

EPR for catalysts based on nickel and cobalt complexes

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Abstract

This review is concerned with data on the composition and structure of intermediate paramagnetic cobalt and nickel compounds in Ziegler-type metal complex catalysts. The problem of reactivity of the intermediate compounds is briefly outlined. General regularities are revealed for the mechanism of formation of the metal complex catalysts. Particular emphasis is made on the structure of intermediates whose EPR spectra explicitly exhibit the effects of vibronic interactions. Vibronic effects are shown to play an important role in the realization of geometric configuration for structures with the pseudodegenerate electronic state. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The EPR method has found wide use in identification of the intermediate compounds and revelation of the correlation between the structural details and activity of the systems. High sensitivity of the EPR method and its selectivity to the paramagnetic compounds set the stage for the studies of the intermediates containing unpaired electrons directly in the catalytic systems, without their isolation from solutions.

Wide possibilities of the EPR method in elucidation of the nature of activity of the nickel and cobalt complex catalysts became evident after revealing the intermediate nickel(I) (1972), and cobalt(0) (1973) compounds stabilized by the electron-donation ligands in these catalysts [1].

This review is concerned with data on the composition and structure of intermediate paramagnetic cobalt and nickel compounds in Ziegler-type metal complex catalysts. The problem of reactivity of the intermediate compounds is briefly outlined.

2. Composition of intermediate compounds

The scheme of preparing Ziegler-type metal complex catalysts consists of sequential addition, to a solution of the initial transition–metal complex, of the compound stabilizing the reduced forms of metals and organometallic compounds. The process of catalyst formation proceeds through a number of intermediate steps, during which the paramagnetic metal complexes emerge, as a rule, in unusual oxidation states. They are ordinarily detected at low (77 K) temperatures.

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2.1. Cobalt intermediate compounds

There are many catalytic systems based on cobalt compounds that are catalytically active in various processes: for instance, hydrogenation of olefins and benzene, isomerization of olefin and other processes [2].

Let us consider the formation of the intermediate compounds in a typical $\text{Co}(\text{Acac})_2\text{-PBu}_3\text{-PhMgBr}$ system that is characterized by the enhanced stability of the $\text{Co}(\text{II})$ phenyl derivatives [3]. After adding tributylphosphine to the solution ($\text{P}:\text{Co} = 2$), the oligomer chains $[\text{Co}(\text{Acac})_2]_n$ dissociate to give the mononuclear high-spin complex of composition $\text{Co}(\text{Acac})_2\text{PBu}_3$. Upon addition to the cooled (down to -30°C) solution of Grignard reagent in diethyl ether, the acetylacetonate groups are sequentially substituted by the phenyl radicals, and the low-spin $\text{Co}(\text{II})$ complexes of $(\text{Acac})\text{CoPh}(\text{PBu}_3)_2$ and $(\text{Bu}_3\text{P})_2\text{CoPh}_2$ compositions appear.

In these conditions, the disubstituted $\text{Co}(\text{II})$ complexes with the methyl [4], benzyl, allyl, and crotyl radicals are identified [5]. The allyl, crotyl, and benzyl radicals form the π -allyl-type bonds with the transition metal, thereby producing the steric hindrances to the coordination of the second phosphine ligand. Because of weaker steric hindrances, a dimethyl analog, unlike the diphenyl complex, is easily coordinated by the third phosphine ligand to give $(\text{Bu}_3\text{P})_3\text{CoMe}_2$.

The monosubstituted $\text{Co}(\text{II})$ derivatives decompose at room temperature with reduction of the transition metal to a diamagnetic $\text{Co}(\text{I})$ compounds, whereas the disubstituted derivatives give two types of paramagnetic $\text{Co}(\text{0})$ compounds, with the relative concentrations dependent on the nature and molar ratio of the components of the system.

