Metal Carbonyl Chemistry. Part 27.[1] Formation of $[Co_3(CCl)(CO)_9]$ by Reaction of the Carbene Precursor $Hg(CCl_3)Ph$ with Octacarbonyldicobalt

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Octacarbonyldicobalt reacts with the dichlorocarbene precursor $Hg(CCl_3)Ph$ at 60 °C in hexane to afford $[Co_3(CCl)(CO)_9]$ in 49% yield. A similar yield of this complex is also obtained at 30 °C, *i.e.* under conditions where appreciable thermal decomposition of $Hg(CCl_3)Ph$ to HgPhCl and CCl_2 does not occur. Trapping experiments using cyclohexene have demonstrated that under both sets of conditions dichlorocarbene is formed. Possible mechanisms to explain the formation of the carbene and $[Co_3(CCl)(CO)_9]$ are discussed.

DICHLOROCARBENE has been detected recently as one of the intermediates formed when octacarbonyldicobalt and the polyhalogenomethanes CCl_4, $CBrCl_3$, or CBr_2Cl_2 react in the non-polar solvent hexane to give the nonacarbonylmethylidynetricobalt cluster complex $[Co_3(CCl)(CO)_9]$ as the major product.[2] In an effort to clarify the mechanistic role of the carbene in the formation of the cluster complex we have investigated the reactions of $[Co_2(CO)_8]$ with the carbene precursor $Hg(CCl_3)Ph$.

The only previous report of a reaction between these two compounds describes reactions carried out in the donor solvents, acetone or tetrahydrofuran, which have been shown to yield $Hg[Co(CO)_4]_2$, Ph_2CO, $CHCl_3$, $CoCl_2$, and only a very small amount of $[Co_3(CCl)(CO)_9]$, together with carbon monoxide.[3] This reaction has not been investigated in any detail, but it is suggested that the appreciable concentration of $[Co(CO)_4]^-$ present under these conditions may lead to nucleophilic displacement of $^-CCl_3$ from $Hg(CCl_3)Ph$, thus giving rise to $CHCl_3$. This, on reaction with $[Co_2(CO)_8]$, could explain the low yield of $[Co_3(CCl)(CO)_9]$ observed.[4] In this present work the reactions were all carried out in hexane, *i.e.* under conditions where disproportionation to $[Co(CO)_4]^-$ is impossible, and a different mechanistic pathway might be anticipated.

