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Nickel(I) Complex as the Final Product of the Sequence of Spontaneous Transformations in the System Ni(Allyl)$_2$–(2,6-Diisopropylphenyl)diazabutadiene

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Abstract—A reaction of Ni(Allyl)$_2$ with bis(2,6-diisopropylphenyl)diazabutadiene gave an imino amide allyl nickel(II) complex (**I**). Complicated rearrangements of the imino amide ligand in the coordination sphere of complex **I** spontaneously yielded a paramagnetic Ni(I) π-allyl complex as a final reaction product. The nickel complexes produced in this system were studied by EPR, IR, and 2D NMR spectroscopy and mass spectrometry. Structure **I** was examined by X-ray diffraction.

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A survey of the literature data on transition metal complexes with allyl ligands since the synthesis of their first representatives [1, 2] till now [3–6] has revealed that the π-allyl structure of transition metal complexes takes an important part in catalytic reactions. This relates to π-allyl fragments both originally present in a transition metal complex or formed immediately in its coordination sphere during reactions of complexes with olefins at a metal complex catalyst. As a rule, a π-allyl complex in catalytic systems is stabilized by various organometallic ligands. A catalytic system based on nickel and palladium diimine complexes has been proposed in [7, 8]. An undoubted advantage of such systems is that lower olefins can be transformed into linear polymers with a considerable α-form content. This type of catalytic systems holds promise as precursors of cationic or electrically neutral allyl nickel and palladium complexes with various diimine ligands including the diazabutadiene fragment [8]. Although such catalytic systems are currently under intensive study, a question is still open as to whether N-containing ligands themselves can be transformed in organometallic complexes. As a result, almost all the mechanisms proposed in the literature for the catalytic cycle ignore possible changes in the nature of the metal–ligand bond and in the structure of the diimine ligand itself [9–15]. One can state that this ligand is most often regarded as an unchangeable entity involved in the catalytic cycle as a "guest" that can either be coordinated to the metal center or quit its coordination sphere intact. Thus, possible transformations of the ligand itself are usually left out. In addition, the catalytic cycle mechanisms considered in the overwhelming majority of relevant studies are based on nickel(0) and nickel(2) complexes. The Ni^{+2} form is regarded as the second most stable species inferior only to colloidal nickel [9, 13–15]. However, some authors do note the formation of nickel(I) complexes from both nickel(II) complexes with allyl [6] and diimine ligands [10, 11].

Furthermore, despite much research dealing with allyl complexes of transition metals, the literature data on nickel allyl systems are very scarce because the attention of researchers is mainly focused on allyl complexes of palladium [16]. Obviously, this is due to both the relatively low stability of allyl complexes of nickel and the limited scope of their study by the most commonly used method (NMR spectroscopy) [17].

In this work, we studied in detail complexation between bisallylnickel(II) and bis(2,6-diisopropylphenyl)diazabutadiene (DAB) by NMR, EPR, and IR spectroscopy; DAB is an efficient, abundant, and synthetically accessible diimine ligand.

EXPERIMENTAL

All manipulations were performed using standard Schlenk ware with an argon–vacuum double manifold glass line. Solvents and volatile components were admitted into the systems by recondensation; solid components were added from evacuated tubes fused to the systems.

NMR spectra were recorded on a Bruker AVANCE 500 spectrometer in sealed evacuated tubes. For reliable assignments of NMR signals and interpretation of the spectra, we employed the APT, DEPT, COSY, NOESY, TOCSY, HMQC, HSQC, and

Chemical shifts δ of the signals in the NMR spectra of the nickel allyl complexes

Complex	$\delta_{H15anti}$	$\delta_{H17anti}$	δ_{H16}	δ_{H15syn}	δ_{H17syn}	δ_{C15}	δ_{C16}	δ_{C17}	δ_{C26}	δ_{C25}	δ_{C24}	δ_{C8}	δ_{C7}
I (THF- d_8)	1.41 $J = 13.0$	1.43 $J = 12.0$	5.34	1.59 $J = 6.0$	1.62 $J = 6.8$	53.6	106.39	50.6	119.48	132.44	37.65	191.36	72.82
II (C_6D_6)	1.83 $J = 13.0$	1.79 $J = 13.0$	5.46	1.62 $J = 6.0$	2.0 $J = 4.3$	53.75	106.43	50.75	18.47	139.49	123.46	183.13	69.4
II (THF-d_8)	1.61	1.43	5.35	1.41	1.59	53.97	106.7	50.71	19.26	140.88	124.18	184.13	69.56
$Ni(Allyl)_2$ [2, 20]	1.67 $J = 14.3$		4.9	3.76 $J = 7.6$									

HMBC techniques. IR spectra were recorded on an Infralyum FT-801 FTIR spectrometer (in KBr pellets pressed in an inert atmosphere or in Nujol between ZnSe windows). Mass spectra were measured on a Varian MAT spectrometer (direct inlet probe). Elemental analysis was carried out on a FLACH 1112 (EA series) analyzer in sealed crucibles filled and encapsulated in an inert atmosphere.

An experimental set of X-ray diffraction data for the imino amide allyl nickel(II) complex (**I**) was collected with its red single crystal (0.22 × 0.18 × 0.05 mm) on a Smart Apex II automated diffractometer (MoK_α radiation, $T = 240$ K, $2.30° \le \theta \le 28.05°$, 7168 independent reflections out of 20928 measured ones, $R_{int} = 0.1354$). The monoclinic unit cell of complex **I** has the following parameters: $a = 16.832(6)$, $b = 10.939(4)$, $c = 18.470(7)$ Å, $\beta = 116.46(2)°$, $V = 3044.7(19)$ Å^3, $P2_1/c$, $Z = 4$, $\rho_{calcd} = 1.129$ g/cm^3, $\mu = 0.658$ mm^{-1}). Structure **I** was solved by the direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. The H atoms were located geometrically and refined together with the non-hydrogen atoms using a riding model. The final residuals are $R_1 = 0.0520$ and $wR_2 = 0.1056$ ($I > 2\sigma(I)$), $R_1 = 0.1784$, $wR_2 = 0.1377$ for all reflections. The comprehensive tables of the coordinates of the basic atoms and the bond lengths and bond angles in structure **I** have been deposited with the Cambridge Crystallographic Data Collection (no. 819771; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and can be made available from the authors upon request.

