Addition Reactions of Tricarbonylcyclo-octatetraene-iron and -ruthenium

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IT has been suggested that tricarbonylcyclo-octatetraeneiron undergoes 1,4-addition reactions with tetracyanoethylene[1] and substituted acetylenes.[2]

Tricarbonylcyclo-octatetraeneruthenium[3] reacts rapidly at room temperature with hexafluoroacetone and with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene to afford respectively the crystalline complexes (II) and (Ib), fully characterised by elemental analyses and molecular-weight measurements. Both complexes show terminal carbonyl bands in their infrared spectra characteristic of a disubstituted $Ru(CO)_3$ group, *e.g.*, (II) shows bands at 2083s, 2019s, and 2015s cm.$^{-1}$ (cyclohexane). The ^{19}F n.m.r. spectrum of (Ib)† had two bands of equal intensity at 58·8 p.p.m. (J_{FF} 13; J_{HF} 5·0) and 63·2 p.p.m. (J_{FF} 13; J_{HF} 0·0), whereas the ^1H n.m.r. spectrum had eight bands of equal intensity at τ_a 3·60 (J_{ae} 8; J_{ab} 11), τ_b 4·45 (J_{ba} 11; J_{bg} 4), τ_c 5·02 (J_{ce} 10; J_{cd} 8), τ_d 5·26 (J_{dc} 8; J_{df} 6), τ_e 5·60 (J_{ea} 8; J_{ec} 10), τ_f 5·95 (J_{fd} 6; J_{fh} 11), τ_g 6·68 (J_{gb} 4; J_{gh} 8), τ_h 8·27 (J_{hf} 11; J_{hg} 8). Proton-decoupling experiments clearly demonstrated the presence of the cyclic arrangement

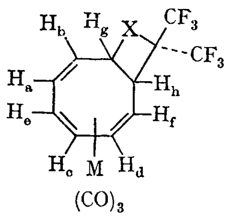
$$\overline{\text{CH}_a\cdot\text{CH}_b\cdot\text{CH}_g\cdot\text{CH}_h\cdot\text{CH}_f\cdot\text{CH}_d\cdot\text{CH}_c\cdot\text{CH}_e}$$

These observations may be rationalised on the basis of the structure (Ib), and are clearly not consistent with these adducts being formed by 1,4-addition reactions *e.g.*, structure (IV).

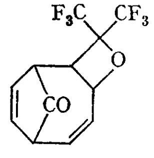
Tricarbonylcyclo-octatetraeneiron reacts at room temperature with $(CF_3)_2C:C(CN)_2$ to afford (Ia); the corresponding reaction with $(CF_3)_2CO$ however leads instead to the formation of *trans*-$C_8H_8Fe_2(CO)_6$ and an organic compound m.p. 76—77°, which is assigned structure (III) on the basis of infrared (band at 1754 s cm.$^{-1}$), ^{19}F n.m.r. (bands at 71·5 p.p.m., J_{FF} 10·5; J_{HF} 2 and 77·9 p.p.m., J_{FF} 10·5; J_{HF} 0·8), and ^1H n.m.r. (bands at τ 3·81, 4·19, 4·9, 6·25, 6·48, and 6·76, relative intensity 2 : 2 : 1 : 1 : 1 : 1) spectroscopy.

These reactions are of especial interest because diene systems normally only undergo 1,4-addition reactions with $(CF_3)_2C:C(CN)_2$[4] and $(CF_3)_2CO$.[5] It is suggested that electronic participation by the metal renders possible an otherwise thermally forbidden[6] concerted 1,2-cycloaddition reaction. Specifically, it is suggested that $(CF_3)_2CO$ and $(CF_3)_2C:C(CN)_2$ react by co-ordination[7] on to the metal leaving the cyclo-octatetraene bonded to the metal as a monodentate ligand; the reaction then proceeds by an allowed[8] 1,2-addition reaction within the co-ordination sphere.

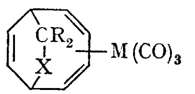
The detailed mechanism of these and related reactions are being investigated.



(Ia) M=Fe, X=C(CN)$_2$
(Ib) M=Ru, X=C(CN)$_2$
(II) M=Ru, X=O



(III)



(IV) R=CF$_3$

(*Received, August 24th,* 1967; *Com.* 910.)

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† Relative to CCl_3F (0·0 p.p.m.); coupling constants in c./sec. Complexes (Ia) and (II) have very similar spectra, and details for (Ib) only are given for brevity.

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