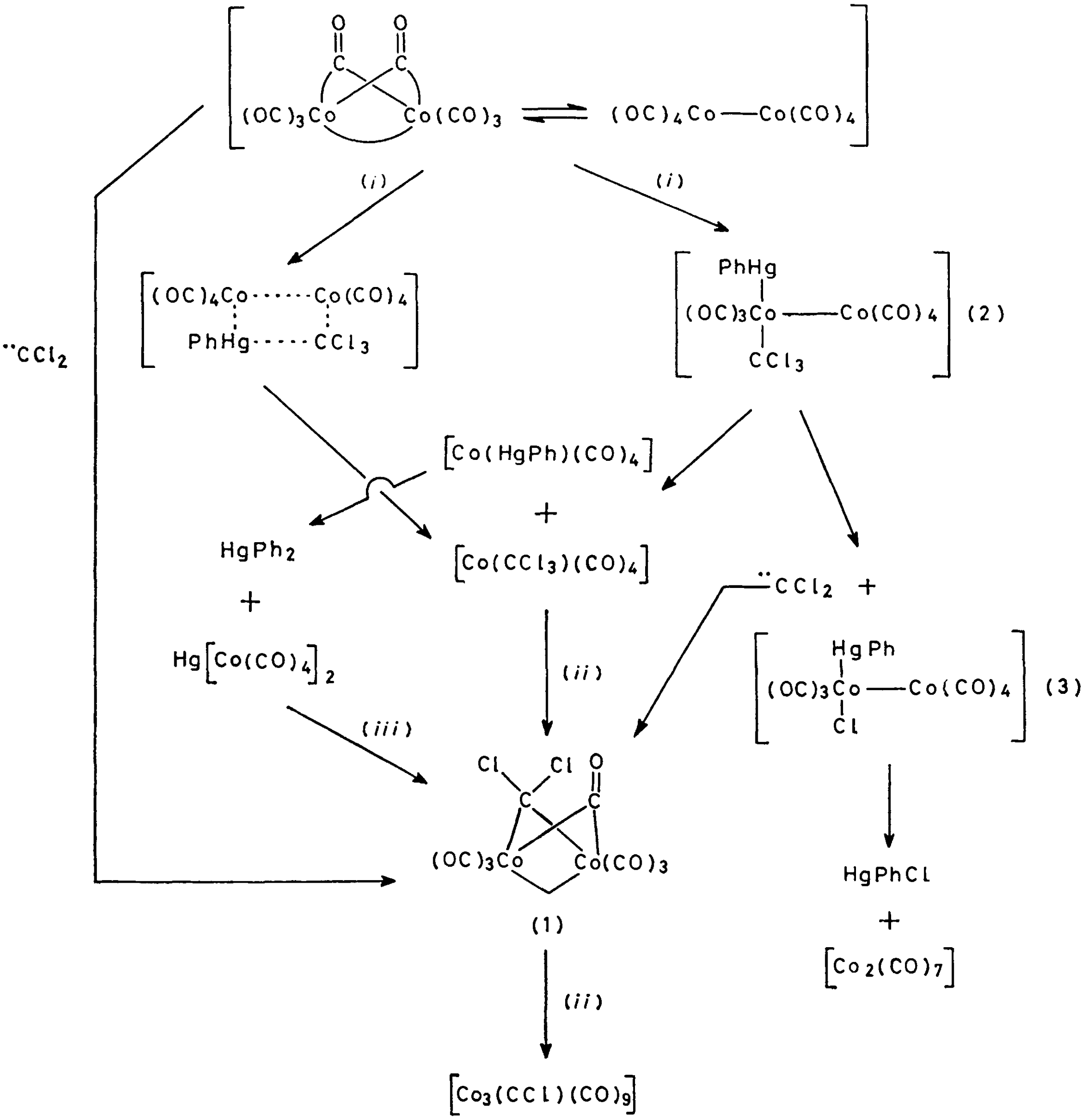
RESULTS AND DISCUSSION

After stirring a mixture of $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$ at 60 °C for 2 h the major product was found to be $[Co_3(CCl)(CO)_9]$ (49%), together with $CoCl_2$, $HgCl_2$, and some $[Co_4(CO)_{12}]$ (15%), which is always formed to some extent on heating $[Co_2(CO)_8]$. Unlike the reaction in polar solvents no $Hg[Co(CO)_4]_2$ was detected among the products. When this reaction was repeated under similar conditions but in the presence of an excess of the carbene trap cyclohexene the yield of $[Co_3(CCl)(CO)_9]$ was reduced to 16%, and 7,7-dichloronorcarane was detected among the products by g.l.c. analysis. Other products of the reaction included $CoCl_2$, $HgCl_2$, HgPhCl (7%), and $HgPh_2$ (8%). The formation of the norcarane and the reduced yield of the cluster complex is evidence that at 60 °C not only is dichlorocarbene being generated by thermal decomposition of $Hg(CCl_3)Ph$, but that the carbene may be involved in cluster formation.

As a further check the reaction between $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$ was repeated at the lower temperature of 30 °C. A control experiment using $Hg(CCl_3)Ph$ in the presence of cyclohexene showed that at this temperature there was no observable dissociation to give dichlorocarbene, and it was confidently anticipated that the reaction with $[Co_2(CO)_8]$ would not lead to cluster formation at this lower temperature. Surprisingly, not only was $[Co_3(CCl)(CO)_9]$ formed, but the yield (51%) was comparable to that obtained at the higher temperature. A careful examination of the reaction products showed the presence of $CoCl_2$, $HgCl_2$, HgPhCl (6%), and $HgPh_2$ (8%), together with a trace of the dichlorocarbene dimerisation product, tetrachloroethylene. Furthermore, when this reaction was repeated at 30 °C but in the presence of an excess of cyclohexene the yield of $[Co_3(CCl)(CO)_9]$ (44%) was not markedly affected, although 7,7-dichloronorcarane was detected among the reaction products, confirming the formation of dichlorocarbene.

