Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF DICOBALT OCTACARBONYL AND RELATED COMPOUNDS WITH *gem*-DIHALIDES

DIETMAR SEYFERTH and MICHELLE D. MILLAR*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (*U.S.A.*)

(Received December 2nd, 1971)

SUMMARY

Dicobalt octacarbonyl and some of its derivatives ($NaCo(CO)_4$, $Co_4(CO)_{12}$, $Hg[Co(CO)_4]_2$, $[Co(CO)_3PPh_3]_2$, $NaCo(CO)_3PPh_3$) react with activated *gem*-dihalides, R_2CX_2, such as dichlorodiphenylmethane, 9,9-dihalofluorenes and dimethyl dibromomalonate, to give the "dimer" olefin, $R_2C{=}CR_2$. The course of this conversion involves formation of the coupling product, $R_2XC{-}CXR_2$, followed by dehalogenation of the latter. These separate steps have been confirmed for activated monohalides (bromodiphenylmethane, 9-bromofluorene, dimethyl bromomalonate) which were readily coupled by cobalt carbonyls, and for activated vicinal dihalides (D,L and *meso*-dibromostilbene, 9,9'-dichlorobisfluorenyl) which cobalt carbonyls readily dehalogenated. A radical mechanism is favored for these processes, and indirect evidence in its favor is presented.

INTRODUCTION

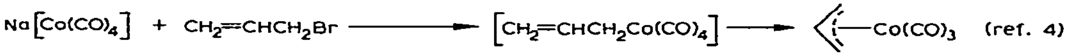
During the course of a study of reactions of organomercury compounds with dicobalt octacarbonyl[1], we had occasion to investigate the reaction of benzyl bromide with $NaCo(CO)_4$ in THF[1c]. The major product, dibenzyl ketone, was the expected one, but a second product, 1,2-diphenylethane (10% yield), also was present. While the formation of the ketone most probably occurred via organocobalt intermediates [$PhCH_2Co(CO)_4$ and $PhCH_2COCo(CO)_4$], it was by no means clear how the coupled hydrocarbon product could have been produced. This reaction aroused our interest in the general topic of reactions of dicobalt octacarbonyl and related compounds with organic halides.

It is well known that dicobalt octacarbonyl and the $Co(CO)_4^-$ anion react with a wide variety of organo trihalides, RCX_3, and with carbon tetrahalides, to give organocobalt cluster complexes, the methylidynetricobalt nonacarbonyls, $RCCo_3(CO)_9$[2]. Reactions of certain organic monohalides with $Co(CO)_4^-$ or $Co_2(CO)_8$ have been reported to give the rather unstable organocobalt tetracarbonyls or secondary products derived from these, *e.g.*:

---

* National Institutes of Health Predoctoral Fellow.

$$Na[Co(CO)_4] + CH_3I \longrightarrow CH_3Co(CO)_4 \quad \text{(ref. 3)}$$


(ref. 4)

$$Na[Co(CO)_4] + PhCH_2Br \longrightarrow PhCH_2Co(CO)_4 \; [\longrightarrow (PhCH_2)_2C{=}O]$$

Only one *gem*-dihalide seems to have been treated with dicobalt octacarbonyl: hexachlorocyclopropane, and this reaction gave a complex organocobalt product in a reaction which may be considered atypical[5]. In view of the lack of information concerning the interaction of *gem*-dihalides with dicobalt octacarbonyl, we felt that an investigation of such reactions might be of interest.

Some information concerning reactions of other metal carbonyls with *gem*-dihalides had been reported by Coffey[6] in 1961. Thus, the action of iron pentacarbonyl on dichlorodiphenylmethane gave tetraphenylethylene in 95% yield [based on eqn. (4)]. The reaction progressed through several highly colored stages and it was

$$2\,Fe(CO)_5 + 2\,Ph_2CCl_2 \rightarrow 10\,CO + FeCl_2 + Ph_2C{=}CPh_2 \tag{4}$$

suggested by Coffey that a carbene intermediate might be involved in this reaction. This olefin synthesis was extended to reactions of $Fe(CO)_5$ with various substituted dichlorodiphenylmethanes and with 9,9-dibromofluorene. However, it was by no means a general reaction and was not observed to occur with many other halides, including carbon tetrachloride, ethyl dibromoacetate, benzotrichloride, chloroform, 2,2-dibromopropane, dichloromethane, diiodomethane, benzyl chloride, benzal chloride, trityl chloride, 1,2-dibromo-1,2-diphenylethane or allyl chloride. Among other metal carbonyls which converted dichlorodiphenylmethane to tetraphenylethylene were $(C_5H_5N)_2W(CO)_4$, $Ni(CO)_4$, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and $HgFe(CO)_4$. Dicobalt octacarbonyl was not examined.

