Reactions of Transition-Metal η^1-Propargyl and η^1-Allenyl Complexes with Sulfur Dioxide and Transition-Metal−Carbon Bond-Cleaving Reactions of the Cycloadducts Which Yield Cyclic Sulfenate Esters

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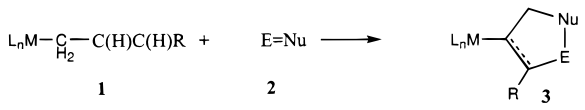
Received January 6, 1998

The preparation of several cyclopentadienyliron dicarbonyl η^1-2-alkynyl and η^1-allenyl complexes is reported. The 3 + 2 cycloaddition reactions of these complexes with sulfur dioxide yielded regioisomeric transition-metal-substituted 1,2-oxathiolen-1-yl oxides (sulfenate esters). One of the η^1-allenyl complex SO_2 cycloadducts has been characterized by X-ray crystallography. The transition metal can subsequently be cleaved from the sulfenate ester containing complexes under oxidative and nonoxidative reaction conditions to produce a variety of new sulfur-containing heterocycles.

Introduction

Cycloaddition reactions between transition-metal η^1-2-alkynyl (**1**) and η^1-allyl complexes (**1**) and unsaturated



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electrophilic reagents (**2**) have been studied in detail over the last 20 years with the pioneering work in this area having been done by the Rosenblum and Wojcicki groups.[1] These 3 + 2 cycloaddition reactions have been shown to yield transition-metal-substituted five-membered-ring heterocycles and carbacycles (**3**) and offer alternative approaches to these ring systems when the metal is subsequently cleaved from the ring.[1−3]

Several years ago, we reported a variant of this 3 + 2 cycloaddition reaction which yields transition-metal-substituted five-membered-ring thiosulfinate esters.[1a,2] More recently, we have explored an example of this reaction, first reported by Wojcicki in 1977,[3] involving the cycloaddition of cyclopentadienyliron dicarbonyl 2-alkynyl complexes with ketenes as a route to cyclopentenones.[4] Five- and six-membered-ring sulfur-containing heterocycles will presumably begin attracting increased attention as synthetic targets because of a recent report that 1,2-dithiolanes and 1,2-dithianes look particularly promising as inhibitors of HIV type 1 replication.[5] This replication inhibition is apparently a result of their ability to attack the conserved zinc fingers (presumably via the sulfur of the heterocycle) of retroviral nucleocapsid proteins causing zinc ejection from the protein.

Experimental Section

General Methods. All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR. All absorptions are expressed in parts per million relative to tetramethylsilane. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc., of Norcross, GA. High-resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, University of Nebraska−Lincoln. Low-resolution EI mass spectra were obtained on a Hewlett-Packard 5989 GC/MS system. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise noted. Cyclopentadienyliron dicarbonyl dimer was purchased from Strem Chemicals and used as received. Phenyllithium and methyllithium solutions, propargyl methyl ether, and copper iodide were purchased from Aldrich Chemical Co. and

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S0276-7333(98)00006-5 CCC: $15.00
Publication on Web 05/21/1998

used as received. Propargyl tosylate, 3-phenyl-2-propyn-1-ol, and 2-butyn-1-ol were purchased from Farchan Laboratories and used as received. 2-butyne-1,4-diol and 3-butyn-2-ol were purchased from Lancaster and used as received. $CpFe(CO)_2$-$CH_2C{\equiv}CR$ (**6a**, R = CH_3)[6] and (**6b**, R = Ph)[6] were synthesized according to literature procedures via addition of a THF solution of the $CpFe(CO)_2$ (Fp) anion (**5**) to a THF solution of the appropriate 2-alkynyl tosylate (**4a,b**). Literature procedures[6] typically use 2-alkynyl halides, but the tosylates are more convenient to work with since they are solids and give routinely higher yields of iron complex. Allenyl complexes, $CpFe(CO)_2CHC{=}C{=}CHR$ (**8a**,**b**, R = H, Me)[6b] and $CpFe(CO)_2CRC{=}C{=}CH_2$ (**10a**, R = CH_2OMe;[7] **10b**, R = CH_2OBn[2b]) were prepared likewise.

4-Methoxy-2-butyn-1-ol. In an adaptation of a literature procedure,[8] propargyl methyl ether (1.00 g, 14.3 mmol) was dissolved in diethyl ether (100 mL) and cooled to −78 °C. A 2.5 M *n*-butyllithium (6.28 mL, 15.7 mmol) solution was added dropwise. The solution was stirred for 1.5 h at −78 °C, and then paraformaldehyde (0.856 g, 28.5 mmol) was added. The reaction mixture was allowed to warm to 25 °C overnight. The mixture was poured into saturated NH_4Cl solution (100 mL) and then extracted with diethyl ether (3 × 50 mL). The solution was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The product, a light yellow oil (1.11 g, 11.1 mmol, 78%), was used without further purification and proved identical by spectroscopic comparison to previously reported material.[9]

General Procedure for Synthesis of Alkynyl Tosylates. In an adaptation of a literature procedure,[10] the propargyl alcohol was dissolved in diethyl ether (100 mL) and *p*-toluenesulfonyl chloride (0.95 equiv) was added. The solution was cooled to −15 °C, and powdered potassium hydroxide (5.0 equiv) was added 1 equiv at a time over 30−45 min. The reaction mixture was then allowed to stir at −15 °C for 90 min. Ice water (100 mL) was then added, and the mixture was extracted with diethyl ether (3 × 50 mL). The solution was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The product was then triturated with petroleum ether (15 mL) and cooled to −78 °C, and the solvent was decanted. The remaining product was dried under vacuum.

1-Tosyl-2-butyne (4a). This compound has been reported without spectroscopic characterization previously.[11] 2-Butyn-1-ol (3.59 g, 0.051 mol), *p*-toluenesulfonyl chloride (9.34 g, 0.049 mol), and potassium hydroxide (14.4 g, 0.257 mol) were reacted using the above procedure to yield the product (**4a**) (10.47 g, 0.047 mol, 91%) as a light yellow solid, mp 43−44 °C. ^{1}H NMR ($CDCl_3$): 7.74 (d, J = 8.2 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 2 H), 4.64 (q, J = 2.1 Hz, 2 H), 2.42 (s, 3 H), 1.70 (t, J = 2.1 Hz, 3 H). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.87; H, 5.40.

