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Conversion of imine ligands in allyl–nickel(II) complexes

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ABSTRACT

Interaction of $Ni(allyl)_2$ and bidentate nitrogen-containing ligands (phenanthroline-1,10; bis(2,6-diisopropylphenyl)diazabutadiene) has been studied. It has been shown that coordination of diimine ligands proceeds with transfer of an allylnickel group to the diimine frame and formation of a covalent Ni–N bond giving rise to imine(amide)Ni(II) complexes. In the case of phenanthroline dearomatization of one heteroaromatic ring takes place. The low-spin imine(amide)allyl complexes $(allyl)Ni(C_{15}H_{15}N_2)$ (**1**) and $(allyl)Ni(C_{29}H_{42}N_2)$ (**3**) have been isolated as crystals and characterized by solution spectroscopy. Combining two molar equivalents of phenanthroline-1,10 with $Ni(allyl)_2$ results in the transfer of both allyl groups and formation of the high-spin imine(amide)Ni(II) complex $Ni(C_{15}H_{15}N_2)_2$ (**2**).

1. Introduction

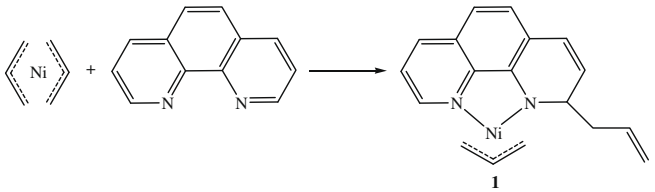
Dimerization and polymerization of olefins are among the most important industrial processes nowadays. Neutral and cationic complexes of nickel are applied in highly effective homogeneous processes of ethylene oligomerization, such as SHOP-process [1–4]. Comparatively recently it has been shown that bidentate diimine nickel complexes can catalyze conversions of low olefins into products of different polymerization degree ranging from dimers to high molecular weight polymers [5]. Of special importance is that diimine nickel complexes may be useful for manufacture of α-olefinic products [6–8].

Diimine ligands allow an extensive varying both the geometric and donor–acceptor properties of catalytically active complexes and thereby a control over properties of the prepared catalysts [9–18]. This gave a great impetus to syntheses of a wealth of new diimine ligands and their metallo-complexes with different transition metals [19–32].

One of the poorest known issues, in our view, is the possibility for imine ligands to be converted within the coordination sphere of a transition metal in the course of catalytic cycle. Is the structure of a nitrogen ligand left intact over the whole life of the catalytically active species? Does the nature of the nitrogen–metal bond alter in the course of the catalyst functioning? In order to shed more light on these intriguing problems we have studied the reaction of bis(allyl)nickel with phenanthroline-1,10 and bis(2,6-diisopropylphenyl)diazabutadiene which can be ranked as classic ligands of Brookhart catalysts. These systems were chosen because they contain nickel complexes bearing an olefin unit bound to the metal atom and an imine ligand within the coordination sphere. In particular, phenanthroline and bis(2,6-diisopropylphenyl)diazabutadiene enable us to assess the behavior of a nitrogen donor atom either integrated in an aromatic system or positioned beyond it.

2. Results and discussion

Addition of one mole equivalent of phenanthroline-1,10 to an ether solution of $Ni(allyl)_2$ at −5 °C makes the yellow solution turn bright green (Eq. (1)). Raising the temperature to 35 °C leaves the coloration unaltered. Evaporation of the volatiles in vacuo gave a green powder which was readily soluble in pentane, benzene, or tetrahydrofurane. Recrystallization from pentane yielded filar crystals which decomposed in air within 10–15 min.



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For the assignment of the confusing ^{1}H and ^{13}C NMR spectra of complex **1** heteronuclear multiple bond coherence methods were applied. The ^{1}H NMR spectrum of complex **1** shows a clear signal at 5.87 ppm which is representative for an allyl group bound to nickel. The signal is displaced to a weak field by comparison with that from the complex Ni(allyl)$_2$ (4.98 ppm). In the HSQC spectrum the signal at 5.87 ppm shows a cross-peak with the ^{13}C signal at 112.65 ppm which is slightly displaced to a strong field relative to that from the complex Ni(allyl)$_2$ (112.91 ppm). All the four protons in the CH_2-groups of the allyl moiety at the nickel atom are non-equivalent (δ = 2.14, 2.57, 2.78, 3.09 ppm) and generally more shielded in comparison with those in Ni(allyl)$_2$ (1.75, 3.09 ppm) [33,34]. The proton signals show cross-peaks with ^{13}C nuclei at 51.32 and 54.90 ppm. Quantitative ^{1}H and ^{13}C NMR spectra detect the complex **1** as two isomers, different in the position of the allyl groups, only. The isomers ratio is about 1:1.15. An independence of the ratio from the used solvent was observed in benzene, toluene and in tetrahydrofurane. The difference in the intensities allowed the assignment of all NMR signals to particular isomers. In 1967 Wilke and co-workers [33] reported that Ni(allyl)$_2$ exists in the form of dynamically equilibrated *cis*- and *trans*-isomers differing by the locations of the allyl moieties. The ratio between these isomers depends strongly on the temperature and ranges from 3:1 at +30 °C to 8:1 at −70 °C. Quantitative NMR spectroscopy was applied from 60 °C up to −83 °C to elucidate the possibility of the transformation between the *cis*- and *trans*-isomers of complex **1**. However, the ratio of the *cis*-, *trans*-isomers was constant in the temperature range. It is noteworthy that both the intensities and the ratio between the signals of the *cis*- and *trans*-isomers left constant for at least two months when a solution was kept in a sealed NMR ampoule. This fact suggests a rather high energy barrier for the interconversion of the *cis*- and *trans*-forms of the complex. The presence of two isomers may testify that the formation of complex **1** proceeds at two reaction centers or according to two different mechanisms.