In separate experiments it has also been demonstrated that the mixture of $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$ in hexane at both 60 and 30 °C is capable of initiating the polymerisation of a 1 : 1 molar mixture of styrene and methyl methacrylate; under similar conditions neither $Hg(CCl_3)Ph$ nor $[Co_2(CO)_8]$ alone cause polymerisation to occur. The yield of $[Co_3(CCl)(CO)_9]$ (43% at 60 °C; 38% at 30 °C) is only slightly affected, if at all, by the presence of the monomers, bearing in mind the experimental difficulties of isolating the cluster from the polymerised product mixture. The characterisation of the polymer from the reaction at 60 and at 30 °C as a 1 : 1 copolymer confirms a free-radical initiation step.[5] Further evidence of this is provided by the fact that when these reactions were repeated under similar conditions, but in the presence of a three-fold excess of the radical scavenger 1,1-diphenyl-2-picrylhydrazyl, polymerisation was inhibited. From these results it is apparent that the interaction of $Hg(CCl_3)Ph$ with $[Co_2(CO)_8]$ both at 60 and 30 °C gives rise to an intermediate or intermediates which readily undergo homolysis to form $^{\bullet}CCl_3$, $Cl^{\bullet}$, $Ph^{\bullet}$, or $^{\bullet}Co(CO)_4$ radicals. It is striking that in every respect these reactions very closely resemble the reactions of $[Co_2(CO)_8]$ with polyhalogenomethanes investigated previously,[2] suggesting that similar intermediates may be involved in both cases.

At 60 °C it is known[6] that $Hg(CCl_3)Ph$ undergoes appreciable dissociation into $^{\cdot\cdot}CCl_2$ and HgPhCl. The marked reduction in the yield of $[Co_3(CCl)(CO)_9]$ when this reaction is carried out in the presence of cyclohexene may indicate that, in the main, cluster formation arises by direct reaction of the carbene with $[Co_2(CO)_8]$, possibly *via* the dichloromethylene-bridged intermediate [(1), see Scheme] proposed previously for the reaction between $[Co_2(CO)_8]$ and polyhalogenomethanes.[2] At 30 °C, since the yield of $[Co_3(CCl)(CO)_9]$ is unaffected by the presence of the carbene trap, and $Hg(CCl_3)Ph$ does not dissociate at this lower temperature, cluster formation must arise by direct interaction of $Hg(CCl_3)Ph$ with $[Co_2(CO)_8]$. Although dichlorocarbene may be involved in cluster formation at the higher temperature the evidence is not entirely unambiguous. If the decomposition of $Hg(CCl_3)Ph$ at this temperature is reversible, as has been demonstrated for $Hg(CBrCl_2)Ph$[6] the reduced yield of cluster in the presence of cyclohexene could simply reflect a reduced concentration of $Hg(CCl_3)Ph$ caused by efficient trapping of the dichlorocarbene by the cyclohexene.* Two possible mechanistic pathways for the reaction between $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$ are outlined in the Scheme. The first involves a four-centre reaction between the mercury compound and $[Co_2(CO)_8]$ to afford the unstable intermediates $[Co(CCl_3)(CO)_4]$ and $[Co(HgPh)(CO)_4]$. This reaction resembles that between HgPhCl and $[Mn(SnMe_3)(CO)_5]$ which is reported to form $SnMe_3Cl$ and $[Mn(HgPh)(CO)_5]$; the latter rapidly disproportionates to $HgPh_2$ and $Hg[Mn(CO)_5]_2$.[7] Alternatively, oxidative addition of $Hg(CCl_3)Ph$ to $[Co_2(CO)_8]$ could occur to give the intermediate [(2), see Scheme]. This could either decompose



SCHEME (*i*) $Hg(CCl_3)Ph$; (*ii*) $[Co_2(CO)_8]$; (*iii*) $[Co(CCl_3)(CO)_4]$

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to the same intermediates, $[Co(CCl_3)(CO)_4]$ and $[Co(HgPh)(CO)_4]$, or it could decompose *via* a 1,2-chlorine shift with elimination of dichlorocarbene to form intermediate (**3**), which might be expected to undergo further breakdown as shown in the Scheme. An oxidative-addition mechanism would require loss of a CO ligand from $[Co_2(CO)_8]$. Attempts to differentiate between the two mechanistic pathways by carrying out the reactions between $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$ at both 30 and 65 °C under a pressure of 50 atm * of carbon monoxide gave $[Co_3(CCl)(CO)_9]$ in yields of 44 and 41% respectively. These yields are not significantly lower than those obtained under an atmosphere of nitrogen. This indicates that CO dissociation is not the rate-limiting step during cluster formation.

