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Formal [2 + 2] and [4 + 2] Cycloaddition Reactions of Iron(II) Acetylide Complexes. X-ray Crystallographic Structure Determinations of [1,2-Bis(diphenylphosphino)ethane](η^5-cyclopentadienyl)(4,4-diphenyl-2-methyl-3-oxo-1-cyclobutenyl)iron(II) and [1,2-Bis(diphenylphosphino)ethane](2-cyano-4-methylene-1-cyclobutenyl)(η^5-cyclopentadienyl)iron(II)

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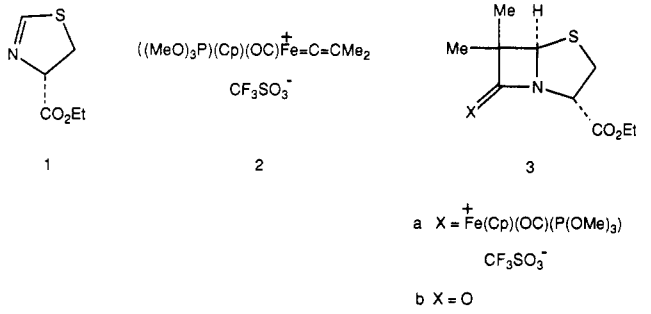
The iron(II) acetylide complexes **8**, **12**, and **13** reacted with diphenylketene, phenylethylketene, 3,3-dimethylbutanoyl chloride, 2-chloroacrylonitrile, diketene, dimethyl methylenemalonate, and 1,3-dicyano-1,3-butadiene to produce the corresponding formal [2 + 2] and [4 + 2] cycloadducts. The structures of (diphos)(Cp)FeC=C(Me)COC(Ph)$_2$ (space group $P2_1/n$ (No. 14), Z = 4, a = 15.187 (2) Å, b = 18.548 (4) Å, c = 15.631 (2) Å, β = 109.16 (1)°, $R(F)$ = 0.077) and (diphos)(Cp)FeC=C(CN)CH$_2$C(=CH$_2$) (space group $Pna2_1$ (No. 33), Z = 4, a = 18.860 (2) Å, b = 10.050 (1) Å, c = 15.733 (4) Å, $R(F)$ = 0.038) were determined by X-ray crystallography.

Recently, we described the synthesis of mono- or bicyclic β-lactams via the formal [2 + 2] cycloaddition reaction of imines or Δ^1-thiazolines with cationic iron(II) vinylidene followed by oxidative demetalation.[1] This chemistry is exemplified by the reaction of **1** and **2** to produce **3a** (72%) and subsequent iodosobenzene oxidation to reveal **3b** (52%). Cationic iron(II) vinylidenes may be prepared



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from the reaction of iron(II) acetylides with electrophiles.[2] Additionally, such vinylidenes readily undergo nucleophilic addition reactions. Thus, in principle, it should be possible to develop useful cyclization chemistry upon the basis of the iron acetylide, iron vinylidene, and vinyliron cascade (Scheme I). Thus, reaction of **4** with the reagent **5** bearing electrophilic and nucleophilic terminii should provide **6** and subsequently **7**. Such cyclization chemistry has precedent in studies on the formal [2 + 2] cycloaddition reaction of iron acetylides with tetracyanoethylene, hexafluoroacetone, phenyl isocyanate, carbon disulfide, and ketenes.[2-4] Representative cycloadducts that have been

Scheme I

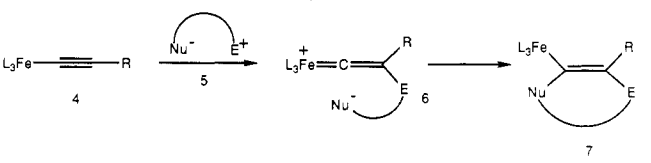

Table I

acetylide	cyclo-adduct	yield, %	acetylide	cyclo-adduct	yield, %
8	**11**	96	**13**	**16b**	96
8	**14a**	76	**13**	**17**	24
12	**14b**	95	**13**	**18**	78
12	**14c**	76	**8**	**20a**	69
12	**14d**	38	**12**	**20b**	61
13	**16a**	70	**8**	**22**	54

reported include the cyclobutene derivatives **9**, **10**, and **11** derived from the acetylide **8**. Herein, we report further studies on the cycloaddition reactions of **8**, **12**, and **13** with acylating agents and electron-deficient alkenes.

Results and Discussion

The iron acetylides **8**,[5] **12**, and **13**[6] were reacted with diphenylketene,[7] ethylphenylketene,[8] 3,3-dimethylbutanoyl

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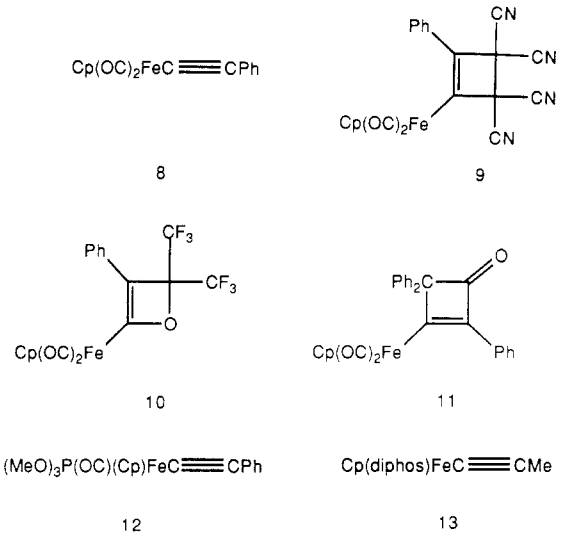
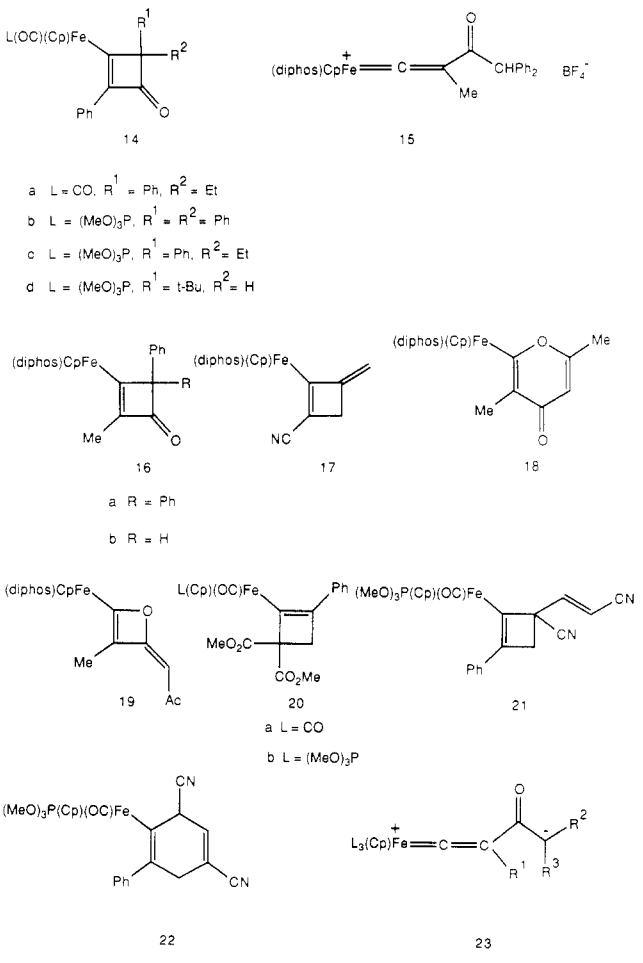


