Journal of Organometallic Chemistry, 187 (1980) 91—102

ORGANOCOBALT CLUSTER COMPLEXES

XXXI *. THE REACTIONS OF BROMO- AND CHLOROMETHYLIDYNETRICOBALT NONACARBONYL WITH THIOLS AND LITHIUM THIOLATES

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(Received July 22nd, 1979)

Summary

The action of alkanethiols on bromomethylidynetricobalt nonacarbonyl in the presence of triethylamine gives thioesters, $RSC(O)CCo_3(CO)_9$, as principal products, but arenethiols react to give tars. A more useful reaction is that between arenethiols and $ClCCo_3(CO)_9$, which gives $ArSCCo_3(CO)_9$ complexes as the principal products. The action of lithium alkane- and arenethiolates on $BrCCo_3(CO)_9$ in hydrocarbon medium leads to formation of thioesters, but in the presence of triethylamine or in diethyl ether solution complexes of type $Co_3(CO)_4(SR)_5$ are formed instead. Possible mechanisms of these reactions are discussed.

Introduction

The formation of $(OC)_9Co_3C$-substituted esters and amides by the reaction of bromomethylidynetricobalt nonacarbonyl (Ia) with alcohols and with aliphatic amines (eq. 1 and 2) has been described in a previous paper of this series

$$BrCCo_3(CO)_9 \xrightarrow{ROH} \underset{(Ib)}{ROC(O)CCo_3(CO)_9} \qquad (1)$$

$$BrCCo_3(CO)_9 \xrightarrow{RR'NH} \underset{(Ic)}{RR'NC(O)CCo_3(CO)_9} \qquad (2)$$

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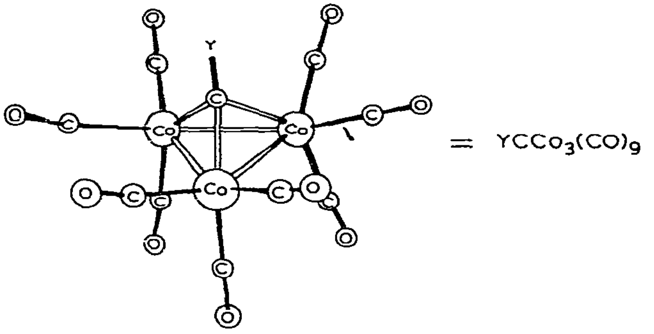
* Part XXX: ref. 1; preliminary communication: ref. 2.

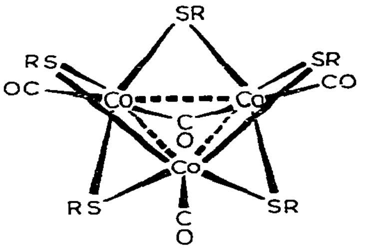
[1]. The reactions with ammonia and primary and secondary amines proceed readily at room temperature and give good product yields. The reactions with alcohols require higher temperatures but also occur readily at room temperature when an excess of triethylamine is present. Such reactions with phenols and with aniline derivatives require the presence of triethylamine when carried out at room temperature. Noteworthy was that such solvolysis of bromomethylidynetricobalt nonacarbonyl occurs with CO migration from cobalt to carbon, necessarily with subsequent replacement of the CO ligand lost from cobalt by an as yet undefined intermolecular process. These reactions occur readily under a nitrogen atmosphere in the absence of external carbon monoxide, but they proceed more rapidly and give better product yields when carbon monoxide is bubbled through the solution while the reaction is taking place.

It was of interest to see if this chemistry of bromomethylidynetricobalt nonacarbonyl could be extended to the preparation of cobalt cluster-substituted thioesters, $RSC(O)CCo_3(CO)_9$ (Id) by reaction with aliphatic and aromatic thiols. Thioesters of this type had been prepared previously by treatment of cobalt cluster acylium salts, $[OCCCo_3(CO)_9]^+ [PF_6]^-$ or $[OCCCo_3(CO)_9]^+ [AlX_4]^- \cdot AlX_3$, with various alkane- and arene-thiols [3,4].

Results and discussion

Alkanethiols react with bromomethylidynetricobalt nonacarbonyl in the presence of triethylamine to give thioesters of type Id in moderate yield. In a typical example, a solution of 4.6 mmol of t-butanethiol, 1.9 mmol of $BrCCo_3(CO)_9$ and 3.6 mmol of triethylamine in 40 ml of benzene was stirred at room temperature for one day while carbon monoxide was bubbled slowly through the solution. Hydrolysis with dilute hydrochloric acid followed by filtration chromatography gave the expected product, $(CH_3)_3CSC(O)CCo_3(CO)_9$, in 45% yield. Similar reactions were carried out with ethane- and n-butanethiol, giving $C_2H_5SC(O)CCo_3(CO)_9$ (44%) and $n\text{-}C_4H_9SC(O)CCo_3(CO)_9$ (33%), respectively. Subsequent reexamination of the $BrCCo_3(CO)_9/C_2H_5SH$ reaction in the presence of triethylamine showed that a second, minor product was present in the



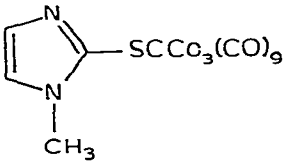


(II)

(Ia, Y = Br;
Ib, Y = ROC(O);
Ic, Y = RR′NC(O);
Id, Y = RSC(O);
Ie, Y = RS)

reaction mixture. This compound, obtained in 10% yield as a red-brown solid, was identified as the thioether, $C_2H_5SCCo_3(CO)_9$. This was a notable difference from the reactions of $BrCCo_3(CO)_9$ with alcohols and amines, in which products of type $ROCCo_3(CO)_9$ and $RR'NCCo_3(CO)_9$ did not appear to have been formed. Previously, complexes of type $RSCCo_3(CO)_9$ (Ie) had been unknown, although an oxygen analog, $CH_3OCCo_3(CO)_9$, had been prepared [5].

