Metal Carbonyl Chemistry. Part XXIII.[1] Dichlorocarbene Formation During the Reactions of Octacarbonyldicobalt with Chlorinated Hydrocarbons

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Trapping experiments using cyclohexene have demonstrated the intermediate formation of dichlorocarbene in the reactions of octacarbonyldicobalt with the compounds $CXCl_3$ (X = Cl or Br) or CBr_2Cl_2 in hexane solvent which give $[ClCCo_3(CO)_9]$ as the major product. Evidence is also presented for the formation of radical intermediates during these reactions, and the mechanism of formation of the cobalt cluster compound is discussed in the light of these findings.

TRIHALOGENO-COMPOUNDS, RCX_3, are well known to form alkylidynenonacarbonyltricobalt complexes, $[RCCo_3(CO)_9]$ upon reaction with octacarbonyldicobalt.[2] These reactions are usually carried out in a donor solvent, such as tetrahydrofuran or acetone, under conditions where disproportionation to $[Co(solvent)_6]^{2+}$ $2[Co(CO)_4]^-$ is known to occur.[3] Under such conditions recent evidence suggests that radical intermediates, formed by attack of the anion on the organohalogen compound, may be involved, but there was no evidence for carbene intermediates.[4] Polar solvents are not essential for cluster formation, and there have been several reports of reactions occurring in non-polar solvents such as benzene or hexane.[5] For example, a 19% yield of $[(CH_3)CCo_3(CO)_9]$ is obtained on reaction of $CH_3{\cdot}CCl_3$ with $[Co_2(CO)_8]$ in pentane at 100 °C.[6] We now report some observations on the reactions of halogenoalkanes with octacarbonyldicobalt in hexane which demonstrate that both radical

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[1] Part XXII, B. L. Booth, R. N. Haszeldine, and I. Perkins, *J.C.S. Dalton*, preceding paper.

[2] G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta. Rev.*, 1970, **4**, 109; B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

[3] W. Hieber, W. Abeck, and J. Sedlmeier, *Angew. Chem.*, 1952, **64**, 480; *Chem. Ber.*, 1953, **86**, 705; W. F. Edgell and J. Lyford, *Inorg. Chem.*, 1970, **9**, 1932.

[4] D. Seyferth and M. D. Millar, *J. Organometallic Chem.*, 1972, **38**, 373.

[5] R. Ercoli, *Chimica e Industria*, 1962, **44**, 565; 1344.

[6] B. L. Booth, R. N. Haszeldine, and P. R. Mitchell, unpublished observations.

and carbene intermediates are formed under these conditions.

When a solution of octacarbonyldicobalt and an excess of carbon tetrachloride in n-hexane was stirred at 70 °C for 7 h the major reaction product was $[ClCCo_3(CO)_9]$ (41%), according to the stoicheiometry:

$$4[Co_2(CO)_8] + CCl_4 \longrightarrow 2[ClCCo_3(CO)_9] + 14CO + 2Co^{II} + 2Cl^-$$

Examination of the product liquor by g.l.c. showed the presence of small amounts of tetrachloroethylene and hexachloroethane.* The similar reactions of $CBrCl_3$ and CBr_2Cl_2 afforded $[ClCo_3(CO)_9]$ as the only metal cluster product in 49 and 42% yields respectively under milder reaction conditions. Tetrachloroethylene and hexachloroethane were again identified as products of the reaction of $CBrCl_3$, while only the former could be detected in the reaction of CBr_2Cl_2. No organic bromine-containing products were observed in either of these reactions, and both reactions gave a pink solid residue which contained Co^{II}, Cl^-, and Br^- ions.

