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

REACTIVITY OF METAL–METAL BONDS. V.

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(Received September 8th, 1967)

INTRODUCTION

In previous papers[1-3], we have examined the reactivity of Sn–Sn, Sn–Mn, and Ge–Mn bonds towards fluoro-olefins. While a variety of olefins was employed, the substituents on the metal atoms were not changed, and so far binary combinations of only three metals have been examined. To obtain a general understanding of the behavior of such covalent metal–metal bonds, further detailed studies are needed of combinations involving other metal atoms, and in which the substituents on the metal atoms are varied. Here we describe some reactions of the Sn–Co bond with two fluorinated olefins, tetrafluoroethylene and trifluoroethylene, and also with trifluoroiodomethane. The reactions of dicobalt octacarbonyl with the same fluorinated compounds have also been studied. In order to gain as much information as possible concerning the mechanism of these reactions, each has been repeated under several different reaction conditions. These involved just heating of the reactants in a nonpolar or a polar solvent, or reaction under ultraviolet irradiation. A preliminary report of this work has appeared elsewhere[4], and more recently, a brief report has appeared of an independent investigation[5] of some reactions of dicobalt octacarbonyl.

EXPERIMENTAL

Standard high-vacuum techniques were employed in the handling of volatile compounds. Thermal reactions were performed in thick-walled Pyrex tubes, while silica tubes were used for reactions requiring ultraviolet irradiation. All solvents were carefully dried and degassed in the vacuum system. Ultraviolet irradiations were made either at 25° with a 200 watt Hanovia lamp at a distance of 3–6 inches or at 70° with a 100 watt lamp in a closed box. Infrared spectra were determined on a Beckman IR-10 or a Perkin–Elmer IR-257 grating spectrophotometer. Carbonyl absorptions were determined accurately on the latter instrument using a × 2.5 or × 10 scale expansion.

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Dicobalt octacarbonyl (Alfa Inorganics Inc.) was purified by dissolution in pentane and removal of impurities by filtration. After evaporation of the solution, the solid was weighed out into reaction tubes, under a nitrogen atmosphere in a dry-box or glove-bag.

Preparation of $R_3SnCo(CO)_4$ *(*$R = CH_3$ *or* C_6H_5*)*[6]

Dicobalt octacarbonyl was dissolved in anhydrous diethyl ether and stirred under nitrogen with a two-fold excess of 1% sodium amalgam until the solution was colorless. Trimethyl- or triphenyltin chloride (80% of theoretical amount) was added and the resultant solution was decanted off the precipitated sodium chloride. Evaporation gave pale yellow-green crystals of $(CH_3)_3SnCo(CO)_4$ (95% yield), m.p. 73–74°, or pale yellow crystals of $(C_6H_5)_3SnCo(CO)_4$ (99% yield), m.p. 120°.

(Trimethyltin)cobalt tetracarbonyl (Found: C, 25.2; H, 1.03. $C_7H_9CoO_4Sn$ calcd.: C, 25.1; H, 0.89%.) shows infrared absorptions (in carbon disulfide and carbon tetrachloride solution) at 2081 (s), 2017 (s), 1987 (vs), 1957 (w); 1200 (vw), 1185 (vw); 770 (s), 725 (m); 548 (s), 526 (m), 500 (w), and 490 (w) cm^{-1}. The proton NMR spectrum shows a single peak at $\delta = -0.633$ ppm relative to internal TMS as standard. It is readily oxidized to a purple solid within a few minutes of exposure to air, but shows good anaerobic thermal stability. The compound sublimes readily, and was recovered quantitatively from pentane solution after heating at 65° for 450 h. Some decomposition occurred in methanol solution on heating at 90° for 48 h. After ultraviolet irradiation of a pentane solution at 60° for 450 h, recovery of the compound was in excess of 75%. Solutions in pentane, carbon tetrachloride, chloroform and carbon disulfide in the absence of air, are stable indefinitely.

(Triphenyltin)cobalt tetracarbonyl (Found: C, 50.7; H, 3.01. $C_{22}H_{15}CoO_4Sn$ calcd.: C, 50.5; H, 2.88%.) shows infrared absorptions at (CCl_4 and CS_2 solution) 3071 (m), 3057 (m), 3015 (w), 2995 (w); 2087 (s), 2026 (s), 1996 (vs), 1970 (w); 1579 (w), 1480 (w), 1430 (s), 1331 (w), 1260 (w), 1190 (w), 1157 (w); 1072 (s), 1020 (w), 998 (s); 729 (s), 698 (s); 550 (vs), 510 (m), 488 (m), 449 (m) cm^{-1}. The proton NMR spectrum shows two singlets (ratio 3:2) at $\delta = -7.67$, and -7.48 ppm relative to internal TMS. The solid compound is comparatively resistant to air oxidation over a period of days, but solutions decompose rapidly in air, particularly when exposed to daylight. Attempts to sublime the compound cause considerable decomposition, but little decomposition occurs when solutions are heated *in vacuo* in the dark. Ultraviolet irradiation of pentane solutions causes slow formation of hexaphenylditin and an unidentified cobalt-containing orange solid. The original solid is moderately soluble in pentane, carbon tetrachloride, chloroform, carbon disulfide, and acetone.

Although both $(CH_3)_3SnCo(CO)_4$ and $(C_6H_5)_3SnCo(CO)_4$ can be recovered unchanged from acetone solutions the infrared spectra of these solutions show, 10 to 15 min after preparation, the carbonyl absorption at 1890 cm^{-1} characteristic[7] of $Co(CO)_4^-$. [In methanol, $(CH_3)_3SnCo(CO)_4$ shows the $Co(CO)_4^-$ absorption at 1905 cm^{-1}.] The infrared spectra of solutions in carbon disulfide, pentane, carbon tetrachloride, etc. are identical with those of the solid compounds.

1. *Reactions with tetrafluoroethylene*

(*a*). Dicobalt octacarbonyl (1.22 g, 3.65 mmole) was sealed with a 10-fold excess of C_2F_4 and left in the dark for 43 days. On opening the tube, the only volatile products were a trace of CO and unreacted C_2F_4. Extraction with pentane followed by vacuum removal of pentane at 60°, left a solid which showed infrared absorptions characteristic of $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $Co_3(CO)_9CCF_3$ [*vide infra*, I (*b*)] and also at 1250, 1180, 1140, 1049 and 910 cm^{-1}. Separation was attempted by chromatography and sublimation, with little success. Ultimately, after decomposition of $Co_2(CO)_8$ by exposure to air, it was possible to separate by chromatography on a silica gel column $Co_3(CO)_9CCF_3$ (0.05 g, 2.7% yield) and $Co_4(CO)_{12}$ (0.213 g, 10% yield) both identified spectroscopically. The latter was doubtless formed when heating the pentane solution of $Co_2(CO)_8$.

