Metal Carbonyl Chemistry. Part XIX.[1] Diels–Alder Reactions of the π-Cyclopentadienyldicarbonyliron Derivative of Hexafluorobicyclo[2.2.0]hexa-2,5-diene

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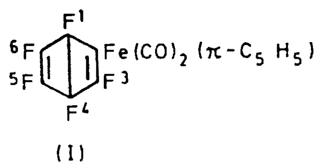
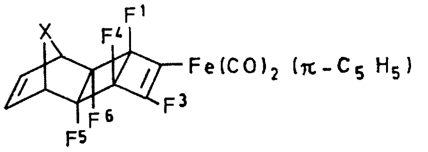
The compound $[(p\text{-}C_6F_5)Fe(CO)_2(\pi\text{-}C_5H_5)]$ reacts with cyclopentadiene, furan, or 2,3-dimethylbuta-1,3-diene to give yellow, air-stable 1 : 1 Diels–Alder adducts in which the *para*-bond is retained. Pyrrole failed to react under similar conditions. The i.r. spectra of the adducts from cyclopentadiene and furan show evidence for the presence of rotational isomers about the iron atom. The adduct from cyclopentadiene has also been prepared in low yield from reaction of 2,3,4,5,6,7-hexafluorotetracyclo[6.2.1.$0^{2,7}$.$0^{3,6}$]undeca-4,9-diene (the Diels–Alder adduct of cyclopentadiene and *para*-hexafluorobenzene) with $Na[Fe(CO_2)(\pi\text{-}C_5H_5)]$, but attempts to prepare the furan and pyrrole adducts by a similar route were unsuccessful.

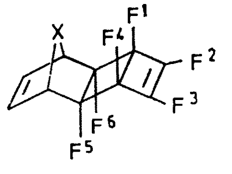
Recent work has shown [2] that hexafluorobicyclo[2.2.0]-hexa-2,5-diene is an active dienophile in the Diels–Alder reaction and gives 1 : 1 and 1 : 2 adducts with a number of dienes. Similar Diels–Alder reactions of some perfluorobicyclo[2.2.0]hex-2-ene derivatives have also been reported in a recent communication.[3] We now describe some reactions of dicarbonyl-π-cyclopentadienyl(pentafluorobicyclo[2.2.0]hexa-2,5-dien-2-yl)iron (I) [1,4] with dienes.



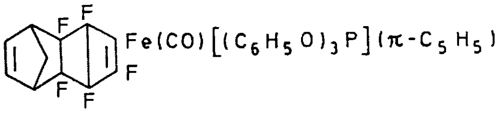
(I)



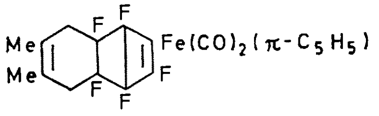
(II) a; X = CH2
b; X = O
c; X = NH



(III) a ; X = CH2
b ; X = O
c ; X = NH



(IV)



(V)

Cyclopentadiene reacts readily with (I) at room temperature in dichloromethane to give a 65% yield of the 1 : 1 adduct (IIa). This adduct may also be obtained in 8% yield from reaction of (IIIa) with sodium π-cyclopentadienyldicarbonylferrate at room temperature. As the i.r. and n.m.r. spectra of the products obtained by these different routes are identical this strongly suggests that the Diels–Alder adduct obtained from compound (IIa) has the same stereochemistry as that of compound (IIIa),[2] and that reaction occurs by *exo*-addition to (I), and by *exo*-addition to the cyclic diene. The ^1H n.m.r. spectrum of (IIa) shows four broad singlets centred at τ 3·47, 5·12, 6·84, and 8·25 with integrated intensities of 2 : 5 : 2 : 2 respectively. The band at τ 5·12 is readily assignable to the $\pi\text{-}C_5H_5$ group, and the presence of three bands due to the cyclopentadiene moiety confirms that a Diels–Alder adduct (1,4-addition) rather than a 1,2-adduct is obtained. Comparison with the ^1H n.m.r. spectrum of (IIIa) enables the following assignments to be made: τ 3·47 (olefinic protons), τ 6·84 (methine protons), and τ 8·25 (methylene-bridge protons). Under

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[1] Part XVIII, B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J.C.S. Dalton*, preceding paper.