When the reaction of carbon tetrachloride was repeated under similar conditions but in the presence of an excess of cyclohexene the yield of $[ClCCo_3(CO)_9]$ was reduced to 29%, and g.l.c. analysis showed the presence of 7,7-dichloronorcarane, but not tetrachloroethylene or hexachloroethane.* The norcarane was also detected among the products of the reactions of $CBrCl_3$ and CBr_2Cl_2 with $[Co_2(CO)_8]$ in the presence of cyclohexene, and again the yields of $[ClCCo_3(CO)_9]$ were reduced by *ca.* 10%. In view of the recent report [4] that radicals may be involved in the reactions of *gem*-dihalides with $[Co_2(CO)_8]$ in tetrahydrofuran solvent, and the knowledge that octacarbonyldicobalt in the presence of CCl_4 and other trichloro-compounds is an effective radical initiator of vinyl polymerisation,[7,8] a check was also carried out to determine whether radicals were also formed under the conditions described above for cluster formation. When the reactions of either CCl_4 or $CBrCl_3$ were repeated under similar conditions but in the presence of a 1 : 1 mixture of methyl methacrylate and styrene both reactions gave a high yield of a white solid shown by i.r. spectroscopy and microanalysis to be a 1 : 1 copolymer. As previously demonstrated [9,10] copolymer formation only occurs upon radical initiation; anionic initiation affords poly(methyl methacrylate) while polystyrene is the product of cationic initiation. In separate experiments it was shown that CCl_4, $CBrCl_3$, $[Co_2(CO)_8]$, or $[Co_4(CO)_{12}]$ do not cause copolymerisation of a 1 : 1 molar solution of methyl methacrylate and styrene under similar conditions. Further evidence in support of radical intermediates comes from the observation that no polymerisation took place when either CCl_4 or $CBrCl_3$ and $[Co_2(CO)_8]$ were heated with the monomers in the presence of a three-fold excess of the radical scavenger, 1,1-diphenyl-2-picrylhydrazyl.† This observed inhibition is not attributable to any reaction of the scavenger with octacarbonyldicobalt as the i.r. spectrum of a mixture of these compounds in hexane at 65 °C remained unchanged even after 6 h. When either CCl_4 or $CBrCl_3$ were also present under these conditions, however, a fairly rapid reaction occurred to give an intractable black solid which contained no metal carbonyl residues, and little hydrazyl was recovered.

The initial reaction between octacarbonyldicobalt and the halogenomethanes could follow one of several alternative pathways as outlined in the Scheme. At the reaction temperature employed it is possible that homolysis of the cobalt–cobalt bond of the bridged or non-bridged [11] forms of $[Co_2(CO)_8]$ could occur with the formation of radicals. This seems unlikely in view of the observation that $[Co_2(CO)_8]$ alone does not catalyse radical polymerisation at 65 °C. An alternative four-centre addition may be envisaged, or, if loss of carbon monoxide occurs initially, it is possible that the halogenomethane oxidatively adds to the co-ordinatively unsaturated cobalt atom. In connection with this last alternative it has been established that when the reaction of CCl_4 and $[Co_2(CO)_8]$ in hexane at 70 °C is carried out under 50 atm of carbon monoxide for 4 h the isolated yield of $[ClCCo_3(CO)_9]$ of 42% is almost identical to that obtained in the absence of CO. The similar reaction of $CBrCl_3$ and $[Co_2(CO)_8]$ in hexane at 40 °C for 4 h under carbon monoxide (50 atm) gave a 43% yield of $[ClCCo_3(CO)_9]$, which is again comparable with the 49% yield obtained under similar conditions in the absence of CO. While this evidence does not necessarily disprove the dissociative mechanism it does indicate that CO dissociation is not a rate-limiting step during cluster formation.

Whatever the mechanism of the initial interaction between octacarbonyldicobalt and halogenomethane it seems reasonable to assume that the products of this reaction will be a tetracarbonylhalogenoalkylcobalt intermediate of type (I) and either $[ClCo(CO)_4]$ or $[BrCo(CO)_4]$, depending on whether CCl_4 or a bromo-derivative is used. These last compounds are known to be unstable above *ca.* −40 °C and to decompose to the cobalt(II) halide and carbon monoxide.[12] Although tetracarbonylfluoroalkylcobalt complexes are reasonably stable at room temperature, the chloro- and bromo-analogues are not known. In an attempt to prepare one of the proposed intermediates, $[(CCl_3)Co(CO)_4]$, the reaction between

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* Percentage yields of C_2Cl_4, C_2Cl_6, and 7,7-dichloronorcarane are not quoted, as they are not really meaningful in view of the fact that an 8—10 molar excess of the halogenomethane was used in these reactions in order to maximise cluster formation.

† Phenolic scavengers, such as 2,4,6-tri-t-butylphenol were avoided as these would almost certainly have caused disproportionation of $[Co_2(CO)_8]$ and a possible change in reaction mechanism.

[7] T. Susuki and J. Tsuji, *J. Org. Chem.*, 1970, **35**, 2982.

[8] Y. Mori and J. Tsuji, *Tetrahedron*, 1972, **28**, 29.