(*b*). Dicobalt octacarbonyl (1.08 g, 3.2 mmole) and C_2F_4 (0.95 g, 9.5 mmole) were dissolved in pentane in a silica Carius tube, which was then sealed and left exposed to daylight at 20° for 10 days. A dense precipitate of long orange crystals was formed. The tube was opened to give a little CO, pentane and unreacted C_2F_4 as the volatile products. Decantation of the remaining solvent left long orange crystals of $(OC)_4CoCF_2CF_2Co(CO)_4$ (0.761 g), m.p. 82°. (Found: C, 27.3; H, 0.0; mol.wt., 500. $C_{10}Co_2F_4O_8$ calcd.: C, 27.2; H, 0.0%; mol.wt., 442.) The principal infrared absorptions differed from those reported previously[8] and were at (CS_2 and CCl_4) 2118 (s), 2051 (s), 2010 (m) [$\nu(C{\equiv}O)$]; 1049 (s) [$\nu(C-F)$]; 678 (s), 527 (m), 551 (s), 488 (w), 465 (w), and 450 (s) cm^{-1}. The ^{19}F NMR spectrum consisted of a single resonance at +31.8 ppm with respect to internal $CFCl_3$. The identity of the product was also established chemically by heating a sample (0.055 g) with excess iodine. Carbon monoxide was evolved as well as a condensible gas identified spectroscopically as C_2F_4 (0.010 g, 81%). Removal of the excess iodine left CoI_2 (0.071 g, 94.5%). A similar reaction with excess bromine gave $CoBr_2$, CO, and $BrCF_2CF_2Br$, identified spectroscopically.

The decanted solvent was evaporated to give a solid which spectroscopically was shown to contain $Co_2(CO)_8$, $Co_4(CO)_{12}$, $Co_3(CO)_9CCF_3$, $(OC)_4CoCF_2CF_2Co(CO)_4$ and a species causing absorption at 1250 (m), 1180 (s), 1140 (m), and 910 (m) cm^{-1}. Treatment with small quantities of pentane gave a further crop (0.263 g, total yield 1.024 g, 73%), of sparingly soluble $(OC)_4CoCF_2CF_2Co(CO)_4$, while chromatographic treatment of the pentane extract on a silica gel column ultimately yielded $Co_4(CO)_{12}$ (0.08 g, 4.5% yield) [infrared absorptions at (CS_2 solution) 2061 (vs), 2054 (vs), 2038 (w), 2027 (w), 1867 (vs) cm^{-1}] and $Co_3(CO)_9CCF_3$ (0.07 g, 4.5% yield), m.p. 134–6°. (Found: C, 26.7; F, 10.0. $C_{11}Co_3F_3O_9$ calcd.: C, 25.9; F, 11.2%.) The infrared spectrum shows absorptions at 2018 (s), 2072 (s), 2055 (s), 2042 (s,sh) [$\nu(CO)$]; 1283 (s), 1115 (s) [$\nu(C-F)$]; 957 (s) [$\nu(C-C)$]; 709, 703 (s); 532 (vs), 506, 496 (s); 445 (w), 395 (w) cm^{-1}. The ^{19}F NMR spectrum shows a single line at $\delta = +51.3$ ppm with respect to internal $CFCl_3$ as standard. The species causing the unassigned infrared absorptions was unstable to air and was not identified.

(*c*). Dicobalt octacarbonyl (0.806 g, 2.37 mmole) and excess C_2F_4 were heated in dry, degassed acetone at 70° for 17 h. On opening the tube, a small amount of carbon monoxide, acetone and unreacted C_2F_4 were removed under vacuum. The remaining material was extracted thrice with pentane and then with chloroform to leave a brown-black solid (0.36 g) containing only Co, F, and H_2O.

The pentane solution was reduced in volume and chromatographed on a silica gel column. The first band (purple) yielded $Co_3(CO)_9CCF_3$ (0.181 g, 15% yield), identified spectroscopically, while the second band (red in color) which was eluted with a pentane/chloroform mixture, was a mixture of $Co_3(CO)_9CCCo_3(CO)_9$ and an unidentified cobalt carbonyl. This mixture was combined with the spectroscopically identical original chloroform extract, and after iterative solvent extraction with pentane and column chromatography yielded firstly the "unknown" cobalt carbonyl* (0.025 g). (Found: C, 33.9; H, 0.0; F, 0.0; Co, 33.1%; mol.wt., 916.) The compound showed infrared absorptions at (CS_2 and CCl_4 solution), 2096 (s), 2062 (vs), 2038 (s); 663 (w); 531 (vs), 507 (s), 500 (s,sh) cm^{-1}. The second fraction was $Co_3(CO)_9CCCo_3(CO)_9$ (0.161 g, 7.7% yield). (Found: C, 27.3; mol.wt., 758. $C_{20}Co_6O_{18}$ calcd.: C, 27.2%; mol.wt., 882.) The infrared spectrum shows absorption at ($CHCl_3$ solution) 2081 (s), 2064 (vs), 2029 (s); 674 (m), 531 (vs), 511 (s), 500 (s), 467 (s), and 425 (s,br) cm^{-1} (*cf.* ref 9).

(*d*). (Trimethyltin)cobalt tetracarbonyl (0.72 g, 2.15 mmole), pentane, and excess C_2F_4 were irradiated for 72 h at 50° in a silica tube, to give a red solution and a precipitate. The only volatile products were pentane, unreacted C_2F_4 and a little carbon monoxide.

