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ALKENYLIRON COMPLEXES. CYCLOADDITION REACTIONS OF ORGANOIRON METALLOALKADIENES

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Summary

The metalloalkadienes, 2-Fp-1,3-butadiene (**5**), 1-Fp-1,3-butadiene (**6**), and 1-Fp-3-methyl-1,3-butadiene (**7**) (Fp = η-$C_5H_5(CO)_2Fe$) form Diels–Alder adducts with a variety of electrophilic dienophiles. Kinetic experiments have demonstrated that **5** is at least 100 times more reactive toward dimethyl acetylene dicarboxylate than 2-trimethylsiloxy-1,3-butadiene. **5** and toluene sulfonyl isocyanate from an imino lactone that is thought to arise via a stepwise process involving ionic species. The synthetic utility of **5** is limited by its low decomposition point (110°C) and the formation of nearly equimolar quantities of the 1,3- and 1,4-positional isomers of cycloadducts derived from several asymmetric dienophiles.

Introduction

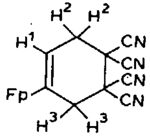
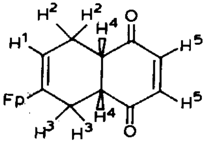
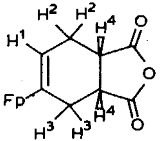
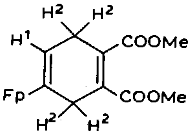
The rate of the Diels–Alder reaction [1] can be enhanced dramatically by combining an electron-rich diene with an electrophilic dienophile. Although a large number of reactive electrophilic dienophiles are known, there has not been a parallel development of reactive dienes. There are a limited number of highly reactive dienes (i.e. cyclobutadiene), but these substances do not necessarily impart synthetic flexibility to the Diels–Alder adducts. The problems of low reactivity and lack of synthetic flexibility have been alleviated partially by the utilization of electron-rich alkadienes bearing substituents such as alkoxy [2], acetoxy [3], and silyl [4]. In particular, Danishefsky's diene ($MeOCH{=}CH(Me_3SiO)C{=}CH_2$) is quite reactive, and the resulting cyclohexenes are transformed readily into useful cyclohexenones [5].

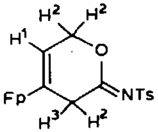
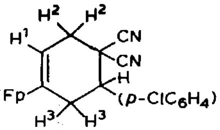
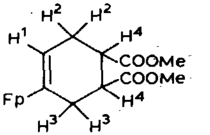
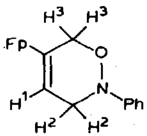
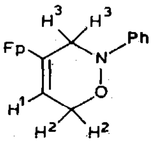
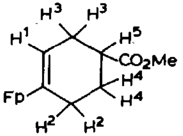
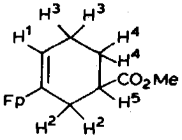
There is a need for highly reactive electron-rich alkadienes containing substituents that can be manipulated into useful functionality. In this sense transition metal groups may be useful substituents. Certain transition metal groups are powerful electron donors when bonded to organic substrates. In particular, the electron donor ability of the Fp group (Fp = η-$C_5H_5(CO)_2Fe$) is attested to by the fact that

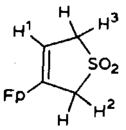
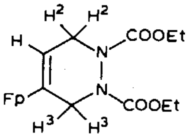
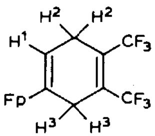
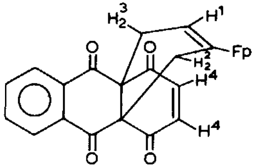
0022-328X/85/$03.30 *(Continued on p. 240)*

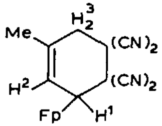
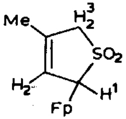
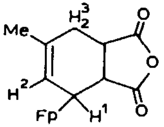
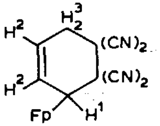
TABLE 1

YIELDS AND SPECTROSCOPIC PROPERTIES OF THE PRODUCTS ISOLATED FROM THE REACTION BETWEEN **5**, **6**, OR **7** AND DIENOPHILES

Reactants	Adduct	Yields (%)	PMR data (τ)						IR data (cm^{-1})
			H^1	H^2	H^3	H^4	Cp	Other	
Tetracyanoethylene and **5**	 (8)	93	4.28 [a]	6.50	6.75	–	4.83	–	2365, 2320 (CN) [d] 2020, 1970 (CO)
p-quinone and **5**	 (9)	85	4.63 [b]	6.98	6.98	7.50	5.25	3.59 (H^5)	2002, 1960 (CO) [d]
Maleic anhydride and **5**	 (10)	77	4.13 [c]	6.72	6.72	7.50	5.21	–	2002, 1945, (CO) [d] 1861, 1769, (C(O)OC(O))
Dimethylacetylene dicarboxalate and **5**	 (11)	90	4.48 [c]	6.90	6.90	–	5.20	6.23 (OMe) 6.17 (OMe)	2015, 1935 (CO) [d]

