Cycloaddition of Alkynes to CpFe(CX)(CY)SR (CX, CY = CO, CS, CNCH$_3$) To Give $\overline{RSFeC}$(=Y)C=C Heterometallacycles[1]

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CpFe(CO)$_2$SC$_6$H$_5$ undergoes a cycloaddition reaction with dimethyl acetylenedicarboxylate (DMAD) to give the five-member heterometallacycle Cp(CO)$\overline{FeS(C_6H_5)C}$(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=O that crystallizes in the monoclinic space group $P2_1/n$ with a = 5.941 (1) Å, b = 18.246 (5) Å, c = 17.311 (5) Å, β = 96.50 (2)°, V = 1864.4 (9) Å^3, and Z = 4. The structure was solved by direct methods followed by least-squares refinement using 2403 independent reflections to a final R value of 0.054 (R_w = 0.065). Compounds of the type CpFe(CX)(CY)SC$_6$H$_5$ have been prepared where CX and CY are pairwise combinations of carbonyl, thiocarbonyl, and methyl isocyanide ligands. These compounds also react with DMAD to yield five-member heterometallacycles. Competition between a carbonyl or a thiocarbonyl ligand with a methyl isocyanide ligand results in preferential incorporation of the isocyanide into the heterometallic ring. Competition between a carbonyl and a thiocarbonyl ligand results in an unprecedented attack on the carbonyl rather than the thiocarbonyl ligand. The regiochemistry of the cycloaddition products favors a concerted mechanism with a highly ordered transition state.

Introduction

The formation and fragmentation of metallacycles is an important and extensively investigated area of organotransition-metal chemistry.[2] *Heterometallacycles* are transition-metal complexes in which the metal is part of a carbacyclic ring containing one or more main-group elements other than carbon. One preparative route to heterometallacycles is cycloaddition of alkenes or alkynes to :X—M≡CY triatomic fragments, where :X is a π-donor ligand (e.g. SR$^-$), CY is a π-acceptor ligand (e.g. CO, CS, CNR), and M is a metal with filled dπ orbitals (e.g. Fe(II)).

Sharp and co-workers have reported the reactivity of CpFe(CO)$_2$SR toward fluoroalkynes to give, among other products, $\overline{RSFeC}$(=O)C=C heterometallacycles.[3] In this paper we describe the similar reaction of CpFe(CO)$_2$SC$_6$H$_4$-p-Z (Z = OMe, H, Cl, NO$_2$) with the more reactive alkyne dimethyl acetylenedicarboxylate (DMAD), to cleanly give the carbomethoxy derivatives 1 (X = Y = O) in high yield. In addition we report the preparation
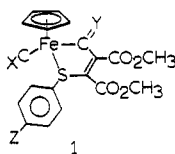
of CpFe(CX)(CY)SC$_6$H$_5$, where ligands CX and CY are pairwise combinations of carbonyl, thiocarbonyl, and methyl isocyanide. These compounds also react with DMAD to give the corresponding heterometallacycles.

It has been suggested that the heterometallic cycloaddition reaction described above proceeds by way of a stepwise, charge-separated pathway (Figure 1, mechanism II).[1a,4] However, such a mechanism seems inconsistent with the formation of 1 (X = S, Y = O, Z = H) when DMAD is reacted with CpFe(CO)(CS)SC$_6$H$_5$. The incor-

poration of the carbonyl ligand into the heterometallacycle of 1 (X = S, Y = O Z = H) contrasts with the preferential attack of thiocarbonyls by simple nucleophiles.[5] This unexpected preferential incorporation of the weaker of two π-acceptor ligands into the heterometallic ring has prompted us to further investigate the mechanism of the cycloaddition reaction of CpFe(CO)$_2$SR and DMAD.

Results and Discussion

The novel cycloaddition of fluoroalkynes and CpFe(CO)$_2$SR reported several years ago by Sharp et al.[3] bears a striking resemblance to [4π + 2π] 1,3-dipolar cycloaddition reactions in organic chemistry. Indeed, CpFe(CO)$_2$SR compounds possess 4π electrons delocalized over the S–Fe–CO fragment, and the fragment is isolobal[7] with the allyl anion. Consequently the symmetry principles developed by Woodward and Hoffman for organic reactions[8] may be used to construct a correlation diagram for the reaction of CpFe(CO)$_2$SR and alkynes (Figure 2). For simplicity only the π-type orbitals of the RS–Fe–CO fragment, which are in the same plane as the reacting π orbitals of the incoming alkyne, are shown in Figure 2. The conventional S and A symmetry labels are used to describe the *approximate* symmetry of the molecular orbitals. The relative energies of the molecular orbitals of the reactants and product are based upon the results of Fenske–Hall molecular orbital calculations.[9–11] The resulting correlation diagram indicates that a symmetry-imposed barrier is not to be expected for a concerted heterometallic cycloaddition reaction.

Figure 2 should not be construed as an attempt to abuse the selection rules of Woodward and Hoffmann. Rather, the correlation diagram is intended to exemplify the similarities between the title reaction and 1,3-dipolar cycloaddition reactions. There has been considerable discussion

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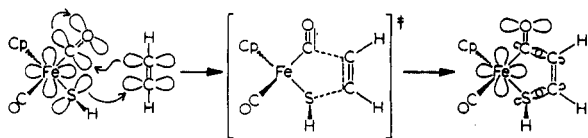
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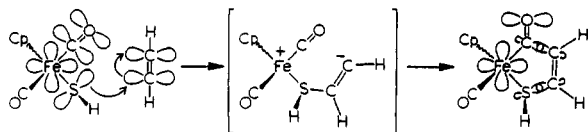
Mechanism I

Mechanism II

Figure 1. Possible mechanisms for the reaction of CpFe(CO)₂SR and alkynes.