1-Tosyl-3-phenyl-2-propyne (4b). 3-Phenyl-2-propyn-1-ol (13.65 g, 0.103 mol), *p*-toluenesulfonyl chloride (18.5 g, 0.100 mol), and potassium hydroxide (28.90 g, 0.515 mol) were reacted using the above procedure to yield the product (**4b**) (24.86 g, 0.0870 mol, 90%) as a light yellow solid, mp 75−77 °C. ^{1}H NMR ($CDCl_3$): 7.84 (d, J = 8.4 Hz, 2 H), 7.32−7.23 (m, 7 H), 4.93 (s, 2 H), 2.37 (s, 3 H). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found: C, 67.24; H, 4.94.

3-Tosyl-1-butyne (7b). This compound has been reported without spectroscopic characterization previously.[11] 3-Butyn-2-ol (2.00 g, 0.029 mol), *p*-toluenesulfonyl chloride (5.16 g, 0.027 mol), and potassium hydroxide (8.00 g, 0.143 mol) were reacted using the above procedure to yield the product (**7b**) (4.54 g, 0.020 mol, 71%) as a white solid, mp 50−51 °C. ^{1}H NMR ($CDCl_3$): 7.79 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.2 Hz, 2 H), 5.14 (dq, J = 6.6, 2.0 Hz, 1 H), 2.42 (s, 3 H), 2.39 (d, J = 2.0 Hz, 1 H), 1.54 (d, J = 6.6 Hz, 3 H). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 59.00; H, 5.41.

1-Tosyl-4-methoxy-2-butyne (9a). 4-Methoxy-2-butyn-1-ol[9] (1.11 g, 0.011 mol), *p*-toluenesulfonyl chloride (2.01 g, 0.011 mol), and potassium hydroxide (3.11 g, 0.056 mol) were reacted using the above procedure to yield the product (**9a**) (2.28 g, 0.009 mol, 85%) as a light yellow oil. ^{1}H NMR ($CDCl_3$): 7.79 (d, J = 7.8 Hz, 2 H), 7.33 (d, J = 7.9 Hz, 2 H), 4.72 (t, J = 1.4 Hz, 2 H), 3.97 (t, J = 1.4 Hz, 2 H), 3.25 (s, 3 H), 2.43 (s, 3 H). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55. Found: C, 56.61; H, 5.55.

1-Tosyl-4-(benzyloxy)-2-butyne (9b). 4-(Benzyloxy)-2-butyn-1-ol[2b] (2.55 g, 0.015 mol), *p*-toluenesulfonyl chloride (2.62 g, 0.014 mol), and potassium hydroxide (4.06 g, 0.072 mol) were reacted using the above procedure to yield the product (**9b**) (3.93 g, 0.012 mol, 87%) as a light yellow oil. ^{1}H NMR ($CDCl_3$): 7.80 (d, J = 8.0 Hz, 2 H), 7.31 (m, 7 H), 4.75 (t, J = 1.4 Hz, 2H), 4.46 (s, 2 H), 4.05 (t, J = 1.4 Hz, 2 H), 2.39 (s, 3 H). Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.44; H, 5.49. Found: C, 65.58; H, 5.52.

General Procedure for Synthesis of Iron Alkynyl and Allenyl Complexes.[2,6,7] The iron anion (**5**) was generated by stirring a THF solution of $[CpFe(CO)_2]_2$ over a 1% sodium amalgam for 5 h. The anion was then added using a double-ended needle to a THF solution of the appropriate alkynyl tosylate cooled to 0 °C. The resulting mixture was allowed to warm to 25 °C over 1 h. The solvent was removed by rotary evaporation. The remaining residue was washed with pentane until the washes were colorless. The pentane was removed by rotary evaporation. The crude product was vacuum-dried and purified by column chromatography on alumina.

Cyclopentadienyl(2-butynyl)dicarbonyliron (6a). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (2.00 g, 5.7 mmol) and then added to a THF solution of 1-tosyl-2-butyne (**4a**) (2.32 g, 10.3 mmol) using the procedure outline above. The crude product was purified by column chromatography on deactivated alumina using 20:1 hexane/diethyl ether. The product (**6a**) (1.66 g, 7.2 mmol, 70%) was obtained as a brown solid, which was identical by spectroscopic comparison to previously reported material.[6b]

Cyclopentadienyl(3-phenyl-2-propynyl)dicarbonyliron (6b). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (10.00 g, 0.028 mol) and then added to a THF solution of 1-tosyl-3-phenyl-2-propyne (**4b**) (15.44 g, 0.054 mol) using the procedure outlined above. The crude product was purified by column chromatography on deactivated alumina using 10% diethyl ether in hexane. The product (**6b**) (10.44 g, 0.036 mol, 66%) was obtained as a brown solid, which was identical by spectroscopic comparison to previously reported material.[6b]

Cyclopentadienyl(propadienyl)dicarbonyliron (8a). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (2.00 g, 5.7 mmol) and then added to a THF solution of propargyl tosylate (**7a**) (2.26 g, 10.8 mmol) using the procedure outlined above. The crude product was purified by column chromatography on deactivated alumina using 50:50 hexane/diethyl ether. The product (**8a**) (1.40 g, 6.5 mmol, 60%) was obtained as a dark red oil, which was identical by spectroscopic comparison to previously reported material.[6b]

Cyclopentadienyl(1,2-butadien-1-yl)dicarbonyliron (8b). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (1.64 g, 4.6 mmol) and was added to a THF solution of **7b** (1.89 g, 8.4 mmol) using the procedure outlined above. The product (**8b**) was obtained as a dark red oil (1.46 g, 6.4 mmol, 75%),

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which was identical by spectroscopic comparison to previously reported material.[6b]

Cyclopentadienyl(4-methoxy-1,2-butadien-3-yl)dicarbonyliron (10a). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (1.66 g, 4.7 mmol) and was added to a THF solution of **9a** (2.28 g, 9.0 mmol) using the procedure outlined previously. The product was obtained as a dark red oil (**10a**) (1.85 g, 7.3 mmol, 79%), which was identical by spectroscopic comparison to previously reported material.[7]

Cyclopentadienyl(4-(benzyloxy)-1,2-butadien-3-yl)dicarbonyliron (10b). The iron anion (**5**) was generated from $[CpFe(CO)_2]_2$ (1.17 g, 3.3 mmol) and was added to a THF solution of **9b** (2.00 g, 6.1 mmol) using the procedure outline previously. The product was obtained as a dark red oil (**10b**) (1.69 g, 5.0 mmol, 83%), which was identical by spectroscopic comparison to previously reported material.[7]