chloride, phenylacetyl chloride, 2-chloroacrylonitrile, diketene, dimethyl methylenemalonate,[9] and 1,3-dicyano-1,3-butadiene[10] to produce the cycloadducts **11**,[3] **14a–d**, **16a,b**, **17**, **18**, **20a,b** and **22** (Table I). The ketene or acid



chloride additions smoothly provided the corresponding cyclobutenone–iron species. The sequence of nucleophilicity of the acetylides is in the order **13** > **12** > **8**, whereas the electrophilicity of the α-carbon in the intermediate vinylidene zwitterions **23** is clearly reversed, with the diphos-substituted system being the least reactive.

(9) Ponticello, I. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3509.
(10) Ponticello, I. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3499. Ahn, K.-D.; Hall, H. K. *Ibid.* **1981**, *19*, 629.

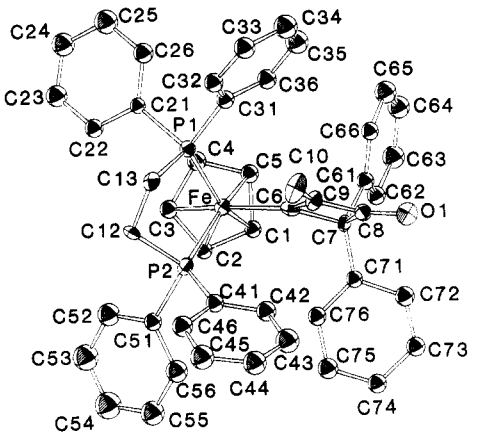


Figure 1. ORTEP drawing of [1,2-bis(diphenylphosphino)-ethane](η⁵-cyclopentadienyl)(4,4-diphenyl-2-methyl-3-oxo-1-cyclobutenyl)iron(II) (**16a**). The thermal ellipsoids are drawn at the 50% probability level.

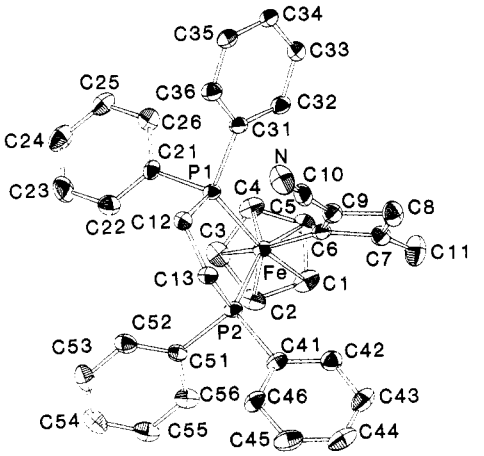


Figure 2. ORTEP drawing of [1,2-bis(diphenylphosphino)-ethane](2-cyano-4-methylene-1-cyclobutenyl)(η⁵-cyclopentadienyl)iron(II) (**17**). The thermal ellipsoids are drawn at the 50% probability level.

Thus, in the addition of **13** to diphenylketene the reaction could be stopped at the intermediate stage with isolation of the acylvinylidene **15**. The structural assignment of this substance was based principally on NMR characteristics (^{1}H NMR δ 1.13 (s, 3 H, Me), 4.78 (s, 1 H, C*H*CO), 5.15 (s, 5 H, vinylidene Cp); ^{13}C NMR δ 366.7 (Fe=*C*), 198.6 (*C*O), 89.4 (Cp)). Additionally, an NMR study established that reaction of **16a** with trifluoroacetic acid (1 equiv) in $CDCl_3$ slowly gave **15** as the trifluoroacetate salt. In contrast with these results, we have not isolated the presumed vinylidene adducts from the reaction of acetylides **8** and **12** with ketenes. The stereochemistry of the reaction deserves comment. Both cycloadducts **14c** and **14d** contain two asymmetric centers (Fe and C-4). ^{1}H NMR spectra indicated that these substances consisted of mixtures of diastereoisomers (**14c**, 4:1; **14d**, 7:3). The identity of the major isomer in each case was not determined.

Acetylide **13** reacted smoothly with 2-chloroacrylonitrile at −78 °C to produce **17**, which was presumably formed via the loss of HCl subsequent to cycloaddition. Diketene also reacted with **13** to provide a mixture of two adducts. Both these substances clearly contained enolized β-dicarbonyl residues (^{1}H NMR δ 5.62 and 5.30; ^{13}C NMR δ 172.9, 110.8). When it stood, the more polar compound rearranged to the less polar product. On the basis of spectroscopic data, the stable product was assigned the γ-pyrone structure **18**. Presumably, the less stable product was the oxete derivative **19**.