Figure 2. Correlation diagram for the reaction of CpFe(CO)₂SR and alkynes.

Figure 3. ORTEP drawing of the 1 (X = Y = O, Z = H) molecule. Atoms are represented by thermal vibration ellipsoids at the 50% probability level, and the labeling scheme is defined. Hydrogen atoms have been omitted for clarity.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for 1 (X = Y = O, Z = H)

Bond Distances			
Fe–S	2.188 (1)	S–C21	1.804 (4)
Fe–C11	2.080 (5)	S–C31	1.778 (4)
Fe–C12	2.105 (4)	C31–C41	1.323 (5)
Fe–C13	2.101 (5)	C41–C5	1.554 (5)
Fe–C14	2.119 (5)	C5–O5	1.205 (5)
Fe–C15	2.091 (4)	C6–O6	1.154 (5)
Fe–C5	1.950 (4)		
Fe–C6	1.735 (4)		

Bond Angles			
S–Fe–C5	87.4 (1)	C32–C31–C41	124.7 (4)
S–Fe–C6	96.6 (1)	C31–C41–C42	123.0 (3)
S–Fe–Cp[a]	123.9 (4)	C31–C41–C5	118.7 (3)
C5–Fe–C6	94.6 (2)	C42–C41–C5	118.2 (3)
C5–Fe–Cp[a]	121.0 (4)	Fe–C5–C41	115.6 (3)
C6–Fe–Cp[a]	124.3 (4)	C41–C5–O5	116.5 (3)
Fe–S–C21	115.8 (1)	Fe–C5–O5	127.8 (3)
Fe–S–C31	102.0 (1)	Fe–C6–O6	175.1 (4)
C21–S–C31	97.2 (2)		
S–C31–C32	119.2 (3)		
S–C31–C41	116.1 (3)		

[a] Cp is the centroid of the cyclopentadienyl ligand.

thiolate ligand on the electron-deficient alkyne to give a charge-separated intermediate that undergoes ring closure by attacking one of the π-acceptor ligands.

Trifluoropropyne and hexafluoro-2-hexyne react with CpFe(CO)₂SR at elevated temperatures or photochemically to give modest yields of the corresponding heterometallacycles.[3] However, the more electrophilic alkyne, dimethyl acetylenedicarboxylate (DMAD), reacts cleanly with CpFe(CO)₂SR at room temperature.[1a,4]

The crystal structure of 1 (X = Y = O, Z = H), one of the cycloadducts of DMAD, was determined. An ORTEP drawing of the molecule is shown in Figure 3, and selected interatomic distances and angles are given in Table I.

The molecular structure of 1 (X = Y = O, Z = H) may be described as a pseudooctahedral piano-stool-type molecule with two of the legs incorporated into a five-member SFeCC=C heterometallacycle. The chelate ligand is best viewed as bonded to the metal through an acyl and a thioether moiety. The Fe–C5 distance (1.950 (4) Å) compares with those reported for CpFe(dppe)C(=O)Ph (1.93 Å)[13] and CpFe(CO)(PPH₃)C(=O)Ph (1.97 Å).[14] The Fe–S bond length (2.188 (1) Å) is significantly shorter than

over the mechanism of organic cycloaddition reactions.[12] Most agree that 1,3-dipolar cycloaddition reactions may proceed by way of either a cyclic transition state or through a charge-separated or diradical intermediate. Similarly, one of two mechanisms seem likely for the cycloaddition of CpFe(CO)₂SR and alkynes (Figure 1). Mechanism I proceeds through a concerted transition state. Mechanism II involves an initial nucleophilic attack by the coordinated
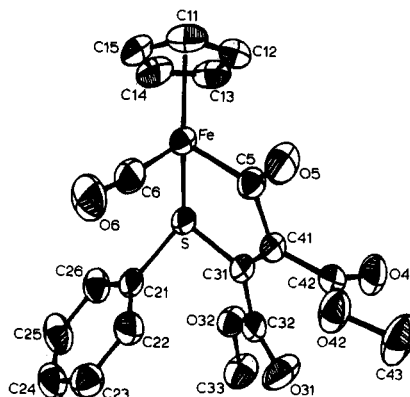
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that reported for the thiolate complex $CpFe(CO)_2SEt$ (2.296 (2) Å).[15] This may reflect a reduction of the filled–filled orbital interactions between the metal and the thiolate ligand.[9,10] The C31–C41 distance (1.323 (5) Å) is comparable to a typical C–C double bond (1.337 (6) Å).[16] The S, C31, C41, and C5 atoms are coplanar. The angle between the S/Fe/C5 and S/C31/C41/C5 least-squares planes is 177.7°; consequently, the heterometallacycle is planar.

