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REACTIONS OF COBALT ACETYLACETONATES WITH TRIMETHYLALUMINIUM IN THE PRESENCE OF 2,2'-DIPYRIDYL

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Summary

The reactions of cobalt(III) acetylacetonate and cobalt(II) acetylacetonate with trimethylaluminium in the presence of 2,2'-dipyridyl (dipy) as an electron donor was studied. A mixture of methylcobalt complexes at a molar ratio dipy/Co of 2/1 was found to be formed from these reactions. Aluminium(III) acetylacetonate or aluminium dimethylacetylacetonate, depending on the molar ratio of reactants, are the other reaction products.

Introduction

A number of papers describe the formation of alkylcobalt complexes from reactions of cobalt acetylacetonates with alkylaluminium compounds in the presence of organic electron donors [1—7]. Many of these complexes have been isolated, their composition and structure have been determined and their properties described. However, the courses of these reactions have not been explained and not all the final and intermediate products have been determined. In our previous paper, the reaction of cobalt(III) acetylacetonate with trimethylaluminium without an electron donor was described and the reaction mechanism proposed [8].

The purpose of the present work was to investigate all the reaction products of cobalt(III) acetylacetonate and cobalt(II) acetylacetonate with trimethylaluminium in the presence of 2,2'-dipyridyl as an electron donor.

Results

The reactions of cobalt(III) acetylacetonate [$Co(acac)_3$] with trimethylaluminium [Me_3Al] in the presence of 2,2'-dipyridyl (dipy) were carried out in benzene at temperatures from 5 to 20°C at various $Me_3Al/Co(acac)_3$ molar ratios, maintaining constant the dipy/$Co(acac)_3$ molar ratio (2/1). The reaction mixture slowly changes colour from dark green via russet to navy blue. This colour is reached after about two hours mixing of reactants.

For $Me_3Al/Co(acac)_3$ molar ratios $\leqslant 3/1$ no gaseous products were formed. For $Me_3Al/Co(acac)_3$ molar ratios $> 3/1$, methane, ethane and ethylene were evolved with the composition given in Table 1.

The following reaction products were isolated: (1) for the $Me_3Al/Co(acac)_3$ molar ratio of 1/1, aluminium(III) acetylacetonate was sublimed (Found: C, 55.52; H, 6.71. $C_{15}H_{21}O_6Al$ calcd.: C, 55.55; H, 6.52%). (2) for the molar ratio $Me_3Al/Co(acac)_3$ of 3/1, aluminium dimethylacetylacetonate was distilled off (Found: Al, 16.82. $C_7H_{13}O_2Al$ calcd.: Al, 17.28%). The identification was confirmed by the PMR spectrum recorded in benzene.

The reaction mixture is paramagnetic. The EPR spectrum is presented in Fig. 1.

In spite of carrying out a number of reactions in various solvents: benzene, toluene, n-pentane, n-heptane, diethyl ether and tetrahydrofuran, attempts of isolation of the cobalt compound formed from the reaction failed. It is slightly soluble in the solvents used. It precipitates from the reaction mixture together with other unidentified products probably resulting from the oxidation processes taking place in the reaction medium.

Attempts were carried out to determine the composition of the cobalt compound in a number of chemical reactions and studies without isolating it from the reaction mixture.

The cobalt compound formed is very active towards oxygen. In contact with air it undergoes immediate decomposition with the formation of diamagnetic products.

1.41 moles of CH_4 per mole of $Co(acac)_3$ are evolved upon hydrolysis of the reaction mixture with water, methanol or a sulphuric acid solution. 46.7% of methane is evolved with respect to the methyl groups introduced as Me_3Al ($Co(acac)_3/Me_3Al$ molar ratio of 1/1).

A slow thermal decomposition of the reaction mixture takes place at ca. 70°C. Gases of the following composition are evolved: 81.2% of CH_4, 18.8% of C_2H_6 and traces of C_2H_4. The amount of gases evolved was 1.20 moles of CH_3 groups per 1 mole of $Co(acac)_3$. It was assumed that one molecule of CH_4 corresponds to one CH_3 group; one molecule of C_2H_6 corresponds to two CH_3 groups).