Let us now dwell in more detail on the composition of the intermediate $\text{Co}(\text{0})$ compounds that contain no phosphine ligands. Because these types of intermediates appear in the absence of the phosphine ligands as well, we consider the results of studying these complexes

in the catalytic $\text{CoX}_2\text{-MR}$ systems, where $\text{M} = \text{AlR}_2$, MgY , or Li and X stands for the acidoligands. The following principal results were obtained [1,4]:

1. The paramagnetic $\text{Co}(\text{0})$ compounds are formed only in cases when the chelate ligand of the starting $\text{Co}(\text{II})$ complex compound contains the oxygen atom or the catalytic systems contains the ether.
2. The paramagnetic $\text{Co}(\text{0})$ compounds are formed only in the medium of aromatic hydrocarbons.
3. The EPR parameters of the intermediate $\text{Co}(\text{0})$ complexes depend on the number and position of the alkyl substituents at alkylbenzene (Fig. 1) and on the extent of substitution of the α -carbon atom in the alkyl group of organometallic compound (Fig. 2), and they are independent of the nature of the main Group metal (aluminum, magnesium, or lithium).

The experimental data allow one to represent the intermediate $\text{Co}(\text{0})$ compounds as an *at*-complex of composition $[(\eta^6\text{-ArH})\text{CoR}(\text{OR}'\text{R}'')]^-$, with a counterion supposedly in the form of a residue of the organometallic compound with $\text{M}^+ = \text{AlR}_2^+$, MgY^+ , or Li^+ .

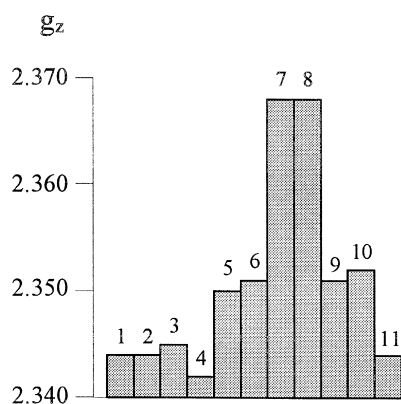


Fig. 1. g_z Values of the $\text{Co}(\text{0})$ complexes $[(\eta^6\text{-ArH})\text{CoEt}(\text{Etacac})]^-$. $\text{ArH} = \text{C}_6\text{H}_6$ (1), MeC_6H_5 (2), EtC_6H_5 (3), *i*- PrC_6H_5 (4), 1,2- $\text{Me}_2\text{C}_6\text{H}_4$ (5), 1,3- $\text{Me}_2\text{C}_6\text{H}_4$ (6), 1,4- $\text{Me}_2\text{C}_6\text{H}_4$ (7), 1,4- $\text{Et}_2\text{C}_6\text{H}_4$ (8), 1,3,5- $\text{Me}_3\text{C}_6\text{H}_3$ (9), 1,2,4,5- $\text{Me}_4\text{C}_6\text{H}_2$ (10), C_6Me_6 (11).

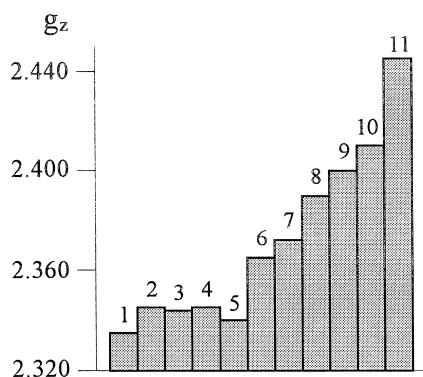


Fig. 2. g_z Values of the Co(0) complexes $[(\eta^6\text{-MeC}_6\text{H}_5)\text{-CoR(Racac)}]^-$. R = Me(1), Et(2), *n*-Pr(3), *n*-Bu(4), Bz(5), Cy(6), *i*-Pr(7), (-)Ment(8,10), Ph(9), GeEt₃(11).

In the presence of phosphine ligands in the system, they are coordinated to cobalt(0). The EPR-based composition of the phosphine complex is $(\eta^6\text{-ArH})\text{CoPR}_3(\text{OR}'\text{R}'')$ [4].

