Electron Spin Resonance Investigations of Some Soluble Organometallic Catalysts

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Abstract: Experimental evidence, supported by theoretical considerations, led to the assumption that Cr from Cr(acac)$_3$AlEt$_3$ systems, with Al:Cr = 10, forms sandwich complexes with aromatic solvents. The values of the coupling constants in the esr spectra of these species are consistent with this assumption and with the variation of the energy of the highest occupied molecular orbital in the alkylbenzenes investigated. For Ti- and VO-containing systems, structures are advanced, based upon the esr spectra.

Recently, several papers dealing with the question of the valence state of the transition ion in organometallic soluble catalysts were published.[1–4] In fact, a precise knowledge of the valence state of the transitional ion can give unique information regarding the mechanism of action of those catalysts.

In a previous paper, we investigated, by means of electron spin resonance spectroscopy (esr), a series of catalytic systems resulting from the interaction of Ti(OC$_4$H$_9$)$_4$, Cr(C$_5$H$_7$O$_2$)$_3$, and VO(C$_5$H$_7$O$_2$)$_2$ with Al(C$_2$H$_5$)$_2$Cl.[5]

A certain influence of the solvent upon the esr spectra of the catalytic systems was observed, and it seemed of interest to subject this influence to a systematic investigation since it may have considerable effects on the specific properties of those catalytic systems.

Experimental Section

The following catalytic systems were investigated: (1) Ti(OC$_4$H$_9$)$_4$–Al(C$_2$H$_5$)$_3$, (2) Cr(C$_5$H$_7$O$_2$)$_3$–Al(C$_2$H$_5$)$_3$, and (3) VO(C$_5$H$_7$O$_2$)$_2$–Al(C$_2$H$_5$)$_3$. Hereafter, the following abbreviations will be used: acac = C$_5$H$_7$O$_2$ = acetylacetonate, Bu = C$_4$H$_9$O = butylate, Et = C$_2$H$_5$ = ethyl.

The systems were prepared by a procedure described elsewhere.[6,7] They were dissolved in different solvents, ultraviolet spectroscopic grade, Merck, which were used without further purifications. The systems investigated, with the molar ratios Al:Me and with the solvents used, are listed in Table I.

The esr spectra were recorded with an X-band spectrometer, Model IFA-06-65, modulated with 141 Kc/3.[8] All measurements were carried at room temperature in sample tubes sealed under argon. The g factors and line widths of the spectra were determined with the aid of a standard sample of potassium peroxylamine disulfonate, which has a g factor of 2.0057 ± 0.0001 and a hyperfine splitting constant of 13.00 ± 0.07 gauss.[9] The number of unpaired spins present in the sample was determined by double integration of the spectra and comparison with a standard.

Table I. The Soluble Organometallic Catalysts Investigated

System	Molar ratio, Al:Me	Solvent
Ti(OBu)$_4$–AlEt$_3$	2	C$_7$H$_{14}$
		C$_6$H$_{12}$
		C$_6$H$_6$
		C$_6$H$_5$CH$_3$
		o-C$_6$H$_4$(CH$_3$)$_2$
		p-C$_6$H$_4$(CH$_3$)$_2$
		C$_6$H$_5$C$_2$H$_5$
Cr(acac)$_3$–AlEt$_3$	3	C$_6$H$_6$
		C$_6$H$_5$CH$_3$
Cr(acac)$_3$–AlEt$_3$	10	C$_7$H$_{14}$
		C$_6$H$_{12}$
		C$_6$H$_6$
		C$_6$H$_5$CH$_3$
		C$_6$H$_5$CH$_2$D
		o-C$_6$H$_4$(CH$_3$)$_2$
		p-C$_6$H$_4$(CH$_3$)$_2$
		C$_5$H$_5$C$_2$H$_5$
VO(acac)$_2$–AlEt$_3$	10	C$_7$H$_{14}$
		C$_6$H$_6$
		C$_6$H$_5$CH$_3$
		p-C$_6$H$_4$(CH$_3$)$_2$
		C$_6$H$_5$C$_2$H$_5$

Results

The results of the esr measurements are listed in Table II, while Figure 1 represents some spectra of the systems used.