The key intermediates formed by both routes are the compounds $[Co(CCl_3)(CO)_4]$ and $[Co(HgPh)(CO)_4]$. There is some evidence to suggest that both these compounds would be unstable under the conditions employed. A previous attempt [2] to prepare $[Co(CCl_3)(CO)_4]$ by the reaction of $Tl[Co(CO)_4]$ with CCl_4 in benzene resulted in the rapid formation of $[Co_3(CCl)(CO)_9]$, TlCl, and $CoCl_2$ together with some tetrachloroethylene and hexachloroethane. The tetrachloroethylene is probably formed by a 1,2-chlorine shift to give $^{\bullet\bullet}CCl_2$ and unstable $[CoCl(CO)_4]$, while hexachloroethane may arise by homolysis to form $^{\bullet}CCl_3$ and $[Co(CO)_4]^{\bullet}$ radicals. Decomposition of $[Co(CCl_3)(CO)_4]$ in the presence of $[Co_2(CO)_8]$ has been shown [2] to give a high yield of $[Co_3(CCl)(CO)_9]$, possibly *via* an intermediate such as (**1**), again with formation of $[CoCl(CO)_4]$, which is known [8] to decompose above −40 °C to $CoCl_2$ and CO. The second, key intermediate $[Co(HgPh)(CO)_4]$ has never been isolated, and attempts to prepare it by the reaction of HgBrPh and $Na[Co(CO)_4]$ have resulted in high yields of the disproportionation products $HgPh_2$ and $Hg[Co(CO)_4]_2$.[3,4] A similar disproportionation reaction has also been observed to occur with $[Co(HgMe)(CO)_4]$ [9] and $[Mo(\eta\text{-}C_5H_5)(HgMe)(CO)_3]$.[10] Although $HgPh_2$ is detected among the products of reaction between $Hg(CCl_3)Ph$ and $[Co_2(CO)_8]$, there was no evidence for the other disproportionation product $Hg[Co(CO)_4]_2$. This suggested the possibility that $Hg[Co(CO)_4]_2$, like $[Co_2(CO)_8]$, might be capable of reaction with $[Co(CCl_3)(CO)_4]$ to form $[Co_3(CCl)(CO)_9]$ and $HgCl_2$. Support for this idea was obtained by the dropwise addition of a solution of $Tl[Co(CO)_4]$ in benzene to a solution of CCl_4 and $Hg[Co(CO)_4]_2$ in benzene at room temperature which gave $[Co_3(CCl)(CO)_9]$ in 45% yield based on the *total* available cobalt. A control experiment has shown that $Hg[Co(CO)_4]_2$ does not react with CCl_4 to form $[Co_3(CCl)(CO)_9]$ under these conditions. Even in the unlikely event that the reaction between $Tl[Co(CO)_4]$ and CCl_4 gives a quantitative conversion into $[Co_3(CCl)(CO)_9]$ this would only account for a 31% yield of the cluster. Thus, a substantial amount of the $[Co_3(CCl)(CO)_9]$ formed must arise by reaction of $[Co(CCl_3)(CO)_4]$ with $Hg[Co(CO)_4]_2$.

From these investigations it is apparent that members of two very different classes of compounds, $Hg(CCl_3)Ph$ and polyhalomethanes, react with octacarbonyldicobalt in apolar solvents by similar mechanistic pathways involving the intermediacy of the compound $[Co(CCl_3)(CO)_4]$.

EXPERIMENTAL

Except where stated, all reactions were carried out under an atmosphere of dry nitrogen. Phenyl(trichloromethyl)mercury [6] was a commercial sample used without further purification; octacarbonyldicobalt was recrystallised from pentane prior to use. All solvents were dried by recommended procedures. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, and g.l.c. analyses were carried out on a Pye 104 gas chromatograph using Florisil. All yields of cobalt complexes are based on cobalt.

Reactions at 60 °C.—(a) *In hexane.* Phenyl(trichloromethyl)mercury (1.04 g, 2.6 mmol) was added to a solution of octacarbonyldicobalt (0.40 g, 1.17 mmol) in hexane (100 cm^3), and the solution stirred at 60 °C for 2 h. The product mixture was filtered to give a dirty pink solid shown by qualitative elemental analysis to contain Co^{II} and Cl^- ions. Concentration of the filtrate followed by chromatography, using hexane as eluant, gave $[Co_3(CCl)(CO)_9]$ (0.18 g, 0.39 mmol, 49%) as a black-violet solid purified by vacuum sublimation, and identified by its m.p. and i.r. spectrum. Further elution with hexane afforded $[Co_4(CO)_{12}]$ (51 mg, 0.09 mmol, 15%).