All (including deuterated) solvents were purchased from Merck. Before use, solvents were placed in standard Schlenk flasks with Teflon valves by recondensation in a vacuum manifold through a U-shaped seal filled with glass beads lined with a K–Na alloy. Solvents were stored over a Na–K mirror.

The complex $Ni(Allyl)_2$ and DAB were prepared as described in [2] and [18], respectively.

Synthesis of complex I [19]. A solution of DAB (1.50 g, 4 mmol) in diethyl ether (100 mL) was slowly (for 30 min) added dropwise at −5°C to a vigorously stirred solution of $Ni(Allyl)_2$ (0.564 g, 4 mmol) in diethyl ether (100 mL). The bright red reaction mixture was stirred at about −5°C for 2 h, filtered, and concentrated in vacuo. The bright red powder that formed was dissolved in pentane (50 mL) at −5°C and the solution was kept in a freezer at −30°C for five days. The bright red crystals that formed as thin plates were filtered off at −30°C and dried in vacuo ($P = 10^{-2}$ mm Hg) at $T = 20$–25°C for 6 h. The crystals are stable under argon, yet rapidly decomposing with self-ignition in air. The yield of complex **I** was 1.07 g (2.08 mmol, 52.0%); no melting was observed up to 60–65°C (decomp.).

For $C_{32}H_{46}N_2Ni$			
Anal. calcd. (%):	C, 74.28,	H, 8.96,	N, 5.41.
Found (%):	C, 75.16,	H, 8.20,	N, 4.92.

HRMS: for $C_{32}H_{46}N_2Ni$ anal. calcd.: −516.3014, measured −516.2994 (−2 mmu).

MS (70 eV, *m/z*, %): 476 (100.0), 516 (74.8).

IR (KBr, ν, cm^{-1}): 1602 ν(C=N), 1105 ν(CCC), 532 δ(CCC).

^{1}H NMR (500 MHz, THF-d_8, 297 K, δ, ppm): 6.95 (d, 1H, CH(3), $^3J_{H3-H4} = 7.12$ Hz), 6.86 (m, 1H, CH(4)), 6.98 (d, 1H, CH(5), $^3J_{H5-H4} = 6.87$ Hz), 4.38 (d, 1H, $CH_2$7, $^2J_{H7'-H7} = 26.5$ Hz), 4.56 (d, 1H, $CH_2$7', $^2J_{H7-H7'} = 27$ Hz), 7.20 (m, 3H, CH(11), CH(12), CH(13)), 1.67 (d, 1H, $CH_2$15, $^3J_{H15-H16} = 5.98$ Hz), 1.61 (d, 1H, $CH_2$15', $^3J_{H15-H16} = 13.2$ Hz), 5.35 (d,

1H, CH(16)), 1.48 (d, 1H, $CH_2$17, $^3J_{H17-H16}$ = 5.98 Hz), 1.40 (d, 1H, $CH_2$17', $^3J_{H17-H16}$ = 14.3 Hz), 4.50 (d, 1H, CH(18)), 1.38 $CH_3$19, $CH_3$20), 3.86 (m, 1H, CH(21)), 1.31 (m, 6H, $CH_3$22, $CH_3$23), 2.88 (m, 2H, $CH_2$24'), 5.73 (m, 1H, CH(25)), 5.01 (m, 2H, $CH_2$26), 3.32 (m, 1H, CH(27)), 1.29 (m, 6H, $CH_3$28, $CH_3$29), 3.67 (m, 1H, CH(30)), 1.22 (m, 6H, $CH_3$31, $CH_3$32).

^{13}C NMR (125 MHz, THF-d_8, 297 K, δ, ppm): 157.84 (C(1)), 147.87 (C(2)), 123.06 (C(3)), 123.54 (C(4)), 123.43 (C(5)), 146.33 (C(6)), 72.82 (C(7)), 191.36 (C(8)), 146.67 (C(9)), 124.41 (C(11)), 127.33 (C(12)), 124.67 (C(13)), 53.61 (C(15)), 106.39 (C(16)), 50.62 (C(17)), 28.44 (C(18)), 26.16, 26.34 (C(19), C(20)), 28.30 (C(21)), 24.49, 25.16 (C(22), C(23)), 37.65 (C(24)), 132.44 (C(25)), 119.48 (C(26)), 29.09 (C(27)), 24.23, 24.14 (C(28), C(29)), 29.29 (C(30)), 24.42, 24.57 (C(31), C(32)).

Synthesis of the complex $C_{32}H_{46}N_2Ni$ (II) [19]. A solution of complex **I** (2.58 g, 5 mmol) in diethyl ether (100 mL) was kept in a Schlenk flask at 20–25°C for 5 h. The solvent was removed in vacuo. The resulting reddish brown powder was dissolved in pentane (50 mL) and kept in a freezer at −30°C for 5 days. The amorphous reddish brown powder that formed was filtered off and dried in vacuo ($P = 10^{-2}$ mm Hg) at 20–25°C for 6 h. According to X-ray powder diffraction data, the product is X-ray amorphous. The product is stable under argon, yet rapidly decomposing with self-ignition in air. The yield of complex **II** was 1.99 g (3.85 mmol, 77.0%), T_m = 97–10°C.

For $C_{32}H_{46}N_2Ni$			
Anal. calcd. (%):	C, 74.28,	H, 8.96,	N, 5.41.
Found (%):	C, 73.42,	H, 8.05,	N, 4.70.

MS (70 eV, *m/z*, %): 476 (100.0), 516 (65.2).

IR (KBr, ν, cm^{-1}): 1641 ν(C=N), 1076 ν(CCC), 532 δ(CCC).

