

Supplementary Material

Dynamic EPR studies of the formation of catalytically active centres in multicomponent hydrogenation systems

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Preliminary Data

Previously [1,2], for systems based on $\text{Co}(\text{acac})_2$ and AlEt_3 , immediately after mixing of the components, a signal in the EPR spectrum was recorded. It was preliminarily interpreted as a signal from the $\text{Co}(0)$ complex. Table S1 shows the corresponding parameters of g-factors and A-constants, and the EPR spectrum itself is depicted in Figure S1.

Table S1. – The EPR parameters of catalytic systems based on $\text{Co}(\text{acac})_2$ –Red–toluene, according to the data of works [1].

№	Solvent/ Arene	Cocatalyst (Red)	g		A	
			g_{\perp}	g_{\parallel}	A_{\perp}	A_{\parallel}
1	Toluene	AlEt_3	2.050	2.355	16.0	56.9
2		$\text{AlEt}_2(\text{OEt})$	2.050	2.355	18.0	56.9
3		$\text{Li}(\text{H-C}_4\text{H}_9)$	2.051	2.362	16.3	59.2
4		$(\text{PhCH}_2)\text{MgCl}$	2.054	2.368	16.9	64.0

The catalysts were formed at 298 K in an argon atmosphere, and their EPR spectra were recorded at 77 K.

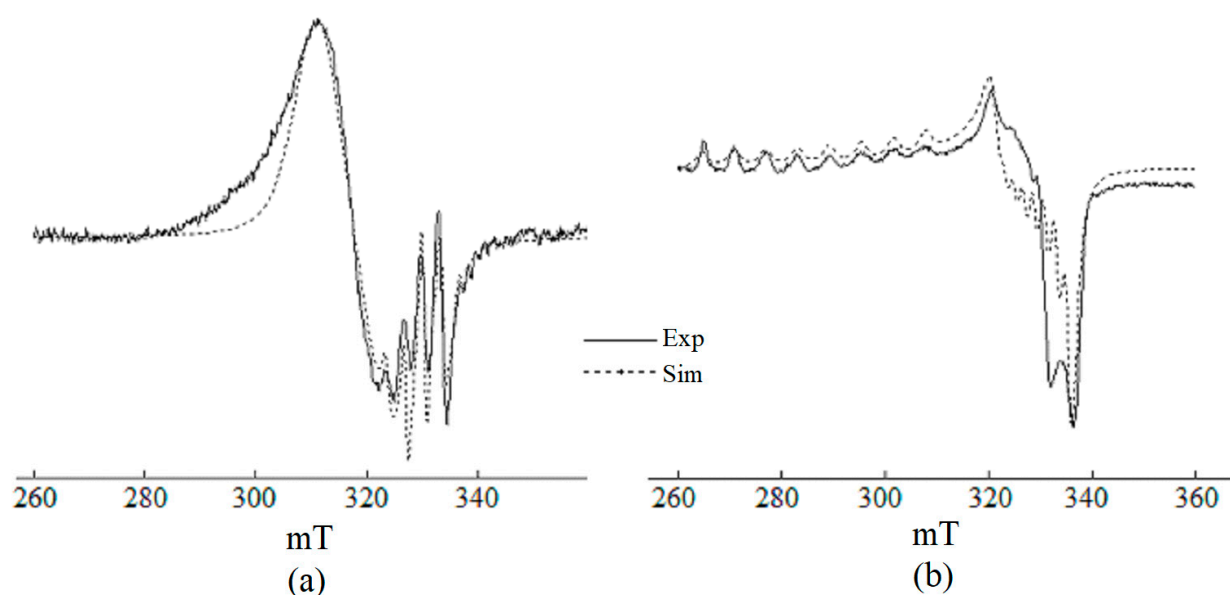


Figure S1. – Real (solid line) and simulated (dashed line) EPR spectra of the $\text{Co}(\text{acac})_2\text{-AlEt}_3$ catalytic system formed in toluene in an argon atmosphere (a) $T = 293\text{ K}$, and (b) $T = 77\text{ K}$, from [1].