Table II. Summary of the Crystal Structure Data for 16a and 17

	16a	17
formula	$C_{52}H_{50}FeOP_2 \cdot 0.65CH_2Cl_2 \cdot CH_3OH$	$C_{37}H_{32}FeNP_2$
M_r	911.71	608.46
cryst size, mm	0.22 × 0.08 × 0.06	0.37 × 0.25 × 0.18
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)
a, Å	15.187 (2)	18.860 (2)
b, Å	18.548 (4)	10.050 (1)
c, Å	15.631 (2)	15.733 (4)
α, deg	90.0	90.0
β, deg	109.16 (1)	90.0
γ, deg	90.0	90.0
V, Å^3	4159 (2)	2982 (1)
Z	4	4
d_{calcd}, g cm^{-3}	1.46	1.36
μ(Mo Kα), cm^{-1}	6.10	6.36
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)	
scan type	$2\theta/\theta$	$2\theta/\theta$
2θ range, deg	4–48	4–55
scan width, deg	0.9 + 0.35 tan θ	0.8 + 0.35 tan θ
no. of unique data	6750	3848
no. of unique data with $I > 3\sigma(I)$	2965	2843
no. of params	286	363
$R(F)$	0.077	0.038
$R_w(F)$	0.086	0.046
GOF	1.81	1.25

Acetylides **8** and **12** reacted with dimethyl methylenemalonate to produce the corresponding cyclobutene complexes **20a** and **20b**. However, acetylide **12** reacted with 1,3-dicyano-1,3-butadiene to produce the mixture of two diastereoisomeric [2 + 2] cycloadducts **21** (^{1}H NMR δ 6.55, 6.51 and 5.91, 5.83 (2 AB q, J = 16 Hz, C*H*=C*H*CN), 4.73, 4.72 (2 s, Cp)) and the two diastereoisomeric [4 + 2] cycloadducts **22** (^{1}H NMR δ 6.66 (br d, 1 H, J = 6 Hz, C*H*CN), 4.79, 4.75 (2 s, 5 H, Cp)). When they were warmed, the unstable [2 + 2] adducts **21** rearranged to produce only the formal Diels–Alder adduct **22**. Chromatography gave **22** as a single undefined stereoisomer.

Most of the substances prepared in this study were authenticated by spectral data and high-resolution molecular ion mass measurements. Most of the products even when crystalline proved difficult to obtain microanalytically pure even after repeated chromatography and/or recrystallization. Thus, in order to substantiate our structural assignments, we have carried out X-ray crystallographic studies on the two representative adducts **16a** and **17**. The results of these studies are summarized in Tables II–IV and in the ORTEP diagrams (Figures 1 and 2). It is clear from these results that iron(II) acetylides readily undergo formal [4 + 2] and [2 + 2] cycloaddition reactions to provide cyclic alkenyl ion complexes.

Experimental Section

All glassware was dried at 150 °C for several hours, or at 250 °C for at least $^1/_2$ h, and then assembled while hot. The apparatus was either evacuated and refilled with O_2-free nitrogen (three cycles) or simply purged with high-purity nitrogen for several minutes. All reactions were run under positive nitrogen pressure unless otherwise noted. Solvents for chromatography were distilled at atmospheric pressure before use. Hexane refers to ACS reagent grade, boiling point range 35–60 °C. Dried Et_2O, hexane, toluene, PhH, and THF were distilled from Na/benzophenone ketyl. Dry dichloromethane was redistilled from calcium hydride. All other reagents were used as supplied (Aldrich) unless otherwise noted.

IR spectra were obtained on a Perkin-Elmer 283 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz), Varian XL-400 (400 MHz), or Varian XL-300 (300 MHz) instrument. ^{13}C NMR spectra were recorded on the Varian instruments at 101 or 75 MHz. All NMR spectra were run as $CDCl_3$ solutions unless otherwise noted, with tetramethylsilane or $CHCl_3$ as an internal reference. Ultraviolet spectra were taken on a Perkin-Elmer 330 spectrophotometer. Melting points were determined on a Reichert hot stage melting point apparatus and are uncorrected. Fast atom bombardment mass spectra were obtained by the Midwest Center for Mass Spectrometry (University of Nebraska, Lincoln, NE) or by the Analytical Services Laboratory of Northwestern University on a VG70-250SE instrument. All column chromatography was performed on E. Merck silica gel 60, 230–400 mesh ASTM. TLC was carried out on E. Merck precoated silica gel 60 F254 plates.

Carbonyl(η^5-cyclopentadienyl)(phenylethynyl)(trimethyl phosphite)iron(II) (12). Method 1. n-BuLi in hexane (1.6 M, 0.3 mL) was added to PhC≡CH (40 μL) in Et_2O (2 mL) at −78 °C. After 90 min, the solution was added via cannula to

Table III. Selected Bond Lengths (Å) and Angles (deg) for 16a

Fe–P1	2.206 (3)	O1–C8	1.26 (1)
Fe–P2	2.245 (3)	C1–C2	1.40 (1)
Fe–C1	2.13 (1)	C1–C5	1.42 (1)
Fe–C2	2.12 (1)	C2–C3	1.41 (1)
Fe–C3	2.10 (1)	C3–C4	1.44 (1)
Fe–C4	2.13 (1)	C4–C5	1.43 (1)
Fe–C5	2.13 (1)	C6–C9	1.38 (1)
Fe–C6	1.94 (1)	C6–C7	1.62 (1)
P1–C13	1.85 (1)	C7–C61	1.58 (1)
P1–C21	1.85 (1)	C7–C71	1.51 (1)
P1–C31	1.83 (1)	C7–C8	1.52 (1)
P2–C12	1.84 (1)	C8–C9	1.40 (1)
P2–C41	1.87 (1)	C9–C10	1.51 (1)
P2–C51	1.84 (1)	C12–C13	1.51 (1)
P1–Fe–P2	85.5 (1)	C1–C5–C4	107 (1)
P1–Fe–C6	98.1 (3)	C7–C6–C9	90.0 (8)
P2–Fe–C6	98.1 (3)	C61–C7–C71	114.4 (8)
C13–P1–C21	101.3 (4)	C6–C7–C8	81.8 (7)
C13–P1–C31	103.8 (5)	O1–C8–C7	131 (1)
C21–P1–C31	98.7 (5)	O1–C8–C9	136 (1)
C12–P2–C41	101.9 (5)	C7–C8–C9	93.0 (8)
C12–P2–C51	102.3 (5)	C6–C9–C8	95.3 (8)
C41–P2–C51	97.9 (5)	C6–C9–C10	135 (1)
C1–C2–C3	109 (1)	C8–C9–C10	130 (1)
C2–C3–C4	108 (1)	P2–C12–C13	108.0 (7)
C3–C4–C5	107.5 (9)	P1–C13–C12	107.9 (7)

