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Preliminary communication

THE ACTION OF THIOLS AND THIOLATES ON HALOMETHYLIDYNETRICOBALT NONACARBONYLS: A MULTIPLICITY OF REACTION PATHS*

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SUMMARY

The action of alkanethiols and of lithium alkanethiolates on bromomethylidynetricobalt nonacarbonyl gave products of type $RSC(O)CCo_3(CO)_9$. This type of product also was obtained in a reaction of $LiSC_6H_5$ with the cobalt complex, but the action of an arenethiol on bromomethylidynetricobalt nonacarbonyl or on the analogous chloro compound in the presence of triethylamine gave $ArSCCo_3(CO)_9$ complexes and products of partial cluster degradation, $Co_3(CO)_4(SAr)_5$. Complexes of type $RSC(O)CCo_3(CO)_9$ decomposed when heated in refluxing benzene under nitrogen, giving decarbonylation products, $RSCCo_3(CO)_9$, in low yield.

Bromomethylidynetricobalt nonacarbonyl, Ia, reacts with alcohols (2,3), phenols (3) and amines (3) with migration of a CO ligand from cobalt to the apical carbon atom to give products, Ib and Ic, respectively, which can be regarded as formally resulting from reaction of the acylium ion $(OC)_9Co_3CCO^+$ with the nucleophilic substrate. The reactions

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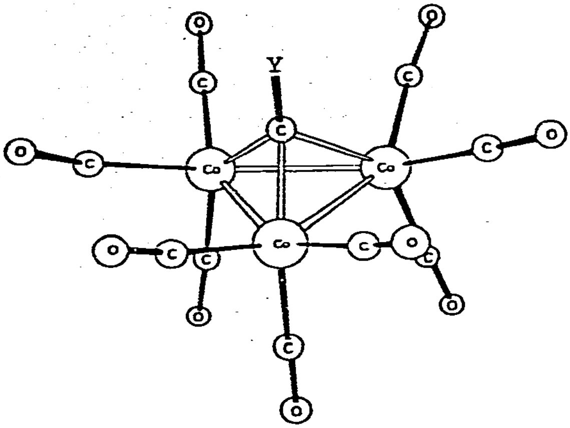
* Part 25 of the series "Organocobalt Cluster Complexes". Part 24: ref. 1.



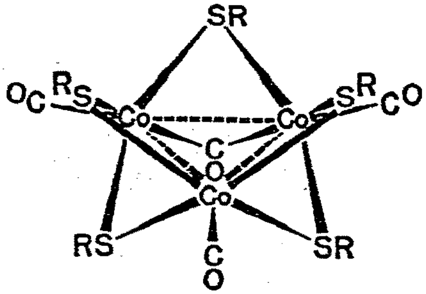
$= RCCo_3(CO)_9$

I a, Y = Br
b, Y = CO_2R
c, Y = $C(O)NR_2$
d, Y = C(O)SR
e, Y = SC_6H_5
f, Y = $SC_6H_4CH_3$-p

with alcohols and phenols are accelerated considerably when carried out in the presence of triethylamine (3). It was of interest to see if such reactions also occur with aliphatic and aromatic thiols to give products of type RSC(O)-$CCo_3(CO)_9$, Id. Such thioesters had been prepared previously in these Laboratories by reaction of the appropriate alkane- or arenethiol with the acylium ions reagents $(OC)_9Co_3CCO^+PF_6^-$ (4) or $(OC)_9Co_3CCO^+AlX_4 \cdot AlX_3^-$ (5).

The reactions of alkanethiols with $BrCCo_3(CO)_9$ in the presence of triethylamine did indeed give products of type Id. The reaction with tert-butanethiol is typical. A solution of 1.99 mmol of Ia, 4.6 mmol of Me_3CSH and 3.6 mmol of triethylamine in 40 ml of dry benzene was stirred at room temperature for 24 hr. while carbon monoxide was bubbled slowly through the solution. The reaction mixture was treated with dilute HCl and the product was isolated from the organic phase by filtration chromatography. Elution with hexane gave 0.27 g of a mixture of Ia and $HCCo_3(CO)_9$ and subsequent elution with dichloromethane resulted in isolation of $Me_3CSC(O)CCo_3(CO)_9$ (5), mp 74-75°, in 45% yield. Similar reactions with ethane- and n-butanethiol gave $C_2H_5SC(O)CCo_3(CO)_9$ (4) (44%) and n-$C_4H_9SC(O)CCo_3(CO)_9$ (33%), respectively.

