THE PREPARATION OF FUNCTIONAL ALKYLIDYNETRICOBALT NONACARBONYL COMPLEXES FROM DICOBALT OCTACARBONYL*

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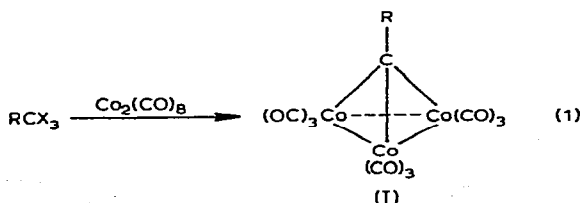
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SUMMARY

Various functionally-substituted methylidynetricobalt nonacarbonyl deri-vatives, $RCCo_3(CO)_9$, where R is D, Me_3Si, $PhMe_2Si$, $(MeO)_2P(O)$, $(EtO)_2P(O)$, $Me_3COC(O)$, $Me_3SiOC(O)$, $Et_2NC(O)$, $CH_3C(O)$, $C_2H_5C(O)$, $n-C_3H_7C(O)$, $Me_2CHC(O)$, $n-C_4H_9C(O)$, $Me_3C(O)$, $PhC(O)$, $p-CH_3C_6H_4C(O)$, $p-BrC_6H_4C(O)$, $HOCH_2$, $HC(O)$, CH_3O and Me_2N, have been prepared by reaction of dicobalt octacarbonyl with the appropriate RCX_3 or $RCHX_2$ (X=Cl or Br) compound.

INTRODUCTION

The most generally applicable synthesis of alkylidynetricobalt nonacarbonyl complexes (I) uses the reaction of dicobalt octacarbonyl with an organic trihalide [eqn. (1)][8]. We and others have developed procedures for the alkylation or arylation of already intact CCo_3 cluster complexes[2,3,7,9], or for their further elaboration[3,6],

$$RCX_3 \xrightarrow{\ Co_2(CO)_8\ } \quad (OC)_3Co \underset{\underset{(CO)_3}{Co}}{\overset{\overset{R}{\underset{|}{C}}}{\diagup\diagdown}} Co(CO)_3 \qquad (1)$$

(I)

but functionally substituted alkylidynetricobalt nonacarbonyl compounds remain few in number. In this paper we describe a number of new functional $RCCo_3(CO)_9$ complexes, prepared by the $RCX_3/Co_2(CO)_8$ reaction. More of interest, we point out the applicability of some $RCHX_2$ compounds as starting materials in such syntheses.

RESULTS AND DISCUSSION

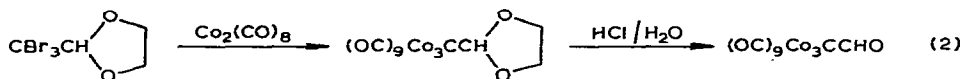A repetition of the previously described preparations of $CH_3CCo_3(CO)_9$ and

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PhCCo$_3$(CO)$_9$ by reaction of dicobalt octacarbonyl with CH$_3$CCl$_3$ and PhCCl$_3$, respectively, using varying reaction conditions established that the optimum molar ratio of Co$_2$(CO)$_8$ to RCX$_3$ was 9/5. This ratio was used throughout the investigation.

Carbonyl-substituted cluster complexes of type (OC)$_9$Co$_3$CC(O)Z became of interest to us as our research in this area progressed. At the time we began our work, esters of type (OC)$_9$Co$_3$CCO$_2$R(R=Me, Et) had been prepared[9] and the acid, (OC)$_9$Co$_3$CCO$_2$H, had been claimed but not characterized or described in any way[10]. Unknown, for instance, were the alcohol (OC)$_9$Co$_3$CCH$_2$OH, the aldehyde (OC)$_9$Co$_3$-CCHO, ketones (OC)$_9$Co$_3$CC(O)R, and amides (OC)$_9$Co$_3$CC(O)NR$_2$, to name just a few simple derivatives*.

Our procedure was refined in the preparation of the known[8] (OC)$_9$Co$_3$CCO$_2$-Et and then extended to the preparation of (OC)$_9$Co$_3$CCO$_2$CMe$_3$ from CCl$_3$CO$_2$-CMe$_3$ and (OC)$_9$Co$_3$CCO$_2$SiMe$_3$ from the hydrolytically sensitive CCl$_3$CO$_2$SiMe$_3$. The yield of the silyl ester was 38%, but that of the tert-butyl ester was only 4%. N,N-Diethyltrichloroacetamide reacted with dicobalt octacarbonyl in THF to give (OC)$_9$Co$_3$CC(O)NEt$_2$ in 19% yield. In our hands, reaction of Co$_2$(CO)$_8$ with tri-chloroacetyl chloride, trichloroacetic anhydride or trichloroacetic acid in THF did not give the expected CCo$_3$(CO)$_9$ derivatives.