The IR spectrum of complex **1** displays a significant displacement of the skeleton vibration bands of phenanthroline rings in the region of 1637–1322 cm^{-1} together with the appearance of new intensive narrow lines at 904 and 846 cm^{-1} attributable to the vibrations of a dearomatized nitrogen heterocycle. Furthermore, in the low-frequency IR region there appears a narrow line at 291 cm^{-1} which can be assigned to the Ni–N vibration [34]. The mass-spectrum of complex **1** has the molecular ion peak m/z 320 with a very low intensity (3.5%). It is quite explicable by a facile detachment of the allyl moiety from the nickel atom during the ionization. It is also supported by a high intensity of the signal at m/z 279 ($M^+-C_3H_5$). All the spectral data are in excellent agreement with those of an X-ray analysis (Fig. 1).

Analysis of the X-ray data as a whole allows one to state that the dearomatized moiety of the formed ligand is characterized by elongation of the ring skeleton bonds (N2–C10 = 1.469 Å, N2–C11 = 1.329 Å, C9–C10 = 1.505 Å) and a short Ni–N bond (N2–Ni = 1.896 Å) that is recognized as a δ-bond, whereas the N1–Ni bond is close by its parameters to the usual diazadiene coordination. As suggested by solution spectroscopy one may assert that the dearomatized moiety of the ligand contains a sp^3-hybridized nitrogen atom, whereas that of the aromatic part remains sp^2-hybridized.

Thus the obtained data support the mechanistic view that phenanthroline reacts with Ni(allyl)$_2$ by formally inserting the C=N moiety into the Ni–C bond of the allyl complex. In the process one of the N-heterocycles undergoes dearomatization which is attended with the formation of a new five-membered metallocycle. Noteworthy, this cycle comprises two Ni–N bonds of fundamentally different character that may play an essential role in the electronic and geometric properties of the resulting amide-imine

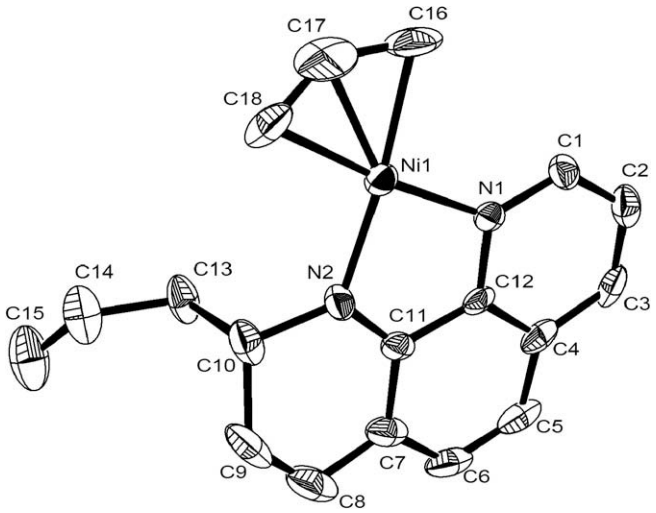
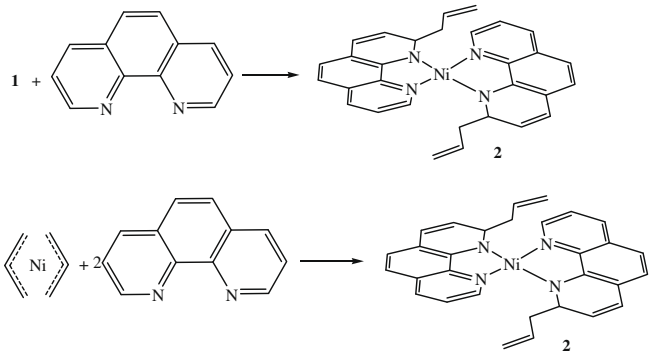


Fig. 1. Molecular structure of **1** (ORTEP plot with hydrogen atoms omitted); distances between selected atoms [Å] and angles [°]: Ni–N1 = 1.921(3), Ni–N2 = 1.896(3), Ni–C17 = 1.969(6), N1–C1 = 1.325(4), N1–C12 = 1.372(4), C1–C2 = 1.383(5), N2–C10 = 1.469(5), N2–C11 = 1.329(5), C10–C9 = 1.505(6), N1–Ni–N2 = 85.14(12), N2–Ni–C18 = 100.97 (16), N1–Ni–C17 = 133.6(3), N2–Ni–C17 = 136.3(2), Ni–N2–C11 = 112.5(2), Ni–N1–C12 = 111.5(2).

complex as a whole. To the best of our knowledge, no reaction associated with a similarly profound altering of an aromatic heterocyclic ligand has been described. We reason that if the ligands of the catalytically active species undergo such dramatic change in both the electronic and geometric structures, it must crucially affect the course of catalysis.



