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Intramolecular rearrangement of the imine–amide ligand within the nickel coordination sphere affected by carbon monoxide

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ABSTRACT

The interactions of the nickel imine–amide allyl complex $\left[D^2\text{-}\left(\overline{C{=}N\hat{\ }N{-}C}\right)Ni(\eta^3\text{-allyl})\right]$ **1** with carbon monoxide and unsaturated hydrocarbons have been studied. It is shown that this complex reacts readily with carbon monoxide to form the nickel(0) diimine carbonyl complex [(2-(1-propenyl)-[1,10]phenanthroline)Ni$(CO)_2$] **2**. During the process the ligand undergoes a deep transformation within the nickel coordination sphere. Specifically, the nickel–nitrogen σ-bond turns to an N-donor bond with aromatization of a ring in the nitrogen-containing ligand. This novel heteroaromatic ligand 2-(1-propenyl)-[1,10] phenanthroline has been isolated; the nickel(0) diimine carbonyl complex **2** has been studied with X-ray diffraction method. The comparative spectral studies of complexes **1**, **2**, and 2-(1-propenyl)-[1,10]phenanthroline have been carried out with UV/vis, IR-FT, and 2D NMR spectroscopy. It has been shown that the planar 16-electron nickel(II) imine–amide allyl complex **1** is indifferent to olefins and acetylenes. Based on the NMR data, this fact can be explained by the inability of the π-δ rearrangement into **1**.

1. Introduction

Polymerization of olefins is still one of the most important industrial processes today and α-olefins are the most valuable products. In 1995 the work of Brookhart et al. [1] on the usage of nickel and palladium α–diimine complexes for polymerization attracted attention of the scientific community at large. It served as a powerful stimulus for studying diimine complexes of transition metals in polymerization of both linear and cyclic olefins [2–7]. Transition metal allyl complexes with nitrogen-containing ligands are the most interesting subjects for investigations as they bear an active metal–carbon bond inside their coordination sphere that makes such systems promising for organic fine chemicals synthesis and metal complex catalysis [8–12].

The least known today is the possibility of transformations of N-containing ligands themselves within transition metal coordination sphere. For this reason almost all catalytic cycle schemes proposed in the literature, including activation and deactivation of the active species, ignore the possibility that the nature of metal–ligand bonds and, furthermore, the diimine ligand itself can alter. It can be stated that ligands are usually regarded as an unchanging unit which can be “hosted” in the metal coordination sphere or driven out of it in the course of catalytic cycle. It is generally accepted that the state of a transition metal can alter radically at different steps of the catalytic cycle, whereas the possibility of any transformations of ligands is neglected as a rule [3,13–19]. Nevertheless, every aspect of the ligand behavior should be understood and intelligently used, because it may be the only way to atom-economic catalytic systems most consistent with the principles of green chemistry.

The possibility of a profound transformation of diimine ligands within the coordination sphere of a nickel π-allyl complex was demonstrated in [20]. The process involves formation of a nickel–nitrogen σ-bond and an imine–amide complex. Interestingly, phenanthroline, usually a stable ligand, looses aromaticity in one of its heteroatomic rings under very mild conditions (Scheme 1):

Our work focuses on the chemical properties of complex **1**, specifically, whether there is a possibility for this spontaneously formed imine–amide complex to undergo further transformations inside the nickel coordination sphere when affected by the conventional catalytic ligands such as olefins, acetylenes, and carbon monoxide. We hope that our research will help in following the ways of how nitrogen-containing ligands transform that could complement the catalytic cycle puzzle and facilitate the development of catalytic systems with desired properties.

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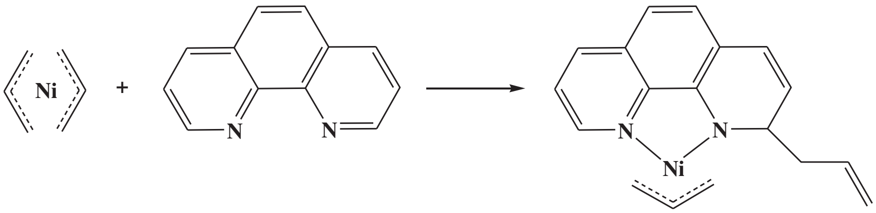

1

Scheme 1.

2. Results and discussion

Nickel di- and monoallyl complexes are classic catalysts for conversions of olefins, dienes and acetylenes [8]. According to an X-ray structural analysis and multinuclear 2D NMR spectroscopy [20] **1** has a planar structure, contains a π-allyl group, an active fragment, and, besides, it is electron-deficient with its 16-electron pattern. On the whole complex **1** meets all the conventional requirements for a catalyst [21]. This complex is to be active in catalytic conversions of unsaturated hydrocarbons or at least in some interactions with them. We tried to initiate reactions between **1** and ethylene, propylene, norbornadiene, styrene, acetylene, and phenylacetylene. The molar ratios between **1** and the unsaturated hydrocarbons varied from 1:1 to 1:100, while the reaction temperature varied from 20 to 70 °C. Under these conditions the NMR spectra of complex **1** remained unchanged. We could observe only a superposition of chemical shifts from **1** and the used unsaturated hydrocarbon. Of special interest is the fact of a total indifference of **1** toward acetylene and phenylacetylene, as it was quite logical to assume loss of the allyl group by acetylenes due to the acetylene acidic proton. This irritating inertness provoked further tests of **1** with carbon monoxide.