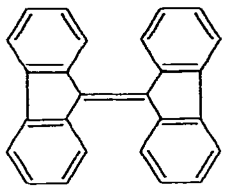
RESULTS AND DISCUSSION

The initial reaction studied was that of dicobalt octacarbonyl with dichlorodiphenylmethane (1/2 molar ratio) in THF at 50°. This reaction produced tetraphenylethylene in 98% yield, based on eqn. (5). Benzene served equally well as reaction solvent. Other cobalt carbonyl derivatives were found to be equally effective as

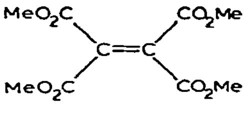
$$2\,Ph_2CCl_2 + Co_2(CO)_8 \rightarrow Ph_2C{=}CPh_2 + 8\,CO + 2\,CoCl_2 \tag{5}$$

reagents for this conversion of dichlorodiphenylmethane to tetraphenylethylene: sodium tetracarbonylcobaltate(−I), mercury bis(tetracarbonylcobaltate), bis[tricarbonyl(triphenylphosphine)cobalt] and tetracobalt dodecarbonyl. The mercury derivative was especially effective when the reaction mixture was irradiated with ultraviolet light (*cf.* ref. 1b).

9,9-Dibromofluorene reacted with dicobalt octacarbonyl to produce bifluorenylidene (I) in high yield, and a similar reaction with dimethyl dibromomalonate gave tetracarbomethoxyethylene (II) in 93% yield. Other *gem*-dihalides which were examined included the following which did not react with dicobalt octacarbonyl in THF: 7,7-dichloro- and 7,7-dibromonorcarane, 2,2-dichloro-1,1,1,3,3,3-hexafluoro-



(I)

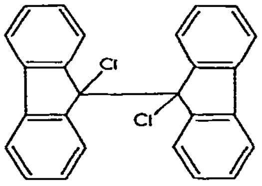


(II)

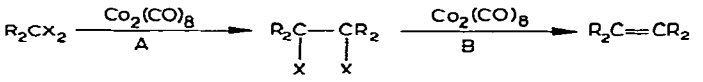
propane, 1,1-dibromo-2,2-diphenylethylene, and the following which reacted quite vigorously but from whose reaction mixtures the expected olefin "dimers" could not be isolated: $PhCCl_2CH_3$, $PhCBr_2CH_3$, $PhCBr_2SiMe_3$, $Br_2C(CN)_2$ and $Cl_2C(COCH_3)_2$.

Although the conversion of *gem*-dihalides to olefins via dicobalt octacarbonyl and its derivatives appears to be a reaction of limited scope, it was of interest to learn more about the nature of the reactions involved. In particular, the question of possible carbene or carbene–cobalt complex intermediates was an intriguing one in view of the intense research activity in the area of transition metal–carbene complexes during recent years.

The possibility of the intervention of carbene complexes was soon disposed of when it was found that 9,9-dichlorofluorene (2 molar equivalents) reacted with dicobalt octacarbonyl (1 molar equivalent) to give two products: the expected olefin (I) (41% yield), and also 9,9'-dichlorobisfluorenyl, (III), in 38% yield. The formation of (I) in high yield from 9,9-dibromofluorene and the formation of a mixture of (I) and (III) from 9,9-dichlorofluorene suggested to us that the 9,9'-dihalobisfluorenyls very likely are intermediates in the 9,9-dihalofluorene-to-(I) conversion. An independent experiment confirmed that the action of $Co_2(CO)_8$ in 50% excess on (III) (in THF at 50°) results in dechlorination of the latter, giving (I) in 86% yield. Thus, the course of the reactions which we report would appear to be that shown in eqn. (6).

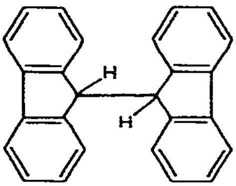


(III)



$$R_2CX_2 \xrightarrow[A]{Co_2(CO)_8} \underset{X}{\underset{|}{R_2C}}-\underset{X}{\underset{|}{CR_2}} \xrightarrow[B]{Co_2(CO)_8} R_2C{=}CR_2 \qquad (6)$$

It was a simple coupling side-reaction ($PhCH_2Br \rightarrow PhCH_2CH_2Ph$) which aroused our interest in this area, and further experiments now showed that such $Co_2(CO)_8$-induced coupling of organic monohalides becomes the main reaction when the halides bear two aryl substituents instead of only one. For example, reaction of bromodiphenylmethane with dicobalt octacarbonyl gave $Ph_2CHCHPh_2$ in 81% yield, while the action of dicobalt octacarbonyl on 9-bromofluorene resulted in formation of (IV) in 67% yield. In similar fashion, $(MeO_2C)_2CHCH(CO_2Me)_2$ was formed in 41% yield by reaction of dimethyl bromomalonate with dicobalt octacarbonyl.