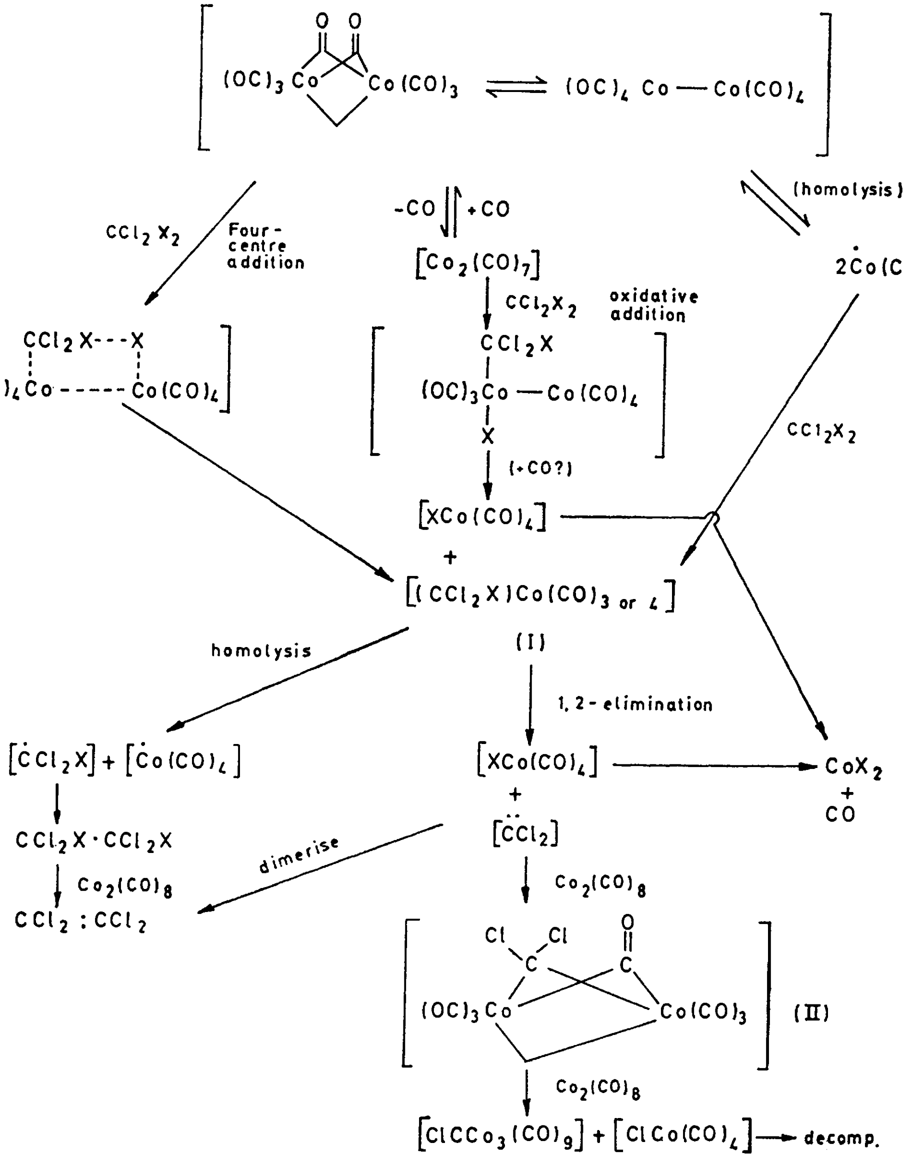
[9] G. Henrici-Olivé and S. Olivé, *J. Organometallic Chem.*, 1973, **52**, C49; ' Polymerisation: catalysis, kinetic mechanisms,' Verlag Chemie, Weinheim, 1969.

[10] C. Walling, E. R. Brigg, W. Cummings, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 48.

[11] K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847; 1964, **47**, 155; *Spectrochim. Acta*, 1963, **19**, 1925; G. Bor, *ibid.*, p. 2065.

[12] M. Pankowski and M. Bigorgne, *Compt. rend.*, 1967, **264**, 1382.