Pentane extraction of the residue left a pale brown solid from which trimethyltin fluoride (0.209 g, 53% yield) was sublimed. An inorganic residue (0.015 g), presumably $CoF_{2-3}\cdot xH_2O$, remained. Chromatography with pentane on silica gel gave a dense purple band which overlapped with and was preceded by a colorless fluorocarbon. Preliminary experiments showed the purple band to contain a colorless oil as well as a purple solid. Many iterative chromatographs separated the fluorocarbon from the oil, but the latter could not be separated completely from the purple compound by chromatography, solvent extraction or sublimation. From the tail of the purple band, however, it was possible to isolate a pure sample of the purple solid, identified spectroscopically as $Co_3(CO)_9CCF_3$ (0.126 g, 11.5% yield). The oil was identified spectroscopically as $(CH_3)_3SnCF_2CF_2Co(CO)_4$, characteristic infrared absorptions were observed at (CS_2 and CCl_4 solution) 2118 (s) 2047 (vs), 2039 (vs) [ν(C≡O)]; 1063 (m), 1038 (m), 1025 (m,sh), 1001 (m) [ν(C–F)]; 770 (m) (CH_3–Sn rock), 725 (w); 689 (s). The proton NMR spectrum ($CDCl_3$ solution with TMS as internal standard) showed only a single peak at $\delta = -0.33$ ppm, with some broadening presumably due to the presence of a paramagnetic impurity. The ^{19}F NMR spectrum (in $CFCl_3$ solution with the solvent as internal standard) consisted of two singlets at +41 and +101 ppm of which the former could be assigned to $-CF_2-$ adjacent to $-Co(CO)_4$ by analogy with $(OC)_4CoCF_2CF_2Co(CO)_4$ (see above).

(*e*). (Trimethyltin)cobalt tetracarbonyl (1.09 g, 3.27 mmole) was dissolved in dry acetone and sealed in a pyrex tube with excess C_2F_4, and then heated at 90° for 36 h. The solution became orange-red and a pale brown precipitate formed. On opening the tube, carbon monoxide, acetone, and unreacted C_2F_4 were found to be the volatile products. The tube contents were extracted first with pentane and then with chloroform, to leave an insoluble pale brown solid. On sublimation, this gave trimethyltin fluoride (0.30 g, 51% yield), identified spectroscopically, and left an involatile powder containing only Co, F, and H_2O.

The pentane extract was chromatographed on a silica gel column to give three products. The first to be eluted was identified as unreacted $(CH_3)_3SnCo(CO)_4$ (0.2 g, 23% recovery). The second product was the characteristically purple solid

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* A referee has pointed out that these data are consistent with a formulation $[Co(CO)_4C]_5$, which requires C, 32.8; Co, 32.2%; mol. wt. 915. We are grateful for this suggestion.

$Co_3(CO)_9CCF_3$ (0.015 g, *ca.* 1% yield), and the third (0.075 g) was identical spectroscopically to the unknown cobalt obtained in reaction 1(*c*) above.

The chloroform extract contained a trace (0.01 g) of an orange solid which showed carbonyl infrared absorptions ($CHCl_3$ solution) at 2005 (m), 2065 (s,br), and 2051 (s,br) cm^{-1}.

(*f*). (Triphenyltin)cobalt tetracarbonyl (1.32 g, 2.54 mmole), dry pentane, and excess C_2F_4 were irradiated at 60° for 96 h. On opening the tube a negligible amount of carbon monoxide was detected and the only volatile products were pentane and unreacted C_2F_4. Extraction of the tube contents with pentane left a brown solid (0.12 g), containing triphenyltin fluoride, hexaphenylditin, and cobalt fluorides, from which hexaphenylditin (0.083 g) was removed by chloroform extraction at 70°. Evaporation of the pentane extract and sublimation at 70° gave a trace of $Co_3(CO)_9CCF_3$, identified spectroscopically, while the remaining material (1.11 g) was spectroscopically identical to the original reactant, apart from very weak peaks at 1190, 1125, and 970 cm^{-1}. Attempts to purify the compound further, by chromatography caused decomposition and gave no separation.

(*g*). (Triphenyltin)cobalt tetracarbonyl (1.67 g, 3.20 mmole), dry acetone and excess C_2F_4, were heated in a sealed tube at 90° for 48 h, to give a deep red solution with a copious precipitate. Carbon monoxide, unreacted C_2F_4 containing some silicon tetrafluoride, and acetone were removed as volatile fractions when the tube was opened. The tube contents were transferred to a dry-box and extracted several times with pentane and then with chloroform. This left a brown solid (1.24 g) which was shown spectroscopically[10] and analytically (Found: C, 47.1. $C_{18}H_{15}FSn$: C, 58.5 %.) to contain about 80 % triphenyltin fluoride, the remainder being cobalt fluorides.

The pentane and chloroform extracts were combined, evaporated and chromatographed on a silica gel column with pentane. The first band (purple) to be eluted contained $Co_3(CO)_9CCF_3$ (0.045 g, 2.8 % yield), identified spectroscopically. On continued elution, adding increasing amounts of benzene to the eluting pentane, a dense orange band eluted. Evaporation followed by sublimation caused considerable decomposition but gave an orange sublimate (0.04 g) identical spectroscopically to the unknown cobalt carbonyl of 1(*c*) above. The tail of this orange band, eluted with a benzene/chloroform mixture, contained several unidentified components in trace amounts.

2. *Reactions with trifluoroethylene*

(*a*). $Co_2(CO)_8$ (0.54 g, 1.57 mmole), dry pentane, and excess C_2F_3H were irradiated at 65° for 72 h. Carbon monoxide was the only volatile product other than pentane and unreacted olefin. Pentane, followed by chloroform, extractions of the tube contents left a brown solid (0.08 g) containing only cobalt fluorides. Column chromatography in pentane of the combined extracts gave first a trace of a purple solid with infrared absorptions at 2110 (m), 2070 (vs), 2050 (s), 1995 (w), 901 (m), and 600 (m) cm^{-1}. Its color indicated this to be a compound of the $Co_3(CO)_9CX$ type, but it is not[9,11] $Co_3(CO)_9CH$, and it could not be investigated further because of the trace amounts. The second band also purple, contained $Co_3(CO)_9CCF_3$, identified spectroscopically, but the yield was very low. Further elution with chloroform, gave a considerable yield of $Co_4(CO)_{12}$.