Reactions of bromomethylidynetricobalt nonacarbonyl with arenethiols, carried out at room temperature in the presence of triethylamine, proceeded quite differently. They occurred virtually instantaneously in the presence of triethylamine to give a green-black tar. (No reaction occurred in the absence of the amine). From the tar could be extracted low yields of thioethers, $ArSCCo_3(CO)_9$, usually contaminated with diaryl disulfides, as well as small amounts of $HCCo_3(CO)_9$. Various modifications in reaction procedures were tried in order to improve the yields. Reactions were carried out in which dichloromethane or triethylamine itself was used as reaction medium, and chloromethylidynetricobalt nonacarbonyl was used in place of the bromo derivative. With $ClCCo_3(CO)_9$ the reactions were slower and more manageable, and moderate yields of $ArSCCo_3(CO)_9$ products could be isolated. Thus in a reaction of $ClCCo_3(CO)_9$ with benzenethiol in the presence of an excess of triethylamine at room temperature $C_6H_5SCCo_3(CO)_9$, a red-orange powder, was obtained in 43% yield. In another such reaction a minor by-product was isolated as a brown powder which was identified by infrared spectroscopy as $Co_3(CO)_4(SC_6H_5)_5$, a complex which had been prepared earlier by Hungarian workers [6] by the reaction of diphenyl disulfide with dicobalt octacarbonyl. The crystal structure of the ethylthio analog, $Co_3(CO)_4(SC_2H_5)_5$, had been determined to be that shown as II by Wei and Dahl [7]. A similar reaction carried out using *p*-toluenethiol in place of benzenethiol gave $p\text{-}CH_3C_6H_4SCCo_3(CO)_9$ in 37% yield, as well as $Co_3(CO)_4(SC_6H_4CH_3\text{-}p)_5$ in 33% yield, based on *p*-toluenethiol. The isolation of $Co_3(CO)_4(SAr)_5$ complexes in these reactions is significant in that it represents the first capture of a trinuclear fragment in the chemical destruction of a $RCCo_3(CO)_9$ complex. Usually complete disruption occurs, with formation of $Co(CO)_4^-$ or of wholly inorganic cobalt species [8,9]. A reaction which proceeded particularly well was that between 2-mercapto-*N*-methylimidazole with $BrCCo_3(CO)_9$ in toluene solution in the presence of triethylamine at room temperature. A 75% yield of III was isolated in the form of brown crystals.



(III)

The known higher acidity of arenethiols (vs. alkanethiols) provided the basis for a possible explanation of the observed difference in reactivity between alkane- and arene-thiols toward bromomethylidynetricobalt nonacarbonyl in the presence of triethylamine. For instance, the pK_a of C_6H_5SH is 6.50 while that of $n\text{-}C_4H_9SH$ is 10.5 [10]. Triethylamine is known to be able to deprotonate arenethiols [11], and the arenethiolate species, ArS^-, could than attack the $BrCCo_3(CO)_9$ cluster complex (at Br or at CO) to give, ultimately, $ArSCCo_3(CO)_9$ (eq. 3). Perhaps such an anion route is not available to alkanethiols.

$$ArSH + Et_3N \rightarrow Et_3NH^+\ SAr^- \xrightarrow{BrCCo_3(CO)_9} ArSCCo_3(CO)_9 + Et_3NH^+\ Br^- \qquad (3)$$

However, if the anion mechanism were operative in the case of the $ArSH/Et_3N/BrCCo_3(CO)_9$ reactions, one might expect that pre-formed alkanethiolate anions would react with $BrCCo_3(CO)_9$ to give $RSCCo_3(CO)_9$ products, rather than the thioesters, $RSC(O)CCo_3(CO)_9$. These ideas were not confirmed by experiment. The reaction of lithium t-butanethiolate, obtained by the action of n-butyllithium on t-butanethiol, with $BrCCo_3(CO)_9$ in benzene gave $(CH_3)_3CSC(O)CCo_3(CO)_9$ in 73% yield, not the thioether $(CH_3)_3CSCCo_3(CO)_9$. Other lithium alkanethiolates reacted similarly. It also was found that lithium arenethiolates react with $BrCCo_3(CO)_9$ in benzene medium with high speed stirring to give $ArSC(O)CCo_3(CO)_9$ in good yield, rather than $ArSCCo_3(CO)_9$, (eq. 4) e.g.:

$$BrCCo_3(CO)_9 \xrightarrow[\text{benzene}]{C_6H_5SLi} C_6H_5SC(O)CCo_3(CO)_9 (62\%, \text{based on } BrCCo_3(CO)_9) \qquad (4)$$