General Procedure for the Synthesis of Metallosulfenate Esters. The appropriate iron allenyl or propargyl complex was dissolved in CH_2Cl_2 (10−15 mL), purged with nitrogen, and cooled to −78 °C. Sulfur dioxide (10 mL) was condensed at −78 °C into the iron complex solution. The reaction mixture was allowed to warm to 25 °C under nitrogen to allow evaporation of excess sulfur dioxide. The solvent was removed by rotary evaporation, and the remaining solid was vacuum-dried. The crude product was purified by recrystallization or column chromatography. Cyclopentadienyl(1-oxo-5-phenyl-1,2-oxathiol-4-en-4-yl))dicarbonyliron (**12b**) and cyclopentadienyl(1-oxo-5-methyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (**12a**) were purified by recrystallization from $CHCl_3$/hexane and were identical by spectroscopic comparison to previously reported material.[3]

Cyclopentadienyl(1-oxo-1,2-oxathiol-3-en-4-yl))dicarbonyliron (14a). The iron allenyl complex **8a** (2.09 g, 9.7 mmol) was treated with SO_2 to generate the crude product, which was purified by column chromatography on silica gel using 50:50 ethyl acetate/pentane to yield a brown solid (**14a**) (1.26 g, 4.5 mmol, 48%): mp 70−71 °C (dec). IR (NaCl): 2016, 1965, 1130, 1094, 934, 847, 833 cm^{-1}. ^1H NMR ($CDCl_3$): 5.78 (d, J = 2.4 Hz, 1 H), 4.89 (s, 5 H), 3.79 (dd, J = 16.3, 2.8 Hz, 1 H), 3.32 (d, J = 16.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$): 215.0, 214.05, 136.64, 99.03, 85.40, 75.65. DEPT ($CDCl_3$): 136.64 (CH), 99.03 (C), 85.40 (CH), 75.65 (CH_2). Anal. Calcd for $C_{10}H_8FeO_4S$: C, 42.89: H, 2.89. Found: C, 42.86; H, 2.89.

Cyclopentadienyl(1-oxo-5-methyl-1,2-oxathiol-3-en-4-yl))dicarbonyliron (14b). The iron allenyl complex **8b** (1.54 g, 6.5 mmol) was treated with SO_2 to generate the crude product, which was purified by column chromatography on silica gel using 50:50 ethyl acetate/pentane to yield a brown gum (**14b**) (0.56 g, 1.9 mmol, 29%) as a mixture of syn and anti diastereomers. IR (NaCl): 2017, 1966, 1115, 912, 847 cm^{-1}. ^1H NMR ($CDCl_3$): syn, 5.54 (d, J = 3.0 Hz, 1H), 4.91 (s, 5 H), 3.60 (dq, J = 7.4, 3.0 Hz, 1 H), 1.42 (d, J = 7.4 Hz, 3 H); anti, 5.45 (d, J = 0.8 Hz, 1 H), 4.89 (s, 5 H), 3.31 (dq, J = 7.5, 0.8 Hz, 1 H), 1.22 (d, J = 7.5 Hz, 3 H). FAB HRMS (*m*/*e*): calcd for (MH^+) ($C_{11}H_{11}FeO_4S$) 294.9728, found 294.9726.

Cyclopentadienyl(1-oxo-3-methylmethoxy-1,2-oxathiol-3-en-4-yl)dicarbonyliron (16a). The iron allenyl complex **10a** (0.75 g, 2.9 mmol) was reacted with SO_2 to generate the crude product, which was purified by column chromatography on silica gel using 100% ethyl acetate to yield a dark red gum (**16a**) (0.48 g, 1.5 mmol, 51%). IR (NaCl): 2016, 1958, 1123, 1086, 839 cm^{-1}. ^1H NMR ($CDCl_3$): 4.94 (s, 5 H), 4.20 (s, 2 H), 3.93 (d, J = 16.6 Hz, 1 H), 3.43 (d, J = 16.4 Hz, 1 H), 3.42 (s, 3 H). ^{13}C NMR ($CDCl_3$): 214.28, 213.97, 146.56, 100.87, 85.78, 68.65, 58.38, 43.45. FAB HRMS (*m*/*e*): calcd for MH^+ ($C_{12}H_{13}FeO_5S$): 324.9885, found 324.9841.

Cyclopentadienyl(1-oxo-3-methylbenzyloxy-1,2-oxathiol-3-en-4-yl)dicarbonyliron (16b). The iron allenyl complex **10b** (1.43 g, 4.3 mmol) was treated with SO_2 to generate the crude product, which was purified by column chromatography on silica gel using 3:1 ethyl acetate/pentane to yield a brown gum (**16b**) (0.81 g, 2.0 mmol, 48%). IR (NaCl): 2017, 1966, 1141, 1125, 1090, 1070, 867, 840 cm^{-1}. ^1H NMR ($CDCl_3$): 7.34 (m, 5 H), 4.85 (s, 5 H), 4.60 (s, 2 H), 4.28 (s, 2 H), 3.92 (d, J = 16.6 Hz, 1 H), 3.43 (d, J = 16.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): 214.21, 213.70, 146.58, 137.86, 128.38, 128.34, 127.75, 100.94, 85.67, 72.57, 66.19, 53.42. Anal. Calcd for $C_{18}H_{16}FeO_5S$: C, 54.02; H, 4.03. Found: C, 53.13; H, 4.08. FAB HRMS (*m*/*e*): calcd for ($M + Na^+$) ($C_{18}H_{16}FeO_5SNa$), 422.9966; found, 422.9955.