^{1}H NMR (500 MHz, THF-d_8, 297 K, δ, ppm): 6.97 (m, 1H, CH(3), HSQC 123.01), 6.84 (m, 1H, CH(4)), 6.94 (m, 1H, CH(5)), 4.79 (d, 1H, CH(7), $^2J_{H7-H7'}$ = 25.0 Hz), 4.57 (d, 1H, CH(7'), $^2J_{H7'-H7}$ = 25.0 Hz), 7.18 (m, 6H, CH(11), CH(12), CH(13)), 1.61 (d, 1H, CH^{anti}15, $^3J_{H15-H16}$ = 12.7 Hz, COSY 5.35, HMBC 53.97), 1.41 (d, 1H, CH^{syn}15, $^3J_{H15-H16}$ = 6.0 Hz, HSQC 53.97), 5.35 (m, 1H, CH(16), COSY 1.43, 1.61, HSQC 106.7), 1.43 (d, 1H, CH^{anti}17, $^3J_{H17-H15}$ = 14.3 Hz, COSY 1.61, 5.35, NOESY 1.59, HSQC 50.71), 1.59 (d, 1H, CH^{syn}17, $^3J_{H17-H16}$ = 6.0 Hz, NOESY 1.43), 4.51 (m, 1H, CH(18)), 1.26 (m, $CH_3$19), 1.29 (m, 3H, $CH_3$20), 3.88 (m, 1H, CH(21)), 1.2 (m, 6H, $CH_3$22, $CH_3$23), 5.7 (m, 1H, CH(24), $^3J_{H24-H25}$ = 16.4 Hz, HSQC 124.18), 6.51 (dq, 1H, CH(25), $^3J_{H25-H26}$ = 7.0 Hz, $^3J_{H25-H24}$ = 16.1 Hz, HSQC 140.88, HMBC 184.13), 1.64 (d, 3H, $CH_3$26, $^3J_{H26-H24}$ = 7.0 Hz, HSQC 19.26), 3.37 (m, 1H, CH(27)), 1.35 (m, 3H), 1.37 $CH_3$29), 3.66 (m, 1H, CH(30)), 1.11 (m, 3H, $CH_3$31), 1.16m, 3H, $CH_3$32).

^{13}C NMR (125 MHz, THF-d_8, 297 K, δ, ppm): 158.17 (C(1)), 123.02 (C(3)), 123.53 (C(4)), 123.43 (C(5)), 146.54 (C(6)), 69.56 (C(7)), 184.13 (C(8)), 147.17 (C(9)), 139.71 (C(10)), 124.17 (C(11)), 127.13 (C(12)), 124.43 (C(13)), 140.20 (C(14)), 53.97 (C(15)), 106.7 (C(16)), 50.71 (C(17)), 28.45 (C(18)), 26.10 (C(19)), 26.26 (C(20)), 28.28 (C(21)), 24.89, 25.15 (C(22), C(23)), 124.18 (C(24)), 140.88 (C(25)), 19.26 (C(26)), 29.22 (C(27)), 23.78 (C(28)), 24.00 (C(29)), 29.42 (C(30)), 24.28 (C(31)), 24.62 (C(32)).

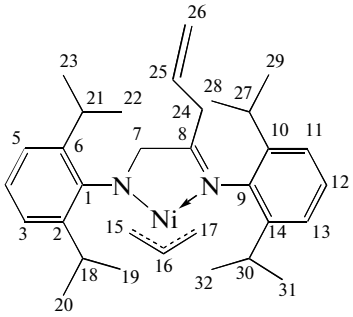
^{1}H NMR (500 MHz, C_6D_6, 297 K, δ, ppm): 7.28 (d, 1H, CH(3), $^3J_{H3-H4}$ = 7.3 Hz), 7.23 (m, 1H, CH(4)), 1.62 (d, 1H, CH(5), $^3J_{H5-H4}$ = 7.2 Hz), 4.67 (d, 1H, $CH_2$7, $^2J_{H7'-H7}$ = 25.30 Hz), 4.90 (d, 1H, $CH_2$7', $^2J_{H7-H7'}$ = 25.0 Hz), 7.06 (m, 3H, CH(11), CH(12), CH(13)), 1.83 (d, 1H, CH_2^{anti}15, $^3J_{H15-H16}$ = 13 Hz, COSY 5.46, NOESY 1.62^-, HSQC 53.75, HMBC 50.75), 1.62 (d, 1H, CH_2^{syn}15, $^3J_{H15-H16}$ = 6.0 Hz, COSY 2.00, 5.46, NOESY 1.83^-, 2.00^+, 5.46^-, HSQC 53.75, HMBC 50.75), 5.46 (m, 1H, CH(16), COSY 1.62, 1.79, 1.83, 2.00, NOESY 1.62, 2.00, HSQC 106.43, HMBC 50.75, 53.75), 2.00 (d, 1H, CH_2^{syn}17, $^3J_{H17-H16}$ = 4.3 Hz, COSY 1.62, 5.46, NOESY 1.62^+, 1.79^-; 5.46^-, HSQC 50.75, HMBC 53.75), 1.79 (d, 1H, CH_2^{anti} 17, $^3J_{H17-H16}$ = 13.0 Hz, COSY 5.46, NOESY 2.00^-, HSQC 50.75, HMBC 53.75), 4.81 (m, 1H, CH(18)), 1.47 (d, 3H, $CH_3$19, $^3J_{H19-H18}$ = 6.7 Hz), 1.53 (d, 3H, $CH_3$20, $^3J_{H20-H18}$ = 6.7 Hz), 4.14 (m, 1H, CH(21)), 1.41 (m, 6H, $CH_3$22, $CH_3$23), 5.64 (d, 1H, CH(24), $^3J_{H24-H25}$ = 16.0 Hz, HSQC 123.46, HMBC 18.47), 5.87 (dq, 1H, CH(25), $^3J_{H25-H26}$ = 6.45 Hz, $^3J_{H25-H24}$ = 16.2 Hz, HSQC 134.49, HMBC 18.47, 183.13), 0.94 (d, 2H, $CH_2$26, $^3J_{H26-H25}$ = 6.54 Hz, HSQC 18.47), 3.46 (m, 1H, CH(27)), 1.1 (m, 3H, $CH_3$28), 1.28 (m, 3H, $CH_3$29), 3.75 (m, 1H, CH(30)), 1.27 (m, 3H, $CH_3$31), 1.15 (m, 3H, $CH_3$32).

^{13}C NMR (125 MHz, C_6D_6, 297 K, δ, ppm): 157.63 (C(1)), 123.23 (C(3)), 123.25 (C(5)), 146.0 (C(6)), 69.4 (C(7)), 183.13 (C(8)), 146.47 (C(9)), 139.06 (C(10)), 123.84 (C(13)), 139.53 (C(14)), 53.75 (C(15)), 106.43 (C(16)), 50.75 (C(17)), 28.02 (C(18)), 24.74 (C(19)), 26.07 (C(20)), 27.88 (C(21)), 25.02–25.9 (C(22), C(23)), 123.46 (C(24)), 139.49 (C(25)), 18.47 (C(26)), 28.48 (C(27)), 23.95 (C(28)), 23.55 (C(29)), 28.67 (C(30), HSQC 3.75), 23.37 (C(31)), 24.28 (C(32)).