When C_6H_5SLi and $BrCCo_3(CO)_9$ were mixed in diethyl ether medium, the reaction took a different course, giving $Co_3(CO)_4(SC_6H_5)_5$ as the only isolable product in 28% yield. This complex also was formed (in 36% yield) when the $C_6H_5SLi/BrCCo_3(CO)_9$ reaction was carried out in benzene in the presence of triethylamine. Other products formed in this reaction included $HCCo_3(CO)_9$ (26%) and a small quantity of a mixture of $C_6H_5SSC_6H_5$ and $C_6H_5SCCo_3(CO)_9$. Chloromethylidynetricobalt nonacarbonyl, which was only very poorly reactive toward C_6H_5SLi in benzene at room temperature, reacted readily in benzene in the presence of triethylamine, giving $Co_3(CO)_4(SC_6H_5)_5$ in 40% yield. This complex was obtained in even higher yield (50%) when the $C_6H_5SLi/ClCCo_3(CO)_9$ reaction was carried out in diethyl ether solution.

Although a discussion of the possible mechanisms of these reactions is speculative at this time, we suggest the following posibilities:

(1) For the formation of the $ArSCCo_3(CO)_9$ complexes, an $S_{RN}1$ mechanism [12]:

$$ArSH + Et_3N \rightarrow ArS^- + Et_3NH^+ \qquad (5)$$

$$ArS^- + ClCCo_3(CO)_9 \rightarrow ArS^{\bullet} + [ClCCo_3(CO)_9]^{\bar{\bullet}} \qquad (6)$$

$$[ClCCo_3(CO)_9]^{\bar{\bullet}} \rightarrow Cl^- + {}^{\bullet}CCo_3(CO)_9 \qquad (7)$$

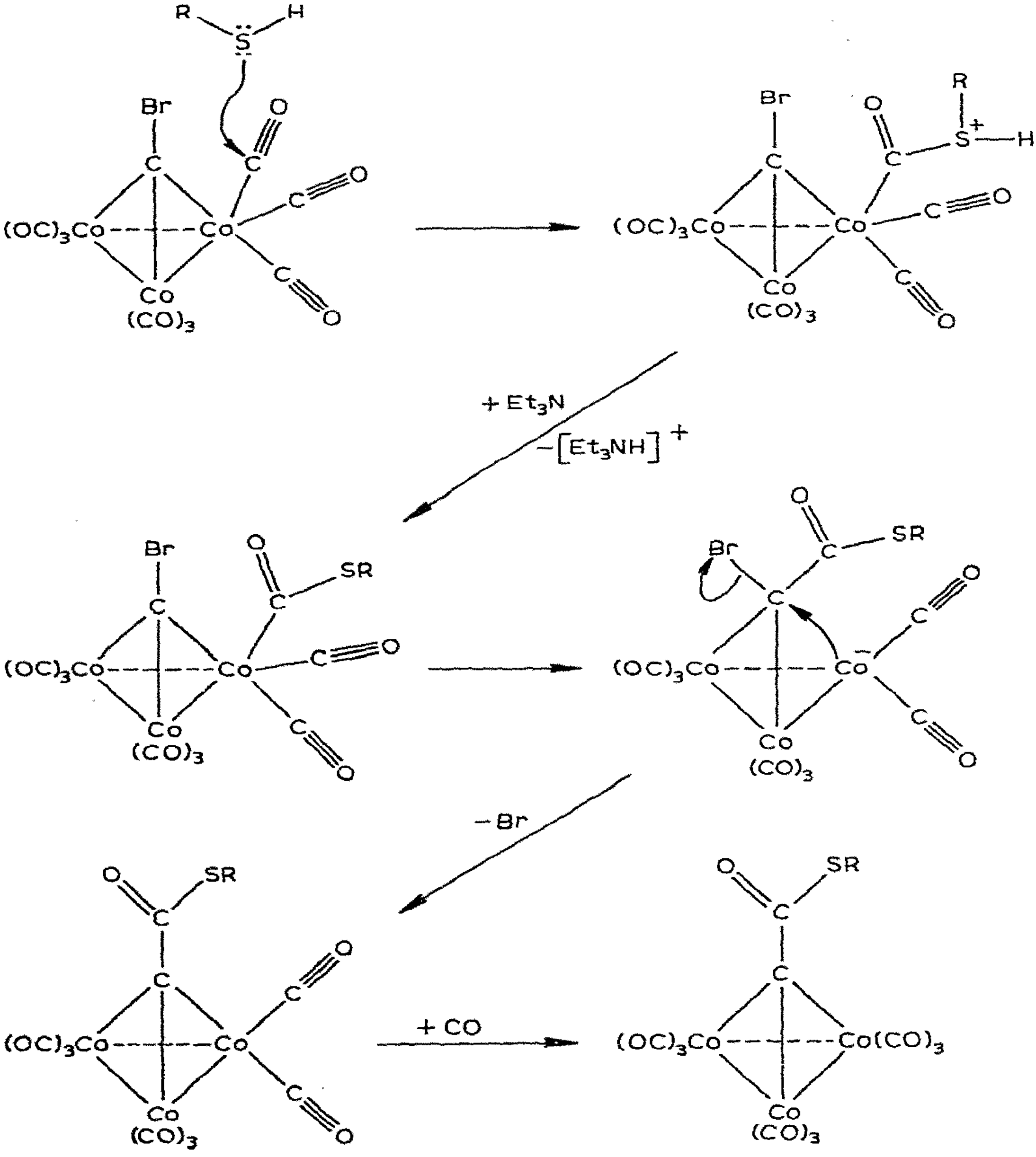
$$ArS^- + {}^{\bullet}CCo_3(CO)_9 \rightarrow [ArSCCo_3(CO)_9]^{\bar{\bullet}} \qquad (8)$$