Table IV. Selected Bond Lengths (Å) and Angles (deg) for 17

Fe–P1	2.158 (1)	N–C10	1.142 (7)
Fe–P2	2.167 (1)	C1–C2	1.428 (8)
Fe–C1	2.112 (5)	C1–C5	1.418 (7)
Fe–C2	2.108 (5)	C2–C3	1.436 (8)
Fe–C3	2.119 (5)	C3–C4	1.426 (7)
Fe–C4	2.094 (4)	C4–C5	1.402 (7)
Fe–C5	2.093 (4)	C6–C7	1.520 (7)
Fe–C6	1.960 (4)	C6–C9	1.377 (7)
P1–C12	1.866 (4)	C7–C8	1.531 (8)
P1–C21	1.849 (5)	C7–C11	1.340 (8)
P1–C31	1.840 (5)	C8–C9	1.536 (7)
P2–C13	1.852 (5)	C9–C10	1.426 (8)
P2–C41	1.849 (4)	C12–C13	1.532 (6)
P2–C51	1.840 (4)		
P1–Fe–C6	91.2 (2)	C4–C5–C1	108.9 (4)
P2–Fe–C6	91.1 (1)	C7–C6–C9	87.7 (4)
P1–Fe–P2	87.50 (5)	C6–C7–C11	139.7 (5)
C21–P1–C31	98.6 (2)	C8–C7–C11	127.8 (5)
C12–P1–C31	106.7 (2)	C6–C7–C8	92.4 (4)
C12–P1–C21	102.1 (2)	C7–C8–C9	81.8 (3)
C41–P2–C51	99.0 (2)	C6–C9–C10	137.4 (5)
C13–P2–C51	103.5 (2)	C6–C9–C8	98.1 (4)
C13–P2–C41	101.5 (2)	C10–C9–C8	124.5 (5)
C2–C1–C5	107.0 (5)	N–C10–C9	176.7 (6)
C1–C2–C3	108.8 (4)	P1–C12–C13	110.9 (3)
C4–C3–C2	106.2 (4)	P2–C13–C12	111.9 (3)
C3–C4–C5	109.1 (4)		

$(MeO)_3P(Cp)(OC)FeI$[11] (73 mg) in Et_2O (2 mL) at −5 °C. After 2 h the solution was reduced in volume to 2 mL (N_2) and chromatographed on silica (eluant hexane) to give **12** (30 mg, 44%): IR ($CDCl_3$) 3020, 2950, 2095, 1970, 1592, 1220, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 2 H, J = 7 Hz), 7.13 (t, 2 H, J = 7 Hz), 7.02 (t, 1 H, J = 7 Hz), 4.76 (s, 5 H), 3.74 (d, 9 H, J = 11.6 Hz); ^{13}C NMR (100.8 MHz, $CDCl_3$) δ 217.4 (d, J = 44 Hz), 130.9, 128.8, 127.7, 124.3, 117.8, 83.4, 77.2, 53.0 (d, J = 5 Hz); mass spectrum (FAB) m/e 374 ($M^{\bullet+}$), 346, 222, 165, 121, 63. High-resolution mass spectrum: calcd for $C_{17}H_{19}FeO_4P$ ($M^{\bullet+}$), 374.0370; found ($M^{\bullet+}$), 374.0377.

Method 2. Acetylide **8** (100 mg) in $(MeO)_3P$ (4 mL) was heated to 180–190 °C for 45 min (sealed tube). Evaporation and chromatography gave **12** (105 mg, 78%).

Dicarbonyl(η⁵-cyclopentadienyl)(3-oxo-2,4,4-triphenyl-1-cyclobutenyl)iron(II) (11). Diphenylketene[7] (21 mg) in CH_2Cl_2 (1 mL) was added to **8** (25 mg) in CH_2Cl_2 (1 mL) at −78 °C. The mixture was warmed up to room temperature and, after 1 h, evaporated. Chromatography on silica (eluant CH_2Cl_2) and recrystallization from $CHCl_2/Et_2O$ gave **11** (41 mg, 96%) as yellow crystals: mp 185–186 °C (lit.[3] mp 189–190 °C); IR ($CHCl_3$) 2038, 1985, 1715, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 2 H, J = 7 Hz), 7.45 (t, 2 H, J = 7 Hz), 7.40–7.24 (m, 11 H), 4.50 (s, 5 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.1, 213.5, 185.1, 166.3, 141.4, 132.8, 129.0, 128.5, 128.2, 127.8, 127.0, 126.8, 86.3, 85.9; mass spectrum (FAB) m/e 473 (M^+ + H), 444, 417, 388, 307, 267, 259, 228, 227. High-resolution mass spectrum (FAB): calcd for $C_{29}H_{20}FeO_3$ (M^+ + H), 473.0840; found (M + H^+), 473.0828. Anal. Calcd for $C_{29}H_{20}FeO_3$: C, 73.74; H, 4.27. Found: C, 73.44; H, 4.22.

Dicarbonyl(η⁵-cyclopentadienyl)(4-ethyl-3-oxo-2,4-diphenyl-1-cyclobutenyl)iron(II) (14a). Reaction of ethylphenylketene[8] with acetylide **8** gave **14a** (29 mg, 76%) as a yellow oil: TLC R_f 0.34 (CH_2Cl_2); IR ($CHCl_3$) 2040, 1987, 1710, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2 H, J = 7.6 Hz), 7.48–7.20 (m, 8 H), 4.65 (s, 5 H), 2.35 (m, 1 H), 2.22 (m, 1 H), 1.00 (t, 3 H, J = 7.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 213.4, 188.9, 166.0, 141.8, 132.7, 128.4, 128.3, 127.5, 127.1, 126.7, 85.7, 81.2, 23.9, 10.3; mass spectrum (FAB) m/e 425 (M + H^+), 369, 340, 259, 227, 219. High-resolution mass spectrum (FAB): calcd for $C_{25}H_{20}FeO_3$ (M + H^+), 425.0840; found (M + H^+), 425.0834. Anal. Calcd for $C_{25}H_{20}FeO_3 \cdot H_2O$: C, 67.87; H, 5.02. Found: C, 68.08; H, 4.78.