p-Toluenesulfonyl isocyanate and **5**	 (12)	88	4.10 [c]	5.18	5.48	–	5.13	2.25 (Ar) 2.85 (Ar) 7.58 (CH_3)	2010m, 1948 (CO) [d] 1571 (C=N)
β,*β*-Dicyano-*o*-chlorostyrene and **5**	 (13)	83	4.43 [c]	7.20	7.20	5.95	5.15	2.70 (Ar)	2300, 2253 (CN) [d] 2007, 1955 (CO)
Dimethylfumarate and **5**	 (14)	70	4.50 [c]	7.60	7.60	7.25	5.28	6.35 (OMe) 6.33 (OMe)	2005, 1935 (CO) [d] 1740, 1720 (C=O)
Nitrosobenzene and **5**	 (15a) and  (15b)	8	4.30 [b]	5.70	6.25	–	5.26 5.24	3.00 (Ar)	2010, 1960 (CO) [e]
Methyl acrylate and **5**	 (16a)  (16b)		4.60 [b]	–	7.70	–	4.39 4.40	6.50 (OMe) 6.51 (OMe) 7.70 H^5	

Sulfur dioxide and **5**	 (17)		4.25 [a]	–	6.49	–	4.85		2010, 1960 [d] (CO) 1282, 110 (SO_2)
Diethylazo-dicarboxylate and **5**	 (18)	91	4.60 [b]	6.00	6.00	–	5.28	6.00 (CH_2) 8.80 (CH_3)	2015, 1985 (CO) [e] 1750 (C=O)
Hexafluoro-2-butyne and **5**	 (19)	85	4.60 [b]	7.05	7.05	–	5.31	–	2010, 1945 (CO) [d]
Quinarzarine-quinone and **5**	 (20)	75	4.50 [b]	–	7.39	3.32	5.15	2.20 (Ar)	2010, 1940 (CO) [d] 1692, 1715 (C=O)

Tetracyano-ethylene and 7	 (21)	6.35 [a]	4.25	7.05	–	4.85	8.24 (Me)	2005, 1960 (CO) [d]
Sulfur dioxide and 7	 (22)	5.92 [b]	4.55	6.68	–	5.09	8.26 (Me)	2005, 1960 (CO) [e] 1330, 1100 (SO_2)
Maleic anhydride and 7	 (23)	7.35 [b]	4.35	7.70	6.78	5.35	8.30 (Me)	2000, 1940 (CO) [e] 1765 (C=O)
Tetracyanoethylene and **6**	 (24)	6.33 [a]	3.80 3.96	6.88	–	4.65	–	2010, 1960 (CO) [d]

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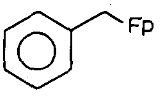
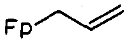
[a] Acetone-d_6. [b] Carbon disulfide. [c] Chloroform-d_1. [d] KBr pellet. [e] Neat.

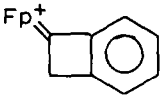
compound **1** is as reactive to proton–deuterium exchange as anisole [6], that the σ-allyl complex **2** is protonated by weak acids such as acetic acid [7] and that the Fp group stabilizes carbenium ions such as the cationic carbene complexes **3** and **4** [8]. Hence, it appears that the attachment of either Fp or $FpCH_2$ to the 1- or 2-positions of the 1,3-alkadienes would activate these dienes toward electrophilic dienophiles.



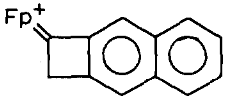
(1)



(2)



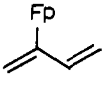
(3)



(4)

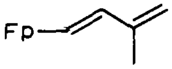
Furthermore, the resulting Diels–Alder adducts would possess either an iron-vinyl or iron-allyl group that could be transformed to useful organic functionality.

Herein, we report the results of our studies of the cycloaddition reactions of the metalloalkadienes 2-Fp-1,3-butadiene (**5**) [9], 1-Fp-1,3-butadiene (**6**) [10], and 1-Fp-3-methyl-1,3-butadiene (**7**) [10].



(5)

(6)



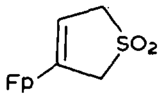
(7)

Results and discussion

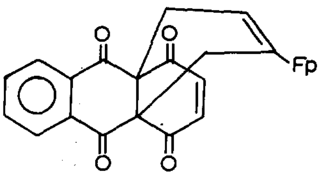
Cycloadducts of 2-Fp-1,3-butadiene

The electron-rich metalloalkadiene, 2-Fp-1,3-butadiene (**5**), readily affords [4 + 2]-cycloadducts as bright yellow solids when allowed to react with symmetrical electrophilic dienophiles. The yields of these cycloadducts (70–93%) are quite good even though no effort was made to maximize them. The dienophiles employed, structures and yields of the cycloadducts, and spectroscopic data are presented in Table 1. Analytical data is presented in Table 2. The proposed cyclohexene and cyclohexadiene structures are in accord with the ^1H NMR spectral data for these substances. Further support for these structures comes from the transformation of the *p*-quinone adduct **9** to the known adduct of butadiene and *p*-quinone by sequential protonation and demetallation (see Scheme 1).

