

THE MECHANISM OF PHOTOINSERTION OF HALOALKENES INTO Fe—C BONDS OF DIENEIRON TRICARBONYLS

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Summary

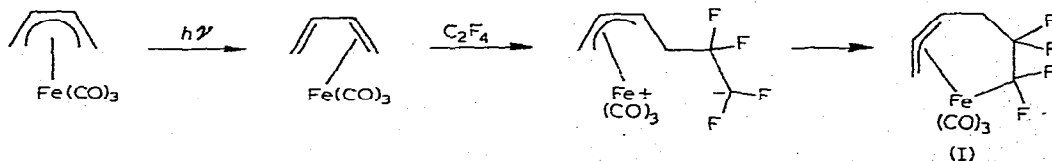
1,1-Dichloro-2,2-difluoroethylene (like other fluoroalkenes) and dieneiron tricarbonyls react photochemically to give products in which the haloalkene has inserted into the Fe—C(1) bond of the diene complex. The reaction is regioselective with respect to both diene and haloalkene. The reaction is shown to occur by (a) photodissociation of a CO ligand from iron; (b) π -complexation of haloalkene; (c) $\pi \rightarrow \sigma$ ligand rearrangements accompanied by CO reattachment. The adducts undergo hydrolysis on silica gel chromatography, to give substituted 2-chlorocyclohexadienoneiron tricarbonyls.

Introduction

Bond and Green and coworkers [1-6] have reported numerous reactions in which tetrafluoroethylene and related haloalkenes undergo photoinsertion into the C(1)—Fe bond of, inter alia, dieneiron tricarbonyls. Since photochemical reactions of such complexes may result from either photodissociation of a CO ligand [7] or from partial photodissociation of the diene, giving a transient (1,2- η)-bonded dieneiron tricarbonyl [8,9] we undertook studies of the mechanism of these reactions.

Bond, Lewis, and Green [5,6] have in the meantime proposed a mechanism (Scheme 1) involving formation of a zwitterion via nucleophilic attack of a

SCHEME 1. Proposed mechanism of photoinsertion.



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(1,2- η)-diene-Fe(CO)₃ species on the haloethylene.

This proposal adequately rationalizes their observed haloalkene regioselectivities, the tendencies of the groups to become bonded to the α -carbon having been found to be CF₃, Cl > F > H. However, a number of problems with this proposal come to mind: (a) photoreactions involving (1,2- η)-bonded diene intermediates usually occur with low quantum yields (≤ 0.04) and compete ineffectively with reactions involving photodissociation of CO, which have higher quantum yields (0.1–0.8) [7,8]; (b) cyclobutadieneiron tricarbonyl derivatives readily give the photoinsertion reaction [4], although no evidence of photochemically generated (1,2- η)-cyclobutadiene complexes could be obtained from studies of reactions with trimethylphosphite, quantum yield ≤ 0.001 [9]; (c) the failure of tetracyanoethylene to react by photoinsertion [9] is difficult to understand in terms of this mechanism; (d) the authors were forced to postulate electrophilic attack by the haloalkene at the coordinated double bond of the putative (1,2- η)-dieneiron tricarbonyl, in contrast to the normal pattern of attack by electrophiles at uncoordinated double bonds, since haloalkenes do not in fact react as electrophiles toward uncoordinated alkenes, but instead react predominantly via diradical intermediates.

Since regioselectivity provides an important clue to mechanism, we chose to use 1,1-dichloro-2,2-difluoroethylene in our studies, with the hope that the superior radical and carbanion-stabilizing ability of the chlorines would provide useful mechanistic evidence. Reactions with butadiene-, 2,3-dimethylbutadiene-, cyclohexadiene-, and also with the unsymmetrical diene complexes 1,3-pentadiene- and 1-phenylbutadiene-iron tricarbonyl were investigated.

Results

Reactions were run at room temperature, by UV irradiation, through GWV or Solidex filters, of solutions of the dieneiron tricarbonyls containing excess 1,1-dichloro-2,2-difluoroethylene. The reaction was followed by IR monitoring of the carbonyl peaks of starting material and adduct. The initially rapid reaction became slower as inorganic byproducts precipitated on the immersion well. Typical yields produced were about 30% of adduct, 40% recovered starting material, and 20% inorganic precipitate.

The reaction clearly results from absorption of light by the diene complex, since dichlorodifluoroethylene is completely transparent at the wavelengths used (> 300 nm). The adduct II is also transparent above 300 nm.

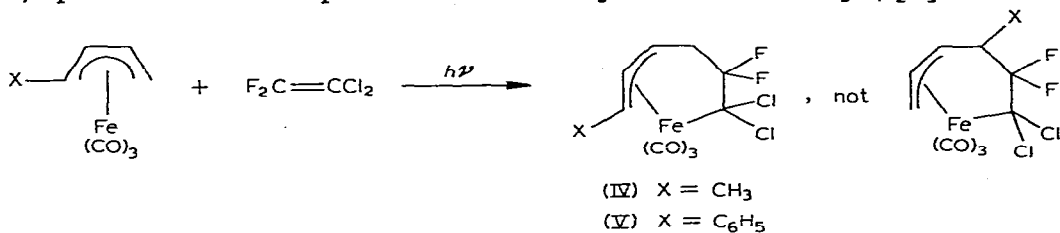
The adducts could be isolated and purified by careful crystallization. In contrast to C₂F₄ adducts, they are in all cases rather unstable, depositing inorganic precipitate on standing one or two days under argon at room temperature. They could be stored safely at -20°C under argon. All showed three carbonyl stretching frequencies at ca. 2080, 2030, and 2010 cm⁻¹, essentially identical to those of the butadieneiron tricarbonyl-tetrafluoroethylene adduct (I) at 2084, 2029, and 2014 cm⁻¹. The structures are based on IR, PMR, mass spectral, microanalytical data, and especially on ¹⁹F NMR data, as compared to the known tetrafluoroethylene adducts [2,4,5,6].

