Reaction of Bis(trifluoromethyl)diazomethane with Transition-metal Complexes

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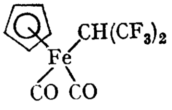
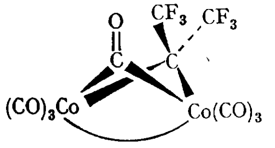
BIS(TRIFLUOROMETHYL)DIAZOMETHANE (I)[1] undergoes a variety of reactions with transition-metal complexes which formally correspond to the insertion of the $C(CF_3)_2$ moiety into a metal–metal, metal–hydrogen, or metal–halogen bond. Recently[2] the insertion of CCl_2 into a tin–tin bond has been reported.

Reaction of π-cyclopentadienyldicarbonyliron dimer with (I) in tetrahydrofuran at room temperature gives (II), a yellow crystalline solid (m.p. 87°). The i.r. spectrum shows terminal carbonyl bands at 2038s and 1991s cm.$^{-1}$; and the ^{19}F and ^{1}H n.m.r. spectra show absorptions at 53·4 p.p.m. (relative to $CFCl_3$ internal) (doublet, J_{HF} 12 c./sec.), τ 5·0 (π-C_5H_5), and τ 7·5 (multiplet) respectively.

Octacarbonyldicobalt reacts with (I) in hexane at room temperature to give (III),† a deep red sublimable air-sensitive solid. The i.r. spectrum shows terminal carbonyl bands at 2124m, 2091s, 2068s, 2061s, 2052sh, and 2025w cm.$^{-1}$, and a strong bridging carbonyl band at 1867 cm.$^{-1}$. The ^{19}F n.m.r. spectrum showed a single unsplit absorption at 49·5 p.p.m.



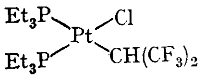
(II)



(III)

(CO)$_5$MnCH(CF$_3$)$_2$

(IV)



(V)

Pentacarbonylmanganese hydride reacts exothermically with (I) to give (IV), a white, crystalline solid with terminal carbonyl bands in the i.r. spectrum at 2134s, 2041s, and 2011s cm.$^{-1}$. The ^{19}F and ^{1}H n.m.r. spectra show absorptions at 53·3 p.p.m. (doublet, J_{HF} 12 c./sec.), and τ 7·0 (multiplet).

Chlorobis(triethylphosphine)platinum hydride does not react with (I) in hexane, until 120°; when the main product is (V), a cream, crystalline solid (m.p. 171°). The ^{19}F and ^{1}H n.m.r. spectra showed absorptions at 50·0 p.p.m. (triplet of double doublets, J_{PtF} 132, J_{HF} 11·5, J_{PF} 17 c./sec.), and τ 6·5 (multiplet), respectively.

The reactions to form (II), (III), and (IV) all proceed at room temperature and, therefore, involve direct attack by the 1,3-dipolar reagent (I) on the transition-metal reactant. It is suggested that in the formation of (II) an intermediate, perhaps analogous to (III), abstracts hydrogen from tetrahydrofuran. Complex (II) is not formed in hydrocarbon solvents.

In the formation of the platinum complex (V), it is suggested that (CF$_3$)$_2$C, generated by thermolysis of (I), co-ordinates with *trans*-(Et$_3$P)$_2$Pt(H)Cl to form a five co-ordinate carbene complex (Et$_3$P)$_2$Pt(H)Cl[(CF$_3$)$_2$C], which rearranges to give (V). The fact that the (Et$_3$P)-ligands are *cis* to each other in (V) provides support for this hypothesis.

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† A structurally related cobalt complex has recently been reported as formed by heating (CO)$_4$CoCF$_2$CF$_2$Co(CO)$_4$ [B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and (in part) J. J. Cox, *Chem. Comm.*, 1967, 529].

[1] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

[2] D. Seyferth and F. M. Armbrecht, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 2790.