Crystallographic Structure Determination of Complex 14a. Single crystals of $CpFe(CO)_2(C_3H_3SO_2)$ (**14a**) are, at 293 K, monoclinic, space group $P2_1/c-C_{2h}^5$ (No. 14), with a = 10.3532(9) Å, b = 9.5692(7) Å, c = 22.708(2) Å, β = 97.931(6)°, V = 2228.2(3) Å^3, and Z = 8 [d_{calcd} = 1.670 g cm^{-3}; μ_a(Mo Kα) = 1.534 mm^{-1}]. A total of 4336 independent absorption-corrected reflections having 2θ(Mo Kα) < 50.8° (the equivalent of 0.8 limiting Cu Kα sphere) were collected on a computer-controlled Siemens P4 autodiffractometer using ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using direct methods" techniques with the Siemens SHELXTL-PC (version 5.0) software package. The resulting structural parameters have been refined to convergence [R_1 (unweighted, based on F) = 0.050 and wR_2 (weighted, based on F^2) = 0.085 for 2449 independent reflections having 2θ(Mo Kα)< 50.8° and $I > 2\sigma(I)$; R_1 (unweighted, based on F) = 0.110 and wR_2 (weighted, based on F^2) = 0.106 for all 4096 reflections; R_1 (unweighted, based on F) = 0.083 and wR_2 (weighted, based on F^2) = 0.095 for 3566 independent reflections having 2θ(Mo Kα) < 50.8° and $I > 0$] using counterweighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^3 or sp^2 hybridization of the carbon atoms and a C−H bond length of 0.98 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for the hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded. All calculations were performed using the SHELXTL-PC (version 5) interactive software package (G. Sheldrick, Siemens, Madison, WI).

Reaction of 12b with HCl To Produce *trans*-Cinnamyl Chloride (17). Complex **12b** (0.100 g, 0.28 mmol) was dissolved in CH_2Cl_2 (12 mL) and cooled to 0 °C. Concentrated HCl (0.047 mL, 0.56 mmol) was added, and the reaction mixture was allowed to warm to 25 °C overnight. The solution was washed with saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The organic extracts were combined and dried with anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the remaining material vacuum-dried. The crude product was purified by column chromatography on silica gel using 1:1 diethyl ether/hexane to elute *trans*-cinnamyl chloride (**17**) (0.030 g, 0.20 mmol, 70%) (identified by ^1H NMR spectroscopic comparison to an authentic sample (Acros)) followed by 1:1 CH_2Cl_2/pentane to elute cyclopentadienyldicarbonyliron chloride (**18**) (0.022 g, 0.10 mmol, 37%) (also identified by spectroscopic comparison to an authentic sample).[12]

Synthesis of Sulfenate Esters (19). General Procedure. The metallosulfenate ester (**12a**,**b**) (150 mg) was dissolved in CH_2Cl_2 (10 mL) and purged with carbon monoxide. Ceric ammonium nitrate (4−8 equiv) was dissolved in methanol or ethanol (15−20 mL) and also purged with carbon monoxide. Both solutions were cooled to −78 °C. The ceric ammonium nitrate solution was then added to the metallosulfenate ester solution by a double-ended needle using CO pressure. The resulting reaction mixture was allowed to warm

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to 25 °C and stir 30 min under a balloon of carbon monoxide. Water (50 mL) was then added and extracted with ethyl acetate (3 × 30 mL). The organic layers were combined and dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation.

4-(Carbomethoxy)-5-methyl-1,2-oxathiol-4-en-1-yl Oxide (19a). Complex **12a** (0.154 g, 0.53 mmol) was treated with ceric ammonium nitrate (1.45 g, 2.65 mmol) in methanol. The crude product was purified by chromatography on a silica gel column at 0 °C using 100% diethyl ether to yield the product as a light yellow oil (0.030 g, 0.17 mmol, 33%). IR (NaCl): 1728, 1437, 1271, 1130, 964, 746, 689 cm^{-1}. ^1H NMR ($CDCl_3$): 5.67 (dq, J = 15.2, 2.4 Hz, 1 H), 5.35 (dq, J = 15.2, 2.4 Hz, 1 H), 3.82 (s, 3 H), 2.41 (t, J = 2.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): 162.34, 155.77, 129.99, 82.18, 52.52, 10.85. Anal. Calcd for $C_6H_8O_4S$: C, 40.90; H, 4.58; Found: C, 41.71; H, 4.48.

4-(Carbomethoxy)-5-phenyl-1,2-oxathiol-4-en-1-yl Oxide (19b). Complex **12b** (0.150 g, 0.42 mmol) was treated with ceric ammonium nitrate (1.84 g, 3.36 mmol) in methanol. The crude product was purified by chromatography on a silica gel prep plate using 3:1 hexane/ethyl acetate to yield the product as a light yellow gum (0.020 g, 0.08 mmol, 20%). IR (NaCl): 1737, 1436, 1275, 1215, 1133, 967, 695 cm^{-1}. ^1H NMR ($CDCl_3$): 7.47 (m, 5 H), 5.90 (d, J = 15.7 Hz, 1 H), 5.58 (d, J = 15.7 Hz, 1 H), 3.73 (s, 3 H). ^{13}C NMR ($CDCl_3$): 161.9, 156.39, 130.33, 129.97, 129.03, 128.57, 127.16, 83.01, 52.56. EI HRMS (*m/e*): calcd for M^+ ($C_{11}H_{10}O_4S$) 238.0316, found 238.0300.

4-(Carboethoxy)-5-phenyl-1,2-oxathiol-4-en-1-yl Oxide (19c). Complex **12b** (0.150 g, 0.42 mmol) was treated with ceric ammonium nitrate (1.84 g, 3.36 mmol) in ethanol. The crude product was purified by chromatography on a silica gel prep plate (1 mm) using 1:1 diethyl ether/hexane to yield the product as a light yellow gum (0.010 g, 0.040 mmol, 9%). ^1H NMR ($CDCl_3$): 7.40−7.54 (m, 5 H), 5.90 (d, J = 15.8 Hz, 1 H), 5.58 (d, J = 15.7 Hz, 1 H), 4.18 (q, J = 7.1 Hz, 2 H), 1.15 (t, J = 7.1 Hz, 3 H). Anal. Calcd for $C_{12}H_{12}O_4S$: C, 57.13; H, 4.79. Found: C, 57.29; H, 4.93.

Reaction of 12a with Methyllithium to yield 20. 12a (0.100 g, 0.34 mmol) was dissloved in 10 mL of freshly distilled THF and was cooled to −78 °C. Methyllithium (1.2 mL, 1.4 M, 1.71 mmol) was added slowly to the flask. The reaction mixture was allowed to stir for 30 min at −78 °C and then saturated NaCl solution (20 mL) was added. The aqueous layer was extracted with diethyl ether (2 × 20 mL). The organic extracts were combined and dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the crude product was vacuum-dried, yielding a dark red gum (0.063 g, 0.20 mmol, 60%). IR ($CDCl_3$): 3155, 2021, 1968, 1436, 1384, 1096, 934, 868, 767. ^1H NMR ($CDCl_3$): 4.93 (s, 5 H), 4.71 (d, J = 10 Hz, 1 H), 4.42 (d, J = 10 Hz, 1 H), 2.49 (s, 3 H), 2.19 (s, 3 H). FAB HRMS (*m/e*): calcd for ($M+Na^+$) ($C_{12}H_{14}O_4FeSNa$), 332.9839, found 332.9862.