[2] M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc.* (*C*), 1971, 90.

[3] W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *Chem. Comm.*, 1971, 709.

[4] D. J. Cook, M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1771.

low resolution the ^{19}F n.m.r. spectrum shows five band systems of approximately equal intensity.* The similarity between the chemical-shift value of the band at lowest field (24·8 p.p.m.), for the vinylic fluorine atom adjacent to the metal atom, when compared with that observed for the similar fluorine atom in compound (I) (29·8 p.p.m.) confirms that Diels–Alder addition occurs across the CF⋮CF bond in (I). The mass spectrum of (IIa) shows a parent ion at *m/e* 410, and peaks at *m/e* 382 and 354 corresponding to stepwise loss of two CO molecules. The major fragmentation pattern observed in the mass spectrum is a retro-Diels–Alder reaction of the parent ion to give cyclopentadiene and $[(C_6F_5)Fe(CO)_2(C_5H_5)]$. The i.r. spectrum of compound (IIa) is interesting in that six bands are observed in the metal carbonyl stretching frequency region.* This contrasts with the spectrum of compound (I) which shows only the expected strong symmetrical doublet in this region. The position and intensities of these bands in the spectrum of (IIa) are independent of the method of preparation of the complex and are unchanged by repeated chromatography or recrystallisation. It is therefore unlikely that these bands could be attributed to the presence of three stereoisomers, and it is considered that they are due to rotamers arising by restricted rotation about the iron–carbon σ-bond. Similar rotational isomerism has been observed previously for the compounds $[(CH_3Cl_2Si)Fe(CO)_2(\pi\text{-}C_5H_5)]$,[5] and acyl derivatives of the type $[(CXH_2{\cdot}CO)Mn(CO)_5]$ (X = F or Cl).[6] A molecular-framework model of compound (IIa) shows that there is some steric interaction between the π-cyclopentadienyl group and the fluorine atoms F^5 and F^6 and also the bridgehead fluorines F^1 and F^4. The interaction between the π-cyclopentadienyl group and atoms F^5 and F^6 is obviously absent in compound (I), and the interaction with the bridgehead fluorines is somewhat reduced due to the increased angle strain in the hexa-2,5-diene system and is such that in this compound the barrier to rotation about the iron–carbon bond is small.

Reaction of compound (IIa) with triphenyl phosphite at room temperature under u.v.-irradiation conditions gives a trace of a yellow solid, which is tentatively assigned the structure (IV) on the basis of its i.r. spectrum.* The spectrum shows a strong band at 1592 cm^{-1} for ν(FC⋮CFe), and although it only shows one band in the metal carbonyl region at 1993 cm^{-1}, this band is very broad (half-width 20 cm^{-1}) and has a pronounced shoulder at 1986 cm^{-1}, which suggests the possibility of rotational isomers, similar to those previously reported[7] for the compound $[(C_6H_5GeI_2)Co(CO)I(\pi\text{-}C_5H_5)]$.

Furan reacts only slowly with compound (I) to yield the 1 : 1 Diels–Alder adduct (IIb) in 68% yield. An attempt to prepare this compound by the alternative reaction of compound (IIIb) with $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ results only in the decomposition of both reactants. The ^1H n.m.r. spectrum shows bands at τ 2·05 (olefinic protons), 3·30 (methine protons), and 4·90 (π-cyclopentadienyl protons) in the intensity ratio of 2 : 2 : 5 respectively. The ^{19}F n.m.r. spectrum is similar to that of (IIa) and exhibits five bands of approximately equal intensity, with a low field band at 27·8 p.p.m. for the vinylic fluorine atom. The mass spectrum is also similar to that of (IIa) in that fragmentation of the parent ion at *m/e* 412 occurs with successive loss of two CO groups, and the major fragmentation pathway is by a retro-Diels–Alder reaction to give the base peak at *m/e* 344 $[(C_6F_5)Fe(CO)_2C_5H_5]^+$. The i.r. spectrum of (IIb) * shows a band at 1588 cm^{-1} [ν(CF⋮CFe)], and again six bands are observed in the metal carbonyl region suggesting that it is a mixture of rotamers.