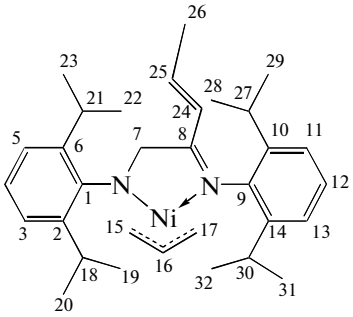
A solution of complex **I** in THF-d_8 was kept in a sealed NMR tube at 25°C while monitoring its transformation by the DEPT-135 ^{13}C NMR technique. The characteristic signals for the C(26) atom were watched. After 3 h, the signal at δ 119.48 (complex **I**)

was completely replaced by the signal at δ 19.27 (complex **II**). The degree of conversion of complex **I** into complex **II** is nearly 100%.

The atomic numbering in structures **I** and **II** is given below:



(I)



(II)

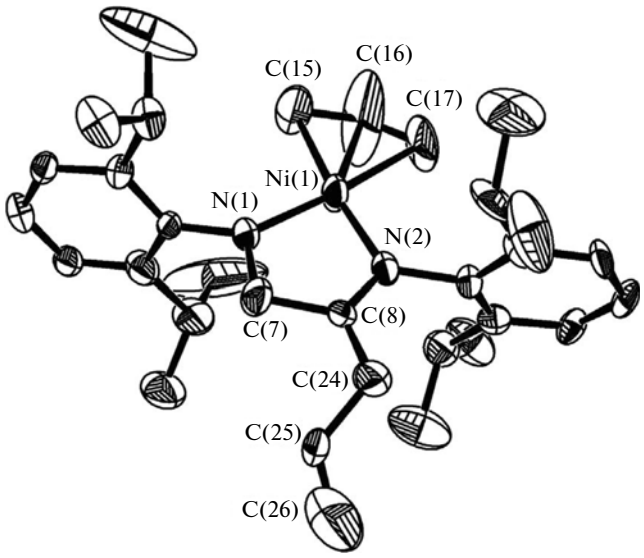
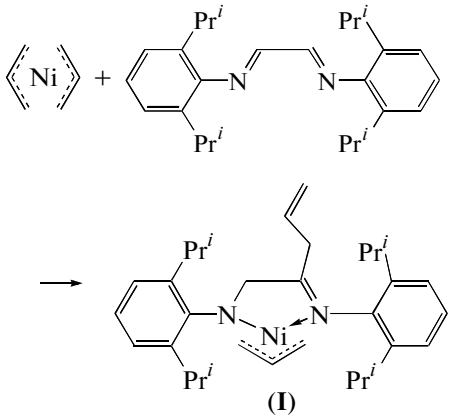


Fig. 1. Molecular structure of complex **I** (X-ray diffraction data). Selected bond lengths and bond angles: Ni–N(1), 1.845(3) Å; Ni–N(2), 1.922(3) Å; Ni–C(15), 1.955(4) Å; Ni–C(16), 1.955(9) Å; Ni–C(17), 1.947(13) Å; C(25)–C(26), 1.13ÅA; C(24)–C(25), 1.320(4) Å; C(8)–C(24), 1.557(3) Å; N(1)–C(7), 1.437(9) Å; N(2)–C(8), 1.287(9) Å; C(7)–C(8), 1.478 Å; N(1)NiN(2), 84.93(12)°; N(2)NiC(17), 102.76(16)°; N(1)NiC(15), 104.01(3)°; C(17)NiC(15), 68.30(6)°; NiN(1)C(7), 113.92(3)°; NiN(2)C(8), 114.92(4)°; C(17)C(16)C(15), 121.16(2)°.

RESULTS AND DISCUSSION

A reaction of a yellow solution of $Ni(Allyl)_2$ with an equimolar amount of DAB in diethyl ether at −5°C produces a bright red solution. The reaction product was precipitated with pentane and cooled to −30°C for crystallization. The resulting bright red platelike crystals are unstable in air; when finely divided, they decompose with self-ignition.

According to X-ray diffraction data (Fig. 1), the product is an imino amide π-allyl nickel(II) complex (**I**). Its formation can be represented by the scheme



(I)

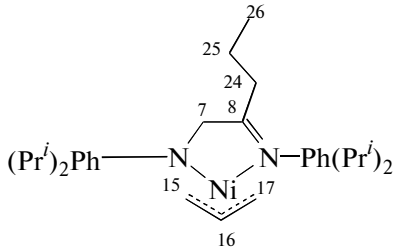
A reaction of $Ni(Allyl)_2$ with DAB does not occur as a simple ligand metathesis; it is accompanied by a complex imino-amide rearrangement in the diazabutadiene fragment of the ligand.

Complex **I** has a molecular structure. The planes of the phenyl rings of the diisopropylphenyl ligands are nearly perpendicular to the plane of the chelate ring: the respective dihedral angles are 88.1° and 82.4°. The Ni–N distances differ substantially (1.846(3) and 1.921(3) Å): for the N atom at the double C=N bond, this distance is noticeably longer. The allyl ligand is disordered over two positions.

To get comprehensive information on the structure of the product of such an unusual reaction, we thoroughly examined complex **I** using 2D homo- and heteronuclear NMR experiments.

In the ^{1}H NMR spectrum of complex **I**, the multiplet at δ 5.35 characteristic of the central proton of the nickel-coordinated allyl group is well resolved [2]. In the HSQC experiment, this signal shows a cross peak with a signal for the ^{13}C nucleus at δ 106.39. According to DEPT-135 data, this carbon atom is bound to only one proton. In the COSY spectrum, the cross peaks at δ 5.35–1.40, 5.3–1.48, 5.35–1.61, and 5.35–1.67 are resolved. In the HSQC spectrum, the signals at δ 1.40 and 1.48 correlate with the signal at δ 50.62 and the signals at δ 1.61 and 1.67 correlate with the signal at

δ 53.61. According to DEPT-135 data, these signals can unambiguously be assigned to the ^{13}C nuclei in the CH_2 groups. When analyzing the degrees of shielding and the coupling constants, one can identify the signals for the *syn*- and *anti*-protons of the π-coordinated allyl group and the corresponding carbon atoms (table). The signals for the terminal protons of the π-allyl group of complex **I** are substantially shifted downfield compared to the analogous signals for $Ni(Allyl)_2$ (table). The fragment of a conventional molecule with atomic numbering is shown below:



All the hydrogen and carbon atoms of the π-allyl group in complex **I** are nonequivalent, in contrast to those in $Ni(Allyl)_2$ [2, 20]. The considerable nonequivalence of the ^{13}C and ^{1}H nuclei in the CH_2 fragments of the πallyl group of complex **I** can be associated with a considerable difference between the shielding abilities of the imine and amide moieties of the ligand. It is difficult to locate the atoms of the π-allyl group relative to the ligand because the TOCSY and NOESY spectra show no selective cross peaks between the protons of the π-allyl group and the protons of the imino amide ligand.