4-Methyl-5-phenyl-1,2-oxathiol-4-en-1-yl Oxide (21). Copper(I) iodide (0.160 g, 0.84 mmol) was added to THF (5 mL). The suspension was thoroughly purged with nitrogen and cooled to −45 °C. Methyllithium (1.4 M, 1.20 mL, 1.68 mmol) was added, and the reaction mixture was allowed to stir at −45 °C (30 min). In another flask, **12b** (0.200 g, 0.56 mmol) was dissolved in THF (10 mL). The solution was purged with nitrogen and cooled to −45 °C. The THF solution of **12b** was then transferred to the cuprate solution by a double-ended needle. The resulting mixture was allowed to stir for 30 min at −45 °C, and then saturated NH_4Cl (25 mL) was added. The aqueous layer was extracted with diethyl ether (3 × 15 mL). The organic extracts were combined and dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the remaining oil was vacuum-dried. The crude product was purified by chromatography (1:1 hexane/Et_2O) on a silica gel prep plate (1 mm) to yield a light yellow gum (0.040 g, 0.21 mmol, 37%). IR (NaCl): 1123, 970, 760, 695 cm^{-1}. ^1H NMR ($CDCl_3$): 7.43−7.39 (m, 5 H), 5.60 (d, J = 15.5 Hz, 1 H), 5.17 (d, J = 15.2 Hz, 1 H), 1.99 (s, 3 H). ^{13}C NMR ($CDCl_3$): 144.0, 140.32, 129.02, 128.96, 128.87, 128.61, 84.72, 11.06. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 62.08; H, 5.21.

1-Methoxy-3-(cyclopentadienyldicarbonylferrio)-3-buten-2-one (22a) from 16a and Ce(IV)/Methanol. Complex **16a** (0.100 g, 0.31 mmol) was treated with ceric ammonium nitrate (0.51 g, 0.93 mmol) in methanol/CH_2Cl_2 under a CO atmosphere as described above for **19**. The crude product was purified by column chromatography on silica gel using 1:1 ethyl acetate/pentane to yield the product as a red-brown oil (0.010 g, 0.036 mmol, 12%). IR (NaCl): 2016 (s), 1952 (s), 1685 (m), 1120 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 5.87 (s, 1 H), 5.59 (s, 1 H), 4.89 (s, 5 H), 4.23 (s, 2 H), 3.42 (s, 3 H). EI HRMS (*m/z*): calcd for (M^+ − CO) ($C_{11}H_{12}O_3Fe$), 248.0136; found (M^+ − CO) 248.0132, (M^+ − 2CO) 220.0183. FAB LRMS (*m/z*): calcd for (MH^+) ($C_{12}H_{13}O_4Fe$) 277.0, found 277.1.

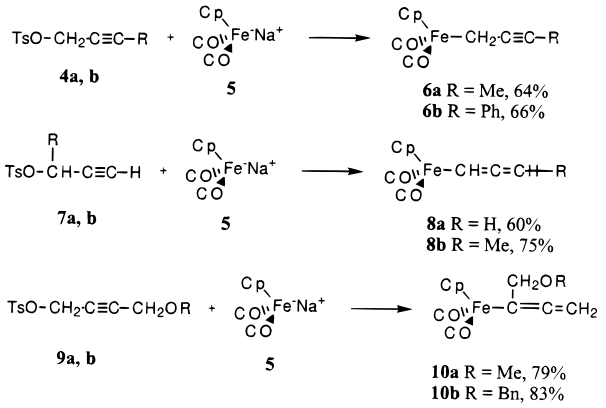
1-(Benzyloxy)-3-(cyclopentadienyldicarbonylferrio)-3-buten-2-one (22b) from 16b and Ce(IV)/Methanol. Complex **16b** (0.100 g, 0.25 mmol) was treated with ceric ammonium nitrate (0.41 g, 0.75 mmol) in methanol/CH_2Cl_2 under a CO atmosphere as described above for **19**. The crude product was purified by column chromatography on silica gel using 1:1 ethyl acetate/pentane to yield the product as a red oil (0.020 g, 0.057 mmol, 23%). IR (NaCl): 2017 (s), 1959 (s), 1713 (m), 1682 (m) 1568 (m), 1116 (m), 1027 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 7.29−7.35 (m, 5 H), 5.84 (s, 1 H), 5.56 (s, 1 H), 4.87 (s, 5 H), 4.61 (s, 2 H), 4.29 (s, 2 H). ^{13}C NMR ($CDCl_3$): 214.99, 208.26, 153.62, 137.65, 130.65, 128.39, 127.99, 127.78, 85.54, 73.07, 72.28. DEPT ($CDCl_3$): 130.65 (CH_2), 128.39 (CH), 127.99 (CH), 127.78 (CH), 85.54 (CH), 73.07 (CH_2), 72.28 (CH_2). EI HRMS (*m/z*): calcd for (M^+ − CO) ($C_{17}H_{16}O_3Fe$) 324.0449, found (M^+ − CO) 324.0440, (M^+ − 2CO) 296.0440. FAB LRMS (*m/z*): calcd for (MH^+) ($C_{18}H_{17}O_4Fe$) 353.0, found 353.1.

1-Methoxy-3-(cyclopentadienyldicarbonylferrio)-3-buten-2-one (22a) from 16a and Dimethylcuprate. Complex **16a** (0.106 g, 0.33 mmol) was reacted with dimethylcuprate generated from the reaction of copper(I) iodide (0.094 g 0.49 mmol) with methyllithium (1.4 M, 0.70 mL, 0.98 mmol) as described above for **21**. The crude product was purified by column chromatography on silica gel using 1:1 ethyl acetate/pentane to yield a red-brown oil (0.010 g, 0.036 mmol, 11%) identical by spectroscopic comparison to the material (**22a**) reported above.