(b) *In the presence of cyclohexene.* Phenyl(trichloromethyl)mercury (1.04 g, 2.60 mmol), $[Co_2(CO)_8]$ (0.88 g, 2.57 mmol), cyclohexene (30 cm^3), and hexane (15 cm^3) were stirred at 60 °C for 3 h to give a brown precipitate and a violet solution. Extraction of the brown solid with cold water and analysis of the pink aqueous extract showed the presence of $CoCl_2$. Further extraction with boiling water gave $HgCl_2$ leaving a grey solid residue, which was separated by t.l.c. (benzene eluant) into diphenylmercury (75 mg, 0.21 mmol, 8%), m.p. 122 °C (lit.,[11] 123—124 °C), and phenylmercury(II) chloride (60 mg, 0.19 mmol, 7%), m.p. 257 °C (lit.,[11] 258—259 °C). The violet filtrate was concentrated under reduced pressure, and g.l.c. analysis (3 m TXP column at 140 °C) of the concentrated solution showed the presence of 7,7-dichloronorcarane. Further concentration gave a violet residue of $[Co_3(CCl)(CO)_9]$ (55 mg, 0.12 mmol, 15%).

(c) *In the presence of a* 1 : 1 *molar mixture of methyl methacrylate and styrene.* A solution of $[Co_2(CO)_8]$ (0.80 g, 2.34 mmol), $Hg(CCl_3)Ph$ (2.08 g, 5.20 mmol), methyl methacrylate (21.7 g, 0.22 mol), and styrene (22.6 g, 0.22 mol) in hexane (10 cm^3) was stirred at 60 °C for 2 h to give a brown solid, which dissolved in acetone to give a purple-brown solution. Careful treatment of this solution with hexane yielded a blue-white precipitate and a violet solution which were separated by filtration. Addition of chloroform to the blue-white solid afforded a pink suspension (1.10 g) which contained 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 (32.4 g, 73%) identified by solubility, i.r. spectroscopy, and analysis (Found: C, 75.4; H, 8.0. Calc. for 1 : 1 copolymer: C, 76.2; H, 7.9%). The violet solution was concentrated and chromatographed to yield $[Co_3(CCl)(CO)_9]$ (0.21 g, 0.66 mmol, 43%) and $[Co_4(CO)_{12}]$ (30 mg).

(d) *In the presence of* 1,1-*diphenyl*-2-*picrylhydrazyl.*

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* Throughout this paper: 1 atm = 101 325 Pa.

Phenyl(trichloromethyl)mercury (1.10 g, 3.50 mmol), $[Co_2(CO)_8]$ (0.40 g, 1.17 mmol), and 1,1-diphenyl-2-picrylhydrazyl (1.80 g, 4.60 mmol) were stirred in hexane (40 cm^3) at 60 °C for 4 h to give a black precipitate (1.8 g) which showed no metal carbonyl bands in its i.r. spectrum. Filtration, evaporation of the purple filtrate, and chromatography of the residue gave 1,1-diphenyl-2-picrylhydrazyl (20 mg) and $[Co_4(CO)_{12}]$ (10 mg).

(*e*) *Under a pressure of carbon monoxide.* A solution of $[Co_2(CO)_8]$ (1.84 g, 5.4 mmol) and $Hg(CCl_3)Ph$ (2.1 g, 5.3 mmol) in hexane (40 cm^3) was placed into a stainless-steel autoclave (300 cm^3), which was then pressurized to 50 atm with carbon monoxide and heated with stirring at 65 °C for 5 h. The product mixture was filtered to give a grey-pink solid shown to consist of a mixture of $CoCl_2$ and $HgCl_2$ (0.61 g), $HgPh_2$ (0.11 g, 0.31 mmol, 6%), and HgPhCl (61 mg, 0.19 mmol, 4%). The violet filtrate was evaporated under reduced pressure and the volatiles were collected at −196 °C. The residue consisted of $[Co_3(CCl)(CO)_9]$ (0.71 g, 1.49 mmol, 41%) and $[Co_4(CO)_{12}]$ (0.12 g, 0.21 mmol, 8%) separated by chromatography (hexane eluant). Fractional distillation of the volatiles and g.l.c. analysis (2 m SE 30 column at 70 °C) of the highest boiling fraction showed the presence of tetrachloroethylene (0.11 mmol).

Reactions at 30 °C.—(*a*) *In hexane.* A solution of $[Co_2(CO)_8]$ (1.8 g, 5.3 mmol) and $Hg(CCl_3)Ph$ (2.08 g, 5.2 mmol) in hexane (50 cm^3) was stirred for 5 h at 30 °C to give a violet solution and grey-brown precipitate, which on filtration and work-up as described previously was found to consist of a mixture of a $CoCl_2$, $HgCl_2$, HgPhCl (0.09 g, 0.27 mmol, 6%), and $HgPh_2$ (0.14 g, 0.04 mmol, 8%). The violet solution was concentrated by removal and collection of the volatile liquids. Chromatography (pentane eluant) of the involatile residue yielded $[Co_3(CCl)(CO)_9]$ (0.86 g, 1.8 mmol, 51%). G.l.c. analysis (2m SE 30 column at 70 °C) of the volatiles after fractional distillation showed tetrachloroethylene (0.11 mmol).