$$[ArSCCo_3(CO)_9]^{\bar{\bullet}} + ClCCo_3(CO)_9 \rightarrow ArSCCo_3(CO)_9 + [ClCCo_3(CO)_9]^{\bar{\bullet}} \qquad (9)$$

etc.

In support of this mechanism, we note that the tricobaltcarbon nonacarbonyl radical has been implicated as an intermediate in a reaction of methylidynetricobalt nonacarbonyl [13] and that radical anions of type $[XCCo_3(CO)_9]^{\bar{\bullet}}$ have been generated chemically and electrochemically and shown to be rather stable, long-lived species [14,15]. Their intervention in these reactions could explain one observation: when triethylamine is added to a solution containing an arenethiol and $ClCCo_3(CO)_9$, the examination of the reaction mixture by thin layer chromatography (TLC) immediately after the addition had been completed showed the absence of any alkylidynetricobalt nonacarbonyl cluster complexes which can be eluted with hexane, i.e., while the starting $ClCCo_3(CO)_9$ appears

SCHEME 1.

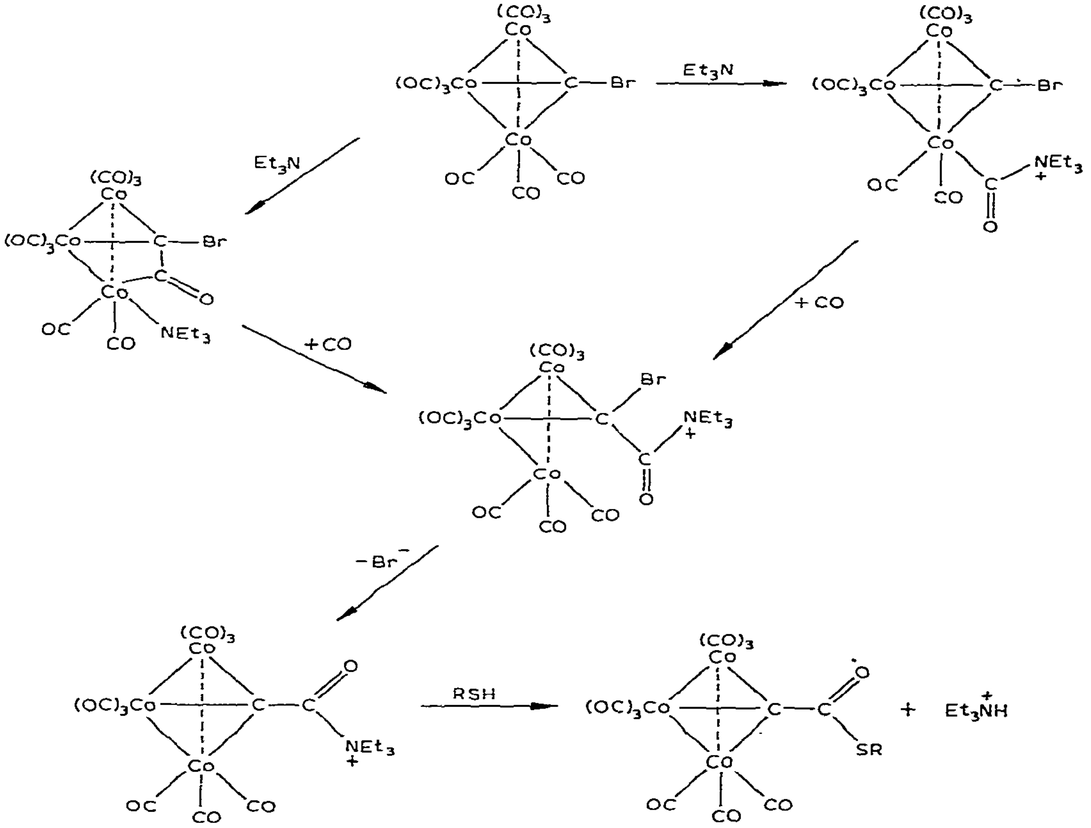


to have reacted, no $ArSCCo_3(CO)_9$ product is present. Also, standard work-up of the reaction mixture immediately after addition gives no products. Only after the solution has been stirred for some hours is the presence of a hexane-elutable product (red-brown spot) apparent, and, after a reaction time of about 18 h, a reasonable yield of $ArSCCo_3(CO)_9$ is obtained. In terms of the mechanism above, the formation of the radical anion, $[ArSCCo_3(CO)_9]^{\cdot-}$, is rapid, but its further reaction to give product is slow. The radical intermediates in this reaction sequence also would explain the observed by-products: ArSSAr ($ArS^{\cdot}$ coupling) and $HCCo_3(CO)_9$ (H atom abstraction by $^{\cdot}CCo_3(CO)_9$). Alkanethiols, being less acidic, show such chemistry to a lesser extent and react with halomethylidynetricobalt nonacarbonyl complexes by alternative pathways.