1-(Benzyloxy)-3-(cyclopentadienyldicarbonylferrio)-3-buten-2-one (22b) from 16b and Dimethylcuprate. Complex **16b** (0.771 g, 1.93 mmol) was reacted with dimethylcuprate generated from the reaction of copper(I) iodide (0.550 g, 2.89 mmol) with methyllithium (1.4 M, 4.13 mL, 5.78 mmol) as described above for **21**. The crude product was purified by column chromatography on silica gel using 1:1 ethyl acetate/pentane to yield a red oil (0.184 g, 0.52 mmol, 27%) identical by spectroscopic comparison to the material (**22b**) reported above.

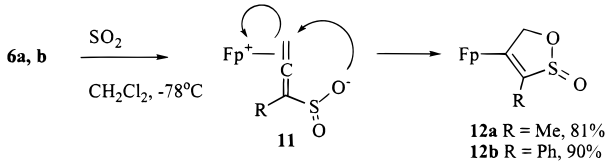
Results and Discussion

The propargyl and allenyl complexes used for cycloadditions were prepared by addition of the $CpFe(CO)_2$ anion (Fp anion) (**5**) to solutions of the appropriate propargyl tosylate.[2,6,7] The tosylates were prepared from the propargyl alcohols using standard conditions.[10] 4-Methoxy-2-butyne-1-ol used to make **9a** was prepared via condensation of the anion of propargyl methyl ether with paraformaldehyde.[8,9] We have reported the preparation of 4-benzyl-2-butyn-1-ol used to make **9b** previously.[2b] Propargyl tosylates of internal alkyl or aryl substituted alkynes (**4a**,**b**) react with the Fp anion in S_N2 reactions to produce 2-alkynyl complexes (**6a**,**b**).



Propargyl tosylates of terminal alkynes (**7a**,**b**) or internal alkynes containing oxygen substituents (**9a**,**b**) react with Fp anion in S_N2' reactions to produce allenes (**8a**,**b** and **10a**,**b**).

Reaction of iron propargyl complexes (**6a**,**b**) with SO_2 was first reported in 1969 by Roustan and Charrier.[13] They reported the products to be SO_2 insertion products, and in 1971 Wojcicki et al.[6a] correctly assigned the product structures as sultines resulting from a 3 + 2 cycloaddition reaction with SO_2. Demetalation to yield S,O-containing heterocycles has not been studied in detail previously. We first repeated Wojcicki's SO_2 experiments with the exception of performing them in CH_2Cl_2 at −78 °C and isolated the 3 + 2 cycloaddition products (**12a**,**b**) in excellent yields as expected.



Iron allenyl complex cycloaddition chemistry has not been studied to the extent propargyl chemistry has. In 1971, Wojcicki et al. reported isolating no SO_2-containing products from a variety of reactions of **8a** with SO_2 at 25 °C or above.[6a] In the mid 1980s, Rosenblum and Watkins reported use of **8a** in 3 + 2 cyclization approaches to hydroazulenes.[14] We have found that all 4 allenyl complexes reported above (**8a**,**b** and **10a**,**b**) will react with SO_2 in CH_2Cl_2 at −78 °C to produce 3 + 2 cycloaddition products (**14a**,**b** and **16a**,**b**), which are regioisomers of the complexes formed by the propargyl cyclizations. These cyclization reactions presumably proceed via intermediates (**13** and **15**) analogous to the one (**11**) reported for the propargyl cyclizations.[6a]

The structure of the cyclization product (**14a**) from the simplest allene was confirmed by X-ray crystallography. A single-crystal X-ray structural analysis of **14a** revealed that it was composed of two crystallographically independent molecules of $CpFe(CO)_2(C_3H_3SO_2)$ as shown in Figure 1a,b. Data collection and refinement parameters are summarized in Table 1 with selected bond lengths and angles, averaged for the two independent molecules, given in Table 2.

(13) Roustan, J.-L.; Charrier, C. *C. R. Acad. Sci. Ser. C,* **1969**, *268*, 2113.

(14) Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316 and references therein.

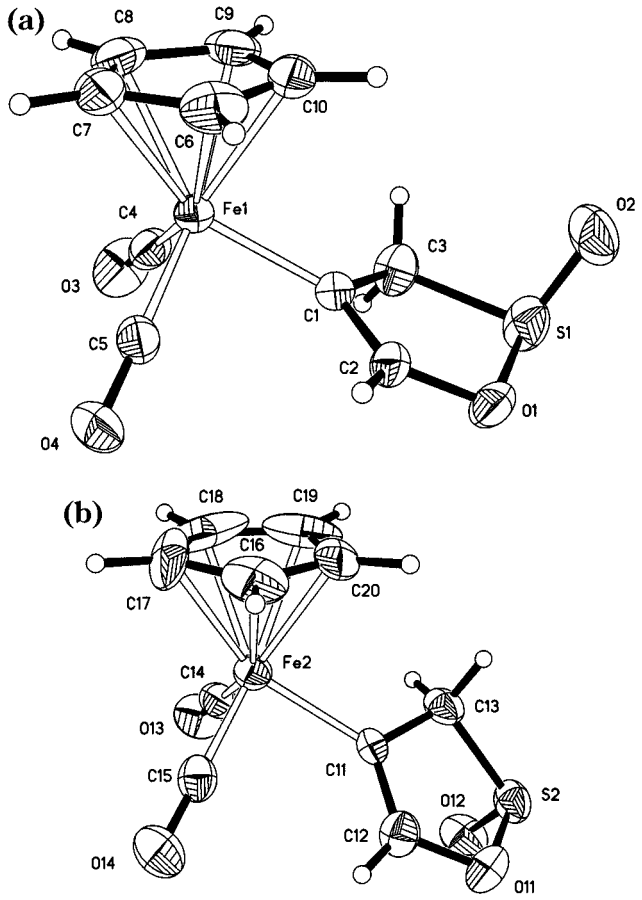


Figure 1. Molecular structures of two crystallographically independent molecules (a, b) present in **14a**.

