Reactions of Fluoro-olefins with Octacarbonyldicobalt

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Nonacarbonyltricobalt derivatives, RCCo(CO)$_9$ have previously been prepared by acidification of the acetylene complexes (R′C$\equiv$CH)Co$_2$(CO)$_6$ (where R′ = H,[1] Bu^n,[1] Me,[2] or Ph[2]) or by reaction of the trihalogenomethane derivatives RCX$_3$ with octacarbonyldicobalt (R = Me,[3] F,[5] Cl,[4,5] H,[4,5] Ph[4], CO$_2$Me,[4,5] or CO$_2$Et[5]; X = Cl. R = H,[4,5] or Br[5]; X = Br. R = H,[4] or I[5]; X = I) or with sodium tetracarbonylcobaltate(−I)[6] (R = Me; X = Cl). We now report the preparation of the compound CF$_3$.CCo$_3$(CO)$_9$ in 60—73% yields by the reaction of the fluoro-olefins CF$_2$:CFX (X = F, Cl, or Br) with octacarbonyldicobalt at 80—100° for several hours in pentane solution.

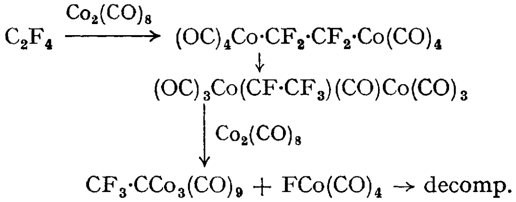
The deep purple solid, CF$_3$·CCo$_3$(CO)$_9$ (m.p. ~190°) was identified by comparison of its i.r. and ^{19}F n.m.r. spectra with those of an authentic sample prepared in low yield from CF$_3$·CClBr$_2$[3] or from CF$_3$·CCl$_3$ and octacarbonyldicobalt. The structure was further confirmed by cleavage with chlorine to give the compound CF$_3$·CCl$_3$ (97% yield), or with anhydrous hydrogen chloride to give the compound CF$_3$·CH$_3$ (70% yield). Under conditions where tetrafluoroethylene gives a high yield of CF$_3$·CCo$_3$(CO)$_9$ the olefins CF$_3$·CF:CF$_2$, CF$_2$:CHF, CF$_2$:CH$_2$, CH$_2$:CHF, PhCF:CF$_2$, or CCl$_2$:CCl$_2$ either do not react or give very low yields (<1%) of purple compounds in amounts insufficient to permit characterisation. An independent investigation of the reaction of tetrafluoroethylene has been reported briefly in a recent note.[7]

Reaction of octacarbonyldicobalt with tetrafluoroethylene under mild conditions (100° for 1 hr., or 20° for several days) gives the compound (CO)$_4$Co·CF$_2$·CF$_2$·Co(CO)$_4$ in 85% yield. The structure of this compound has been confirmed by comparison with an authentic sample prepared by the reaction of tetrafluorosuccinyl chloride with sodium tetracarbonylcobaltate(−I); its reaction with chlorine gives a 77% yield of the compound CF$_2$Cl·CF$_2$Cl. The ^{19}F n.m.r. spectrum agrees with that of the compound obtained previously in 30% yield by a similar route,[8,9] but the m.p. (97—98°) is distinctly higher than that reported[9] (80° with decomposition) and the i.r. spectrum differs appreciably from the more complex spectrum reported earlier, specifically in the absence of the strong impurity bands at 1218, 785, and 767 cm.$^{-1}$. When the compound (CO)$_4$Co·CF$_2$·CF$_2$·Co(CO)$_4$ is kept under the conditions used for the direct conversion of octacarbonyldicobalt into CF$_3$·CCo$_3$(CO)$_9$, the last compound is obtained in 75% yield; this reaction is inhibited by carbon monoxide.

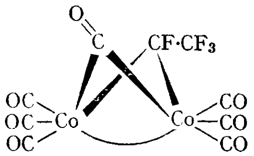
At 40—45° compound (CO)$_4$Co·CF$_2$·CF$_2$·Co(CO)$_4$ slowly loses carbon monoxide over several days *in vacuo* to give a red, crystalline solid (m.p. 57—58°; 98% yield); the reaction is completely inhibited by 1 atm. of carbon monoxide. Elemental analysis of this new compound is consistent with a formula C$_2$F$_4$Co$_2$(CO)$_7$, and ^{19}F n.m.r. shows only two absorptions at 50·0 p.p.m. (quartet, J = 12 c./sec.) and 70·8 p.p.m. (doublet, J = 12 c./sec.) upfield from CFCl$_3$ reference and solvent with an intensity ratio of 1 : 3 respectively, consistent with the presence of a CF$_3$·CF group. The i.r. spectrum shows bands due to terminal metal carbonyl groups at 2122s, 2087vs, 2067vs, 2060vs, and 2019w cm.$^{-1}$, and a strong band at 1866 cm.$^{-1}$ attributed to a bridging metal carbonyl.

Reaction of the compound with anhydrous hydrogen chloride in hexane at 100° (16 hr.) gives the compound $CF_3\cdot CH_2F$ (56% yield). This novel compound is therefore considered to be (I), and the spectroscopic evidence suggests that only one of the forms (II or III) is present.

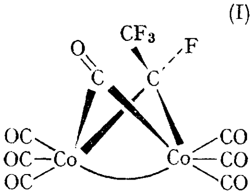
The compound (I) reacts with phosphorus ligands with displacement of two terminal carbonyl groups to give $L(OC)_2Co(CF\cdot CF_3)(CO)Co(CO)_2L$ [$L = Ph_3P$, $Bu^n{}_3P$, $(PhO)_3P$, or $P(O\cdot CH_2)_3CEt$], as evidenced by the retention of the bridging carbonyl in the i.r. spectra and the simplicity of the band pattern in the terminal metal carbonyl region. Compound (I) can be heated at 100° in hexane for 14 hr. without decomposition, and is thus relatively stable thermally. It reacts readily with octacarbonyldicobalt under these conditions, however, to form $CF_3\cdot CCo_3(CO)_9$ (61% yield), thus showing that (I) is an intermediate in the formation of $CF_3\cdot CCo_3(CO)_9$ *via* the sequence



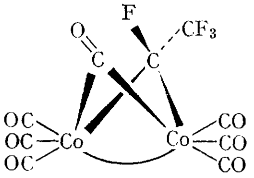
$$\begin{array}{c} C_2F_4 \xrightarrow{Co_2(CO)_8} (OC)_4Co\cdot CF_2\cdot CF_2\cdot Co(CO)_4 \\ \downarrow \\ (OC)_3Co(CF\cdot CF_3)(CO)Co(CO)_3 \\ \downarrow {\scriptstyle Co_2(CO)_8} \\ CF_3\cdot CCo_3(CO)_9 + FCo(CO)_4 \rightarrow \text{decomp.} \end{array}$$



(I)



(II)



(III)

The reactions of the olefins $CF_2{:}CFCl$ and $CF_2{:}CFBr$ with octacarbonyldicobalt to give $CF_3\cdot CCo_3(CO)_9$ are presumed to occur by a similar mechanism, although so far it has not proved possible to isolate compounds analogous to $(OC)_4Co\cdot CF_2\cdot CF_2\cdot Co(CO)_4$ or (I) under mild conditions.

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