Quinazarinquinone, which has two potential dienophilic sites – the external and internal carbon–carbon double bonds – forms a cycloadduct **20** via the internal double bonds only. Not surprisingly, sulfur dioxide gave the substituted sulfolene **17**.



(17)

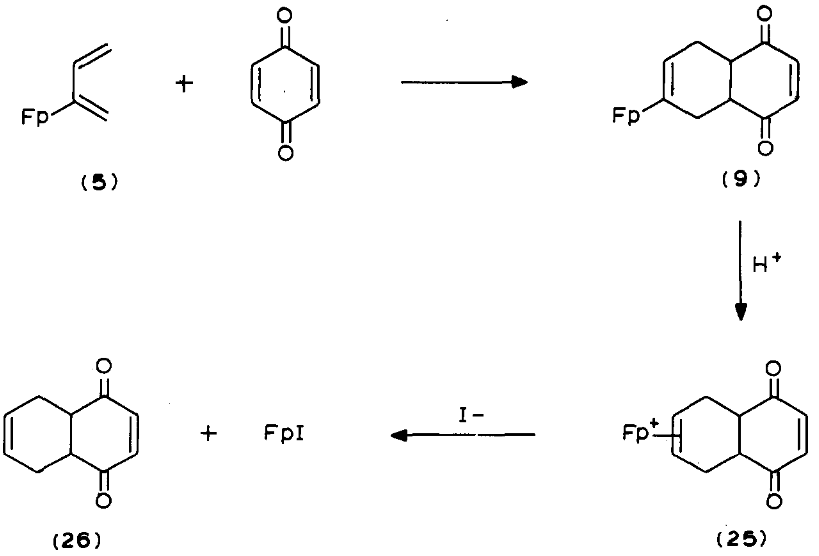


(20)

TABLE 2

IRON ANALYSES AND MELTING POINTS OF CYCLOADDUCTS

Adduct	Empirical formulae	M.p. (°C)	Iron analyses (Found (calcd.)(%))
8	$C_{17}H_{10}FeN_4O_2$	228–229	15.84 (15.60)
9	$C_{17}H_{14}FeO_4$	101	16.46 (16.53)
10	$C_{15}H_{12}FeO_5$	136	17.04 (17.07)
11	$C_{17}H_{16}FeO_6$	106	14.96 (15.05)
12	$C_{19}H_{17}FeNO_5S_2$	121–122	13.37 (13.11)
13	$C_{21}H_{15}ClFeN_2O_2$	145–146	13.25 (13.38)
14	$C_{17}H_{18}FeO_6$	104	15.45 (14.97)
15	$C_{17}H_{15}FeNO_3$	oil	15.91 (16.61)
17	$C_{11}H_{10}FeO_4S$	–	19.39 (19.04)
18	$C_{17}H_{20}FeN_2O_6$	oil	13.80 (13.86)
19	$C_{15}H_{10}F_6FeO_2$	65	14.44 (14.28)
20	$C_{25}H_{16}FeO_6$	184	11.69 (11.96)
21	$C_{18}H_{12}FeN_4O_2$	–	15.37 (15.05)



SCHEME 1

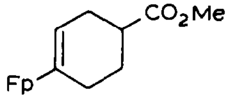
TABLE 3

SECOND ORDER RATE CONSTANTS FOR THE REACTIONS BETWEEN 5 AND DIMETHYL ACETYLENE DICARBOXYLATE IN VARIOUS SOLVENTS AT 70°C

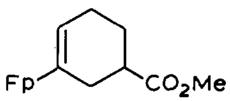
Solvent	D^{12} [a]	k ($\times 10^{-3}$) ($\text{mol}^{-1}\ \text{s}^{-1}$)
Cyclohexane	2	1.10
Nitromethane	35	1.4
Acetonitrile	36	1.70

[a] Dielectric constant.

Since Fp(vinyl) and Fp(η^1-allyl) complexes are both known to react with electrophilic dienophiles via ionic intermediates [11], and since **5** contains both the vinyl and η^1-allyl moieties, there was the distinct possibility that these cycloadducts were the result of a stepwise polar mechanism rather than a concerted (Diels–Alder) mechanism. In order to distinguish between the polar and concerted pathways, the rate constants for the reaction between **5** and dimethyl acetylene dicarboxylate were determined as a function of the polarity of the solvent. As can be seen from the data in Table 3, the small variation in the rate constant in going from nonpolar cyclohexane to moderately polar nitromethane or acetonitrile supports the non-polar (Diels–Alder) mechanism. Dimethyl maleate and a variety of asymmetric electrophilic alkenes such as ketene, ethoxymalonitrile or cyclopent-2-eneone failed to react with **5** at temperatures below 110°C, the decomposition point of the diene. Methyl acrylate reacted sluggishly: after 120 h in refluxing dichloroethane, 70% of **5** was recovered along with a white solid (unidentified) and a dark brown oil. This oil was identified as an equimolar mixture of the isomeric cycloadducts of methyl acrylate, **16**, admixed with Fp_2. Although the three components of this mixture could not be separated, the ^{1}H NMR and IR spectra support the characterization of these substances as the [4 + 2]-cycloadducts (Table 1).