The DEPT-135 ^{13}C NMR spectrum of complex **I** contains one signal at δ 119.48 for the sp^2-hybridized carbon atom of the CH_2 group, which correlates in the HSQC spectrum with the signal at δ 5.01. These signals belong to the terminal CH_2 group at the double bond of the 1-propenyl substituent. Analysis of the HSQC, HMBC, COSY, NOESY, and DEPT-135 data allowed us to assign the signals for the other nuclei of the propenyl fragment (table).

The CH_2 group at the N atom covalently bonded to nickel can unambiguously be identified since the ^{1}H NMR spectrum exhibits doublets atδ 4.56 and 4.38 for two nonequivalent protons. In the NOESY spectrum, the doublet a δ 4.56 shows a cross peak with the signal at δ 3.86 for the proton at the tertiary C atom of the isopropyl substituent of the phenyl ring of the ligand. We used this signal to determine the relative positions of the substituted phenyl rings and the other fragments in complex **I** (for detailed assignments, see Experimental). In the HMBC spectrum, the signals at δ 4.56 and 4.38 correlate with the signal at δ 191.36 for the carbon atom at the nickel-coordinated N atom. According to the DEPT-135 data, this carbon atom is quaternary.

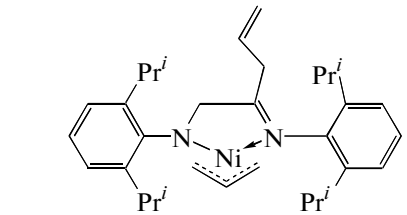
The IR spectrum of complex **I** shows a band at 1602 cm^{-1} ($\nu(C{=}N)_{imine}$). This band is shifted by ~24 cm^{-1} to the lower frequencies compared to an analogous band in the spectrum of the free ligand, which agrees with the literature data [21] on the vibrational frequency changes upon the metal–nitrogen coordination bonding in diimine ligands. The carbon framework of the π-allyl group absorbs at 1105 (ν(CCC)) and 532 cm^{-1} (δ(CCC)) [22, 23].

The mass spectrum of complex **I** shows a pronounced molecular ion peak with m/z 516 ($I_{rel} > 70\%$). In mass spectra recorded for ethyl complexes of nickel under comparable conditions, the molecular ion peak intensities do not exceed 5% [24]. A comparative analysis allows one to state that the π-allyl group in complex **I** is coordinated to the metal atom more strongly than in other organometallic nickel complexes and is less prone to dissociation under electron impact.

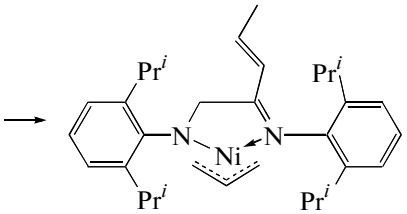
Thus, the X-ray diffraction data fully agree with the data from 2D NMR and IR spectroscopy and mass spectrometry.

In the crystalline state, complex **I** is stable for at least 90 days. In sealed evacuated tubes, its bright red solutions in THF and benzene at 20–25°C turn reddish brown in 3 to 4 h. The NMR spectra show considerable changes suggesting a "migration" of the double bond. In this respect, the DEPT-135 ^{13}C NMR spectra are most illustrative (Fig. 2). The signals at 119.48 ($H_2C{=}$), 132.44 (HC=), and 37.65 (CH_2) for the propenyl fragment with the terminal CH_2 group of complex **I** are replaced by the signals at δ 19.26 (terminal CH_3), 140.88 (HC=), and 124.16 (HC=) for the propenyl fragment with the terminal methyl group of complex **II** (Fig. 2).

According to the NMR data obtained, one can state that complex **I** in solution undergoes a spontaneous transformation into complex **II**:



(I)



(II)