In contrast to these results, benzenethiol reacted almost instantaneously with bromomethylidynetricobalt nonacarbonyl at room temperature in the presence of triethylamine and with carbon monoxide bubbling through the reaction mixture to give a mixture of $C_6H_5SCCo_3(CO)_9$, Ie, and diphenyl disulfide, as well as much tar. A more manageable reaction occurred between $ClCCo_3(CO)_9$ and benzenethiol in dichloromethane in the presence of triethylamine and under carbon monoxide. The reaction was slower (14 hr. at room temperature) and again much tar was formed. However, hexane extraction of the nonvolatiles, column chromatography and subsequent recrystallization of the hexane-soluble fraction gave $C_6H_5SCCo_3(CO)_9$, mp 55-57°, an orange-red powder, in 40% yield. (No reaction occurred in the absence of triethylamine). This is the first $(OC)_9Co_3C$ cluster complex with an organosulfur function attached directly to the apical carbon atom. Extraction of the hexane-insoluble portion of the reaction product with benzene gave a brown powder which decomposed around 230° and which was identified on the basis of its infrared spectrum as the known $Co_3(CO)_4(SC_6H_5)_5$. This compound had been prepared previously by Klumpp, Bor and Markó (6) by reaction of dicobalt octacarbonyl with diphenyl disulfide. The crystal structure of the ethylthio analog, $Co_3(CO)_4(SC_2H_5)_5$, had been determined by Wei and Dahl (7), and the cobalt-sulfur cluster II was shown to be present. The isolation of $Co_3(CO)_4(SC_6H_5)_5$ from the $ClCCo_3(CO)_9/C_6H_5SH/Et_3N$ reaction represents the first example of the interception of an intermediate in the chemical destruction of a $RCCo_3(CO)_9$ cluster complex. Usually, complete disruption of the $Co_3(CO)_9$ unit to $Co(CO)_4^-$ or wholly inorganic cobalt species occurs (8).



II

A similar reaction occured between chloromethylidynetricobalt nonacarbonyl and p-toluenethiol in the presence of triethylamine and under carbon monoxide. Column chromatography (silicic acid) gave p-$CH_3C_6H_4SCCo_3(CO)_9$, If, a brick-red solid, mp 96-97°, in 37% yield on elution with hexane, as well as $Co_3(CO)_4(SC_6H_4CH_3\text{-p})_5$, a brown powder, mp∿200° (dec), in 33% yield on elution with benzene.

The difference in the products formed in these reactions of alkanethiols and arenethiols was most intriguing, but careful reexamination of the reactions of $BrCCo_3(CO)_9$ with alkanethiols showed that $RSCCo_3(CO)_9$ and $Co_3(CO)_4(SR)_5$ type products were formed here as well. In some cases (e.g., n-C_4H_9SH) they were obtained in only trace yields, but in the $C_2H_5SH/BrCCo_3(CO)_9/Et_3N$ reaction a 10% yield of $C_2H_5SCCo_3(CO)_9$, a red-brown solid, mp 103-105° (dec), as well as a trace of $Co_3(CO)_4(SC_2H_5)_5$ were obtained.

In view of these results, the reactions of bromomethylidynetricobalt nonacarbonyl with lithium thiolates were examined since it was possible that in $ArSH/Et_3N$ systems the active reagent is the thiolate anion. Surprisingly, when a slurry of lithium benzenethiolate (via n-C_4H_9Li + C_6H_5SH) in benzene reacted with $BrCCo_3(CO)_9$ (high speed stirring at room temperature for 12 hr.), the product which was isolated in 67% yield was the initially sought $C_6H_5SC(O)CCo_3(CO)_9$ (4). When this reaction was carried out in the presence of triethylamine or in diethyl ether medium, the only sulfur-containing cobalt product was $Co_3(CO)_4(SC_6H_5)_5$. A reaction of $LiSCMe_3$ with $BrCCo_3(CO)_9$ in benzene gave $Me_3CSC(O)$-$CCo_3(CO)_9$ in 70% yield.

In a previous paper we had noted the facile thermal decarbonylation of $(OC)_9Co_3C$-substituted ketones (9). Thus it was possible that when $ArSCCo_3(CO)_9$ complexes were formed in these reactions they were not the primary products but rather that they were produced by decarbonylation of the initially formed $ArSC(O)CCo_3(CO)_9$. In an experiment in which a solution of p-$CH_3C_6H_4SC(O)CCo_3(CO)_9$ in benzene was heated at reflux under nitrogen for 2 hr. this complex decomposed completely and the decarbonylation product, If, was isolated in 14% yield. In similar fashion, $Me_3CSC(O)CCo_3(CO)_9$ was decarbonylated to $Me_3CSCCo_3(CO)_9$ (13% yield). Less severe conditions did not result in decarbonylation, and we must conclude that when $ArSCCo_3(CO)_9$ type products are formed in the $ArSH/BrCCo_3(CO)_9/Et_3N$ reactions, they are primary, not secondary, reaction products.

The mechanism of the reaction which produces the $ArSCCo_3(CO)_9$ complexes remains unknown to date. Direct nucleophilic substitution reactions of halomethylidynetricobalt nonacarbonyl complexes are extremely unlikely since the apical carbon atom is so highly hindered. For this reason, other processes, some of which may involve initial attack at cobalt, must obtain. Electron transfer mechanisms also are quite possible, and for the $ArSCCo_3(CO)_9$-forming reaction an $S_{RN}1$ mechanism (10) could be discussed. Clearly, further experimental work is required.

Other routes to the novel $RSCCo_3(CO)_9$ complexes are under investigation and will be reported in due course. All new compounds were characterized by combustion analysis and IR and NMR spectroscopy.

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