A number of 1,1,1-trichloromethyl ketones reacted well with dicobalt octa-carbonyl in THF to give the expected (OC)$_9$Co$_3$CC(O)R ketones in good yield (Table 1), but the reaction of hexachloroacetone with dicobalt octacarbonyl did not result in either of the expected ketones, (OC)$_9$Co$_3$CC(O)CCl$_3$ or [(OC)$_9$Co$_3$C]$_2$CO. Chloral also reacted vigorously with dicobalt octacarbonyl, but none of the aldehyde, (OC)$_9$Co$_3$CCHO, could be isolated from the reaction mixture. This aldehyde could, however, be prepared in very low yield by the reaction of an appropriate acetal with dicobalt octacarbonyl, followed by hydrolysis [eqn. (2)]. The alcohol, (OC)$_9$Co$_3$-CCH$_2$OH, was a by-product. The latter had been sought in vain by previous workers[12]

$$\text{CBr}_3\text{CH} \underset{\text{O}}{\overset{\text{O}}{\diagdown}} \xrightarrow{\text{Co}_2\text{(CO)}_8} \text{(OC)}_9\text{Co}_3\text{CCH} \underset{\text{O}}{\overset{\text{O}}{\diagdown}} \xrightarrow{\text{HCl/H}_2\text{O}} \text{(OC)}_9\text{Co}_3\text{CCHO} \qquad (2)$$

who had found that reaction of CCl$_3$CH$_2$OH or CBr$_3$CH$_2$OH with dicobalt octa-carbonyl gave the reduced product, CH$_3$CCo$_3$(CO)$_9$, instead. Such reduction ap-peared to be a general phenomenon since analogous reactions with appropriate halogenated alcohols which should have given (OC)$_9$Co$_3$CC(Me)OH and (OC)$_9$Co$_3$-CCMe$_2$OH resulted in formation of (OC)$_9$Co$_3$CC$_2$H$_5$ and (OC)$_9$Co$_3$CCHMe$_2$, respectively**.

In our hands, 2,2,2-trichloroethanol did react with dicobalt octacarbonyl in THF at 55° to give (OC)$_9$Co$_3$CCH$_2$OH, but its yield was only 0.8%. A better (but still low) yield of 4% of this compound was obtained by allowing dicobalt octacarbo-nyl to react with the silyl-protected alcohol derivative, CCl$_3$CH$_2$OSiMe$_3$, in place of the free alcohol and hydrolyzing the reaction mixture. A similar procedure with CBr$_3$CH$_2$OSiMe$_3$ gave (OC)$_9$Co$_3$CCH$_2$OH in 5% yield. The use of temperatures

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* A patent[11] had claimed such compounds without further specification, and in the complete absence of any kind of supporting data, we can only regard this claim as questionable.

** Although this novel reduction was recommended[12] as a synthesis of alkylidynetricobalt nonacar-bonyls, the yields were too low (3–9%) to make this route at all attractive.

TABLE 1

PREPARATION OF ALKYLIDYNETRICOBALT NONACARBONYL COMPOUNDS FROM DICOBALT OCTACARBONYL[a]

| Starting halide	Product (% yield)	M.p. (°C)
CCl_4[b]	$ClCCo_3(CO)_9$ (46)	131–133
CBr_4[c]	$BrCCo_3(CO)_9$ (43)	131–133 (dec.)
CI_4	$ICCo_3(CO)_9$ (5)	97–99 (dec.)
CI_4 (in CCl_4)	$\begin{cases} ICCo_3(CO)_9 \text{ (9 parts)} \\ ClCCo_3(CO)_9 \text{ (1 part)} \end{cases}$ (17)	
$CHBr_3$	$HCCo_3(CO)_9$ (34)	105–107 (dec.)
$CDBr_3$	$DCCo_3(CO)_9$ (27)	105–107 (dec.)
CH_3CCl_3	$CH_3CCo_3(CO)_9$ (43)	183–184
$C_6H_5CCl_3$	$C_6H_5CCo_3(CO)_9$ (29)	105–107
$C_6H_5CHCl_2$	$C_6H_5CCo_3(CO)_9$ (34)	
Me_3SiCCl_3	$Me_3SiCCo_3(CO)_9$ (41)	Dec. without melting
$PhMe_2SiCCl_3$	$PhMe_2SiCCo_3(CO)_9$ (50)	75
Me_3SiCBr_3	$Me_3SiCCo_3(CO)_9$ (6)	
$CCl_3P(O)(OMe)_2$	$(MeO)_2P(O)CCo_3(CO)_9$ (27)[e]	128 (dec.)
$CCl_3P(O)(OEt)_2$	$(EtO)_2P(O)CCo_3(CO)_9$ (42)[e]	81–82
$CCl_3CO_2C_2H_5$	$(OC)_9Co_3CCO_2C_2H_5$ (53)	45–46
$CCl_3CO_2CMe_3$	$(OC)_9Co_3CCO_2CMe_3$ (4)	48–49
$CCl_3CO_2SiMe_3$	$(OC)_9Co_3CCO_2SiMe_3$ (38)	60–62
CCl_3CONEt_2	$(OC)_9Co_3CCONEt_2$ (19)	58–60
CH_3COCCl_3	$CH_3COCCo_3(CO)_9$ (40)	Dec. without melting
$C_2H_5COCCl_3$	$C_2H_5COCCo_3(CO)_9$ (40)	74 (dec.)
$n\text{-}C_3H_7COCCl_3$	$n\text{-}C_3H_7COCCo_3(CO)_9$ (49)	51–52
$Me_2CHCOCCl_3$	$Me_2CHCOCCo_3(CO)_9$ (37)	150–153 (dec.)
$n\text{-}C_4H_9COCCl_3$	$n\text{-}C_4H_9COCCo_3(CO)_9$ (53)[e]	56–57
$Me_3CCOCCl_3$	$Me_3CCOCCo_3(CO)_9$ (24)	155–157 (dec.)
$PhCOCCl_3$	$PhCOCCo_3(CO)_9$ (33)	68–69
$p\text{-}BrC_6H_4COCCl_3$	$p\text{-}BrC_6H_4COCCo_3(CO)_9$ (32)	106–108 (dec.)
$p\text{-}MeC_6H_4COCCl_3$	$p\text{-}MeC_6H_4COCCo_3(CO)_9$ (41)	64–65
CCl_3CH_2OH	$(OC)_9Co_3CCH_2OH$ (0.8)	155–156
$CCl_3CH_2OSiMe_3$[d]	$(OC)_9Co_3CCH_2OH$ (4)	
$CBr_3CH_2OSiMe_3$[d]	$(OC)_9Co_3CCH_2OH$ (5)	
$CBr_3CH{\overbrace{}\atop}^{O}_{O}$[d]	$\begin{cases} (OC)_9Co_3CCHO \text{ (3)} \\ (OC)_9Co_3CCH_2OH \text{ (2)} \end{cases}$	Dec. ca. 130° without melting
CH_3OCHCl_2	$CH_3OCCo_3(CO)_9$ (27)	172–173 (dec.)
$[ClCH=N^+Me_2]Cl^-$	$Me_2NCCo_3(CO)_9$ (26)[e]	