Tl[Co(CO)$_4$],[13] which is covalent and soluble in non-polar solvents, and CCl$_4$ was investigated. When carbon tetrachloride was added dropwise to a solution of the thallium salt a rapid reaction occurred to give [ClCCo$_3$(CO)$_9$] (72%), TlCl, and CoCl$_2$. When inverse addition was used, that is, the dropwise addition of Tl[Co(CO)$_4$] in benzene to a solution of CCl$_4$ in benzene at room temperature, the yield of [ClCCo$_3$(CO)$_9$] was reduced to 20%, and tetrachloroethylene and hexachloroethane were detected among the products. The addition of [Co$_2$(CO)$_8$] to [(CCl$_3$)Co(CO)$_4$], formed *in situ* by the dropwise addition of carbon tetrachloride to a benzene solution of Tl[Co(CO)$_4$] {molar ratios of Tl[Co(CO)$_4$] : CCl$_4$: [Co$_2$(CO)$_8$] *ca.* 1 : 8 : 2}, gave [ClCCo$_3$(CO)$_9$] in 56% yield based on the total amount of cobalt. Of this total less than half could have been formed by reaction of Tl[Co(CO)$_4$] with CCl$_4$, and the remainder must arise by reaction between the [(CCl$_3$)Co(CO)$_{3\text{ or }4}$] and [Co$_2$(CO)$_8$]. A control reaction carried out using [Co$_2$(CO)$_8$] and CCl$_4$ alone under similar conditions gave no cluster complex. These results are readily explained if the initially formed [(CCl$_3$)Co(CO)$_4$] reacts rapidly with either Tl[Co(CO)$_4$] or [Co$_2$(CO)$_8$], when these are present in excess, to form [ClCCo$_3$(CO)$_9$]. In the absence of an excess of the cobalt carbonyls the [(CCl$_3$)Co(CO)$_4$] undergoes appreciable decomposition to C$_2$Cl$_4$ and C$_2$Cl$_6$ with a corresponding reduction in the yield of [ClCCo$_3$(CO)$_9$]. There is evidence that this decomposition can occur both by an α-chloro-elimination mechanism and by homolysis of the carbon–cobalt σ-bond to give $\dot{C}Cl_3$ and $\dot{C}o(CO)_4$ radicals (see Scheme). Evi-



SCHEME

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[13] S. E. Pedersen, W. R. Robinson, and D. P. Schussler, *J. Organometallic Chem.*, 1973, **43**, C44.

dence of the latter pathway is given by the isolation of a 1 : 1 copolymer of methyl methacrylate and styrene formed in 70% yield, together with $[ClCCo_3(CO)_9]$ (17%), when a solution of $Tl[Co(CO)_4]$ in benzene is added at room temperature to a solution of the monomers (1 : 1 molar ratio) in carbon tetrachloride. Thallium tetracarbonylcobaltate alone does not cause copolymerisation under these conditions. Evidence for the competing α-chloro-elimination has been obtained by addition of $Tl[Co(CO)_4]$ in benzene to a mixture of CCl_4 and cyclohexene at room temperature and detection of the trapped carbene as 7,7-dichloronorcarane. There are very few well authenticated examples of α-halogeno-elimination reactions occurring with α-alkyl transition-metal complexes, although it is a well known reaction of certain main-group organometallic compounds. The most convincing example of this reaction in organotransition-metal chemistry is the iridium(I) compound, $[Ir(CO)(PPh_3)_2(CH_2Cl)]$, obtained from diazomethane and *trans*-$[IrCl(CO)(PPh_3)_2]$, which appears to rearrange to the five-co-ordinate carbene complex $[IrCl(CO)(PPh_3)_2(CH_2)]$.[14] An analogous carbene complex $[IrCl(CO)(PMePh_2)_2\{C(CF_3)_2\}]$ has also been reported,[15] but this is stable as the five-co-ordinate species, and shows no tendency to rearrange to a four-co-ordinate compound by insertion of the carbene ligand into the Ir–Cl bond. It should be noted, however, that the postulated 1,2-shift of a chlorine atom to the cobalt atom does not necessarily imply that free dichlorocarbene is present in these reactions. It is conceivable that norcarane formation could occur by reaction of complexed carbene with cyclohexene. Similarly, tetrachloroethylene formation may arise by carbene dimerisation, but equally it could be formed by the dehalogenation of hexachloroethane by octacarbonyldicobalt, as demonstrated recently for other vicinal dihalides.[4]

