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 Å^2 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.

Acknowledgment. We thank Dr. K. Christensen for assistance with the NMR experiments and Professors D. L. Lichtenberger and R. S. Glass for helpful discussions. Financial support of this work by National Institutes of Health is gratefully acknowledged. We also appreciate the constructive criticism of a reviewer.

Registry No. 1 (X = Y = O, Z = H), 107939-81-1; 1 (X = S, Y = O, Z = H), 107939-82-2; 1 (X = O, Y = NCH_3, Z = H), 107939-83-3; 1 (X = S, Y = NCH_3, Z = H), 107939-84-4; CpFe(CO)(CS)I, 96307-26-5; CpFe(CO)(CS)Cl, 96307-28-7; $CpFe(CS)(CNCH_3)I$, 96307-70-9; $CpFe(CO)(CS)SC_6H_5$, 107939-78-6; $CpFe(CO)(CNCH_3)SC_6H_5$, 107939-79-7; $CpFe(CS)(CNCH_3)SC_6H_5$, 107939-80-0; $[CpFe(CO)_2(CS)]PF_6$, 33154-56-2; $CNCH_3$, 593-75-9; C_6H_5SH, 108-98-5; $CpFe(CO)_2SC_6H_5$, 12110-44-0; DMAD, 762-42-5; CCl_4, 56-23-5; $CDCl_3$, 865-49-6; CD_2Cl_2, 1665-00-5; CD_3COCD_3, 666-52-4; $CNCD_3$, 2206-26-0.

Supplementary Material Available: Listings of the anisotropic thermal parameters and hydrogen atom fractional coordinates for 1 (X = Y = O, Z = H) (3 pages); a listing of structure factors for 1 (X = Y = O, Z = H) (17 pages). Ordering information is given on any current masthead page.

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Cycloaddition of Alkenes and Alkynes to $CpFe(CO)_2PR_2$ To Give $(R)_2\overline{PFeC(=O)C\underset{..}{-}C}$ Heterometallacycles[1]

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$CpFe(CO)_2P(C_6H_5)_2$ undergoes a cycloaddition reaction with dimethyl acetylenedicarboxylate to give the five-member heterometallacycle $Cp(CO)\overline{FeP(C_6H_5)_2C(CO_2CH_3){=}C(CO_2CH_3)C}{=}O$ 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) Å^3, 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). $CpFe(CO)_2P(C_6H_5)_2$ 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 $CpFe(CO)_2P(C_6H_5)_2$ catalyzes the isomerization of excess dimethyl maleate to dimethyl fumarate. These results indicate that the cycloadditions of $CpFe(CO)_2P(C_6H_5)_2$ 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 $Cp(CX)\overline{FeS(R)C{=}C}{=}Y$ 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 $R\ddot{S}{-}Fe{=}CY$ triatomic fragment.[1,2]

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

(2) Ashby, M. T.; Enemark, J. H. *Organometallics*, preceding paper in this issue.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for 1

	Bond Distances		
Fe-P	2.168 (2)	P-C21	1.839 (6)
Fe-C11	2.093 (9)	P-C21′	1.806 (6)
Fe-C12	2.106 (7)	P-C31	1.826 (6)
Fe-C13	2.118 (7)	C31-C41	1.318 (8)
Fe-C14	2.089 (7)	C41-C5	1.540 (9)
Fe-C15	2.091 (8)	C5-O5	1.206 (8)
Fe-C5	1.957 (7)	C6-O6	1.146 (9)
Fe-C6	1.750 (8)		
	Bond Angles		
P-Fe-C5	86.0 (2)	P-C31-C32	126.5 (5)
P-Fe-C6	97.3 (2)	P-C31-C41	113.6 (5)
P-Fe-Cp[a]	125.7 (4)	C32-C31-C41	119.9 (6)
C5-Fe-C6	88.0 (3)	C31-C41-C42	123.7 (6)
C5-Fe-Cp[a]	124.7 (4)	C31-C41-C5	119.3 (6)
C6-Fe-Cp[a]	124.0 (4)	C42-C41-C5	116.9 (6)
Fe-P-C21	117.5 (2)	Fe-C5-C41	116.5 (5)
Fe-P-C21′	120.4 (2)	C41-C5-O5	116.8 (6)
Fe-P-C31	102.8 (2)	Fe-C5-O5	126.7 (5)
C21-P-C21′	103.9 (3)	Fe-C6-O6	175.5 (8)
C21-P-C31	103.4 (3)		
C21′-P-C31	107.2 (3)		