[a] Reactions in THF solution unless otherwise indicated. [b] Carbon tetrachloride used as solvent. [c] Benzene used a solvent. [d] Reaction mixture was hydrolyzed to obtain the products indicated. [e] Air-unstable.

higher than 50–55° resulted in lower yields of the hydroxymethyl derivative and in formation of some of the reduced complex, $(OC)_9Co_3CCH_3$.

Methylidynetricobalt nonacarbonyl complexes with organometallic or organometalloidal functions at the apical carbon atom also were sought. In previous studies, we had found that phenyl(trichloromethyl)mercury reacts with dicobalt octacarbonyl in THF not to give $PhHgCCo_3(CO)_9$, but rather $PhHgCo(CO)_4$ and CCl_3^- in the first step[13]. The ultimate products after several further steps were Hg-

$[Co(CO)_4]_2$, $CHCl_3$, benzophenone, and carbon monoxide. The reaction of some of the chloroform produced with dicobalt octacarbonyl gave chloromethylidynetricobalt nonacarbonyl as a minor by-product. Trimethyl(trichloromethyl)tin was found to react with dicobalt octacarbonyl in similar fashion. The expected Me_3Sn-$CCo_3(CO)_9$ was not formed. Instead, the $Co(CO)_4^-$ anion formed by the action of the THF solvent on $Co_2(CO)_8$ displaced the CCl_3^- anion from tin, giving $Me_3SnCo(CO)_4$, which could be isolated. The major cobalt carbonyl product was $Co_4(CO)_{12}$ (33%), and a small amount of $ClCCo_3(CO)_9$ was formed as well. Trimethyl(trichloromethyl)-silane, on the other hand, did react with dicobalt octacarbonyl to give the CCo_3 cluster complex, $Me_3SiCCo_3(CO)_9$ in 41% yield, and $PhMe_2SiCCo_3(CO)_9$ was prepared in 50% yield by a similar reaction with $PhMe_2SiCCl_3$. Esters of trichloromethylphosphonic acid also reacted with dicobalt octacarbonyl, giving $(OC)_9Co_3$-$CP(O)(OR)_2$ esters (R = Me and Et), which, however, were not air-stable, in contrast to most derivatives of methylidynetricobalt nonacarbonyl.

A most intriguing preparation of $ClCCo_3(CO)_9$ is that based on the reaction of the cobalt tetracarbonyl anion with chloroform [eqn. (3)][14].