(*b*) *In presence of cyclohexene.* When $Hg(CCl_3)Ph$ (2.10 g, 5.30 mmol), $[Co_2(CO)_8]$ (1.80 g, 5.30 mmol), cyclohexene (30 cm^3), and hexane (20 cm^3) were stirred at 30 °C for 5 h the products were a brown solid mixture of $CoCl_2$ and $HgCl_2$ (0.62 g), HgPhCl (90 mg, 0.29 mmol, 5%), and $HgPh_2$ (0.12 g, 0.34 mmol, 6%) and a violet solution. Concentration of the latter under vacuum and g.l.c. analysis (3m TXP column at 140 °C) of the concentrate showed the presence of 7,7-dichloronorcarane. Evaporation to dryness gave a violet residue of $[Co_3(CCl)(CO)_9]$ (0.74 g, 0.55 mmol, 44%).

(*c*) *In the presence of methyl methacrylate and styrene.* A mixture of $[Co_2(CO)_8]$ (1.8 g, 5.3 mmol), $Hg(CCl_3)Ph$ (2.1 g, 5.3 mmol), methyl methacrylate (21.7 g, 0.22 mol), styrene (22.6 g, 0.22 mol), and hexane (15 cm^3) was stirred at 30 °C for 2.0 h to give a 1 : 1 copolymer of methyl methacrylate and styrene (34.8 g, 79%) (Found: C, 74.5; H, 8.0. Calc. for 1 : 1 copolymer: C, 76.2; H, 7.9%), $[Co_3(CCl)(CO)_9]$ (0.69 g, 1.45 mmol, 38%), and $CoCl_2$ (0.84 g).

(*d*) *In the presence of* 1,1-*diphenyl*-2-*picrylhydrazyl.* Reaction between $Hg(CCl_3)Ph$ (1.10 g, 3.50 mmol), $[Co_2(CO)_8]$ (0.40 g, 1.17 mmol), and 1,1-diphenyl-2-picrylhydrazyl (1.80 g, 4.60 mmol) in hexane (40 cm^3) at 30 °C for 4 h gave a black solid (1.9 g) which showed no metal carbonyl bands in its i.r. spectrum. Only 1,1-diphenyl-2-picrylhydrazyl (30 mg) was recovered.

(*e*) *Under a pressure of carbon monoxide.* A mixture of $[Co_2(CO)_8]$ (1.84 g, 5.4 mmol) and $Hg(CCl_3)Ph$ (2.1 g, 5.3 mmol) in hexane (40 cm^3) was stirred at 30 °C for 5 h in a stainless-steel autoclave pressurized to 50 atm with carbon monoxide. The products were identified as $CoCl_2$ and $HgCl_2$ (0.57 g), $HgPh_2$ (0.16 g, 0.05 mmol, 9%), HgPhCl (0.14 g, 0.45 mmol, 8%), and $[Co_3(CCl)(CO)_9]$ (0.71 g, 1.59 mmol, 44%). Tetrachloroethylene (0.06 mmol) was also detected by g.l.c. analysis.

Reaction of $Tl[Co(CO)_4]$ *with* CCl_4 *in the Presence of* $Hg[Co(CO)_4]_2$.—An orange solution of $Tl[Co(CO)_4]$ (3.41 g, 9.08 mmol) in benzene (50 cm^3) was added dropwise to a solution of carbon tetrachloride (1.60 g, 10.4 mmol) and $Hg[Co(CO)_4]_2$ (5.50 g, 10.1 mmol) in benzene (50 cm^3) over a period of 0.5 h, and the reaction mixture was stirred at room temperature for 1.0 h. A pink solid product was filtered, washed with hexane, and shown to contain a mixture of $CoCl_2$, TlCl, and $HgCl_2$. The purple filtrate was concentrated and chromatographed to give $[Co_3(CCl)(CO)_9]$ (2.10 g, 4.40 mmol, 45%) on elution with hexane. Further elution with benzene gave $Hg[Co(CO)_4]_2$ (1.80 g, 3.30 mmol, 33%).

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