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

This paper shows that $\mathrm{CpFe(CO)_2PR_2}$ undergoes analogous cycloaddition reactions with alkynes. However, in contrast to $\mathrm{CpFe(CO)_2SR}$, $\mathrm{CpFe(CO)_2PR_2}$ also reacts with alkenes to form unstable saturated heterometallacycles that have been characterized in situ.

Results and Discussion

The heterometallacycles $\mathrm{Cp(CO)FeP(R)_2C{=}CC{=}O}$ are prepared upon treatment of $\mathrm{CpFe(CO)_2PR_2}$ with an electron-deficient alkyne. The sulfur analogues $\mathrm{Cp(CO)FeS(R)C{=}CC{=}O}$ have been prepared by a similar route.[1-3] Some difficulty was encountered in obtaining $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ in pure form. When $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$[4] was prepared in oxo solvents (e.g. THF) or in solvents which were not rigorously dried and degassed, significant quantities of $\mathrm{CpFe(CO)_2PO(C_6H_5)_2}$ and other impurities were obtained. The problem is further complicated in that $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ does not readily crystallize, and it is not stable to chromatography. However, suitably pure solutions of $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ could be prepared by using dry benzene as a solvent. When prepared in situ, $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ reacts cleanly with dimethyl acetylenedicarboxylate and methyl propiolate to give 1 and 2, respectively. Only one regioisomer was obtained for the latter reaction. The somewhat less reactive $\mathrm{CpFe(CO)_2P(C_6F_5)_2}$ also reacts with dimethyl acetylenedicarboxylate to give the corresponding heterometallacycle 3.

The $\mathrm{Cp(CO)FeP(R)_2C{=}CC{=}O}$ compounds were characterized by chemical analysis and by comparing their NMR and IR spectra to their sulfur analogues. In addition, 1 was characterized by single-crystal X-ray crystallography. An ORTEP drawing of the molecule and the labeling scheme are shown in Figure 1. Table I lists selected interatomic distances and angles.

The structure of 1 is similar to the sulfur analogue.[1,2] The chelate ligand is bonded to the metal through an acyl group and tertiary phosphine group. The Fe–P distance in 1 (2.168 (2) Å) compares with those reported for

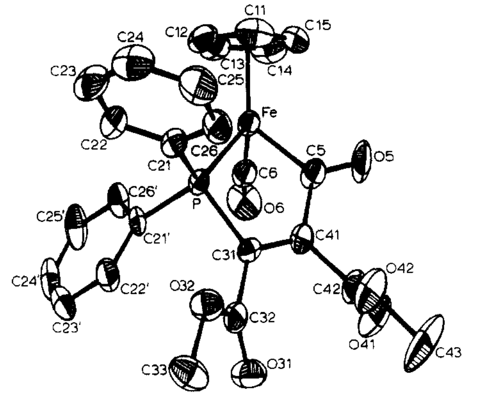

Figure 1. ORTEP drawing of 1.

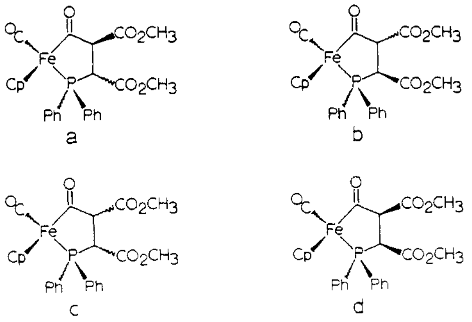

Figure 2.