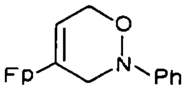


(**16a**)

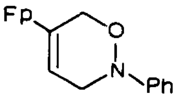


(**16b**)

The formation of equimolar amounts of the positional isomers **16a** and **16b** from methyl acrylate is unusual in that the previously reported Diels–Alder adducts of methyl acrylate were exclusively the 1,4-isomer or a mixture of the 1,4- and 1,3-isomers in which the 1,4-isomer clearly predominated (Table 4) [13]. Similarly, nitrosobenzene which gives only one isomeric cycloadduct with either 2-methyl-1,3-butadiene or 2-chloro-1,3-butadiene [14], gave a 2/3 mixture of isomers **15a** and **15b**.



(**15a**)

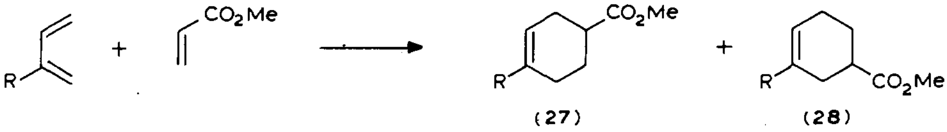


(**15b**)

The relative yields of **15a** and **15b** are essentially invariant in solvents of different polarity: cyclohexane (3/5), acetonitrile (3/5) or methylene chloride (2/3). Thus is appears that both of these isomers are formed via the same reaction pathway, most likely the Diels–Alder reaction.

TABLE 4

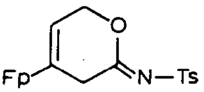
RELATIVE YIELDS OF CYCLOADDUCTS OF METHYL ACRYLATE AND VARIOUS 1,3-BUTADIENES



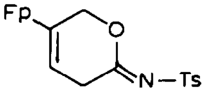
R	*T*. (°C)	Ratio **27**/**28**	Yield (%)	Ref.
OCH_2CH_3	160	**27** only	50	13
CH_3	20	5.4/1	54	13
C_6H_5	150	4.5/1	73	13
Cl	160	**27** only	60	13
CN	95	**27** only	86	13
Fp	83	2/3 or 3/2		This work

Our initial contention that **5** would be a highly reactive diene in the Diels–Alder reaction is borne out by the observation that **5** is two orders of magnitude more reactive toward dimethyl acetylene dicarboxylate than 2-trimethylsiloxy-1,3-butadiene (TMSB) (Table 5). Competition experiments show that **5** is, by at least a factor of three, more reactive toward tetracyanoethylene than TMSB.

The reaction between *p*-toluene sulfonyl isocyanate and **5** and the resulting cycloadduct are anomalous in several ways. First, in contrast to methyl acrylate and nitrosobenzene, *p*-toluene sulfonyl isocyanate afforded only one product, which was identified as the imino lactone **12a**.



(12a)



(12b)

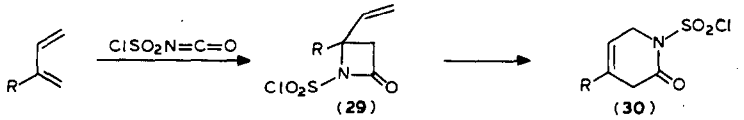
This structural assignment is predicated on analyses of the ^1H NMR and IR spectra of the cycloadduct. The absence of a strong absorption in the 1760–1600 cm^{-1} region of the IR spectrum of **12a** indicated the absence of a carbonyl group. The strong absorption observed at 1571 cm^{-1} is, however, typical of the imine absorption (1600–1550 cm^{-1}) of imino lactones [15,16]. In the ^1H NMR spectrum

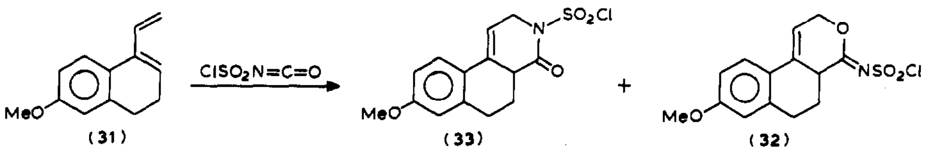
TABLE 5

RATE CONSTANTS FOR THE REACTIONS BETWEEN 5 OR 2-TRIMETHYLSILOXY-1,3-BUTADIENE (TMSB) AND EXCESS DIMETHYL ACETYLENE DICARBOXYLATE IN ACETONITRILE-d_3 AT 70°C