Discussion

A. Ti(OBu)$_4$–AlEt$_3$. The esr spectra yielded by the systems with the molar ratio Al:Ti = 2 show two signals, one with g = 1.959 ± 0.001, with a well-resolved hyperfine structure of 11 components. These components have the intensity 1:2:3:4:5:6:5:4:3:2:1 and may be thus reasonably ascribed to the equivalent interaction of the unpaired spin with two ^{27}Al nuclei (^{26}Al, I = $^5/_2$) in agreement with the arguments advaned by Djabiev, *et al.*[3]

The other signal with g = 1.979, extremely narrow, $\Delta H_{1/2}$ = 4.5 gauss, arises also from the interaction of the aluminum alkyl with the titanium derivative, but it seems difficult to ascribe it to a certain species.

Based upon these data it looks plausible that the system has the structure[3]

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(1) S. V. Shiulydin, N. N. Tikhomirova, A. E. Shilov, and A. K. Shilova, *Zh. Strukt. Khim.*, **2**, 740 (1961).

(2) G. Sartori, E. Cervone, A. Furlani, and I. Collamati, *Ric. Sci.*, **32**, 385 (1962).

(3) T. S. Djabiev, R. D. Sabirova, and A. E. Shilov, *Kinetika i Kataliz*, **5**, 441 (1964).

(4) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, **81**, 161 (1965).

(5) C. Nicolau and E. Angelescu, *Rev. Roumaine Chim.*, 10, 27 (1965).

(6) I. V. Nicolescu and E. Angelescu, *J. Polymer Sci.*, A3, 1227 (1965).

(7) I. V. Nicolescu and E. Angelescu, *ibid.*, in press.

(8) I. Pascaru, *Nucl. Instr. Methods*, **26**, 333 (1964).

(9) J. E. Wertz, D. C. Reitz, and F. Dravnieks in "Free Radicals in Biological Systems," Academic Press Inc., New York, N. Y., 1962, p 186.

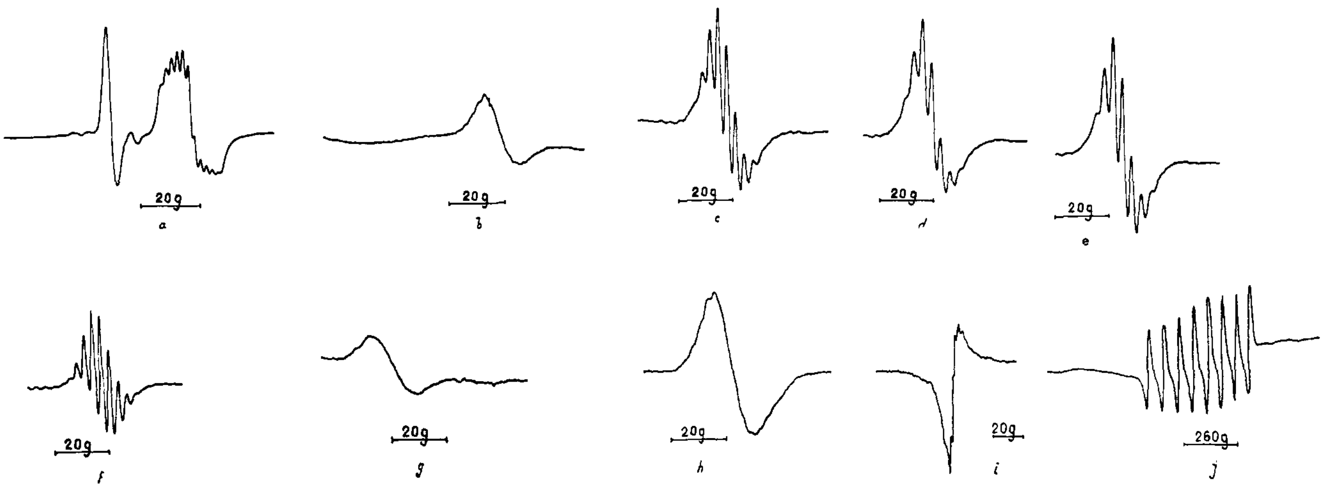
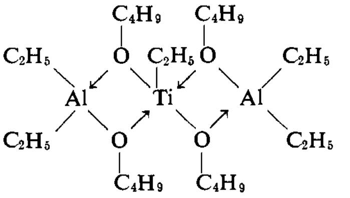