$\mathrm{CpFe(CO)(PPh_3)C({=}O)Ph}$ (2.17 Å)[5] and related phosphine compounds.[6,7] The Fe–C5 distance (1.957 (7) Å) is similar to those reported for other Fe(II)–acyl complexes, e.g. $\mathrm{CpFe(dppe)C({=}O)Ph}$ (1.93 Å)[8] and $\mathrm{CpFe(CO)(PPh_3)C({=}O)Ph}$ (1.97 Å).[5] Within experimental error, the Fe–C5 distance is identical with the related distance in $\mathrm{Cp(CO)FeS(C_6H_5)C(CO_2CH_3){=}C(CO_2CH_3)C{=}O}$,[1,2] as is the C31–C41 distance (1.312 (8) Å) which is comparable to a typical C–C double bond (1.333 (7) Å).[9] The P, C31, C41, and C5 atoms are coplanar; the P–C31–C41–C5 torsion angle is −0.7°. The heterometallacyclic ring is slightly puckered; the angle between the P/Fe/C5 and P/C31/C41/C5 planes is 167.9°. The related angle for $\mathrm{Cp(CO)FeS(C_6H_5)C(CO_2CH_3){=}C(CO_2CH_3)C{=}O}$ is 177.7°.[1,2]

The phosphide complex $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ also reacts with a variety of electron-deficient alkenes. This is in sharp contrast to the related thiolate complex $\mathrm{CpFe(CO)_2SC_6H_5}$, which is unreactive toward alkenes.[1,2] The reactivity of $\mathrm{CpFe(CO)_2P(C_6H_5)_2}$ may be attributed to the greater nucleophilicity of the phosphide as compared to that of the thiolate ligand.[10] Alkenes are known to be less

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(8) Felkin, H.; Meunier, B.; Pascard, C.; Prange, T. *J. Organomet. Chem.* **1977**, *135*, 361.

(9) *CRC Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Ed.; CRC: Boca Raton, FL, 1978; p F-215.

(10) We have carried out Fenske–Hall molecular orbital calculations on the model compound $\mathrm{CpFe(CO)_2PH_2}$.[1,11] The results of the calculation for $\mathrm{CpFe(CO)_2PH_2}$ are very similar to those reported for $\mathrm{CpFe(CO)_2SH}$.[12] The principal differences are attributable to the spatial nature and character of the heteroatom lone pairs. The calculations predict somewhat greater heteroatom character in the Fe–X (X = S, P) antibonding HOMO for $\mathrm{CpFe(CO)_2PH_2}$ as compared to that for $\mathrm{CpFe(CO)_2SH}$. Accordingly, the phosphide ligand is expected to be more nucleophilic than the thiolate ligand when bound to the $\mathrm{CpFe(CO)_2}$ group.

(11) Ashby, M. T. Ph.D. Dissertation, University of Arizona, 1986.

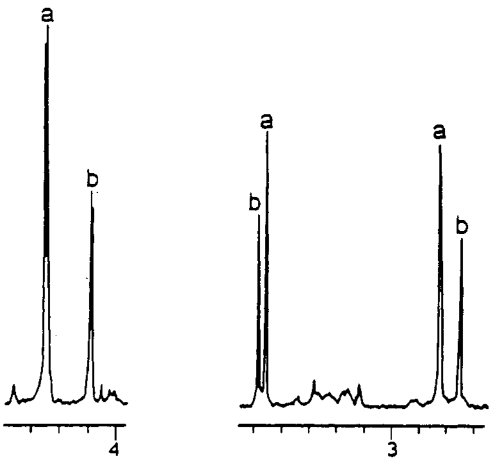

Figure 3.

susceptible to nucleophilic attack than are alkynes.[13] The relatively less nucleophilic phosphide complex $CpFe(CO)_2P(C_6F_5)_2$ is unreactive toward even the most electrophilic alkenes (e.g. TCNE).