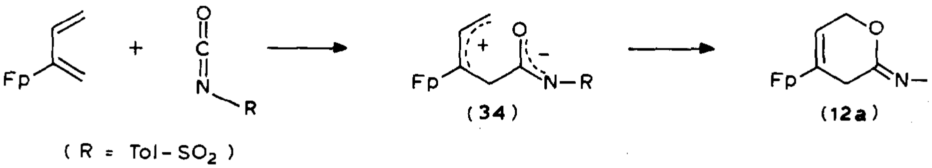
Diene	*k* (mol^{-1} s^{-1})
5	1.3×10^{-3}
TMSB	5.7×10^{-6}

of **12a** the two proton multiplet observed at τ 6.40 is assigned to the methylene protons adjacent to the imine group. For other imino lactones this resonance is observed near τ 6.60 [16]. The two proton multiplet at τ 5.48 is assigned to the methylene protons adjacent to the oxygen. Irradiation of the τ 5.48 resonance caused the vinyl proton multiplet at τ 4.10 to collapse to a broad singlet, whereas irradiation of the multiplet at τ 6.40 had only a slight effect on the vinyl resonance. This data is consonant with the structure **12a** in which the electrophilic carbon of the isocyanate group has become bonded to C(1) of the diene ligand of **5**. These observations are interpreted in terms of a stepwise cycloaddition of *p*-toluene sulfonyl isocyanate to **5** via dipolar intermediates. Although the chemistry of *p*-toluene sulfonyl isocyanate is not well developed, the chemistry of chlorosulfonyl isocyanate is well established [15–19]. Of particular interest is the addition of chlorosulfonyl isocyanate to substituted butadienes [19]. At 0°C, the initial product is *β*-lactam **29** which subsequently rearranges to *δ*-lactam **30** at 40°C.



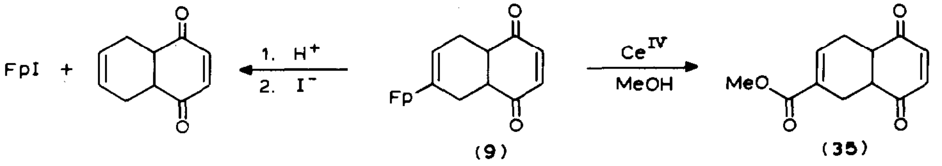


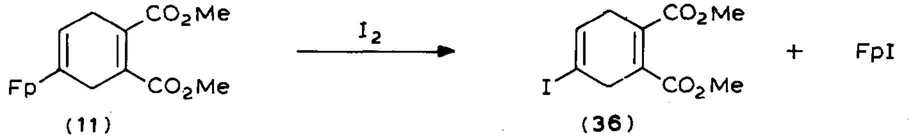
Diene **31** gave both the *δ*-lactam **33** and the imino lactone **32**, which slowly rearranged to **33**. The formation of the thermodynamically less stable imino lactone **12a** suggests that ionic intermediates are involved in the cycloaddition process and that the initial ring closure is charge controlled. We suggest that the addition of *p*-toluene sulfonyl isocyanate to **5** proceeds via initial electrophilic attack at C(1) of the diene ligand. Charge controlled ring closure of the resulting zwitterionic intermediate **34** affords the observed imino lactone.



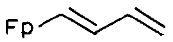
Demetallation of the cycloadducts of 5

Methods for effecting the demetallation of the cycloadducts were investigated briefly. Sequential protonation of **9** and demetallation of the resulting alkene complex were discussed earlier as a method of transforming the C–Fp to the H–C linkage. **9** also undergoes the expected oxidative carbonylation to afford the ester in 40% yield. The C–Fp bond in **11** was cleaved by iodine to afford **36**, which could not be obtained free of FpI.

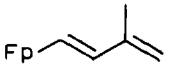




None of the cycloadducts reacted with sulfur dioxide.



(6)



(7)

Cycloaddition reactions of 1-Fp-1,3-butadienes

Qualitatively the 1-Fp-1,3-butadienes **6** and **7** appear to be as reactive toward electrophile dienophiles as **5**. Unfortunately, except for the tetracyanoethylene adduct of **7**, these cycloadducts could not be obtained in pure form. These purification problems may be attributed to the formation of diastereomers and the intrinsic instability of some of these cycloadducts. Whereas the cycloadducts from the reactions between **5** and dienophiles afford vinyl-Fp complexes, the cycloadducts that result from the reactions between **6** or **7** and dienophiles are secondary allyl complexes. The instability of secondary allyl-Fp complexes has been documented [20]. Consequently, the characterization of these cycloadducts rests to a large degree on analyses of their ^{1}H NMR and IR spectra which are consonant with the assigned cyclohexene or cyclohexadiene structures (Table 1).

Conclusion

At the inception of this work it was hypothesized that metalloalkadienes such as **5**, **6** and **7** would be highly reactive dienes in [4 + 2]-cycloadditions, and that the presence of the Fp group in these cycloadducts would allow the convenient introduction of a variety of organic functional groups. (C–H, C–X, carbonyl groups). In part the hypothesis is correct: these metallobutadienes are more reactive than 2-trimethylsiloxy-1,3-butadiene and readily form cycloadducts with symmetrical dienophiles. The utility of these dienes is, however, severly limited by their lack of thermal stability above 110°C and their failure to react with most monosubstituted electrophilic alkenes. Although a small yield of cycloadduct was obtained from methyl acrylate and **5**, the product was an equimolar mixture of the 1,3- and 1,4-cycloadducts. A similar product distribution was obtained from nitrosobenzene. This lack of specificity further limits the utility of **5** in the Diels–Alder reaction. Finally, the 1-Fp-butadiene complexes tended to give impure products that readily decomposed when purification was attempted.