$$Co(CO)_4^- + CHCl_3 \xrightarrow{\text{THF}} \underset{(20\%)}{ClCCo_3(CO)_9} + \underset{(trace)}{HCCo_3(CO)_9} \tag{3}$$
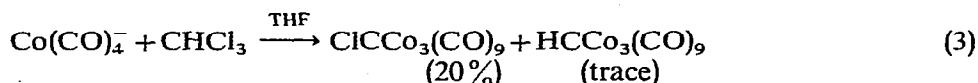
Since some RCX_3 compounds of interest in $RCCo_3(CO)_9$ synthesis are not readily available, this raises the possibility that the respective $RCHX_2$ compounds, if available, might serve in their place. We have found that this is the case, with limitations, and have used this change in the standard $RCX_3/Co_2(CO)_8$ procedure to good advantage. Benzal chloride reacted with dicobalt octacarbonyl in THF to give $PhCCo_3(CO)_9$ in 34% yield. Of greater interest was the synthesis of the as yet unknown functional cluster derivatives $CH_3OCCo_3(CO)_9$ (27% yield) and $Me_2NCCo_3(CO)_9$ (26% yield) by the reactions of dicobalt octacarbonyl with CH_3OCHCl_2 and $[CHCl=NMe_2]^+$-Cl^-, respectively. The dimethylamino-substituted cluster could be protonated with hexafluorophosphoric acid to give the isolable $[Me_2NHCCo_3(CO)_9]^+PF_6^-$, but it resisted attempted alkylation with trialkyloxonium salts*. Such syntheses appear to be restricted to the more reactive *gem*-dihalo compounds. Methyl dichloroacetate, 1,1-dichloroethane and trimethyl(dibromomethyl)silane did not react with dicobalt octacarbonyl even after prolonged heating. α,α-Dichloroacetophenone, ethyl dibromoacetate and dichloromethyl acetate[15] did react with dicobalt octacarbonyl, but no CCo_3 cluster products could be isolated from their reaction mixtures. Nevertheless, the $RCHCl_2$-based route should be of general value in the synthesis of alkoxymethylidyne- and aminomethylidynetricobalt nonacarbonyls since the required organic starting materials are readily available from esters and amides of formic acid.

In conclusion, we note that the interesting question concerning the mechanism of the reactions of RCX_3 and $RCHX_2$ compounds with dicobalt octacarbonyl remains unanswered. Various suggestions have been made[8,16], but direct experimental proof is lacking. The yields of $RCX_3/Co_2(CO)_8$ reactions in general are not high (up to 50% when the reactions proceed well), and a detailed knowledge of their

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* The chemistry of $CH_3OCCo_3(CO)_9$ and $Me_2NCCo_3(CO)_9$, as well as of higher alkyl analogs, is under investigation.

mechanism may well lead to productive modifications of the present procedure.

The $RCX_3/Co_2(CO)_8$ reactions carried out during the course of the present study are summarized in Table 1. Included are some of the results we obtained with reactions described previously by others in order to provide a calibration of the yields. Worth noting among these are the preparations of iodomethylidynetricobalt nonacarbonyl and deuteriomethylidynetricobalt nonacarbonyl. The material prepared in THF medium in the case of the former was contaminated with $HCCo_3$-$(CO)_9$, as shown by ^{1}H NMR, and the $ICCo_3(CO)_9$ and $HCCo_3(CO)_9$ could not be separated by column chromatography. Furthermore, the yield was low. The poor solubility of carbon tetraiodide in THF may have been responsible for this, and since CI_4 reacted much more rapidly and vigorously with dicobalt octacarbonyl than did CCl_4, in which CI_4 has fair solubility, a reaction was tried in which carbon tetrachloride was used as the reaction medium. The yield of product was improved, but according to its elemental analysis, a roughly 9/1 mixture of iodomethylidyne- and chloromethylidynetricobalt nonacarbonyl had been formed. Deuteriomethylidynetricobalt nonacarbonyl, a useful compound for mechanistic studies of methylidynetricobalt nonacarbonyl reactions, can be prepared in high purity from $DCBr_3$ and dicobalt octacarbonyl. Subsequent brominolysis of the $DCCo_3(CO)_9$ formed and mass spectrometric analysis of the $DCBr_3$ produced indicated an isotopic purity virtually identical to that of the $DCBr_3$ used in the original preparation (99.0 %).

EXPERIMENTAL

General comments

Melting points were obtained using a Büchi melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 257 or 457A grating IR spectrophotometer, NMR spectra using a Varian Associates T60 or a Perkin–Elmer R20 spectrometer. Chemical shifts are reported in δ units (ppm) downfield from internal TMS. Column chromatography was accomplished for the most part using a 40×600 mm column fitted with a fritted glass disc and Teflon stopcock. In most instances, 100 mesh Mallinckrodt reagent grade silicic acid served well. The elution solvents used were: (A) n-hexane; (B) 20 % (v/v) benzene/80 % hexane; (C) benzene; (D) dichloromethane; (E) 5 % diethyl ether/95 % dichloromethane. Thin layer chromatography (TLC) was carried out using Eastman Chromagram Sheet No. 6060.

Dicobalt octacarbonyl was purchased from Strem Chemical Co.

Preparation of starting materials

(a) Trichloromethylcarbinols

$CCl_3CH(OH)Et$[17] and $CCl_3CH(OH)Pr$-n[17] were prepared by the sodamide procedure[18], $CCl_3CH(OH)Bu$-n[17] and $CCl_3CH(OH)CMe_3$ by the procedure which uses CCl_3MgCl[19], $CCl_3CH(OH)Pr$-i[17] via CCl_3Li[20], and $CCl_3CH(OH)Ph$[18] by reaction of chloroform and KOH with benzaldehyde[17]. The Friedel–Crafts procedure (arene + chloral + $AlCl_3$)[21] served in the preparation of $CCl_3CH(OH)C_6H_4CH_3$-p[22] and $CCl_3CH(OH)C_6H_4Br$-p[23]. The tert-butyl derivative, m.p. 49° (sublimes at 60°/ 0.08 mmHg) is a new compound. (Found: C, 35.19; H, 5.42. $C_6H_{11}Cl_3O$ calcd.: C, 35.06; H, 5.39 %.) NMR (CCl_4): δ 1.27 (s, 9 H), 3.17 (s, 1 H) and 3.85 ppm (s, 1 H).