Considerable difficulty was encountered in our attempts to purify the cycloaddition products obtained from the reaction $CpFe(CO)_2P(C_6H_5)_2$ and alkenes. The source of these difficulties became evident when the reactions of dimethyl maleate and dimethyl fumarate with $CpFe(CO)_2P(C_6H_5)_2$ were followed by ^1H NMR spectroscopy. The carbomethoxy groups on the alkenes proved a probe of the stereospecificity of the cycloaddition reaction. Figure 2 illustrates the four stereoisomers possible when $CpFe(CO)_2P(C_6H_5)_2$ is reacted with dimethyl maleate and dimethyl fumarate. When somewhat less than 1 equiv of alkene was added to a C_6D_6 solution of $CpFe(CO)_2P(C_6H_5)_2$, which had been generated in situ by addition of excess $CpFe(CO)_2I$ to $LiP(C_6H_5)_2$, the same two stereoisomers of 4 were observed (Figure 3), which were assigned to the less sterically demanding trans isomers. Figure 3 shows the two regions in the ^1H NMR spectrum that are most informative. The doublets observed at ca. 4.2 ppm are assigned to the cyclopentadienyl ligands. The four singlets between 2.7 and 3.5 ppm are attributed to the carbomethoxy groups of the heterometallacycles. The ^1H NMR spectrum in Figure 3 reveals the *thermodynamic* ratio of the two heterometallacycles (vide infra); accordingly, the assignment of the spectrum has been made by assuming that the more sterically demanding isomer (**4b**, the one with three adjacent bulky groups) will be less abundant.

The observation of only two diastereoisomers is evidence for a stepwise mechanism involving rotation about the C–C bond of the alkene prior to ring closure. The high stereospecificity in the reaction of dimethyl maleate is surprising. The reason for the high stereospecificity and the reason for the difficulty encountered in purifying 4 became obvious when more than 1 equiv of dimethyl maleate was added to the C_6D_6 solution of $CpFe(CO)_2P(C_6H_5)_2$. A rapid conversion of excess dimethyl maleate to dimethyl fumarate was observed. This observation suggests that 4 undergoes retro fragmentation to give $CpFe(CO)_2P(C_6H_5)_2$ and the, possibly, isomerized alkene. Thus, $CpFe(CO)_2P(C_6H_5)_2$ appears to be a catalyst for the isomerization of dimethyl maleate to dimethyl fumarate (Figure 4). This observation also lends credence to our assignment of the two stereoisomers of 4 as the trans isomers.

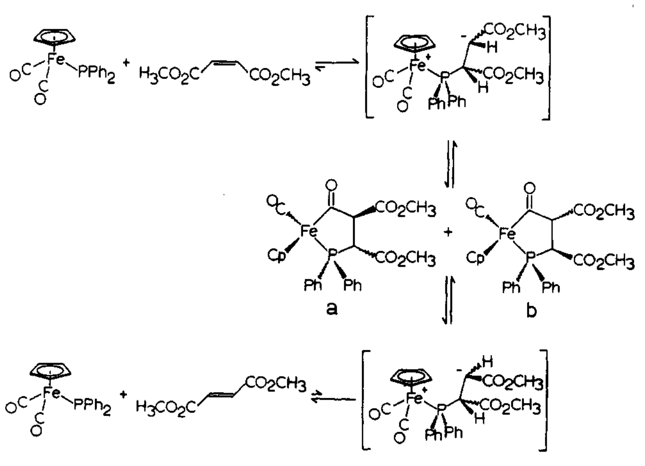

Figure 4.

While the in situ ^1H NMR experiments were conducted, we noted that the ratio of the two diastereomeric heterometallacycles does not remain constant as a function of time. Indeed, the kinetic ratios are not the same when $CpFe(CO)_2P(C_6H_5)_2$ is reacted with dimethyl maleate and dimethyl fumarate, nor are the kinetic ratios the same as the thermodynamic ratios. However, eventually the same thermodynamic ratio (**4a**:**4b** = 1.2:1) is obtained regardless of whether dimethyl maleate or dimethyl fumarate is used. With the assumption that the assignment in Figure 3 is correct, the initial spectrum observed when excess dimethyl fumarate is added to $CpFe(CO)_2P(C_6H_5)_2$ indicates that **4b** is most abundant. The final spectrum shows that isomer **4a** is most abundant. In contrast, the initial spectrum observed when excess dimethyl maleate is added to $CpFe(CO)_2P(C_6H_5)_2$ indicates that the reaction results in a kinetic preference of **4a**. As expected, the final thermodynamic ratio of **4a** and **4b** is the same as the final ratio for the reaction of dimethyl fumarate.