Experimental

Infrared spectra were recorded on a Perkin–Elmer Model 180 spectrophotometer, calibrated with polystyrene. ^{1}H NMR (60 MHz) spectra were obtained on a JEOL

C-60HL NMR spectrometer using tetramethylsilane as an internal standard.

Iron analyses were performed in this laboratory. The organometallic compounds were oxidized to ferric salts by a mixture of aqua regia and perchloric acid. The ferric salts were then reduced to ferrous salts by aluminum wire, and these solutions were titrated with potassium dichromate in the presence of barium diphenylamine sulfonate. Carbon and hydrogen analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York. Melting points were determined in sealed capillaries and are uncorrected.

In general, all reactions were carried out under an atmosphere of dinitrogen.

2-Fp-1,3-butadiene [9], 1-Fp-1,3-butadiene [10] and 1-Fp-3-methyl-1,3-butadiene [10] were prepared as previously described. All solvents were reagent grade and were dried and degassed before use. Deuterated solvents and dienophiles were commercially available and were used as received.

Reaction between $CH_2=CFpCH=CH_2$ and tetracyanoethylene. Tetracyanoethylene, 0.55 g (4.3 mmol), was added to a solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol) in 20 ml of methylene chloride, at 22°C. After the solution had stood for 0.5 h, petroleum ether was added to effect the precipitation of a green solid, which was collected by vacuum filtration. Reprecipitation of this solid from methylene chloride by the addition of petroleum ether gave 1.35 g (93%) of **8** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and β,β-dicyano-o-chlorostyrene. After a solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and β,β-dicyano-*o*-chlorstyrene in 30 ml of 1,2-dichloroethane had been refluxed for 2 h, the solvent was removed by rotary evaporation to afford a red oil. Dissolution of this oil in methylene chloride followed by the addition of petroleum ether gave 1.5 g (83%) of **13** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and maleic anhydride. A solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and maleic anhydride, 0.42 g (4.3 mmol), in 30 ml of 1,2-dichloroethane was refluxed for 1.5 h. After the mixture had cooled to 20°C, petroleum ether was added. A yellow precipitate was obtained by cooling this solution to −78°C. Reprecipitation of this solid from methylene chloride by the addition of petroleum ether afforded 1.1 g (80%) of **10** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and dimethyl acetylene dicarboxylate. After a solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and dimethyl acetylene dicarboxylate, 0.61 g (4.3 mmol), in 30 ml of 1,2-dichloroethane and been refluxed for 1.5 h, the solvent was removed by rotary evaporation to afford a red oil. Trituration of this oil with petroleum ether gave a brown solid which was crystallized from cyclohexane to give 1.4 g (90%) of **11** as a yellow solid.

Reaction between $CH_2=CFpCH=CH_2$ and p-quinone. Cooling a solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and *p*-quinone, 0.46 g (4.2 mmol), in 30 ml of 1,2-dichloroethane, which had been refluxed for 1.5 h, afforded 0.02 g of an unidentified black solid, which was removed by filtration. The filtrate was concentrated by rotary evaporation to a green oil. Dissolution of this oil in hot petroleum ether (30–60°C), followed by filtration and cooling of the filtrate to −78°C gave 1.22 g (85%) of **9** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and p-toluene sulfonyl isocyanate. A solution of *p*-toluene sulfonyl isocyanate, 0.7 g (4.3 mmol), and $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), in 20 ml of methylene chloride was stirred for 3 min at 22°C. The solvent then evaporated in a stream of dinitrogen gas to afford a brown solid.

Reprecipitation of this solid from methylene chloride by the addition of petroleum ether gave 1.5 g (88%) of **12** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and nitrosobenzene. A solution of nitrosobenzene, 0.5 g (4.4 mmol), and $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), in 30 ml of methylene chloride was stirred for 20 h at 24°C. The oil resulting from removal of the solvent by rotary evaporation was dissolved in a minimum amount of benzene and then chromatographed on neutral activity III alumina (30 × 4 cm). Elution with 1/1 benzene/petroleum ether afforded 1.32 g (88%) of a yellow oil which was found to be a 3/2 mixture of the positional isomers **15a** and **15b**.

Reaction between $CH_2=CFpCH=CH_2$ and diethyl azodicarboxylate. A solution of diethyl azodicarboxylate, 0.75 g (4.3 mmol), and $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), in 30 ml of methylene chloride was stirred magnetically at 24°C for 2 h. The orange oil resulting from removal of the solvent by rotary evaporation was dissolved in a minimum amount of petroleum ether and then chromatographed on neutral activity III alumina (30 × 4 cm). Elution with petroleum ether afforded, after removal of the solvent by rotary evaporation, 1.6 g (91%) of **18** as an orange oil.

