ESR study of π-allyl Co(II) complexes in Ziegler type catalytic systems

V. V. Saraev,★ Yu. S. Levkovskii, A. E. Komolova, V. A. Gruznykh, M. Gomboogiin, and F. K. Schmidt

Irkutsk State University,
1 ul. K. Marksa, 664033 Irkutsk, Russian Federation

ESR study of the interaction between the components of the catalytic system Co(acac)$_2$—PBu$_3$—LiBu in the presence of butadiene revealed the formation of stable paramagnetic cobalt complexes containing a PBu$_3$ ligand and butadiene molecules. Complexes (η^3-R)$_2$CoPBu$_3$ (where R is allyl, crotyl, benzyl) have been synthesized by ordinary methods *in situ*, in order to identify the structures of the complexes. ESR parameters and geometry of the central core have been determined. The influence of the nature of phosphine ligands on the parameters of the ESR spectra has been studied. The general regularities in the ESR spectra of (η^3-R)$_2$CoPBu$_3$ and the complexes formed in the catalytic system have been revealed.

Key words: Ziegler type catalytic systems; π-allyl complexes of Co(II), ESR study.

Complexes with metal—carbon bonds that form through the interaction of the components of a catalytic system or in the course of the reaction are known to be responsible for catalysis by Ziegler—Natta type systems. It has been shown previously[1,2] that the reduction of cobalt to the zero-valent state with the formation of paramagnetic Co(II) complexes occurs in catalytic systems based on Co(II)-organic and organometallic compounds of nontransition metals. Later, ESR spectroscopy revealed intermediate alkyl and hydride derivatives of Co(II) formed during the formation of catalytic systems, and the routes of their transformations were studied. There is doubtless interest in the fine details of the interaction of hydride and alkyl Co(II) complexes with unsaturated compounds resulting in the alkyl and allyl intermediates through which the catalytic process occurs.

The aim of this work is to study allyl Co(II) complexes in Ziegler type catalytic systems using ESR methods.

Experimental

Dehydrated cobalt bis-acetylacetonate and cobalt dichloride were used. Solvents were purified by known methods and distilled under argon. Tributylphosphine and *n*-butyllithium were synthesized by previously described procedures.[3,4] Grignard reagents were used as 0.5 *M* solutions in ether. Reactions between components of the catalytic system were performed at 233 K under argon in a vessel with a "branch" for the ESR analysis. ESR spectra were registered on a Rubin spectrometer (operating frequency 9.6 GHz) at 77 K in toluene solutions. The diphenylpicrylhydrazyl radical and Mn^{2+} in MgO served as standards.

Results and Discussion

There are data[5] indicating that paramagnetic phosphine complexes of the (PBu$_3$)Co(acac)$_2$ type are formed in the system Co(acac)$_2$—PBu$_3$ in toluene. After the introduction of LiBu into the system, the initial signal in the ESR spectrum disappears and a signal characteristic of the phosphine-arene Co(0) complexes appears (*cf.* Ref. 5). In the presence of butadiene in the system, the aforementioned Co(0) complex is not formed. In this case the quantitative transformation of the high-spin (PBu$_3$)Co(acac)$_2$ complex into a paramagnetic complex occurs; the ESR spectrum of the latter (Fig. 1) corresponds to spin $S = 1/2$ and is a tri-axial anisotropic signal, in which there is a HFS from one Co nucleus and a poorly resolved HFS from one nucleus with $I = 1/2$.

It should be mentioned that the transformation of the initial signal in the ESR spectrum into the signal presented in Fig. 1 occurs with the formation of a series of intermediate paramagnetic compounds, which are extremely unstable and have not been identified so far (Fig. 2). The signal presented in Fig. 1 is observed also in the case when CoCl$_2$(PBu$_3$)$_2$ is the initial complex. Under these conditions, the detection of similar signals unambiguously indicates that ligands of the initial cobalt compound are absent in the studied complexes.