To investigate the selectivity of the cycloaddition of DMAD with respect to the π-acceptor ligand, the compounds $CpFe(CX)(CY)SC_6H_5$ were prepared where ligands CX and CY are pairwise combinations of carbonyl, thiocarbonyl, and methyl isocyanide. $CpFe(CO)(CS)SC_6H_5$ was prepared in modest yield from $CpFe(CO)(CS)I$. We prepared $CpFe(CO)(CS)I$ from $[CpFe(CO)_2(CS)]PF_6$ and KI in THF in high yield and free of detectable quantities of $CpFe(CO)_2I$. Recently, a more elaborate and less effective (ca. 50% yield from $[CpFe(CO)_2(CS)]PF_6$) procedure for the preparation of $CpFe(CO)(CS)I$ has been reported.[17] Interestingly, these workers suggest that the reaction of $[CpFe(CO)_2(CS)]PF_6$ and KI is a less desirable route because with use of this method their product was contaminated with significant quantities of $CpFe(CO)_2I$, which is difficult to separate from $CpFe(CO)(CS)I$. In our hands the amount of $CpFe(CO)_2I$ contaminate was found to be approximately proportional to the amount of $[CpFe(CO)_3]PF_6$ that contaminated the $[CpFe(CO)_2(CS)]PF_6$. The use of $[CpFe(CO)_2(CS)]PF_6$ free of $[CpFe(CO)_3]PF_6$ gave $CpFe(CO)(CS)I$ without detectable quantities of $CpFe(CO)_2I$. Similarly, $CpFe(CO)(CS)Cl$ was prepared by using LiCl. The use of NaCl gave significantly lower yields of $CpFe(CO)(CS)Cl$. $CpFe(CO)(CNCH_3)SC_6H_5$ was prepared in high yield from $CpFe(CO)_2SC_6H_5$ and 1 equiv of methyl isocyanide. $CpFe(CNR)_2SC_6H_5$ (R = C_6H_4-m-OMe and C_6H_4-m-CF_3) was prepared from $CpFe(CO)_2SC_6H_5$ and 2 equiv of the corresponding isocyanide.[18] $CpFe(CS)(CNCH_3)SC_6H_5$ was prepared from $CpFe(CS)(CNCH_3)I$ rather than from $CpFe(CO)(CS)SC_6H_5$ because the latter compound may only be prepared in modest yields.

Mechanism II (Figure 1) involves an intramolecular nucleophilic attack on the CX or CY ligand of $[CpFe(CX)(CY)(L)]^+$. The better π-acceptor ligand of CX and CY is expected to be more susceptable toward nucleophiles because π^* (CX or CY) is at relatively lower energy. This preferential affinity of π-acceptor ligands toward nucleophiles has been termed "LUMOphilic" attack.[19a] The relative π-acceptor ability of carbonyl, thiocarbonyl, and isocyanide ligands is CS > CO > CNR.[5,19] Accordingly, methoxide ion reacts at the thiocarbonyl ligand for both $[CpFe(CO)_2(CS)]PF_6$[20] and $[CpFe(CNR)_2(CS)]PF_6$[21] to give $CpFe(L)_2C(=S)OCH_3$. Reaction of C_6F_5Li with $[CpFe(CNR)_2(CO)]PF_6$ reportedly gives a mixture of products.[22]

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Table II. Effect of Z on the Reaction Rate of $CpFe(CO)_2SC_6H_4$-p-Z and DMAD[a]

Z	[Z], mol L^{-1}	[DMAD], mol L^{-1}	k,[b] L mol^{-1} s^{-1}	k_{rel}
OMe	0.05	0.05	9.9 (5) × 10^{-2}	423
H	0.05	0.05	2.63 (4) × 10^{-2}	112
H	0.05	0.20	2.59 (6) × 10^{-2}	111
Cl	0.05	0.05	8.3 (3) × 10^{-3}	36
NO$_2$	0.05	0.50	2.34 (12) × 10^{-4}	1

[a] In chloroform-d_1 at 20 ± 1 °C. [b] The number in parentheses is the estimated standard deviation in the least significant digit.

Table III. Effect of Solvent Polarity on the Reaction Rate of $CpFe(CO)_2SC_6H_4$-p-Z and DMAD[a]

solvent	k, L mol^{-1} s^{-1}	k_{rel}
carbon tetrachloride	3.08 (6) × 10^{-3}	1.0
chloroform-d_1	2.63 (4) × 10^{-2}	8.5
dichloromethane-d_2	1.82 (3) × 10^{-2}	5.9
acetone-d_6	5.3 (3) × 10^{-3}	1.7
acetonitrile-d_3	2.73 (6) × 10^{-2}	8.9

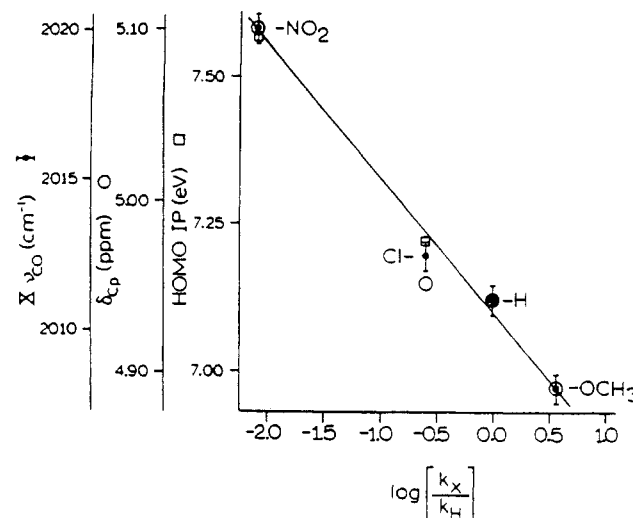[a] Z = H; [Z] = 0.05 mol L^{-1}; [DMAD] = 0.05 mol L^{-1}; T = 20 ± 1 °C.

Figure 4. Hammett relationship between the rate of reaction of $CpFe(CO)_2SC_6H_4$-p-Z with DMAD and selected spectroscopic properties of $CpFe(CO)_2SC_6H_4$-p-Z.