Figure 1. Electron spin resonance spectra of the investigated systems (ν = 9325 Mc/sec, 298°K, modulation = 0.75 g): (a) $Ti(OBu)_4$–$AlEt_3$ with Al:Ti = 2 in toluene; (b) $Cr(acac)_3$–$AlEt_3$ with Al:Cr = 10 in benzene; (c) in toluene; (d) in o-xylene; (e) in p-xylene; (f) in ethylbenzene; (g) in isopropylbenzene; (h) $Cr(acac)_3$–$AlEt_3$ with Al:Cr = 3 in toluene; (i) $Cr(acac)_3$–$AlEt_3$ in toluene–CH_2D (Al:Cr = 10); (j) $VO(acac)_2$–$AlEt_2$ with Al:V = 10 in toluene.



The fivefold coordination of the Ti^{+3} ion may account for the high instability of the complex in contact with air and is in agreement with the hypothesis advanced by Cosse[10] of the nature of active centers in the heterogenous Ziegler–Natta systems.

It must be stressed that the esr spectra of the Ti-containing systems are rather indifferent to the influence of the solvent, having the same features in all solvents used.

B. $Cr(acac)_3$–$AlEt_3$. The system with Al:Cr = 3, in benzene or toluene, yielded an unstructured esr spectrum with the g factor of 1.987 ± 0.001 and the half line width (measured between the point of maximum slope) of 31.2 gauss.

Increasing the Al:Cr ratio to 10, a different signal appeared, structured in the case of substituted benzenes (with the exception of isopropylbenzene) and unstructured in benzene. In aliphatic solvents no narrow signal could be detected.

The esr spectra recorded with $Cr(acac)_3$–$AlEt_3$ in alkylbenzenes strongly suggest that Cr forms sandwich complexes with the aromatic solvents. Indeed the g factor of 1.987 ± 0.001, the coupling constants ranging constants ranging from 2.7 gauss (for ethylbenzene) to 3.78 gauss (for o-xylene), as well as the hyperfine structure detected are very similar to those observed by other authors on $Cr(C_6H_6)_2^+$ [11a] and $Cr(C_6H_5–C_6H_5)_2^+$.[11b] The g factors are identical with ours, as are the coupling constants and the number of hyperfine components.

Table II. Parameters of the Esr Spectra Observed

System	Molar ratio, Al:Me	Solvent	Hyperfine structure	g factor	Coupling constant a, gauss
$Ti(OBu)_4$–$AlEt_3$	2	All solvents used	2 signals one without	1.979 ± 0.001	...
			one with 11 components	1.959 ± 0.001	1.98
$Cr(acac)_3$–$AlEt_3$	3	C_6H_6	...	1.987 ± 0.001	...
		$C_6H_5CH_3$	...	1.987 ± 0.001	...
$Cr(acac)_3$–$AlEt_3$	10	C_7H_{14}	...	...	...
		C_6H_{12}	...	...	...
		C_6H_6	...	1.987 ± 0.001	...
		$C_6H_5CH_3$	7 lines	1.987 ± 0.001	3.11
		$C_6H_5CH_2D$	7 lines	1.987 ± 0.001	2.90
		o-$C_6H_4(CH_3)_2$	7 lines	1.988 ± 0.001	3.78
		p-$C_6H_4(CH_3)_2$	7 lines	1.987 ± 0.001	3.24
		$C_6H_5C_2H_5$	9 lines + weak statellites	1.987 ± 0.001	2.7
		C_6H_5-i-C_3H_7	...	1.991 ± 0.001	...
$VO(acac)_2$–$AlEt_3$	10	All solvents used	8 lines	1.9915 ± 0.0003	46.8