Carbonyl(η⁵-cyclopentadienyl)(3-oxo-2,4,4-triphenyl-1-cyclobutenyl)(trimethyl phosphite)iron(II) (14b). Diphenylketene (58 mg) in CH_2Cl_2 (4 mL) was added to acetylide **12** (93 mg) in CH_2Cl_2 (4 mL) at −78 °C. The reaction mixture was to warmed to room temperature and, after 2 h, evaporated. Chromatography gave **14b** (134 mg, 95%) as yellow needles: mp 164–165 °C (from CH_2Cl_2/Et_2O); IR ($CHCl_3$) 3000, 2960, 2930, 1960, 1700, 1660, 1605, 1498 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 2 H, J = 7.2 Hz), 7.50 (d, 2 H, J = 7.2 Hz), 7.42–7.32 (m, 5 H), 7.25–7.18 (m, 6 H), 4.27 (s, 5 H), 3.57 (d, 9 H, J = 11.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 238.2 (d, J = 34 Hz), 218.0 (d, J = 45 Hz), 186.4 (d, J = 4 Hz), 166.9 (d, J = 4 Hz), 143.7, 142.5, 134.5, 130.0, 129.7, 129.3, 128.3, 127.8, 127.7, 127.4, 126.7, 126.3, 125.9, 87.0, 84.0, 52.9 (d, J = 8.5 Hz); mass spectrum (FAB) m/e 569 (M + H^+), 388, 346, 301, 273, 267, 245. High-resolution mass spectrum (FAB): calcd for $C_{31}H_{29}FeO_5P$ (M + H^+), 569.1180; found (M + H^+), 569.1181. Anal. Calcd for $C_{31}H_{29}FeO_5P$: C, 65.51; H, 5.14; P, 5.45. Found: C, 64.99; H, 5.11; P, 5.13.

Carbonyl(η⁵-cyclopentadienyl)(4-ethyl-3-oxo-2,4-diphenyl-1-cyclobutenyl)(trimethyl phosphite)iron(II) (14c). Reaction of acetylide **12** and ethylphenylketene gave **14c** (76%) as a yellow oil containing two diastereoisomers (4:1): TLC R_f 0.28 (CH_2Cl_2/MeOH 19:1); IR ($CHCl_3$) 3002, 2960, 1955 br, 1690 br, 1608, 1582, 1500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77*, 7.75 (2 d, 2 H, J = 7 Hz), 7.46–7.09 (m, 8 H), 4.59, 4.26* (2 s, 5 H), 3.53*, 3.34 (2 d, 9 H, J = 10.8 Hz), 2.50*, 2.48 (2 m, 1 H), 2.20, 1.99* (2 m, 1 H), 1.07, 1.05* (2 t, 3 H, J = 7.5 Hz) (asterisks designate signals for the major diastereoisomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ (major diastereoisomer) 240.5 (d, J = 36 Hz), 218.2 (d, J = 48 Hz), 190.4, 165.4, 142.8, 134.5, 128.8, 128.4, 128.0, 127.8, 127.6, 127.5, 126.4, 126.0, 83.7, 82.0, 52.6 (d, J = 8 Hz), 25.5, 10.4; mass spectrum (FAB) m/e 521 (M + H^+), 369, 340, 301, 273, 245, 219. High-resolution mass spectrum (FAB): calcd for $C_{27}H_{29}FeO_5P$ (M + H^+), 521.1180; found (M + H^+), 521.1187.

Carbonyl(η⁵-cyclopentadienyl)[4-(1,1-dimethylethyl)-3-oxo-2-phenyl-1-cyclobutenyl](trimethyl phosphite)iron(II) (14d). Reaction of $^tBuCH_2COCl$ (51.2 μL), Et_3N (51.4 μL), and **12** (138 mg) gave **14d** (55 mg, 38%) as a yellow oil containing two diastereoisomers (7:3): TLC R_f 0.29 (CH_2Cl_2/MeOH); IR (film) 2945, 2860, 1945 br, 1790, 1690 br, 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68, 7.47* (2 d, 2 H, J = 7.6, 7.2 Hz), 7.43–7.18 (m, 3 H), 4.74 (s, 5 H), 3.56, 3.37* (2 d, 9 H, J = 10.8, 11.1 Hz), 3.30, 3.26* (2 s, 1 H), 1.13*, 1.05 (2 s, 9 H) (asterisks designate signals for the major diastereoisomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.7*, 226.5 (2 d, J = 38 Hz), 218.2*, 217.5 (d, J = 50, 48 Hz), 187.6*, 186.7, 169.2, 169.1*, 134.8*, 134.6, 127.9, 127.7, 127.3, 126.5, 126.3, 84.0 (d, J = 4 Hz), 83.5, 83.3* (2 d, J = 3 Hz), 52.5 (d, J = 7 Hz), 52.2* (d, J = 7 Hz), 33.9*, 33.3, 29.2*, 29.1 (asterisks designate signals for the major diastereoisomer); mass spectrum (FAB) m/e 474, 473 (M + H^+), 302, 301, 292, 277, 245. High-resolution mass spectrum (FAB): calcd for $C_{23}H_{29}FeO_5P$ (M + H^+), 473.1180; found (M + H^+), 473.1179.

[1,2-Bis(diphenylphosphino)ethane](η⁵-cyclopentadienyl)[2-(diphenylacetyl)-2-methylethylidene]iron(II) Tetrafluoroborate (15). To a solution of **13**[6] (24 mg) in dry CH_2Cl_2 (4 mL) at −78 °C was added diphenylketene[7] (10 μL). In a separate vessel, a solution of titanium(IV) isopropoxide (13 μL) in dry CH_2Cl_2 (1 mL) was prepared and transferred via cannula into the acetylide solution. The reaction mixture was warmed up to room tempreature with stirring. After 3 h, the reaction mixture was cooled to −78 °C and tetrafluoroboric acid (7 μL) was added. The mixture was warmed to room temperature, the solvent evaporated under a stream of nitrogen, and the residue recrystallized to afford **15** as bright orange crystals (17 mg, 47%): mp 182–183 °C dec (from CH_2Cl_2/MeCN); IR (KBr) 1570, 1433, 1262, 1096, 1044 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55–7.32 (m, 16 H), 7.22 (m, 6 H), 7.58–7.08 (m, 4 H), 6.76 (m, 4 H), 5.15 (s, 5 H), 4.78 (s, 1 H), 3.16 (m, 2 H), 2.73 (m, 2 H), 1.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 366.7 (t, J = 31 Hz), 198.6, 138.6, 135.9, 135.4, 133.6, 132.7, 131.7, 131.3, 129.3, 128.9, 128.5, 127.1, 89.4, 62.2, 29.0 (t, J = 22 Hz), 9.24; mass spectrum (FAB) m/e 753 (M^+), 715, 355, 341, 331, 325, 263, 221, 191, 115, 106. Mass spectrum (FAB): calcd for $C_{48}H_{43}FeOP_2^+$ (M^+), 753.2138; found (M^+), 753.2108.