Spectroscopic data for the adducts are given in Table 1. The mass spectra showed very weak or undetectable parent peaks, QFe(CO)₃, but strong peaks

due to loss of 1–3 CO molecules, $QFe(CO)_{2-0}$; and in most cases peaks due to $QFe(CO)_{3-0} - HCl$; $QFe(CO)_{1,0} - HCl - HF$; $QFe - HF$; $Q - FCl$; $Q - FCl_2$; $Q - Cl_2F$, and $Q - HCl$.

Bond and Green have reported data for numerous tetrafluoroethylene adducts, in which the β -fluorines fall at average chemical shifts of 101 ppm from $CFCI_3$ (range 95–120 ppm) with 2J of 222 Hz, and α -fluorines average 74 ppm (range 66–91), with 2J 236 Hz [1-6]. Our data thus indicate that the adducts from dichlorodifluoroethylene (ca. 97 ppm and 211 Hz) have β -fluorines, not α . This is further supported by the agreement of the proton–fluorine coupling constants of our adducts with those reported [1-6] for the β -fluorines of the C_2F_4 adducts, and by the hydrolysis products obtained from the adducts (vide infra). Both IR and ^{19}F NMR spectra of the initial reaction mixtures gave no sign whatever of isomeric adducts; thus the reactions appear to be regiospecific with respect to the haloethylenes, only the $-FeCCl_2CF_2-$ isomer being detectable in each case.

The reaction is also found to be regiospecific with respect to the diene complex, since both 1-phenylbutadiene- and 1,3-pentadiene-iron tricarbonyl gave only one adduct. The coupling of F(1) to two hydrogens, H(5) and H(6), requires these adducts to be IV and V, in which the haloethylene has coupled to the unsubstituted end of the diene complex. Similar results have been reported for the 1,3-pentadiene- and isoprene-iron tricarbonyl adducts with C_2F_4 [5].



The reaction, although normally run at room temperature, is very facile. Thus, irradiation at $-50^\circ C$ of a hexane solution of butadieneiron tricarbonyl and dichlorodifluoroethylene, followed by determination of an infrared spectrum at $-40^\circ C$, showed the final adduct (II) already formed. Very little inorganic precipitate accompanied adduct formation under these conditions, and no intermediates could be detected.

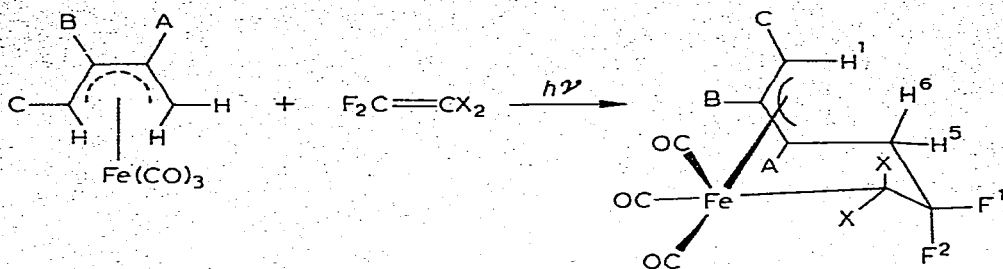
A clue to the mechanism was provided by the observation that addition of dichlorodifluoroethylene to a $-50^\circ C$ THF solution of the butadiene complex which had been irradiated for 15 hours at $-50^\circ C$ also cleanly gave the 1 : 1 adduct, as shown by IR.

Most significantly, irradiation of butadieneiron tricarbonyl and excess dichlorodifluoroethylene in toluene under a ^{13}CO atmosphere gave the adduct II containing $60 \pm 10\%$ of ^{13}CO in excess of normal. Recovered diene complex contained less than 13 atom % excess ^{13}CO . Thus, formation of adduct is accompanied by substantial CO exchange.

