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REACTION BETWEEN COBALT(III) ACETYLACETONATE AND TRIMETHYLALUMINIUM

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Summary

The reaction between cobalt(III) acetylacetonate and trimethylaluminium at a molar ratio of $Me_3Al/Co(acac)_3$ of 1/1 has been investigated. When a benzene solution of trimethylaluminium was added to a benzene solution of cobalt (III) acetylacetonate, IR spectra and volumetric gas analysis show that the latter is reduced via stable cobalt(II) acetylacetonate to metallic cobalt. Aluminium(III) acetylacetonate was also formed. The gaseous products of this reaction were methane, ethane, and ethylene. A reaction mechanism is suggested.

Introduction

To establish the oligomerization mechanism for dienes the composition and structure of the catalytic species has to be obtained. It is of value to study the reactions of transition metal compounds with various organoaluminium compounds. In this paper we present our results on the reaction of cobalt(III) acetylacetonate with trimethylaluminium.

The reaction of cobalt(III) acetylacetonate with triethylaluminium has been described in the literature, but authors are not unanimous regarding the course of the reaction. Tamai [1] states that the reaction proceeds via a gradual reduction of cobalt [$Co^{III} \rightarrow Co^{II} \rightarrow Co^0$]. Nicolescu [2] has studied the reaction of $Cr(acac)_3$ and $Co(acac)_3$ with Et_3Al and ascertained that the final oxidation state of chromium and cobalt is +2. This is not in line with Sartori's [3] studies in which the reduction of Cr^{3+} to Cr^0 in the reaction of $Cr(acac)_3$ with Et_3Al is postulated.

Results and discussion

Cobalt(III) acetylacetonate reacts with trimethylaluminium in benzene solution at room temperature to give metallic cobalt, aluminium acetylacetonate and a mixture of methane, ethane and ethylene (eqn. 1). During the reaction

$$3\,\mathrm{Co(acac)_3} + 3\mathrm{(CH_3)_3Al} \rightarrow 3\,\mathrm{Co^0} + 3\,\mathrm{Al(acac)_3} + [\mathrm{CH_4} + \mathrm{C_2H_6} + \mathrm{C_2H_4}] \qquad (1)$$

the colour of the reacting mixture changes from green via violet-red to black. Hydrolysis of the reaction products does not lead to evolution of gaseous products. This proves that all the hydrolyzable methyl groups take part in reaction 1.

After the solvent was distilled off, the reaction products were sublimed to give aluminium acetylacetonate (anal. found: C, 55.74; H, 6.89; Al + O, 37.37. Calcd.: C, 55.60; H, 6.48; Al + O, 37.92%). The identification was confirmed by IR and NMR studies.

The residue is an active form of metallic cobalt. It violently reacts with air, methanol and water. Hydrogen chloride reacts with the metal giving $\mathrm{CoCl_2}$ and hydrogen.

The amount and contents of the gases formed in reaction 1 are shown in Table 1. The yield of gases was calculated on the basis of the methyl groups used. It has been accepted that one methyl group gives a methane molecule, and two methyl groups give a molecule of ethylene or ethane. The rate of evolution of gases, initially low, rises considerably after 40% of the trimethylaluminium has been added.

The IR spectra of the reaction mixtures, for the molar ratio $\mathrm{Al/Co} < 1$ confirmed that the reduction of cobalt(III) acetylacetonate to metallic cobalt proceeds via stable cobalt(II) acetylacetonate. For the molar ratio Al/Co of 1/3 we observed a decrease of the intensity of the 1284 $\mathrm{cm^{-1}}$ band, attributed to stretching vibrations of C—C + $\mathrm{C{-}CH_3}$ for $\mathrm{Co(acac)_3}$ and the appearance of new 1261 $\mathrm{cm^{-1}}$ and 1288 $\mathrm{cm^{-1}}$ bands attributed to the same vibrations for $\mathrm{Co(acac)_2}$ and $\mathrm{Al(acac)_3}$ [4, 5]. We also observed a decrease of the intensity of the 466 $\mathrm{cm^{-1}}$ band attributed to the stretching vibrations of $\mathrm{Co^{III}{-}O}$ bond, and the appearance of a 490 $\mathrm{cm^{-1}}$ band (stretching vibrations of Al—O), and overlapping bands at 422 $\mathrm{cm^{-1}}$ (stretching vibrations of $\mathrm{Co^{II}{-}O}$) and 425 $\mathrm{cm^{-1}}$ (out of plane bending $\mathrm{Al(acac)_3}$) [4, 5]. Analogous observations for the reaction between cobalt acetylacetonate and triethylaluminium were made by Tamai [1].

