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Supplementary Material Available: Textual presentation of the X-ray analysis, tables of structure determination data, atomic coordinates, thermal parameters, bond distances and angles, dihedral, vector-plane, and torsion angles, least-squares planes, and nonbonded distances, and ORTEP diagrams for 4 (22 pages); a listing of structure factors for 4 (33 pages). Ordering information is given on any current masthead page.

Cycloaddition Reactions of Transition-Metal 2-Alkynyl Complexes with a Disulfur Monoxide Source. Transition-Metal-Mediated Syntheses of Five-Membered-Ring Thiosulfinate Esters

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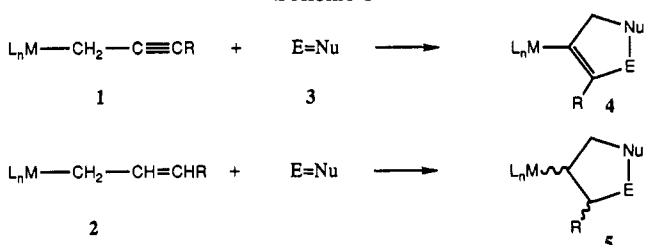
Reactions of cyclopentadienyl- and (pentamethylcyclopentadienyl)iron dicarbonyl 2-alkynyl complexes as well as cyclopentadienylmolybdenum tricarbonyl 2-alkynyl complexes with 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (37) have been shown to yield transition-metal-substituted five-membered-ring thiosulfinate esters in moderate to excellent yield. The transition metal can subsequently be cleaved from these cyclic metallothiosulfinate esters with ceric ammonium nitrate to yield carboethoxy-substituted five-membered-ring thiosulfinate esters. Reactions of chiral, racemic 2-alkynyl complexes with 37 also yield five-membered-ring thiosulfinate esters as the kinetic products of cyclization. The diastereoselectivity of these cycloadditions can be altered by the addition of $MgBr_2$.

Introduction

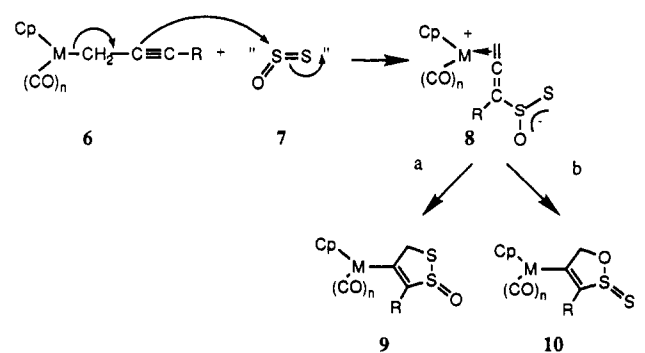
Cycloaddition reactions between transition-metal 2-alkynyl (1) and η^1 -allyl complexes (2) and unsaturated electrophilic reagents (3) have been studied in detail over the last 20 years by a number of research groups.¹ These 3+2 cycloaddition reactions have been shown to yield transition-metal-substituted five-membered-ring heterocycles and carbocycles (4, 5) (Scheme I), and they offer

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Scheme I

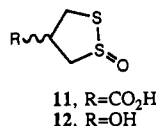


Scheme II

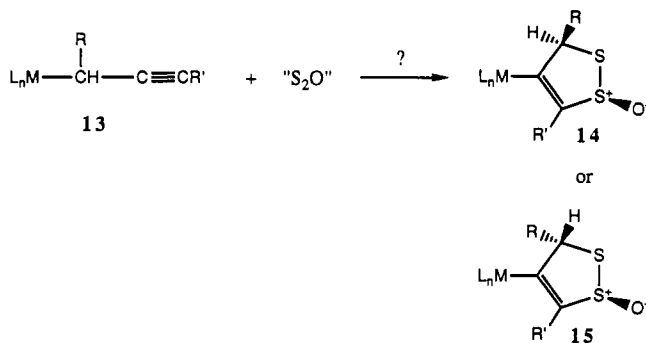


organic chemists alternative approaches to these ring systems when the metal is subsequently cleaved from the ring.^{1a,c-h,2}

We have been studying a variant of this reaction (Scheme II), which can yield transition-metal-substituted five-membered-ring thiosulfinate esters (9).² If the metal could be removed from these complexes 9 in high yield, then one would have access to analogues of naturally occurring thiosulfinate esters 11 (R = CO₂H) (asparagusic acid S-oxides, plant growth regulators)³ and 12 (R = OH) (Brugeriols, isolated from mangroves).⁴ Other cyclic thiosulfinate esters have been shown to be tumor growth inhibitors.⁵



Last, since certain thiosulfinate esters are known to be optically stable,⁶ we were interested in studying the diastereoselectivity of cyclization reactions between chiral, racemic 2-alkynyl complexes (13) and "S₂O" as a route to diastereomerically pure transition-metal-substituted five-membered-ring thiosulfinate esters (14, 15).



Experimental Section

General Comments. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 1330 or a Perkin Elmer 1620 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian VXR 200 instrument. All absorptions are expressed in parts per million relative to TMS. Nuclear Overhauser effect difference spectra were recorded by using the method of Hall and Sanders.⁷ Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA. Mass spectral analyses were performed by the Mid-West Center for Mass Spectrometry at the University of Nebraska—Lincoln. Melting points were determined on a Mel-Temp apparatus and reported uncorrected.