The reactions of $CpFe(CX)(CY)SC_6H_5$ (CX = CS, CY = CO; CX = CO, CY = CNCH$_3$; CX = CS, CY = CNCH$_3$) with DMAD unexpectedly give 1 (X = S, Y = O, Z = H), 1 (X = O, Y = NCH$_3$, Z = H), and 1 (X = S, Y = NCH$_3$, Z = H), respectively. Accordingly, the trend for preferential attack on the π-acceptor ligands by DMAD appears to be CNR > CO > CS. These results are inconsistent with mechanism II. The order may be consistent with Mechanism I in that the relative strength of the Fe–CX π bond, which is weakened in the cyclic transition state, is CS > CO > CNR.

The kinetics of the cycloaddition reactions of DMAD with $CpFe(CO)_2SC_6H_4$-p-Z (Z = OMe, H, Cl, NO$_2$) were studied by ^{1}H NMR spectroscopy as a function of Z (Table II). Compounds for which Z is an electron-donating substituent react faster. Furthermore, the reaction rates correlate with the spectroscopic properties of $CpFe(CO)_2SC_6H_4$-p-Z,[9,10] most importantly with the HOMO ionization potential (Figure 4). The correlation observed between the reaction rate and the spectroscopic results for $CpFe(CO)_2SC_6H_4$-p-Z provide additional support for the

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electronic model of CpFe(CO)$_2$SR previously described.[9,10] The dependence of the reaction rate on the substituent Z is consistent with both mechanisms I and II.

If the reaction proceeds by mechanism II, then the charge-separated intermediate might be trapped in protic solvents.[23] However, the reaction of CpFe(CO)$_2$(SC$_6$H$_5$) with DMAD in methanol gives primarily 1 (X = Y = O, Z = H). The small and apparently random relationship between solvent polarity and the rate constant (Table III) is similar to that observed for many organic [4π + 2π] cycloaddition reactions.[12a]

Summary

Several new RSFeC(=Y)C=C heterometallacycles have been prepared by the cycloaddition of CpFe(CX)-(CY)SC$_6$H$_4$-p-Z (CX = CY = CO; CX = CS, CY = CO; CX = CO, CY = CNCH$_3$; CX = CS, CY = CNCH$_3$) and DMAD. The crystal structure of one of these cycloadducts 1 (X = Y = O, Z = H) has been determined. The regiochemistry observed for the cycloaddition of CpFe(CX)-(CY)SC$_6$H$_5$ and DMAD appears inconsistent with the stepwise mechanism previously proposed for the reaction.[1a,4] The observed regiochemistry and the kinetics of the cycloaddition reactions of CpFe(CO)$_2$(SC$_6$H$_4$-p-Z) with DMAD are most consistent with a concerted mechanism involving a highly ordered cyclic transition state that is electronically similar to the [4π + 2π] 1,3-dipolar cycloaddition reactions in organic chemistry. These results for the cycloaddition of CpFe(CX)(CY)SR with alkynes contrast with the cycloadditions of CpFe(CO)$_2$PR$_2$ with alkenes (described in the following paper)[6] which appear to involve an intermediate which permits rotation about the C-C bond of the reacting alkene.

Experimental Section

Solvents were dried by routine methods.[24] Solution manipulations were carried out by using standard Schlenk and septum/syringe techniques under argon. The deuteriated solvents and dimethyl acetylenedicarboxylate were purchased from Aldrich and used as received. The CpFe(CO)$_2$SC$_6$H$_4$-p-Z compounds,[9,10,25] [CpFe(CO)$_2$(CS)]PF$_6$,[26] and methyl isocyanide[27] were prepared by literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument. NMR chemical shifts are reported in δ vs. Me$_4$Si. For the ^{1}H NMR spectra an internal standard of Me$_4$Si was used as a reference. For the ^{13}C NMR spectra the CDCl$_3$ resonance was assigned 77.00 ppm. Infrared spectra were obtained on a Perkin-Elmer Model 983 spectrophotometer as CHCl$_3$ solutions between NaCl plates. Elemental analysis were carried out by Atlantic Microlab, Atlanta, GA.

CpFe(CO)(CS)I. [CpFe(CO)$_2$(CS)]PF$_6$ (3.00 g, 8.20 mmol) and KI (1.50 g, 9.00 mmol) was placed in a 100-mL Schlenk flask together with a magnetic stirrer bar. Dry THF (50 mL) was added, and the slurry was degassed with argon. The mixture was refluxed 10 h, the THF was removed with a rotary evaporator, and the remaining brown residue was extracted with benzene (2 × 20 mL) which was filtered through Celite to remove the salts. The benzene was removed with a rotary evaporator to leave dark brown crystals which were washed with pentane (2 × 10 mL) to give CpFe-(CO)(CS)I (2.53 g, 97%). On occasion a brown oil resulted which crystallized upon adding the pentane. Recrystallization from Et$_2$O/pentane gave an analytically pure sample of CpFe(CO)(CS)I as dark brown crystals: IR (CHCl$_3$, cm^{-1}) 2029 (CO), 1310 (CS); ^{1}H NMR (CDCl$_3$, ppm) 5.10 (s, 5 H, Cp); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm) 322.1 (CS), 212.3 (CO), 87.5 (Cp). Anal. Calcd for C$_7$H$_5$-

IOSFe (319.93): C, 26.28; H, 1.58; S, 10.02. Found: C, 26.36; H, 1.61; S, 10.07.