Reaction between $CH_2=CFpCH=CH_2$ and dimethyl fumarate. A solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and dimethyl fumarate, 0.72 g (4.3 mmol), in 30 ml of methylene chloride was refluxed for 96 h. Trituration of the orange oil resulting from the removal of the solvent by rotary evaporation gave 1.1 g of a yellow solid which was found by ^1H NMR spectroscopy to be a 4/1 mixture of **14** and dimethyl fumarate. This solid was added to hot ligroin and filtered to yield 0.54 g (32%) of **14** as a yellow powder.

Reaction between $CH_2=CFpCH=CH_2$ and hexafluoro-2-butyne. A solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), and hexafluoro-2-butyne in 30 ml of methylene chloride was sealed in a glass ampule at −78°C. The reaction mixture was then allowed to stand at 24°C for 3 h, after which time the volatile components were removed in vacuo to afford a dark oil. This oil was dissolved in a minimum amount of petroleum ether and then percolated through a column of alumina. Elution with petroleum ether gave a yellow oil, which when crystalized from petroleum ether, gave 1.25 g (85%) of **19** as bright yellow crystals.

Reaction between $CH_2=CFpCH=CH_2$ and sulfur dioxide. A solution of sulfur dioxide, 15 ml, and $CH_2=CFpCH=CH_2$, 0.89 g (3.8 mmol), was stirred at −78°C for 3 min. Methylene chloride, 10 ml, was then added and the resulting solution warmed to room temperature. Evaporation of the solvent gave a brown solid which when crystalized from methylene chloride/petroleum ether gave 0.93 g (85%) of **17** as a yellow solid.

Reaction between $CH_2=CFpCH=CH_2$ and methyl acrylate. A solution of $CH_2=CFpCH=CH_2$, 1.0 g (4.3 mmol), methyl acrylate, 1.0 g (14.3 mmol), and hydroquinone, 0.01 g (0.1 mmol), in 30 ml of 1,2-dichloroethane was refluxed for 120 h. The red oil resulting from concentration of the reaction mixture by rotary evaporation was chromatographed on neutral activity I alumina (40 × 4 cm). Elution with benzene afforded an unidentified white solid (m.p. 92°C). Further elution with benzene gave 0.3 g of a brown oil which was characterized solely by ^1H NMR spectroscopy as a mixture of Fp_2 and the positional isomers **16a** and **16b**.

Reaction between $FpCH=CHCMe=CH_2$ and tetracyanoethylene. A solution of $FpCH=CHCMe=CH_2$, 0.280 g (1.15 mmol), and tetracyanoethylene, 0.05 g (0.39 mmol), in 5 ml of methylene chloride was allowed to stand at 22°C for 0.5 h. The slow addition of petroleum ether effected the precipitation of 0.11 g (79%) of **21** as a yellow powder.

Reaction between FpCH=CHCMe=CH$_2$ and sulfur dioxide. 5 ml of sulfur dioxide were condensed into a flask containing 0.39 g (1.5 mmol) of FpCH=CHCMe=CH$_2$ at −78°C. The resulting solution was warmed to 24°C and the excess sulfur dioxide was allowed to evaporate. The residual yellow oil was shown by ^{1}H NMR and IR spectroscopy to be impure **22**. Attempts to prepare an analytically pure sample of **22** were not successful.

Reaction between FpCH=CHCMe=CH$_2$ and p-quinone. A solution of *p*-quinone, 0.22 g (2.05 mmol), and FpCH=CHCMe=CH$_2$, 0.5 g (2.05 mmol), in 20 ml of 1,2-dichloroethane was refluxed for 1 h. The residue resulting from the evaporation of the solvent in a stream of dinitrogen gas was extracted with petroleum ether and then methylene chloride. A black and insoluble solid, 0.0206 g, remained, but it was not further characterized. The combined extracts were condensed to a dark oil. The ^{1}H NMR spectrum of this material was complex, exhibiting a number of cyclopentadienyl resonances. This material was not further examined.

Reaction between FpCH=CHCMe=CH$_2$ and maleic anhydride. A solution of FpCH=CHCMe=CH$_2$, 0.55 g (2.3 mmol), and maleic anhydride, 0.20 g (2.03 mmol), in 20 ml of 1,2-dichloroethane was refluxed for 15 min. The residue resulting from the evaporation of the solvent in a stream of dinitrogen gas was extracted with petroleum ether and then methylene chloride. Evaporation of the methylene chloride extract gave 0.62 g (89%) of **23** as a brown oil. Trace impurities, visible in the ^{1}H NMR spectrum of this substance, could not be removed because of decomposition when column chromatography was attempted, and the failure of this material to crystallize at low temperature.

Reaction between FpCH=CHCH=CH$_2$ and tetracyanoethylene. A solution of FpCH=CHCH=CH$_2$, 0.10 g (0.44 mmol), and tetracyanoethylene, 0.057 g (0.44 mmol), in 5 ml of methylene chloride was allowed to stand at 22°C for 0.5 h. During this period the color of the reaction mixture changed from orange to green. Evaporation of the solvent afforded a green oil that was then dissolved in a minimum amount of methylene chloride. The addition of petroleum ether effected the precipitation of 0.05 g of green crystals identified by ^{1}H NMR and IR spectroscopy as **24** contaminated with tetracyanoethylene.