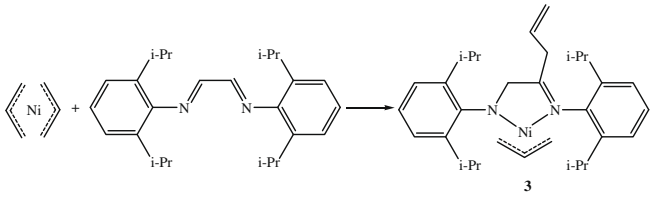
(2)

To test complex **1** for a possible introduction of the second phenanthroline molecule we have carried out its reaction with one mole equivalent of phenanthroline.

When phenanthroline was added to an ether solution of complex **1** the color of the reaction mixture turned from bright green to greenish-brown. A similar change can be seen when the reaction proceeds in pentane, tetrahydrofurane, or benzene. Vacuum evaporation gave a greenish-brown powder which during recrystallizations gave no crystals suitable for X-ray analysis. The ^{1}H NMR spectrum of the compound contains very broad and grossly shifted signals, whereas the ^{13}C spectrum has no signals apart from those of the solvent. Varying the concentration and solvents (THF, C_6D_6, acetone, toluene, and pyridine) did not improve the resolution. The product appears to be a paramagnetic material. Its EPR spectrum contained no signals from both the powdered complex and its solutions at 296–77 K. This may be explained by the high-spin state of a tetrahedral d^8-complex of Ni(II). The mass-spectrum does not display the molecular ion that seems to result from a low stability of the complex and its decomposition in the course of the

ionization. The peak at the maximum m/z (222) is assigned to the molecular ion of the protonated ligand $C_{15}H_{15}N_2^+$. In the IR spectrum of complex **2** one can see lines located close to those of complex **1** together with novel intensive narrow bands at 812 and 728 cm^{-1} in the region expected of the dearomatized heterocycle and at 1531, 1420 and 1405 cm^{-1} in the region of the skeleton vibrations of aromatic rings. In the low-frequency IR region of Ni–N vibrations a broadened band appears at 238 cm^{-1} that is shifted toward lower frequencies, as compared with complex **1**. Clearly the IR spectrum contains a second set of bands which is consistent with a tetrahedral structure of complex **2**. Thus the second phenanthroline unit is inserted into the second Ni–C allyl bond to form a high-spin tetrahedral nickel(II) complex **2**. We have also prepared this complex by reacting $Ni(allyl)_2$ with two mole equivalents of phenanthroline (Eq. (2)).

When one mole equivalent of bis(2,6-diisopropylphenyl)diazabutadiene was added to an ether solution of $Ni(allyl)_2$ at 0–5 °C the color of the reaction mixture turned from yellow to bright red. Crystallization from pentane at −30 °C gave bright red plates of complex **3** (Eq. (3)). The ^1H NMR spectrum of complex **3** contains the well resolved multiplet at 5.35 ppm from one proton which is characteristic of the allyl group bound to nickel. The signal is somewhat displaced to a strong field relative to the analogous signal of complex **1** and significantly displaced to a weak field relative to that of $Ni(allyl)_2$ (4.98 ppm) [33,34].

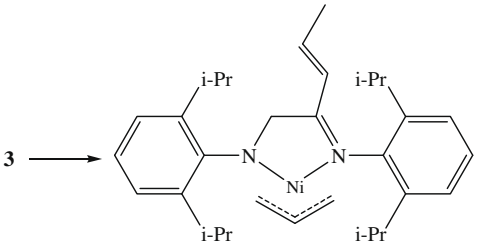


(3)

In the HSQC spectrum the signal at 5.35 ppm has the cross-peak with the ^{13}C signal at 106.39 ppm which is, in contrast to complex **1**, significantly displaced to a strong field by comparison with that of $Ni(allyl)_2$ (112.91 ppm). All the four proton of the CH_2-groups of the allyl moiety at the nickel are non-equivalent (δ = 1.4, 1.43, 1.58 and 1.61 ppm) and, in general, much less shielded compared to those of complex **1**. Hence it may be suggested that the ligand of complex **3** exhibits generally more acceptor properties than the ligand of complex **1** does. The double bond position in the allyl moiety of the nitrogen-containing ligand is uniquely determined by the DEPT-135 signals at 119.48 ppm (H_2C=), 132.44 ppm (HC=) and 37.65 ppm (CH_2). When compared with the free ligand the IR spectrum of complex **3** has the $\nu(C{=}N)_{imine}$ band at 1602 cm^{-1} shifted by about 24 cm^{-1} to low frequency which correlates quite well with published data on coordination shifts in diimine ligands [21].

In the mass-spectrum of complex **3** the molecular ion peak at m/z 516 is pronounced, whereas the peak at m/z 476 ($M^+-C_3H_5$) has the highest intensity. This suggests a rather facile dissociation of an allyl moiety from the nickel.