Discussion

The results, especially the CO exchange, strongly support a mechanism involving initial photodissociation of CO (Scheme 2), rather than partial photodis-

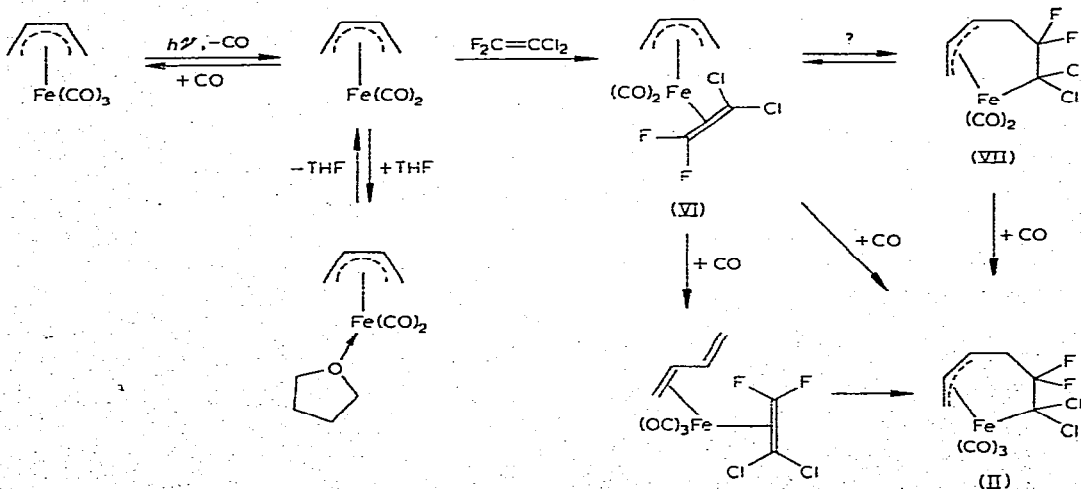
TABLE 1
SPECTROSCOPIC DATA FOR DIENEIRON TRICARBONYL-HALOETHYLENE ADDUCTS^a



Adduct	A	B	C	X	$\nu(\text{CO})$	δ_1	δ_C	δ_B
I	H	H	H	F	2084, 2029, 2014	2.25	2.6	ca. 4.1
II	H	H	H	Cl	2087, 2037, 2016	2.52	2.90	ca. 3.9
III	CH ₃	CH ₃	H	Cl	2078, 2027, 2002	2.6	2.9	1.4
IV	H	H	CH ₃	Cl	2080, 2030, 2007	ca. 1.9	1.22	ca. 3.6
V	H	H	Ph	Cl	2081, 2032, 2009	2.2	ca. 7.2	5.35

^a All NMR data in ppm downfield from reference compound: tetramethylsilane for protons and fluorotrichloromethane for ¹⁹F, measured in benzene-*d*₆ solutions. *J*'s are coupling constants in Hz. IR spectra measured in hexane or cyclohexane solutions.

SCHEME 2. Mechanism of photoinsertion reaction.

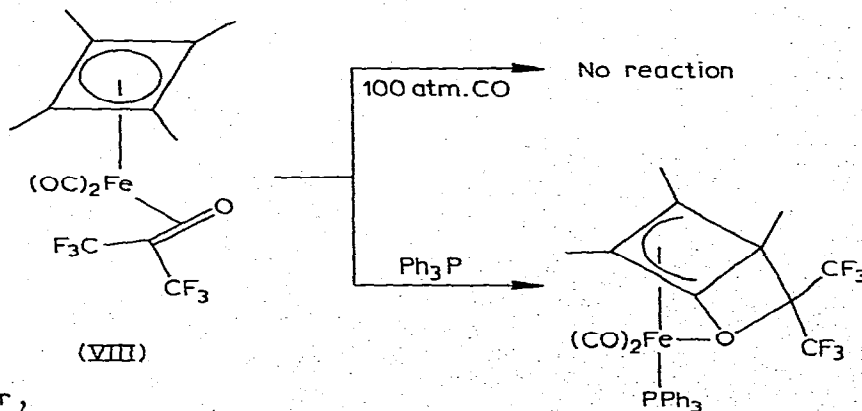


sociation of the diene as previously [5,6] proposed.

Intermediates analogous to VI have been isolated from photolysis of cyclobutadieneiron tricarbonyl in the presence of dimethyl maleate or fumarate [10] and evidently do not in those cases react further. The detailed mechanism of the $\pi \rightarrow \sigma$ conversion VI \rightarrow II cannot be fully determined from our results. However, η -tetramethyl-(1,2- η)-cyclobutadiene-hexafluoroacetoneiron tricarbonyl (VIII analogous to VI), which does not undergo the $\pi \rightarrow \sigma$ conversion under CO pressure, does rearrange in the presence of phosphines [4]; this suggests that the reaction

δ_A	δ_5	δ_6	J_{1B}	J_{1C}	J_{CB}	$J_{5F(1)}$	$J_{6F(1)}$	$\Phi_{F(1)}$	$\Phi_{F(2)}$	${}^2J_{FF}$
ca. 3.8	ca. 1.3	ca. 1.8	13	—	7	35.6	14	116.7	109.5	223
ca. 3.9	0.6–2.2	—	12.5	—	7	34	11	100.1	94.1	211
1.3	ca. 1.1	1.9	—	2.5	—	33	12	101.2	94.7	212
ca. 3.6	ca. 1.9	ca. 1.9	—	6	—	33	12	99.7	95.6	210
ca. 4.0	1.5–3.0	—	7	—	—	32	12	99.5	94.5	212

requires a “push” from an entering ligand, and does not proceed through an unsaturated intermediate like VII.