It was shown that in the presence of other cocatalysts, namely $\text{AlEt}_2(\text{OEt})$, $\text{Li}(\text{H-C}_4\text{H}_9)$ and $(\text{PhCH}_2)\text{MgCl}$, a much less intense and often distorted signal was also observed in the EPR spectrum. The approximate parameters of these signals are presented in Table S1. The study of these paramagnetic structures is hindered by the facts that (1) they are extremely reactive and (2) they are very sensitive to water or atmospheric oxygen. Therefore, the data shown in Table S1 and Figure S1 were poorly reproduced due to the imperfection of the used experimental techniques. It should be noted that the values of g - and A - (Table S1) are presented as they were given in [1,2]. During the current study, many methods for the working with catalytic systems were improved, including those related to the EPR spectra, so the values of g - and A - were refined in the paper, as well as in Supplementary information.

The experimental work carried out in recent years has not only produced reproducible results, but has also established a number of factors that significantly affect the intensity and stability of the described paramagnetic signals.

Experimental Section

General Procedures

Solvents (toluene, octane, hexane, and diethylether) and **substrates** (styrene, 1-hexene, and cyclohexene) were purified using standard procedures [3]. Toluene, octane, and hexane were further dried by distillation from LiAlH_4 using a distillation column and were stored in an argon atmosphere over molecular sieve 4 \AA in sealed tubes. After being purified from peroxides, diethyl ether was distilled from sodium benzophenone ketyl and was stored in an argon atmosphere over sodium foil in sealed tubes. As determined by the Fisher method [4], the water concentration in octane, hexane, and toluene was $\sim 1.1 \cdot 10^{-3}\text{ mol/L}$ and the water concentration in diethyl ether was $1.6 \cdot 10^{-3}\text{ mol/L}$.

***p*-Xylene** (1,4-dimethylbenzene), **mesitylene** (1,3,5-trimethylbenzene), **durene** (1,2,4,5-tetramethylbenzene), and **1,2,3,4,5,6-hexamethylbenzene** were dried via standard procedures [5] and were stored in an argon atmosphere in sealed tubes.

***n*-Butanol** was refluxed over freshly calcined CaO (12.5 g) for 4 h in an argon atmosphere and was then distilled using a Vigreux column. The distillate was boiled over sodium and was then distilled off, and the fraction boiling at 117 °C ($n_D^{25} = 0.80572$) was collected [6].

Ethanol was refluxed over freshly calcinated CaO under argon and distilled over needle column. Further, it was boiled and distilled over sodium collecting the fraction, which boiled at 78 °C [5].

Argon (Argon Gas Purity, 99.998 %) was purified from moisture and oxygen by consecutive passing through the columns filled with P₂O₅, granulated alkali, molecular sieves SAA and powdered copper heated to 200 °C.

Hydrogen (Brand 1, National standard No. P51673-2000) was purified from oxygen and water traces by consecutive passing through the columns filled with nickel-chromium catalyst and SAA zeolites.

Triethylaluminum [1] was purified by distillation in vacuum at 48-49 °C / 1 Hg mm. It was stored in ampoules under an argon atmosphere. AlEt₃ was diluted in Schlenk tube in hexane or in octane under argon. Concentration of AlEt₃ solution was determined by volumetric analysis removing aliquot of the solution with water. Purity of AlEt₃ was checked by the PMR method: $\delta_{CH_2} = 0.45$ ppm (q, $^1J = 8.24$ Hz), $\delta_{CH_3} = 1.22$ ppm (t, $^1J = 8.24$ Hz.).

Benzylmagnesium chloride ((PhCH₂)MgCl) was synthesized via a standard procedure [7] using a solution of **butyllithium** Li(*n*-Bu) (Acros Organics) in hexane. The butyllithium concentration was determined via a standard procedure [8].

Ethoxydiethylaluminum (AlEt₂(OEt)) was obtained from AlEt₃ solution in hexane by dropping of the desired quantity of C₂H₅OH under continuous cooling at T = -10 °C and stirred in an argon atmosphere [1].

Commercial **lithium tetrahydroaluminate** LiAlH₄ ("Sigma-Aldrich", CAS Number 16853-85-3) was used without additional crystallization. A specimen of LiAlH₄ was dissolved in THF and the obtained solution was filtered through the Schott filter. Concentration of LiAlH₄, determined from the amount of hydrogen evolved upon the hydrolysis, was about 95–98% in theory. ²⁷Al NMR spectrum (THF, δ , ppm): 98 (quint: $^1J_{Al-H} = 173$ Hz) [1].