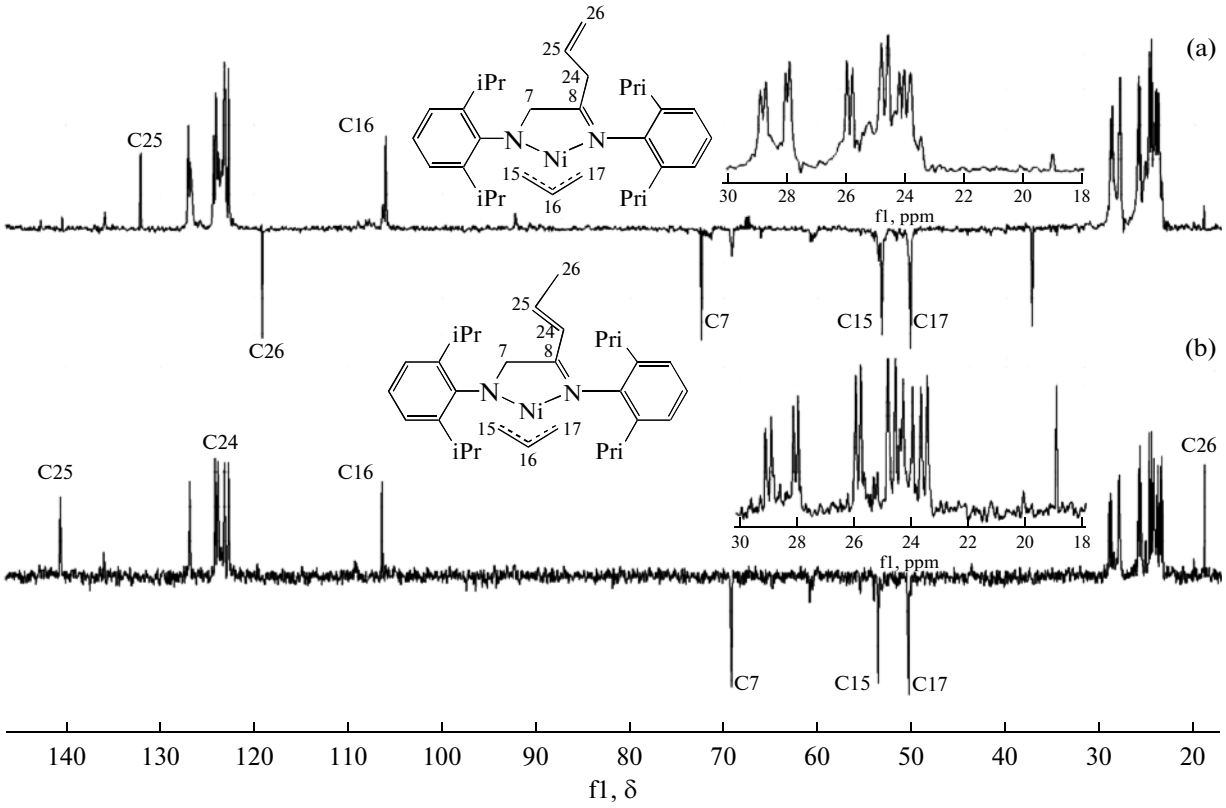


Fig. 2. DEPT-135 ^{13}C NMR spectra of complex **I** (a) immediately upon its dissolution and (b) after 4 h (THF-d_8, a sealed evacuated tube).

All our attempts to obtain complex **II** in the crystalline state failed. Both bulk crystallization and zone refining gave only reddish brown X-ray amorphous powders that are extremely unstable in air. Because of this, the structure of complex **II** is mainly concluded from 2D NMR data.

The multiplet for the central proton of the π-allyl group in complex **II** appears at δ 5.46 and correlates in the HSQC spectrum with the signal at δ 106.43, which, according to the DEPT-135 data, belongs to the carbon atom bound to only one proton. In the HMBC spectrum, the signal at δ 5.46 correlates with the signals at δ 50.75 and 53.75 for the terminal carbon atoms of the π-allyl group, either of which is bound to two protons (DEPT-135 data). The HSQC spectrum contains cross peaks at δ 53.75–1.83, 53.7–1.62, 50.7–1.79, and 50.75–2.0. Thus, the signals in the ^1H NMR spectrum at δ 1.83, 1.62, 1.79, and 2.0 can unambiguously be assigned to the terminal protons of the allyl group (Fig. 3).

According to the HSQC and HMBC data, the protons with the signals at δ 1.83 and 1.62 are bound to the carbon atom with the signal at δ 53.75, while the protons with the signals at δ 1.79 and 2.0 are bound to the carbon atom with the signal at δ 50.75. All the four signals for the terminal protons are split into doublets. For the doublets at δ 1.62 (J = 13 Hz) and 1.79 (J = 13 Hz), the COSY spectrum shows an intense cross peak at δ 5.46. In combination with the values of the coupling constants, this allows unambiguous assignment of these doublets to the *anti*-protons of the allyl group (Fig. 4).

Accordingly, the doublets at δ 1.83 (J = 6 Hz) and 2.0 (J = 4.3 Hz) correspond to the *syn*-protons. The COSY experiment reveals spin-spin couplings of these protons with each other and with the central proton of the π-allyl group. These cross peaks are much less intense than those in the COSY spectrum between the central and *anti*-protons.

Analysis of the NMR data for the π-allyl fragment of complex **II** reveals an unusual inversion of the chemical shifts of the signals for its *syn*- and *anti*-protons. As a rule, the *anti*-protons in allyl complexes of transition metals are more strongly shielded than the *syn*-protons [2, 20]. In complex **II**, the opposite is observed for the protons at the C(15) atom (the atomic numbering is the same as in table): the signal for the *syn*-proton is shifted upfield compared to the signal for the *anti*-proton. The NOESY spectrum shows distinct cross peaks for all the four terminal protons of the π-allyl group (Fig. 4), including exchange cross peaks for the *syn*- and *anti*-protons [25]. This exchange can

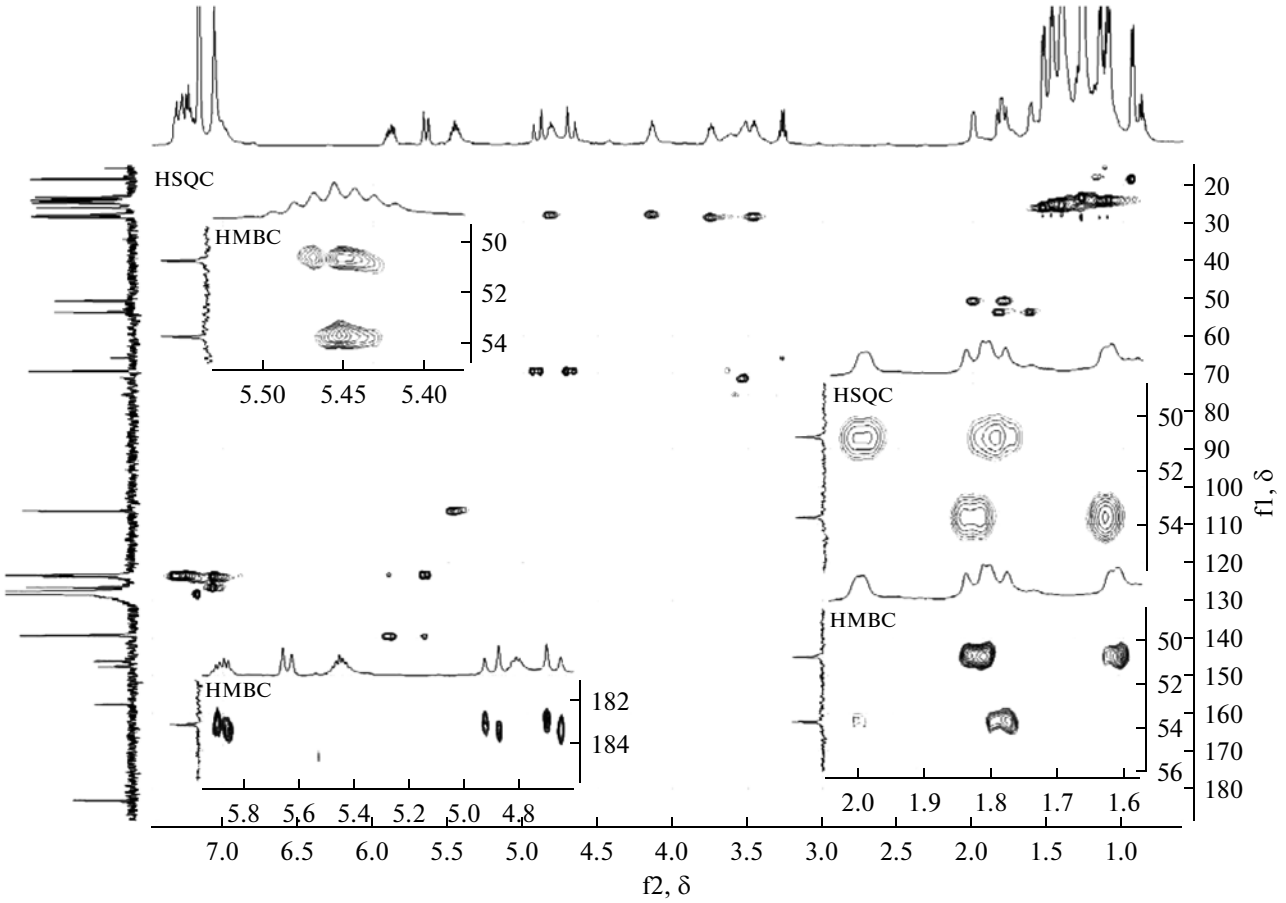
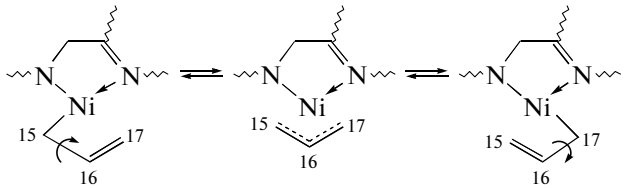