We conclude that the reaction of $CpFe(CO)_2Pr_2$ with alkenes precedes through a stepwise mechanism that apparently involves an intermediate that allows rotation about the C–C bond of the reacting alkene. This contrasts with the concerted pathway proposed for the reaction of $CpFe(CO)_2SR$ with alkynes.[1,2] The dissimilar mechanisms for these superficially comparable reactions may be a consequence of the subtle differences in the spatial nature and character of the phosphide and thiolate ligand lone pairs, the steric influence of the additional substituent of the phosphide ligand,[11] and the differing dipolarophiles.

Experimental Section

Solvents were dried by routine methods prior to use.[14] Solution manipulations were carried out by using standard Schlenk techniques under an argon atmosphere. The ^1H and ^{31}P NMR spectra were obtained as $CDCl_3$ and C_6D_6 solutions on a Bruker WM-250 spectrometer. The ^1H chemical shifts are reported in δ vs. an internal standard of Me_4Si. The ^{31}P chemical shifts are reported in δ vs. an external standard of phosphoric acid. Infrared spectra were obtained on a Perkin-Elmer PE-983 spectrophotometer as $CHCl_3$ solutions between NaCl plates. Diphenylphosphine was purchased from Strem Chemicals. Dimethyl acetylenedicarboxylate, methyl propiolate, dimethyl maleate, dimethyl fumarate, and *n*-butyllithium were purchased from Aldrich. Bis(pentafluorophenyl)phosphinous chloride was prepared from (pentafluorophenyl)magnesium bromide and phosphorus trichloride.[15] $CpFe(CO)_2I$[16] and $CpFe(CO)_2P(C_6H_5)_2$[17]

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(12) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L., submitted for publication.

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were prepared by published procedures. CpFe(CO)$_2$P(C$_6$H$_5$)$_2$[4] was prepared in situ as described below. Elemental analysis were performed by Atlantic Microlabs, Atlanta, GA.

Cp(CO)FeP(C$_6$H$_5$)$_2$C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)C=O (1). To a 100-mL Schlenk flash was added 50 mL of *dry* benzene. After the solution was thoroughly degassed with argon, diphenylphosphine (0.60 mL, 0.64 g, 3.5 mmol) was added by syringe, followed by *n*-butyllithium (1.4 mL, 2.6 M in hexane). The pale yellow solution was vigorously stirred 5 min during which time a yellow oil separated from the benzene. CpFe(CO)$_2$I (1.00 g, 3.3 mmol) was added, and the resulting brown slurry was vigorously stirred ca. 2 h during which time the yellow oil slowly reacted and the solution turned red. The resulting reaction mixture was filtered through a fine airless frit to remove most of the salts. To the benzene solution of CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ was added dimethyl acetylenedicarboxylate (0.40 mL, 0.46 g, 3.3 mmol), and the solution turned brown instantly. The reaction mixture was stirred 1 h, and the volatiles were removed with a rotary evaporator to give a brown oil. The oil was dissolved in a minimum amount of CH$_2$Cl$_2$ and chromatographed on a silica gel column (2 × 30 cm). [CpFe(CO)$_2$]$_2$ and unidentified organic compounds were eluted off the column with CH$_2$Cl$_2$. A brown band, which was followed closely by an unidentified blue compound, was eluted off the column with increasing concentrations of ethyl ether. The brown band was collected as a single fraction, and the solvent was removed with a rotary evaporator to give **1** as a brown oil which solidified when pumped on (1.12 g, 68%): IR (CHCl$_3$, cm^{-1}) 1953 (FeCO), 1726 (CC(=O)OR), 1589 (FeC(=O)R); ^{1}H NMR (CDCl$_3$, ppm) 7.92–8.00 (m, 2 H, Ph), 7.30–7.62 (m, 8 H, Ph), 4.45 (d, 5 H, J_{P-H} = 1.38 Hz, Cp), 3.81, 3.60 (s, 6 H, CO$_2$CH$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, ppm) 113.26. Anal. Calcd for C$_{25}$H$_{21}$O$_6$PFe (504.27): C, 59.55; H, 4.20. Found: C, 59.36; H, 4.38.