(*b*). $Co_2(CO)_8$ (1.68 g, 4.9 mmole), dry acetone, and excess C_2F_3H were heated at 90° for 7 days, and then left at room temperature for a further 4 weeks. Carbon monoxide, acetone, and unreacted olefin were removed as volatile products. The tube contents were extracted with pentane until the washing were colorless and then in the same way with chloroform. A brown solid (0.89 g) remained containing only Co, F, and H_2O. Treatment of the pentane solution on a silica gel column gave first a trace of a purple fraction, presumably a $Co_3(CO)_9CX$ compound, with infrared bands at 2107 (m), 2057 (vs), 2041 (s), 2022 (w,sh) cm^{-1}. With the addition of increasing amounts of benzene to the eluting pentane, a second purple fraction eluted. This yielded a small amount of $Co_3(CO)_9CCF_3$. Next an orange fraction was eluted which contained the same unknown cobalt carbonyl (0.097 g) as in reaction 1(*c*) above. Further elution of the column with chloroform gave a deep red product identified as $Co_3(CO)_9C{-}CCo_3(CO)_9$, and this was combined with the original chloroform extract. Treatment of the latter on a silica gel column gave pure $Co_3(CO)_9C{-}CCo_3(CO)_9$ (0.603 g, 14% yield). The last of this fraction to come off the column was contamined with a small amount of a further product.

(*c*). The reaction of $(CH_3)_3SnCo(CO)_4$ and C_2F_3H under ultraviolet irradiation at 60° in pentane was performed several times, and the following is typical. After 108 h under the above conditions, the reaction mixture was deep red. Carbon monoxide, pentane, and unreacted olefin were recovered under vacuum. Pentane extraction of the residue left a brown solid from which trimethyltin fluoride was recovered by sublimation. This left a residue of hydrated cobalt fluorides.

Treatment of the pentane extract on a silica gel column gave two fractions of which the first was unreacted $(CH_3)_3SnCo(CO)_4$ (*ca.* 85% recovery) and the second $Co_3(CO)_9CCF_3$.

(*d*). (Trimethyltin)cobalt tetracarbonyl (1.17 g, 3.51 mmole) dissolved in dry methanol was heated with excess C_2F_3H at 90° for 72 h. Only carbon monoxide, methanol, and unreacted olefin were recovered on vacuum fractionation. The tube contents were extracted with pentane until the washings were colorless, to leave a pink solid. Sublimation at 0.01 mm and 130° gave trimethyltin fluoride (0.42 g, 65% yield), identified spectroscopically and a pink residue of $CoSiF_6 \cdot xH_2O$, (0.48 g, *ca.* 44% yield), identified by positive qualitative tests for Co^{2+} and SiF_6^{2-} only, and by the infrared bands (Nujol mull) at 3510 (m,br), 1650 (m,br) (H_2O); and 725 (s,br) cm^{-1} (SiF_6^{2-}).

The pentane solution, chromatographed on silica gel, gave three fractions. The first, separated in only trace amounts, was red and had infrared absorptions at 2105 (m), 2005 (vs), 2040 (s), and 2020 (m) cm^{-1}. The second fraction was orange (*ca.* 0.005 g) with infrared absorptions at 2096 (s), 2062 (vs) and 2038 (s) cm^{-1}, identifying it as the unknown cobalt carbonyl isolated in reaction 1(*c*) above. The third fraction, eluted with benzene, was a purple solid which sublimed at 60° and which was identified as $Co_3(CO)_9CCH_2COOCH_3$ (0.10 g, 5.5% yield). (Found: C, 30.5; H, 1.0; mol.wt., 492. $C_{13}H_5Co_3O_{11}$ calcd.: C, 30.4, H, 0.97%; mol.wt., 514.) Infrared absorptions were observed at 2106 (s), 2056 (vs), 2041 (vs), 2023 (s,sh), 1981 (vw) [ν(C≡O)]; 1743 (s) [ν(>C=O); 1635 (vw); 1465 (w), 1437 (w), 1368 (w), 1141 (ms) [ν(C–O–C)]; 1008 (m) [ν_{asymm}(C–O–C)]. The proton NMR spectrum consisted of two singlets, ratio 3 : 2, at $\delta = -3.75$ ($-CO_2CH_3$) and $\delta = -4.6$ (–CH–) with respect to internal TMS.

After elution of this third fraction, elution of the silica gel column with methanol gave a small amount of an impure unidentified organic oil.

(*e*). (Trimethyltin)cobalt tetracarbonyl (0.71 g, 2.12 mmole), acetone and excess C_2F_3H were heated at 90° for 36 h. Vacuum fractionation gave carbon monoxide, acetone, and unreacted olefin. Pentane and then chloroform extractions left a brown solid which on vacuum sublimation gave trimethyltin fluoride (0.303 g, 77 %) (Found: C, 19.9; H, 5.12. C_3H_9FSn calcd.: C, 19.7; H, 4.92 %.) and left a brown powder whose analyses corresponded to $CoF_{2.8} \cdot 4.5\ H_2O$. (0.21 g, ca. 53 % yield) (Found: Co, 30.8; F, 27.4 %.)

The pentane and chloroform extracts were combined and treated chromatographically on a silica gel column. Elution with pentane gave the unknown cobalt carbonyl (0.08) of 1(*c*) above, with infrared absorptions at 2096 (s), 2062 (vs), 2038 (s), 663 (m), 531 (vs), 507 (s), and 500 (sh) cm^{-1}. Chloroform eluted an air-sensitive hydrated fluorine-containing carbonyl product whose constitution suggests that it may be a precursor of the inorganic fluoride (0.03 g). (Found: C, 40.5; H, 3.0; Co, 15.4 %; F, 11.6; mol.wt., 1100.) Infrared absorptions at 3350 (w), 2104 (m), 2058 (vs), 2041 (s); 1640 (w); 667 (w), 608 (w), 531 (s), 508 (s) cm^{-1}.

(*f*). Irradiation of (triphenyltin)cobalt tetracarbonyl with excess C_2F_3H in pentane at 60° for 150 h caused little reaction with *ca.* 90 % recovery of the tin–cobalt compound. This also contained some $Co_4(CO)_{12}$ identified spectroscopically, the only other product being hexaphenylditin (*ca.* 6 % yield).

(*g*). (Triphenyltin)cobalt tetracarbonyl (1.52 g, 2.92 mmole), acetone and excess C_2F_3H were heated at 90° for 48 h. A deep orange solution with a copious precipitate resulted. Vacuum fractionation gave carbon monoxide, acetone and unreacted C_2F_3H. Pentane, and then chloroform extractions in a dry nitrogen atmosphere left a brown cobalt-containing solid (1.01 g) whose infrared spectrum showed the presence of both water and phenyl groups. Sublimation at 240°, 0.01 mm, with a −196° probe yielded pure triphenyltin fluoride. (Found: C, 57.6; H, 4.10. $C_{18}H_{15}FSn$ calcd.: C, 58.5; H, 4.07 %.) The infrared spectrum also agreed with that reported[4]. However, quantitative separation was not achieved. The yield of unsublimed triphenyltin fluoride was calculated from the carbon and hydrogen analytical data. The combined yield was 70 %. The residue was cobalt fluorides.