Double integration of the esr spectra indicated that only four chromium ions out of 1000 are forming such complexes, the rest being probably involved in bimetallic complexes with $Al(C_2H_5)_3$. Since gas chro-

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[10] P. Cosse, *J. Catalysis*, **3**, 80 (1964).

[11] (a) R. D. Feltham, P. Sogo, and M. Calvin, *J. Chem. Phys.*, **26**, 1354 (1957); (b) I. D. Tzvetkov, V. V. Voevodsky, G. A. Razuvaev, I. V Sorokin, and G. A. Dormatchev, *Dokl. Akad. Nauk SSSR*, **115**, 118 (1957).

matographic measurements yielded two molecules of C_2H_4 for the reduction of one molecule of $Cr(acac)_3$, it seems reasonable to assume that Cr^{+3} is reduced in the sandwich complexes to Cr^+; these compounds thus have a relatively stable electronic structure.

The neutrality of the solution is due to the formation of $(AlEt_4)^-$ anions.

No conclusions concerning the bimetallic complex, assumed to concentrate the catalytic activity of the system, emerge from the results reported in this paper. It seems plausible that it may have the structure postulated by Sartori, *et al.*,[2] with a zerovalent chromium bonded to six oxygen atoms by dative bonds from the later.

The *g* factors of our spectra, markedly differing from the *g* factor of free radicals, show that the unpaired electron giving rise to the spectra belongs in each case to Cr. Moreover, the coupling constants observed are close to those found in the benzene negative (or positive) ion, namely 3.75 gauss. The total splitting of each spectra is about 27 gauss.

Based upon these facts the possibility of formation of sandwich complexes between Cr and aromatics, in our experimental conditions, seems to be established. Furthermore, since the 3d orbital of Cr is energetically between the highest occupied molecular orbital (HOMO) and the lowest empty molecular orbital (LEMO) of the aromatics,[12] one can build the following scheme for the bonding in the sandwich complexes.

$$\begin{array}{lll}
\varphi_{\mathrm{LEMO}} & \cdots\cdots\cdots\cdots & \Phi_{\mathrm{LEMO}} \approx \varphi_{\mathrm{LEMO}} - c_2\varphi_{3\mathrm{d}} \\
\varphi_{3\mathrm{d}} & \cdots\cdots\cdots\cdots & \Phi_{3\mathrm{d}} \approx \varphi_{3\mathrm{d}} - c_1\varphi_{\mathrm{HOMO}} + c_2\varphi_{\mathrm{LEMO}} \\
\varphi_{\mathrm{HOMO}} & \cdots\cdots\cdots\cdots & \Phi_{\mathrm{HOMO}} \approx \varphi_{\mathrm{HOMO}} + c_1\varphi_{3\mathrm{d}}
\end{array}$$

$$c_1 \approx \frac{w(3\mathrm{d},\ \mathrm{HOMO})}{E_{\mathrm{d}} - E_{\mathrm{HOMO}}} \ll 1; \quad c_2 \cong \frac{w(3\mathrm{d}_1\ \mathrm{LEMO})}{E_{\mathrm{LEMO}} - E_{\mathrm{d}}} \qquad (1)$$

It is difficult to tell *a priori* whether the interaction of the 3d orbitals will be stronger with the HOMO or the LEMO of the ligand. Nevertheless, the coupling constants in the esr spectra, measuring the unpaired spin density—probably on the ligand molecules, roughly increase going from benzene to alkylbenzenes.