These complexes can be classified as low-spin Co(II) complexes with a d^7 electron configuration or Co(0) complexes with a d^9 electron configuration. In the first case, stabilization of Co(II) is possible due to the formation of π-crotyl ligands in the reaction of unstable alkyl and hydride Co(II) complexes with butadiene. In the second case, stabilization of Co(0) can occur through

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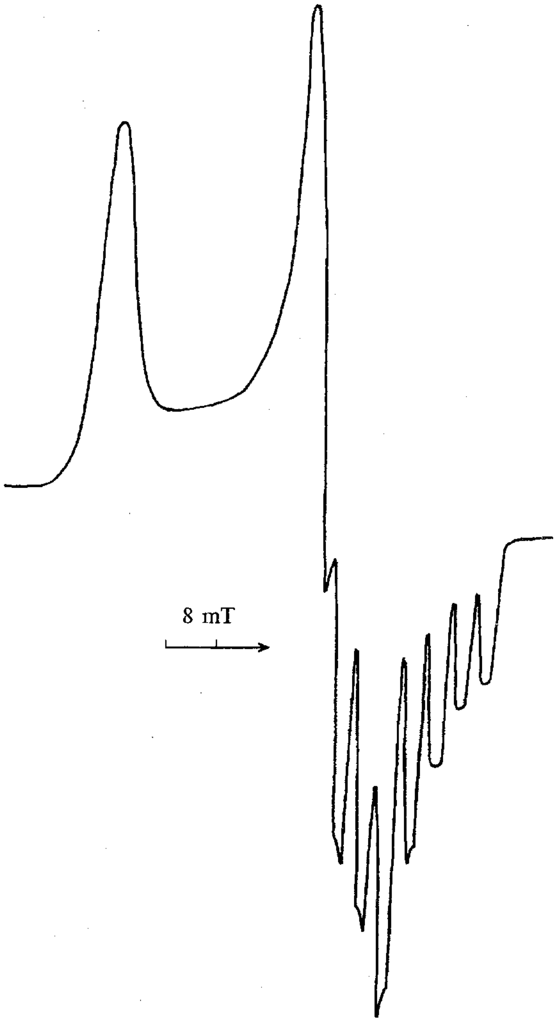


Fig. 1. ESR spectrum of the Co(acac)$_2$—PBu$_3$—LiBu—butadiene system.

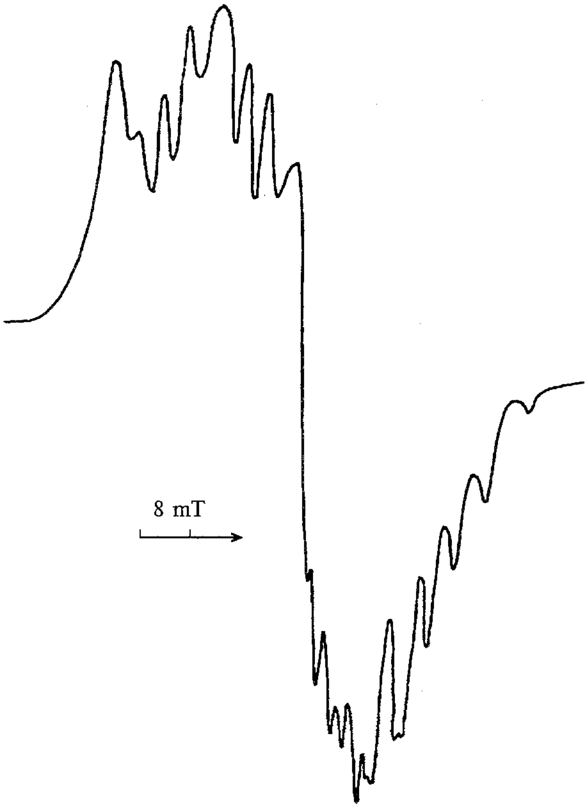


Fig. 2. ESR spectrum of the Co(acac)$_2$—PBu$_3$—LiBu—butadiene system 2 min after the components were mixed.

the coordination of butadiene. It was proposed that the signal observed relates to π-crotyl Co(II) complexes.