When carbon monoxide was admitted to a bright green ether solution of **1** in a flow reactor, the color quickly changed to bright red followed by a partial fading during 10–14 h. Using GC–MS it was established that the moment of the initial color change was accompanied by formation of acrylic aldehyde in the amount equimolar to the nickel. Further the content of acrylic aldehyde stayed constant in the course of the process.

When the change in the coloration ceased, the crystalline (1:1)-adduct consisting of complex **2** and 2-(1-propenyl)-[1,10]phenanthroline (**pphen**) was obtained from the solution. We studied the molecular structure of the adduct with X-ray structural analysis (the structure is shown on Fig. 1; the crystal packing is given in Supplementary material).

According to NMR data, dissolution of the adduct in THF or toluene does not bring about an interaction between **2** and **pphen**. The ^{1}H NMR spectrum shows a simple superposition of signals from **2** and **pphen** (Fig. 2). The solution contained **2** and **pphen** in approximately equimolar amounts as follows from the corresponding integral intensities of the ^{1}H NMR signals. Analysis of the TOCSY and NOESY spectrum reveals no mutual cross-peaks for **2** and **pphen**.

Analysis of the summation of the obtained data suggests that **1** and CO react in the following way (Scheme 2):

Among the products **pphen** and tetracarbonylnickel should be taken out. Their presence is explained by Scheme 3.

According to Scheme 2, the reaction of complex **1** and carbon monoxide involves reduction of nickel(II) to nickel(0) and formation of the dicarbonyl complex together with the profound transformation of the ligand, specifically, the ring aromatization and migration of the double bond within the propenyl substituent.

Attempts to separate **2** and **pphen** using crystallization from different solutions failed. The crystalline adduct, prepared according to Scheme 2, was divided into complex **2** and **pphen** only chromatographically. The isolated individual complex **2** was subjected to crystallization from different solvents (pentane, diethyl ether, toluene, THF, and mixtures). Unfortunately, complex **2** always precipitated as an X-ray amorphous bright red powder.

When **1** reacted with CO under isobaric conditions in a non-flow reactor ($P = 1$ kg/cm^2, 20 °C), the initial bright green color of the solution quickly turned bright red. The absorption of the gas ceased when the molar ratio of CO:Ni reached 3. From the obtained solution a powdery bright red X-ray amorphous product was prepared with the yield of 90–92%. Its spectra were identical to those of complex **2**. Using GC–MS it was also established that the reaction of

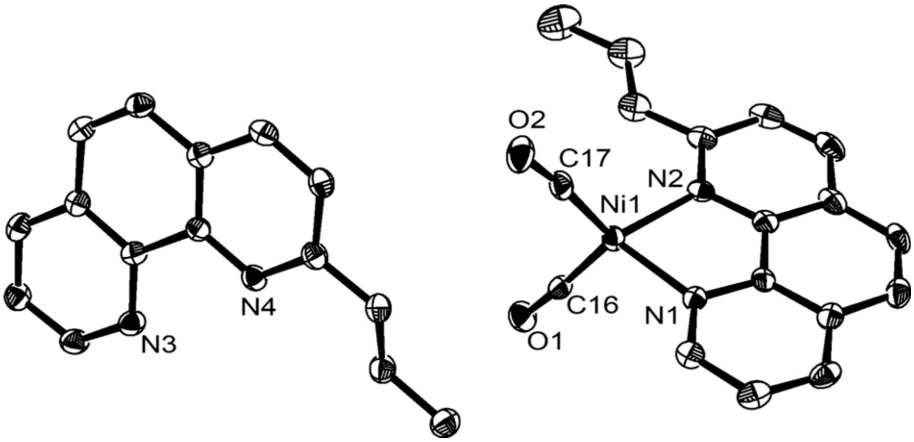

Fig. 1. Molecular structure of adduct of **2** and **pphen**. (ORTEP plot with hydrogen atoms omitted); distances between selected atoms [Å] and angles [°]: Ni–N1 = 2.015(2), Ni–N2 = 2.052(2), Ni–C16 = 1.747(3), Ni–C17 = 1.760(3), C16–O1 = 1.160(4), C17–O2 = 1.151(4), N1–Ni–N2 = 81.47(10), N1–Ni–C16 = 114.42 (12), N2–Ni–C17 = 118.11(12), N2–Ni–C16 = 113.12(12), N1–Ni–C17 = 112.10(12), C16–Ni–C17 = 113.76(14).