Exactly how cluster formation occurs on reaction of $[Co_2(CO)_8]$ with the intermediates, $[(CCl_2X)Co(CO)_4]$, is still a matter for conjecture. It is tempting to suggest that it arises by attack of dichlorocarbene, either free or complexed, on octacarbonyldicobalt to give a chloroalkyl-bridged complex (II). Such a reaction would explain the reduced yield of $[ClCCo_3(CO)_9]$ obtained in the presence of the carbene-trap, cyclohexene, and it would also explain why only the chloro-cluster complex is formed on reaction of CCl_2Br_2, since it is reasonable to suppose that a 1,2-bromine shift to cobalt would occur in preference to chlorine migration. Since the isolation of the alkyl-bridged complex, $[(OC)_3Co(CO)(CF{\cdot}CF_3)Co(CO)_3]$,[16] shown to be an intermediate in the formation of $[(CF_3)CCo_3(CO)_9]$ from C_2F_4 and $[Co_2(CO)_8]$, there have been other recent indications that intermediates of this type may be involved in several reactions leading to alkylidynenonacarbonyltricobalt complexes. These include the reaction of dimethylketen with $[Co_2(CO)_8]$ which affords the compounds $[RCCo_3(CO)_9]$ ($R = CMe{:}CH_2$ or $CHMe_2$),[17] and the preparation of $[(OC)_9Co_3C(O{\cdot}SiPh_2)Co(CO)_4]$ from Ph_2SiH_2 and $[Co_2(CO)_8]$.[18] Also of interest, in relation to this present investigation, is the report that photolysis of a mixture of CF_2Br_2 and $[Co(CO)_3NO]$ gives the CF_2-di-μ-bridged complex, $[(OC)_3Co(CF_2)(CF_2)Co(CO)_3]$, by a reaction thought to involve the intermediate $[(CF_2Br)Co(CO)_{3\text{ or }4}]$.[19]

An unsuccessful attempt to study the reaction of dichlorocarbene with $[Co_2(CO)_8]$ by addition of the carbonyl to a solution of the carbene-precursor, $NaO{\cdot}CO{\cdot}CCl_3$, in benzene under reflux, gave only $[Co_4(CO)_{12}]$ (74%), together with a residue which contained Co^{II}, Cl^-, and Na^+ ions. It is evident that under these conditions the conversion of $[Co_2(CO)_8]$ into $[Co_4(CO)_{12}]$ is faster than its reaction with $\ddot{C}Cl_2$ or $NaO{\cdot}CO{\cdot}CCl_3$. We are currently investigating the reactions of other dichlorocarbene precursors which form the carbene under milder conditions.

EXPERIMENTAL

Except where stated, all reactions were carried out under an atmosphere of dry nitrogen. The tetrahalogenomethanes and cyclohexene were dried over anhydrous calcium chloride, and hexane and benzene were dried over sodium sand. All solvents and liquid reactants were distilled immediately before use. Routine i.r. spectra were recorded on a Perkin-Elmer 137 spectrometer, and solution spectra on a Perkin-Elmer 257 instrument. Mass spectra were obtained on an A.E.I. MS902 mass spectrometer. G.l.c. analyses utilised a Pye 104 chromatograph, while solid–liquid chromatographic separations were carried out on Florisil. All yields of cobalt complexes are based on cobalt.

Reaction of Octacarbonyldicobalt with Carbon Tetrachloride.—(a) *In hexane.* When carbon tetrachloride (21·4 g, 139 mmol) was added to a solution of octacarbonyldicobalt (4·5 g, 13·2 mmol) in hexane (100 ml) and the solution was stirred at 65 °C for 7 h, filtration of the product mixture gave a dirty pink residue (1·9 g) shown by elemental analysis to contain Co^{II} and Cl^- ions. The volatiles were removed from the filtrate under reduced pressure, and were separated by fractional distillation. G.l.c. analysis (2 m SE30 column at 72 °C) of the highest boiling fraction showed the presence of tetrachloroethylene (0·03 mmol). The involatile residue was taken up in hexane and g.l.c. analysis (3 m TXP column at 142 °C) showed the presence of hexachloroethane (0·03 mmol). Concentration of the hexane solution under reduced pressure, and chromatography of the residual liquor using pentane as eluant yielded $[ClCCo_3(CO)_9]$ (1·70 g, 3·6 mmol, 40%) as a black-violet solid, purified by vacuum sublimation at 40 °C, and identified by m.p. and i.r. spectroscopy. Further elution gave $[Co_4(CO)_{12}]$ (0·21 g, 0·37 mmol, 6%).

(b) *In the presence of cyclohexene.* Carbon tetrachloride (12·7 g, 82·6 mmol), octacarbonyldicobalt (1·2 g, 3·5 mmol), and cyclohexene (40 ml) heated at 70 °C for 6 h in hexane

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[14] E. D. Mango and I. Dvoretzsky, *J. Amer. Chem. Soc.*, 1966, **88**, 1654.

[15] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *Chem. Comm.*, 1968, 170; *J. Chem. Soc.* (*A*), 1969, 1872.

[16] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, *J. Chem. Soc.* (*A*), 1969, 691.

[17] D. A. Young, *Inorg. Chem.*, 1973, **12**, 482.

[18] S. A. Fieldhouse, A. H. Cleland, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *J. Chem. Soc.* (*A*), 1971, 2536.