TABLE 1

AMOUNT AND COMPOSITION OF GASEOUS PRODUCTS OF THE REACTION OF $Co(acac)_3$ WITH Me_3Al IN THE PRESENCE OF DIPY FOR $Me_3Al/Co(acac)_3$ (MOLAR RATIOS >3/1)

Experiment	Molar ratio $Me_3Al/Co(acac)_3$	Quantity of gases evolved (cm^3/mmol $Co(acac)_3$)	Composition of gases			Number of methyl groups evolved as gas per 1 mol of $Co(acac)_3$
			CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	
1	5/1	26.5	85.1	13.3	1.6	1.39
2	7/1	25.0	89.3	10.3	0.4	1.26
3	8/1	30.5	90.8	8.6	0.6	1.49
4	10/1	35.0	93.4	6.6	traces	1.66

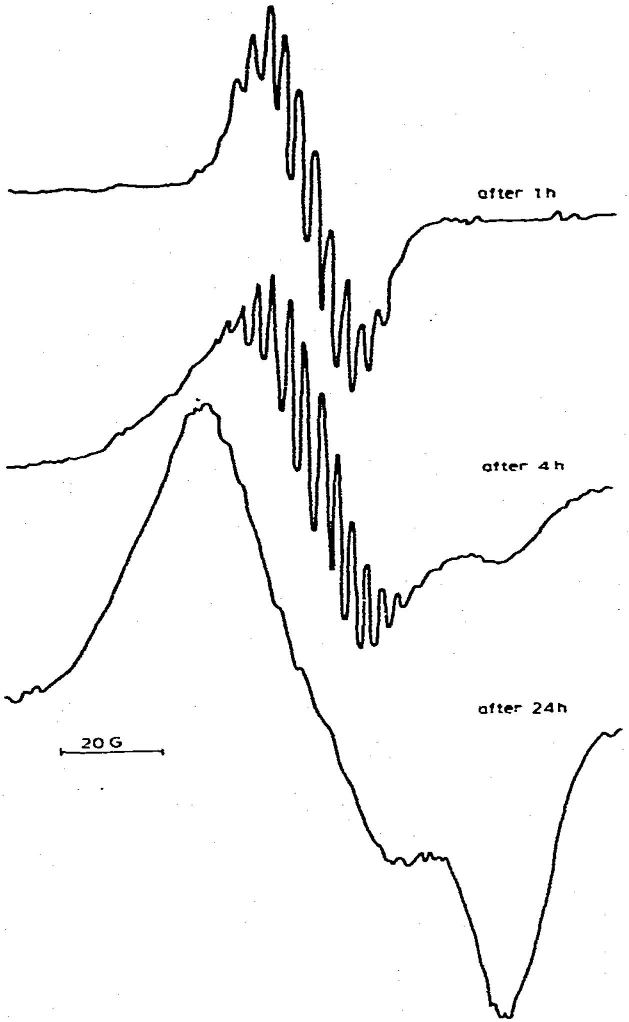

Fig. 1. EPR spectrum of the reaction mixture of cobalt(III) acetylacetonate with trimethylaluminium in the presence of 2,2'-dipyridyl for Co(acac)$_3$/Me$_3$Al/dipy (molar ratios 1/1/2).

The reaction of Co(acac)$_3$ with Me$_3$Al in the presence of dipy at constant Me$_3$Al/Co(acac)$_3$ molar ratios of 1/1 was studied, but with different dipy/Co(acac)$_3$ molar ratios. The reaction course for the dipy/Co(acac)$_3$ molar ratio $> 2/1$ is identical to that for molar ratio 2/1. No gaseous products are formed. The presence of free dipy was found in the reaction mixture. For the dipy/Co(acac)$_3$ molar ratio $< 2/1$, however gaseous products are formed with the composition presented in Table 2. The composition of the gases is similar to that of the gases evolved from the reaction of Co(acac)$_3$ with Me$_3$Al carried out without an electron donor [8].

The reaction of cobalt(II) acetylacetonate with trimethylaluminium in the

TABLE 2

AMOUNT AND COMPOSITION OF GASEOUS PRODUCTS OF THE REACTION OF $Co(acac)_3$ WITH Me_3Al IN THE PRESENCE OF dipy FOR dipy/$Co(acac)_3$ (MOLAR RATIOS <2/1)

Experiment	Molar ratio dipy/$Co(acac)_3$	Quantity of gases evolved (cm^3/mmol $Co(acac)_3$)	Composition of gases		
			CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)
1	0.5/1	32	79.2	19.7	1.1
2	1/1	22	73.4	25.0	1.6
3	1.5/1	10	69.8	28.0	2.2

presence of dipy was also studied. The reaction was carried out analogously with the reactions of cobalt(III) acetylacetonate. All studies carried out (EPR spectra, hydrolysis, thermal decomposition) showed that the same kind of cobalt compound is formed as in reactions of cobalt(III) acetylacetonate. The remaining reaction products were isolated and identified. Aluminium(III) acetylacetonate or aluminium dimethylacetylacetone were found to be formed depending on the molar ratio of the reactants.

The reactions of $Co(acac)_2$ proceed much more rapidly than those of $Co(acac)_3$. The colour of the reaction mixture changes immediately on dropwise addition of the Me_3Al solution.