However,

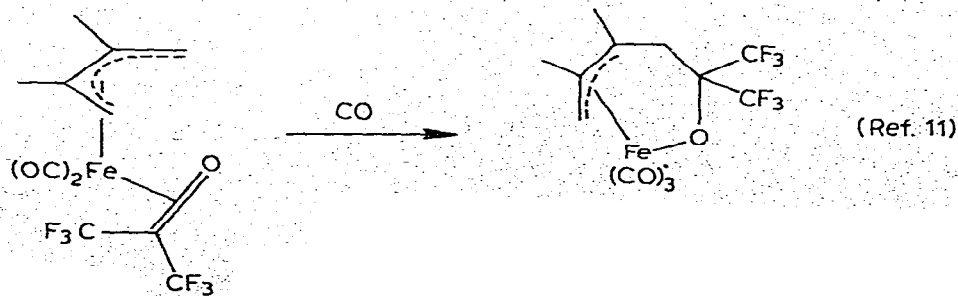
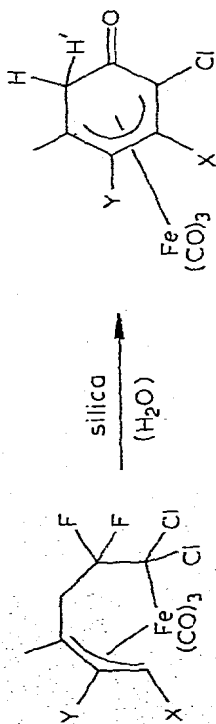


TABLE 2
SPECTROSCOPIC DATA FOR HYDROLYSIS PRODUCTS FROM $C_2F_2Cl_2$ ADDUCTS ^a

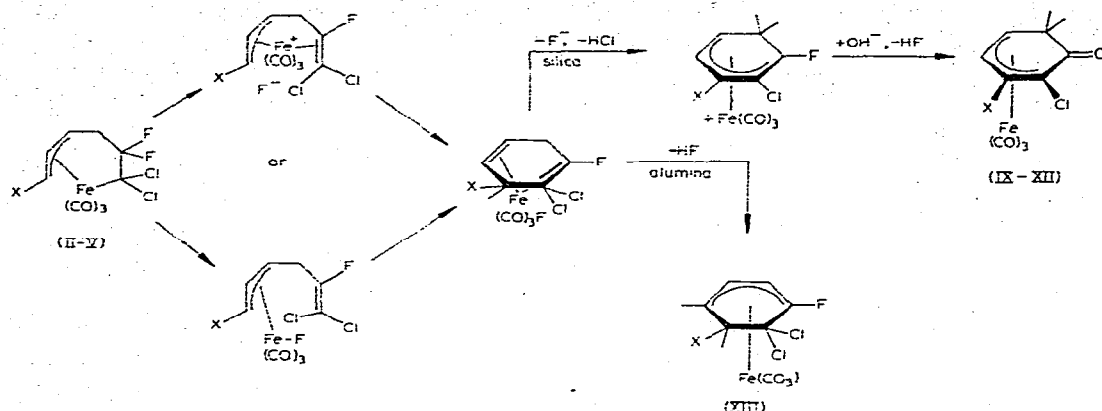


X	Y	Z	Prod- uct	Starting material	$\nu(CO)$ (cm^{-1})	δX	δY	δZ	δH	$\delta H'$	JHH'	JYZ	JZH,ZH'
H	H	H	IX	II	2068, 2012, 1999, 1690 ^b	5.25	4.33	2.08	ca. 2.2	1.7	17	4	—
H	CH ₃	CH ₃	X	III	2061, 2006, 1987, 1704	5.14	(1.35)	(0.86)	2.3	2.0	18	—	—
CH ₃	H	H	XI	IV	2062 ^c , 2002 ^c , 1993 ^c , 1690 ^b	(1.90)	4.52	2.05	2.2	ca. 1.7	16	6	1
C ₆ H ₅	H	H	XII	V	2068 ^d , 2012 ^d , 2000 ^d , 1685 ^d	(ca. 7.2)	4.82	ca. 1.9	ca. 2.2	ca. 1.7	18	5	1.4

^a All data as in Table 1, except as noted. ^b CCl₄ solution. ^c C₆H₆ solution. ^d CHCl₃ solution.

tural assignments previously made. They are explicable in terms of the activating effect of the iron in adducts II-V on the β -fluorines (Scheme 3).

SCHEME 3. Proposed mechanism for hydrolytic rearrangement of adducts.



Experimental

All reactions and manipulations were carried out under argon. Reaction solvents were analytical grade; all other solvents were freshly distilled before use. IR spectra were recorded on Perkin-Elmer Model 457 or 621 spectrophotometers, NMR spectra on Varian A-60A or Bruker HX-60E. Mass spectra were measured on a Varian MAT instrument at 70 eV ionizing voltage, using the direct inlet. Microanalyses were performed by Dornis and Kolbe, Mülheim. 1,1-Dichloro-2,2-difluoroethylene and tetrafluoroethylene were used as obtained from PCR, Inc.