Synthesis of **LiAlH(*tert*-BuO)₃** was performed by alcoholysis of LiAlH₄ with *tert*-butanol in THF at 30 °C for 48 h according to the procedure described in [9], molar ratio [*tert*-BuOH]/[LiAlH₄] = 3. The reaction was monitored by the ²⁷Al NMR spectroscopy method. ²⁷Al NMR, δ , ppm (THF): 78 s [1].

Bis(acetylacetonato)cobalt samples were synthesized via a procedure reported in the literature [10].

Co(acac)₂·2H₂O was synthesized by combining an aqueous solution of CoCl₂·6H₂O (0.2 mol, 47.6 g) with an aqueous solution of Na(acac) (0.4 mol, 48.8 g) [10]. The resulting Co(acac)₂

precipitate was vacuum dried (40–50°C/14 Torr) for 3 h. The crystalline hydrate synthesized in this way, $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, was a pale pink powder.

$\text{Co}(\text{acac})_2 \cdot 0.5\text{H}_2\text{O}$ was synthesized by dehydrating the crystalline hydrate $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ by azeotropic distillation with toluene. The resulting lilac powder was vacuum dried (40–50°C/2 Torr) for 10 h [1].

Anhydrous $\text{Co}(\text{acac})_2$, a dark lilac powder, was obtained by sublimating $\text{Co}(\text{acac})_2 \cdot 0.5\text{H}_2\text{O}$ at 105–110°C/0.1 Torr [1].

The water content of the bis(acetylacetonato)cobalt samples was determined by thermogravimetric analysis combined with differential scanning calorimetry on an STA 449 F3 Jupiter thermoanalytical system (Netzsch, Germany) under the following conditions: nitrogen supply rate, 30 mL/min; heating rate, 5 K/min.

Experimental protocols

All manipulations were carried out in an inert atmosphere (dry, deoxygenated argon) using Schlenk techniques.

The interactions between $\text{Co}(\text{acac})_2$ and AlEt_3 or another reductant (Red) (Red = $\text{AlEt}_2(\text{OEt})$, $\text{Li}(n\text{-Bu})$, or $(\text{PhCH}_2)\text{MgCl}$) at different ratios between the initial reactants were studied in a dry and deoxygenated argon and/or hydrogen atmosphere. For example, a solution of a reductant in octane (Red = AlEt_3 or $\text{AlEt}_2(\text{OEt})$), tetrahydrofuran (Red = $(\text{PhCH}_2)\text{MgCl}$), or hexane (Red = $\text{Li}(n\text{-Bu})$) was added to a stirred solution of $\text{Co}(\text{acac})_2$ (0.0256 g, $1 \cdot 10^{-4}$ mol) in toluene (9 mL). The total volume of the system was 10 mL. The Red/Co molar ratio was varied between 1 and 25, depending on the reductant type. The resulting solution was analysed at different points in time by EPR spectroscopy at room temperature and at the liquid nitrogen temperature.

The $\text{Co}(\text{acac})_2$ –Red reaction systems were prepared for EPR spectroscopy using the following method: after the cobalt reaction, the mixture was prepared as described above. The transfer of sample solutions into 4 mm pre-pumped and argon-filled ampoules was carried out according to the Schlenk technology [11].

EPR spectra were recorded on a ESP 70-03 XD/2 spectrometer (the Experimental Design Office of Special Equipment of Belarus State University, Republic of Belarus) with a working frequency of 9.3 GHz. The spectrometer's sweep ranges were calibrated using diphenylpicrylhydrazyl of the *N,N*-diphenyl-*N'*-picrylhydrazyl radical (DPPH).