Reaction between FpCH=CHCH=CH$_2$ and p-quinone. A black precipitate formed immediately when FpCH=CHCH=CH$_2$, 0.20 g (0.87 mmol) and *p*-quinone were mixed in 1 ml of nitromethane-d_3. The supernatant liquor was separated from the precipitate and evaporated to afford FpCH=CHCH=CH$_2$, which was identified by ^{1}H NMR spectroscopy. The black solid, which did not exhibit any absorptions in the 2100–1900 cm^{-1} region of its IR spectrum, was not further examined.

Protonation of 9 by hexafluorophosphoric acid

Hexafluorophosphoric acid (65%), 0.21 g (0.089 mmol), was added to a solution of 0.3 g (0.089 mmol) of **9** in 20 ml of diethyl ether at 0°C. The precipitate which formed immediately was collected by filtration and then reprecipitated from acetone by the addition of diethyl ether to afford 0.32 g (75%) of **25** as an analytically pure orange solid. ^{1}H NMR (CD$_3$NO$_2$): τ 3.39 (s, 2, CH=CH), 4.35 (s, 2, CH=CH), 4.49 (s, 5, Cp), 6.75 (m, 2, CH), 7.75 (m, 4, CH$_2$). IR (KBr): 2075, 2021 (C≡O), 1675 (C=O) cm^{-1}. (Found: Fe, 11.28. $C_{17}H_{15}F_6FeO_4P$ calcd.: Fe, 11.53%). This salt was further characterized by demetallation with sodium iodide in acetone to afford **26** which was identified by comparison of its melting point and spectroscopic properties to those of an authentic sample of **26**. M.p. 56–58°C. ^{1}H NMR (CS_2): τ 3.51 (s, 2, CH_2), 4.45 (m, 2, CH_2), 6.91 (m, 2, CH), 7.75 (m, 4, CH_2).

Oxidation of 9 with ceric ammonium nitrate

Ceric ammonium nitrate, 1.56 g (2.57 mmol), was added to a stirred solution of 0.3 g (0.9 mmol) of **9** in 10 ml of methanol at 0°C. The solution was allowed to stand at 24°C for 15 min and then an equal volume of water was added. The resulting solution was filtered through Celite which was then washed with diethyl ether until the filtrate was only slightly colored. The filtrate was extracted twice with 100 ml of water. These extracts were combined and then washed with two 50 ml portions of diethyl ether. The ether fractions were combined and dried over anhydrous sodium sulfate. Rotary evaporation of the solvent gave 0.123 g of a yellow oil. Recrystallation of this oil from carbon disulfide gave 0.08 g (40%) of **35** as a white solid. (m.p. 92–93°C). ^{1}H NMR ($CDCl_3$): τ 2.84 (s, 2, CH=CH), 3.10 (m, 1, HC=C), 6.28 (s, 3, OCH_3), 6.75 (m, 2, CH), 7.40 (m, 4, CH_2); IR (KBr): 1707 (CO_2Me), 1678 (C=O) cm^{-1} (Found: C, 65.52; H, 5.62. $C_{12}H_{12}O_4$ calcd.: C, 65.44; H, 5.49%).

Reaction between 11 and I_2

Iodine, 1.0 g (4.0 mmol), was added to a solution of **11**, 1.5 g (4.0 mmol), in 25 ml of methylene chloride at −78°C. The solution was then warmed to 24°C and stirred at this temperature for 20 min. The solution was then washed (2 × 15 ml) with an aqueous 10% solution of $NaHSO_3$ and then with distilled water (2 × 40 ml). After the organic phase had been dried over anhydrous magnesium sulfate, the solvent was removed in vacuo to afford a purple solid. This material was identified by ^{1}H NMR spectroscopy to be a mixture of **36** and FpI. Attempts to separate the two components by column chromatography resulted in gross decomposition. **36**: ^{1}H NMR (CS_2): τ 3.50 (m, 1, HC=C), 6.40 (s, 6, OCH_3), 7.42 (m, 4, CH_2).

Kinetics

Solutions of dienes (0.5 *M*) were mixed with at least a five-fold excess of dienophile at 70°C. The course of the reaction was then monitored by ^{1}H NMR spectroscopy. The reactions were in all cases first order with respect to complex. The reactions between **5** or 2-trimethylsiloxy-1,3-butadiene (TMSB) and TCNE were too fast to monitor by ^{1}H NMR spectroscopy. Therefore, an experiment was performed in which four equivalents of both **5** and TMSB in acetone-d_6 were allowed to compete for one equivalent of TCNE. ^{1}H NMR analysis of the cycloadducts (which could not be separated) shows that **5** was at least 2.5 times more reactive than TMSB. Higher diene to dienophile ratios were not satisfactory because of difficulties in performing the ^{1}H NMR analysis of the products.

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