Cp(CO)FeP(C$_6$H$_5$)$_2$C(H)=C(CO$_2$CH$_3$)C=O (2). Treatment of CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ (ca. 1.7 mmol) with methyl propiolate (0.15 mL, 0.14 g, 1.7 mmol) using conditions similar to those employed to prepare **1** gave **2** (0.58 g, 78%) as a yellow solid. The product was characterized spectroscopically: IR (CHCl$_3$, cm^{-1}) 1947 (FeCO), 1729 (CC(=O)OR), 1592 (FeC(=O)R); ^{1}H NMR (CDCl$_3$, ppm) 7.88–7.92 (m, 2 H, Ph), 7.85 (d, 1 H, J_{P-H} = 6.38 Hz, PCH=C), 7.55–7.58 (m, 3 H, Ph), 7.34–7.38 (m, 3 H Ph), 7.09–7.17 (m, 2 H, Ph), 4.48 (d, 5 H, J_{P-H} = 1.23 Hz, Cp), 3.78 (s, 3 H, CO$_2$CH$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, ppm) 105.20.

Cp(CO)FeP(C$_6$F$_5$)$_2$C(CO$_2$CH$_3$)=C(CO$_2$CH$_3$)CO (3). To a 100-mL Schlenk flask was added CpFe(CO)$_2$P(C$_6$F$_5$)$_2$ (0.15 g, 0.28 mmol) and 20 mL CH$_2$Cl$_2$. After the solution was degassed with argon, several drops of dimethyl acetylenedicarboxylate was added and the solution turned brown. The reaction was followed by TLC (siliga gel/ethyl ether) to completion in ca. 30 min. The CH$_2$Cl$_2$ was removed with a rotary evaporator, and the resulting brown residue was extracted with a minimum amount of CH$_2$Cl$_2$. The extract was chromatographed on Florisil (1 × 30 cm) eluting with ethyl ether to give a brown band which was collected as a single fraction. The ether was removed with a rotary evaporator to give a brown oil which was dissolved in 10 mL of CH$_2$Cl$_2$, and 10 mL of pentane was added. The resulting solution was reduced in volume with a rotary evaporator to give **3** as fine yellow crystal which were filtered, washed with pentane (2 × 15 mL), and dried under vacuum (0.11 g, 58%). The product was characterized spectroscopically: IR (CHCl$_3$, cm^{-1}) 1967 (FeCO), 1727 (CC(=O)OR), 1602 (FeC(=O)R); ^{1}H NMR (CDCl$_3$, ppm), 4.71 (s, 5 H, Cp), 3.84, 3.71 (s, 6 H, CO$_2$CH$_3$).