Lithium arenethiolates react with $BrCCo_3(CO)_9$ with retention of the $CCo_3(CO)_9$ cluster only in the absence of donor solvents. Hence, in their reactions with $BrCCo_3(CO)_9$ the strong cation solvation which makes radical anion formation favorable is not possible and here also an alternate route is preferred.

(2) For the formation of the $RSC(O)CCo_3(CO)_9$ complexes a more complicated mechanism in which RSH or $(RSLi)_x$ acts as a nucleophile and attacks at a coordinated carbon monoxide ligand (Scheme 1). With alkanethiols the deprotonation by triethylamine does not occur to any appreciable extent [16].

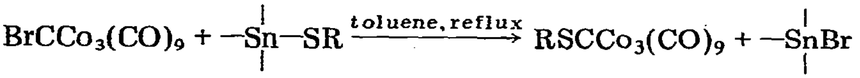
SCHEME 2



However, alkanethiols still may behave as nucleophiles, and they are better nucleophiles than arenethiols [17]. We suggest that the alkanethiol attacks a coordinated carbon monoxide ligand reversibly. In the resulting adduct, formally a protonated metal thioester, the proton is more acidic, hence more labile than in the alkanethiol, and deprotonation by triethylamine (a necessary reagent in these reactions) occurs readily. Transfer of the thioester function to the apical carbon atom, possibly with concerted loss of Br^-, follows and subsequently CO transfer to the vacant coordination site occurs. An alternate mechanism may be considered in which the triethylamine is more than a deprotonating agent (Scheme 2).

These suggested mechanisms seem reasonable, but they are speculative. However, they may serve to suggest further experiments in the development of the chemistry of these cobalt cluster complexes.

In another paper [18] we have described a useful route to $RSCCo_3(CO)_9$ and $ArSCCo_3(CO)_9$ complexes by the reaction of methyltin alkane- and arenethiolates with bromomethylidynetricobalt nonacarbonyl (eq. 10). Thus we can



$$BrCCo_3(CO)_9 + -\overset{|}{\underset{|}{Sn}}-SR \xrightarrow{toluene,\,reflux} RSCCo_3(CO)_9 + -\overset{|}{\underset{|}{Sn}}Br \qquad (10)$$

now prepare either $RSCCo_3(CO)_9$ or $RSC(O)CCo_3(CO)_9$ cluster complexes from a given thiol at will by using either the thiol or its appropriate metal derivative.

Experimental

General comments

The reactions were carried out in a three-necked round-bottomed flask of appropriate size which was equipped with a magnetic stir-bar, a nitrogen inlet tube if carried out under nitrogen or a gas dispersion tube if carbon monoxide was bubbled through the reaction mixture. When the reactions were carried out above room temperature, a reflux condenser and a thermometer were added.

The standard work-up involved pouring the reaction mixture into 100 ml of cold 10% hydrochloric acid, separating and drying the organic layer ($MgSO_4$ or Na_2SO_4), filtering and then concentrating the filtrate at reduced pressure (rotary evaporator). Column chromatography and filtration chromatography were used extensively for the separation of products. Column chromatography was performed using a 40 × 600 mm column fitted with a fritted-glass disk and a Teflon stopcock. Filtration chromatography was carried out using a 60 ml filter funnel fitted with a fritted glass disk. In general, silicic acid (Mallinckrodt reagent, 100 mesh) was used as the chromatographic support and eluents used included hexane, dichloromethane, benzene and diethyl ether. Thin layer chromatography (TLC) served well for monitoring the progress of reactions (Eastman Chromagram Sheet 6060). The intense colors of the alkylidynetricobalt nonacarbonyl complexes made chemical visualization unnecessary. Solid samples in general were further purified by sublimation (50—60°C at 0.02—0.07 mmHg) or by recrystallization.

Infrared spectra were recorded using a Perkin—Elmer model 457A infrared spectrophotometer. The characteristic stretching frequencies in the 2200—2000 cm^{-1} region of the terminal CO ligands always are much more intense than the rest of the bands in the spectrum. Therefore, the sample was diluted after the initial spectrum was recorded, so that an accurate spectrum of these frequencies could be recorded. In general, spectra were taken using 0.1 mm sodium chloride cells. Proton NMR spectra were recorded using a Varian Associates T60 spectrometer. Chemical shifts are given in δ units, ppm downfield from internal tetramethylsilane.

Dicobalt octacarbonyl was purchased from Strem Chemicals, Inc. and its reactions with carbon tetrabromide and carbon tetrachloride gave $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ [5]. The alkane- and arene-thiols were commercial products.

Reaction of bromomethylidynetricobalt nonacarbonyl with alkanethiols

The standard apparatus was charged with 1.00 g (1.9 mmol) of the cobalt complex, 0.5 ml (4.7 mmol) of n-butanethiol, 0.5 ml (3.6 mmol) of triethylamine and 40 ml of benzene. The mixture was stirred at room temperature for 24 h while carbon monoxide was bubbled slowly through it. Standard work-up was followed by filtration chromatography. Hexane eluted a trace of a red-orange material which was not identified due to lack of substance. Dichloromethane eluted n-$C_4H_9SC(O)CCo_3(CO)_9$ which was purified by sublimation at 50° C in vacuo to give 0.35 g (33%), m.p. 52—53° C.