Fig. 3. HSQC and HMBC spectra of complex **II** in C_6D_6. The insets in the main spectrum are placed in the areas free from cross peaks.

be effected only by rotation of the terminal CH_2 groups, which is possible if the η^3–π- and η^1–σ-forms of the allyl group in complex **II** are in equilibrium:



Our data agree well with data on such an exchange in allyl complexes of palladium thoroughly examined by NOESY NMR spectroscopy [4, 5]. Therefore, complex **II** exists in solution as both the η^3–π and η^1–σ-allyl forms.

In the IR spectrum of complex **II**, the band $\nu(C{=}N)_{imine}$ is shifted by 39 cm^{-1} to the higher frequencies (1641 cm^{-1}) compared to an analogous band for complex **I**. This is consistent with the formation of a conjugated system of double bonds during the isomerization of the propenyl substituent. The band at 1076 cm^{-1} ν(CCC)) due to the vibrations of the π-allyl carbon framework is broadened and shifted by 29 cm^{-1} to the lower frequencies compared to that for complex **I**. The position of the band δ(CCC) remains virtually unchanged (532 cm^{-1}).

The mass spectrum of complex **II** shows a pronounced molecular ion peak with m/z 516 (I_{rel} = 65%), which also suggests insignificant dissociation of the π-allyl group under electron impact.

In a sealed evacuated NMR tube, a solution of complex **II** remains stable for several hours (NMR data), whereupon the ^1H and ^{13}C NMR signals broaden and disappear in 24 h (except the signals for the solvent). The reddish brown solution turns dark brown. The EPR spectrum of the resulting dark brown solution shows an intense signal (Fig. 5) characteristic of Ni(I) complexes [26].

Therefore, allyl complex **II** in solution spontaneously decomposes with time, Ni(II) being reduced to Ni(I). It is worth noting that the resulting paramagnetic complex remains stable in a sealed tube at room

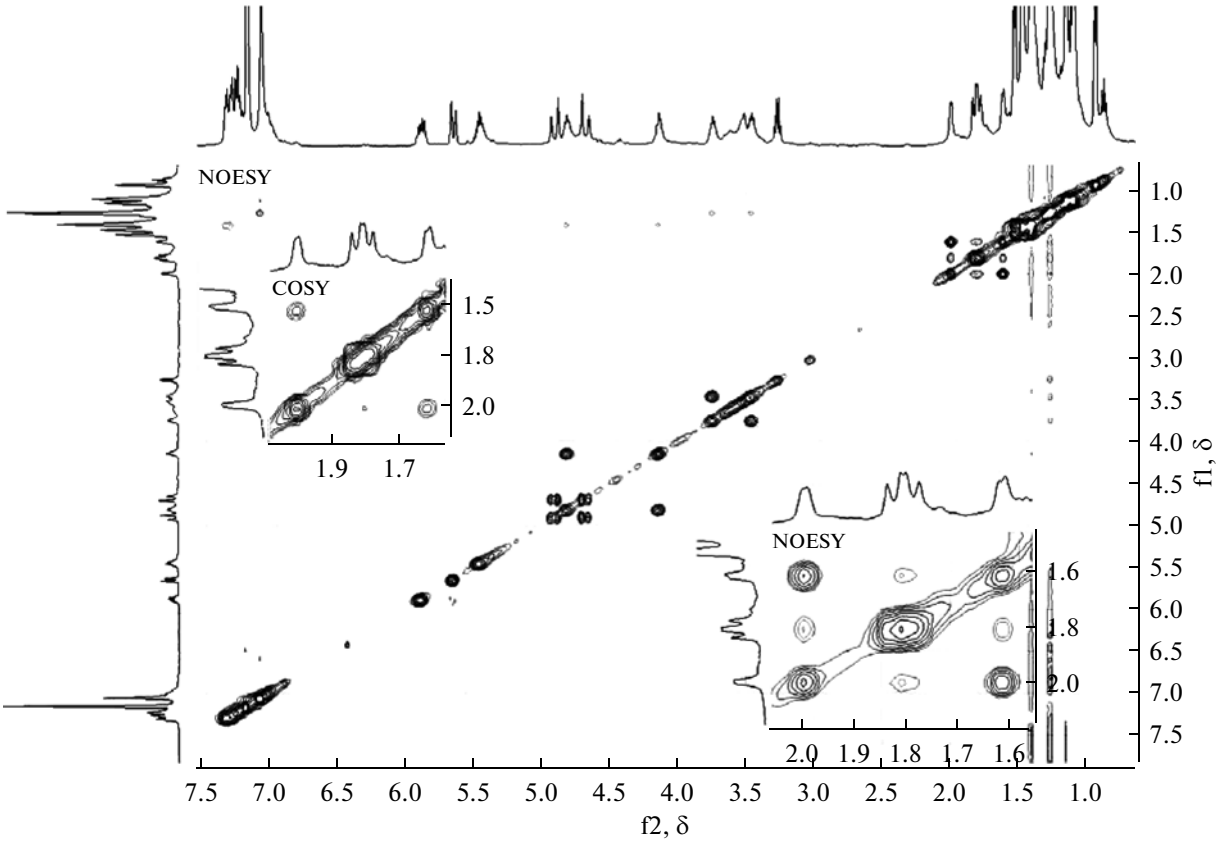


Fig. 4. NOESY and COSY spectra of complex **II** in C_6D_6. The insets in the main spectrum are placed in the areas free from cross peaks.