(b). Trichloromethyl ketones

Oxidation of the trichloromethylcarbinols by chromium trioxide in glacial acetic acid[17] served well in the preparation of the ketones. Prepared thus were the known CCl_3COEt[17], $CCl_3COPr\text{-}n$[17], CCl_3COPh[24,25], $CCl_3COC_6H_4CH_3\text{-}p$[26], and $CCl_3COC_6H_4Br\text{-}p$[27]. The following new compounds were characterized:

$CCl_3COC_4H_9\text{-}n$. B.p. 95° (28 mmHg), n_D^{20} 1.4633, $v(C{=}O)$ 1755 cm^{-1}. (Found: C, 35.39; H, 4.48. $C_6H_9Cl_3O$ calcd.: C, 35.50; H, 4.45%.)

$CCl_3COCHMe_2$. B.p. 72–75° (28 mmHg), n_D^{20} 1.4501, $v(C{=}O)$ 1752 cm^{-1}. (Found: C, 31.82; H, 3.82. $C_5H_7Cl_3O$ calcd.: C, 31.69; H, 3.72%.)

CCl_3COCMe_3. B.p. 70–72° (13 mmHg), n_D^{20} 1.4648, $v(C{=}O)$ 1725 cm^{-1}. (Found: C, 35.46; H, 4.49; Cl, 51.77. $C_6H_9Cl_3O$ calcd.: C, 35.41; H, 4.45; Cl, 52.27%.)

(c). Trichloromethyl compounds of silicon, tin and phosphorus

(i). *Silicon.* A solution of trichloromethyllithium was prepared by dropwise addition of 0.1 mol of chloroform in 25 ml of dry THF to 62.5 ml of n-butyllithium (1.6 M, 0.1 mol) in hexane diluted with 100 ml of THF, 25 ml of diethyl ether and 25 ml of pentane and cooled to −115°. The reagent solution was stirred at this temperature for 2 h and then 0.099 mol of PhMe$_2$SiCl in 50 ml of THF was added dropwise. The reaction mixture was stirred for 2 h at about −115°, warmed to room temperature and the solvents were removed at reduced pressure. The residue was trap-to-trap distilled at 0.25 mmHg (pot temperature to 120°) and the distillate was recrystallized from pentane to give 13.1 g (54%) of PhMe$_2$SiCCl$_3$, m.p. 27–28°. (Found C, 42.61; H, 4.40. $C_9H_{11}Cl_3Si$ calcd.: C, 42.62; H, 4.33%)

A similar procedure was used in the preparation of Me$_3$SiCCl$_3$, a known compound.

(ii). *Tin.* Trimethyltrichloromethyltin was prepared by the reaction of (dimethylamino)trimethyltin with trimethyltin chloride[28].

(iii). *Phosphorus.* Dimethyl- and diethyltrichloromethylphosphonate were prepared by the Arbuzov reaction of carbon tetrachloride with the respective trialkyl phosphite[29].

(d). Other compounds

(i). *Trimethylsilyl trichloroacetate.* Hexamethyldisilazane (Dow Corning Corp., 32 g, 0.2 mol) was added, with stirring under nitrogen, slowly to a solution of 0.60 mol of trichloroacetic acid in 500 ml of dry diethyl ether. The reaction mixture was stirred at room temperature for 20 h, concentrated at atmospheric pressure and filtered. The filtrate was treated with pyridine to remove unconverted acid and filtered. Vacuum distillation of the filtrate thus obtained gave 27.5 g (29%) of CCl$_3$CO$_2$SiMe$_3$, b.p. 69–70° (10 mmHg), n_D^{25} 1.4375, $v(C{=}O)$ 1750 cm^{-1}. (Found: C, 25.49; H, 4.05; Cl, 45.21. $C_5H_9Cl_3O_2Si$ calcd.: C, 25.49; H, 3.85; Cl, 45.15%.)

(ii). *Trimethyl(2,2,2-trichloroethoxy)silane.* Hexamethyldisilazane (0.10 mol) was added rapidly, with stirring under nitrogen, to 30.0 g (0.20 mol) of 2,2,2-trichloroethanol (Aldrich) in 150 ml of dry diethyl ether and the reaction mixture was stirred and heated at reflux for 18 h. Distillation gave 43 g of liquid boiling at 53–54° (12 mmHg) which GLC showed to be a mixture of the starting alcohol (1 part) and the desired product (1.4 parts). The product was separated by GLC (20% Carbowax 20 M on Chromosorb P at 110°) to give 12.6 g (29%) of CCl$_3$CH$_2$OSiMe$_3$, n_D^{25} 1.4421. (Found:

C, 26.97; H, 4.88; Cl, 48.15. $C_5H_{11}Cl_3OSi$ calcd.: C, 27.10; H, 5.01; Cl, 48.00%.)
NMR (CCl_4): δ 0.22 (s, 9 H, Me_3Si) and 4.08 ppm (s. 2 H. CH_2).