CpFe(CO)(CS)Cl. Treatment of [CpFe(CO)$_2$(CS)]PF$_6$ (0.50 g, 1.4 mmol) with LiCl (0.10 g, 2.4 mmol) using conditions similar to those employed to prepare CpFe(CO)(CS)I gave CpFe(CO)-(CS)Cl as red crystals (0.22 g, 68%): IR (CHCl$_3$, cm^{-1}) 2042 (CO), 1315 (CS); ^{1}H NMR (CDCl$_3$, ppm) 5.13 (s, 5 H, Cp).

CpFe(CS)(CNCH$_3$)I. Freshly distilled methyl isocyanide (0.13 g, 10.0 mmol) was added to a 50-mL Schlenk flask followed by 15 mL of dry THF and a magnetic stirrer bar. The solution was degassed with argon, and CpFe(CO)(CS)I (1.00 g, 3.13 mmol) was added as a solid. The solution was refluxed and the reaction followed by IR to completion in 4 h. The volatiles were removed under vacuum. The remaining residue was extracted with benzene (2 × 5 mL). The benzene extract was filtered through Celite and column chromatographed on silca gel (2 × 15 cm) eluting with benzene to give two small brown bands followed by a large green band, which was collected as a single fraction. The solvent was removed with a rotary evaporator to give green crystals that were washed with pentane (2 × 10 mL) and dried to give CpFe-(CS)(CNCH$_3$)I (0.96 g, 92%): IR (CHCl$_3$, cm^{-1}) 2189 (CNCH$_3$), 1290 (CS); ^{1}H NMR (CdCl$_3$, ppm) 4.87 (s, 5 H, Cp), 3.59 (s, 3 H, CNCH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm) 326.9 (CS), 296.6 (CN), 86.3 (CP). Anal. Calcd for C$_8$H$_8$NISFe (332.98): C, 28.86; H, 2.42; N, 4.21; S, 9.63. Found: C, 28.84; H, 2.46; N, 4.21; S, 9.60.

CpFe(CO)(CS)SC$_6$H$_5$. To a 50-mL Schlenk flask was added NaH (0.12 g, 5.2 mmol), 25 mL of dry THF, and a magnetic stirrer bar. After the solution was degassed with argon, thiophenol (0.53 mL, 0.57 g, 5.2 mmol) was added via syringe. When H$_2$ evolution had ceased, CpFe(CO)(CS)I (1.50 g, 4.7 mmol) was added as a solid. The resulting brown solution was stirred 30 min, and the volatiles were removed under vacuum to give a brown residue that was extracted with a minimum amount of benzene and chromatographed on silca gel (2 × 20 cm). Elution with benzene first gave a light brown band of phenyl disulfide which was followed by a green band. The latter band was collected as a single fraction and the benzene was removed with a rotary evaporator to give CpFe(CO)(CS)SC$_6$H$_5$ as maroon crystals (0.32 g, 23%). On occasion a brown oil was obtained after the benzene was removed, which could be made to crystallize from benzene/pentane: IR (CHCl$_3$, cm^{-1}) 2020 (CO), 1307 (CS); ^{1}H NMR (CDCl$_3$, ppm) 7.56 (m, 2 H, Ph), 7.10–7.2 (m, 3 H, Ph), 4.99 (s, 5 H, Cp). Anal. Calcd for C$_{13}$H$_{10}$OS$_2$Fe (302.20): C, 51.67; H, 3.34; S, 21.22. Found: C, 51.59, H, 3.39; S, 21.11.

CpFe(CO)(CNCH$_3$)SC$_6$H$_5$. To a 100-mL Schlenk flask was added CpFe(CO)$_2$SC$_6$H$_5$ (2.00 g, 6.7 mmol), 30 mL of dry THF, and a magnetic stirrer bar. After the solution was degassed with argon, methyl isocyanide (0.50 mL) was added via syringe. After being stirred ca. 10 min, the solution turned red with gas loss. The solution was stirred another 20 min, and the volatiles were removed under reduced pressure to give a dark red oil that was extracted with benzene (2 × 10 mL). The benzene extract was filtered through a plug of Florisil (2 × 10 cm). The Florisil column was washed with additional benzene (20 mL), and the benzene was removed from the combined solutions with a rotary evaporator to give CpFe(CO)(CNCH$_3$)SC$_6$H$_5$ as a dark red oil (1.98 g, 95%). CpFe(CO)(CNCH$_3$)SC$_6$H$_5$ could not be made to crystallize: IR (CHCl$_3$, cm^{-1}) 2178 (CNCH$_3$), 1975 (CO); ^{1}H NMR (CDCl$_3$, ppm) 7.48–7.51 (m, 2 H, Ph), 6.96–7.07 (m, 3 H, Ph), 4.70 (s, 5 H, Cp), 3.32 (s, 3 H, CNCH$_3$). Anal. Calcd for C$_{14}$H$_{13}$NOSFe (299.18): C, 56.21; H, 4.38; N, 4.68; S, 10.72. Found: C, 54.21; H, 4.28; N, 4.39; S, 9.98.