The combined pentane and chloroform extracts were treated chromatographically on silica gel, eluting with pentane. At least five fractions were separated, most of which occurred in only trace amounts and were not identified. The third eluted component was an orange material which showed infrared bands at 2096 (s), 2062 (vs), and 2038 (s) cm^{-1} thus showing it to be the unknown cobalt carbonyl of 1(*c*) above.

3. *Reactions with trifluoroiodomethane*

(*a*). Dicobalt octacarbonyl (0.90 g, 2.64 mmole) was allowed to react with excess CF_3I at 85° for 110 h. Considerable carbon monoxide was evolved, with unreacted CF_3I being the only other volatile product. The tube contents were extracted first with pentane and then with chloroform, in each case until the washings were colorless, leaving a brown solid (0.23 g) which contained only cobalt and fluorine.

Chromatography on silica gel of the pentane extract gave $Co_3(CO)_9CF$ (0.344 g, 28.3 %) (Found: C, 26.3; F, 4.48. $C_{10}Co_3FO_9$ calcd.: C, 26.1; F, 4.13 %.) Infrared absorptions were observed at 2110 (m), 2067 (s,sh), 2058 (vs), 2042 (vs), 2028 (s), 1984 (vw); 1164 (s); 638 (s), 620 (m,sh), 531 (s), 521 (m,sh), and 502 (s) cm^{-1}. The

^{19}F NMR spectrum showed a singlet at −44.5 ppm with respect to internal $CFCl_3$. Elution of the column with chloroform gave a fraction which was combined with the original chloroform extract and treated again on a silica gel column to give $Co_3(CO)_9C{-}CCo_3(CO)_9$ (0.083 g, 3.6% yield). Further elution with methanol gave a reddish fraction which on evaporation gave $CoI_2 \cdot 2\,H_2O$ (0.295 g, 32% yield).

(*b*). Dicobalt octacarbonyl (0.90 g, 2.64 mmole) was irradiated with excess CF_3I at 30° for 180 h. The volatile products were carbon monoxide, C_2F_6 (0.01 g) identified spectroscopically, unreacted CF_3I and a fraction which condensed at −45° containing $CF_3Co(CO)_4$ (see below) and $Co_3(CO)_9CF$. Prolonged pumping on the reaction tube, and repeated trap-to-trap distillations of the volatile fraction gave a pure sample of $CF_3Co(CO)_4$ (0.04 g, 6.2% yield). (Found: mol.wt., 230, 250. $C_5CoF_3O_4$ calcd.: mol.wt., 240.) Saturated vapor pressure at 20° is 1.4 mm. The infrared spectrum (vapor showed absorptions at 2137 (m), 2071 (vs,sh), 2066 (vs), 2061 (vs,sh), 2026 (m), 2005 (w), 1960 (vs); 1096 (s), 1060 (s,sh), 1057 (s), 710 (w), 559 (m), 454 (m), 376 (m) cm^{-1}.

The contents of the reaction tube were extracted with pentane in a dry-box to leave a black solid from which $CoI_2 \cdot 2\,H_2O$ (0.146 g, 16%) was extracted with chloroform. The pentane extract after heating to convert unreacted $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and treatment on a silica gel column, gave $Co_3(CO)_9CF$ (0.06 g, 4.4%) and $Co_4(CO)_{12}$ (0.462 g, 30.5%).

(*c*). (Trimethyltin)cobalt tetracarbonyl (0.50 g, 1.50 mmole) and excess CF_3I were heated at 70° for 36 h, and carbon monoxide, and unreacted CF_3I were then removed under vacuum. Extraction of the residue with pentane, followed by sublimation of the insoluble material, gave trimethyltin fluoride (0.14 g, 51% yield). (Found: C, 19.9; H, 5.12. C_3H_9FSn: C, 19.7; H, 4.92%.) Dry ammonia gas was bubbled through the pentane extract and the white precipitate was filtered off, dried, and identified as $(CH_3)_3SnI \cdot NH_3$ (0.141 g, 30.5%). (Found: C, 11.6; H, 3.9; N, 4.5; I, 40.8. $C_3H_{12}INSn$ calcd.: C, 11.6; H, 3.9; N, 4.85; I, 41.1%.) The purple filtrate was treated chromatographically on silica gel to give a trace of $(CH_3)_3SnCo(CO)_4$, and $Co_3(CO)_9CF$ (0.20 g, 29%). A trace of $Co_3(CO)_9CCF_3$, identified spectroscopically was also eluted off the column.

Under more forcing conditions (7 days at 70° followed by 3 weeks at room temperature) the above procedures yielded from $(CH_3)_3SnCo(CO)_4$ (1.90 g, 5.66 mmole) a brown cobalt fluoride (0.70 g) in addition to trimethyltin fluoride (0.596 g, 58%), trimethyltin iodide as the ammine (0.72 g, 41%) and $Co_3(CO)_9CF$ (0.30 g, 11.5%).

(*d*). (Trimethyltin)cobalt tetracarbonyl (0.703 g, 2.10 mmole) was irradiated with excess CF_3I at 50° for 48 h. Treatment as in reaction 3(*c*) gave $CF_3Co(CO)_4$ (0.015 g, 3%) as a volatile fraction condensing at −45°, trimethyltin fluoride (0.182 g, 47.6%) and an involatile solid (0.08 g), presumably cobalt fluorides. Treatment of the pentane extract with dry ammonia gas precipitated $(CH_3)_3SnI \cdot NH_3$ (0.225 g, 35% yield), while treatment of the filtrate yielded $Co_3(CO)_9CF$ (0.226 g, 23.4% yield). Evaporation of the chloroform extract yielded $CoI_2 \cdot 2\,H_2O$ (0.03 g, 3% yield).

(*e*). (Triphenyltin)cobalt tetracarbonyl and excess CF_3I were allowed to react under irradiation for 5 days at 30°. Approximately 90% of the starting material was recovered, in addition to small amounts of cobalt iodide and $Co_3(CO)_9CF$.