The identical procedure using t-butanethiol (same scale) gave t-$C_4H_9SC(O)CCo_3(CO)_9$, m.p. 74—75° C (lit. [4] m.p. 74—75° C), in 45% yield.

A similar reaction was carried out with ethanethiol (same scale). The reaction mixture was poured into 100 ml of water and the material dissolved in the organic layer was chromatographed on a silicic acid column. Hexane eluted a red band which yielded 0.1 g (0.2 mmol, 10%) of a red-brown solid, m.p. 113—115° C (dec.) which was identified as $C_2H_5SCCo_3(CO)_9$. Further elution with copious amounts of hexane gave a trace amount of material which was identified as $Co_3(CO)_4(SC_2H_5)_5$ on the basis of its IR spectrum [6]. Finally, benzene eluted a purple-brown band which yielded, after sublimation at 40° C and 0.01 mmHg, 0.20 g (0.4 mmol, 19%) of $C_2H_5SC(O)CCo_3(CO)_9$, m.p. 61—62° (lit. [3] m.p. 61—62° C), whose IR spectrum was identical to that of an authentic sample [19]. In another reaction carried out on the same scale in essentially the same manner filtration chromatography of the reaction products using dichloromethane as eluent followed by sublimation of the solid thus obtained gave $C_2H_5SC(O)CCo_3(CO)_9$ in 44% yield.

Reaction of bromomethylidynetricobalt nonacarbonyl with lithium alkanethiolates

A 300 ml, three-necked flask equipped with a gas inlet tube, a gas outlet tube to a Nujol bubbler, a pressure-equalizing addition funnel and a magnetic stir-bar was flushed with carbon monoxide and charged with 1.00 g (1.92 mmol) of $BrCCo_3(CO)_9$ and 100 ml of dry benzene. The addition funnel was charged with 0.49 ml (4.4 mmol) of t-butanethiol and 50 ml of benzene. The lithium t-butanethiolate was formed by addition of 1.8 ml of 2.37 *M* (4.3 mmol) of n-butyllithium in hexane (Alfa/Ventron) to the solution in the addition funnel. The latter became cloudy, but no precipitate formed.

The $(CH_3)_3CSLi$ solution then was added with stirring to the $BrCCo_3(CO)_9$

during a period of 15 min under an atmosphere of carbon monoxide. The progress of the reaction was monitored by TLC; it was allowed to proceed until the starting cluster had been consumed, which took about 2 h. Standard workup was followed by column chromatography (silicic acid). Hexane eluted a trace of $BrCCo_3(CO)_9$. Benzene eluted a dark brown band from which was obtained, after sublimation, 0.8 g (1.4 mmol), 73% yield) of $(CH_3)_3CSC(O)CCo_3(CO)_9$, m.p. 74—75°C.

Similar reactions between $BrCCo_3(CO)_9$ and lithium alkanethiolates gave n-$C_4H_9SC(O)CCo_3(CO)_9$ and $(CH_3)_2CHSC(O)CCo_3(CO)_9$.

Reaction of chloromethylidynetricobalt nonacarbonyl with arenethiols

The standard apparatus was flushed with carbon monoxide and charged with 1.14 g (2.4 mmol) of $ClCCo_3(CO)_9$, 0.75 ml (5 mmol) of benzenethiol and 50 ml of dichloromethane. The mixture was stirred to effect solution while carbon monoxide was bubbled through it. Then 5.0 ml (36 mmol) of triethylamine was added by syringe. After the addition had been completed, TLC indicated no compounds which moved in hexane were present. The reaction mixture was stirred at room temperature in a stream of carbon monoxide for 18 h. At the end of this time TLC indicated the presence of a new product, which moved in hexane, as a red-brown spot.

The reaction mixture was poured in 100 ml of water. The organic layer was washed with two 100 ml portions of water, dried over $MgSO_4$ and evaporated at reduced pressure. The residue was chromatographed on a silicic acid column. Hexane eluted a red-brown band which yielded 0.50 g (0.91 mmol, 43%) of $C_6H_5SCCo_3(CO)_9$, m.p. 56—57°C.

When an identical reaction was attempted, but with hydrolysis immediately following the addition of triethylamine, no products were isolated.

A reaction of $ClCCo_3(CO)_9$ (2.4 mmol) with *p*-toluenethiol (5.0 mmol) in the presence of triethylamine (5.0 ml) in 50 ml of dichloromethane (18 h, at room temperature under a stream of CO) gave 0.5 g (0.89 mmol, 37%) of *p*-$CH_3C_6H_4SCCo_3(CO)_9$, a brown-red solid, m.p. 96—97°C. This product was eluted from the silicic acid column by hexane; benzene eluted a brown oil. Extraction of the latter with pentane and cooling the pentane solution to —30°C gave 0.3 g of brown powder, m.p. ca. 200°C (dec), which was identified by comparison of its IR spectrum with that of the C_6H_5SH-derived compound [6] as $Co_3(CO)_4(SC_6H_4CH_3\text{-}p)_5$; the yield was 0.33 mmol (33% based on *p*-$CH_3C_6H_4SH$). IR ($CHCl_3$): 2945w, 2950w, 2920m, 2050(sh), 2010vs. (terminal CO), 1825s (bridging CO), 1480m and 1300w cm^{-1}.