Reaction of butadieneiron tricarbonyl with 1,1-dichloro-2,2-difluoroethylene

A solution of 1.738 g (8.96 mmol) butadieneiron tricarbonyl in 120 ml pentane in a GWV-glass filter immersion-well photoapparatus was degassed with a slow stream of argon for thirty minutes. 5 ml (ca. 58 mmol) dichlorodifluoroethylene was added, degassing continued for five more minutes, and photolysis was begun with a medium-pressure 250 W mercury lamp. After 8 hours, IR spectroscopy of the reaction mixture indicated product and starting material in comparable amounts. No other significant carbonyl absorptions appeared. The mixture was filtered into a 200-ml 2-neck flask to remove insoluble material, and the volume reduced to 20 ml by pumping. The solution was cooled to -78°C and filtered under argon, giving 0.919 g of product II (28%) as a light yellow solid. After drying under vacuum (10^{-2} Torr) for several hours, II was a near-white solid. Anal: Found: C, 33.03; H, 2.22; Cl, 21.57; F, 11.58; Fe, 16.96. $\text{C}_9\text{H}_6\text{Cl}_2\text{F}_2\text{FeO}_3$ calcd.: C, 33.07; H, 1.85; Cl, 21.69; F, 11.62; Fe, 17.08%. Mass spectrum: Major peaks at m/e 298, 270, 242 [$\text{C}_6\text{H}_6\text{Cl}_2\text{F}_2\text{Fe}(\text{CO})_{2-0}$]; 263, 235, 207 [$\text{C}_6\text{H}_6\text{ClF}_2\text{Fe}(\text{CO})_{2-0}$]; 214 and 186 [$\text{C}_6\text{H}_4\text{ClFFe}(\text{CO})_{1,0}$]; 150 ($\text{C}_6\text{H}_5\text{ClF}_2$); 132 ($\text{C}_6\text{H}_6\text{ClF}$); 97 ($\text{C}_6\text{H}_6\text{F}$); all with appropriate isotopic peaks.

^{19}F NMR of the filtrate showed some additional II, and large singlets at 107.9

and 113.9 ppm. No sign of any adduct isomeric with II was detectable. Evaporation of the filtrate gave 0.713 g of a yellow oil, identified by IR spectroscopy as primarily unreacted butadieneiron tricarbonyl (ca. 40%).

In another run, using 1.250 g diene complex (6.44 mmol) and 3 ml (ca. 35 mmol) dichlorodifluoroethylene in cyclohexane and photolyzing for 4 h with the apparatus attached to a gas buret, 1.45 mmol of gas was found to be evolved. The insoluble material was dissolved in distilled water and an aliquot was analyzed spectrophotometrically for iron(II) using 1,10-phenanthroline, which indicated 0.81 mmol iron(II) to have been formed (13%). Product II was isolated in 24% yield (0.498 g).

Reaction of 2,3-dimethylbutadieneiron tricarbonyl with dichlorodifluoroethylene

The reaction was run as above, using 0.886 g diene complex (4.00 mmol) and 3 ml (ca. 35 mmol) dichlorodifluoroethylene, and photolyzing the solution in 80 ml cyclohexane for 5 h through a Solidex filter. Filtration yielded 0.332 g of near-white solid, after washing in cyclohexane and drying in vacuo. Evaporation of the filtrate gave a yellow oil, which was recrystallized from hexane at -78°C , giving a near-white solid (III) m.p. $77-82^{\circ}\text{C}$ (dec.). IR and PMR spectra: Table 1. Mass spectrum: Major peaks at m/e 326, 298, and 270 [$\text{C}_8\text{H}_{10}\text{Cl}_2\text{F}_2\text{Fe}(\text{CO})_{2-0}$]; 318, 290, and 262 [$\text{C}_8\text{H}_9\text{ClF}_2\text{Fe}(\text{CO})_{3-1}$]; 250 ($\text{C}_8\text{H}_9\text{Cl}_2\text{FFe}$); 242 and 214 [$\text{C}_8\text{H}_8\text{FClFe}(\text{CO})_{1,0}$]; 160 ($\text{C}_8\text{H}_{10}\text{FCl}$); 145 ($\text{C}_7\text{H}_7\text{FCl}$); 125 ($\text{C}_8\text{H}_{10}\text{F}$); and 109 ($\text{C}_7\text{H}_6\text{F}$); all with appropriate isotopic patterns.

In another run, 1.619 g (7.29 mmol) of complex and 4 ml (ca. 45 mmol) dichlorodifluoroethylene in 80 ml dry ether were photolyzed for 6 h. Adduct III was obtained in 17% crude yield by filtration of the reaction mixture, evaporation of the filtrate in vacuo, and recrystallization of the residue from toluene/hexane at -78°C , m.p. 80°C (dec.). ^{19}F NMR spectrum: Table 1. A ^{19}F NMR spectrum of the mother liquor showed peaks due to III and numerous byproducts, but none around 74 ppm attributable to the regioisomeric adduct.

Reaction of 1,3-pentadieneiron tricarbonyl with dichlorodifluoroethylene

Diene complex (0.597 g, 2.90 mmol) and 3 ml (ca. 35 mmol) dichlorodifluoroethylene in 120 ml hexane were photolyzed as above for 7 h through a GWV glass filter. Filtration left an inorganic residue which was dried for 18 hours, then submitted for microanalysis: Anal: Found: C, 2.10; H, 3.30; Fe, 35.03; Cl, 27.13; F, 9.46%. Mol. ratios: C, 0.28; H, 5.25; Fe, 1.00; Cl, 1.22; F, 0.79.