The same reactants heated at 90° for 48 h gave an exceedingly complex reaction although some unreacted $(C_6H_5)_3SnCo(CO)_4$ was recovered. Further identification of products was not possible, although it was clear from the IR spectra that CF_3–aryl compounds were present.

DISCUSSION

Reactions with fluoroolefins

The behaviour of dicobalt octacarbonyl with tetrafluoroethylene has been studied by Wilkinson *et al.*[8] who reported that in the absence of solvent, at room temperature, formation of the insertion product occurred readily. It is described as forming orange crystals which are moderately stable in air but are unstable in solution. In our current studies, this reaction could not be reproduced. However, employing pentane as solvent and standing the tube in daylight over a period of days, a 73 % yield of $(OC)_4CoCF_2CF_2Co(CO)_4$ was obtained. Additionally, $Co_3(CO)_9CCF_3$ and $Co_4(CO)_{12}$ were formed in low yield. The infrared spectrum of $(OC)_4CoCF_2CF_2Co(CO)_4$ shows only a single C–F stretching frequency in the infrared at 1049 cm^{-1} and lacks the strong peaks earlier reported by Wilkinson *et al.* at 1218, 785, and 767 cm^{-1}. These were presumably due to impurities probably arising from other fluoroolefins present with C_2F_4 (*cf.* also ref. 5).

In acetone, the mode of reaction differs greatly. No insertion product was formed and extensive decarbonylation, fluorination and also catenation of the cobalt occurred, as proven by the considerable yield of hydrated cobalt fluorides and lower yields of $Co_3(CO)_9CCF_3$, $(OC)_9Co_3C$–$CCo_3(CO)_9$ and an unidentified cobalt carbonyl. This latter compound containing only cobalt and carbon and presumably oxygen, was produced in a number of other reactions in acetone described below, and although consistent analytical and spectroscopic data were obtained, it has not yet been possible to fit these with any reasonable formulation*.

(Trimethyltin)cobalt tetracarbonyl, on irradiation with tetrafluoroethylene in pentane gave an insertion product $(CH_3)_3SnCF_2CF_2Co(CO)_4$ (*ca.* 47 %) thus being similar to the behaviour of the Sn–Mn and Ge–Mn analogues[2,3]. Also formed were $Co_3(CO)_9CCF_3$ (12 %) trimethyltin fluoride (53 %), and a little cobalt fluoride.

Under thermal conditions in acetone, the reaction parallels that of $Co_2(CO)_8$ in that $Co_3(CO)_9CCF_3$, cobalt fluorides and the "unknown" cobalt carbonyl were formed, but no insertion product. The only tin-containing product was trimethyltin fluoride.

The Sn–Co bond in (triphenyltin)cobalt tetracarbonyl is very much less reactive than its methyltin analogue in respect to reaction under UV irradiation in pentane with tetrafluoroethylene, since negligible reaction occurred.

However, under thermal conditions in acetone there was extensive conversion to cobalt fluorides, triphenyltin fluorides, with lower yields of the "unknown" cobalt carbonyl and $Co_3(CO)_9CCF_3$, at a rate very similar to the methyltin compound. The mode and rate of reaction of the tin–cobalt compounds with tetrafluoroethylene in acetone are thus similar (*vide infra*).

For the three carbonyl compounds, therefore, where photochemical reaction in pentane with tetrafluoroethylene occurs, it does not proceed far beyond formation of insertion products. On the other hand reaction at 70–90° in acetone resulted

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* See footnote p. 604.

largely in fluorination; a type of behaviour which is unexpected for a fluoroolefin under such mild conditions.

Dicobalt octacarbonyl, under irradiation with trifluoroethylene in pentane reacted only to a negligible extent, giving low yields of compounds of the $Co_3(CO)_9CR$ type, principally $Co_3(CO)_9CCF_3$. Some conversion to $Co_4(CO)_{12}$ occurred. No insertion product was formed.

On heating in acetone over a long period the same reactants gave cobalt fluorides as the principal products along with a good yield of $[Co_3(CO)_9C-]_2$ and traces of other tricobalt enneacarbonyl species.

The cobalt fluorides formed in this and most other cases were hydrated and while the Co/F ratio varied with the conditions of the experiments, the mean ratio was *ca.* Co/F = 1 : 2.5. The formation of water in a fluorination process in glass is to be expected, and although the stoichiometry suggests that the fluoride products are mixtures of Co^{II} and Co^{III} fluorides, a formulation such as $CoF_2 \cdot xHF$ cannot be ruled out.

(Trimethyltin)cobalt tetracarbonyl reacted much less readily with C_2F_3H than with C_2F_4 under irradiation in pentane, and as with $Co_2(CO)_8$, no insertion products were formed. Small yields were obtained of trimethyltin fluoride, cobalt fluorides, and $Co_3(CO)_9CCF_3$. Again under thermal conditions in acetone fluorination was the principal reaction, giving $(CH_3)_3SnF$ and $CoF_{2.8} \cdot 4.5\ H_2O$, and also the unknown cobalt carbonyl. Stopping the reaction after a few hours yielded an unstable red solid hydrated fluorinated cobalt carbonyl presumably a precursor to the cobalt fluoride in addition to the above products.

(Trimethyltin)cobalt tetracarbonyl was also heated with trifluoroethylene in methanol and here very different products were obtained due to the chemical participation of the solvent. Instead of hydrated cobalt fluorides, a high yield of hydrated cobalt hexafluorosilicate was obtained. It is not at all clear why the hexafluorosilicate should be formed in this case, and only cobalt fluorides in other reactions, unless the greater solubility of cobalt fluorides in methanol facilitates the reaction with silicon tetrafluoride to give the SiF_6^{2-} salt. Trimethyltin fluoride was also formed, in 65% yield so that fluorination is the principal reaction. The other product of significant yield (5.5%) was identified as $Co_3(CO)_9CCH_2COOCH_3$. This has clearly been formed by the methanolysis of a compound $Co_3(CO)_9CX$, similar to the methanolysis reported by Bor, Marko and Marko[9]. They described the reaction $Co_3(CO)_9CX + CH_3OH + CO \rightarrow Co_3(CO)_9CCOOCH_3$. In the present case, the solvolyzed compound is most likely $Co_3(CO)_9CCH_2F$, the methanolysis proceeding as follows:

$$Co_3(CO)_9CCH_2F + CH_3OH + CO \rightarrow Co_3(CO)_9CCH_2COOCH_3 + HF$$

The eliminated HF will further favor the formation of cobalt hexafluorosilicate as described above, but the quantity of hydrogen fluoride produced by this means is insufficient to account for the high yield of the hexafluorosilicate.