EPR spectra simulation

Theory

Generally, the EPR spectrum generally consists of lines caused by various transitions between energy levels. For most systems, the energy sublevels, into which the ground level splits in a magnetic field, and the EPR spectrum can be calculated by solving the spin Hamiltonian (SH) of the form:

$$H = \beta(g_x H_x B_x + g_y H_y B_y + g_z H_z B_z) + \left\{ D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 + S_y^2) \right\} + (A_x I_x S_x + A_y I_y S_y + A_z I_z S_z), \quad (1)$$

where β is Bohr magneton ($9.27404 \cdot 10^{-24}$ J/T); H_x, H_y, H_z are magnetic field components; S_x, S_y, S_z are components of the electron spin operator; I_x, I_y, I_z are components of the kernel spin operator; g_x, g_y, g_z are g-factor components of spectroscopic splitting; D, E are splitting parameters in the zero field; A_x, A_y, A_z are components of the hyperfine coupling constant (HFC).

The first term of expression (1) characterizes the Zeeman interaction of the electron magnetic moment with an external magnetic field. The D value serves as a measure of the axial distortion of cubic symmetry, and the E value is a measure of the axial symmetry distortion. For the systems with $S = 1/2$, the splitting in the zero field is absent. The third term represents the HFC of unpaired electrons with atomic nuclei that have nonzero magnetic moments. This notation assumes that g, D , and A have common principal axes.

For a more accurate description of the EPR spectrum, two more terms should be added to SH (1):

$$- \beta_N (g_{Nx} H_x B_x + g_{Ny} H_y B_y + g_{Nz} H_z B_z) + P \left\{ \left[I_z^2 - \frac{1}{3} I(I+1) \right] + \eta (I_x^2 + I_y^2) \right\}, \quad (2)$$

where β_N and g_N are nuclear Bohr magneton and nuclear g-factor, respectively; P is a quadrupole interaction constant; η is an asymmetry parameter of the quadrupole interaction.

The first term of equation (2) characterizes the nuclear Zeeman interaction, which is significant only if the energy $\beta_N g_N H$ – is comparable to the HFC constant. The second term of equation (2) determines the interaction of the nuclei quadrupole moments with the electric field, due to which the forbidden transitions can be observed.

According to the vivid expression of McGarvey [12], SH is a "crossroad" where the experimenter and theorist meet. An experimenter using EPR spectra determines such signal parameters as g, A, D, E , and P , while a theorist finds a correspondence between these parameters and the structure of paramagnetic compounds.

Practice

The model EPR spectra were calculated on a GPU-Tesla computer cluster using the EasySpin module for the MatLab software suite [13], taking into account only the Zeeman electron and the hyperfine interaction in the first order of approximation. The concentration of the spins was calculated by comparison with the reference sample representing a $\text{Cu}(\text{acac})_2$ solution, as the areas of the EPR signals assigned to $\text{Co}(0)$ were compared with the areas of the signals of $\text{Cu}(\text{acac})_2$ solutions of a certain concentration. All the compared signals were obtained under strictly identical conditions for the EPR survey [14, 15].

A general description of methods and examples of working with Easyspin are available at easyspin.org.

The *pepper* function was used for solid-state EPR spectra of frozen systems, and the *garlic* function for solution EPR spectra. A discussion of these functions can be found in [13] or easyspin.org.

Table S2. – The data used to simulation of the EPR spectra of systems based on Co(acac)₂–Red in toluene

№	Cocatalyst (Red)	Spectrum component	<i>g</i>			<i>A</i> , MHz		
			<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃	<i>A</i> ₁	<i>A</i> ₂	<i>A</i> ₃
1	AlEt ₃	Co(0) centre	2.017	2.071	2.354	19.4	38.4	195.0
		Al centre	2.019	2.085	2.346	88.0	8.7	192.0
2	(PhCH ₂)MgCl	Co(0) centre	2.017	2.068	2.369	24.4	38.4	192.0
		Mg centre	2.017	2.062	2.299	24.4	38.4	39.0
3	Li(<i>n</i> -C ₄ H ₉)	Co(0) centre	2.017	2.071	2.364	12.4	38.4	192.0
		Li centre	2.028	2.045	2.277	12.0	58.7	80.0

It is of note that the relative values corresponding to each specific signal in the spectrum are not given deliberately. The case is that the values of *g*-factors in different experiments are approximately the same, if the samples are taken under near-identical conditions. Table S2 shows values that, on average, correspond to most of the recorded spectra. However, the relative amounts for each specific signal of various experiments differ significantly. From the point of view of mathematical statistics, it is impossible to describe this by one figure, since this paper is based on the results of about 1000 experiments.