CpFe(CS)(CNCH$_3$)SC$_6$H$_5$. To a dry 50-mL Schlenk flask was added NaH (0.08 g, 3.3 mmol), 20 mL of dry THF, and a magnetic stirrer bar. After the solution was degassed with argon, thiophenol (0.35 mL, 0.39 g, 3.4 mmol) was added via syringe. When the H$_2$ had ceased evolving from the solution, CpFe(CS)(CNCH$_3$)I (1.00 g, 3.0 mmol) was added as a solid. The resulting brown solution was stirred 2 h at which time the volatiles were removed under vacuum to give a brown oil. The oil was extracted with a minimum amount of ethyl ether and chromatographed on silica gel (2 × 20 cm) eluting with ethyl ether to give a light brown band of phenyl disulfide followed closely by a brown band which was collected as a single fraction. Removal of the ethyl ether with a rotary evaporator gave CpFe(CS)(CNCH$_3$)SC$_6$H$_5$ as a red/brown oil (0.94 g, 99%) which could not be made to crystallize: IR

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(CHCl$_3$, cm^{-1}) 2185 (CNCH$_3$), 1286 (CS); ^{1}H NMR (CDCl$_3$, ppm) 7.57–7.60 (m, 2 H, Ph), 6.99–7.10 (m, 3 H, Ph), 4.82 (s, 5 H, Cp), 3.39 (s, 3 H, CNCH$_3$). Anal. Calcd for C$_{14}$H$_{13}$NS$_2$Fe (315.24): C, 53.34; H, 4.16; N, 4.44; S, 20.34. Found: C, 53.32; H, 4.26; N, 4.33; S, 19.58.

Cp(CO)FeS(C$_6$H$_5$)C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=O (1 (X = Y = O, Z = H)). To a 50-mL round-bottom flask fitted with a rubber septum was added CpFe(CO)$_2$SC$_6$H$_5$ (1.00 g, 3.5 mmol), 20 mL of CH$_2$Cl$_2$, and a magnetic stirrer bar. After the solution was degassed with argon, DMAD (0.47 mL, 0.54 g, 3.8 mmol) was added via syringe. The reaction was followed by IR spectroscopy to completion in 30 min. The solvent was removed with a rotary evaporator. The remaining brown solid was extracted with 15 mL of CHCl$_3$ and filtered through a plug of glass wool. Pentane (25 mL) was added, and the solution was cooled to ~78 °C (acetone/dry ice) to give a brown precipitate which was collected on a frit, washed with pentane (2 × 20 mL), and dried to give 1 (X = Y = O, Z = H) (1.27 g, 85%) as a brown solid: IR (CHCl$_3$, cm^{-1}) 1964 (FeC=O), 1730 (CC(=O)OR), 1596 (FeC(=O)R); ^{1}H NMR (CDCl$_3$, ppm) 7.38–7.41 (m, 5 H, Ph), 4.70 (s, 5 H, Cp), 3.88 (s, 3 H, C(=O)CCO$_2$CH$_3$), 3.62 (s, 3 H, SCCO$_2$CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm) 260.8 (FeC(=O)R), 215.7 (FeC=O), 166.0, 161.4 (CO$_2$), 156.6, 148.8, 135.7, 130.0, 129.9, 129.2, 128.8, 128.3 (C=C, Ph), 84.0 (Cp), 53.2, 52.6 (CH$_3$). Anal. Calcd for C$_{19}$H$_{16}$O$_6$SFe (428.25): C, 53.29; H, 3.77; S, 7.49. Found: C, 53.54; H, 3.86; S, 7.56.

Cp(CS)FeS(C$_6$H$_5$)C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=O (1 (X = S, Y = O, Z = H)). Treatment of CpFe(CO)(CS)SC$_6$H$_5$ (0.15 g, 0.50 mmol) with DMAD (0.06 mL, 0.07 g, 0.50 mmol) using conditions similar to those employed to prepare 1 (X = Y = O, Z = H) gave 1 (X = S, Y = O, Z = H) (0.05 g, 24%) as a brown solid. The reaction is quantitative by ^{1}H NMR: IR (CHCl$_3$, cm^{-1}) 1731 (CC(=O)OR), 1605 (FeC(=O)R), 1284 (FeC=S); ^{1}H NMR (CDCl$_3$, ppm) 7.37–7.55 (m, 5 H, Ph), 4.80 (s, 5 H, Cp), 3.90 (s, 3 H, C(=O)CCO$_2$CH$_3$), 3.64 (s, 3 H, SCCO$_2$CH$_3$). Anal. Calcd for C$_{19}$H$_{16}$O$_5$S$_2$Fe (444.31): C, 51.36; H, 3.72; S, 12.59. Found: C, 51.36; H, 3.72; S, 12.59.

Cp(CO)FeS(C$_6$H$_5$)C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=NCH$_3$ (1 (X = O, Y = NCH$_3$, Z = H)). To a 25-mL round-bottom flask fitted with a rubber septum was added CpFe(CO)(CNCH$_3$)SC$_6$H$_5$ (0.71 g, 2.4 mmol), 10 mL of CH$_2$Cl$_2$, and a magnetic stirrer bar. After the solution was degassed with argon, DMAD (0.30 mL, 0.35 g, 2.4 mmol) was added via syringe. The reaction was followed by IR spectroscopy to completion in 30 min. The reaction mixture was filtered through Celite, and the solvent was removed under vacuum to give a brown oil. The oil was washed with pentane (2 × 10 mL) and dried under high vacuum to give 1 (X = O, Y = NCH$_3$, Z = H) as a sticky brown solid. 1 (X = O, Y = NCH$_3$, Z = H) does not appear to be stable to storage, even under an argon atmosphere in the absence of light. The product was characterized spectroscopically: IR (CHCl$_3$, cm^{-1}) 1950 (FeC=O), 1724 (CC(=O)OR); ^{1}H NMR (CDCl$_3$, ppm) 7.27–7.32 (m, 5 H, Ph), 4.66 (s, 5 H, Cp), 3.93 (s, 3 H, C(=NCH$_3$)CCO$_2$CH$_3$), 3.65 (s, 3 H, SCCO$_2$CH$_3$), 3.55 (s, 3 H, CNCH$_3$).