The reaction between 1.9 mmol of $BrCCo_3(CO)_9$ and 5.0 mmol of *p*-toluenethiol in the presence of 10 ml of triethylamine in 20 ml of dichloromethane at room temperature was virtually instantaneous and gave a tarry product. The latter was extracted with hexane. Column chromatography of the hexane extracts, hexane eluent, gave first a small quantity of $HCCo_3(CO)_9$ (by IR), then a bright red-orange band from which was obtained 0.20 g (19%) of *p*-$CH_3C_6H_4SCCo_3(CO)_9$.

Reaction of bromomethylidynetricobalt nonacarbonyl with 2-mercapto-N-methylimidazole

The standard apparatus was flushed with carbon monoxide and charged with

1.00 g (1.92 mmol) of the cobalt complex in 50 ml of toluene. Carbon monoxide was bubbled through this solution for 10 min and then 0.46 g (4.0 mmol) of 2-mercapto-*N*-methylimidazole was added. Subsequently, 5.0 ml of triethylamine was added and the mixture was stirred at room temperature with carbon monoxide bubbling through it for 18 h. After the solvent had been removed at reduced pressure, the residue was chromatographed on a silicic acid column. Pentane eluted a faint purple band which was discarded. Elution with benzene removed a brown band which yielded, after recrystallization from hexane, 0.80 g (1.44 mmol, 75% yield) of *N*-methylimidazole-2-thiomethylidynetricobalt nonacarbonyl as brown prisms, m.p. 140° C (dec.). The mass spectrum (70 eV) showed the molecular ion at *m/e* 554 and major fragment ions corresponding to the successive loss of the nine CO ligands at *m/e* 526, 498, 470, 442, 414, 386, 358, 330 and 302, as well as the $[M - 9\ CO - C_2H_2]^+$ fragment.

Reaction of bromomethylidynetricobalt nonacarbonyl with lithium arenethiolates

A 200 ml three-necked Morton (creased) flask equipped with a carbon monoxide inlet tube, a gas outlet tube leading to a Nujol bubbler and a high speed stirring apparatus (Labline Catalog No. 1280) was flushed with carbon monoxide and charged with 0.43 ml (4.2 mmol) of benzenethiol in 100 ml of dry benzene. Then 1.8 ml of 2.37 *M* n-butyllithium in hexane (4.3 mmol) was added. A white precipitate of lithium benzenethiolate formed immediately. To this slurry was added 1.0 g (1.92 mmol) of $BrCCo_3(CO)_9$ and the mixture was stirred at high speed at room temperature in a stream of carbon monoxide for 12 h. The reaction mixture subsequently was poured into 100 ml of water and the organic layer was washed with two 100 ml portions of water, dried and evaporated at reduced pressure. The residue was chromatographed on a silicic acid column. Elution with hexane gave trace amounts of a purple and a red band. Elution with benzene yielded, after recrystallization from hexane, 0.67 g (1.2 mmol, 62%) of $C_6H_5SC(O)CCo_3(CO)_9$, m.p. 91—92° C (dec.) (lit. [3] m.p. 91.5—92.5° C), whose spectral data were in agreement with those reported.

Similar reactions with the appropriate lithium arenethiolates gave *p*-$CH_3C_6H_4SC(O)CCo_3(CO)_9$ [4], *p*-$CH_3OC_6H_4SC(O)CCo_3(CO)_9$, *p*-$ClC_6H_4SC(O)CCo_3(CO)_9$ and *p*-$FC_6H_4SC(O)CCo_3(CO)_9$.

A similar reaction of $BrCCo_3(CO)_9$ (1.92 mmol) and C_6H_5SLi (4.2 mmol) in benzene carried out in the presence of 0.5 ml of triethylamine (10 h at room temperature under CO) was worked up in the same way. Chromatography of the reaction residue on silicic acid with hexane gave first a purple band which yielded 0.22 g (0.5 mmol, 26% yield) of $HCCo_3(CO)_9$ (by IR) and, upon further elution, 0.1 g of a red solid whose IR spectrum indicated it to be a mixture of diphenyl disulfide and $C_6H_5SCCo_3(CO)_9$. Elution with benzene yielded 0.25 g (0.3 mmol, 36% based on C_6H_5SH) of brown powder which was identified as $Co_3(CO)_4(SC_6H_5)_5$ by comparison of its IR spectrum with that of an authentic sample prepared by the method of Klumpp et al. [6].

A reaction of 1.92 mmol of $BrCCo_3(CO)_9$ and 4.3 mml of C_6H_5SLi in 100 ml of diethyl ether was carried out using the same procedure. TLC showed that no $BrCCo_3(CO)_9$ was present after the addition had been completed. After hydrolysis with 100 ml of 10% hydrochloric acid the organic layer was separated and evaporated. The residue was chromatographed on a silicic acid column. Benzene eluted 0.2 g (28% based on C_6H_5SH) of $Co_3(CO)_4(SC_6H_5)_5$.