When a solution of complex **3** is kept at 20–25 °C for 4 h, the bright red color of the solution turns reddish-brown. The process is attended with the clear replacement of the initial DEPT ^{13}C NMR signals at 119.48 ppm. (H_2C=), 132.44 ppm (HC=), and 37.65 ppm (CH_2) of the allyl moiety with CH_2-terminal group in complex **3** by the signals at 19.27 ppm (from terminal CH_3-group), 140.89 ppm (HC=), 124.10 ppm (HC=) of the propenyl moiety with terminal CH_3-group in complex **4** (Eq. (4)). The other parts of complexes **3** and **4** remain similar and the NMR signals alter insignificantly (see Section 3).



(4)

Thus, complex **3** in solution (toluene, benzene, THF, ether, pentane) undergoes a spontaneous isomerization into complex **4** which remains unaltered in solution for two months at least. The isomerization of complex **3** is attributable to a thermodynamical stabilization of complex **4** by conjugation of double bonds. From reddish-brown solutions of complex **4** in pentane, benzene, or THF a reddish-brown powder was obtained which was readily soluble but failed to form crystals suitable for X-ray analysis.

Addition of bis(2,6-diisopropylphenyl)diazabutadiene to complexes **3** and **4** does not cause a reaction. NMR spectra show no change except for appearance of the signals from the free ligand. According to NMR data the reaction of $Ni(allyl)_2$ with two mole equivalents of bis(2,6-diisopropylphenyl)diazabutadiene also gives complexes **3** and **4** and free bis(2,6-diisopropylphenyl)diazabutadiene. These observations suggest that free diimine ligands do not readily replace an imine-amide ligand at the nickel center.

The transformation of an imine ligand in the coordination sphere of a transition metal proceeding through formal insertion of a C=N moiety into the M–C bond was previously demonstrated for organometallic complexes $Zr(CH_2Ph)_4$ and $Hf(CH_2Ph)_4$ when combined with 2,5-bis(*N*-aryliminomethyl)pyrrole [23,35]. Alkylation of a diene in the reaction between diethyl zinc and bis(2,6-diisopropylphenyl)diazabutadiene was also described to form an imine(amide)ethylzinc complex [36]. Similar reactions of organonickel complexes are without precedent.

Exemplifying two classic ligands in Brookhart-type catalytic systems, we have demonstrated principal alterations of the ligand molecule by dearomatization of the aromatic heterocycle and the formation of imine(amide)nickel complexes. This reactivity of diimine ligands is bound to affect catalytic cycles of nickel complexes comprising Brookhart-type ligands. The observed dearomatization of phenanthroline under ambient conditions provides access to amide(allyl)nickel complexes and is of general interest in synthesis.

3. Experimental section

3.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials.

Infrared spectra were measured for specimens pressed in KBr tablets under argon on an Infralum FT-801 FT spectrometer. Mass spectra were obtained on a Varian MAT spectrometer.

^1H and ^{13}C NMR spectra were obtained from a Bruker AVANCE 500. Assignment of ^{13}C and ^1H signals was supported by APT, DEPT, COSY, NOESY, TOCSY, HMQC, HSQC, HMBC spectra. Melting points were measured in capillaries sealed under argon and are uncorrected. The elemental analysis of the complexes was performed on a FLACH 1112 analyzer (EA series).

3.2. Crystal structure analysis

Selected crystals were kept under paraffin oil for protection against humidity. For single crystal data collection the crystals were placed in premounted Cryoloops from Hampton Research

Table 1
Crystal data for compound **1**.

	1
Empirical formula	$C_{18}H_{18}N_2Ni$
Formula mass	321.05
Crystal size (mm)	0.20 × 0.10 × 0.02
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.8871(4)
b (Å)	19.0290(10)
c (Å)	7.8769(4)
β (°)	99.265(4)
V (Å^3)	1462.64(12)
Z	4
$D_{calcd.}$ (g/cm^3)	1.458
μ (Mo Kα) (mm^{-1})	1.320
Temperature (K)	100(2)
Data collected range (°)	$4.7 \geqslant 2\theta \geqslant 52.74$
h	$-12 \geqslant h \geqslant 12$
k	$-23 \geqslant k \geqslant 22$
l	$-7 \geqslant l \geqslant 9$
Number of reflections measured	8586
Number of unique data	2976 (R_{int} = 0.0483)
Parameters	209
Goodness-of-fit (GOF) on F^2	0.970
R_1 [$I \geqslant 2\sigma(I)$]	0.0426
wR_2 (all data)	0.0876

and cooled down to 100 K, covered with a protecting oil film. Data collection was performed using an Xcalibur diffractometer from Oxford Diffraction, equipped with the Enhance source option and Sapphire CCD detector in φ and ω-scan mode, respectively. The structure was solved by direct methods using SHELXS und refined using SHELXL-97. H atoms were added at idealized positions (see Table 1).

The Ni(allyl)$_2$ complex and bis(2,6-diisopropylphenyl)diazabutadiene were prepared according to [33,13], respectively. Phenanthroline-1,10 and all the used solvents were purchased (Merck).

3.3. Synthesis of *1*

A cold solution (−5 °C) of phenanthroline-1,10 (0.54 g, 3 mmol) in 50 ml of diethyl ether was slowly, during 30 min, added by drops to a vigorously stirred solution of Ni(allyl)$_2$ (0.423 g, 3 mmol) in 50 ml of diethyl ether keeping the temperature at −5 °C. The resulting bright green reaction mixture was kept stirring at this temperature for 2 h followed by filtration. The filtrate was evaporated in vacuo to give a bright green powder. This was dissolved in 20 ml of pentane and kept in at −30 °C for three days. Thin green needles were formed that were filtered off at −30 °C and dried for 6 h at 10^{-2} mbar, 20 °C. The product is stable in argon but air-sensitive.

