Regiospecific Formation of Cyclopropylcarbinyl Compounds in the **Reaction of But-3-envliron Complexes with Electrophilic** and Radical Reagents

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3-Methylbut-3-enyldicarbonyl- η^5 -cyclopentadi-Summary environ(II) reacts regiospecifically with free radicals (Cl₃C•, Br₃C•, ArSO₂•) and with electrophiles (CF₃CO₂H) at the δ -carbon of the butenyl ligand, resulting in displacement of the metal and the formation of cyclopropylcarbinyl compounds in high yield.

ONE of the most interesting features of the chemistry of σ -bonded organoiron complexes of the type RFe(CO)₂- $(\eta^5-C_5H_5)$ is the number of different sites at which they are susceptible to attack by external reagents.¹ For example, attack has been detected at the metal,² at the α -carbon of of alkyl ligands,³ at the γ -carbon of allyl ligands,⁴ and at the ortho- and para-carbons of benzyl ligands,5 in each case with different immediate consequences. We now report two novel and closely related reactions in which there is regiospecific attack of reagents on the δ -carbon of a but-3-envl ligand.

Thus, 3-methylbut-3-enyldicarbonyl- η^{5} -cyclopentadienyliron(II) (1; 0.5 mol dm^{-3} in CDCl₃) reacts with trifluoroacetic acid $(0.5 \text{ mol dm}^{-3})$ to give a nearly quantitative yield of 1,1-dimethylcyclopropane (2a) [¹H n.m.r. singlets at $\delta 0.22(4H)$ and 1.07(6H)] and trifluoroacetatodicarbonylcyclopentadienyliron(II),⁵ within a few seconds at ambient (*=radical or cation) temperature (equation 1).

Fe(CO)₂(C₅H₅)
$$\xrightarrow{R'x}$$
 \xrightarrow{R} + XFe(CO)₂(C₅H₅) (1)
(1)
a; R' = R = H, X = CF₃CO₂
b; R' = CCl₃SO₂, R = CCl₃, X = Cl
c; R' = R = CBr₃, X = Br

d; $\mathbf{R}' = \mathbf{R} = \operatorname{ArSO}_{2}, \mathbf{X} = \mathbf{I}$

Complex (1) reacts more slowly with trichloromethanesulphonyl chloride⁶ and with carbon tetrabromide⁷ in CH_2Cl_2 to give 1-methyl-1-(β , β , β -trichloroethyl)cyclopropane (2b) and 1-methyl-1-(β,β,β -tribromoethyl)cyclopropane (2c), respectively (isolated in ca. 65% yield); for (2b) ¹H n.m.r. δ 2.73 (s, 2H), 1.30 (s, 3H), and 0.38 and 0.63 (m, 4H); ${}^{13}C$ n.m.r. δ 99.9 (CCl₃), 63.2 (CH₂), 23.3 (CH₃), and 14.0 (C_2H_4) p.p.m.; for (2c), ¹H n.m.r. δ 3.09 (s, 2H), 1.34 (s, 3H), and 0.47 and 0.66 (m, 4H); ¹³C n.m.r. δ 67.3 (CH₂), 39.9 (CBr_3) , 23·1 (CH_3) , 17·6 (1C), and 14·3 (C_2H_4) p.p.m. In the corresponding reaction of (1) with toluene-4-sulphonyl iodide,⁶ only (2c) could be isolated (in 70% yield); ¹H n.m.r. δ 3.03 (s, CH_2), 1.20 (s, CH_3), 2.36 (s, Ar CH_3), and 0·34 (s, C₂H₄); ¹³C n.m.r. δ 65·6 (CH₂), 21·3 (CH₃), 22·6 (CH₃), 11.0 (1C), and 12.9 (C₂H₄) p.p.m.

$$R^{*} + Fe(CO)_{2}(C_{5}H_{5})$$

$$R + Fe(CO)_{2}(C_{5}H_{5}) \rightarrow R + Fe(CO)_{2}(C_{5}H_{5}) (2)$$

$$R'X + \dot{F}e(CO)_2(C_5H_5) \longrightarrow \dot{R} + XFe(CO)_2(C_5H_5)$$
 (3)

We propose that these reactions proceed by a direct attack of the electrophile (CF_3CO_2H) or the radical (Cl_3C_2, Cl_3C_2) Br_3C_{\bullet} , or $ArSO_{2^{\bullet}}$) on the δ -carbon of the butenyl ligand with synthronous or subsequent (probably the latter) cyclisation and expulsion of the metal complex (equation 2). By analogy with the more extensively studied reaction of the same free radical precursors with allylcobalt(III) complexes^{6,7} it is to be expected that the radical displacement of equation (2) would be followed by the further reaction of the displaced paramagnetic iron complex with the radical precursor $(R'X = Br_3CBr, ArSO_2I, etc.)$ to generate the attacking radical of equation (2) as shown in equation (3). The combination of equations (2) and (3) thus provides the propagation steps of a chain reaction.

Electrophilic attack on the δ -carbon of a but-3-envl ligand of a metal complex with formation of a cyclopropane

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derivative has been observed previously with some but-3envltin(IV) complexes⁸ and with but-3-envlcobalt(III) complexes,⁹ though not with CF₃CO₂H as reagent. The homolytic displacement is a novel process, of potential importance in organic synthesis, which we have also detected with a number of but-3-envlcobalt(III) complexes.10

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