[1,2-Bis(diphenylphosphino)ethane](4,4-diphenyl-2-methyl-3-oxo-1-cyclobutenyl)(η⁵-cyclopentadienyl)iron(II) (16a). To a solution of **13** (36.9 mg) in CH_2Cl_2 (1 mL) at −78 °C was added dropwise a solution of diphenylketene (17 mg) in CH_2Cl_2 (0.5 mL). The cold bath was removed and the reaction mixture warmed up to room temperature and stirred for 1 h, whereupon the solvent was removed *in vacuo* and the crude residue recrystallized to provide **16a** (35.2 mg, 70%): mp 169–171 °C (from CH_2Cl_2/Et_2O); IR (KBr) 3053, 1668, 1473, 1433, 1263, 986, 691 cm^{-1}; UV ($CHCl_2$) λ_{max} 392 (ε = 6800); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.70–7.16 (m, 30 H), 4.01 (s, 5 H), 2.85 (br s, 4 H), 0.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 246.8 (t, J = 22 Hz), 189.9, 162.5, 144.8, 142.6 (t, J = 17 Hz), 136.2 (t, J = 16 Hz), 132.9, 131.0, 130.9, 130.1, 129.9, 129.0, 128.3, 128.2, 127.0, 125.3, 88.0, 81.2, 29.8 (t, J = 20 Hz), 12.1; mass spectrum (FAB) m/e 753 (M + H^+), 621, 519, 219, 183, 154, 136. Mass spectrum (FAB): calcd for $C_{48}H_{42}FeOP_2$ (M + H^+), 753.2138; found (M + H^+), 753.2136.

[1,2-Bis(diphenylphosphino)ethane](2-methyl-3-oxo-4-phenyl-1-cyclobutenyl)(η⁵-cyclopentadienyl)iron(II) (16b). $PhCH_2COCl$ was refluxed over PCl_5 for 1 h and then distilled (82 °C, 6 mmHg). Et_3N was stirred over CaH_2 for 2 days and redistilled (90 °C). To a solution of **13** (91.9 mg) in dry Et_2O and CH_2Cl_2 (1:1, 2 mL) at 3 °C was added Et_3N (22 μL). To this mixture was added dropwise a solution of $PhCH_2COCl$ (22 μL) in dry Et_2O (1 mL). The reaction mixture was kept at 0–5 °C for 10 min and then was extracted with H_2O (3 × 5 mL), and the extract was dried ($MgSO_4$), filtered, and evaporated and the residue recrystallized to give **16b** (103.4 mg, 96%) as an orange powder: mp 144–146 °C (from CH_2Cl_2/Et_2O); IR (KBr) 1684, 1433, 1253, 1094, 978, 742, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.83 (t, 2 H, J = 8.6 Hz), 7.52–7.16 (m, 21 H), 7.02 (t, 2 H, J = 8.1 Hz), 4.06 (s, 5 H), 3.09 (m, 1 H), 3.01–2.82 (m, 1 H), 2.57–2.38

(11) Haines, R. J.; DuPreez, A. L.; Marais, L. L. *J. Organomet. Chem.* **1970**, *24*, C26.

(m, 3 H), 0.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 187.6, 161.8 (d, J = 4.3 Hz), 144.5, 144.1, 144.0, 140.4 (d, J = 28.5 Hz), 138.0, 137.7, 137.2, 134.3 (d, J = 10.7 Hz), 133.3 (d, J = 10.3 Hz), 132.0, 130.8 (t, J = 4.6 Hz), 130.6 (d, J = 8.9 Hz), 130.3, 130.2, 129.7 (d, J = 32.6 Hz), 128.8 (t, J = 6.1 Hz), 128.4, 128.2, 128.1, 128.0, 127.8 (d, J = 8.5 Hz), 126.0, 81.3, 80.2, 29.4 (dd, J = 15.4, 32.3 Hz), 27.8 (dd, J = 15.2, 23.8 Hz), 11.53; mass spectrum (FAB) m/e 677 ($M + H^+$), 519, 431, 426, 306, 119, 103. Mass spectrum (FAB): calcd for $C_{42}H_{38}FeOP_2$ ($M + H^+$), 677.1825; found ($M + H^+$), 677.1825.

[1,2-Bis(diphenylphosphino)ethane](2-cyano-4-methylene-1-cyclobutenyl)(η^5-cyclopentadienyl)iron(II) (17). To a solution of **13** (67.1 mg) in dry CH_2Cl_2 (4 mL) at 0 °C was added 2-chloroacrylonitrile (20.6 mg) in CH_2Cl_2 (25 mL) dropwise over a period of several hours. Upon completion of addition, the reaction mixture was stirred at room temperature for 1 h and concentrated and the residue purified by chromatography on alumina (basic, grade III; 1:99 $MeOH/CH_2Cl_2$) to give **17** (17.9 mg, 24%) as bright yellow-orange crystals: mp >220 °C dec (from CH_2Cl_2/Et_2O); IR (KBr) 3070, 2930, 2175, 1640, 1490, 1440, 1410, 1390 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 (br s, 4 H), 7.42–7.27 (m, 12 H), 7.19 (br s, 4 H), 4.58 (s, 1 H), 4.30 (s, 5 H), 4.08 (s, 1 H), 3.02 (m, 2 H), 2.79 (s, 2 H), 2.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 213.9 (t, J = 28 Hz), 158.9, 143.6 (m), 137.4 (m), 133.0 (t, J = 4.8 Hz), 131.6 (t, J = 3.7 Hz), 129.3, 128.7, 127.9 (t, J = 4.4 Hz), 127.7 (t, J = 4.6 Hz), 121.9, 103.0, 80.3, 42.9, 29.2 (dd, J = 21.3, 21.3 Hz); mass spectrum (FAB) m/e 610 ($M + H^+$), 519, 219, 183, 154. Mass spectrum (FAB): calcd for $C_{37}H_{33}FeNP_2$ ($M + H^+$), 610.1515; found ($M + H^+$), 610.1497.