Further, the simulated spectra for the Co-containing and M-containing fragments (M = Al, Li, Mg) of paramagnetic sites are presented separately. In addition, the total spectrum obtained by combination of the above spectra for each of the model systems (see Figures S2–S4) is given. The contribution of the ferromagnetic resonance signal is not taken into account in this case.

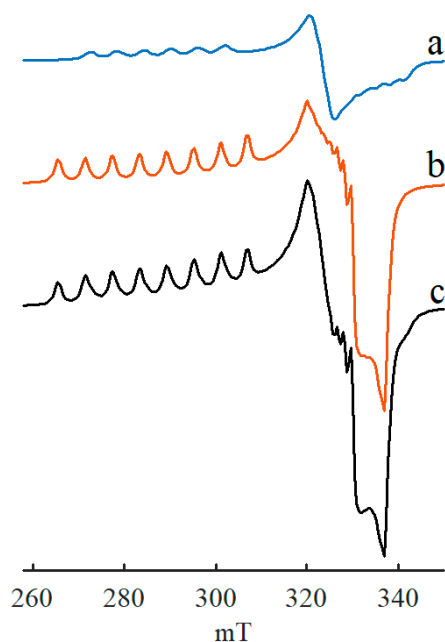


Figure S2. – Simulated subspectra of Al-containing fragment (a) and Co-containing fragment of (c) simulated spectrum shown in Figure 10.

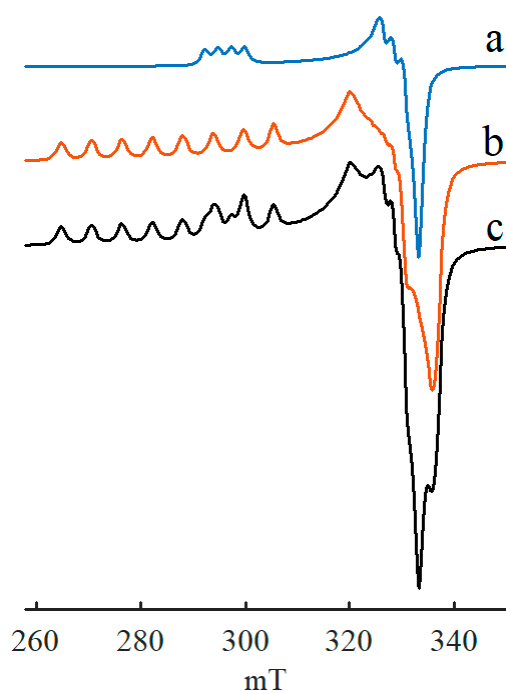


Figure S3. – Simulated subspectra of Li-containing fragment (a) and Co-containing fragment of (c) simulated spectrum shown in Figure 11(a).

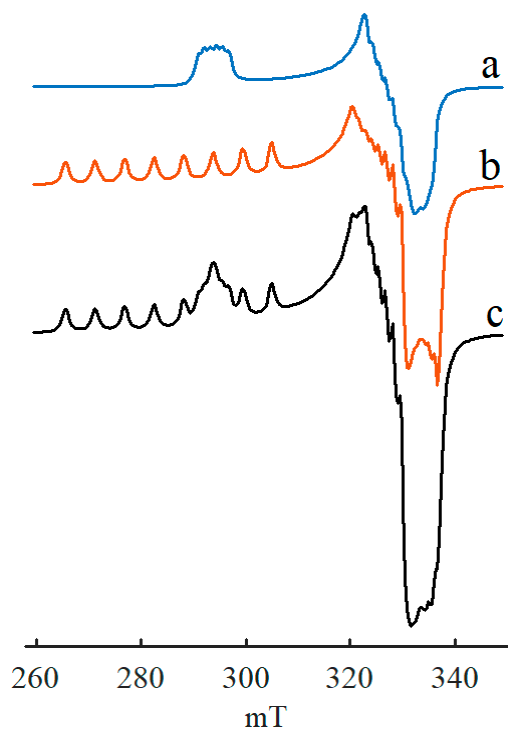


Figure S4. – Simulated subspectra of Mg-containing fragment (a) and Co-containing fragment of (c) simulated spectrum shown in Figure 11(b).

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