Evaporation of the filtrate left a pale yellow residue whose ^{19}F NMR spectrum (Table 1) showed only adduct IV, and a singlet at 107.6 ppm. Recrystallization from hexane at -78°C gave IV as near-white solid, m.p. $83-85^{\circ}\text{C}$ (dec.). IR and NMR spectra: Table 1. MS: major peaks at m/e 312, 284, and 256 [$\text{C}_7\text{H}_8\text{Cl}_2\text{F}_2\text{Fe}(\text{CO})_{2-0}$]; 221 ($\text{C}_7\text{H}_8\text{ClF}_2\text{Fe}$); 200 ($\text{C}_7\text{H}_8\text{Cl}_2\text{F}_2$); 146 and 111 ($\text{C}_7\text{H}_8\text{Cl}_{1,0}\text{F}$); 131 and 96 ($\text{C}_6\text{H}_5\text{Cl}_{1,0}\text{F}$); and 95 ($\text{C}_6\text{H}_4\text{F}$), all with appropriate isotopic peaks. Anal: Found: C, 35.58; H, 2.85; Cl, 19.10; F, 10.28; Fe, 15.06. $\text{C}_{10}\text{H}_8\text{Cl}_2\text{F}_2\text{FeO}_3$ calcd.: C, 35.23; H, 2.36; Cl, 20.80; F, 11.15; Fe, 16.38%.

Reaction of 1-phenylbutadieneiron tricarbonyl with dichlorodifluoroethylene

1.053 g (3.90 mmol) diene complex and 4 ml (ca. 45 mmol) dichlorodifluoro-

ethylene in 140 ml hexane were photolyzed for 6.5 h through GWV glass as described previously. Filtration and evaporation of the reaction mixture gave 0.649 g of a yellow solid, m.p. 85–90°C (dec.). Recrystallization from hexane/toluene at –78°C gave 0.482 g of V (31% yield). Evaporation of the mother liquor left a yellow solid, IR of which showed predominantly starting diene complex, plus some additional V. IR and NMR spectra: Table 1.

Reaction of cyclobutadieneiron tricarbonyl with dichlorodifluoroethylene

Photolysis of a solution of 1.00 g (5.21 mmol) cyclobutadieneiron tricarbonyl and 3 ml (ca. 35 mmol) dichlorodifluoroethylene in 80 ml cyclohexane through Solidex for 4 h produced a large quantity of inorganic precipitate, but IR of the reaction solution showed little or no adduct. The mixture was filtered and the filtrate evaporated down, leaving 0.612 g of a brown oil, TLC of which (silica, hexane) showed starting material as the only mobile substance. After drying in vacuo, the solid was submitted for analysis: Found: Fe, 25.10; Cl, 22.39; F, 9.68. Mol. ratios: Fe, 1.00; Cl, 1.40; F, 1.13.

Reaction of cyclohexadieneiron tricarbonyl with dichlorodifluoroethylene

A solution of 1.101 g (5.00 mmol) cyclohexadieneiron tricarbonyl and 3 ml (ca. 35 mmol) dichlorodifluoroethylene in 140 ml hexane was photolyzed through GWV for 5 h. IR spectroscopy showed only starting material, but some precipitate had formed on the filter. This was removed, the solution again degassed, and photolysis continued for an additional 17 h. Filtration gave 0.565 g of inorganic precipitate and a filtrate, which left 0.757 g of a pale yellow oil on evaporation. The IR spectrum in the metal carbonyl region showed only starting material in significant amount; peaks at 1800, 1750, and 1710 cm^{-1} also indicated organic carbonyl compounds. Gas chromatographic analysis showed at least 24 components; the three largest had apparent molecular weights of 158 ($\text{C}_8\text{H}_8\text{FCI?}$), 130 ($\text{C}_6\text{H}_4\text{FCI?}$) and 142 ($\text{C}_8\text{H}_8\text{F}_2?$).

Reaction of dichlorodifluoroethylene with photolyzed butadieneiron tricarbonyl in THF at –50°C

A solution of 0.144 g (0.75 mmol) butadieneiron tricarbonyl in 200 ml THF (freshly distilled from LiAlH_4 under argon) was cooled to –50°C in a jacketed photoapparatus by circulating coolant through the jacket and lamp well, and photolyzed through GWV at –50°C, with a very slow continuous flow of argon through the solution. After 15 h, photolysis was discontinued, 3 ml (ca. 35 mmol) dichlorodifluoroethylene was added, and the solution allowed to warm to room temperature. Evaporation of the solvent gave a brown oil, whose IR spectrum (in cyclohexane) showed starting material (2052, 1985, 1976 cm^{-1}) and adduct II (2084, 2036, 2013 cm^{-1}).

Reaction of butadieneiron tricarbonyl with dichlorodifluoroethylene at –50°C

A solution of 0.250 g (1.29 mmol) butadieneiron tricarbonyl and 1 ml (ca. 12 mmol) dichlorodifluoroethylene in 200 ml hexane was cooled to –50°C as above while degassing with argon. After 3 h of photolysis through GWV at ca –50°C the solution was transferred to a Dry Ice-cooled flask under argon pressure, and stored at –78°C. An IR spectrum taken at –40°C showed only peaks due to

starting material and adduct II. The solution was warmed to room temperature and filtered, leaving 0.039 g of inorganic precipitate. Evaporation of the filtrate left 0.241 g of residue which was subjected to pump vacuum for 2 h then recrystallized from hexane at -78°C , giving 0.10 g (31%) of near-white II m.p. 78°C (dec.). Identification followed from IR and NMR spectra.