Materials. 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, (pentamethylcyclopentadienyl)iron dicarbonyl dimer, and cyclopentadienylmolybdenum tricarbonyl dimer were purchased from Strem

Chemicals and used as received. 2-Butyn-1-ol, 3-phenyl-2-propyn-1-ol, 2-butyne-1,4-diol, 3-hexyn-2-ol, and 4-heptyn-3-ol were purchased from Farchan Laboratories and used as received. 4-methyl-4-penten-2-yn-1-ol was purchased from K & K Laboratories and used as received. 4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (37) was synthesized according to a literature procedure.^{8b}

The 2-alkynyl chlorides and bromides used in the syntheses of the 2-alkynyl transition-metal complexes were synthesized from the corresponding alcohol and thionyl chloride or phosphorus tribromide according to reported procedures and are listed as follows with references: 3-chloro-1-phenylpropyne (20),⁹ 1-chloro-2-butyne (21),¹⁰ 1-bromo-2-butyne (24),¹¹ 3-bromo-1-phenylpropyne (25),¹² and 5-bromo-2-methyl-1-penten-3-yne (22).¹³

4-(Benzyloxy)-2-butyne-1-ol (34).¹⁴ The following is an adaptation of a procedure used for monobenylation of 1,4-cyclohexanediol.¹⁵ 2-Butyne-1,4-diol (10.00 g, 0.12 mol) was dissolved in tetrahydrofuran (150 mL). Sodium hydride (60% dispersion in mineral oil) (4.88 g, 0.12 mol) was washed with petroleum ether and then added to this solution. After the NaH addition was complete, the solution was heated at reflux (2 h). While reflux was maintained, benzyl bromide (14.3 mL, 0.12 mol) was added to this solution. The solution was maintained at reflux for 36 h. The solution was cooled to 0 °C, and 1.2 N HCl (50 mL) was cautiously added. The solution was extracted with diethyl ether (2 × 50 mL). The combined ether layers were washed with water (50 mL) and dried (MgSO₄), and the solvent was removed by rotary evaporation to yield a light brown oil. The crude product was purified by column chromatography on silica. The monobenzylated product 34 was eluted with 10% hexane in diethyl ether and is a light yellow liquid: 8.60 g, 48.86 mmol (41%); IR (CDCl₃) 3609, 3417, 3033, 2864, 2248, 1496, 1455, 1385, 1353, 1124, 1070, 1010 cm⁻¹; ¹H NMR (CDCl₃) δ 7.39–7.29 (m, 5 H), 4.59 (s, 2 H), 4.29 (t, J = 1.5 Hz, 2 H), 4.20 (t, J = 1.5 Hz, 2 H), 2.8 (br s, 1 H). Anal. Calcd for C₁₁H₁₂O₂: C, 75.00; H, 6.82. Found: C, 75.06; H, 6.90.

1-(Benzyloxy)-4-bromo-2-butyne (23). 4-(Benzyloxy)-2-butyne-1-ol (34) (5.00 g, 28.41 mmol) was dissolved in anhydrous diethyl ether (100 mL), and pyridine (0.2 mL) was added. Phosphorus tribromide (2.7 mL, 28.4 mmol) was dissolved in anhydrous diethyl ether (15 mL) and added dropwise to the alcohol. After this addition the solution was refluxed (2 h). The solution was then cooled to 0 °C and washed with water (25 mL) followed by saturated sodium bicarbonate solution (25 mL). The solution was dried (MgSO₄) and the solvent removed by rotary evaporation and high vacuum. The product 23 (light yellow liquid) was used without further purification: 6.14 g, 25.69 mmol, (90%); IR (CDCl₃) 2861, 2360, 2252, 1496, 1454, 1211, 1073 cm⁻¹; ¹H NMR (CDCl₃) δ 7.36–7.33 (m, 5 H), 4.58 (s, 2 H), 4.21 (t, J = 1.8 Hz, 2 H), 3.95 (t, J = 1.8 Hz, 2 H). Anal. Calcd for C₁₁H₁₁BrO: C, 55.23; H, 4.60. Found: C, 55.06; H, 4.69.

General Procedure for Synthesis of 2-Alkynyl Tosylates. Propargyl alcohol in dry diethyl ether (5–10 mL) at 0 °C was treated with 1.4 M methyllithium in ether (1.1 equiv). MeLi was added dropwise via syringe. To this solution *p*-toluenesulfonyl chloride (1.01 equiv) was added at 0 °C. The reaction mixture was stirred for 10–20 min at 0 °C and then warmed to room temperature over 1.5 h. The mixture was poured into cold water (20 mL) and extracted with ether (2 × 30 mL). The solution was dried (MgSO₄), and the solvent was removed under reduced pressure and high vacuum. The yellow oils thus obtained were triturated with petroleum ether (30 mL) at 25 °C. The solution was then cooled to –78 °C and the solvent was decanted, leaving

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a light yellow gum, which was dried under high vacuum.

2-Tosyl-3-hexyne (18). 3-Hexyn-2-ol (5.51 g, 56.26 mmol) was deprotonated with methyllithium (42.2 mL, 59.1 mmol, 1.4 M in diethyl ether), and then *p*-toluenesulfonyl chloride (10.73 g, 56.26 mmol) was added. After workup and trituration, the product 18 was obtained as a light yellow liquid: 8.91 g, 35.30 mmol (63%); IR (C_6D_6) 2983, 2940, 2880, 2262, 1599, 1496, 1360, 1177, 1098, 1048, 995 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.80 (d, $J = 7.3$ Hz, 2 H), 7.41 (d, $J = 7.3$ Hz, 2 H), 5.18 (tq, $J = 7.3, 2.9$ Hz, 1 H), 2.42 (s, 3 H), 1.99 (dq, $J = 7.5, 2.9$ Hz, 2 H), 1.52 (d, $J = 7.3$ Hz, 3 H), 0.93 (t, $J = 7.5$ Hz, 3 H). Anal. Calcd for $C_{15}H_{18}SO_3$: C, 61.88; H, 6.39; S, 12.71. Found: C, 60.86; H, 6.24; S, 12.50. The propargyl tosylates are known to be extremely reactive compounds,¹⁶ and repeated attempts to obtain a more satisfactory carbon analysis failed.