An attempt to prepare the similar compound (IIc) by reaction of (I) with pyrrole was unsuccessful even at 60 °C for 4 days. The only product isolated was $[(C_6F_5)Fe(CO)_2(\pi\text{-}C_5H_5)]$, presumably formed by rearrangement of the starting material. In view of this competing rearrangement reaction no attempts were made to use more forcing conditions or longer reaction times. An attempt to prepare (IIc) by reaction of compound (IIIc) with $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ resulted only in the decomposition of the starting materials.

The reaction of (I) with 2,3-dimethylbuta-1,3-diene is extremely slow and gives only a 5% yield of the 1 : 1 adduct (V) after one month at room temperature. This compound was characterised from spectroscopic data only as insufficient material was available for elemental analysis. The mass spectrum shows a parent ion at *m/e* 426, and other fragments arising by stepwise loss of CO, accompanied by cleavage of methyl groups and/or loss of fluorines. This yields a series of fragments of high *m/e* values which can be formed by several interconnecting pathways. The retro-Diels–Alder cleavage of the parent ion is another major fragmentation pathway and gives rise to peaks at *m/e* 344 $[(C_6F_5)Fe(CO)_2(C_5H_5)]^+$, 316 $[(C_6F_5)Fe(CO)(C_5H_5)]^+$, 288 $[(C_6F_5)Fe(C_5H_5)]^+$, and 82 $[C_6H_{10}]^+$. In contrast to the other Diels–Alder adducts described in this work compound (V) shows only two metal carbonyl bands at 2042 and 1992 cm^{-1} in its i.r. spectrum,* although due to the limited quantity of material available the spectrum was run on a chloroform solution, which gives poorer resolution than the cyclohexane solvent employed when examining the metal carbonyl region of the other adducts. Other bands in the spectrum at 1712 cm^{-1} ν[C(CH_3)⋮C(CH_3)] and 1587 cm^{-1} ν(CF⋮CFe) are entirely consistent with the structure assigned to this compound.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer, and n.m.r. spectra on a Varian HA 100 instrument operating at 100·0 MHz for protons and 94·1 MHz for ^{19}F nuclei. Mass spectra were obtained on an

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* See Supplementary Publication No. 21250 (3 pp.); for details of the supplementary publications scheme, see Notice to Authors. No. 7, *J.C.S. Dalton*, 1974, Index issue.

[5] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 2773.

[6] F. Calderazzo, K. Noack, and U. Schaerer, *J. Organometallic Chem.*, 1966, **6**, 265.

[7] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 523.

A.E.I. MS902 mass spectrometer operating at an ionising energy of 70 eV. Molecular-weight determinations were carried out using a Mechrolab vapour pressure osmometer. Dicarbonyl-π-cyclopentadienyl(pentafluorobicyclo[2.2.0]-hexa-2,5-dien-2-yl)iron was prepared from hexafluorobicyclo-[2.2.0]hexa-2,5-diene as reported previously.[1,4] 2,3,4,5,6,7-Hexafluorotetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene, 2,3,4,5,6,7-hexafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene, and 2,3,4,5,6,7-hexafluoro-11-azatetracyclo-[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene were prepared as reported elsewhere.[2] Cyclopentadiene, furan, pyrrole, and 2,3-dimethylbuta-1,3-diene were commercial samples freshly distilled before use. Except where stated all manipulations were carried out under an atmosphere of dry nitrogen.