(IV)

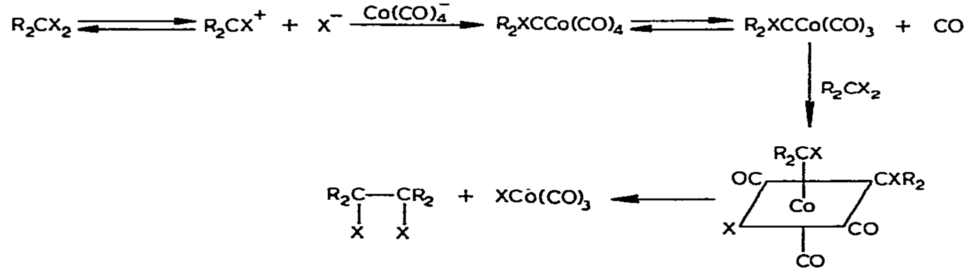
Thus, it seems reasonable to assume that the coupling reaction (A) is the first step in the $R_2CX_2/Co_2(CO)_8$ reaction.

The second step, dehalogenation of a vicinal dihalide, also occurs readily with suitably activated compounds. In one example, *meso*-1,2-dibromostilbene was converted to *trans*-stilbene in 93% yield by the action of dicobalt octacarbonyl in THF. Similar dehalogenation could be achieved in 93% yield using $NaCo(CO)_4$. D,L-Dibromostilbene also gave *trans*-stilbene (91%) on debromination with $Co_2(CO)_8$.

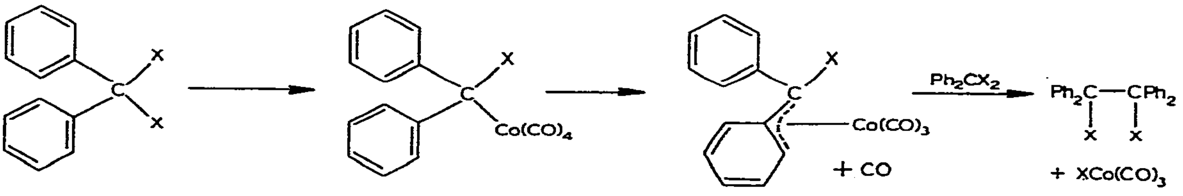
These experiments thus have provided evidence which supports the reaction course shown in eqn. (6). It now became of interest to learn more about the nature of the interaction of the activated organic mono- and dihalides and cobalt carbonyl compounds. First, we note that the reactive species in THF most probably is the $Co(CO)_4^-$ anion. Its sodium salt by itself is capable of causing this coupling–dehalogenation sequence. In THF solution, $Co_2(CO)_8$ also is a source of the $Co(CO)_4^-$ anion through its solvent-induced redox disproportionation (ref. 1a and references cited therein), and it is quite likely that $Hg[Co(CO)_4]_2$ and $Co_4(CO)_{12}$ also give this ion on reaction with THF.

We considered the possibility of at least three types of reaction which in principle could lead to the observed coupled products from activated *gem*-dihalides.

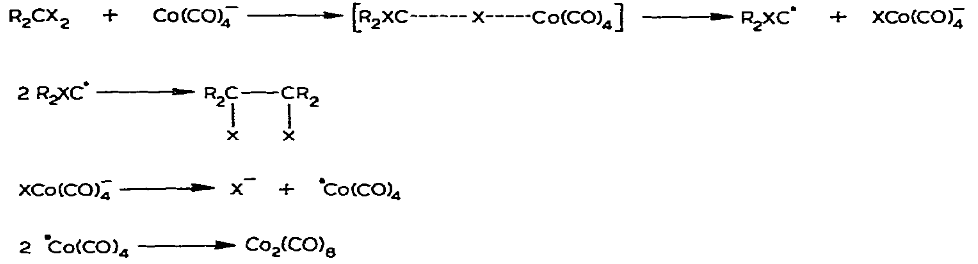
(1). A polar mechanism, most likely of the S_N1 type in view of the apparent restrictions on R in R_2CX_2 for a successful coupling reaction. The formation of the coupled product occurs in an oxidative addition–elimination sequence after formation of an organocobalt intermediate:



(2). A variation of (1), in which a π-benzyl or π-oxapropenyl species is an intermediate:



(3). A radical mechanism involving atom transfer from carbon to cobalt in the initial step:



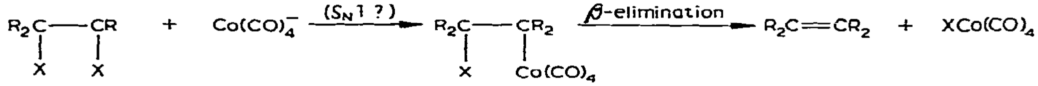
$$R_2CX_2 + Co(CO)_4^- \longrightarrow [R_2XC\text{-----}X\text{-----}Co(CO)_4]^- \longrightarrow R_2XC^{\bullet} + XCo(CO)_4^-$$

$$2\,R_2XC^{\bullet} \longrightarrow R_2C(X)\text{—}CR_2(X)$$

$$XCo(CO)_4^- \longrightarrow X^- + {}^{\bullet}Co(CO)_4$$

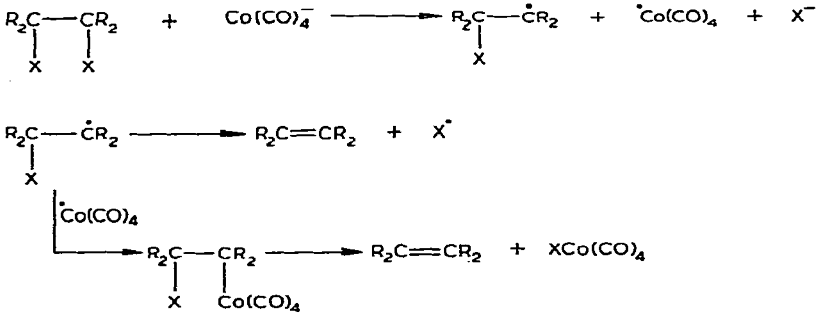
$$2\,{}^{\bullet}Co(CO)_4 \longrightarrow Co_2(CO)_8$$