Yield 632 mg (1.9 mmol), 66%.

Decomp. 82–90 °C. Anal. Calc. for $C_{18}H_{18}N_2Ni$ (321.04): C, 67.34; H, 5.65; N, 8.73; Ni, 18.28. Found: C, 67.50; H, 6.05; N, 8.93%.

HRMS: $C_{18}H_{18}N_2Ni$ calculated – 320.0823, measured – 320.0822.

HRMS: $C_{15}H_{13}N_2Ni$ ($M^+-C_3H_5$) calculated – 279.0432, measured – 279.04223.

MS (70 eV): m/z (%) = 39(36.9), 58(45.7), 98(28.5), 140(53.2), 180(74.3), 238(100.0), 279(80.5), 320(3.5).

IR (KBr) cm^{-1}: 3407(vs), 3021(m), 2915(m), 1637(s), 1616(s), 1589(s), 1542(s), 1506(s), 1463(s), 1396(s), 1376(s), 1124(s), 989(vs), 904(s), 846(s), 804(s), 786(s), 728(d), 711(s), 673(s), 646(s), 291(Ni–N, s).

Isomer A (*cis*-isomer).

^{1}H NMR (500 MHz, [D$_8$]THF, 297 K): δ = 8.31 (m, 1H, CH1), 7.94 (m,1H, CH2), 7.14(m, 1H, CH3), 6.75(d, $^3J_{HH}$ = 3.48 Hz, 1H, CH5), 6.26 (d, $^3J_{HH}$ = 9.64 Hz, 1H, CH6), 6.24 (m, 1H, CH8), 5.28 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 9.65 Hz, 1H, CH9), 4.32(m, 1H, CH10), 2.34 (m, 1H, $CH_2$13), 2.57 (m, 1H, $CH_2$13'), 5.96 (m, 1H, CH14), 4.95 (m, 2H, $CH_2$15), 2.14 (d, $^2J_{HH}$ = 12.8 Hz, 1H, $CH_2$16), 2.78 (d, $^2J_{HH}$ = 6.61 Hz, 1H, $CH_2$16'), 5.67 (m, 1H, CH17), 2.57 (d, $^2J_{HH}$ = 13.00 Hz, 1H, $CH_2$18), 3.09 (dd, $^3J_{HH}$ = 3.09 Hz, $^2J_{HH}$ = 12.73 Hz, 1H, $CH_2$18') ppm (Fig. 2).

^{13}C NMR (125 MHz, [D$_8$]THF, 297 K): δ = 148.93 (d, $^1J_{CH}$ = 180.6 Hz, C1), 138,22 (d, $^1J_{CH}$ = 161.26 Hz, C2), 121.51 (d, $^1J_{CH}$ = 157.74 Hz, C3), 130,93 (s, C4), 128.27 (d, $^1J_{CH}$ = 157.75 Hz, C5), 105.22 (d, $^1J_{CH}$ = 168.22 Hz, C6), 116.67 (s, C7), 125.65 (d, $^1J_{CH}$ = 157.74 Hz, C8), 123.57 (d, $^1J_{CH}$ = 158.9 Hz, C9), 63.96 (C10), 155.77 (s, C11), 143.58 (s, C12), 49.56 (C13), 136.17 (C14), 116.37 (t, $^1J_{CH}$ = 154.26 Hz, C15), 48.42 (C16), 109.95 (d, $^1J_{CH}$ = 159.9 Hz, C17), 55.28 (C18) ppm (Fig. 2).

Isomer B (*trans*-isomer)

^{1}H NMR (500 MHz, [D$_8$]THF, 297 K): δ = 8.31 (m, 1H, CH1), 7.95 (m, 1H, CH2), 7.14(m, 1H, CH3), 6.77(d, $^3J_{HH}$ = 3.48 Hz, 1H, CH5), 6.26 (d, $^3J_{HH}$ = 6.33 Hz, 1H, CH6), 6.28 (m, 1H, CH8), 5.29 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 9.67 Hz, 1H, CH9), 4.42(m, 1H, CH10), 2.14 (m, 1H, CH13), 2.34 (m, 1H, CH13'), 5.96 (m, 1H, CH14), 5.01 (m, 2H, $CH_2$15), 2.24 (d, $^2J_{HH}$ = 13.36 Hz, 1H, $CH_2$16), 2.89 (d, $^2J_{HH}$ = 6.75 Hz, 1H, $CH_2$16'), 5.87 (m, 1H, CH17), 3.10 (dd, $^3J_{HH}$ = 7.18 Hz, $^2J_{HH}$ = 12.67 Hz, 1H, $CH_2$18'), 2.51 (d, $^2J_{HH}$ = 13.10 Hz, 1H, $CH_2$18) ppm (Fig. 2).