Cp(CS)FeS(C$_6$H$_5$)C(CO$_2$CH)=C(CO$_2$CH$_3$)C=NCH$_3$ (1 (X = S, Y = NCH$_3$, Z = H)). Treatment of CpFe(CS)(CNCH$_3$)SC$_6$H$_5$ (0.12 g, 0.40 mmol) with DMAD (0.06 g, 0.40 mmol) using conditions similar to those employed to prepare 1 (X = O, Y = NCH$_3$, Z = H) gave 1 (X = S, Y = NCH$_3$, Z = H) as a light brown solid: IR (CHCl$_3$, cm^{-1}) 1724 (CC(=O)OR), 1275 (FeC=S); ^{1}H NMR (CDCl$_3$, ppm) 7.18–7.37 (m, 5 H, Ph), 4.80 (s, 5 H, Cp), 3.94 (s, 3 H, C(=NR)CCO$_2$CH$_3$), 3.67 (s, 6 H, SCCO$_2$CH$_3$ and FeC(NCH$_3$)R).

Reaction of CpFe(CO)$_2$SC$_6$H$_5$ and DMAD in Methanol. CpFe(CO)$_2$SC$_6$H$_5$ (0.30 mL, 0.10 M in CD$_3$OD) and DMAD (0.30 mL, 0.10 M in CD$_3$OD) were mixed, and the ensuing reaction was followed by ^{1}H NMR spectroscopy to completion in ca. 15 min. The principal product observed was 1 (X = Y = O, Z = H). Other products included unreacted CpFe(CO)$_2$SC$_6$H$_5$ (7%) and two uncharacterized products (8 and 4%, respectively).

Reaction Kinetics of CpFe(CO)$_2$SC$_6$H$_5$-p-Z and DMAD. Similar procedures were used to determine the rate constants for the reaction of DMAD with the CpFe(CO)$_2$SC$_6$H$_4$-p-Z compounds (Table II). In a typical experimental 0.5 mL of a 0.10 M solution

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Table IV. Crystallographic Data for 1 (X = Y = O, Z = H)

(A) Cell Parameters

formula	C$_{19}$H$_{16}$O$_6$SFe
fw	428.25
cryst color	brown
cryst shape	parallelpiped
cryst size, mm	0.5 × 0.18 × 0.15
cryst orientatn	ϕ axis = [100]
cryst system	monoclinic
space group	$P2_1/n$
a,[a] Å	5.941 (1)
b, Å	18.246 (5)
c, Å	17.311 (5)
β, deg	96.50 (2)
V, Å^3	1864.4 (9)
Z	4
d_{calcd}, g cm^{-3}	1.53
μ, cm^{-1}	6.4

(B) Measurement and Treatment of Intensity Data

radiatn	Mo Kα (λ = 0.710 73 Å), monochromatized by a graphite crystal
data collectn method	$\theta/2\theta$ scan
scan speed, deg min^{-1}	variable (3.0–29.3) as a function of reflctn intensity
scan range (2θ), deg	Mo Kα_1 – 1.0 to Mo Kα_2 + 1.0
ratio of total bkgd time to peak scan time	0.5
std reflctns	(200), (060), (004), recollected every 197 reflctns
max dev of stds, %	<2
max 2θ, deg	50
no. of unique data	3518
no. of data used	2403, $I > 3\sigma(I)$
final residuals	
R	0.054
R_w	0.065

[a] The cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range 11–25°.

of DMAD was added to 0.5 mL of a 0.10 M solution of CpFe(CO)$_2$SC$_6$H$_4$-p-Z. After the two reactants were mixed, the resulting solution (0.05 M in both DMAD and CpFe(CO)$_2$SC$_6$H$_4$-p-Z) was transferred to an NMR tube. The concentration of CpFe(CO)$_2$SC$_6$H$_4$-p-Z was monitored as a function of time by integrating the ^{1}H NMR resonance corresponding to the cyclopentadienyl ligand. Plots of the reciprocal of CpFe(CO)$_2$SC$_6$H$_4$-p-Z concentration vs. time were linear, as expected for second-order kinetics. Rate constants and their estimated standard deviation were obtained by a least-squares fit of the data.[28] The rate constants from replicate experiments were reproducible within two estimated standard deviations. In one experiment, the concentration of DMAD (0.20 M) was chosen to be four times that of CpFe(CO)$_2$SC$_6$H$_4$ (0.05 M) so as to establish the first-order dependence of the reaction rate on the concentration of DMAD. A higher concentration of DMAD (0.50 M) was used in its reaction with CpFe(CO)$_2$SC$_6$H$_4$-p-NO$_2$ so that the reaction rate would proceed on a convienient time scale. All of the kinetics experiments were conducted at 20 ± 1 °C unless otherwise noted.

Crystal Structure. Crystals of 1 (X = Y = O, Z = H) suitable for structure determination were obtained by slow evaporation in the air of a solution containing the compound dissolved in ethyl ether. The crystals were obtained as brown parallelpipeds.

