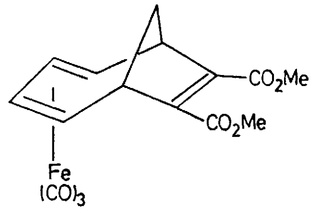
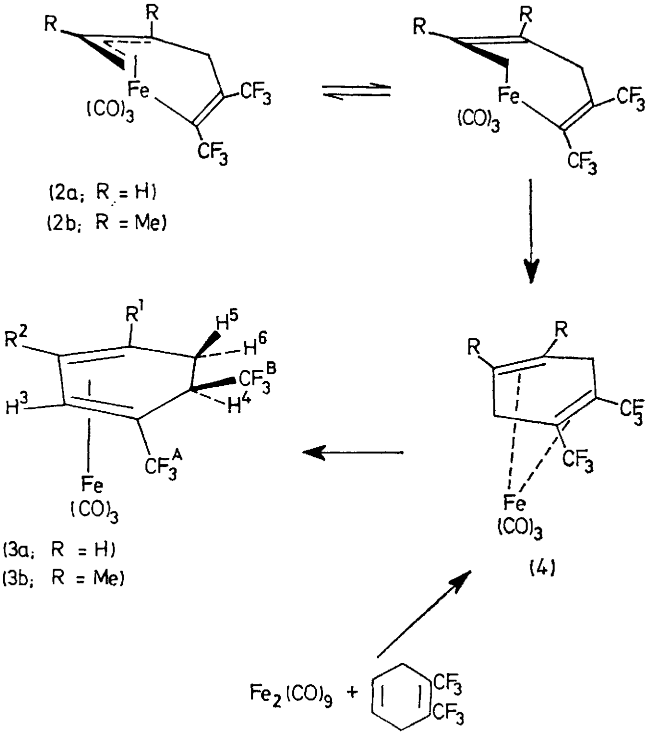
Stepwise Diels–Alder Addition of Hexafluorobut-2-yne to Co-ordinated 1,3-Dienes

By ROBERT DAVIS, MICHAEL GREEN,* and RUSSELL P. HUGHES
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Tricarbonyl(butadiene or 2,3-dimethylbutadiene)iron react with hexafluorobut-2-yne in a stepwise fashion yielding, as the final products, substituted tricarbonyl(cyclohexa-1,3-diene)iron complexes.



(1)



(2a; R = H)
(2b; R = Me)

(3a; R = H)
(3b; R = Me)

(4)

SCHEME

THE ability of a transition metal to lift symmetry imposed restrictions on the cycloadditions of organic ligands attached to itself is still a topic of controversy. An elegant series of experiments has recently demonstrated that formation of complex (1), in the reaction of tricarbonyl(cycloheptatriene) iron and dimethyl acetylenedicarboxylate, arises, after initial u.v. irradiation to create a co-ordination site, from thermally induced carbon–carbon bond formation.[1] The overall reaction, to yield (1), was classified as a $({}_{2}\pi + {}_{6}\pi)$ cycloaddition, normally a thermally 'forbidden' reaction. Analogous reactions were observed with tricarbonyl(cyclo-octatriene)iron, or tricarbonyl(cyclo-octatetraene)iron, and dimethyl acetylenedicarboxylate.[1]

It has previously been demonstrated in this laboratory that u.v. irradiation, at 20°, of hexane solutions of tricarbonyl(butadiene)iron, or tricarbonyl-(2,3-dimethylbutadiene)iron, and hexafluorobut-2-yne (HFB), yielded the 1 : 1 adducts (**2a,b**) arising from the oxidative linkage of two of the termini of the organic ligands.[2] We now report that thermolysis of complexes (**2a,b**) occurred readily in refluxing hexane, to yield the substituted cyclohexa-1,3-diene complexes [(**3a**), m.p. 28—30°, ν_{CO} (hexane) 2071s, 2010s, and 2001s cm^{-1}] and [(**3b**), m.p. 63°, ν_{CO} (hexane) 2063s, 2004s, and 1991s cm^{-1}] respectively.†

Complexes (**3**) can only arise from a further, thermally induced reductive cyclisation involving a linkage of the remaining two termini of the organic ligand in (**2**), to yield intermediate cyclohexa-1,4-diene complexes (**4**) (see Scheme). Under the experimental conditions, such complexes (**4**) are expected to undergo the previously established facile 1,3-hydrogen shift to yield the cyclohexa-1,3-diene ligand in complexes (**3**). In agreement, 1,2-bis(trifluoromethyl)-cyclohexa-1,4-diene reacted with [$Fe_2(CO)_9$] in refluxing hexane to produce low yields of complex (**3a**). The regio-specificity of the 1,3-hydrogen shift in the above system is noteworthy.

A previous example of the reductive linking of a metal–*sp*^{3} carbon σ-bond and a metal–*sp*^{2} carbon σ-bond has been described in the case of a methyl–rhodium(III)–vinyl ligand system.[4]

The overall reaction described above involves a stepwise Diels–Alder addition of HFB to a co-ordinated 1,3-diene, a process which is a thermally 'allowed' concerted reaction in the absence of the transition metal. It is possible that the reaction of but-2-yne with butadiene, catalysed by [Fe-$(C_8H_8)_2$], and yielding 1,2-dimethylcyclohexa-1,4-diene,[5] proceeds *via* a similar reaction path.[6] That such a normally facile concerted process should occur in an unequivocally stepwise fashion under the influence of a transition metal implies that previously reported examples of concerted

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† N.m.r. data (numbering as in Scheme): [complex (**3a**); (^{1}H; 100 MHz; $CDCl_3$; 34°) at τ 4·07 (d, H^3), 4·63 (d, d, H^2), 6·91 (d, d, t, H^1), 7·03 (d, d, q, H^4), 7·61 (d, d, d, H^6) and 8·00 (d, d, d, H^5); (^{19}F; 94 MHz; $CDCl_3$; 34°) at 56·64 (q, $CF_3{}^A$) and 66·46 (d, q, $CF_3{}^B$) p.p.m. rel. to $CFCl_3$]; [complex (**3b**); (^{1}H; 100 MHz; $CDCl_3$; 34°) at τ 4·33 (s, H^3), 7·04 (d d, q, H^4), 7·56 (d, d, H^6), 7·83 (s, $CH_3{}^2$), 8·11 (d, d, H^5), and 8·37 (s, $CH_3{}^1$); (^{19}F; 94 MHz; $CDCl_3$; 34°) at 56·56 (q, $CF_3{}^A$) and 66·88 d, q, $CF_3{}^B$) p.p.m. rel. to $CFCl_3$]. Satisfactory microanalytical and mass spectral data have also been obtained for complexes (**3a,b**).

'forbidden' reactions promoted by transition metals should be re-examined, with a view to eliminate completely the possibility of stepwise addition.

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