^{13}C NMR (125 MHz, [D$_8$]THF, 297 K): δ = 149.04 (d, $^1J_{CH}$ = 190.42 Hz, C1), 138,25 (d, $^1J_{CH}$ = 150.2 Hz, C2), 121.55 (d, $^1J_{CH}$ = 172.04 Hz, C3), 131,06 (s, C4), 128.31 (d, $^1J_{CH}$ = 148.58 Hz, C5), 105.04 (d, $^1J_{CH}$ = 168.22 Hz, C6), 116.90 (s, C7), 125.87 (d, $^1J_{CH}$ = 156.7 Hz, C8), 123.59 (d, $^1J_{CH}$ = 159.3 Hz, C9), 62.82 (C10), 155.77 (s, C11), 143.84 (s, C12), 48.89 (C13), 136.04 (C14), 116.19 (t, $^1J_{CH}$ = 153.22 Hz, C15), 51.32 (C16), 112.65 (d, $^1J_{CH}$ = 160.16 Hz, C17), 54.90 (C18) ppm (Fig. 2).

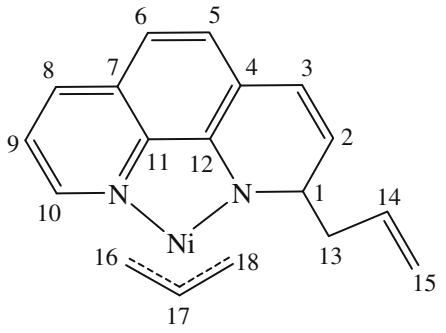


Fig. 2. Numbering scheme of carbon atoms in **1**.

3.4. Synthesis of *2*

A solution of phenanthroline-1,10 (0.36 g, 2 mmol) in 30 ml of diethyl ether was slowly, during 30 min, added by drops to a vigorously stirred solution of **1** (0.642 g, 2 mmol) in 30 ml of diethyl ether at 20 °C. The greenish-brown reaction mixture was kept stirring for 2 h followed by filtration. The filtrate was evaporated to give a greenish-brown powder. This was dissolved in 20 ml of pentane-ether (5:1 v/v) at 20–25 °C. The solution was kept in a refrigerator at −30 °C for three days to obtain a greenish-brown amorphous precipitate. This was filtered off at −30 °C and dried in vacuum for 6 h at 10^{-2} mbar, 20 °C. The product is stable in argon but air-sensitive.

Yield 470 mg (0.94 mmol), 47%.

Decomp. 126 – 128 °C. Anal. Calc. for $C_{30}H_{26}N_4Ni$ (501.25): C, 71.88; H, 5.23; N, 11.18; Ni, 11.71. Found: C, 71.05; H, 5.52; N, 10.93%.

MS (70 eV): *m*/*z* (%) = 39(65.7), 50.0(51.4), 51(50.4), 63(61.2), 180(100.0), 193(58.9), 207(36.7), 221(42.8).

IR (KBr) cm^{-1}: 3401(w), 3023(m), 2823(m), 1620(s), 1548(s), 1569(s), 1531(s), 1506(s), 1468(s), 1447(s), 1420 (s), 1405(s), 1390(s), 1362(s), 1316(s), 1236(s), 1198(s), 1122(s), 989(vs), 906(s), 844(s), 830(s), 812(s), 795(s), 770(s), 728(d), 686(s), 636(s), 238(Ni–N, w).

3.5. Synthesis of **3**

A cold solution (−5 °C) of (2,6-diisopropylphenyl)diazabutadiene (1.50 g, 4 mmol) in 100 ml of diethyl ether was slowly, during 30 min, added by drops to a vigorously stirred solution of $Ni(allyl)_2$ (0.564 g, 4 mmol) in 100 ml of diethyl ether keeping the temperature at −5 °C. The resulting bright red reaction mixture was kept at this temperature for another 2 h followed by filtration. The filtrate was evaporated to give a bright red powder. This was dissolved in 50 ml of pentane at −5 °C. The solution was kept in a refrigerator at −30 °C for five days to obtain a crystalline precipitate as thin bright red plates. The crystals were filtered off at −30 °C and dried in vacuum for 6 h at 10^{-2} mbar, 20 °C). The product is stable in argon but air-sensitive.

Yield 1.07 g (2.08 mmol), 52%.

Decomp. 60 – 65 °C. Anal. Calc. for $C_{32}H_{46}N_2Ni$ (517.41): C, 74.28; H, 8.96; N, 5.41; Ni, 11.34. Found: C, 75.16; H, 8.20; N, 4.92%.

HRMS: $C_{32}H_{46}N_2Ni$ calculated – 516.3014, measured – 516.29939 (−2 mmu).

MS (70 eV): *m*/*z* (%) = 41(24.9), 59(13.9), 186(13.0), 228(43.2), 418(33.4), 434(42.9), 476(100.0), 516(74.8).

IR (KBr) cm^{-1}: 3052(m), 3012(s), 2960(s), 2923(s), 2865(s), 2740(m), 2688(s), 1932(s), 1913(s), 1872(s), 1847(s), 1812(s), 1783(s), 1762(s), 1602(N=C,s) 1571(s), 1461(d), 1363(s), 1355(s), 1313(vs), 1253(s), 1105(s), 1076(vs), 987(vs), 919(s), 892(s), 794(s), 754(d), 568(s), 532(s).