[19] F. Seel and G.-V. Röschenthaler, *Z. anorg. Chem.*, 1971, **386**, 297.

(25 ml) gave a dirty pink precipitate of CoCl$_2$. Filtration and g.l.c. analysis (3 m TXP column at 140 °C and 2 m SE30 column at 140 °C) of the filtrate after concentration showed the presence of 7,7-dichloronorcarane. Further concentration of the filtrate under reduced pressure, and sublimation of the violet residue *in vacuo* at 45 °C gave [ClCCo$_3$(CO)$_9$] (0·32 g, 0·67 mmol, 29%).

(c) *In the presence of a* 1 : 1 *molar mixture of methyl methacrylate and styrene.* A hexane (10 ml) solution of carbon tetrachloride (12·7 g, 82·6 mmol), octacarbonyldicobalt (1·60 g, 4·68 mmol), methyl methacrylate (21·7 g, 0·22 mol), and styrene (22·6 g, 0·22 mol) was stirred at 60 °C for 4 h to give a violet solid. The solid was filtered off and taken up in acetone to give a turquoise solution from which a dirty white solid precipitated upon addition of hexane. The white solid was filtered off, giving a violet filtrate, which on concentration yielded [ClCCo$_3$(CO)$_9$] (0·54 g, 1·13 mmol, 36%). Addition of chloroform to the dirty white solid gave a pink solid suspension, shown by analysis to contain Co^{II} and Cl$^-$ ions, and a colourless solution, which on treatment with methanol gave a white 1 : 1 copolymer of methyl methacrylate and styrene (39·6 g, 89% recovery) identified by i.r. spectroscopy, solubility measurements, and microanalysis [Found: C, 75·1; H, 7·9. Calc. for 1 : 1 copolymer: C, 76·2; H, 7·9%].

(d) *In the presence of* 1,1-*diphenyl*-2-*picrylhydrazyl.* A hexane solution (20 ml) of carbon tetrachloride (7·95 g, 51·6 mmol), octacarbonyldicobalt (0·40 g, 1·17 mmol), methyl methacrylate (21·7 g, 0·22 mol), styrene (22·6 g, 0·22 mol), and 1,1-diphenyl-2-picrylhydrazyl (1·6 g, 4·06 mmol) was stirred at 60 °C for 8 h, and gave a black precipitate (1·39 g), which contained no metal carbonyl bands in its i.r. spectrum. After filtration, the pale mauve filtrate was evaporated to dryness and was found to contain no 1 : 1 copolymer.

A similar black precipitate (1·34 g) was obtained when a solution of octacarbonyldicobalt (0·40 g, 1·17 mmol), carbon tetrachloride (2·40 g, 15·6 mmol), and 1,1-diphenyl-2-picrylhydrazyl (1·8 g, 4·6 mmol) in hexane (40 ml) was heated at 65 °C for 7 h.

(e) *Under a pressure of carbon monoxide.* Carbon tetrachloride (15·1 g, 98 mmol), octacarbonyldicobalt (2·5 g, 7·3 mmol), and hexane (50 ml) were stirred at 70 °C for 4 h in a stainless-steel autoclave (300 ml capacity) pressurised to 50 atm with carbon monoxide. Filtration of the product mixture gave a dirty pink residue containing Co^{II} and Cl$^-$ ions, and a violet solution which was shown, using the work-up procedure described in (a) above, to contain small amounts of tetrachloroethylene and hexachloroethane, [ClCCo$_3$(CO)$_9$] (0·98 g, 2·06 mmol, 42%), and [Co$_4$(CO)$_{12}$] (0·24 g, 0·42 mmol, 12%).

Reaction of Octacarbonyldicobalt with Bromotrichloromethane.—(a) *In hexane.* A solution of bromotrichloromethane (3·02 g, 15·2 mmol) and octacarbonyldicobalt (4·5 g, 13·2 mmol) in hexane was stirred at 40 °C for 2 h to give a dirty pink solid (2·14 g) shown by qualitative elemental analysis to contain Co^{II}, Br$^-$, and Cl$^-$ ions. Using a work-up procedure similar to that described previously for the reactions with carbon tetrachloride, the product solution was shown to contain small amounts of tetrachloroethylene and hexachloroethane, together with the major product [ClCCo$_3$(CO)$_9$] (2·06 g, 4·32 mmol, 49%) [Found: C, 25·1; H, 0·3%. *M*, 477 (mass spect.). Calc. for C$_{10}$O$_9$ClCo: C, 25·2; H, 0·0%. *M*, 477], and [Co$_4$(CO)$_{12}$] (30 mg).