temperature for more than a year. The nickel oxidation state can change through cleavage of both the covalent Ni–C bond and the Ni–N bond. Because the ^{14}N nuclei show no hyperfine structure, it is impossible to specify the type of the Ni–N bond in the paramagnetic complex. Some structural information for the complex can be obtained by analyzing the *g* tensor ($g_x = 2.186$, $g_y = 2.143$, and $g_z = 2.024$). The ratio of the components of the *g* tensor (g_x, $g_y > g_z$) suggests a trigonal structure of the complex [27]. While comparing the greatest component of the *g* tensor (2.186) with analogous parameters for typical amide complexes of nickel(I) of the formula (Nacnac)NiL (where Nacnac is β-diketiminate and L is bis(diphenylphosphino)methane [28], tricyclohexylphosphine [28], and THF [29]), one should note that the greatest components of the *g* tensor for β-diketiminate complexes of nickel(I) (2.43–2.54) differ greatly from the pure spin value, though these complexes contain spectrochemically "strong" ligands such as bis(diphenylphosphino)methane or tricyclohexylphosphine. On the other hand, the same parameter, e.g., for a cyclopentadienyl complex of Ni(I) with bipyridyl CpNi(Bipy) (2.184 [30]), is nearly as great as the component of the *g* tensor for the complex under study. The aforesaid data suggest that the spontaneous decomposition of complex **II** and the reduction of Ni(II) to Ni(I) are due to the transformation of the Ni–N bond from the covalent bond to a coordination one without elimination of the allyl group from the coordination sphere. In

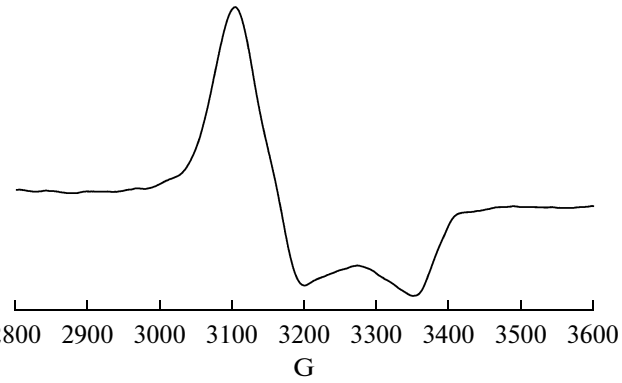
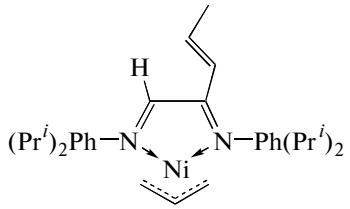


Fig. 5. EPR spectrum of Ni(I) complex **III** in THF-d_8, at 77 K.

this case, the paramagnetic complex can be formulated as the most plausible structure **III**:

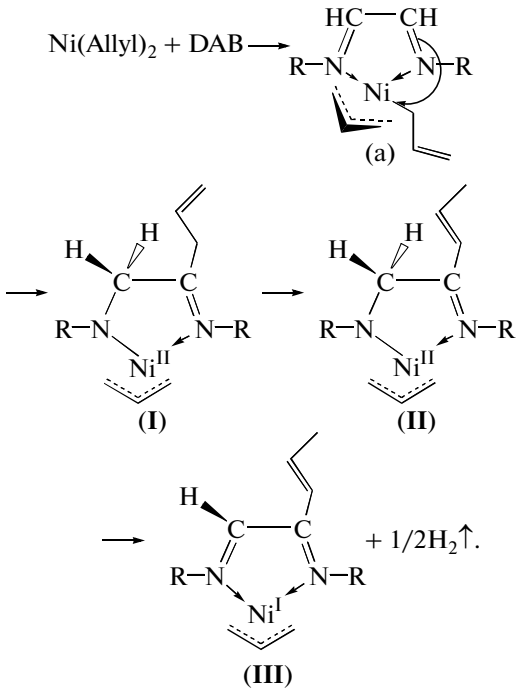


(III)

The transformation of diamagnetic nickel(II) complex **II** into paramagnetic nickel(I) complex **III** retaining the allyl group is suggested by the absence of the NMR signals (except those for the solvent) in the system after the intensity of the EPR signal reaches a maximum value. If the allyl fragment were eliminated, the NMR spectrum would contain the signals for propene or its transformation products (the transformation of complex **II** into complex **III** was studied in a sealed NMR tube).

Thus, diamagnetic nickel complex **I** in THF in a sealed tube rapidly isomerizes into diamagnetic complex **II**, which is completely transformed in 48 h into paramagnetic complex **III** as the final product. Despite the thermodynamic stability of nickel(I) complex **III**, we failed to isolate it in the individual state. Concentration of a solution of complex **III** resulted in the formation of a resinous product extremely susceptible to oxygen and moisture traces. Elemental analysis data for the resinous product are close to formula **III**.

Based on the results obtained in this study, we can propose the following scheme reflecting all the observed transformations:



According to the above scheme, the first step of the reaction of the nickel bis(π-allyl) complex with DAB involves the formation of an intermediate complex (a), in which at least one η^3–π-allyl group exists in the η^1–σ-allyl form. The coordination sphere of complex (a) undergoes a rearrangement that can formally be regarded as insertion of the activated double C=N bond into the metal–carbon bond. This rearrangement gives intermediate imino amide π-allyl complex **I**, which isomerizes with time into 2-propenyl complex **II** containing a stable system of conjugated double bonds. In the final step of the process, a spontaneous reduction of Ni(II) to Ni(I) leads to nickel(I) complex **III**.

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