^{1}H NMR (500 MHz, [D_8]THF, 297 K): δ = 6.95 (d, $^3J_{HH}$ = 7.12 Hz, 1H, CH3), 6.86 (m, 1H, CH4), 6.98(d, $^3J_{HH}$ = 6.87 Hz 1H, CH5), 4.37(d, $^2J_{HH}$ = 26.34 Hz, 1H, $CH_2$7), 4.55 (d, $^2J_{HH}$ = 26.34 Hz, 1H, $CH_2$7'), 7.20 (m, 3H,CH11–CH13), 1.44 (d, $^2J_{HH}$ = 4.96 Hz, 1H, $CH_2$15), 1.59 (d, $^2J_{HH}$ = 12.90 Hz, 1H, $CH_2$15'), 5.34(m, 1H, CH16), 1.43 (d, $^2J_{HH}$ = 7.96 Hz, 1H, $CH_2$17), 1.62 (d, $^2J_{HH}$ = 12.94 Hz, 1H, $CH_2$17'), 4.50 (m, 1H, CH18), 1.38 (m, 3H, $CH_3$19), 1.40 (m, 3H, $CH_3$20), 3.86 (m, 1H, CH21), 1.31 (m, 6H, $CH_3$22, $CH_3$23), 2.88 (m, 2H, CH24), 5.73 (m, 1H, CH25), 5.01 (m, 2H, CH26), 3.32 (m, 1H, CH27), 1.29 (m, 6H, $CH_3$28, $CH_3$29), 3.61 (m, 1H, CH30), 1.22 (m, 6H, $CH_3$31, $CH_3$32) ppm (Fig. 3).

^{13}C NMR (125 MHz, [D_8]THF, 297 K): δ = 157.84(C1), 147.87(C2), 123.43(C3), 123.06(C4), 123.54(C5), 146.33(C6), 72.82(C7), 191.36(C8), 146.67(C9), 139.26(C10), 124.41(C11), 127.33(C12), 124.67(C13), 139.61(C14), 50.62(C15), 106.39(C16), 53.61(C17), 28.44(C18), 26.16(C19), 26.34(C20), 28.30(C21), 24.49(C22), 25.16(C23), 37.65(C24), 132.44(C25), 119.48(C26), 29.09(C27), 24.14(C28), 24.23(C29), 29.29(C30), 24.42(C31), 24.57(C32) ppm (Fig. 3).

3.6. Synthesis of **4**

(a) A solution of complex **3** (2.58 g, 5 mmol) in 100 ml of diethyl ether was kept in a Schlenk flask at 20–25 °C for 5 h and then evaporated to give a reddish-brown powder. This was dissolved in 50 ml of pentane and kept in a refrigerator at −30 °C for five days to obtain an amorphous reddish-brown precipitate which was filtered off and dried for 6 h at 10^{-2} mbar, 20 °C. The product is stable in argon but air-sensitive. Yield 1.99 g (3.85 mmol), 77%. m.p. 97 – 100 °C 60 – 65 °C. Anal. Calc. for $C_{32}H_{46}N_2Ni$ (517.41): C, 74.28; H, 8.96; N, 5.41; Ni, 11.34. Found: C, 73.42; H, 8.05; N, 4.70%. MS (70 eV): *m*/*z* (%) = 31(12.1), 41(29.8), 59(18.8), 74(30.0), 186(13.56), 228(43.4), 418(32.4), 434(40.7), 476(100.0), 516(65.2).IR (KBr) cm^{-1}: 3052(m), 3012(s), 2960(s), 2923(s), 2865(s), 2740(m), 2688(s), 1932(s), 1913(s), 1872(s), 1847(s), 1812(s), 1783(s), 1762(s), 1641(N=C, s), 1490(s), 1384(d), 1313(vs), 1253(s), 1218(s), 1205(s), 1076(vs), 987(vs), 919(s), 873(s), 794(s), 754(d), 568(s), 532(s).^{1}H NMR (500 MHz, [D_8]THF, 297 K): δ = 6.94 (m, 1H, CH3), 6.84 (m, 1H, CH4), 6.97(m, 1H, CH5), 4.57(d, $^2J_{HH}$ = 24.81 Hz, 1H, $CH_2$7), 4.78 (d, $^2J_{HH}$ = 25.24 Hz, 1H, $CH_2$7'), 7.18 (m, 3H,CH11–CH13), 1.43 (d, $^2J_{HH}$ = 13.8 Hz, 1H, $CH_2$15), 1.59 (d, $^2J_{HH}$ = 6.25 Hz, 1H, $CH_2$15'), 5.35(m, 1H, CH16), 1.41 (d, $^2J_{HH}$ = 8.89 Hz, 1H, $CH_2$17), 1.60 (d, $^2J_{HH}$ = 12.88 Hz, 1H, $CH_2$17'), 4.51 (m, 1H, CH18), 1.26 (m, 3H, $CH_3$19), 1.29 (m, 3H, $CH_3$20), 3.88 (m, 1H, CH21), 1.20 (m, 6H, $CH_3$22, $CH_3$23), 5.70 (d, $^3J_{HH}$ = 15.7 Hz, 2H, CH24), 6.52 (m, 1H, CH25), 1.64 (d, $^3J_{HH}$ = 6.98 Hz, 3H, $CH_3$26), 3.37 (m, 1H, CH27), 1.35 (m, 3H, $CH_3$28), 1.37(m, 3H, $CH_3$29), 3.66 (m, 1H, CH30), 1.11 (m, 3H, $CH_3$31), 1.16(m, 3H, $CH_3$32) ppm (Fig. 4).^{13}C NMR (125 MHz, [D_8]THF, 297 K): δ = 158.17(C1), 148.02(C2), 123.43(C3), 123.02(C4), 123.53(C5), 146.54(C6), 69.56(C7), 184.13(C8), 147.17(C9), 139.71(C10), 124.17(C11), 127.13(C12), 124.43(C13), 140.20(C14), 50.72(C15), 106.71(C16), 53.97(C17), 28.45(C18), 26.10(C19), 26.26(C20), 28.28(C21), 24.89(C22), 25.15(C23), 124.10(C24), 140.89(C25), 19.27(C26), 29.22(C27), 23.78(C28), 24.00(C29), 29.42(C30), 24.28(C31), 24.62(C32) ppm (Fig. 4).^{1}H NMR (500 MHz, C_6D_6, 297 K): δ = 7.27 (m, 1H, CH3), 7.23 (m, 1H, CH4), 7.32(m, 1H, CH5), 4.68(d, $^2J_{HH}$ = 25.30 Hz, 1H, $CH_2$7), 4.90 (d, $^2J_{HH}$ = 25.30 Hz, 1H, $CH_2$7'), 7.06 (m, 3H,CH11–CH13), 1.79 (d, $^2J_{HH}$ = 12.98 Hz, 1H, $CH_2$15), 2.00 (d, $^2J_{HH}$ = 4.27 Hz, 1H,

