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XI*. REACTION OF HYDRIDOTETRACARBONYLCOBALT WITH FLUORO-OLEFINS

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SUMMARY

The reaction between $HCo(CO)_4$ and $CF_2{=}CFCl$ under thermal or UV irradiation conditions has been found to give a low yield of $CHF_2{-}CFCl{-}Co(CO)_4$. The olefins $CF_2{=}CCl_2$, $CF_2{=}CHF$ or $CF_2{=}CH_2$ do not give stable adducts under similar conditions.

Tetrafluoroethylene is well known to undergo insertion reactions with a number of transition metal hydrides to give stable adducts[2]. The olefins $CF_2{=}CFCl$ and $CF_2{=}CCl_2$ have also been shown to give $CHFCl{-}CF_2{-}Re(CO)_5$ and $CHCl_2{-}CF_2{-}Re(CO)_5$ respectively as the only products upon reaction with $HRe(CO)_5$[3]. Hydridopentacarbonylmanganese similarly reacts with the olefin $CF_2{=}CFCl$ under both UV irradiation and thermal conditions to give mixtures of the two possible adducts, although when olefin pressures of >1 atm are employed the isomer $CHFCl{-}CF_2{-}Mn(CO)_5$ is the major product formed[4,5]. A mixture of the isomers $CHF_2{-}CCl_2{-}Mn(CO)_5$ and $CHCl_2{-}CF_2{-}Mn(CO)_5$ is also obtained from the reaction between $HMn(CO)_5$ and $CF_2{=}CCl_2$, but again formation of the more stable isomer, $CHCl_2{-}CF_2{-}Mn(CO)_5$, is favoured when long reaction times and a large excess of the olefin are employed[4,6]. The reaction between $CF_2{=}CFCl$ and $HCo(CO)_4$, previously reported[6] to give only the hydrogenated product $CHF_2{-}CHFCl$, has now been reinvestigated and is reported herein.

When an excess of chlorotrifluoroethylene was caused to react with hydridotetracarbonylcobalt at 0°, either under a pressure (2–3 atm) of the olefin for 18 days, or on UV irradiation of the mixture for 6 h, a low yield (2–4%) of a pale yellow, volatile oil was obtained. The IR spectrum of the oil showed three bands in the metal carbonyl stretching frequency region, a weak band at 2990 cm^{-1} [ν(C–H)], medium C–F stretching vibrations at 1114, 1097 and 1007 cm^{-1}, and a band at 819 cm^{-1} assigned to a C–Cl stretching vibration, indicating that the compound is a 1/1 adduct. On the basis of C–F stretching vibrations reported previously[7] for other fluorocarbon–transition metal carbonyls the bands at 1114 and 1097 cm^{-1} are assigned to fluorine

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* For Part X see ref. 1.

atoms bonded to the carbon atom (C_β) furthest from the cobalt atom, and the band at 1007 cm^{-1} to the C_α–F bond.

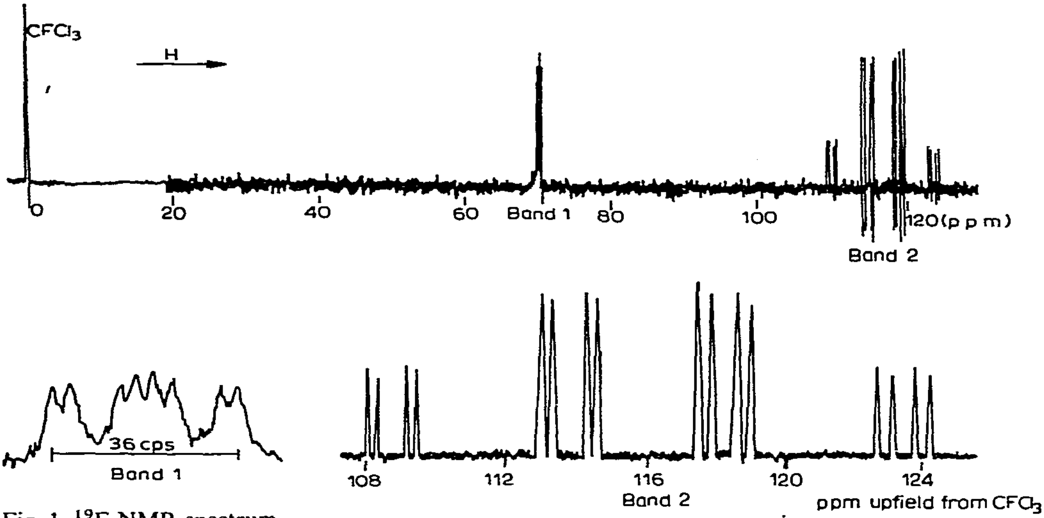

Fig. 1. ^{19}F NMR spectrum.

The ^{19}F NMR spectrum (Fig. 1) recorded on a 20% solution in cyclohexane showed two bands centred at 69.7 and 116.6 ppm upfield from $CFCl_3$. The pattern of the high field band can only arise from the presence of a $-CHF_2$ group in which the two fluorine atoms are non-equivalent. This gives rise to an AB pattern, in which each member is split into a doublet by the proton [$J(F_\beta-H)$ 60.1; $J(F'_\beta-H)$ 56.9 Hz]* and further split into doublets by the fluorine atom on the α-carbon atom [$J(F_\alpha-F'_\beta)$ 20.4; $J(F_\alpha-F_\beta)$ 11.8 Hz]. The pattern of the low field band arises by coupling of F_α with F_β and F'_β, and further splitting [$J(F_\alpha-H)$ 3.4 Hz] occurs by coupling of F_α with the proton on the β-carbon atom. The ^{1}H NMR spectrum (Fig. 2) recorded on a 20% solution in cyclohexane, which was also used as a reference, showed a single band centred at −4.10 ppm from cyclohexane (τ *ca.* 4.47)** split into a doublet by F_β, and again into a doublet by F'_β; further splitting into doublets occurs by coupling of the proton with F_α. The spectroscopic data thus establishes the structure of the adduct as the isomer $CHF_2-CFCl-Co(CO)_4$. No evidence could be obtained for even small amounts (< 5%) of the other possible isomer $CHFCl-CF_2-Co(CO)_4$, which, on the basis of previous observations[4,5,6] on the $HMn(CO)_5$/fluoro-olefin adducts might be expected to be more stable than the isomer isolated.