3-Tosyl-4-heptyne (19). 4-Heptyn-3-ol (6.14 g, 54.74 mmol) was deprotonated with methyllithium (41.1 mL, 57.6 mmol, 1.4 M in diethyl ether), and then *p*-toluenesulfonyl chloride (10.44 g, 54.76 mmol) was added. After workup and trituration, the product 19 was obtained as a light yellow liquid: 8.56 g, 32.13 mmol (59%); IR ($CDCl_3$) 3609, 2979, 2940, 2880, 2254, 1917, 1599, 1496, 1307, 1189, 1176, 1120, 1098, 1078 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.80 (d, $J = 7.8$ Hz, 2 H), 7.32 (d, $J = 7.8$ Hz, 2 H), 5.00 (tt, $J = 7.4, 1.9$ Hz, 1 H), 2.43 (s, 3 H), 1.99 (dq, $J = 7.4, 1.9$ Hz, 2 H), 1.79 (p, $J = 7.4$ Hz, 2 H), 0.97 (t, $J = 7.4$ Hz, 3 H), 0.92 (t, $J = 7.4$ Hz, 3 H). Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.12; H, 6.81; S, 12.04. Found: C, 63.00; H, 6.82; S, 11.95.

Synthesis of Transition-Metal 2-Alkynyl Complexes. $CpFe(CO)_2CH_2C\equiv CR$ ($R = CH_3$ (29),¹⁷ Ph (28))¹⁸ and $CpMo(CO)_2CH_2C\equiv CR$ ($R = CH_3$ (40),¹⁷ Ph (41))¹⁹ were synthesized according to literature procedures via addition of a THF solution of the appropriate metal anion to a THF solution of the 2-alkynyl chloride or bromide. The other 2-alkynyl complexes were synthesized similarly as outlined below.

(Pentamethylcyclopentadienyl)(2-butynyl)dicarbonyliron (32). The iron anion (generated via stirring a THF solution (15 mL) of $[Me_5C_5Fe(CO)_2]_2$ (2.00 g, 4.04 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of 1-bromo-2-butyne (24) (1.10 g, 8.08 mmol) in THF. The crude product was purified by sublimation (72 °C, 1 mmHg) to give 32 as an orange-red solid: 1.02 g, 3.39 mmol (42%), mp (acetone/petroleum ether) 92–94 °C; IR ($CDCl_3$) 2901, 2862, 1979, 1925, 1418, 1362, 1070, 1038 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.85 (s, br, 2 H), 1.78 (s, 3 H), 1.74 (s, 15 H). HRMS (m/e): calcd for $C_{15}H_{20}FeO$ ($M^+ - CO$), 272.0863; found, 272.0834.

(Pentamethylcyclopentadienyl)(2-(1-hydroxy)butenyl)dicarbonyliron (35). The iron anion (generated via stirring a THF solution (15 mL) of $[Me_5C_5Fe(CO)_2]_2$ (2.00 g, 4.04 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of 1-bromo-2-butyne (24) (1.10 g, 8.08 mmol) in THF (15 mL). The solution was allowed to stir at 0 °C for 2 h. The solvent was removed by rotary evaporation. Purification of the crude product was attempted by column chromatography on alumina. Elution with 5% diethyl ether in petroleum ether yielded recovered iron dimer (0.600 g, 30%), and the iron alkenyl complex 35 was eluted with 5% ethanol in diethyl ether. The solvent was removed by rotary evaporation to give a dark yellow solid: 0.62 g, 1.94 mmol (24%); mp (acetone/petroleum ether) 108–112 °C; IR ($CDCl_3$) 3600, 3400, 2920, 2860, 1990, 1940, 1640, 1450, 1335, 1180 cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.35 (tq, $J = 9.3, 2.7$ Hz, 1 H), 4.04 (dd, $J = 5.7, 2.7$ Hz, 2 H), 1.79 (d, $J = 9.3$ Hz, 3 H), 1.76 (s, 15 H), 1.54 (t, $J = 5.7$ Hz, 1 H) (exchanges with D_2O). Anal. Calcd for $C_{18}H_{22}FeO_3$: C, 60.41; H, 6.92. Found: C, 60.36; H, 6.99.

(Pentamethylcyclopentadienyl)(3-phenyl-2-propynyl)dicarbonyliron (33). The iron anion (generated via stirring a THF solution (15 mL) of $[Me_5C_5Fe(CO)_2]_2$ (2.00 g, 4.04 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of 3-chloro-1-phenylpropyne (20) (1.60 g, 8.08 mmol) in THF (15 mL). The crude product was purified by column chromatography on

alumina and eluted with petroleum ether/diethyl ether (10:1) to give 33 as a yellow-brown solid: 0.79 g, 2.18 mmol (27%); mp (acetone/petroleum ether) 115 °C dec; IR ($CDCl_3$) 3065, 2962, 2885, 1995, 1940, 1598, 1435, 1319, 1301, 1240, 1132, 1079, 1040 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.65–7.20 (m, 5 H), 1.78 (s, 15 H), 1.38 (s, 2 H). Anal. Calcd for $C_{21}H_{22}FeO_2$: C, 69.65; H, 6.08. Found: C, 69.77; H, 6.17.

Cyclopentadienyl(4-methyl-4-penten-2-ynyl)dicarbonyliron (30). The iron anion (generated via stirring a THF solution (15 mL) of $[CpFe(CO)_2]_2$ (2.00 g, 5.65 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of 5-bromo-2-methyl-1-penten-3-yne (22) (1.80 g, 11.33 mmol) in THF (15 mL). The crude product was purified by column chromatography on alumina and eluted with petroleum ether/diethyl ether (20:1) to yield 30 as a yellow-brown solid: 0.61 g, 2.37 mmol (21%); mp (acetone/petroleum ether) 147–149 °C dec; IR ($CDCl_3$) 2921, 2254, 2014, 1958, 1608 cm^{-1} ; 1H NMR ($CDCl_3$) δ 5.08 (br s, 1 H), 5.02 (br s, 1 H), 4.80 (s, 5 H), 1.85 (s, 3 H), 1.73 (s, 2 H). Anal. Calcd for $C_{13}H_{12}FeO_2$: C, 60.94; H, 4.69. Found: C, 60.77; H, 4.76.