(iii). Trimethyl(2,2,2-tribromoethoxy)silane. Essentially the same procedure was used in the reaction of 0.056 mol of hexamethyldisilazane with 0.102 mol of 2,2,2-tribromoethanol (Aldrich) in 50 ml of ether (40 h at reflux). Distillation gave 34.15 g (94%) of the title compound, b.p. 59–61° (1 mmHg), n_D^{25} 1.5064. (Found: C, 16.84; H, 3.12; Br, 67.63. $C_5H_{11}Br_3OSi$ calcd.: C, 16.92; H, 3.12; Br, 67.54%.)
NMR (CCl_4): δ 0.28 (s, 9H, Me_3Si) and 4.23 ppm (s, 2H, CH_2).

Reactions of trihalomethyl compounds with dicobalt octacarbonyl

The general procedure was as follows: A three-necked flask of appropriate volume equipped with a serum cap, nitrogen inlet tube and solids transfer tube was evacuated, filled with dry nitrogen and charged with dicobalt octacarbonyl. The transfer tube was removed and replaced with an overhead stirrer. The solvent and the trihalomethyl compounds then were added by syringe. The mixture was stirred at room temperature, or warmed if necessary, to maintain a steady evolution of gas. After gas evolution had ceased, the reaction mixture was cooled and filtered with suction. The filtrate was treated with an equal volume of 10% aqueous HCl and the products were extracted with an equal volume of pentane or hexane. The organic layer was washed several times with equal volumes of water and dried over $MgSO_4$. The solvent was removed at reduced pressure to leave the crude product. A Co_2-$(CO)_8$/RCX_3 ratio of 9/5 was used throughout the course of this study. In general, the preparations were carried out starting with about 40 to 100 mmol of dicobalt octacarbonyl. On the order of 150 ml of dry THF per 50 mmol of dicobalt octacarbonyl was used. The crude product was purified either by sublimation *in vacuo*, recrystallization from hexane or column chromatography, or by a combination of these. Pertinent data concerning these reactions and the products formed are summarized in Tables 1 and 2.

Reaction times varied considerably, being a function of the trihalomethyl compound used. A reaction time of 3–4 h at 50° was sufficient in the case of the trichloromethyl ketones, but in other cases longer reaction times were required (*e.g.*, 72 h in the case of $PhMe_2SiCCl_3$).

The preparation of $(OC)_9Co_3CCOEt$ is described as an example of this procedure. A 500 ml three-necked flask equipped as described above was charged with 18.7 g (55 mmol) of dicobalt octacarbonyl and 150 ml of dry THF (distilled from sodium benzophenone ketyl). The mixture was stirred until the carbonyl had dissolved and then 5.5 g (31 mmol) of CCl_3COEt was added slowly by syringe. The reaction mixture was stirred at 45° for 3 h, cooled to room temperature and treated with 150 ml of 10% aqueous hydrochloric acid. The aqueous layer was separated and extracted twice with 150 ml portions of hexane. The combined organic layer and washings were washed with three portions of water and dried over anhydrous $MgSO_4$. Filtration was followed by removal of solvents at reduced pressure. The residue was recrystallized from hexane to give 6.2 g (40%) of product, n.p. 74° (dec.).

In the preparation of $(OC)_9Co_3CCO_2SiMe_3$ the reaction mixture was evaporated and extracted with hexane without an intervening hydrolysis step. In the case of the reactions with the 2,2,2-trihaloethoxysilanes, the reaction mixtures were hydrolyzed as above in order to obtain the $(OC)_9Co_3CCH_2OH$ directly. The di-