With the purpose of elucidating the mechanism of the formation of the allyl structures, we performed the synthesis of complexes (PBu$_3$)Co(η^3-C$_3$H$_5$), (PBu$_3$)Co(η^3-CH$_2$C$_6$H$_5$), (PBu$_3$)Co(η^3-C$_4$H$_7$). The commonly accepted procedures were used involving organomagnesium compounds, and without isolation of the complexes from the solution. The obtained spectra of the allyl and crotyl complexes almost coincide, and differ from those of the benzyl complex and the system with butadiene. According to literature data,[3] the bond between the benzyl ligand and the central atom is also a π-allyl type bond.

Despite the differences in the shapes of the ESR spectra of the synthesized complexes (Figs. 3 and 4), it can be noted that each of the eight HFC lines from the Co nucleus (I = 7/2) splits into two lines of additional HFC from one phosphorus nucleus (I = 1/2). This attests to the existence of one phosphine ligand in the coordination sphere, despite the fact that there is an excess of phosphine in the system, and allows one to assume that the bidentate ligands attached to the cobalt ion through π-bonds form five-coordinated compounds, which, unlike the σ-alkyl derivatives,[5] are overwhelmingly more stable.

According to the previously given theory,[5] the triaxial anisotropy of the g-factor in the five-coordinated complex is caused by the fact that the geometry of the complex is an intermediate form between a tetragonal pyramid and a trigonal bipyramid (Fig. 5). The spectra of the π-complexes essentially differ in the values of the constants of the additional HFC with the phosphorus nucleus (≈10), which also indicates geometric peculiarities of complexes of this type.

In order to determine the sensitivity of the parameters of the ESR spectrum to the nature of the coordinating ligands, we studied the influence of the nature of the phosphine ligand on the ESR spectra of allyl and benzyl complexes. Table 1 presents the corresponding parameters for complexes with PPh$_3$ and (C$_6$H$_{11}$)$_3$P, which show an inconsiderable difference in the anisotropy of the g-factor caused, apparently, both by electron and steric factors. We did not succeed in the determination of the z-component of the g-factor and the HFC constants due to the weak resolution of the ESR spectrum.

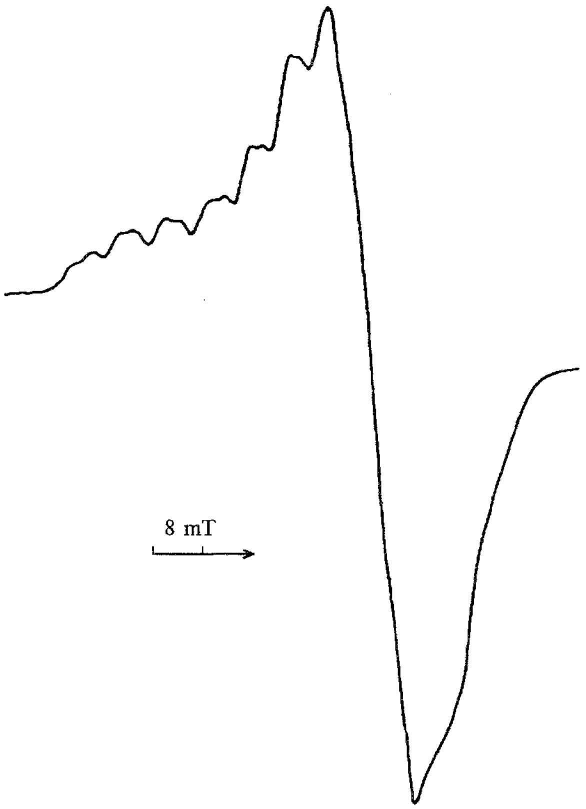
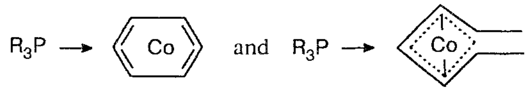


Fig. 3. ESR spectrum of $PBu_3Co(\eta^3\text{-}CH_2C_6H_5)_2$.