Cyclopentadienyl(3-(4-benzyloxy)-1,2-butadienyl)dicarbonyliron (31). The iron anion (generated via stirring a THF solution (15 mL) of $[CpFe(CO)_2]_2$ (2.00 g, 5.65 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of 1-(benzyloxy)-4-bromo-2-butyne (23) (2.70 g, 11.30 mmol) in THF (15 mL). The solution was allowed to stir at 0 °C for 2 h. The solvent was then removed by rotary evaporation. The crude product was chromatographed on alumina and eluted with petroleum ether/diethyl ether (20:1) to give a trace of a compound that may be the S_N2 substitution product as a yellow gum (1H NMR ($CDCl_3$) δ 7.39–7.21 (m, 5 H), 4.61 (s, 2 H), 4.55 (s, 5 H), 4.15 (t, $J = 2$ Hz, 2 H), 1.85 (t, $J = 2$ Hz, 2 H), followed by 31 as a dark yellow solid: 1.27 g, 4.07 mmol (36%); mp (1,2-dichloroethane/petroleum ether) 98 °C dec; IR ($CDCl_3$) 2924, 2860, 2254, 2020, 2007, 1959, 1359, 1129, 1073, 1028 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.36–7.25 (m, 5 H), 4.82 (s, 5 H), 4.53 (s, 2 H), 4.11 (apparent t, $J = 3.0$ Hz, 2 H), 3.94 (apparent t, $J = 3.0$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 215.4, 201.4, 138.8, 128.2, 127.8, 127.3, 85.7, 82.4, 80.3, 71.8, 63.5. FAB HRMS (m/e for MH^+ ($C_{18}H_{17}FeO_3$): calcd, 337.0527; found, 337.0534.

2-(η^5 -Cyclopentadienyl)dicarbonylferrio)-3-hexyne (26). The iron anion (generated via stirring a THF solution (15 mL) of $[CpFe(CO)_2]_2$ (1.02 g, 2.87 mmol) over a 1% sodium amalgam for 3 h) was added to a solution of tosylate 18 (1.51 g, 5.98 mmol) in THF (20 mL) at 0 °C. The solution was then allowed to stir at 25 °C for 14 h. The solvent was removed by rotary evaporation without heat and the product extracted from the residue with pentane (100 mL). If desired, this material may be chromatographed on deactivated alumina with pentane/diethyl ether (10:1). The product 26 was obtained as an amber oil: 1.33 g, 5.15 mmol (90%); IR (C_6D_6) 2967, 2926, 2873, 2015, 1962, 1097, 1060, 1046, 1016 cm^{-1} ; 1H NMR (C_6D_6) δ 4.20 (s, 5 H), 2.90 (tq, $J = 7.2, 2.0$ Hz, 1 H), 2.18 (dq, $J = 8.0, 2.0$ Hz, 2 H), 1.62 (d, $J = 7.2$ Hz, 3 H), 1.10 (t, $J = 8.0$ Hz, 3 H). HRMS (m/e): calcd for $C_{13}H_{14}O_2Fe$, 258.0335; found, 258.0334. This compound was found to be thermally unstable and a satisfactory elemental analysis could not be obtained. It is best synthesized and used immediately thereafter.

3-(η^5 -Cyclopentadienyl)dicarbonylferrio)-4-heptyne (27). The iron anion (generated via stirring a THF solution (15 mL) of $[CpFe(CO)_2]_2$ (0.310 g, 0.876 mmol) over a 1% sodium amalgam for 3 h) was added into a solution of tosylate 19 (0.446 g, 1.677 mmol) in THF (25 mL). The solution was then allowed to stir at 25 °C for 23 h. The solvent was removed by rotary evaporation without heat and the product extracted from the residue with pentane (100 mL). If desired, this material may be chromatographed on deactivated alumina with pentane/diethyl ether (10:1). The product 27 was obtained as an amber oil: 0.402 g, 1.477 mmol (88%); IR (C_6D_6) 2928, 2628, 2872, 2005, 1953, 1613, 1550, 1458, 1433, 1108, 1069, 1000 cm^{-1} ; 1H NMR (C_6D_6) δ 4.21 (s, 5 H), 2.75 (dt, $J = 5.2, 2.8$ Hz, 1 H), 2.18 (dq, $J = 7.8, 2.8$ Hz, 2 H), 1.78 (m, 2 H), 1.32 (t, $J = 7.8$ Hz, 3 H), 1.12 (t, $J = 7.0$ Hz, 3 H). Anal. Calcd for $C_{14}H_{16}O_2Fe$: C, 61.79; H, 5.89. Found: C, 61.70; H, 5.96.

Synthesis of Metallothiosulfinate Esters. General Procedure. The transition-metal 2-alkynyl complex (100–200 mg) was dissolved in tetrahydrofuran (5 mL). 4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (37) (1.0–2.0 equiv) was also dissolved

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in THF (15–20 mL), and the solution was added dropwise to the transition-metal 2-alkynyl complex solution at room temperature. After 2–4 h at room temperature, TLC analysis (silica gel, petroleum ether/diethyl ether, 20:1) showed complete disappearance of the iron 2-alkynyl complex. After 24 h there was only partial disappearance of the corresponding molybdenum 2-alkynyl complexes. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel. 2,3-Diphenylbutadiene (38) and any unreacted 2-alkynyl complex were eluted with petroleum ether/diethyl ether (20:1). Elution with 10% ethanol in diethyl ether yielded the metallothiosulfinate esters.

Cyclopentadienyl(4-(1-oxo-5-methyl-1,2-dithiol-4-enyl))-dicarbonyliron (44). The iron 2-alkynyl complex 29 (0.100 g, 0.435 mmol) was treated with dithiin 1-oxide (37) (0.24 g, 0.86 mmol) in THF. The metallothiosulfinate ester 44 was eluted as a brown solid: 0.0946 g, 0.305 mmol (70% yield); mp (acetone/petroleum ether) 148–150 °C; IR (CDCl₃) 2930, 2882, 2022, 1982, 1590, 1429, 1139, 1042 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 4.98 (s, 5 H), 4.82 (d, br, *J* = 16.0 Hz, 1 H), 4.33 (d, br, *J* = 16.0 Hz, 1 H), 2.42 (s, br, 3 H). FAB HRMS (*m/e*): calcd for MH⁺ (C₁₁H₁₁FeO₃S₂), 310.9499; found, 310.9501.