(Triphenyltin)cobalt tetracarbonyl does not react readily with trifluoroethylene under irradiation, even at 60°. The carbonyl was recovered to the extent of 90%, the remainder being converted to $Co_4(CO)_{12}$ and hexaphenylditin. In acetone as polar medium, however, a rapid reaction occurred in which the principal products were cobalt fluorides, triphenyltin fluoride, the "unknown" cobalt carbonyl and an involatile organic oil which was not investigated further.

Thus the reactions of the 3 carbonyls in acetone with trifluoroethylene are qualitatively similar to those with tetrafluoroethylene. However, photochemical reactions in pentane with trifluoroethylene produce little reaction and no insertion products.

The results of these fluoroolefin reactions may be rationalized as follows. In pentane, $R_3SnCo(CO)_4$ ($R = CH_3$, C_6H_5) exist as molecular species with a single Sn–Co covalent bond, and $Co_2(CO)_8$ exists as 55% non-bridged $(OC)_4Co$–$Co(CO)_4$[13]. With C_2F_4 the reaction with $(CH_3)_3SnCo(CO)_4$ and $Co_2(CO)_8$ is insertion of the C–C skeleton into the metal–metal bond. Substituting CH_3 by C_6H_5 in $R_3SnCo(CO)_4$ greatly reduces relative reactivity presumably by the inverse inductive effect strengthening the Sn–Co bond. The production of $Co_3(CO)_9CCF_3$ in the $Co_2(CO)_8$ reaction is reported[5] to proceed by decarbonylation and rearrangement of the insertion product followed by further reaction with $Co_2(CO)_8$. In the $(CH_3)_3SnCo(CO)_4$ reaction, however, the elimination of $(CH_3)_3SnF$ from the insertion product must leave species such as $CF_2{=}CFCo(CO)_4$ which clearly may facilely rearrange and react further to give $Co_3(CO)_9CCF_3$. With trifluoroethylene in pentane, negligible reaction occurred with all three carbonyls and no insertion products were formed. Comparison with earlier work[2,3] suggests that tetrafluoroethylene is the only two carbon fluoroolefin to form a stable insertion product in a metal–metal bond under these conditions.

In a polar solvent such as acetone, however, a novel and particularly significant feature in the chemistry of such metal–metal bonded compounds was observed. Whereas in non-polar solvents (pentane, CS_2, etc.) the infrared spectrum of the Sn–Co compounds is identical with the solids, in acetone solution within some 15 minutes after the solutions have been prepared, the only carbonyl infrared absorption band is at 1890 cm^{-1} (vs) characteristic[7] of the $Co(CO)_4^-$ ion. However, evaporation of these solutions yields the original compound. Thus it is clear that ionization proceeds in acetone.

$$R_3SnCo(CO)_4 + \text{solvent} \rightleftarrows R_3Sn^+(\text{solvent}) + Co(CO)_4^-$$

Similarly $(CH_3)_3SnCo(CO)_4$ in methanol shows the $Co(CO)_4^-$ adsorption at 1905 cm^{-1}. Dicobalt octacarbonyl in acetone dissociates irreversibly to $Co(CO)_4^-$ and such species as $Co^{II}(\text{acetone})_6$[14].

The similarity in reaction rate and products of $(CH_3)_3SnCo(CO)_4$ and $(C_6H_5)_3SnCo(CO)_4$ on reaction with C_2F_4 and C_2F_3H in acetone are thus explained, since as with $Co_2(CO)_8$ the initial reaction will be nucleophilic attack of $Co(CO)_4^-$ on the olefin (*cf.* ref. 15), *e.g.*:

$$Co(CO)_4^- + C_2F_4 \rightarrow F^- + CF_2{=}CFCo(CO)_4$$

Certainly an intermediate such as $CF_2{=}CFCo(CO)_4$ can reasonably be supposed to undergo further attack and rearrangement to yield $Co_3(CO)_9CCF_3$ while the production of F^- will account at least in part for the final formation of R_3SnF and/or cobalt fluorides. A similar reaction sequence of $Co(CO)_4^-$ attack on $CF_2{=}CFH$ leading to $C_2F_2HCo(CO)_4$ as an instable intermediate will account for the first step in the related reactions of $Co_2(CO)_8$ and $R_3SnCo(CO)_4$ ($R = CH_3$, C_6H_5) with C_2F_3H in acetone and $R_3SnCo(CO)_4$ ($R = CH_3$) in methanol. It appears that further reaction and rearrangement of $C_2F_2HCo(CO)_4$ leads to formation of a tricobalt nonacarbonyl $CFH_2Co_3(CO)_9$ which itself then reacts further.

Reactions with trifluoroiodomethane

Trifluoroiodomethane is known[16] to react readily under UV irradiation by homolytic fission to $CF_3{}^\bullet$ and $I^\bullet$. On irradiating dicobalt octacarbonyl in excess CF_3I at 30° for 180 h, although reaction was not extensive, the products were readily identified as $CF_3Co(CO)_4$ (6%), $Co_3(CO)_9CF$ (4.5%) and CoI_2 (16%) [under the same conditions virtually no reaction was observed with $Co_4(CO)_{12}$].

Under thermal conditions (85° for 180 h) in the dark, however, $CF_3Co(CO)_4$ was not among the products. A considerable quantity of cobalt fluoride and cobalt iodide was formed, in addition to $Co_3(CO)_9CF$ (28%) and interestingly involving formation of a C–C bond, $(OC)_9Co_3C{-}CCo_3(CO)_9$. Although the molar yield of the latter is only 3.6%, it is a useful preparative method since previously reported syntheses[9] have given even lower yields [*cf.* also $C_2F_4+Co_2(CO)_8$ in acetone in which the yield was 7.7%].

With (trimethyltin)cobalt tetracarbonyl and trifluoroiodomethane under thermal conditions (70°, 36 h) high yields of trimethyltin fluoride and trimethyltin iodide were obtained. The cobalt was obtained in the form of $Co_3(CO)_9CF$ contaminated with a trace of $Co_3(CO)_9CCF_3$. Interestingly, on applying more forcing conditions (70°, 7 days) trimethyltin fluoride (50%) and trimethyltin iodide (41%) were again produced, but the yield of $Co_3(CO)_9CF$ fell from 29% to 11.5% and cobalt fluorides were produced.

