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Preliminary communication

The effect of substitution on the reactivity of dienium complexes of tricarbonyliron

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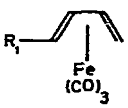
SUMMARY

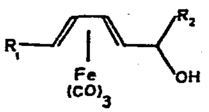
Treatment of dienium complexes of tricarbonyliron with tertiary amines leads to either addition or proton abstraction depending upon the substitution pattern.

Dehydration has proved an effective method for extending conjugation in tricarbonyliron complexes[1,2]. High yields have been obtained in cyclic systems when the reaction was carried out in two steps[2] (dehydroxylation and deprotonation). Attempts to extend these and other synthetic reactions to acyclic compounds point to reactivity differences between cyclic and acyclic systems.

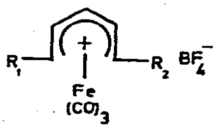
Acylation of diene-Fe(CO)$_3$ (I)[3,4] followed by reduction with sodium borohydride gave the alcohols (II). Dehydroxylation of (II) with fluoroboric acid produced the salts (III) in high yield. Addition of excess tertiary amine (R = Me, Et) to a methylene chloride solution of (III) afforded (V) in the case of (IIIa) and quaternary ammonium salts in the case of both



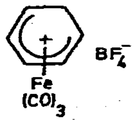
(I)



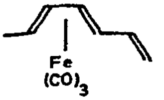
(II)



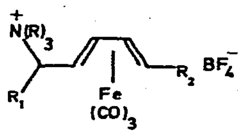
(III)



(VI)



(V)



(IV)

(a) R$_1$=R$_2$=Me
(b) R$_1$=H, R$_2$=Me
(c) R$_1$=H, R$_2$=Et

(IIIb) and (IIIc)[*]. The structure of (V) was deduced from spectroscopic data and by its conversion in acid to symmetrical (IIIa). It is clear from IR spectra of (IVb) and (IVc) on the other hand that they contain both BF_4^- and "neutral" MC–O. It was not possible to deduce from the NMR spectrum of (IVb) the site of NMe_3 addition. The very different behaviour of (IIIa) however supports the assignment of structure (IV).

It has been pointed out that cyclic dienium salts are more stable than their acyclic analogues[5]. For example tricarbonylcyclohexadieniumiron (VI) is unreactive towards neutral water[6] while the reaction with (IIIa) and (IIIc) is essentially complete, [pH 3 was measured for 10^{-3} M solutions]. This could represent a greater positive charge on the metal in the cyclic case and also that no great difference exists between (IIIa) and (IIIc) in this respect. It is possible therefore that the tertiary amine reaction is controlled by steric factors. Attempts to substitute CO in (III) by I^- were unsuccessful and this could also point to a lower positive charge on the metal in (III) than in (VI).

In Table 1 are presented the IR spectra for some of the compounds.

TABLE 1

IR SPECTRA (R = Et) (Nujol mull, cm^{-1})

	$\nu(MC-O)$			$\nu(BF_4^-)$
IIIa	2105	2040	2060	1060
IIIb	2120		2060	1060
IIIc	2120		2060	1060
IVb	2050		1960	1050
IVc	2050		1960	1050
V[a]	2050		1940	–

[a] Liquid film.

REFERENCES

1 D.J. Ehntholt and R.C. Kerber, *Chem. Commun.*, (1970) 1451.
2 B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, *J. Chem. Soc. Dalton*, (1972) 2076.
3 E.O. Greaves, G.R. Knox and P.L. Pauson, *Chem. Commun.*, (1969) 1124.
4 R.E. Graf and C.P. Lillya, *J. Amer. Chem. Soc.*, 94 (1972) 8282.
5 J.E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 85 (1963) 3955.
6 E.O. Fischer and R.D. Fischer, *Angew. Chem.*, 72 (1960) 919.

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[*] All new compounds gave satisfactory elemental analyses.