Reaction of chloromethylidynetricobalt nonacarbonyl with lithium benzenethiolate

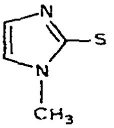
A reaction of 2.1 mmol of $ClCCo_3(CO)_9$ with 4.2 mmol of C_6H_5SLi in benzene (high speed stirring) at room temperature for 15 h gave a 56% recovery of the starting cobalt complex and only a trace of $C_6H_5SC(O)CCo_3(CO)_9$. Reactions carried out in benzene in the presence of triethylamine (as with $BrCCo_3(CO)_9$) or in diethyl ether gave $Co_3(CO)_4(SC_6H_5)_5$ as major product, in yields of 40 and 50%, respectively, based on benzenethiol. In the reaction carried out in the presence of triethylamine $HCCo_3(CO)_9$ was a by-product.

Decarbonylation of p-$CH_3C_6H_4SC(O)CCo_3(CO)_9$

The possibility was considered that the formation of $ArSCCo_3(CO)_9$-type products in the $ClCCo_3(CO)_9$/ArSH/Et_3N reactions was due to decarbonylation

TABLE 1

NEW SULFUR-SUBSTITUTED METHYLIDYNETRICOBALT NONACARBONYL COMPLEXES [a]

R in $RCCo_3(CO)_9$	M.p. (°C)	Analysis (Found (calcd.)) (%)		IR ($CHCl_3$) ν(C=O) (cm^{-1})	NMR ($CDCl_3$) (ppm)
		C	H		
C_2H_5S	113—115	28.78 (28.71)	1.12 (1.00)		1.21 (t, J 7 Hz, 3 H, CH_3) 3.20 (q, J 7 Hz, 2 H, CH_2)
C_6H_5S	55—57	35.02 (34.93)	0.98 (0.92)		7.45 (broad) [b]
p-$CH_3C_6H_4S$	96—97	36.27 (36.19)	1.28 (1.25)		2.48 (s, 3 H, CH_3) [b] 7.08—7.52 (AB m, 4 H, Ph)
	140 (dec.)	30.28 (30.34)	1.03 (0.91)		3.58 (s, 3 H, CH_3) 6.83 and 7.70 (two m, =CH)
n-$C_4H_9SC(O)$	52—53	32.50 (32.28)	1.68 (1.63)	1630	0.87—1.83 (m, 7 H) [a] 3.07 (t, J 7 Hz, 3 H, CH_3)
p-$CH_3OC_6H_4SC(O)$	109.5—110	35.57 (35.55)	1.36 (1.16)	1663	3.25 (s, 3 H, OCH_3) 6.2—7.0 (m, 4 H, Ph)
p-$ClC_6H_4SC(O)$	98—99	33.19 (33.34)	0.74 (0.65)	1672	6.2—7.0 (m, 4 H, Ph)
p-$FC_6H_4SC(O)$	101—102	34.37 (34.26)	0.93 (0.68)	1670	6.2—7.1 (m, 4 H, Ph)
$(CH_3)_2CHSC(O)$	69—70.5	31.01 (30.91)	1.38 (1.30)	1630	2.5 (d, J 6 Hz, 3 H, CH_3) 3.95 (m, 1 H, $Me_2C\underline{H}$)

[a] These complexes all showed the band pattern characteristic of the $CCo_3(CO)_9$ cluster in the terminal carbonyl region of their IR spectra (ca. 2100m, 2065vs, 2050s, 2015(sh), 1985w cm^{-1}. [b] In CCl_4 solution.

of initially formed $ArSC(O)CCo_3(CO)_9$. (Note the facile decarbonylation of ketones of type $ArC(O)CCo_3(CO)_9$ [20]).

A solution of 0.59 g (1.0 mmol) of p-$CH_3C_6H_4SC(O)CCo_3(CO)_9$ in 40 ml of benzene was stirred and heated at reflux under nitrogen for 2 h. At the end of this time TLC showed a red-orange spot of high R_f. The reaction mixture was cooled to room temperature and the solvent removed at reduced pressure. The residue was taken up in hexane and subsequent filtration chromatography (hexane eluent) yielded 0.08 g (14%) of p-$CH_3C_6H_4SCCo_3(CO)_9$ whose IR spectrum was identical to that of an authentic sample.

A similar decomposition study was made with $Me_3CSC(O)CCo_3(CO)_9$. After this complex had been heated in refluxing benzene under nitrogen for 2 h, TLC showed a red spot of high R_f, no starting thioester and decomposition products of 0 R_f. Filtration chromatography (hexane) followed by recrystallization from hexane gave 0.10 g (13% yield) of $Me_3CSCCo_3(CO)_9$, m.p. 63—64°C (dec.) as an orange-red powder: lit. [18] m.p. 63—64°C (dec.).

On the basis of these results it is considered unlikely that the $RSCCo_3(CO)_9$ products formed in the $ArSH/XCCo_3(CO)_9/Et_3N$ reactions were formed by a decarbonylation process.

New compounds

New compounds prepared during the course of this study are listed in Table 1 together with their characterizing data.

Acknowledgment

The authors are grateful to the National Science Foundation for support of this research.

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