Diels–Alder Reactions of Dicarbonyl-π-cyclopentadienyl-(pentafluorobicyclo[2.2.0]*hexa*-2,5-*dien*-2-*yl)iron*.—(a) *With cyclopentadiene*. A solution of (I) (150 mg, 0·43 mmol) and dicyclopentadiene (150 mg, 2·3 mmol) in dry dichloromethane (3 ml) was sealed *in vacuo* in a Pyrex tube (10 ml) and shaken for 12 h at room temperature. Removal of the volatiles (20 °C/10 mmHg) gave a pale yellow solid, which on chromatography (alumina; n-hexane eluant) gave starting material (I) (10 mg). Further elution with chloroform gave *dicarbonyl-π-cyclopentadienyl-*(2,3,5,6,7-*pentafluorotetracyclo*-[6.2.1.0^{2,7}.0^{3,6}]*undeca*-4,9-*dien*-4-*yl)iron* (IIa) (120 mg, 0·27 mmol, 65%) as pale yellow crystals, m.p. 123—124 °C [Found: C, 53·0; H, 3·0; F, 23·4%; *M*, 418 (benzene), 410 (mass spectroscopy). $C_{18}H_{11}F_5FeO_2$ requires C, 52·7; H, 2·7; F, 23·2%; *M*, 410].

(b) *With furan*. A solution of (I) (100 mg, 0·29 mmol) in furan (4 ml) was shaken for 3 days at room temperature in a tube sealed under vacuum. Removal of the excess of furan gave a yellow solid which was chromatographed (alumina) to give recovered (I) (<10 mg; n-hexane eluant) and *dicarbonyl-π-cyclopentadienyl*(2,3,5,6,7-*pentafluoro*-11-*oxatetracyclo*[6.2.1.0^{2,7}.0^{3,6}]*undeca*-4,9-*dien*-4-*yl)iron* (IIb) (83 mg, 0·20 mmol, 68%), m.p. 172—174 °C, upon elution with chloroform [Found: C, 49·7; H, 2·5; F, 22·7%; *M*, 420 (benzene), 412 (mass spectroscopy). $C_{17}H_9F_5FeO_3$ requires C, 49·5; H, 2·2; F, 23·0%; *M*, 412].

(c) *With pyrrole*. A mixture of (I) (105 mg, 0·30 mmol), pyrrole (1·0 g, 15·0 mmol), and chloroform (3 ml), sealed *in vacuo* in a Pyrex tube (15 ml), was heated at 60 °C for 4 days. Removal of the chloroform (20 °C/0·5 mmHg) gave an orange oil, which was extracted with light petroleum (b.p. 30—40 °C; 3 × 10 ml), and the combined extracts were washed with water (2 × 10 ml) to remove traces of pyrrole. On drying the extract ($MgSO_4$), and removal of the solvent (20 °C/0·5 mmHg), a yellow solid (38 mg, 0·11 mmol, 36%) was obtained, which was identified by i.r. spectroscopy as dicarbonyl(pentafluorophenyl)-π-cyclopentadienyliron.[8]

(d) *With* 2,3-*dimethylbuta*-1,3-*diene*. When a solution of (I) (105 mg, 0·30 mmol) in 2,3-dimethylbuta-1,3-diene (3 ml) in a sealed tube was kept at room temperature for 1 month in the absence of light, removal of the volatile materials gave a yellow solid. Chromatography of this solid on alumina (light petroleum eluant) gave recovered (I) (12 mg, 0·035 mmol, 11%) and further elution with chloroform gave *dicarbonyl-π-cyclopentadienyl*(4,5-*dimethyl*-1,2,7,8,10-*pentafluorotricyclo*[6.2.0.0^{2,7}]*deca*-4,9-*diene*-9-*yl)iron* (V) (6 mg, 0·014 mmol, 5%) as a yellow solid, m.p. 165—167 °C, which may be recrystallised from a mixture of chloroform–light petroleum (b.p. 40—60 °C) at −20 °C [Found: *M*, 426 (mass spectrum). $C_{19}H_{15}F_5FeO_2$ requires *M*, 426].