The reactions between the Co(0) at-complexes $[(\eta^6\text{-ArH})\text{Co}(\text{ROR}'\text{R}'')]^-$ and α -olefins (ethylene, propylene, 1-hexene, styrene) results in the conversion of the at-complexes into the Co(0) olefin π -complexes supposedly of composition $(\eta^6\text{-ArH})\text{Co}(\text{CH}_2 = \text{CHR})(\text{OR}'\text{R}'')$ [1]. Direct evidence for the absence of alkyl groups in the π -complexes was obtained in the experiments in which sodium naphthalide was used as the reducer.

The reaction between the Co(0) phosphine complexes $(\eta^6\text{-ArH})\text{CoPPh}_3(\text{OR}'\text{R}'')$ and styrene results in the substitution of the ether by styrene in the coordination sphere of Co(0) [1]. The analogous EPR-spectra are observed for the solutions of π -complex $\text{Co}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_3$ in toluene [6] and of a product of interaction between the $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ complex and butyl vinyl ether and methyl methacrylate in benzene [7]. It is likely that, in these cases, the phosphine ligands are also substituted in part by arene.

Intermediates that form in the reactions between the Co(II) hydride or alkyl complexes and unsaturated compounds are of particular interest. For example, in the presence of butadi-

ene, the reaction between $\text{Co}(\text{Acac})_2\text{PBU}_3$ and LiBu yields a number of paramagnetic crotyl π -complexes [5].

Carbon monoxide also reacts efficiently with Co(0) complexes. For example, in the presence of CO, the phosphine $(\eta^6\text{-ArH})\text{CoPBU}_3(\text{OR}'\text{R}'')$ complex, which appears in the $\text{Co}(\text{Acac})_2\text{-PBU}_3\text{-AlEt}_3$ system, converts during several hours into the paramagnetic trinuclear cluster of composition $\text{EtAlCo}_3(\text{CO})_9$ [8].

2.2. Nickel intermediate compounds

A wide range of catalytic systems based on the nickel compounds are used for the catalytic transformations of hydrocarbons in a variety of reactions: hydrogenation, isomerization, dimerization and co-dimerization of unsaturated compounds, and for other processes [2].

Let us consider the formation of the intermediate paramagnetic compounds in the typical $\text{Ni}(\text{Acac})_2\text{-PBU}_3\text{-AlEt}_2\text{Cl}$ system with a variable amount of aluminum diethyl chloride and fixed molar ratio P:Ni = 4 [1]. The addition of a small amount of aluminum diethyl chloride (Al:Ni = 4) leads to the appearance of the bridged Ni(I) complex of composition $(\text{Bu}_3\text{P})_2\text{NiCl} \cdot \text{ClAlEt}_2$. The concentration of this complex is maximal at Al:Ni = 8. With a further increase in the amount of aluminum diethyl chloride, the phosphine ligands are gradually displaced from the first coordination sphere of Ni(I). The transformation of the intermediate compounds is accompanied by a partial reduction of Ni(I) to Ni(0). The Ni(I) σ -alkyl derivatives are not stabilized in solution.

The intermediate Ni(I) compounds are also found in the reactions between the nickel(II) naphthenate or phenylenediimide [9] complexes and aluminum dialkylchloride and also between the nickel(II) diisopropylsalicylate complex and Grignard reagents [10].

The EPR data on the Ni(I) phosphine complexes obtained at the surface of silicon oxide by reducing the Ni(II) ions with the organo-

phosphorus compounds are also available [11,12].

Aluminum alkylhalides are functioning not only as the reducers and active ligands, but also as the oxidizers of the Ni(0) complexes. For example, quantitative formation of the tricoordinated Ni(I) complex $(\text{Ph}_3\text{P})_2\text{NiCl}$ occurs in the reaction of aluminum ethyldichloride with $\text{Ni}(\text{PPh}_3)_4$ and $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ in toluene ($\text{Al}:\text{Ni} = 3$ and 1, respectively) [1]. An increase in the concentration of AlEtCl_2 first leads to the formation of the bridged $(\text{Ph}_3\text{P})_2\text{NiCl} \cdot \text{ClAlEtCl}$ complex and next to sequential displacement of the phosphine ligands.