Cp(CO)FeP(C$_6$H$_5$)$_2$C(CO$_2$CH$_3$)(H)C(CO$_2$CH$_3$)(H)C=O (4). CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ was prepared as described above. The benzene was removed under vacuum, and a quantity of the remaining red oil was redissolved in benzene-d_6. A ^{1}H NMR spectrum of the resulting solution revealed only one resonance between 0 and 6 ppm, which was assigned to the cyclopentadienyl ligand of CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ (4.12 ppm). The region between 6.8 and 7.9 ppm integrated to be significantly greater than that predicted for two phenyl groups. Four separate experiments were performed by using the benzene-d_6 solution of CpFe(CO)$_2$P(C$_6$H$_5$)$_2$. To separate aliquots was added less than 1 equiv dimethyl fumarate, greater than 1 equiv of dimethyl fumurate, less than 1 equiv dimethyl maleate, and greater than 1 equiv dimethyl maleate. The ensuing reactions were monitored by ^{1}H NMR spectroscopy until equilibrium had been reached. When less than 1 equiv of alkene was added, the alkene was completely consumed. Accordingly, when greater than 1 equiv of alkene was added, the CpFe(CO)$_2$P(C$_6$H$_5$)$_2$ was completely consumed. In each experiment, the principal iron-containing product was **4**; only two of a possible four diastereomers were observed. The heterometallacycles were characterized spectroscopically: IR (CHCl$_3$, cm^{-1}) 1954, 1921 (FeCO), 1728 (CO$_2$CH$_3$), 1592 (FeC(=O)R); ^{1}H NMR (CHCl$_3$, ppm) 4.57 (d, 5 H, J = 0.98 Hz, Cp (**4a**)), 4.35 (d, 5 H, J = 1.28 Hz, Cp (**4b**)), 3.78 (s, 3 H, FeCCCO$_2$CH$_3$ (**4b**), 3.70 (s, 3 H, FeCCCO$_2$CH$_3$ (**4a**)), 3.26 (s, 3 H, FePCCO$_2$CH$_3$ (**4a**)), 3.08 (s, 3 H, FePCCO$_2$CH$_3$ (**4b**)); ^{1}H NMR (C$_6$D$_6$, ppm) 4.24 (d, 5 H, J = 1.2 Hz, Cp (**4a**)), 4.08 (d, 5 H, J = 1.2 Hz, Cp (**4b**)), 3.48 (s, 3 H, FeCCCO$_2$CH$_3$ (**4a**)), 2.74 (s, 3 H, FePCCO$_2$CH$_3$ (**4b**)). The resonances corresponding to the methine and phenyl protons were not assigned.

Table II. Crystallographic Data for 1 at 25 °C

(A) Cell Parameters

formula	C$_{25}$H$_{21}$O$_6$PFe
fw	504.27
cryst color	yellow
cryst shape	parallelepiped
cryst size, mm	0.25 × 0.18 × 0.08
cryst orientatn	random
cryst system	monoclinic
space group	$P2_1/a$
a, Å[a]	17.058 (5)
b, Å	8.713 (3)
c, Å	17.418 (7)
β, deg	117.94 (2)
V, Å^3	2287 (1)
Z	4
d_{calcd}, g cm^{-3}	1.46
d_{obsd},[b] g cm^{-3}	1.51
μ, cm^{-1}	7.6

(B) Measurement and Treatment of Intensity Data

radiatn	Mo Kα (λ = 0.71073 Å), monochromatized by a graphite crystal
data collectn method	$\theta/2\theta$ scan
scan speed, deg min^{-1}	variable ($2 < 2\theta < 45°$ at 1.5–14.5 and $45 < 2\theta < 60°$ at 1.0–5.0) 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	(600), (040), (004), recollected every 97 reflctns
max deviation of stds, %	<1
max 2θ, deg	60
no. of unique data	6432
no. of data used	2320, $I > 3\sigma(I)$
final residuals	
R	0.061
R_w	0.068

[a] The cell dimensions were obtained from a least-squares refinement of setting angles of 22 reflections in the 2θ range 5.3–21.8°. [b] Density was determined by the flotation method using water/ZnBr$_2$.

Crystal Structure. Crystals of **1** suitable for X-ray analysis were obtained from slow evaporation of a methanol solution. A single crystal was selected and mounted on a glass fiber with epoxy cement. Diffraction measurements were carried out by using a

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Table III. Atomic Coordinates for the Non-Hydrogen Atoms in 1