A well-formed crystal was selected and mounted on a Syntex P2$_1$ autodiffractometer. The longest dimension of the crystal was approximately parallel to the ϕ axis. The results from automatic centering, indexing, and least-squares routines and the axial photographs were consistent with a primitive monoclinic lattice. Data were collected for a unique quadrant by using the conditions listed in Table IV. The procedures followed in data collection

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Table V. Atomic Coordinates for the Non-Hydrogen Atoms of 1 (X = Y = O, Z = H)

atom	x	y	z
Fe	0.89980 (9)	0.61833 (3)	0.36951 (3)
S	0.6795 (2)	0.53884 (5)	0.30340 (5)
C11	0.9941 (8)	0.7081 (3)	0.4399 (3)
C12	0.8272 (9)	0.7306 (2)	0.3801 (3)
C13	0.6322 (8)	0.6892 (3)	0.3878 (3)
C14	0.6733 (8)	0.6429 (3)	0.4520 (3)
C15	0.8936 (8)	0.6541 (3)	0.4840 (2)
C21	0.7682 (6)	0.4444 (2)	0.3128 (2)
C22	0.9631 (7)	0.4203 (2)	0.2858 (2)
C23	1.0142 (8)	0.3455 (3)	0.2907 (3)
C24	0.8732 (9)	0.2981 (2)	0.3232 (3)
C25	0.6823 (8)	0.3232 (2)	0.3506 (3)
C26	0.6263 (7)	0.3975 (2)	0.3459 (3)
C31	0.7484 (6)	0.5527 (2)	0.2072 (2)
C32	0.6398 (7)	0.5053 (2)	0.1430 (2)
C33	0.3252 (9)	0.4294 (3)	0.1013 (3)
O31	0.7208 (6)	0.4953 (2)	0.0839 (2)
O32	0.4484 (5)	0.4764 (2)	0.1610 (2)
C41	0.8993 (6)	0.6046 (2)	0.1984 (2)
C42	0.9564 (7)	0.6297 (2)	0.1200 (2)
C43	1.2468 (8)	0.6464 (3)	0.0395 (3)
O41	0.8265 (5)	0.6618 (2)	0.0743 (2)
O42	1.1693 (5)	0.6162 (2)	0.1106 (2)
C5	1.0146 (6)	0.6443 (2)	0.2719 (2)
O5	1.1562 (5)	0.6894 (2)	0.2616 (2)
C6	1.1188 (7)	0.5580 (2)	0.3984 (2)
O6	1.2601 (5)	0.5181 (2)	0.4230 (2)

and processing have been described elsewhere.[29] An absorption correction was not applied because the transmission factors only range from 0.86 to 0.89. The space group $P2_1/n$ was unambiguously determined by the systematic absences of $0k0$ for $k = 2n$ + 1 and $h0l$ for $h + l = 2n + 1$. The structure was solved on the University of Arizona Control Data Corp. Cyber 175 running

programs previously described.[29] An E map calculated by using 400 reflections with the largest values of $|E|$ revealed the positions of all of the non-hydrogen atoms. Least-squares refinement was based upon 2402 reflections having $F_o^2 > 3\sigma(F_o^2)$. The methods used in refinement have also been described.[29] The hydrogen atoms attached to the cyclopentadienyl and phenyl rings were included as fixed contributors by assuming trigonal geometry about the carbon atoms and C–H = 0.95 Å.[30] Each hydrogen atom was assigned an isotropic thermal factor 1 Å² greater than the atom to which it was bonded. Refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.054$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ = 0.065, and $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$ where p, the factor to prevent overweighting of strong reflections, was set equal to 0.03.

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Cycloaddition of Alkenes and Alkynes to CpFe(CO)$_2$PR$_2$ To Give (R)$_2$PFeC(=O)C≃C Heterometallacycles[1]

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CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ undergoes a cycloaddition reaction with dimethyl acetylenedicarboxylate to give the five-member heterometallacycle Cp(CO)FeP(C$_6$H$_5$)$_2$C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=O that crystallizes in the monoclinic space group $P2_1/a$ with a = 17.058 (5) Å, b = 8.713 (3) Å, c = 17.418 (7) Å, β = 117.94 (2)°, V = 2287 (1) Å³, and Z = 4. The structure was solved by direct methods followed by least-squares refinement using 2320 independent reflections to a final R value of 0.061 (R_w = 0.068). CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ also reacts with dimethyl maleate and dimethyl fumarate. The cycloadditions of these alkenes are stereoselective, but not stereospecific. The reactions of these alkenes are also reversible, and CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ catalyzes the isomerization of excess dimethyl maleate to dimethyl fumarate. These results indicate that the cycloadditions of CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ with dimethyl maleate and dimethyl fumarate proceed by a stepwise mechanism that allows rotation about the C–C bond of the reacting alkene.

Introduction

In the preceding paper[2] the reactions of CpFe(CX)(CY)SR (CX, CY = CO, CS, CNCH$_3$) with alkynes to give

Cp(CX)FeS(R)C=C=Y heterometallacycles are described. Molecular orbital calculations have shown that these cycloaddition reactions are electronically similar to [$4\pi + 2\pi$] 1,3-dipolar cycloaddition reactions in organic chemistry. The regiochemistry of the heterometallacycles formed from various pairwise combinations of CX and CY eliminates a stepwise, charge-separated reaction pathway and favors concerted cycloaddition of the alkyne to the RS—Fe=CY triatomic fragment.[1,2]

(1) Presented in part: Ashby, M. T.; Enemark, J. H. *Abstracts*, XIIth International Conference on Organometallic Chemistry, Vienna, Austria, Sept. 1985; No. 65.

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