Cyclopentadienyl(4-(1-oxo-5-phenyl-1,2-dithiol-4-enyl))-dicarbonyliron (45). The iron 2-alkynyl complex 28 (0.200 g, 0.684 mmol) was treated with 37 (0.39 g, 1.37 mmol) in THF. The metallothiosulfinate ester 45 was eluted as a light brown solid: 0.182 g, 0.489 mmol (72% yield); mp (acetone/petroleum ether) 148 °C dec; IR (CDCl₃) 3080, 2930, 2042, 1985, 1540, 1431, 1140, 1058 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 7.72 (s, br, 5 H), 4.96 (d, *J* = 16.0 Hz, 1 H), 4.73 (s, 5 H), 4.53 (d, *J* = 16.0 Hz, 1 H); ¹³C NMR (CDCl₃) δ 213.0, 158.2, 151.0, 136.0, 131.5, 128.4, 128.3, 85.8, 59.6. FAB HRMS (*m/e*): calcd for MH⁺ (C₁₆H₁₃FeO₃S₂), 372.9655; found, 372.9664.

Cyclopentadienyl(4-(1-oxo-5-propenyl-1,2-dithiol-4-enyl))-dicarbonyliron (46). The iron 2-alkynyl complex (30) (0.100 g, 0.391 mmoles) was treated with 37 (0.240 g, 0.86 mmol) in THF. The metallothiosulfinate ester 46 was eluted as a light brown solid: 0.0734 g, 0.218 mmol (56% yield); mp (acetone/petroleum ether) 125–129 °C; IR (CDCl₃) 3030, 2980, 2010, 1975, 1585, 1420, 1390, 1125, 1080 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 5.42 (s, br, 1 H), 5.15 (s, br, 1 H), 4.94 (s, 5 H), 4.83 (d, br, *J* = 16.0 Hz, 1 H), 4.42 (d, br, *J* = 16.0 Hz, 1 H), 2.06 (s, 3 H). Anal. Calcd for C₁₃H₁₂FeO₃S₂: C, 46.43; H, 3.57. Found: C, 46.91; H, 3.88. EI HRMS (*m/e*): calcd for C₁₃H₁₂FeO₃S₂, 336.1873; found, 336.1898.

(Pentamethylcyclopentadienyl)(4-(1-oxo-2-methyl-1,2-dithiol-4-enyl))-dicarbonyliron (42). The iron 2-alkynyl complex 32 (0.100 g, 0.333 mmol) was treated with 37 (0.094 g, 0.329 mmol) in THF. The metallothiosulfinate ester 42 was eluted as a dark brown solid: 0.090 g, 0.237 mmol (74% yield); mp (acetone/petroleum ether) 82–84 °C; IR (CDCl₃) 2980, 2915, 2001, 1956, 1451, 1370, 1089 (SO), 1038 cm⁻¹; ¹H NMR (CDCl₃) δ 4.68 (d, br, *J* = 16.0 Hz, 1 H), 4.24 (d, br, *J* = 16.0 Hz, 1 H), 2.39 (s, br, 3 H), 1.68 (s, 15 H). Anal. Calcd for C₁₈H₂₀FeO₃S₂: C, 50.53; H, 5.26; S, 16.84. Found: C, 50.74; H, 5.20; S, 16.66.

(Pentamethylcyclopentadienyl)(4-(1-oxo-5-phenyl-1,2-dithiol-4-enyl))-dicarbonyliron (43). The iron 2-alkynyl complex 33 (0.180 g, 0.497 mmol) was treated with 37 (0.143 g, 0.500 mmol) in THF. The metallothiosulfinate ester 43 was eluted as a dark brown solid: 0.178 g, 0.403 mmol (81% yield); mp (1,2-dichloroethane/petroleum ether) 135–137 °C dec; IR (CDCl₃) 3062, 2978, 2925, 2005, 1960, 1601, 1566, 1450, 1050 (SO) cm⁻¹; ¹H NMR (CDCl₃) δ 7.48 (m, 2 H), 7.33 (m, 3 H), 4.89 (d, *J* = 16.0 Hz, 1 H), 4.48 (d, *J* = 16.0 Hz, 1 H), 1.61 (s, 15 H); ¹³C NMR (CDCl₃) δ 169.3, 150.6, 135.7, 132.1, 128.2, 128.0, 96.7, 59.1, 9.5. Anal. Calcd for C₂₁H₂₂FeO₃S₂: C, 57.01; H, 4.98; S, 14.48. Found: C, 56.91; H, 4.96; S, 14.40.

Cyclopentadienyl(4-(1-oxo-5-phenyl-1,2-dithiol-4-enyl))-tricarbonylmolybdenum (48). The molybdenum 2-alkynyl complex 41 (0.190 g, 0.528 mmol) was treated with 37 (0.220 g, 0.769 mmol) in THF (20 mL). Analysis of the reaction by TLC (silica gel, 10:1, petroleum ether/diethyl ether) still showed unreacted 41 after 24 h. Heating the solution at this stage led to decomposition of starting material and products. The solvent was removed by rotary evaporation, and the crude product was chromatographed on silica gel. Elution with petroleum ether/

diethyl ether (10:1) yielded 2,3-diphenylbutadiene (38; identical with an authentic sample²⁰ by spectral comparison; 0.150 g, 95% recovery) followed by unreacted 41 (0.100 g, 53%). Elution with 10% ethanol in diethyl ether yielded 48 as a dark yellow-brown solid: 0.100 g, 0.227 mmol, (43%); IR (CDCl₃) 3060, 2058, 1965, 1618, 1439, 1061 cm⁻¹; ¹H NMR (CDCl₃) 7.52–7.35 (m, 5 H), 5.35 (s, 5 H), 5.09 (d, *J* = 16.0 Hz, 1 H), 4.51 (d, *J* = 16.0 Hz, 1 H). Anal. Calcd for C₁₇H₁₂MoO₄S₂: C, 46.37; H, 2.75; S, 14.56. Found: C, 46.22; H, 2.82; S, 14.36.