This mechanism is analogous to those proposed for the reactions of organic halides with pentacyanocobaltate(II)[7] and of chromium(II)[8] with organic halides. Dehalogenation then could involve either a polar mechanism:



$$R_2C(X)\text{—}CR(X) + Co(CO)_4^- \xrightarrow{(S_N1\ ?)} R_2C(X)\text{—}CR_2(Co(CO)_4) \xrightarrow{\beta\text{-elimination}} R_2C{=}CR_2 + XCo(CO)_4$$

or a radical process similar to that proposed above:



$$R_2C(X)\text{—}CR_2(X) + Co(CO)_4^- \longrightarrow R_2C(X)\text{—}\dot{C}R_2 + {}^{\bullet}Co(CO)_4 + X^-$$

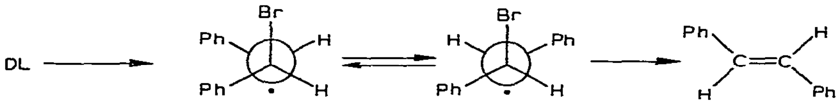
$$R_2C(X)\text{—}\dot{C}R_2 \longrightarrow R_2C{=}CR_2 + X^{\bullet}$$

$$R_2C(X)\text{—}\dot{C}R_2 \xrightarrow{{}^{\bullet}Co(CO)_4} R_2C(X)\text{—}CR_2(Co(CO)_4) \longrightarrow R_2C{=}CR_2 + XCo(CO)_4$$

$$2\,{}^{\bullet}Co(CO)_4 \rightarrow Co_2(CO)_8$$

It would be helpful to have a knowledge of the organocobalt products of these reactions. In view of the ultimate degradation of $Co_2(CO)_8$ to $Co(THF)_6[Co(CO)_4]_2$ in THF medium, such knowledge could be difficult or impossible to achieve when dicobalt octacarbonyl, $NaCo(CO)_4$, $Hg[Co(CO)_4]_2$ or $Co_4(CO)_{12}$ are used as starting material. However, triphenylphosphine–cobalt carbonyl species are more stable in THF than the analogous cobalt carbonyl compounds, and for this reason we carried out experiments with $NaCo(CO)_3PPh_3$ in place of $NaCo(CO)_4$. In the two reactions examined, those with Ph_2CHBr and with Ph_2CCl_2, the expected organic products were formed in good yield ($Ph_2CHCHPh_2$ and $Ph_2C{=}CPh_2$, respectively). In each case, the organocobalt product, formed rapidly in almost quantitative yield, was the dimer, $Ph_3P(OC)_3Co\text{–}Co(CO)_3PPh_3$. This finding is more in line with the radical anion mechanism than with the polar mechanisms.

A second piece of evidence was the finding that D,L-dibromostilbene gave *trans*-stilbene on reaction with dicobalt octacarbonyl. This result rules out a concerted *anti* elimination process on the basis of the work of Miller *et al.*[9]. These authors found that the geometry of substituents on the stilbene produced by debromination of D,L-1,2-dibromostilbene depended on the nature of the dehalogenation agent. Two-electron reductants gave an *anti* elimination, producing *cis*-stilbene. On the other hand, one-electron reductants (Fe^{II}, Cr^{II}, R_3SnH, etc.) gave *trans*-stilbene *via* a free-radical mechanism. In this process, the relatively stable benzylic species (V) first equilibrates with (VI) by internal rotation before it encounters another molecule of reductant. In this connection we note that the conversion of Ph_2CCl_2 to $Ph_2C{=}CPh_2$ via intermediate $Ph_2ClCCClPh_2$ can also be achieved using ferrous chloride in DMSO solution[10]. (A free radical mechanism was postulated.)

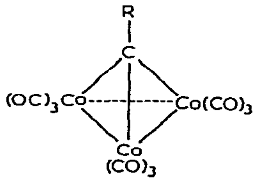


(V) (VI)

Finally, the results obtained when an activated optically active monohalide was treated with dicobalt octacarbonyl also are consistent with the operation of a radical mechanism. A 2/1 mixture of dimethyl D,L- and *meso*-diphenylsuccinate was produced by reaction of dicobalt octacarbonyl with D-$PhCHBrCO_2Me$. For a free-radical mechanism, one would ideally expect a 1/1 ratio of D,L and *meso* isomers, but because of steric considerations and other factors, such a ratio could well deviate from unity.