Table 1. Crystal Data and Structure Refinement for $CpFe(CO)_2(C_3H_3SO_2)$ (14a)

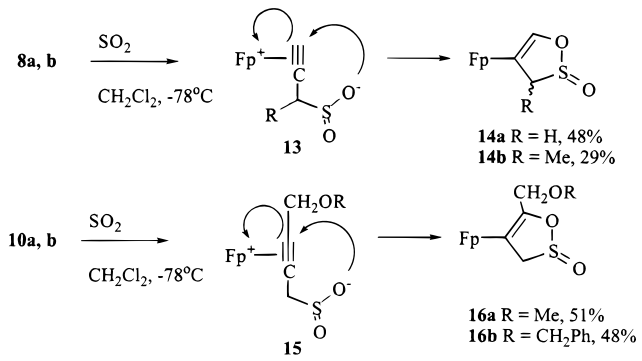
empirical formula	$C_{10}H_8FeO_4S$
fw	280.08
temp	293(2) K
wavelength	0.710 73 Å
cryst system	monoclinic
space group	$P2_1/c$-C_{2h}^5 (No. 14)
unit cell dimens	a = 10.3532(9) Å
	b = 9.5692(7) Å, b = 97.931(6)°
	c = 22.708(2) Å
V, Z	2228.2(3) Å^3, 8
D(calcd)	1.670 g·cm^{-3}
abs coeff	1.534 mm^{-1}
range of rel transm factors	0.843−1.000
F(000)	1136
cryst size	0.35 × 0.40 × 0.40 mm
2θ range for data collcn	4.5−50.8°
limiting indices	$0 \le 12$, $0 \le k \le 11$, $-27 \le l \le 27$
reflcns collcd	4336
indepdt reflcns	4096 [R(int) = 0.0216]
refinement method	full-matrix least-squares on F^2
data/restraints/params	3566/0/290
goodness-of-fit on F_2	1.007
final R indices	
2449 $I > 2\sigma(I)$ data	R_1 = 0.0499, wR_2 = 0.0846
R indices (all 4096 data)	R_1 = 0.1096, wR_2 = 0.1057
R indices (3566 data, $I > 0$)	R_1 = 0.0828, wR_2 = 0.0952
extinction coeff	0.0012(2)
largest diff peak and hole	0.285 and −0.315 e/Å^3

The average Fe−C_{vinyl} bond length is 1.978(5) Å, in agreement with values previously observed in other $CpFe(CO)_2$ complexes containing a sulfur γ to Fe or a five-membered ring system [1.991(7) Å in $CpFe(CO)_2(CMeCHSO_2(C_6H_5))$,[15] 2.008(7) Å in $CpFe(CO)_2(C_3H_2(C_6H_5)S_2O)$,[2b] and 1.997(8) Å in $CpFe(CO)_2(C_4H_5SO_2)$[16]].

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Crystalline $CpFe(CO)_2(C_3H_3SO_2)$ (14a)[a]

param	value[b]	param	value[b]
	Bond Lengths		
Fe_1-C_4	1.749(6,4,8,4)	Fe_1-C_{6-10}	2.081(6,15,41,10)
Fe_1-C_1	1.978(5,7,7,2)	Fe_1-C_p	1.724(-,2,2,2)[c]
S_1-O_1	1.635(4,3,3,2)	O_3-C_4	1.143(5,2,4,4)
S_1-O_2	1.466(4,2,2,2)		
S_1-C_3	1.806(5,2,2,2)	C_6-C_7	1.371(10,24,46,10)
O_1-C_2	1.428(6,7,7,2)		
C_1-C_2	1.301(6,1,1,2)	C_1-C_3	1.512(6,3,3,2)
	Bond Angles		
$C_pFe_1C_1$	121.3(-,14,14,2)[c]	$O_1S_1O_2$	108.1(2,5,5,2)
$C_pFe_1C_4$	125.5(-,3,5,4)[c]	$O_2S_1C_3$	105.9(3,7,7,2)
$C_4Fe_1C_5$	94.5(2,5,5,2)	$O_1S_1C_3$	91.9(2,2,2,2)
$C_4Fe_1C_1$	90.0(2,16,27,4)	$C_2O_1S_1$	109.9(3,1,1,2)
$Fe_1C_4O_3$	178.8(5,5,10,4)	$C_2C_1C_3$	108.9(5,2,2,2)
$Fe_1C_1C_2$	128.8(4,9,9,2)	$C_7C_6C_{10}$	108.0(7,9,17,10)
$Fe_1C_1C_3$	122.3(3,7,7,2)	$C_1C_3S_1$	106.0(3,2,2,2)
		$C_1C_2O_1$	118.4(5,1,1,2)

[a] Bond lengths and angles have been averaged for the two crystallographically-independent molecules. Entries in the table are labeled in agreement with Figure 1a, molecule 1. [b] The first number in parentheses followed an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviation from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average light. [c] The symbol Cp is used to represent the center of gravity for the cyclopentadienyl ring designated by carbon atoms C_6-C_{10} in Figure 1a and carbon atoms $C_{16}-C_{20}$ in Figure 1b. These values are therefore listed without estimated standard deviations.

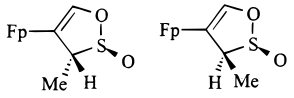


The average Fe−C(carbonyl) distance is 1.749(6) Å and the average $Fe-C_p$ centroid distance is 1.724 Å in agreement with those previously observed.[2b,15,16] The average C═C bond of the cyclized ring is 1.301(6) Å, shorter than the values of 1.336(9) and 1.330(10) Å in $CpFe(CO)_2(CMeCHSO_2(C_6H_5))$[15] and $CpFe(CO)_2(C_3H_3(C_6H_5)S_2O)$,[2b] respectively, and similar to the value of 1.312(12) Å in $CpFe(CO)_2(C_4H_5SO_2)$.[16] The average C−C bond length for the two isomers is 1.512(6) Å, within the range observed for similar five-membered ring complexes (1.485(12)−1.503(9) Å).[2b,16] Both molecules also exhibit large exocyclic angles at the vinyl carbon (127.9(4) and 123.0(3)° for molecule 1 and 129.6(4) and 121.6(3)° for molecule 2) with the larger angle involving the methine carbon and the smaller angle involving the methylene carbon of the ring.

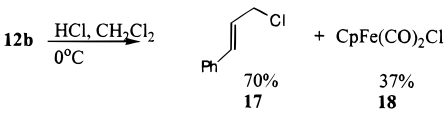
Complex **14b** was produced as a 2.3:1 mixture of diastereomers. The major diastereomer (**14b**-anti) had the anti orientation of the oxygen and methyl groups as proven by shift reagent studies (Table 3).[17] The methine proton in the major diastereomer shifted downfield by 1.29 ppm when treated with $Eu(FOD)_3$, whereas the methyl only shifted downfield by 0.33 ppm. The syn diastereomer showed the exact opposite trend in shifts (methyl moved downfield more than the methine) as expected. Allylic coupling from the alkene H to the methine was much larger in the syn (**14b**) (allylic J = 3.0 Hz) compared to the anti (**14b**) (allylic J = 0.8 Hz) diastereomer. In our earlier thiosulfinate ester syntheses,[2b] we had seen some effect of Lewis acid additives on 3 + 2 cycloaddition stereochemistry so we also tried the cycloaddition to produce **14b** in the presence of $MgBr_2$ (−78 °C to −45 °C). The cyclization still occurred, but the stereochemistry was little affected (1.9:1 *anti*/*syn*).