[1,2-Bis(diphenylphosphino)ethane](η^5-cyclopentadienyl)(3,6-dimethyl-4-oxo-2-pyranyl)iron(II) (18). Diketene was distilled immediately before use (50–52 °C, 55 mmHg). To a solution of **13** (63.1 mg) in $CHCl_2$ (3 mL) at −20 °C was added very slowly, dropwise, diketene (17 μL) in CH_2Cl_2 (5 mL). Upon completion of addition, the cold bath was warmed slowly for approximately 0.5 h (to 0 °C) and was removed and the reaction mixture stirred at room temperature. The reaction progress was monitored by TLC (silica gel, 1:9 $MeOH/CH_2Cl_2$; R_f 0.36). After 1 h, the reaction mixture was filtered through a pad of silica gel with 1:9 $MeOH/CH_2Cl_2$. Rose-colored base-line material remained on the silica, and the bright yellow forerun was concentrated and rechromatographed (silica; $MeOH/CH_2Cl_2$ 1:39–1:19) to give **18** and **19** (56.9 mg, 78%) as a mixture of isomers. These were separable by careful rechromatography. The more polar isomer **19** slowly converted completely to the pyrone form **18**, which was crystalline, on standing: mp >200 °C dec (from CH_2Cl_2/Et_2O); IR (**18**, film) 3060, 2950, 1730 m, 1645, 1550 cm^{-1}; IR (**19**, film) 3360, 3050, 2940, 1725 w, 1641, 1550 cm^{-1}; UV (**18**, CH_2Cl_2) λ_{max} 445 (ε = 5400); ^1H NMR ($CDCl_3$, 400 MHz; **18**) δ 7.38–7.22 (m, 16 H), 7.12 (m, 4 H), 5.62 (s, 1 H), 4.30 (s, 5 H), 2.41 (m, 2 H), 2.28 (m, 2 H), 1.26 (s, 3 H), 0.89 (s, 3 H); ^1H NMR ($CDCl_3$, 400 MHz, **19**) δ 7.48–7.23 (m, 16 H), 7.13 (m, 4 H), 5.30 (s, 1 H), 4.31 (s, 5 H), 2.41 (m, 2 H), 2.28 (m, 2 H), 1.75 (impurity), 1.28 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR ($CDCl_3$, 101 MHz; **18**) δ 172.9, 167.3, 141.6, 140.6, 138.9 (t, J = 20.3 Hz), 132.5 (t, J = 4.3 Hz), 132.2 (t, J = 4.4 Hz), 129.1 (d, J = 6.4 Hz), 127.8 (m), 110.8, 79.5, 27.5 (t, J = 21 Hz), 17.7, 15.0; mass spectrum (FAB) m/e 643 ($M + H^+$), 519, 454, 426, 400, 385, 329, 248. Mass spectrum (FAB): calcd for $C_{38}H_{36}FeO_2P_2$ ($M + H^+$) 643.1618; found ($M + H^+$), 643.1596.

Dicarbonyl(η^5-cyclopentadienyl)[4,4-bis(methoxycarbonyl)-2-phenyl-1-cyclobutenyl]iron(II) (20a). Dimethyl methylenemalonate[9] (24.2 mg) in $CHCl_3$ (50 mL) was added dropwise over 2 h to acetylide **8** (33.4 mg) in $CHCl_3$ (5 mL). Evaporation and chromatography on silica (eluant CH_2Cl_2) gave **20a** (35 mg, 69%) as a yellow oil: TLC R_f 0.34 (CH_2Cl_2); IR ($CHCl_3$) 2040, 1980, 1730, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 2 H, J = 7.2 Hz), 7.36 (t, 2 H, J = 7.2 Hz), 7.23 (t, 1 H, J = 7.2 Hz), 4.84 (s, 5 H), 3.77 (s, 6 H), 3.49 (s, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 170.8, 163.7, 149.5, 136.1, 127.1, 125.9, 123.5, 84.4, 61.7, 51.0, 39.4; mass spectrum (FAB) m/e 423 ($M + H^+$), 422, 367, 366, 365, 307, 281, 279. High-resolution mass spectrum: calcd for $C_{21}H_{18}FeO_6$ ($M + H^+$), 423.0531; found ($M + H^+$), 423.0506.

Carbonyl(η^5-cyclopentadienyl)[4,4-bis(methoxycarbonyl)-2-phenyl-1-cyclobutenyl](trimethyl phosphite)iron(II) (20b). The high-dilution reaction between **12** (45 mg) and dimethyl methylenemalonate (24.2 mg) gave **20b** (38 mg, 61%) as a yellow oil: TLC R_f 0.41 (hexane/Et_2O/Et_3N 49:49:2); IR ($CHCl_3$) 1965 br, 1730 br, 1605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2 H, J = 7.6 Hz), 7.31 (t, 2 H J = 7.6 Hz), 7.17 (t, 1 H, J = 7.6 Hz), 4.64 (s, 5 H), 3.80 (s, 3 H), 3.69 (s, 3 H), 3.56 (d, 9 H, J = 10.8 Hz), 3.54 (d, 1 H, J = 11.2 Hz), 3.28 (d, 1 H, J = 11.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.5 (d, J = 48 Hz), 172.5, 172.3, 165.1, 138.3, 127.5, 125.8, 124.3, 83.8, 62.9, 52.0, 51.6 (d, J = 7 Hz), 39.6; mass spectrum (FAB) m/e 519 ($M + H^+$), 490, 366, 307, 245. High-resolution mass spectrum (FAB): calcd for $C_{23}H_{27}FeO_8P$ ($M + H^+$), 519.0871; found ($M + H^+$), 519.0876.

Carbonyl(η^5-cyclopentadienyl)(4,6-dicyano-2-phenylcyclohexa-1,4-dien-1-yl)(trimethyl phosphite)iron(II) (22). 1,3-Dicyano-1,3-butadiene[10] (58 mg) in $CHCl_3$ (80 mL) was added dropwise over 2 h to **12** (150 mg) in $CHCl_3$ (10 mL). Evaporation gave a yellow oil that contained **21** (3:2) and **22** (3:2) both as mixtures of diastereoisomers: ^1H NMR (400 MHz, $CDCl_3$; **21**) δ 6.55, 6.51 (2 d, 1 H, J = 16.4 Hz), 5.91, 5.83 (2 d, 1 H, J = 16.4 Hz), 4.73, 4.72 (2 s, 5 H), 3.68, 3.65 (2 d, 9 H, J = 10.8 Hz); ^1H NMR (400 MHz, $CDCl_3$; **22**) δ 6.66 (br d, 1 H, J = 6 Hz), 4.79, 4.75 (2 s, 5 H), 3.48, 3.35 (2 d, 9 H, J = 10.8 Hz). The cyclobutenes **21** were too unstable to be isolated. Thus, the crude product in $CHCl_3$ (90 mL) was heated to reflux for 20 min and evaporated. Chromatography on silica (eluant CH_2Cl_2) gave **22** (105 mg, 54%) as a yellow oil containing a single diastereoisomer: TLC R_f 0.43 (CH_2Cl_2); IR (film) 3040, 2970, 2860, 2230, 1950 br, 1640, 1608 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, 2 H, J = 7 Hz), 7.27 (t, 1 H, J = 7 Hz), 7.11 (d, 2 H, J = 7 Hz), 6.66 (br d, 1 H, J = 6 Hz), 4.75 (s, 5 H), 4.74 (m, 1 H), 3.48 (d, 9 H, J = 11.4 Hz), 3.29 (br s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.9 (d, J = 49 Hz), 147.5, 144.9, 138.5, 137.1, 136.5, 130.0, 128.0, 126.4, 118.9, 118.0, 115.8, 83.6, 52.4 (d, J = 6 Hz), 44.3 (d, J = 9 Hz), 38.7; mass spectrum (FAB) m/e 479 ($M + H^+$), 478 ($M^{+\cdot}$), 460, 358, 326, 308, 307. High-resolution mass spectrum: calcd for $C_{23}H_{23}FeN_2O_4P$ ($M^{+\cdot}$), 478.0745; found ($M^{+\cdot}$), 478.0762.