On the basis of these indirect results we favor a radical process of the type indicated for the cobalt carbonyl/*gem*-dihalide reactions. However, we emphasize that these results, while consistent with a radical mechanism, by no means prove it. Furthermore, we note that this conclusion with regard to mechanism should *not* be generalized to R_2CX_2–other metal carbonyl systems, where other mechanisms well may be operative.

The conversion of organic trihalides, RCX_3, to alkylidynetricobalt nonacarbonyl derivatives (VII) could well proceed via radical intermediates of the type discussed above:



(VII)

$$RCX_3 + Co(CO)_4^- \rightarrow [RX_2C\ldots X\ldots Co(CO)_4]^- \rightarrow R\dot{C}X_2 + X^- + {}^{\cdot}Co(CO)_4$$

$$R\dot{C}X_2 + {}^{\cdot}Co(CO)_4 \rightarrow RCX_2Co(CO)_4$$

$$RCX_2Co(CO)_4 + Co(CO)_4^- \rightarrow R\dot{C}XCo(CO)_4 + X^- + {\cdot}Co(CO)_4$$

$$R\dot{C}XCo(CO)_4 + {\cdot}Co(CO)_4 \rightarrow RCX[Co(CO)_4]_2$$

etc., to give finally $RC[Co(CO)_4]_3$. Closure of the open organocobalt species to the condensed structures could occur at both the bis- and tris(cobalt tetracarbonyl)-substituted stages. The yields obtained in such reactions in general are not high (20–60 %), and it has not been established if coupling reactions are complicating side-processes. In any case, the formation of organocobalt species very likely results from the higher reactivity of the $R\dot{C}X_2$ radicals compared to the very stable (hence more selective) $R_2\dot{C}X$ radicals encountered in the present study. Such a radical process, it may be noted, provides a satisfactory explanation for the displacement of hydrogen by cobalt carbonyl moieties in the formation of $ClCCo_3(CO)_9$ from $HCCl_3$[2] and, as we have now observed, of $PhCCo_3(CO)_9$ from $PhCHCl_2$.

EXPERIMENTAL

General comments

All reactions involving cobalt carbonyls were carried out under an atmosphere of prepurified nitrogen. The organic halides used in this study all were known compounds. They were prepared by standard literature procedures and had physical and/or spectroscopic properties in agreement with those given in the literature. Dicobalt octacarbonyl was purchased from Strem Chemicals, Inc. THF was distilled from lithium aluminum hydride prior to use. Infrared spectra were obtained using a Perkin–Elmer Model 337 B or 257 infrared spectrophotometer. Unless otherwise specified, the reactions were carried out in a three-necked, round-bottom flask of appropriate size equipped with a reflux condenser, pressure-equalizing addition funnel, nitrogen inlet tube and a magnetic stirring assembly. All glassware was flame-dried prior to use.

Reactions of dichlorodiphenylmethane with cobalt carbonyls

(*a*). *Dicobalt octacarbonyl.* To 4.7 g (13.7 mmole) of dicobalt octacarbonyl in 60 ml of THF was added a solution of 6.5 g (27.4 mmole) of dichlorodiphenylmethane in 40 ml of THF. The reaction mixture was stirred and heated at 50° for 3 h. During this time gas evolution was observed and the originally red-brown reaction mixture became green in color. The mixture was treated with 300 ml of water and then was extracted with three 200 ml portions of carbon tetrachloride. The combined organic layers were dried ($MgSO_4$) and evaporated at reduced pressure. The residual solid was crystallized from ethanol/dichloromethane to give 4.5 g (98 %) of tetraphenylethylene, m.p. 223–224° (lit.[11] m.p. 223–224°).

A similar reaction carried out on approximately the same scale in 70 ml of dry benzene required 8 h at 50° before CO evolution ceased and a clear solution containing a blue-green precipitate had formed. Evaporation of the benzene solution and crystallization of the residue gave 3.48 g (99.5 %) of tetraphenylethylene, m.p. 219°.

(*b*). *Sodium tetracarbonylcobaltate*(*−I*). A solution of 4.10 g (12.0 mmole) of $Co_2(CO)_8$ in 100 ml of THF was added slowly to an amalgam prepared from 2.0 g (87 mg-atom) of sodium and 300 g of mercury. The mixture was stirred at room temperature under nitrogen for 10 h and then the $Co(CO)_4^-$ solution was decanted from the mercury under nitrogen into another flask equipped in the usual manner.

To this solution was added 9.7 g (41 mmole) of dichlorodiphenylmethane, and the reaction mixture was heated at 50°, with stirring, for 8 h. A solution of 2.0 g of iodine in 20 ml of absolute methanol was added to destroy the unreacted $Co(CO)_4^-$, and subsequently the mixture was treated with crushed sodium thiosulfate to remove the excess of iodine. Water (400 ml) was added. Extraction with two 150 ml portions of hexane followed. The organic layers were evaporated and the residue was crystallized to give 6.1 g (90%) of tetraphenylethylene.