atom	*x*	*y*	*z*
Fe	0.17544 (6)	0.1435 (1)	0.61157 (6)
P	0.3021 (1)	0.1910 (2)	0.7237 (1)
C11	0.1292 (6)	0.366 (1)	0.5692 (5)
C12	0.1899 (5)	0.324 (1)	0.5387 (5)
C13	0.1550 (6)	0.198 (1)	0.4851 (4)
C14	0.0748 (6)	0.158 (1)	0.4832 (5)
C15	0.0579 (5)	0.262 (1)	0.5337 (5)
C21	0.3325 (4)	0.3934 (8)	0.7521 (4)
C22	0.3977 (5)	0.4589 (9)	0.7370 (5)
C23	0.4143 (6)	0.6144 (9)	0.7527 (5)
C24	0.3673 (5)	0.703 (1)	0.7826 (5)
C25	0.3032 (5)	0.636 (1)	0.7968 (5)
C26	0.2848 (5)	0.4815 (9)	0.7820 (4)
C21′	0.4026 (4)	0.1044 (8)	0.7334 (4)
C22′	0.4823 (4)	0.101 (1)	0.8122 (4)
C23′	0.5570 (5)	0.029 (1)	0.8175 (5)
C24′	0.5544 (5)	−0.040 (1)	0.7466 (5)
C25′	0.4785 (5)	−0.029 (1)	0.6666 (5)
C26′	0.4037 (4)	0.0381 (9)	0.6618 (4)
C31	0.2860 (4)	0.1195 (8)	0.8138 (4)
C32	0.3551 (4)	0.1105 (9)	0.9076 (4)
C33	0.4652 (5)	0.251 (1)	1.0261 (4)
O31	0.3687 (4)	−0.0018 (7)	0.9510 (3)
O32	0.3967 (3)	0.2441 (6)	0.9351 (3)
C41	0.2039 (4)	0.0790 (8)	0.7910 (4)
C42	0.1731 (5)	0.023 (1)	0.8541 (4)
C43	0.1569 (6)	0.100 (1)	0.9771 (5)
O41	0.1488 (4)	−0.1024 (7)	0.8564 (3)
O42	0.1805 (3)	0.1379 (8)	0.9080 (3)
C5	0.1328 (5)	0.0968 (9)	0.6955 (4)
O5	0.0565 (3)	0.0815 (9)	0.6801 (3)
C6	0.1912 (5)	−0.054 (1)	0.6052 (4)
O6	0.1957 (4)	−0.1833 (7)	0.5970 (4)

Syntex $P2_1$ autodiffractometer with the conditions summarized in Table II. Examination of the axial photographs and representative data suggested a primitive monoclinic lattice. The data set revealed the systematic absences $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$, which unambiguously, determined the space group to be $P2_1/a$, a nonstandard setting of $P2_1/c$ (No. 14). A total of 6432 unique and observed reflections were collected in the quadrant $+h$, $+k$, $\pm l$. Lorentz and polarization corrections were applied; no absorption correction was applied. Transmission factors range from 0.86 to 0.94.

The structure determination and subsequent refinement were performed on a PDP 11/34a computer running the SDP series of crystallographic programs.[18] The positions of the heavy atoms were determined by direct methods, and the remaining atoms were located in succeeding difference Fourier syntheses. The positions of the cyclopentadienyl and phenyl hydrogen atoms were calculated by assuming trigonal geometry about their bonded carbons and a C–H bond length of 0.96 Å.[19] These hydrogen atoms, but not those bound to the methyl groups, were assigned an arbitrary isotropic thermal parameter of $B = 5.0$ Å^2 and included as fixed contributors in the final structure factor calculations. The effect of the real and imaginary components of anomalous dispersion for the iron and phosphorus atoms were included the structure factor calculations. Only the 2320 reflections having $F_0^2 > 3\sigma(F_0^2)$ were used in the refinement. The final cycles of refinement included 298 variable parameters and converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.061$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.068$, 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. The highest peak in the final difference electron density map had a height of 0.52 e Å^{-3} and was located 0.47 Å from C33. Most of the highest peaks were attributed to the hydrogen atoms bound to C33 and C43.

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Registry No. **1**, 107819-49-8; **2**, 107819-50-1; **3**, 107819-51-2; **4a**, 107819-52-3; **4b**, 107910-95-2; $CpFe(CO)_2I$, 12078-28-3; $CpFe(CO)_2P(C_6F_5)_2$, 33198-53-7; $CpFe(CO)_2P(C_6H_5)_2$, 38816-40-9; diphenylphosphine, 829-85-6; methyl propiolate, 922-67-8; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6.

Supplementary Material Available: Listing of anisotropic thermal parameters and hydrogen atom fractional coordinates for 1 (3 pages); a listing of structure factors for 1 (17 pages). Ordering information is given on any current masthead page.

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