Cyclopentadienyl(4-(1-oxo-5-methyl-1,2-dithiol-4-enyl))-tricarbonylmolybdenum (47). The molybdenum 2-alkynyl complex 40 (0.100 g, 0.340 mmol) and 37 (0.106 g, 0.370 mmol) were allowed to react in THF (15 mL) as outlined above for 48. Chromatography using conditions outlined above for 48 yielded 47 as a dark green-brown solid: 0.057 g, 0.150 mmol (44%); mp (petroleum ether/acetone) 131–132 °C; IR (CDCl₃) 2985, 2941, 2890, 2055, 1970, 1055 cm⁻¹; ¹H NMR (CDCl₃) 5.60 (s, 5 H), 4.78 (dq, *J* = 16.0, 2.0 Hz, 1 H), 4.24 (dq, *J* = 16.0, 2.0 Hz, 1 H), 2.28 (apparent t, *J* = 2.0 Hz, 3 H) HRMS FAB (*m/e*): calcd for MH⁺ - CO (C₁₁H₁₁Mo⁹²O₃S₂), 346.9210; found 346.9220.

Synthesis of Thiosulfinate Esters. General Procedure. The procedure used here is analogous to one used by Reger et al. in cleaving iron-sp² carbon bonds.²¹ The metallothiosulfinate ester (50–100 mg) was dissolved in CH₂Cl₂/CH₃CH₂OH (1:1, 12 mL), and purged with CO. Ceric ammonium nitrate (3.0 equiv) was dissolved in ethanol (15–20 mL) and also purged with CO. Both solutions were cooled to -78 °C and maintained at that temperature for 0.25 h. The ceric ammonium nitrate solution was then transferred under CO pressure into the metallothiosulfinate ester solution. The combined solutions were then maintained at -78 °C for a further 0.5 h after the addition was complete. The solution was then warmed to room temperature while remaining under the CO atmosphere. The reaction was monitored by TLC analysis (silica gel; 5% ethanol in diethyl ether). When TLC showed that all the starting material had reacted (0.5–1.0 h), the solvent was removed by rotary evaporation. The crude product was dissolved in acetone and filtered through a cotton plug to remove the ceric salts. These cyclic thiosulfinate esters (50–52) have proven to be thermally sensitive compounds, and we have been unable to obtain satisfactory elemental analyses for them.

4-Carboethoxy-5-methyl-1,2-dithiol-4-ene 1-Oxide (50). The metallothiosulfinate ester 44 (0.100 mg, 0.322 mmol) was treated with ceric ammonium nitrate (0.53 g, 0.97 mmol). The crude product was purified on a Harrison Research Chromatotron (silica gel), and the ester 50 was eluted with petroleum ether/diethyl ether (1:1) as a light yellow oil: 0.032 g, 0.155 mmol (48%); IR (CDCl₃) 2950, 2860, 1705, 1620, 1565, 1420, 1352, 1280, 1210, 1080 (SO) cm⁻¹; ¹H NMR (CDCl₃) 4.96 (dq, *J* = 16.0, 2.0 Hz, 1 H), 4.51 (dq, *J* = 16.0, 2.0 Hz, 1 H), 4.30 (q, *J* = 7.0 Hz, 2 H), 2.62 (apparent t, *J* = 2.0 Hz, 3 H), 1.35 (t, *J* = 7.0 Hz, 3 H). EI HRMS (*m/e*): calcd for C₈H₈O₂S₂ (M⁺ - OEt), 160.9731; found, 160.9744.

4-Carboethoxy-5-phenyl-1,2-dithiol-4-ene 1-Oxide (51). The metallothiosulfinate ester 45 (0.090 g, 0.241 mmol) was treated with ceric ammonium nitrate (0.395 g, 0.721 mmol). The crude product was purified on a Harrison Research Chromatotron (silica gel), and the ester 51 was eluted with 100% diethyl ether as a light yellow solid: 0.046 g, 0.172 mmol (72%) (similar procedures with metallothiosulfinate esters (43, 48) also yielded 51 in 66% and 59% yields, respectively); mp (1,2-dichloroethane/petroleum ether) 172 °C dec; IR (CDCl₃) 3158, 3063, 2985, 2938, 1712, 1560, 1464, 1375, 1311, 1282, 1238, 1078 (SO) cm⁻¹; ¹H NMR (CDCl₃) 7.90–7.60 (m, 5 H), 5.15 (d, *J* = 18.0 Hz, 1 H), 4.69 (d, *J* = 18.0 Hz, 1 H), 4.09 (q, *J* = 7.0 Hz, 2 H), 1.05 (t, *J* = 7.0 Hz, 3 H). FAB HRMS (*m/e*): calcd for MH⁺ (C₁₂H₁₃O₃S₂), 269.0306; found, 269.0312.

4-Carboethoxy-5-propenyl-1,2-dithiol-4-ene 1-Oxide (52). The metallothiosulfinate ester 46 (0.150 g, 0.446 mmol) was treated with ceric ammonium nitrate (0.734 g, 1.339 mmol). The crude product was purified on a silica prep plate (1.0 mm). The ester 46 was isolated as a yellow gum (*R*_f = 0.55, in 50% diethyl ether

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Table I. Synthesis of Iron 2-Alkynyl Complexes^a

metal anion	alkyne	2-alkynyl complex	% yield
CpFe(CO) ₂ Na ⁺ (16)	MeCH(OTs)C≡CEt (18)	FpCH(Me)C≡CEt (26)	90
	EtCH(OTs)C≡CEt (19)	FpCH(Et)C≡CEt (27)	88
	PhC≡CCH ₂ Cl (20)	FpCH ₂ C≡Ph (28)	74
	MeC≡CCH ₂ Cl (21)	FpCH ₂ C≡CMe (29)	48
	CH ₂ =(Me)C≡CCH ₂ Br (22)	FpCH ₂ C≡C(Me)=CH ₂ (30)	27
	PhCH ₂ OCH ₂ C≡CCH ₂ Br (23)	FpC(CH ₂ OCH ₂ Ph)=C=CH ₂ (31)	36
Cp*Fe(CO) ₂ -Na ⁺ (17)	MeC≡CCH ₂ Br (24)	Fp*CH ₂ C≡CMe (32)	42
	PhC≡CCH ₂ Br (25)	Fp*CH ₂ C≡CPh (33)	24