TABLE 2

NEW $RCCo_3(CO)_9$ COMPOUNDS PREPARED

Compound R in $RCCo_3(CO)_9$	Color	Analysis, found (calcd.) (%)		IR, C≡O bands, (cm⁻¹)	NMR (δ) (ppm)	Purified by method(s)[a]
		C	H			
D	Red	27.20 (27.12)		(CCl₄) 2105 m, 2060 vs, 2045 s, 2025 w, 1980 vw		A
Me₃Si	Purple	30.17 (30.37)	1.68 (1.76)	(CS₂) 2110 m, 2065 s, 2040 s, 2020 w, 1985 vw	(CDCl₃) 0.41 (s, Me₃Si)	B
PhMe₂Si	Purple-black	37.55 (37.54)	2.04 (1.96)	(CCl₄) 2110 m, 2065 s, 2040 s, 2020 w, 1950 w	(CCl₄) 0.67 (s, Me₂Si), 7.3–7.8 (m, Ph)	B
(MeO)₂P(O)	Purple-black	26.90 (26.45)	1.32 (1.10)	(CHCl₃) 2105 s, 2060 vs, 2042 vs, 2020 m, 1970 w, ν(P=O) 1232s	(CDCl₃) 4.0 (d, J 11 Hz, MeO)	C (ether); B
(EtO)₂P(O)	Purple-black	29.65 (29.09)	1.99 (1.74)	(CHCl₃) 2110 s, 2065 vs, 2050 vs, ν(P=O) 1235 s	(CDCl₃) 1.42 (t, J 7 Hz, CH₃-), 4.26 (quintet, J 7 Hz, OCH₂)	C (CHCl₃) B
Me₃COC(O)	Purple	33.01 (33.24)	1.54 (1.67)	(CCl₄) 2111 m, 2065 vs, 2045 s, 2020 w, 1985 vw, ν(C=O) 1675 s	(CDCl₃) 1.58 (s, Me₃C)	A
Me₃SiOC(O)	Red-purple	30.00 (30.13)	1.67 (1.63)	(CCl₄) 2112 m, 2065 vs, 2045 s, 2020 w, 1980 vw, ν(C=O) 1670 s	(CDCl₃) 0.37 (s, Me₃Si)	A
Et₂NC(O)	Black	32.97 (33.30)	2.44 (2.59)	(CCl₄) 2110 m, 2065 vs, 2045 s, 2020 w, 1955 vw, ν (C=O) 1575 s	(CDCl₃) 1.18 (t, J 7 Hz, CH₃), 3.60 (q, J 7 Hz NCH₂)	B
CH₃C(O)	Red-black	29.91 (29.79)	0.78 (0.62)	(CCl₄) 2120 w, 2070 s, 2053 s, 2040 w, 1990 vw, ν(C=O) 1640 s	(CDCl₃) 2.60 (s, CH₃)	B
C₂H₅C(O)	Purple-black	31.67 (31.35)	1.17 (1.01)	(CCl₄) 2110 m, 2065 vs, 2040 s, 2020 w, 1990 w, ν(C=O) 1645 s	(CCl₄) 1.27 (t, J 7 Hz, CH₃), 2.83 (q, J 7 Hz CH₂)	A or B
n-C₃H₇C(O)	Purple-black	32.54 (32.85)	1.46 (1.36)	(CCl₄) 2112 vs, 2062 vs, 2050 s, 2038 w, 1970 w, ν(C=O) 1640 s	(CCl₄) 1.05 (t, J 7 Hz, CH₃) 1.85 [sextet, J 7 Hz, C:C–C–CH₂–] 2.83 [t, J 7 Hz, (O)C–CH₂–]	B
Me₂CHC(O)	Purple-black	32.84 (32.85)	1.34 (1.36)	(CCl₄) 2115 s, 2065 vs, 2050 vs, 2038 w, 1975 w, ν(C=O) 1635 s	(CCl₄) 1.33 (d, J 7 Hz, Me₂C) 3.13 (quintet, J 7 Hz, ⟩CH)	B

Compound	Color	Analysis (found / calc.)		IR	NMR	Method
n-$C_4H_9C(O)$	Purple-black	34.51 (34.24)	2.02 (1.72)	(CCl₄) 2110 s, 2062 vs, 2048 vs, 2038 w, 1965 w, ν(C=O) 1635 s	(CCl₄) 1.0 (t, J 7 Hz, CH₃) 1.2–2.1 [m, (O)C–C–CH₂–CH₂–] 2.9 [t, J 7 Hz, (O)C–CH₂–]	B
Me₃C(O)	Dark violet	34.35 (34.24)	1.80 (1.72)	(CCl₄) 2110 s, 2062 vs, 2048 vs, 2038 w, 1965 w, ν(C=O) 1618 s	(CCl₄) 1.38 (s, Me₃C)	B
PhC(O)	Dark brown	37.59 (37.40)	1.05 (0.92)	(CCl₄) 2112 s, 2064 vs, 2050 vs, 2040 w, 1970 w, ν(C=O) 1610 m	(CCl₄) 7.47 (m, 3 H) } Ph 7.87 (m, 2 H)	B
p-CH₃C₆H₄C(O)	Black	38.45 (38.60)	1.45 (1.25)	(CCl₄) 2110 s, 2065 vs, 2048 vs, 2038 w, 1970 w, ν(C=O) 1611 s	(CCl₄) 2.61 (s, CH₃), 7.64 (A₂B₂ q, J 8 Hz)	B
p-BrC₆H₄C(O)	Violet	32.66 (32.64)	0.74 (0.64)	(CCl₄) 2110 s, 2062 vs, 2050 vs, 2038 w, 1975 w, ν(C=O) 1610 s	(CCl₄) 7.65 (A₂-B₂ q, J 8 Hz)	B
HOCH₂	Red	28.15 (27.99)	0.78 (0.64)	(CCl₄) 2120 m, 2065 vs, 2050 vs, 2035 s, 1995 s, ν(O–H) 3630 m	(CDCl₃) 2.50 (t, J 6 Hz, OH) 5.21 (d, J 6 Hz, CH₂)	C (benzene) and A
HC(O)[b]	Black	c				C (benzene) and A
CH₃O	Red-black	27.89 (27.99)	0.80 (0.64)	(CCl₄) 2108 m, 2065 vs, 2040 s, 2020 w, 1985 w	(CDCl₃) 4.05 (s, OCH₃)	A
Me₂N	Brown			(CCl₄) 2105 m, 2065 vs, 2045 s, 2020 w, 1985 vw	(CDCl₃) 3.18 (s, Me₃N)	B
Me₂HN⁺ (PF₆⁻ salt)	Black	22.51 (22.84)	1.44 (1.12)[d]		[(CD₃)₂CO] 2.77 (s)	

ᵃ Method A: sublimation ~50° in vacuo. Method B: recrystallization from hexane. Method C: column chromatography (elution solvent). ᵇ Characterized by G. H. Williams; cf. ref. 7. ᶜ Extremely air-sensitive, not analyzed. ᵈ Found: N, 2.22. Calcd.: N, 2.22%.

alkylphosphono-substituted methylidynetricobalt nonacarbonyls were found to be air-unstable and thus all operations were carried out under a nitrogen atmosphere.