At the surface of aluminum or silicon oxide, the surface-immobilized $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ complex undergoes considerable structural changes and oxidation of Ni(0) to Ni(I) under the action of AlEtCl_2 [13].

The aluminum bromide-mediated oxidation of Ni(0) to Ni(I) was proved for the cyclooctadiene Ni(0) complex [14].

Boron trifluoride etherate also exhibits oxidizing activity. For instance, in the reaction of the $\text{Ni}(\text{PPh}_3)_4$ with $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{B}:\text{Ni} = 2$), Ni(0) is oxidized to Ni(I) to form a tricoordinated $[\text{Ni}(\text{PPh}_3)_3]^+\text{BF}_4^-$ complex of the cationic type [15]. Upon increasing the amount of $\text{BF}_3 \cdot \text{OEt}_2$ in the system, the phosphine ligands are sequentially displaced from the coordination sphere of Ni(I).

The interaction of $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ complex with $\text{BF}_3 \cdot \text{OEt}_2$ brings to an oxidizing connection of the latter and formation of Ni(II) complex which disproportionation with a Ni(0) complex, forming Ni(I) complexes containing Ni–F and Ni–B valent bonds [16]. In the presence of coordinated olefins (ethylene, vinylbenzene), the disproportionation reaction was slowed down and in reactionary system there was an accumulation of Ni(II) complexes.

The reaction between the coordinately unsaturated $(\text{Ph}_3\text{P})_2\text{NiCl}$ complex and α -olefins results in the substitution of the phosphine ligand by olefins in the coordination sphere of Ni(I) [1]. The Ni(I) π -complexes with ethylene, vinyl

acetate, butadiene, 4-methyl-2-pentene, 1-hexene, isoprene, and styrene were identified [17].

Reactions of styrene and butadiene with the cationic Ni(I) complex give rise to the sequential substitution of the phosphine ligands and formation of the cationic Ni(I) π -complexes of various composition. It is established that the substitution of two phosphine ligands is followed by the oligomerization of unsaturated hydrocarbons, during which nickel is retained in the paramagnetic state [18]. Since the discovery of intermediate Ni(I) compounds in the catalytic systems of Ziegler type many efforts have been undertaken to elucidate the role of the Ni(I) complex compounds in coordination catalysis. Some researches arrived at the conclusion that the Ni(I) complexes play an important role for regeneration of catalytically active Ni(II) hydrides but are inactive in the processes of unsaturated hydrocarbon transformations because of the low kinetic stability of the Ni(I) alkyl derivatives [2]. Thus, the possibility of Ni(I) participation in the transformations of unsaturated hydrocarbons [18] is demonstrated by the reactions of styrene and butadiene oligomerization.

3. Geometric structures of the intermediates in the degenerate or pseudodegenerate electronic state

The wide use of transition metals in catalysis is primarily due to their ability to form the σ - and π -bonds with other molecules and ligands. This ability is determined by the presence of geometrically different and, most importantly, energetically close valence orbitals in the transition elements. In this context, there is an increased interest in the transition-metal compounds in the degenerate or pseudodegenerate electronic state.

In the heteroligand structures, the orbital degeneracy is removed, and the effect of vibronic interaction on the geometric and electronic

structure of the complexes manifests itself in the form of the Jahn–Teller pseudoeffect. In the case of the pseudodegeneracy, the use of the traditional methods for description of the adiabatic potential is complicated by the necessity of rigorous determination of the ground-state function, otherwise one can arrive at erroneous conclusions. These restrictions are irrelevant within the approach that was elaborated for the heteroligand molecules [19].

According to this approach, the substitution effects are suggested to be treated as a perturbation of the homoligand molecule [20–23]. For example, according to the vibronic model and EPR data, the planar $[\text{Ni}(\text{Dpe})_2]^+$ complex is tetragonal, while the compositionally analogous Co(II) complex is rhombic [20]. The bridged Ni(I) complexes of composition $(\text{R}_3\text{P})_2\text{NiCl} \cdot \text{ClAlEt}_2$ are not strictly tetragonal, although the *cis*-positioned ligands provide the axial anisotropy for the EPR parameters. Fig. 3 displays the dependence of g_{\parallel} on the cone angle φ characterizing the phosphine steric volume. Hence, the steric interactions partially suppress the vibronic effects, so that the tetragonal structures tend to take the tetrahedral geometry.