Table 3. ^{1}H NMR Chemical Shifts of Methyl and Methine Protons in 14b-anti and -syn

	δ ($CDCl_3$)	δ w/Eu ($FOD)_3$	$\Delta\delta$
14b-anti methyl (d, J = 7.5 Hz)	1.22	1.55	0.33
14b-anti methine (dq, J = 7.5, 0.8 Hz)	3.31	4.60	1.29
14b-syn methyl (d, J = 7.4 Hz)	1.42	2.27	0.85
14b-syn methine (dq, J = 7.4, 3.0 Hz)	3.60	3.98	0.38

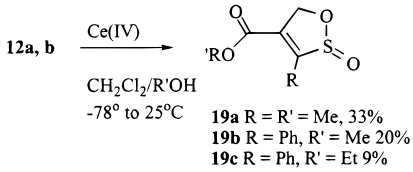


We then proceeded to investigate methods for the cleavage of the iron−carbon bonds in complexes **12**, **14**, and **16**. The methods most often used by organometallic chemists to remove organic ligands from CpFe(CO)(L)(R) complexes are protonolysis, halogenolysis, and oxidative carboxylation[18] so these methods were investigated here first. Protonolysis of **12b** did produce iron−carbon bond cleavage but also resulted in SO_2 extrusion to produce *trans*-cinnamyl chloride (**17**, 70%) as well as recovered iron in the form of $CpFe(CO)_2Cl$ (**18**, 37%).[12] Related ring-opening reactions of sultines have been reported previously.[19]

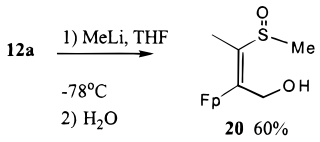


Oxidative carboxylation of **12a,b** did produce the desired esters (**19**), but the isolated yields were not as high as we had hoped for. The known susceptibility of cyclic sulfinate esters to alcohol-induced ring openings[19,20] is most likely responsible for the lower than expected yields of esters (**19**).

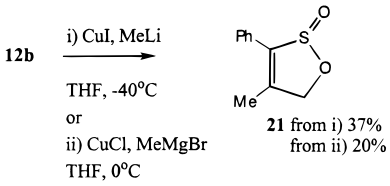
(15) Patel, P. P.; Welker, M. E.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4519.
(16) Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 1971.
(17) (a) Kato, A.; Numata, M. *Tetrahedron Lett.* **1972**, 203. (b) Legler, L. E.; Jindal, S. L.; Murray, R. W. *Tetrahedron Lett.* **1972**, 3907. (c) Yanagawa, H.; Kato, T.; Kitahara, Y. *Tetrahedron Lett.* **1973**, 1073.
(18) For some recent relevant examples and a review (e) see: (a) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. (b) Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M. A. *Organometallics* **1988**, *7*, 2553. (c) Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181. (d) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (e) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.
(19) Liskamp, R. M. J.; Zeegers, H. J. M.; Ottenheijm, H. C. J. *J. Org. Chem.* **1981**, *46*, 5408.
(20) Jung, F.; Sharma, N. K.; Durst, T. *J. Am. Chem. Soc.* **1973**, *95*, 3420.



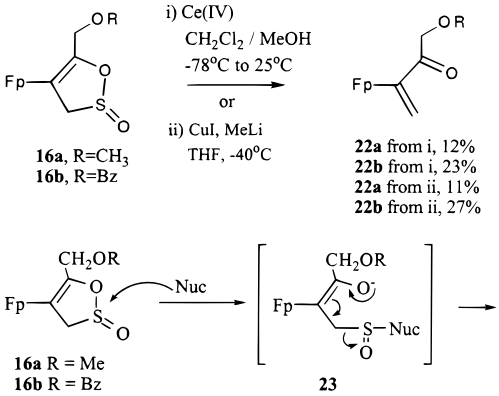
We then investigated nonoxidative demetalations by analogy to cyclopentenone demetalations we had reported in 1995.[4] We examined reactions of **12a**,**b** with nucleophiles such as alkyllithiums and cuprates. When **12a** was treated with MeLi, ring opening to produce sulfone (**20**) occurred. This is an expected result on the basis of analogy to reported reactions of alkyllithiums and Grignard reagents with cyclic sulfenate esters.[21]



However, when **12b** was treated with a cuprate generated from MeLi or MeMgBr, we were able to isolate the demetalated cyclic sulfenate ester (**21**). Isolated yields again were probably diminished to some extent by competitive ring-opening reactions of **12b** and **21** that these nucleophilic conditions might induce.[21]



Last, we investigated demetalation of the cycloadducts (**16a**,**b**) prepared from the allenyl complex cyclizations. To our surprise, these complexes reacted with Ce(IV) in methanol and dimethylcopper lithium to produce identical, new α,β-unsaturated acyl complexes (**22a**,**b**). We propose that these complexes (**22a**,**b**) result from initial nucleophilic ring opening of the sulfenate esters (**16a**,**b**).[19−21] Loss of a sulfur-containing species from the β-position of **23** would account for the observed products (**22a**,**b**).



In summary, Fp propargyl and allenyl complexes react with sulfur dioxide in 3 + 2 cycloaddition reactions. These cycloaddition reactions produce regioisomeric transition-metal-substituted sulfenate esters in good yields. The iron-substituted sulfenate esters can be demetalated under oxidative and nonoxidative reaction conditions to produce unusual, sulfur-containing heterocycles. The biological activities of these heterocycles will be reported in due course.

Acknowledgment. We thank the NIH NIGMS and the Camille and Henry Dreyfus Foundation (Henry Dreyfus Teacher-Scholar Award to M.E.W, 1994−99) for their support. Low-resolution mass spectra were obtained on an instrument purchased with the partial support of NSF (Grant CHE-9007366). The Nebraska Center for Mass Spectrometry (NSF Grant DIR9017262) performed high-resolution mass spectral analyses.

Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and anisotropic displacement parameters for **14a** (16 pages). Ordering information is given on any current masthead page.

OM980006L

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