TABLE 1

THE CONTENTS AND YIELD OF GASEOUS PRODUCTS FROM THE 1/1 REACTION OF COBALT ACETYLACETONATE WITH TRIMETHYLALUMINIUM

Expt.	Contents (%)			Yield (%)
	$\mathrm{CH_4}$	$\mathrm{C_2H_6}$	$\mathrm{C_2H_4}$	
1	72.2	26.0	1.8	66.0
2	78.0	20.5	1.5	63.7
3	76.8	21.6	1.6	64.9

From chromatographic studies of the solvent after the reaction, we ascertained the presence of a small amount of toluene and a few unidentified hydrocarbons that might be the products of oligomerization of ethylene formed in the reaction.

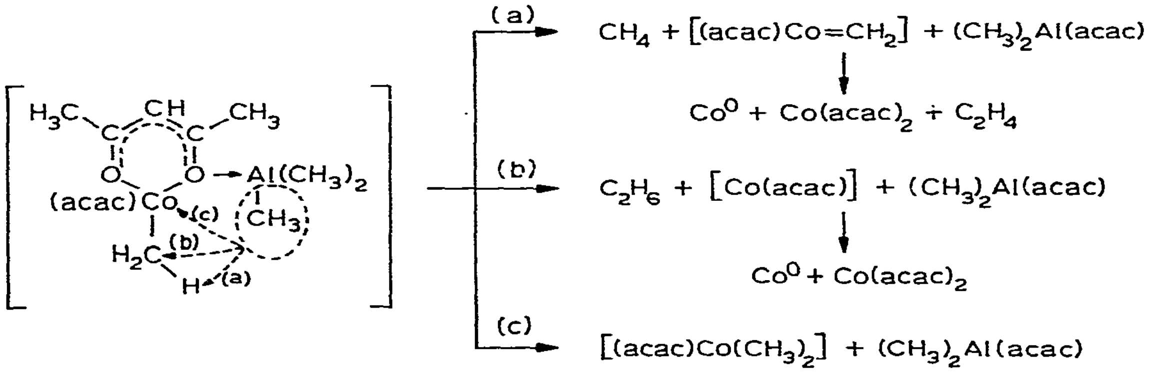
From the mass spectrum of the gases formed in the cobalt(III) acetylacetonate and trimethylaluminium reaction in deuteriobenzene solution, the presence of CH_4, CH_3D and C_2H_6 was confirmed. The quantity of CH_3D in the studied mixture of gases was about 10%.

These observations suggest that the reaction proceeds by more than one route. On the basis of all the results, we propose the following reaction scheme: the first stage of the reaction is the formation of a donor—acceptor complex of cobalt(III) acetylacetonate with trimethylaluminium, and later, the migration of a methyl group from aluminium to cobalt with a simultaneous formation of aluminium dimethylacetylacetonate (eqn. 2).

$$\mathrm{Co(acac)_3 + (CH_3)_3Al \rightarrow \underset{(I)}{[(acac)_2CoCH_3]} + (CH_3)_2Al(acac)} \qquad (2)$$

The intermediate I may form a complex with another molecule of trimethylaluminium or aluminium dimethylacetylacetonate:

The displacement of an electron pair towards the aluminium atom causes an increase of the negative charge on the carbon atom bonded to aluminium and consequently the methyl group could undergo nucleophilic substitution at the hydrogen (a), carbon (b) or cobalt (c) atoms.