^aCp = cyclopentadienyl; Fp = CpFe(CO)₂; Cp* = Me₅Cp; Fp* = Cp*Fe(CO)₂.

in hexane): 0.060 g, 0.259 mmol (58%); IR (CDCl₃) 3154, 2980, 2928, 1697, 1519, 1469, 1379, 1231, 1106 (SO) cm⁻¹; ¹H NMR (CDCl₃) 5.38 (m, 1 H), 5.24 (m, 1 H), 5.02 (d, *J* = 18.0 Hz, 1 H), 4.54 (d, *J* = 18.0 Hz, 1 H), 4.28 (q, *J* = 7.0 Hz, 2 H), 2.08 (apparent t, *J* = 2.0 Hz, 3 H), 1.18 (t, *J* = 7.0 Hz, 3 H). EI HRMS (*m/e*): calcd for C₉H₁₂O₃S₂ 232.3222; found, 232.3202.

Cyclopentadienyl(4-(1-oxo-5-ethyl-3-methyl-1,2-dithiol-4-enyl))dicarbonyliron (58). The chiral propargyliron complex 26 (0.530 g, 2.054 mmol) was treated with dithiin 1-oxide (37; 0.300 g, 1.110 mmol) in THF (3 mL) and allowed to stir for 4.5 h. The crude metallothiosulfinate ester was purified (silica, 2-mm prep plate, 10:1 pentane/diethyl ether, *R_f* = 0.35) and obtained as a yellow solid (58): 0.023 g, 0.07 mmol (6%). During purification, significant decomposition (brown origin material) was noted. IR (C₆D₆): 2969, 2933, 2013, 1958, 1620, 1600, 1450, 1372, 1092, 1026 cm⁻¹. ¹H NMR (C₆D₆): 5.38 (q, *J* = 6.7 Hz, 1 H), 4.22 (s, 5 H), 2.51 (q, *J* = 7.3 Hz, 2 H), 1.78 (d, *J* = 6.7 Hz, 3 H), 1.25 (t, *J* = 7.3, 3 H). HRMS (*m/e*): calcd for C₁₃H₁₄FeO₃S₂, 337.9734; found, 337.9743.

Cyclopentadienyl(4-(1-oxo-3,5-diethyl-1,2-dithiol-4-enyl))dicarbonyliron (53, 54) and Cyclopentadienyl(4-(2-thio-3,5-diethyl-1,2-oxathiol-4-enyl))dicarbonyliron (55, 56). The chiral racemic propargyliron complex 27 (0.156 g, 0.573 mmol) was treated with dithiin 1-oxide (37; 0.186 g, 0.649 mmol) in THF (3 mL). The reaction mixture was allowed to stir for 2 h. The crude metallothiosulfinate ester was purified (silica, diethyl ether, *R_f* = 0.4) and obtained as a yellow solid as a 1.3:1 mixture of diastereomers (54:53): 0.164 g, 0.466 mmol (40%); IR (C₆D₆) 3234, 3110, 3076, 3048, 2967, 2023, 1971, 1618, 1613, 1065 (SO) cm⁻¹. ¹H NMR (C₆D₆): anti (54), 4.75 (apparent dt, *J* = 8.3, 2.7 Hz, 1 H), 3.95 (s, 5 H), 3.12 (m, 1 H), 2.55 (m, 1 H), 2.2-1.4 (m, 2 H, -CH₂ overlapping in syn and anti), 1.10 (t, *J* = 7.7 Hz, 3 H), 0.87 (t, *J* = 8.1 Hz, 3 H); syn (53), 4.42 (dd, *J* = 9.3, 3.3 Hz, 1 H), 4.01 (s, 5 H), 2.77 (m, 1 H), 2.30 (m, 1 H), 2.2-1.4 (m, 2 H, -CH₂ overlapping in syn and anti), 1.27 (t, *J* = 9.7 Hz, 3 H), 1.13 (t, *J* = 7.3 Hz, 3 H). EI HRMS (*m/e*): calcd for M⁺ - O (C₁₄H₁₆FeO₂S₂), 335.9944; found, 335.9940. Trace amounts of 55 and 56 were also noted in the crude product ¹H NMR spectrum.

The chiral racemic propargyliron complex 27 (0.314 g, 1.155 mmol) was treated with dithiin 1-oxide (37, 0.357 g, 1.248 mmol) in THF (3 mL). The reaction mixture was allowed to stir for 3 h. The crude metallothiosulfinate ester was purified (silica, diethyl ether, *R_f* = 0.4) and obtained as a yellow solid as a 1.3:1 mixture of diastereomers (54:53): 0.164 g, 0.466 mmol (40% yield). The spectral data are analogous to those reported above. 55 and 56 (silica, diethyl ether, *R_f* = 0.45) were also obtained as a yellow solid as a 1.3:1 (55:56) mixture: 0.068 g, 0.193 mmol (17% yield); IR (C₆D₆) 2969, 2933, 2027, 1975, 1622, 1613, 1587, 1509, 1158 cm⁻¹. ¹H NMR (C₆D₆): anti (56): 5.42 (dd, *J* = 5.5, 1.1 Hz, 1 H), 3.88 (s, 5 H), 2.75 (m, 1 H), 2.22 (m, 1 H), 1.75-1.32 (m, -CH₂ overlapping syn and anti), 1.16 (t, *J* = 5.9 Hz, 3 H), 0.92 (t, *J* = 6.9 Hz, 3 H); syn (55) 5.02 (dd, *J* = 7.3, 1.8 Hz, 1 H), 3.95 (s, 5 H), 2.55 (m, 1 H), 1.95 (m, 1 H), 1.75-1.32 (m, -CH₂ overlapping syn and anti), 1.28 (t, *J* = 6.7 Hz, 3 H), 1.21 (t, *J* = 6.9 Hz, 3 H). HRMS (*m/e*): calcd for C₁₄H₁₆FeO₃S₂, 351.9890; found, 351.9893.