Reaction of butadieneiron tricarbonyl with dichlorodifluoroethylene under $^{13}\text{C}^{18}\text{O}$

40 ml of a solution made by dissolving 0.312 g of complex and 4 ml (ca. 45 mmol) dichlorodifluoroethylene in enough toluene to make 50.0 ml was transferred to a flask fitted with two stopcock outlets (1.29 mmol complex and ca. 37 mmol haloalkene). One was connected to a $^{13}\text{C}^{18}\text{O}$ reservoir and the other to a pump and an argon reservoir. The solution was frozen in liquid nitrogen and the flask evacuated to 5×10^{-3} Torr, then the pump closed off and the flask warmed to room temperature. $^{13}\text{C}^{18}\text{O}$ was then admitted from the reservoir, and the pressure in the flask restored to 1 atm by admitting argon. The pressure in the reservoir was restored to ca. 1 atm by admitting 77.6 ml of argon at 22°C and 755 mm. The initial gas in the reservoir was 55.5% $^{13}\text{C}^{18}\text{O}$, 2.7% $^{12}\text{C}^{18}\text{O}$, and 41.8% Ar, so that 1.75 mmol $^{13}\text{C}^{18}\text{O}$ was introduced. The solution was photolyzed for 1 h at 19°C using an external 1600 W xenon lamp, then the flask was attached through a -130°C cooled trap (pentane slush bath) to a reservoir. The trap and reservoir were evacuated to 5×10^{-3} Torr, then gas from the reaction flask expanded into the reservoir through the trap. Mass spectrometric analysis of the gas indicated 55% argon, 26% $^{12}\text{C}^{18}\text{O}$, and 19% $^{13}\text{C}^{18}\text{O}$. The reaction flask was refilled with argon, the solution transferred to a two-neck round-bottom flask, and the solvent was stripped off, giving 0.389 g of a yellow oil. A cold finger was inserted into the flask, the flask evacuated, and the cold finger cooled with liquid nitrogen to recover butadieneiron tricarbonyl. Mass spectrometric analysis of this crude recovered starting material at m/e 194–197 showed less than 13 atom % excess $^{13}\text{C}^{18}\text{O}$. The residue after removal of the starting material (0.202 g yellow solid) was predominantly adduct II as shown by IR spectroscopy. Mass spectrometric analysis at m/e 298–301 indicated 47% $\text{C}_6\text{H}_6\text{Cl}_2\text{F}_2\text{Fe}(^{12}\text{C}^{18}\text{O})_3$, 45% $\text{C}_6\text{H}_6\text{Cl}_2\text{F}_2\text{Fe}(^{13}\text{C}^{18}\text{O})(^{12}\text{C}^{18}\text{O})_2$, and 8% $\text{C}_6\text{H}_6\text{Cl}_2\text{F}_2\text{Fe}(^{13}\text{C}^{18}\text{O})_2(^{12}\text{C}^{18}\text{O})$. (Values $\pm 10\%$, corrected for natural $^{13}\text{C}^{18}\text{O}$). Rapid chromatography of the residue on silica gel, followed by recrystallization from hexane at -78°C gave 0.101 g of adduct II, m.p. 81°C (dec.), identified by IR spectroscopy.

Hydrolysis of II on alumina

Butadieneiron tricarbonyl (1.408 g, 7.26 mmol) and $\text{C}_2\text{Cl}_2\text{F}_2$ (5 ml, ca. 58 mmol) were photolyzed in cyclohexane as described above, for 4 h. Filtration and evaporation of the solvent left 1.585 g of material, predominantly II (IR spectroscopy), which was chromatographed on basic alumina. Gas was evolved from the column. Elution with hexane gave first a yellow band, which yielded 0.163 g (12%) of recovered butadieneiron tricarbonyl on collection and evaporation. Hexane then eluted an orange band, collection and evaporation of which gave 0.209 g of an amber oil, (XIII, 9%). The IR spectrum (CCl_4) showed $\nu(\text{CO})$ at 2057, 1997, and 1986 cm^{-1} . The ^1H NMR spectrum (CCl_4) showed resonances at δ (ppm) ca. 5.5 ((br.) m, 2, H(2) and H(3)), 1.9 (d, 1, J 7 Hz, H(4)), 1.5 (d, 1, J 8 Hz, H(5)), and 0.6 (d, 1, J 8 Hz, H(5')). The ^{19}F NMR spectrum (C_6H_6)

showed a resonance at 112.2 ppm (from CFCl_3), with $J(\text{F}-\text{H}(2))$ 26.5 Hz, and $J(\text{F}-\text{H}(5)) = J(\text{F}-\text{H}(5')) \approx 1$ Hz. The mass spectrum showed peaks at m/e 306, 278, 250, and 222 ($\text{C}_6\text{H}_5\text{Cl}_2\text{FFe}(\text{CO})_{3-0}$), 186 ($\text{C}_6\text{H}_4\text{ClFFe}$), 112 ($\text{C}_6\text{H}_5\text{Cl}$), 96 ($\text{C}_6\text{H}_5\text{F}$), 91 (FeCl), and 77 (C_6H_5), all with appropriate isotopic peaks. These data indicate that XIII is 6,6-dichloro-1-fluorocyclohexa-1,3-dieneiron tricarbonyl.