The preparation of $DCCo_3(CO)_9$ was accomplished using $DCBr_3$ containing 99.4% D (by mass spectrometry). In its NMR spectrum the resonance at δ 12.08 ppm (in $CDCl_3$) characteristic of $HCCo_3(CO)_9$ was absent. A 1.32 g sample of this $DCCo_3$-$(CO)_9$ in 70 ml of carbon tetrachloride was treated with 2.16 g (12.5 mmol) of bromine at room temperature for 30 min. The resulting blue precipitate was filtered. The filtrate was concentrated using a 9 in. Vigreux column and the remaining liquid was trap-to-trap distilled at 0.05 mmHg. GLC analysis of the distillate showed the presence of $DCBr_3$ (23%). Mass spectrometry established that it was 99.0% $DCBr_3$.

The preparation of $ICCo_3(CO)_9$ was carried out by adding a slurry of 47.0 g (90 mmol) of carbon tetraiodide in 250 ml of benzene to a solution of 0.135 mol of $Co_2(CO)_8$ in 250 ml of 3/1 carbon tetrachloride/fluorotrichloromethane at $-40°$. The reaction mixture was allowed to warm slowly to $0°$, at which temperature gas evolution began. A reaction period of 8 h at $0°$ and 14 h at room temperature was followed by the usual work-up. The material obtained (8.18 g) appeared to be a mixture of $ICCo_3(CO)_9$ and $ClCCo_3(CO)_9$ according to its analysis. (Found: C, 21.69; I, 19.46. $C_{10}Co_3IO_9$ calcd.: C, 21.15; I, 22.38%.) The analyses obtained indicate the presence of an 87/13 mixture of the iodo and chloro derivatives.

Reactions of dihalomethyl compounds with dicobalt octacarbonyl

(a). *Methyl dichloromethyl ether.* The ether (4.70 g, 41 mmol) was added by syringe to a solution of 73 mmol of $Co_2(CO)_8$ in 200 ml of THF (usual procedure). After a slow reaction had been allowed to proceed for 1 h at room temperature, the reaction mixture was heated at $50°$ until CO evolution ceased. The usual work-up (hydrolysis followed by sublimation) gave 6.21 g (27%) of $(OC)_9Co_3COCH_3$ as red-black crystals.

(b). *N,N-Dimethylchloroformamidinium chloride.* A slurry of 5.3 g (41 mmol) of *N,N*-dimethylchloroformamidinium chloride[30] in 20 ml of dry THF was added to 74.5 mmol of dicobalt octacarbonyl in 200 ml of THF. A vigorous evolution of CO resulted. The mixture was heated at $50°$ for 2 h and then was filtered under nitrogen. (Further operations had to be carried out in the absence of oxygen because the product was air-unstable.) Evaporation of the filtrate at reduced pressure was followed by extraction of the residue with hexane. Evaporation of the hexane extracts left 6.3 g of brown solid (26%) which was not analyzed, rather it was converted to its stable ammonium salt.

A 2.5 g (5.1 mmol) sample of $Me_2NCCo_3(CO)_9$ was dissolved under nitrogen in 50 ml of propionic anhydride. To this solution was added 2.0 g of 65% aqueous HPF_6 (13.7 mmol of acid). The reaction mixture was stirred at room temperature for 1 h and then was treated with 200 ml of anhydrous diethyl ether. The resulting black precipitate (2.01 g, 80%) was washed with chloroform and dried.

Reaction of trimethyl(trichloromethyl)tin with dicobalt octacarbonyl

A solution of 41 mmol of dicobalt octacarbonyl in 150 ml of dry THF was prepared under nitrogen and 22.8 mmol of Me_3SnCCl_3 was added by syringe. The mixture was stirred and heated at $50°$ for 12 h. The solvent was removed at reduced pressure and the residue extracted with two 400 ml portions of boiling n-heptane.

A black solid precipitated when the heptane extracts were cooled to $-78°$. Recrystallization from heptane gave 3.5 g (33%) of $Co_4(CO)_{12}$ (identified by IR). The residue from the heptane extraction was sublimed at 0.1 mmHg (room temperature) to give 0.85 g (11%) of $Me_3SnCo(CO)_4$, m.p. 74–75° (lit.[31] m.p. 73–75°), with IR and NMR spectra in accord with those reported[31]. Further sublimation (40° at 0.1 mm-Hg) gave 0.78 g (7%) of $ClCCo_3(CO)_9$, m.p. 130–131°, identified by spectroscopic comparison with an authentic sample.

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