(b) *In the presence of cyclohexene.* When bromotrichloromethane (1·51 g, 7·63 mmol) was added to a solution of octacarbonyldicobalt (3·01 g, 8·8 mmol) in cyclohexene (40 ml) immediate effervescence occurred and the mixture was stirred for a further 2 h at room temperature. Filtration of the product mixture gave a dirty pink solid (1·72 g) which contained Co^{II}, Br$^-$, and Cl$^-$ ions, and the filtrate was concentrated by removal of most of the volatiles under reduced pressure. G.l.c. analysis (3 m TXP column at 140 °C) of the concentrate showed the presence of 7,7-dichloronorcarane. Further concentration of the filtrate, followed by chromatography of the residue, gave [ClCCo$_3$(CO)$_9$] (0·87 g, 1·81 mmol, 31%) and [Co$_4$(CO)$_{12}$] (20 mg).

(c) *In the presence of a* 1 : 1 *molar mixture of methyl methacrylate and styrene.* A solution of bromotrichloromethane (3·02 g, 15·2 mmol), octacarbonyldicobalt (1·58 g, 4·62 mmol), methyl methacrylate (21·7 g, 0·22 mol), and styrene (22·6 g, 0·22 mol) in hexane (10 ml) was stirred at 40 °C for 1·5 h to give [ClCCo$_3$(CO)$_9$] (0·54 g, 1·13 mmol, 37%), and a 1 : 1 copolymer of methyl methacrylate and styrene (38·2 g, 86% recovery) identified by i.r. spectroscopy, solubility, and microanalysis. A pink solid (0·41 g) containing Co^{II}, Cl$^-$, and Br$^-$ ions was also isolated from the reaction mixture.

When this reaction was repeated in the presence of 1,1-diphenyl-2-picrylhydrazyl (1·8 g, 4·6 mmol) with bromotrichloromethane (2·53 g, 12·8 mmol), octacarbonyldicobalt (0·40 g, 1·17 mmol), methyl methacrylate (21·7 g, 0·22 mol), and styrene (22·6 g, 0·22 mol) stirred in hexane (20 ml) at 40 °C for 6 h, no copolymer formation occurred, and the only product was a black precipitate (1·21 g), which showed no metal carbonyl bands in its i.r. spectrum.

(d) *Under a pressure of carbon monoxide.*—A 300 ml stainless-steel autoclave was charged with bromotrichloromethane (1·61 g, 8·13 mmol), octacarbonyldicobalt (2·1 g, 6·14 mmol), and hexane (50 ml), pressurised to 50 atm with CO, and heated at 40 °C for 4 h with stirring. The product mixture was filtered to give a pink solid (0·70 g) containing Co^{II}, Br$^-$, and Cl$^-$ ions, and a violet filtrate shown to contain small amounts of tetrachloroethylene, and hexachloroethane, together with [ClCCo$_3$(CO)$_9$] (0.83 g, 1.74 mmol, 43%) and [Co$_4$(CO)$_{12}$] (0.19 g, 0.33 mmol, 11%).

Reaction of Octacarbonyldicobalt with Dibromodichloromethane.—(a) *In hexane.* When dibromodichloromethane (2·74 g, 11·3 mmol) was added to a solution of octacarbonyldicobalt (1·50 g, 4·39 mmol) in hexane (50 ml) at room temperature there was vigorous effervescence and precipitation of a green solid. The mixture was stirred for 2·0 h at 35 °C before filtration of the green precipitate (1·25 g), which turned pink on exposure to air, and was shown by analysis to contain Co^{II}, Br$^-$, and Cl$^-$ ions. Evaporation of the violet filtrate under reduced pressure and examination of the volatiles by g.l.c. showed the presence of tetrachloroethylene. Chromatographic separation of the involatile residue yielded [ClCCo$_3$(CO)$_9$] (0·58 g, 1·22 mmol, 42%) [Found: C, 25·4; H, 0·2%. *M*, 477 (mass spect.). Calc. for C$_{10}$O$_9$ClCo: C, 25·2; H, 0·0%. *M*, 477], identified by i.r. spectroscopy and m.p.