The reaction mixtures and products isolated were treated with a benzene solution of iodine. In spite of carrying out the reaction in identical conditions the elemental analysis results of isolated iodination products varied.

Discussion

The results of iodination permit one to suggest that a mixture of various cobalt complexes is formed in the reactions of cobalt acetylacetonates with trimethylaluminium in the presence of dipy.

Reactions carried out at various dipy/$Co(acac)_3$ molar ratios showed that in the cobalt complexes formed, the dipy/Co molar ratio was 2/1.

In reactions carried out at dipy/$Co(acac)_3$ molar ratios >2/1 an excess of dipy remains in the reaction mixture. However, at dipy/$Co(acac)_3$ molar ratios <2/1, a partial reduction of cobalt(III) to cobalt(0) takes place, as in reactions of Me_3Al with $Co(acac)_3$ carried out without an electron donor [8].

The thermal decomposition of the reaction mixture at 70°C suggests that methyl groups σ-bonded with cobalt are present in the complexes formed. Neither of the methylaluminium compounds present in the mixture (trimethylaluminium or aluminium dimethylacetylacetonate) undergoes thermal decomposition at such a low temperature.

The evolution of gaseous products in reactions with an excess of trimethylaluminium is a further proof of the presence of methyl groups linked by σ-bonds with cobalt. The decomposition of alkyl complexes of transition metals with an excess of organoaluminium compounds is described in the literature [9,10]. The fact that the decomposition of cobalt complexes takes place only for $Me_3Al/Co(acac)_3$ molar ratios >3/1 is well explained by the decomposition mechanism proposed by Yamamoto [9]. For lower molar ratios there is no free Me_3Al in the reaction mixture, only $Me_2Al(acac)$, which being a weaker Lewis acid does not cause a destabilization of the Co—CH_3 bond.

From the amount of gases evolved during the thermal decomposition of reaction mixtures and in reactions with an excess of Me_3Al, it can be suggested that the number of methyl groups bonded with cobalt is 1 or 2. Complexes are probably formed, containing both one and two methyl groups bonded directly with cobalt. The presence of cobalt(II) compounds is also confirmed by the paramagnetism of the reaction mixtures.

On the basis of studies carried out it can be stated that in the reactions of cobalt acetylacetonates with trimethylaluminium in the presence of dipy cobalt complexes are formed with the formula $(CH_3)_nCo(dipy)_2$, where $n = 1$ or 2.

The formation of complexes containing an acetylacetonate group in the molecule, or complexes of the oligomer or polymer type, cannot be excluded.

In reactions of $Co(acac)_3$ and $Co(acac)_2$ with Me_3Al in the presence of dipy, identical products are formed. This confirms the reduction of the oxidation degree of cobalt in $Co(acac)_3$. The difference between the rates of these reactions shows that the reduction of Co^{3+} to Co^{2+} is the slowest step of the reaction of $Co(acac)_3$ with Me_3Al in the presence of dipy.

Experimental

Trimethylaluminium [11] and cobalt(III) acetylacetonate [12] were prepared by methods described in the literature. Cobalt(II) acetylacetonate (P.O.Ch., Gliwice) was dried in vacuo, and then sublimed at 100°C under a pressure of 10^{-3} Torr. 2,2'-Dipyridyl (P.O.Ch., Gliwice) was dried at 70°C under a pressure of 10^{-1} Torr.

Solvents were dried and deoxidized by heating with potassium and benzophenone until the mixture reached a navy-blue colour, then they were distilled in a dry and deoxygenized nitrogen atmosphere.

All the reactions were carried out in a dry, deoxygenated nitrogen atmosphere, in a glass apparatus equipped with a magnetic stirrer and dropper.

Elemental analysis was carried out on a Perkin—Elmer, model 240, analyzer. PMR spectra were recorded on JEOL JNM-C-60H or 100H apparatus. EPR spectra were recorded on JEOL JES ME-3X apparatus.

Course of a typical experiment

1.070 g (3.0 mmol) of $Co(acac)_3$ and 0.936 g (6.0 mmol) of dipy in 15 cm^3 of benzene were introduced into the reaction vessel. The mixture was cooled to the freezing point of benzene (about 6°C). A cooled solution of 0.29 cm^3 (3.0 mmol) of Me_3Al in 5 cm^3 of benzene was then slowly added dropwise with stirring. After completion of the dropwise addition (about 20 min), the mixture was still kept at 6°C for 30 min, and then left to heat up to room temperature with continuous stirring.

Reactions were also carried out changing the order of the addition of substrates. To suspensions of the $Me_3Al \cdot$ dipy complex in benzene a solution of $Co(acac)_3$ in benzene was slowly added dropwise.

The reaction mixtures thus obtained were hydrolyzed, thermally decomposed or iodinated.

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