Under UV irradiation at 50°, $CF_3Co(CO)_4$ and CoI_2 were produced in addition to $(CH_3)_3SnF$, $(CH_3)_3SnI$, $Co_3(CO)_9CF$ and CoF_x.

The reaction of (triphenyltin)cobalt tetracarbonyl with trifluoroiodomethane under UV irradiation was characteristically not extensive and no $CF_3Co(CO)_4$ was detected. Reaction under thermal conditions was more extensive but extremely complex and CF_3–aryl species were among the products, which included $Co_3(CO)_9CF$.

It seems very probable that both under irradiation and with heating the initial step in these reactions with trifluoroiodomethane is homolytic cleavage to $CF_3{}^\bullet$ and $I^\bullet$ radicals, although under the latter conditions a pseudo-halogen type of addition may also be a significant process. With $Co_2(CO)_8$, although reaction under irradiation was not extensive, it almost certainly will occur through formation of $CF_3Co(CO)_4$ and $ICo(CO)_4$ which rearrange to give $Co_3(CO)_9CF$, cobalt iodide and carbon monoxide. Under thermal conditions where reaction is more extensive, $Co_3(CO)_9C{-}CCo_3(CO)_9$ and cobalt fluorides are also formed, the latter apparently arising from breakdown of $Co_3(CO)_9CF$. In the reactions of $(CH_3)_3SnCo(CO)_4$, it is perhaps significant that $(CH_3)_3SnCF_3$ was not identified as a product since it has reasonable stability[17] at 70°. However, the various carbonyl species present may well catalyse this decomposition hence accounting in part for the high yield of trimethyltin fluoride. As in the fluoroolefin reactions the Sn–Co bond in the triphenyltin compounds is much less reactive than in its trimethyltin analogue.

With respect to the chemistry of metal–metal bonded compounds, in addition to the nature of the tin–cobalt compounds in polar and non-polar solvents, an obvious point of interest in all these reactions is the ease with which tricobalt nonacarbonyl derivatives are formed in nearly all of the reactions described here. The $Co_3(CO)_9C$– skeleton clearly has very great stability and hence its formation appears to be energetically favoured.

The spectroscopic data obtained for many of the above compounds provide several points worthy of comment. With respect to the NMR data, the most significant feature is observed in the proton and ^{19}F NMR spectra of the $Co_3(CO)_9CX$ derivatives. In all cases, there is a large shift downfield for protons or fluorine atoms attached to the bridging carbon atom or to the adjacent carbon atom. These nuclei are therefore poorly shielded when compared with similarly bonded organic compounds. The same compounds show interesting features in their infrared spectra. Previous workers[9,18] have suggested that the characteristic features of these spectra include four carbonyl stretching vibrations at 2110–2116 (medium intensity, a singlet), 2047–2070 (strong, doublet), and 2016–2040 (medium, singlet), and four Co–C–O bending modes at 650–600, 527–532 (strong), 503–509 (strong), and 470–480 (weak) cm^{-1}. This earlier data for the carbonyl stretching region, together with results obtained in the present study, are included in Table 1. Clearly the frequencies change somewhat as the substituent on the $Co_3(CO)_9C-$ tetrahedron is varied, and the change is most marked when the substituent is CF_3. These frequency shifts have been attributed[9] to the electronegativity, or more precisely the inductive effects, of the substituents. Certainly, the greater the electron withdrawal from the $Co_3(CO)_9C-$ tetrahedron, the higher should be the carbonyl stretching frequencies. The observed results are therefore consistent with the high electron-withdrawing properties of the CF_3 groups, effects which are apparently transmitted through the $Co_3(CO)_9C-$ tetrahedron. It is also significant that similar variations in carbonyl frequencies in the compounds $R_3SnCo(CO)_4$ are observed with changes in R. This electronic effect is therefore also transmitted through the Sn–Co bond. A full discussion of these effects in terms of metal–metal and carbonyl stretching frequencies has been given elsewhere[19].

TABLE 1

CARBONYL STRETCHING FREQUENCIES FOR $Co_3(CO)_9CX$ DERIVATIVES

X	Solvent	Frequencies (cm^{-1})					
$CCo_3(CO)_9$	$CHCl_3$	2081 s	2064 vs		2039 w	2029 s	2011 w
CF_3	CCl_4	2118 m	2072 vs		2055 s	2042 s,sh	
CH_3	C_6H_{12}	2102 m	2052 vs		2038 s	2018 w	
H	C_6H_{12}	2106 m	2057 vs		2042 s	2023 w	
Cl	C_6H_{12}	2109 m	2062 vs		2046 s	2030 w	
F	CCl_4	2110 m	2067 vs	2058 vs	2042 vs	2028 s	1984 w
C_6H_5	C_6H_{12}	2101 m	2054 vs		2040 s	2021 w	
$COOCH_3$	C_6H_{12}	2111 m	2065 vs		2047 s	2034 w	
CH_2COOCH_3	CCl_4	2106 m	2056 vs		2041 vs	2023 s	

ACKNOWLEDGEMENTS

The financial support of the National Research Council, Ottawa, and the Science Research Council, London, England, is gratefully acknowledged.

SUMMARY

The reactions of dicobalt octacarbonyl and $R_3SnCo(CO)_4$ ($R = CH_3$ or C_6H_5)

with tetrafluoroethylene, trifluoroethylene or trifluoroiodomethane have been investigated, and found to be dependent on the reaction conditions employed. Under ultraviolet irradiation in a non-polar solvent such as pentane, reactions with the olefins yield insertion products such as $(OC)_4CoCF_2CF_2Co(CO)_4$ as the principal products. However, under thermal conditions in acetone fluorination by the olefin is extensive, yielding cobalt fluorides, the triorganotin fluoride and significant amounts of tricobalt nonacarbonyl derivatives, principally $Co_3(CO)_9CCF_3$. In the polar medium these reactions probably occur through nucleophilic attack of the $Co(CO)_4^-$ ion on the olefins. The reactions with trifluoroiodomethane were notable in that good yields of the $Co_3(CO)_9CX$ derivatives, such as $Co_3(CO)_9CF$ and $Co_3(CO)_9CC(Co)_3(CO)_9$, were obtained under both ultraviolet irradiation and under thermal conditions. In all of these reactions $(C_6H_5)_3SnCo(CO)_4$ was noticeably less reactive than its trimethyltin analogue.

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