According to the vibronic model and EPR data, the Ni(I) complexes of composition $(\text{R}_3\text{P})_3\text{NiX}$, where R = Ph, Bu, OBU; X = Cl,

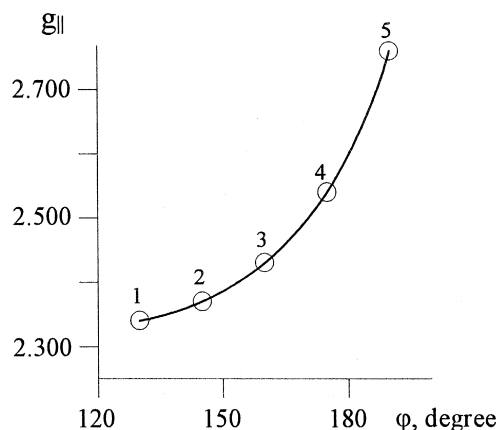


Fig. 3. g_{\parallel} Values as a function of the cone angle φ in the phosphine ligand of the Ni(I) complexes $(\text{R}_3\text{P})_2\text{NiCl} \cdot \text{ClAlEt}_2$. R = Bu(1), Ph(2), *i*-Pr(3), Cy(4), $\text{C}_6\text{H}_4\text{Me-o}$.

Br, J, exhibit the trigonal structure, with the molecular orbital of the unpaired electron oriented along the direction of the Ni–P bond [21–24].

An increase in the volume of the alkyl group R in the Co(0) arene at-complexes $[(\eta^6\text{-MeC}_6\text{H}_5)\text{CoR}(\text{Racac})]^-$ results in an increase in g_z (Fig. 2). Consequently, the steric interactions partially suppress the vibronic effects, so that the structure tends to be axially symmetric. A sharp distinction between the EPR parameters of the complexes with para-xylene and para-ethylbenzene (Fig. 1) indicates that the symmetry of the ground state coincides with the antisymmetric orbital of the arene and that the electronic effects of substitution at the benzene ring partially suppress the vibronic effects in complexes [25].

4. Conclusion

The experimental data on the composition of the intermediate cobalt and nickel compounds and dynamics of their transformation in chemical reactions allow one to reveal the following general regularities of the mechanism of formation of the cobalt and nickel complex catalysts.

The interaction between the transition-metal salts and organometallic compounds results in replacing the acidoligands by alkyl groups. The transition-metal alkyl derivatives decompose when reducing the central atom to the zero oxidation state. The low-valence atoms are stabilized in solutions by phosphines and arenes. The transition metal in zero oxidation state undergoes oxidation under the action of the halogen-containing Lewis acids. In the catalytic systems, the organometallic compounds decompose with formation of the clusters containing the bonding between the transition and main group metals. The transition-metal ions in low oxidation state readily enter the donor-acceptor interaction with the unsaturated compounds. The Ni(I) complexes play an important role not only

for regeneration of catalytically active Ni(II) hydrides but are active participants in the transformations of unsaturated hydrocarbons.

The data on the structure of the intermediate compounds strongly suggest the relevance of the vibronic effects in realization of a certain geometric configuration, and, hence, of the appropriate electronic state even in cases when the degeneracy is absent. Moreover, the vibronic effects in the heteroligand structures become more significant than in the homoligand structures because of a redistribution of the Jahn–Teller stabilization energy between the potential-surface minima. These observations are at the basis of vibronic concept of coordination catalysis [26], according to which a broad spectrum of catalytic reactions with the low-symmetry active complexes can be described in terms of the dynamic Jahn–Teller effect by representing the active complex as a result of the ligand substitution in the high-symmetry structures.

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