Benzyl complexes with PPh_3 and $(C_6H_{11})_3P$ are not formed: decomposition accompanied by the liberation of arene Co(0) is observed. This apparently occurs due to steric hindrances.

Thus, parameters of the ESR spectra (see Table 1) of the synthesized complexes change substantially in the transition from the allyl (crotyl) complex to the benzyl complex and the system with butadiene. Hence, one cannot affirm that the signal in the ESR spectrum of the $Co(acac)_2$—PBu_3—butadiene system does not refer to allyl structures. The parameters of the ESR spectrum contradict neither the zero-valent nor the bivalent state of cobalt in π-complexes of the type



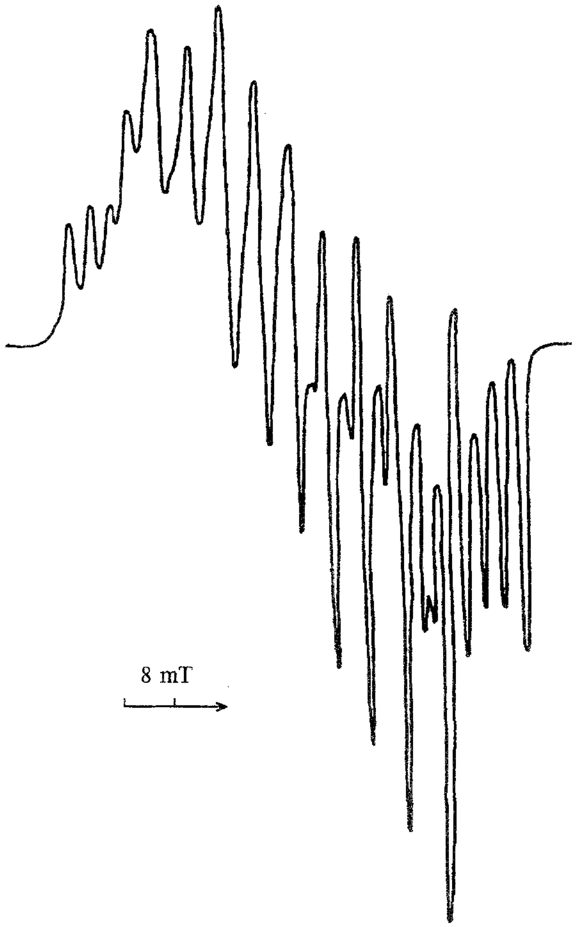


Fig. 4. ESR spectrum of $PBu_3Co(\eta^3\text{-}C_3H_5)_2$.

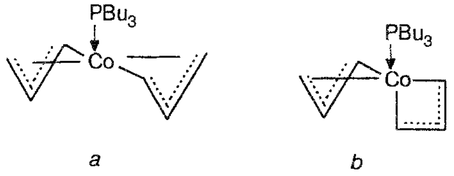


Fig. 5. Geometry of the π-allyl cobalt complexes: tetragonal pyramid (*a*) and trigonal bipyramid (*b*).

Table 1. Parameters of the ESR spectra of cobalt complexes

Complex	*g*-Factor			*a*(Co)			*a*(P)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
$Co(acac)_2$—PBu_3—LiBu—butadiene	2.01	2.12	2.40	4.9	—	—	1.0	—	—
$PBu_3Co(\eta^3\text{-}CH_2C_6H_5)_2$	2.06	2.06	2.29	—	—	7.3	—	—	2.0
$PBu_3Co(\eta^3\text{-}C_3H_5)_2$	2.00	2.12	2.29	3.3	5.9	3.5	13.2	11.8	10.5
$PBu_3Co(\eta^3\text{-}C_4H_7)_2$	2.00	2.12	2.30	3.3	5.6	3.3	13.2	11.2	9.9
$PhPCo(\eta^3\text{-}C_3H_5)_2$	1.99	2.12	—	3.1	5.2	—	12.4	10.4	—
$(C_6H_{11})_3PCo(\eta^3\text{-}C_3H_5)_2$	1.98	2.13	—	2.8	5.2	—	11.2	10.4	—

Further investigations are needed to refine the valent state of cobalt.

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