(*c*). *Sodium (triphenylphosphine)tricarbonylcobaltate(−1).* To an amalgam prepared from 2.0 g of sodium and 100 g of mercury was added 18.2 g (22.4 mmole) of bis[(triphenylphosphine)tricarbonylcobalt] in 200 ml of THF. The slurry was stirred under nitrogen for 6 days at room temperature. The resulting yellow solution was transferred to another reaction flask and 5.33 g (22.4 mmole) of dichlorodiphenylmethane in 10 ml of THF was added. A red-brown solid precipitated immediately. The reaction mixture was stirred at room temperature under nitrogen for 40 h and then was filtered under nitrogen. The solid thus separated was washed with water and acetone to give 17.8 g (98%) of $[Ph_3P(CO)_3Co]_2$, identified by means of its infrared spectrum. The filtrate was washed with water and extracted with dichloromethane. Evaporation of the organic layers gave 2.85 g (72%) of tetraphenylethylene. In another such reaction, a 90% yield of this product was obtained.

(*d*). *Tetracobalt dodecacarbonyl.* A mixture of 1.8 g (3.14 mmole) of tetracobalt dodecacarbonyl and 2.98 g (12.56 mmole) of dichlorodiphenylmethane in 50 ml of THF was stirred and heated at 60° for 3 h. Work-up as in (*a*) gave tetraphenylethylene in 94% yield.

(*e*). *Bis(cobalt tetracarbonyl)mercury.* A mixture of 3.0 g (5.5 mmole) of $Hg[Co(CO)_4]_2$ and 3.1 g (13.6 mmole) of dichlorodiphenylmethane in 50 ml of THF was stirred and heated at 45° for 48 h. Metallic mercury (0.68 g, 50%) was filtered and the filtrate was worked up as in (*a*) to give 0.75 g (41%) of tetraphenylethylene.

In another reaction, 20 mmoles of dichlorodiphenylmethane and 10 mmole of the mercury compound in 100 ml of THF were irradiated (in a quartz flask) with a 100 watt high pressure Hanovia utility UV lamp for 48 h at 45° (with stirring). Metallic mercury was recovered in 88% yield (1.76 g), and the usual work-up of the organic layer gave tetraphenylethylene in 78% yield.

(*f*). *Bis[(triphenylphosphine)tricarbonylcobalt].* A mixture of 4.05 g (5 mmole) of the cobalt compound and 10 mmoles of dichlorodiphenylmethane in 250 ml of THF was stirred and heated at 55° for 20 h. To the solution then was added 20 mmole of iodomethane. The resulting mixture was heated to reflux, cooled and filtered. Further work-up of the filtrate as in (*a*) gave tetraphenylethylene in 60% yield.

Reactions of other gem-dihalides with dicobalt octacarbonyl

(*a*). *9,9-Dibromofluorene.* A mixture of 2.0 g (5.9 mmole) of $Co_2(CO)_8$ and 3.74 g (11.5 mmole) of 9,9-dibromofluorene in 60 ml of THF was stirred and heated for 4 h at 50°. Filtration was followed by evaporation of the filtrate to leave 2.0 g of orange solid. The latter was dissolved in dichloromethane and chromatographed on a 4×41 cm silicic acid (Mallinckrodt) column using dichloromethane as eluent. A red band was eluted, while a thin dark band did not move. The red solution was evaporated to give 1.7 g of bisfluorenylidene (90%), m.p. 169–174°. Recrystallization from ethanol/dichloromethane gave material of m.p. 184–186° in 74% yield; lit.[12] m.p. 189–190°.

(*b*): *9,9-Dichlorofluorene*. A mixture of 5.9 mmole of $Co_2(CO)_8$ and 2.75 g (11.7 mmole) of 9,9-dichlorofluorene in 65 ml of THF was stirred and heated at 55° for 3 h. Filtration was followed by evaporation of the filtrate and extraction of the residue with 30 ml of chloroform. The residue (0.90 g, 38%) was identified as 9,9'-dichlorobisfluorenyl, m.p. 237–240°; lit.[13] m.p. 236°. The chloroform extracts were evaporated to leave a red oil which was chromatographed as in (*a*) to give 0.79 g (41%) of bisfluorenylidene, m.p. 186–187°.

(*c*). *Dimethyl dibromomalonate*. A mixture of 10.7 g (31.6 mmole) of $Co_2(CO)_8$ and 9.7 g (41 mmole) in 140 ml of THF was stirred and heated at 55° for 1 h. To the cooled reaction mixture was added 300 ml of water and the resulting liquid was extracted twice with dichloromethane and twice with pentane. The combined organic layers were dried and evaporated. Recrystallization of the solid residue from ethanol gave 7.6 g (93%) of tetracarbomethoxyethylene, m.p. 111–115°. Recrystallisation raised the m.p. to 119–120°; lit.[14] m.p. 119–120°.