Hydrolysis of II on silica

A 2.00 g sample of crude reaction product obtained as above from photolysis of 1.951 g (10.1 mmol) butadieneiron tricarbonyl and excess dichlorodifluoroethylene was chromatographed on silica gel. Hexane eluted starting material (0.354 g, 18%). The product (IX) was eluted with 10% ether in benzene as a golden yellow band. Evaporation of the solvent left 0.784 g (29%) of an oily solid, which was recrystallized from hexane/toluene at -78°C to give IX as ochre needles, m.p. 114°C (dec.). Anal.: Found: C, 40.30; H, 2.03; Cl, 13.42; Fe, 20.91. $\text{C}_9\text{H}_5\text{ClFeO}_4$ calcd.: C, 40.27; H, 1.88; Cl, 13.21; Fe, 20.81%. The mass spectrum showed peaks at m/e 268, 240, 212, and 184 ($\text{C}_6\text{H}_5\text{ClOFe}(\text{CO})_{3-0}$), 156 ($\text{C}_5\text{H}_5\text{ClFe}$), 148 ($\text{C}_6\text{H}_4\text{OFe}$), 128 ($\text{C}_6\text{H}_5\text{ClO}$), 120 ($\text{C}_5\text{H}_4\text{Fe}$) and 91 (FeCl), all with appropriate isotopic peaks.

Hydrolysis of III on silica

The crude product from 4 h irradiation of 1.15 g of 2,3-dimethylbutadieneiron tricarbonyl (5.18 mmol) with excess dichlorodifluoroethylene in hexane (1.24 g, predominantly III and starting material (IR spectroscopy)) was chromatographed on silica. Hexane eluted, as a yellow band, 0.317 g of starting complex (28% recovery). A 30% ether/benzene mixture eluted, as an orange band, 0.237 g of yellow solid (X), 15% yield. Recrystallization from hexane/toluene at -78°C gave yellow crystals, m.p. $118-120^\circ\text{C}$. Anal.: Found: C, 44.44; H, 3.10; Cl, 12.01; Fe, 18.84. $\text{C}_{11}\text{H}_9\text{ClFeO}_4$ calcd.: C, 44.56; H, 3.06; Cl, 11.96; Fe, 18.84%. The mass spectrum showed peaks at m/e 296, 268, 240 and 212 ($\text{C}_8\text{H}_9\text{ClOFe}(\text{CO})_{3-0}$), 197 ($\text{C}_7\text{H}_6\text{ClOFe}$), 176 ($\text{C}_8\text{H}_8\text{OFe}$), 148 ($\text{C}_7\text{H}_8\text{Fe}$), 121 ($\text{C}_5\text{H}_5\text{Fe}$), and 91 (FeCl), all with appropriate isotopic peaks.

Hydrolysis of IV on silica

The crude product from 5.5 h irradiation of 1.113 g (5.35 mmol) of pentadieneiron tricarbonyl with excess dichlorodifluoroethylene in hexane was chromatographed on silica. Elution with hexane gave 0.489 g (44%) of recovered starting material. Elution with 30% ether/hexane gave 0.352 g of a yellow-orange solid (XI, 27% yield), which was recrystallized from hexane/toluene to give fine yellow needles, m.p. $133-135^\circ\text{C}$ (dec.). Anal.: Found: C, 42.42; H, 2.76; Cl, 12.52; Fe, 19.74. $\text{C}_{10}\text{H}_7\text{ClFeO}_4$ calcd.: C, 42.52; H, 2.50; Cl, 12.55; Fe, 19.77%. The mass spectrum showed peaks at m/e 282, 254, 226, and 198 ($\text{C}_7\text{H}_7\text{ClOFe}(\text{CO})_{3-0}$), 162 ($\text{C}_7\text{H}_6\text{OFe}$), 134 ($\text{C}_6\text{H}_6\text{Fe}$), 107 ($\text{C}_7\text{H}_7\text{O}$) and 91 (FeCl), all with appropriate isotopic peaks.

Hydrolysis of V on silica

A 0.227 g portion of V (0.56 mmol) was chromatographed on silica. Elution with 40% ether/hexane gave 0.141 g (73%) of X, as an ivory-colored solid, m.p.

175°C (dec.). The mass spectrum showed peaks at m/e 344, 316, 288, and 260 ($C_{12}H_9ClOFe(CO)_3$), 232 ($C_{11}H_9ClFe$), 196 ($C_{11}H_8Fe$), 141 ($C_{11}H_9$), and 115 (C_9H_7). Anal.: Found: C, 48.06; H, 2.81; Cl, 10.21; Fe, 16.08. $C_{15}H_9ClFeO_4$ calcd.: C, 52.29; H, 2.63; Cl, 10.29; Fe, 16.21%.

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