* 1988, 38, 3098; (b) J. P. Perdew, *Phys. Rev. B* 1986, 33, 8822; *erratum*: J. P. Perdew, *Phys. Rev. B* 1986, 34, 7406.
- [17] (a) O. Treutler, R. Ahlrichs, J. Chem. Phys. 1995, 102, 346; (b)
 K. Eichkorn, O. Treutler, O. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 240, 283; (c) K. Eichkorn, F. Weigend,
 O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119.
- [18] (a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, 242, 652; (b) F. Haase, R. Ahlrichs, *J. Comput. Chem.* **1993**, 14, 907; (c) F. Weigand, M. Häser, *Theor. Chem. Acc.* **1997**, 97, 331; (d) F. Weigand, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, 294, 143.
- [19] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571.
- [20] P. Deglmann, F. Furche, R. Ahlrichs, Chem. Phys. Lett. 2002, 362, 511.
- [21] (a) R. Bauernschmitt, M. Häser, O. Treutler, R. Ahlrichs, *Chem. Phys. Lett.* 1997, 264, 573; (b) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* 1996, 256, 454; (c) R. Bauernschmitt, R. Ahlrichs, *J. Chem. Phys.* 1996, 104, 9047; (d) H. Weiss, R. Ahlrichs, Häser, *J. Chem. Phys.* 1993, 99, 1262; (e) F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, *J. Am. Chem. Soc.* 2000, 122, 1717; (f) F. Furche, *Dichtefunktionalmethoden für elektronisch angeregte Zustände*, Dissertation, Universität Karlsruhe, 2002.
- [22] (a) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.