Attempted reactions between $HCo(CO)_4$ and the olefins CF_2=CCl_2, CF_2=CHF or CF_2=CH_2 at 0° for 3 weeks failed to give isolable adducts. The reactions with CF_2=CCl_2 or CF_2=CHF under UV irradiation conditions at 0° for 9 h gave traces of volatile, yellow oils, but these proved to be unstable above 0° and could not be adequately characterised.

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* Coupling constants were calculated from the average values measured from the spectrum by applying a previously reported method of correction[8].

** Based on cyclohexane τ 8.57.

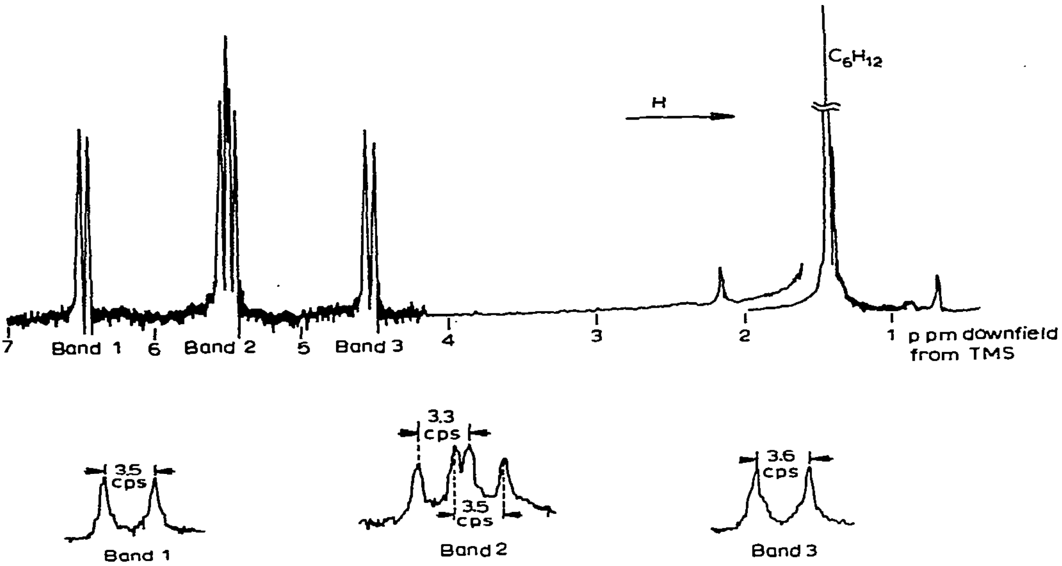

Fig. 2. ^{1}H NMR spectrum.

EXPERIMENTAL

Hydridopentacarbonylcobalt was prepared from octacarbonyldicobalt by a previously described method[9]. Chlorotrifluoroethylene, 1,1-dichlorodifluoroethylene, 1,1-difluoroethylene and trifluoroethylene were commercial samples. ^{19}F and ^{1}H NMR spectra were recorded on a Perkin–Elmer R10 spectrometer, and IR spectra were recorded on a Perkin–Elmer 21 spectrophotometer. Irradiation reactions were carried out in a 1-*l* photochemical reactor using a 125 W UV lamp.

Reaction between hydridotetracarbonylcobalt and chlorotrifluoroethylene

(*a*). *Under pressure.* Hydridotetracarbonylcobalt [20.5 mmoles, prepared from octacarbonyldicobalt (5.26 g, 15.4 mmoles)], pentane (80 ml), and chlorotrifluoroethylene (3920 ml, 20.4 g, 175 mmoles) were sealed in a "Dreadnought" glass tube (300 ml) and put aside at 0° for 18 days. On opening the tube volatile products were transferred to a vacuum line and were found to contain carbon monoxide (31 ml, 1.4 mmoles, 2%), pentane and unreacted chlorotrifluoroethylene, together with (1-chloro-1,2,2-trifluoroethyl)tetracarbonylcobalt (0.10 g, 0.4 mmole, 2%) as a slightly volatile, yellow oil. (Found: C, 25.3, H, 0.6; Cl, 12.3; F, 20.3. $C_6HClCoF_3O_4$ calcd. C, 25.0; H, 0.4; Cl, 12.3; F, 19.8%.) Its IR spectrum recorded on a vapour sample showed bands at 2990 w, 2143 s, 2073 vs, 2037 m, 1389 w, 1351 m, 1253 w, 1160 m, 1114 m, 1097 m, (sh), 1055 w, 1007 m, 819 s cm^{-1}.

(*b*). *Under UV irradiation conditions.* When a solution of hydridotetracarbonylcobalt (34.3 mmoles) and chlorotrifluoroethylene (4060 ml, 21.1 g, 181 mmoles) in pentane (380 ml) was irradiated for 6 h at 0° and for a further 4 h at 10°, fractional distillation of the volatile products *in vacuo* gave (1-chloro-1,2,2-trifluoroethyl)tetracarbonylcobalt (0.40 g, 1.4 mmoles, 4%). Recrystallisation of a non-volatile reaction residue from pentane gave octacarbonyldicobalt (1.7 g, 5.0 mmoles, 29%).

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