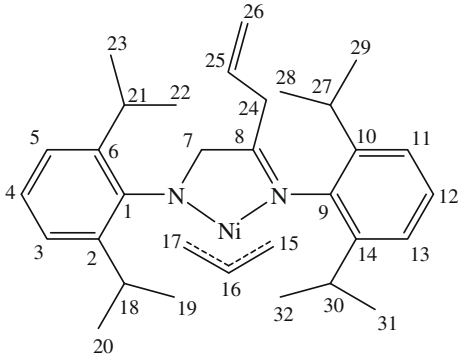


Fig. 3. Numbering scheme of carbon atoms in **3**.

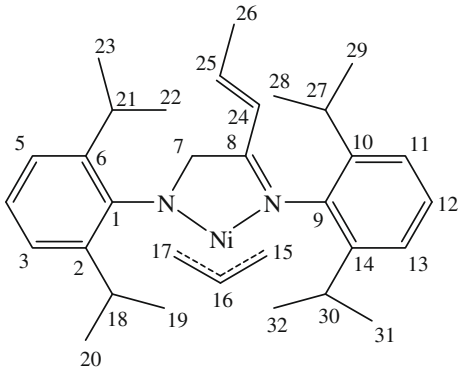


Fig. 4. Numbering scheme of carbon atoms in **4**.

$CH_2$15'), 5.46(m, 1H, CH16), 1.62 (d, $^2J_{HH}$ = 5.36 Hz, 1H, $CH_2$17), 1.83 (d, $^2J_{HH}$ = 12.98 Hz, 1H, $CH_2$17'), 4.81 (m, 1H, CH18), 1.47 (m, 3H, $CH_3$19), 1.53 (m, 3H, $CH_3$20), 4.14 (m, 1H, CH21), 1.41 (m, 6H, $CH_3$22, $CH_3$23), 5.65 (d, $^3J_{HH}$ = 15.8 Hz, 2H, CH24), 5.88 (dk, $^3J_{HH}$ = 6.97 Hz, $^3J_{HH}$ = 16.2 Hz 1H, CH25), 0.94 (d, $^3J_{HH}$ = 6.53 Hz, 3H, $CH_3$26), 3.46 (m, 1H, CH27), 1.28 (m, 3H, $CH_3$28), 1.37(m, 3H, $CH_3$29), 3.75 (m, 1H, CH30), 1.10 (m, 3H, $CH_3$31), 1.15(m, 3H, $CH_3$32) ppm (Fig. 4).^{13}C NMR (125 MHz, C_6D_6, 297 K): δ = 157.99(C1), 147.96(C2), 123.55(C3), 123.79(C4), 123.58(C5), 146.37(C6), 69.69(C7), 183.46(C8), 146.80(C9), 139.41(C10), 123.87(C11), 126.95(C12), 124.18(C13), 139.85(C14), 51.09(C15), 106.76(C16), 54.09(C17), 28.36(C18), 26.23(C19), 26.42(C20), 28.20(C21), 25.01(C22), 25.35(C23), 123.77(C24), 139.82(C25), 18.81(C26), 28.81(C27), 23.70(C28), 23.89(C29), 29.00(C30), 24.29(C31), 24.62(C32) ppm (Fig. 4).

(b) A solution of complex **3** in THF-D8 sealed in an NMR-tube was monitored with NMR-DEPR ^{13}C method using the signals of the C26 atom (Fig. 4) as distinctive ones. After 3 h at 25 °C the signal at 119.48 ppm (complex **3**) was completely replaced by the signal at 19.27 ppm (complex **4**). The transformation of complex **3** into complex **4** is almost 100%.

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Appendix A. Supplementary material

CCDC 730019 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.010.

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