Reaction of 2,3,4,5,6,7-*Hexafluorotetracyclo*[6.2.1.0^{2,7}.0^{3,6}]-*undeca*-4,9-*diene with Sodium Dicarbonyl-π-cyclopentadienylferrate*.—A solution of (IIIa) (77·5 mg, 3·1 mmol) in dry tetrahydrofuran (10 ml) was added to a solution of sodium dicarbonyl-π-cyclopentadienylferrate [prepared from bis(dicarbonyl-π-cyclopentadienyliron) (510 mg, 1·45 mmol) and 1% sodium amalgam] in tetrahydrofuran (50 ml), and the mixture was stirred for 2 h at room temperature. Removal of the solvent (20 °C/1 mmHg) gave an air-sensitive brown solid, which was extracted (3 × 25 ml) with light petroleum (b.p. 40—60 °C). Concentration of the combined extracts to *ca*. 10 ml and chromatography (alumina; light petroleum eluant) gave (IIa) (100 mg, 0·24 mmol, 8%), identified by i.r., n.m.r., and mass spectroscopy.

Attempted Reaction of 2,3,4,5,6,7-*Hexafluoro*-11-*oxatetracyclo*[6.2.1.0^{2,7}.0^{3,6}]*undeca*-4,9-*diene with Sodium Dicarbonyl-π-cyclopentadienylferrate*.—A solution of (IIIb) (380 mg, 1·5 mmol) in dry tetrahydrofuran (5 ml) was added to the sodium salt [from bis(dicarbonyl-π-cyclopentadienyliron) (265 mg, 0·75 mmol)] in tetrahydrofuran (25 ml) and the mixture was stirred for 3 h at room temperature. Removal of the solvent, followed by chromatography (alumina; light petroleum eluant) gave a yellow oil (<5 mg) which showed no metal carbonyl bands or bands in the C–F region of its i.r. spectrum.

Attempted Reaction of 2,3,4,5,6,7-*Hexafluoro*-11-*azatetracyclo*[6.2.1.0^{2,7}.0^{3,6}]*undeca*-4,9-*diene with Sodium Dicarbonyl-π-cyclopentadienylferrate*.—A solution of (IIIc) (600 mg, 2·4 mmol) and the sodium salt [from bis(dicarbonyl-π-cyclopentadienyliron) (425 mg, 1·2 mmol)] in tetrahydrofuran (45 ml) was stirred at room temperature for 1 h. Chromatography (alumina; chloroform eluant) gave only a trace of bis(dicarbonyl-π-cyclopentadienyliron) and no other products were detected.

Reaction of Dicarbonyl-π-cyclopentadienyl(2,3,5,6,7-*pentafluorotetracyclo*[6.2.1.0^{2,7}.0^{3,6}]*undeca*-4,9-*dien*-4-*yl)iron with Triphenyl Phosphite*.—A solution of (IIa) (115 mg, 0·28 mmol), and triphenyl phosphite (80 mg, 0·26 mmol) in dry n-hexane (15 ml) was irradiated (Hanovia UVS 500 lamp) for 2 h at room temperature. Removal of the solvent and chromatography (alumina) of the residue gave, on elution with a 1 : 1 mixture of chloroform–light petroleum (b.p. 40—60 °C), a yellow solid (40 mg), shown by i.r. spectroscopy to be unchanged (IIa) containing a small amount of the pentafluorophenyl isomer. Elution with chloroform gave a yellow solid (3 mg), tentatively identified as *carbonyl-π-cyclopentadienyl*(2,3,5,6,7-*pentafluorotetracyclo*[6.2.1.0^{2,7},-0^{3,6}]*undeca*-4,9-*dien*-4-*yl)(triphenyl phosphite)iron* (IV) (*ca*. 1·5% yield).

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[8] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1837.