(b) *In the presence of cyclohexene.* Dibromodichloromethane (2·74 g, 11·3 mmol) and octacarbonyldicobalt (1·5 g, 4·39 mmol) in cyclohexene (40 ml) stirred at 35 °C for 2 h gave a dirty pink precipitate (1·25 g) and a product solution which was shown by g.l.c. analysis to contain 7,7-dichloronorcarane. Removal of the volatiles under reduced pressure gave a black-violet residue of [ClCCo$_3$(CO)$_9$] (0·46 g, 0·97 mmol, 33%) and [Co$_4$(CO)$_{12}$] (30 mg).

Reaction of Thallium Tetracarbonylcobaltate and Carbon

Tetrachloride.—(a) *In benzene.* Carbon tetrachloride (2·40 g, 15·6 mmol) was added to an orange solution of thallium tetracarbonylcobaltate (2·64 g, 7·04 mmol) in benzene (60 ml), which was then stirred at room temperature for 2·0 h to give a fawn precipitate (2·2 g) which contained Tl^+, Co^{2+}, and Cl^- ions. After filtration, the purple filtrate was concentrated under reduced pressure to afford $[ClCCo_3(CO)_9]$ (0·81 g, 1·7 mmol, 72%).

When a solution of thallium tetracarbonylcobaltate (2·39 g, 6·37 mmol) in benzene (50 ml) was added dropwise to a solution of carbon tetrachloride (2·40 g, 15·6 mmol) in benzene (30 ml) over a period of 0·5 h, and the mixture stirred at room temperature, a precipitate of cobalt(II) chloride (0·61 g) and thallium(I) chloride (1·46 g) was obtained. The filtrate was evaporated under reduced pressure to give a deep violet residue, which was taken up in the minimum amount of hexane and analysis by g.l.c. (3 m TXP column at 142 °C) showed the presence of hexachloroethane. Concentration of the hexane solution then yielded $[ClCCo_3(CO)_9]$ (0·20 g, 0·42 mmol, 20%). The volatile products and solvent stripped from the filtrate, were fractionally distilled and the high boiling residue was analysed by g.l.c. (2 m SE30 column at 76 °C) which showed the presence of tetrachloroethylene.

(b) *In the presence of octacarbonyldicobalt.* Carbon tetrachloride (6·72 g, 43·7 mmol) was added to a solution of thallium tetracarbonylcobaltate (2·04 g, 5·44 mmol) in benzene (50 ml), and after the solution had darkened with precipitation of thallium(I) chloride, a solution of octacarbonyldicobalt (3·7 g, 10·8 mmol) in benzene (40 ml) was added. The mixture was then stirred for 2 h at room temperature, and filtered to give a solid containing cobalt(II) chloride (0·72 g) and thallium(I) chloride (0·48 g). Concentration of the purple filtrate gave $[ClCCo_3(CO)_9]$ (1·45 g, 3·04 mmol, 56%).

(c) *In the presence of cyclohexene.* The dropwise addition of thallium tetracarbonylcobaltate (2·14 g, 5·71 mmol) in benzene (40 ml) to a solution of carbon tetrachloride (2·40 g, 15·6 mmol) in cyclohexene (10 ml) at room temperature gave cobalt(II) chloride (0·54 g) and thallium(I) chloride (1·12 g) after 1 h. After filtration, the filtrate was concentrated to 5 ml and analysis of this by g.l.c. (3 m TXP column at 142 °C) indicated the presence of 7,7-dichloronorcarane. Further concentration of the solution gave $[ClCCo_3(CO)_9]$ (0·19 g, 0·40 mmol, 21%).

(d) *In the presence of a* 1 : 1 *molar mixture of methyl methacrylate and styrene.* A solution of thallium tetracarbonylcobaltate (2·26 g, 6·03 mmol) in benzene (40 ml) was added to a solution containing carbon tetrachloride (2·40 g, 15·6 mmol), methyl methacrylate (21·7 g, 0·22 mol), and styrene (22·6 g, 0·22 mol) at room temperature, and the mixture was stirred for 3 h to give a purple precipitate. This was taken up in acetone, and hexane was added dropwise to the solution to precipitate a mixture of white and pink solids, which was filtered to give a purple filtrate. Concentration of the filtrate yielded $[ClCCo_3(CO)_9]$ (0·16 g, 0·34 mmol, 17%). Chloroform was added to the mixture of white and pink solids to give a suspension which was filtered and shown to be a mixture of cobalt(II) chloride (0·48 g) and thallium(I) chloride (1·16 g). Methanol was added to the colourless filtrate to give a white solid, 1 : 1 copolymer of methyl methacrylate and styrene (31·1 g, 70% recovery) (Found: C, 74·7; H, 8·1. Calc. for 1 : 1 copolymer: C, 76·2; H, 7·9%).

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