Coupling of monohalides with cobalt carbonyls

(*a*). *Bromodiphenylmethane*. A mixture of 1.6 g (4.7 mmole) of $Co_2(CO)_8$ and 4.63 g (18.7 mmole) of bromodiphenylmethane in 70 ml of THF was stirred and heated at 50° for 3 h. Filtration was followed by evaporation of the filtrate to leave 1.7 g (55%) of *sym*-tetraphenylethane, m.p. 200–202°. Recrystallization from hexane/dichloromethane raised the m.p. to 211°; lit.[15] m.p. 211°.

A similar reaction between 4.1 mmole of $Co_2(CO)_8$ and 16.3 mmole of the bromide in 80 ml of dry benzene (2 h at 50°) gave the coupling product in 81% yield.

Another reaction was carried out with $NaCo(CO)_3PPh_3$. A solution of this salt in 200 ml of THF was prepared from the amalgam from 2 g of sodium and 100 g of mercury and 13.8 g (17.0 mmole) of $[(Ph_3P)(CO)_3Co]_2$ (stirring for 5 days). The yellow solution which was produced was transferred under nitrogen into the reaction flask and 8.4 g (34 mmole) of bromodiphenylmethane in 10 ml of THF was added. A red-brown precipitate formed immediately. The reaction mixture was stirred at room temperature for 26 h and filtered under nitrogen to give 13.2 g (96%) of $[(Ph_3P)(CO)_3Co]_2$ (identified by IR). The filtrate was treated with 600 ml of water and then extracted with two 250 ml portions of dichloromethane. The organic solution was dried and evaporated. The yellow residue was chromatographed on a silicic acid column (chloroform eluent) to give 4.1 g (75%) of *sym*-tetraphenylethane, m.p. 210–211°.

(*b*). *9-Bromofluorene*. A mixture of 2.9 mmole of $Co_2(CO)_8$ and 2.89 g (12.3 mmole) of the bromide in 60 ml of dry benzene was stirred and heated at 50° for 3½ h. Filtration, evaporation of the filtrate and crystallization of the residue from ethanol/benzene gave 1.30 g (67%) of bisfluorenyl, m.p. 243–245°; lit.[16] m.p. 246°.

(*c*). *Dimethyl bromomalonate*. A mixture of 29.9 mmole of $Co_2(CO)_8$ and 25.0 g (119 mmole) of the bromide in 100 ml of THF was stirred and heated at 45° for 24 h. The reaction mixture was treated with 400 ml of water and then extracted with four 250 ml portions of benzene. The organic layer was dried and evaporated to leave a viscous brown liquid. Heating at reduced pressure removed the volatile components whose redistillation gave 3.9 g (15.5%) of the starting bromide. The dark solid residue was crystallized from dichloromethane/carbon tetrachloride to give, in two crops, 6.25 g (40%) of *sym*-tetracarbomethoxyethane, m.p. 134–135°; lit.[17] m.p. 135°.

(*d*). *Methyl D,L-bromophenylacetate.* A mixture of 14.0 mmole of $Co_2(CO)_8$ and 11.2 g (48 mmole) of the bromide in 110 ml of THF was stirred at room temperature for 13 h. The reaction mixture was treated with 500 ml of water and then extracted with three 300 ml portions of dichloromethane. The organic layer was evaporated to leave a brown solid which was extracted with three 50 ml portions of boiling methanol. The methanol-insoluble residue was crystallized from hot acetone to give 1.2 g (17%) of dimethyl *meso*-diphenylsuccinate, m.p. 218–219°; lit.[18] m.p. 221–222°. From the methanol solution there was obtained 2.1 g (29%) of dimethyl D,L-diphenylsuccinate, m.p. 169–172°; lit.[19] m.p. 171–178°.

(*e*). *Methyl D-bromophenylacetate.* A mixture of 15 mmole of $Co_2(CO)_8$ and 10.0 g (43.7 mmole) of optically active methyl bromophenylacetate, $[\alpha]_D^{25}$ +19°, (lit.[20] $[\alpha]_D$ +30° for presumably optically pure material) in 90 ml of THF was stirred at room temperature for 17 h. Work-up as in (*d*) gave 2.6 g (43%) of dimethyl D,L-diphenylsuccinate and 1.4 g (23%) of dimethyl *meso*-diphenylsuccinate.

In another similar experiment in which an excess of the optically active ($[\alpha]_D^{25}$ +29.6°) bromide was used [44 mmole to 1.0 mmole of $Co_2(CO)_8$], the recovered (46%) starting bromide was still optically active ($[\alpha]_D^{25}$ +29.2°). A 1.25/1 mixture of dimethyl D,L- and *meso*-diphenylsuccinate was produced in low yield.

Dehalogenation of vicinal dihalides with dicobalt octacarbonyl

(*a*). *9,9′-Dichlorobisfluorenyl.* A mixture of 3.2 mmole of $Co_2(CO)_8$ and 0.85 g (2.13 mmole) of the dichloride in 70 ml of THF was stirred and heated at 50° for 4 h. The mixture was treated with 300 ml of water and extracted with two 100 ml portions of benzene. Evaporation of the organic layer gave 0.7 g of red solid which was recrystallized from ethanol/dichloromethane. Bisfluorenylidene, m.p. 187–189°, was obtained in 86% yield (0.6 g).