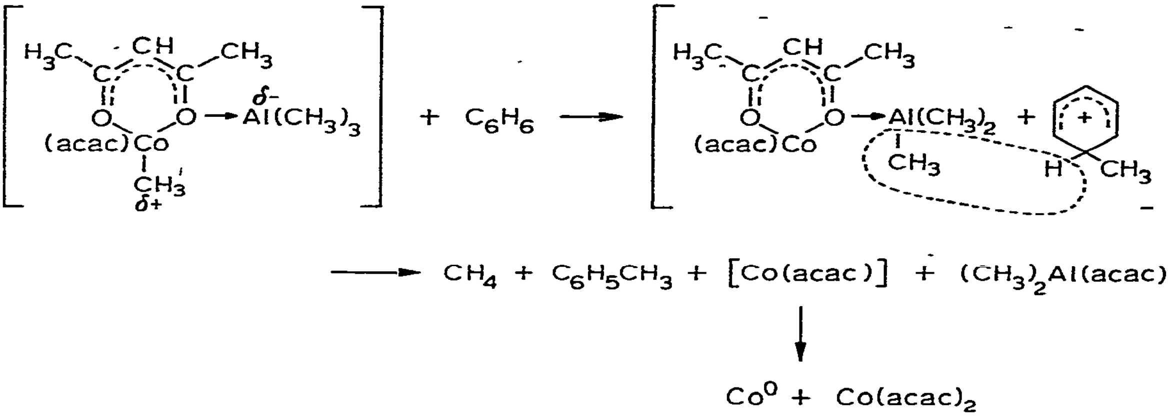


The unstable cobalt dimethylacetylacetonate formed in step (c) may decompose with the evolution of ethane or methane and ethylene:

$$\begin{array}{ccccc} \mathrm{CH_4 + [(acac)Co{=}CH_2]} & \leftarrow & \mathrm{[(acac)Co(CH_3)_2]} & \rightarrow & \mathrm{[(acac)Co] + C_2H_6} \\ \downarrow & & & & \downarrow \\ \mathrm{Co^0 + Co(acac)_2 + C_2H_4} & & & & \mathrm{Co^0 + Co(acac)_2} \end{array}$$

$Co(acac)_2$ formed as an intermediate product reacts with $(CH_3)_3Al$ analogously to $Co(acac)_3$.

As a result of the electronic displacement towards the aluminium atom and the formation of a partial positive charge on the methyl group bonded to cobalt, electrophilic substitution of a solvent molecule can occur according to the following scheme:



Experimental

Trimethylaluminium [6] and cobalt(III) acetylacetonate [7] were obtained by methods described in the literature. Benzene (P.O.Ch., Gliwice) was dried with sodium and distilled in a nitrogen atmosphere. IR spectra were recorded on a Zeiss UR10 spectrometer; absorption cell thickness 0.15 mm. Mass spectra were recorded on a LKB9000 apparatus.

All the reactions were carried out in a dry, deoxygenated nitrogen atmosphere, in a glass apparatus equipped with a stirrer and dropper. The gases evolved were collected in a gas-burette above a saturated solution of sodium chloride.

Course of a typical experiment. To 1.5034 g (4.22 mmol) of $Co(acac)_3$ in 10 ml of benzene 0.4 ml (4.20 mmol) of $(CH_3)_3Al$ was slowly dropped in at room temperature, waiting after every drop until the gas evolution stopped. 146 ml of gas at standard conditions was evolved with the following contents: 72.2% (4.69 mmol) CH_4; 26.0% (1.69 mmol) C_2H_6; 1.8% (0.12 mmol) C_2H_4.

Calculation example. Data: 4.22 mmol $Co(acac)_3$ and 4.20 mmol $(CH_3)_3Al$ = 12.60 mmole CH_3. 4.69 mmol CH_4 corresponds to 4.69 mmol CH_3; 1.69 mmol C_2H_6 corresponds to 3.38 mmol CH_3; and 0.12 mmol C_2H_4 corresponds to 0.24 mmol CH_3. Total 8.31 mmol CH_3.

Reaction yield η based on the methyl groups: $\eta = (8.31/12.60) \times 100 = 66\%$.

The quantity of methyl groups evolved as ethylene (0.24 mmol) and not evolved as a gas (4.29 mmol) is approximately equal to the quantity of methyl groups evolved as methane (4.69 mmol), which is in line with the proposed reaction scheme.

References

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