The HOMO and LEMO of C_6H_6 are

$$\mathrm{HOMO}\begin{cases} \varphi_{\bar{1}} = \dfrac{1}{2}(\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6) \\ \varphi_1 = \dfrac{1}{\sqrt{12}}(2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \\ \qquad\qquad\qquad \varphi_5 + \varphi_6) \end{cases} \qquad (2)$$

$$\epsilon_1 = \epsilon_{\bar{1}} = \alpha + \beta$$

$$\mathrm{LEMO}\begin{cases} \varphi_2 = \dfrac{1}{\sqrt{21}}(2\varphi_1 - \varphi_2 - \varphi_3 + 2\varphi_4 - \varphi_5 - \varphi_6) \\ \varphi_{\bar{2}} = \dfrac{1}{2}(\varphi_2 - \varphi_3 + \varphi_5 - \varphi_6); \ \epsilon_2 = \epsilon_{\bar{2}} = \alpha - \beta \end{cases} \qquad (3)$$

The two-electron heteroatom model for CH_3[13] gives

$$\alpha_{\mathrm{CH_3}} = \alpha + 2\beta$$

and

$$\beta_{\mathrm{C-CH_3}} \approx 0.6\beta \qquad (4)$$

The interaction with CH_3 will enhance the energy of φ_2 and φ_1 (ϵ_2 and ϵ_1) leaving unchanged the energy of $\varphi_{\bar{2}}$ and $\varphi_{\bar{1}}$ ($\epsilon_{\bar{2}}$ and $\epsilon_{\bar{1}}$). Thus the alkylbenzenes will possess the same LEMO as benzene but higher HOMO's leading to lower ionization potentials. Thus, in eq 1, going from benzene to alkylbenzene, c_1 will increase while c_2 remains constant. This fact suggests that the strongest interaction in this case should be the $\varphi_{3\mathrm{d}}$ – HOMO one.

The unpaired spin will be located on $\phi_{3\mathrm{d}}$ where $\varphi_{3\mathrm{d}}$ is predominant, thus explaining the value of the *g* factor of 1.987 different from that of free radicals, and characteristic of chromium salts.

The results obtained with isopropylbenzene may be due to steric hindrance which increases the Cr^+–ligand distance and lessens *W*.

In the case of toluene and of xylene the methyl group is probably arranged with two hydrogens of the CH_3 group in the plane of the complex and only slightly shifted toward Cr^{+3} with respect to the phenylic cycle. The esr measurement with $C_6H_5CH_2D$ support this interpretation, the coupling constants in this case being smaller than those observed in $C_6H_5CH_3$ solutions (2.90 gauss instead of 3.11).

Such a configuration is not possible in isopropylbenzene and is more difficult in ethylbenzene.

C. $VO(acac)_2$–$AlEt_3$. The esr spectra of these systems show the characteristic ^{51}V splitting ($I = {}^7/_2$) with eight lines. Even with lower sweep of the magnetic field and with low amplitude modulation, we could not detect any hyperfine structure superposed on the eight vanadium lines. In toluenic solutions, Shiulydin, *et al.*,[1] and Natta, *et al.*,[4] working with VCl_4–$AlEt_3$ systems, detected a seven-line hyperfine structure identical with that one which we observed in the toluenic solution of chromium-containing systems, superimposed on each of the eight components due to ^{51}V.

It seems reasonable to ascribe this structure to a sandwich complex with toluene produced by the above catalyst, and not to a $VCl_2 \cdot 2AlEt_2Cl$ system as has been suggested.[1,4]

Conclusions

The esr investigations suggest that the $Cr(acac)_3$–$AlEt_3$ system is involved in the formation of a sandwich complex by Cr with aromatic solvents. This hypothesis is supported by the shape, hyperfine structure, and *g* factor of the esr spectra obtained in different solvents and by structural arguments.

For $Ti(OBu)_4$–$AlEt_3$ an interaction of the unpaired spin with two equivalent ^{22}Al nuclei has been detected.

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(12) H. B. Gray, *J. Chem. Educ.*, **41**, 2 (1964).

(13) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter V.