(*b*). *meso-Dibromostilbene.* A mixture of 2.1 g (6.1 mmole) of $Co_2(CO)_8$ and 4.2 g (12.3 mmole) of the dibromide in 90 ml of THF was stirred and heated at 55° for 6 h. Fifty ml of toluene was added to the reaction mixture which subsequently was concentrated to 40 ml at reduced pressure and filtered. Evaporation of the filtrate and crystallization of the residue from ethanol gave 2.05 g (93%) of *trans*-stilbene, m.p. 124–124.5°; lit.[21] m.p. 125°.

A similar reaction carried out in benzene gave *trans*-stilbene in 64% yield.

In another experiment, 17.9 mmole of *meso*-dibromostilbene was treated with ca. 6 mmole of $NaCo(CO)_4$ in 120 ml of THF (50° for 12 h). The reaction mixture was treated with 700 ml of water, extracted with diethyl ether and the extracts were evaporated. Crystallization of the residue from ethanol gave 3.1 g (93%) of *trans*-stilbene, m.p. 123–125°.

(*c*). *D,L-Dibromostilbene.* A reaction carried out as in (*b*) between 29.4 mmole of $Co_2(CO)_8$ and 27.2 mmole of the dibromide in 90 ml of THF for 14 h at 50° gave *trans*-stilbene, m.p. 123–124°, in 91% yield as the sole product.

Reaction of benzal chloride with dicobalt octacarbonyl

A mixture of 34.8 g (102 mmole) of $Co_2(CO)_8$ and 9.15 g (57 mmole) of benzal chloride in 240 ml of THF was prepared and slowly warmed and stirred under nitrogen. At 40°, gas evolution was observed. The reaction mixture was heated at 55° for 6 h and then stirred overnight at room temperature. Subsequently, it was treated with 250 ml of 3 *N* HCl and extracted with pentane. Evaporation of the organic layer gave a dark solid which was recrystallized from hexane to give 11.2 g (34%) of $PhCCo_3(CO)_9$, m.p. 100–104°. A second recrystallization raised the m.p. to 106–108°; lit.[2] 105–107°.

In another reaction, in which 58.7 mmole of $Co_2(CO)_8$ was treated with 117.4 mmole of benzal chloride in 120 ml of THF (48 h at 45°), the isolated yield of $PhCCo_3(CO)_9$ was 16%.

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation (Grants GP 6466X and GP 31429X) for generous support of this research and to the Public Health Service for the award of a fellowship to M.D.M. (5 FO1 GM44391).

REFERENCES

1 (a). D. Seyferth and R. J. Spohn, *J. Amer. Chem. Soc.*, 91 (1969) 3037;
(b). D. Seyferth and R. J. Spohn, *J. Amer. Chem. Soc.*, 91 (1969) 6192;
(c). D. Seyferth and R. J. Spohn, *Trans. N.Y. Acad. Sci., Ser. II*, 33 (1971) 625.
2 G. Palyi, F. Piacenti and L. Marko, *Inorg. Chim. Acta Rev.*, 4 (1970) 109.
3 W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, 13b (1958) 192.
4 R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 82 (1960) 750; 83 (1961) 1097.
5 D. Seyferth, R. J. Spohn, M. R. Churchill, K. Gold and F. R. Scholer, *J. Organometal. Chem.*, 23 (1970) 237.
6 C. E. Coffey, *J. Amer. Chem. Soc.*, 83 (1961) 1623.
7 J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 87 (1965) 5361.
8 C. E. Castro and W. C. Kray Jr., *J. Amer. Chem. Soc.*, 85 (1963) 2768.
9 I. M. Mathai, K. Schug and S. I. Miller, *J. Org. Chem.*, 35 (1970) 1733.
10 T. Shirafuji, Y. Yamamoto and H. Nozaki, *Bull. Chem. Soc. Jap.*, 44 (1971) 1994.
11 R. E. Buckles and G. M. Matlock, *Org. Syn.*, 31 (1951) 104.
12 C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, (1929) 2357.
13 L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, 69 (1947) 470.
14 B. B. Corson, R. K. Hazen and J. S. Tomas, *J. Amer. Chem. Soc.*, 50 (1928) 913.
15 P. J. Montague, *Recl. Trav. Chim. Pays-Bas*, 25 (1906) 379.
16 C. Graebe and H. Stindt, *Justus Liebigs Ann. Chem.*, 291 (1896) 1.
17 J. Walker and J. R. Appleyard, *J. Chem. Soc.*, 67 (1895) 768.
18 G. F. Wright, *J. Amer. Chem. Soc.*, 61 (1939) 2106.
19 R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, 27 (1962) 1067.
20 P. Walden, *Z. Phys. Chem. (Leipzig)*, 17 (1895) 706.
21 L. F. Fieser, *J. Chem. Educ.*, 31 (1954) 291.