

Preliminary communication

SYNTHESIS AND PROPERTIES OF ALKOXYALKYLIDINETRICOBALT NONACARBONYL CLUSTER COMPLEXES

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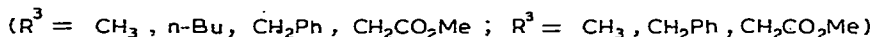
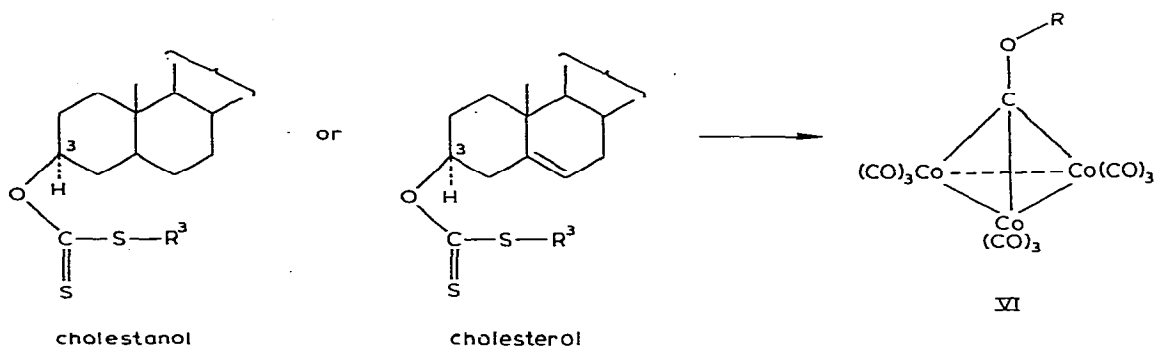
Summary

The title compounds are obtained in fair to good yield by desulfurization of *S*-alkyl xanthates in reactions with dicobalt octacarbonyl. The cluster structure is supported by mass spectroscopic and NMR data, and evidence is presented for an elimination step leading to desulfurization. These air-stable complexes are active catalysts for hydroformylation of olefins.

We have recently described complexation of *S*-alkyl dithiocarbonates (or *S*-alkyl xanthates) $R_2CHC(=S)SR^3$ with $Fe_2(CO)_9$ to afford binuclear complexes for which the $C(=S)S$ group functions as a six electron ligand towards the $Fe_2(CO)_6$ moiety [1]. In the course of our investigations of activation of C—H bonds we are studying the reactions of molecular complexes of xanthates with oxidizing agents, and it was of interest to prepare other complexes containing other transition metals. We report below the unexpected results obtained from the reaction of *S*-alkyl xanthates with $Co_2(CO)_8$.

Organic xanthates are easily obtained in one step from the corresponding alcohols [2], and various R^3 substituents can be introduced by quenching the dithiocarbonate with the appropriate halide. When cholestanyl or cholesteryl xanthates (Scheme 1) were allowed to react in diethyl ether at room temperature under nitrogen with a slight excess of cobalt carbonyl, purple crystalline compounds were readily formed, and isolated in 50–65% yield after chromatography on silica plates.

The complexes I (from cholestanol) and II (from cholesterol) all have the same characteristics, and their 1H NMR spectra show the same pattern indicating elimination of the R^3 group. α -Cholestanol, adamantanethanol and menthol-*S*-methyl xanthates similarly give complexes III, IV and V, respectively, with loss of the substituent on sulfur.



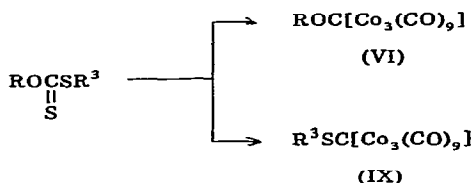
SCHEME 1. In complex VI, R correspond to the squeueleton of α - or β -cholestanol, cholesterol, adamantan-ethanol or menthol.

From microanalytical data and the mass spectra of the complexes we conclude that there is complete desulfurization, with formation of alkoxyalkylidinetricobalt nonacarbonyl clusters corresponding to formula VI.

In addition to the molecular peak, the mass spectra of complexes IV and V show successive loss of nine carbonyls, while for complexes I, II and III the fragment of highest mass was always the $[\text{R}-\text{O}]^+$ group. Infrared spectra are indicative of the carbonyl ligands (complex absorption at $2000\text{--}2100\text{ cm}^{-1}$) and the ^1H NMR spectra show an upfield shift for H(3) or H(1) (1.5 to 1.7 ppm), while the ^{13}C NMR spectra show a downfield shift (12 ppm) for C(3) (compared with that in the starting material).

Alkylalkylidinetricobalt nonacarbonyl clusters are usually prepared by the action of $\text{Co}_2(\text{CO})_8$ on trihalides RCX_3 [3], and very few alkoxy-substituted clusters like VI have been prepared. Our method provides a new and very convenient route to clusters VI, at least in cases in which the xanthate is derived from a secondary alcohol.

Intervention of the anion $^-\text{Co}(\text{CO})_4$ followed by a radical pathway has been proposed to rationalize the conversion of RCX_3 into $\text{RC}[\text{Co}_3(\text{CO})_9]$ [4]. A similar route would account for the formation of cluster VI and desulfurization by successive loss of ^-SR and $^-\text{SCo}(\text{CO})_4$ species. When *S*-methyl xanthates derived from 2,4,6-trimethylphenol (VII) and α -ferrocenylmethylcarbinol (VIII) were allowed to react as above with $\text{Co}_2(\text{CO})_8$, the major complex from VII and the only one from VIII were the cluster species $\text{CH}_3\text{SC}[\text{Co}_3(\text{CO})_9]$ (IX), which were isolated in good yield. These results argue for an elimination step and whether the cluster VI or IX is formed appears to depend on the relative strengths of the C—O or C—S bonds (Scheme 2).



SCHEME 2

The clusters I, II, III and V are optically active, and so we examined their activity as asymmetric catalysts for hydroformylation of olefins. They are very good catalysts for hydroformylation of various linear and cyclic olefins, but no asymmetric induction could be detected, which suggests that the catalytically active species may not contain the chiral entity.

Acknowledgement

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