Perfluoro-allenyl and -butadienyl Transition Metal Complexes

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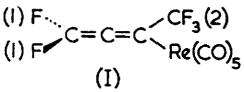
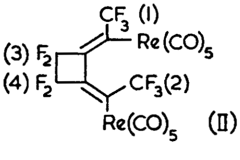
A NUMBER of stable perfluoro-alkyl, -aryl, and -alkenyl transition-metal complexes have been prepared.[1] We now describe synthetic routes to perfluoro-allenyl and -butadienyl metal carbonyl complexes.

Treatment of hexafluorobut-2-yne with carbonyl metal anions gives two types of complex, *e.g.*, the anion $[Re(CO)_5]^-$ affords complexes (I) and (II). The infrared spectrum of the allenic complex (I) showed terminal carbonyl stretching frequencies at

2148m (A_1^{1b}), 2070w (B_1), 2042s (E) and 2012s (A_1^{1a}), *i.e.*, $XRe(CO)_5$, with an additional band at 1992s cm.$^{-1}$ (allenic asymmetric stretching vibration). The ^{19}F n.m.r. spectrum showed a triplet at 62·0 p.p.m.* ($J_{F(1)F(2)}$ = 4c./sec.) and quartet 112·2 p.p.m. ($J_{F(1)F(2)}$ = 4c./sec.) with intensities of 3 : 2 respectively. The allenic complex (I) represents the first example of an allene σ-bonded to a transition metal.



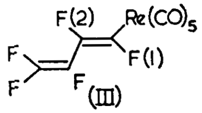
(I)

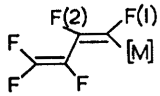


(II)

Molecular weight measurements demonstrated that the yellow crystalline complex (II), m.p. 138—138·5, is a dimer of the allenic complex (I). The The infrared spectrum showed terminal carbonyl stretching frequencies at 2148m (A_1^{1b}), 2070vw (B_1), 2050sh (E), 2040s (E) and 2012s (A_1^{1a}) and an additional band at 1619m cm.$^{-1}$ (C=C.Re). The band at 1992 cm.$^{-1}$ present in (I) was absent in the dimer. The ^{19}F n.m.r. spectrum contained three bands at 44·2 p.p.m. [complex multiplet, CF_3 (2)] 51·6 p.p.m. [quarter, J_{FF} = 2c./sec., CF_2 (3) and (4)] and 64·0 p.p.m. [complex multiplet, CF_3 (1)] with intensities of 3 : 4 : 3, respectively, suggesting that complex (II) has the structure illustrated. It is suggested that the cyclobutane ring present in (II) is puckered so as to relieve steric interaction.

A perfluorobutadienyl metal complex has previously been obtained[2] by treatment of carbonyl π-cyclopentadienylnickel iodide with vinylmagnesium bromide. Reaction of the anions $[Re(CO)_5]^-$ and $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with perfluorobuta-1,3-diene gives the perfluorobutadienyl complexes (III), ν_{max} 2144m (A_1^{1b}), 2073m (B_1), 2038s (E), 2012s (A_1^{1a}), 1785sh, 1773s (C=C), 1632m (C=C·Re) cm.$^{-1}$; $J_{F(1)F(2)}$ = 136·5 c./sec.; and (IVa), ν_{max} 2040s, 1993s (C≡O), 1763s (C=C), 1673s (C=C·Fe); $J_{F(1)F(2)}$ = 41·0 c./sec. It is of particular interest that in the reaction of $[Re(CO)_5]^-$ the *trans*-perfluorobutadienyl complex is obtained, whereas with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ the *cis*-complex is obtained.





(IVa) M = π-$C_5H_5Fe(CO)_2$
(IVb) M = $Mn(CO)_5$

The other isomers were also isolated in low yield and characterised.

The manganese pentacarbonyl analogue was not formed by reaction of the less reactive[3] $[Mn(CO)^5]^-$ anion with perfluorobuta-1,3-diene. However, ultraviolet irradiation of a solution of $CF_2 = CF{\cdot}CF{=}CF_2$ and $Me_3SnMn(CO_5)$ in pentane led to the formation of Me_3SnF and the *cis*-manganese pentacarbonyl complex (IV b), ν_{max} 2132m (A_1^{1b}), 2073m (B_1), 2039s (E), 2010s (A_1^{1a}), 1763s (C=C), 1665s (C=CMn); $J_{F(1)F(2)}$ = 34·0 c./sec.; presumably *via* insertion of the diene into the metal–metal bond followed by elimination of Me_3SnF. Although the insertion of a simple fluoro-olefin into metal–metal bonds has been reported[4] this example represents the first example of an insertion of a diene into a metal–metal bond.

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* Relative to $CClF_3$ (0·0 p.p.m.) increasing to high field.

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