X-ray Data Collection and Structure Determination. A summary of the crystallographic data is presented in Table II. All measurements were performed at −120 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 69 Å). Accurate cell parameters were determined by least-squares refinement applied to the setting angles of 25 high-angle reflections. Intensities of four standard reflections were monitored every 3 h of X-ray exposure, showing no significant decay. All calculations were performed on a MicroVAX 3600 computer using the TEXSAN crystallographic software package.[12]

Compound 16a. Only a very small crystal could be selected for the measurements. The crystal diffracted very weakly, and no significant intensities were observed in the range above 2θ = 48°. The structure was solved by direct methods (MITHRIL).[13] During the structure solution a difference Fourier map showed the presence of a molecule that was identified as the CH_2Cl_2 solvent molecule. This molecule was significantly disordered, and it was refined with an occupancy of 0.65. Further calculations indicated the presence of another solvent molecule that was assigned as the methanol solvent molecule. The molecule was also severely disordered, and an attempt of refinement led to unacceptable metric parameters. Consequently, the parameters of the O and C atoms of the molecule were fixed in the final refinement. The full-matrix least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms, except for the ring and solvent carbon atoms and the oxygen atom of the methanol solvent molecule, yielded the final R of 0.077 (R_w = 0.084). The significant disorder of the solvent molecules contributed to higher than usual values of the R factors. Most of the H atoms showed on the difference Fourier maps. The H atoms were included in the final refinement as fixed contributors to the structure factors.

Compound 17. The structure was solved by heavy-atom techniques (SHELXS 86).[14] Full-matrix least-squares refinement

(12) Swepston, P. N. "TEXSAN Crystallographic Program Package"; Molecular Structure Corp.: College Station, TX, 1986.

(13) Gilmore, G. N. "MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data"; University of Glasgow: Glasgow, Scotland, 1983.

with anisotropic displacement parameters for all non-hydrogen atoms gave the final R of 0.038 (R_w = 0.046). All hydrogen atoms were found in the difference Fourier maps and were included in the refinement as fixed contributors to the structure factors. The final difference map was essentially featureless, with the highest peak being 0.14 e Å^{-3}.

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(14) Sheldrick, G. M. "SHELXS-86: A Program for Crystal Structure Determination"; University of Göttingen, Göttingen, FRG, 1986.

Supplementary Material Available: Tables of positional and thermal parameters for **16a** and **17** (4 pages); listings of structure factors (41 pages). Ordering information is given on any current masthead page.

Insertions of Unactivated Olefins into the Hydrosulfido Ligand of a Cationic Cyclopentadienylmolybdenum Complex

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The cationic complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ ([1]SO_3CF_3) has been reacted with a series of terminal and internal olefins to form the cationic product in which the olefin has inserted into the S–H bond of the bridging ligand. The reaction has been found to be reversible for most olefins. The regiochemistry of the insertion reaction has been studied, and relative rates of insertion have been determined as olefin substituents were varied. For reactions involving internal olefins, the kinetic insertion products were found to rearrange to more stable products. A mechanism for the olefin insertion reaction has been proposed that involves attack of an electrophilic sulfido ligand in **1** on the more electron-rich carbon of the olefin. Secondary products have been isolated from many of the reaction solutions and characterized by spectroscopic data. The secondary products result from air oxidation of **1** and further reaction of this oxidized derivative with olefins.

Introduction

The cationic complex of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]X$ ([1]X; X = SO_3CF_3, BF_4) has been found to undergo interesting reactions with organic oxygen-[1] and nitrogen-containing[2] substrates that result in the cleavage of the carbon–heteroatom bond. In some cases an intermediate reaction step has been proposed that involves S–H addition to an unsaturated substrate.[2] In previous work we have established that μ-SH ligands in cyclopentadienylmolybdenum dimers do undergo addition reactions with certain unsaturated molecules. For example, a neutral molybdenum(III) complex that contained a nucleophilic μ-SH ligand reacted with olefins activated by electron-withdrawing groups.[3] A few other examples of the insertion of activated olefins into an SH ligand in nucleophilic complexes have also been reported.[4,5] We expected the reactivity of the SH ligand in **1** to differ significantly from that of previously studied systems because this cationic molybdenum(IV) derivative should be both more acidic and more electrophilic in character than the previously reported SH complexes. In this paper, we describe the reactivity of the SH ligand in **1** with respect to addition to carbon–carbon double bonds. This system provides the first example of the addition of a coordinated SH ligand to a series of unactivated olefins. A unique feature of the olefin insertions into this metallothiol complex is the reversibility of the reactions.

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Results

Regiochemistry of Olefin Insertion Products. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ reacted with alkenes to form cationic products with μ-alkanethiolate ligands. The list of alkenes that have been used in this study and the resulting alkanethiolate products are given in Table I. Products of the reactions have been isolated and characterized by NMR and mass spectroscopy and, in most cases, by elemental analyses; these data are summarized in Table II. In the reactions of the hydrocarbon-containing terminal olefins, Markovnikov addition products were isolated in every case. Regioselectivity was greater than 95%. The insertion reactions with these olefins were also monitored by NMR spectroscopy, and the data confirmed that the kinetic products showed the same regiochemistry as the isolated complexes indicated in Table I. The reactions with the terminal disubstituted olefins were carried out at low temperature in order to isolate the Markovnikov addition products with tertiary carbons in

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