The chiral racemic propargyliron complex 27 (0.286 g, 1.052 mmol) was treated with dithiin 1-oxide (37; 0.316 g, 1.104 mmol) in THF (3 mL). The reaction mixture was allowed to stir for 6 h. The crude metallothiosulfinate ester was purified (silica, 2.0-mm prep plate, diethyl ether, *R_f* = 0.45) and obtained as a yellow solid as a 1.3:1 mixture of diastereomers (55:56): 0.178 g, 0.508 mmol (48% yield). The spectral data were analogous to those given above. 53 and 54 were seen in trace amounts by ¹H

NMR spectra of the crude product.

MgBr₂-Aided Synthesis of Cyclopentadienyl(4-(1-oxo-5-ethyl-1,2-dithiol-4-enyl))dicarbonyliron (53, 54). The chiral propargyliron complex 27 (0.15 g, 0.54 mmol) was dissolved in THF (5 mL), and MgBr₂ (0.05 g, 0.27 mmol) was added. Due to the acid sensitivity of 27, a small amount (5-10 mg) of anhydrous sodium carbonate was also added to react with traces of *m*-chlorobenzoic acid sometimes present in 37. This solution was treated with 37 (0.17 g, 0.61 mmol) in THF (5 mL). The solution was allowed to stir for 5.25 h at room temperature; then water (2 mL) was added, and the aqueous layer was extracted with ether (15 mL). The crude product ¹H NMR spectrum showed 53 and 54 (2:1) and a trace of 55/56. The crude product was purified (silica, diethyl ether), and 53 and 54 (2:1) were obtained as a yellow solid: 0.18 g, 0.51 mmol (95% yield). The spectral data were analogous to those reported above.

X-ray Data Collection for C₁₆H₁₂O₃S₂Fe (45): monoclinic, *P*2₁/*n*, *a* = 10.081 (4) Å, *b* = 14.992 (5) Å, *c* = 10.227 (3) Å, β = 93.96 (2)°, *V* = 1542 (1) Å³, *Z* = 4, *D*(calcd) = 1.60 g cm⁻³. Of 2582 data collected (Nicolet R3m, 4° ≤ 2θ ≤ 48°, 294 K) 85 were rejected due to background imbalance from a minor, but unavoidable, twin contribution. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were idealized. A 10% disordered S(2) was modeled at two sites; the minor site is S(2'). The phenyl ring was constrained to a rigid hexagon. For 1644 independent, observed data (3σ_{*F*}) *R*(*F*) = 6.84%, *R*(*wF*) = 7.01%, GOF = 1.746, Δ/σ = 0.03, and Δ(ρ) = 1.94 e Å⁻³. All computations used SHELXTL (5.1) software (G, Sheldrick, Nicolet XRD, Madison, WI).

Results and Discussion

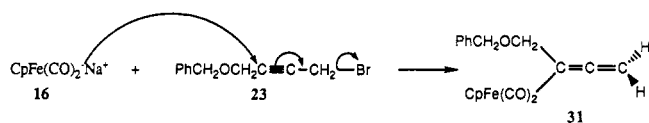
Synthesis of 2-Alkynyl Complexes. All the transition-metal 2-alkynyl complexes used in the cyclization studies were prepared by using procedures analogous to those reported previously (addition of a THF solution of the appropriate metal anion to a THF solution of the 2-alkynyl electrophile).¹⁷⁻¹⁹ All the 2-alkynyl electrophiles were synthesized by using literature procedures or procedures analogous to those in the literature (see Experimental Section for details). In our hands, yields of 2-alkynyl complexes are highest when 2-alkynyl tosylates are used and the use of 2-alkynyl chlorides proved superior to the use of 2-alkynyl bromides as electrophiles (Table I).^{18,22} A similar trend has been noted previously in syntheses of CpFe(CO)₂(allyl) complexes.^{1c,o} All these 2-alkynyl complexes are slightly air sensitive as solids and moderately air sensitive in solution except 26, which was found to be thermally and air sensitive and is heat synthesized and used immediately thereafter.

Unexpected chemistry was noted in two cases during attempted syntheses of iron 2-alkynyl complexes. When 1-(benzyloxy)-4-bromo-2-butyne (23) (prepared via monobenylation of 2-butyne-1,4-diol to yield 4-(benzyloxy)-2-butyne-1-ol (34) followed by treatment with PBr₃) was treated with cyclopentadienyliron dicarbonyl anion (16),²³ we isolated the σ-allene complex (31) (36%) rather

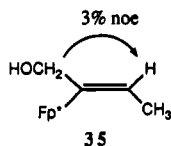
(22) Churchill, M. R.; Wormald, J.; Ross, D. A.; Thomasson, J. E.; Wojcicki, A. *J. Am. Chem. Soc.* 1970, 92, 1795.

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than the 2-alkynyl complex.²⁴ η^1 -Allene complexes have been isolated in three cases previously²⁵ from reactions of iron anion (16) and 2-alkynyl bromides or benzenesulfonates, and our formulation of the allenic structure for 31 is based in part on comparison to literature spectroscopic data. Complex 31 exhibited two peaks in the metal carbonyl region of the infrared spectrum (2020, 1959 cm^{-1}) plus a strong shoulder (1955 cm^{-1}) on the 1959 peak. This shoulder is in the region where the allene would be expected to absorb.²⁵ In the ^1H NMR spectrum, the terminal allenic protons are observed as a triplet (δ 3.94, $J = 3.0$ Hz).^{25b,c} This chemical shift and long-range coupling is consistent with that seen previously. Last, the ^{13}C NMR spectrum from 31 shows two absorptions above 200 ppm (201.4, 215.4). The absorption at 215.4 ppm is in the range expected for the metal carbonyls²⁶ and the 201.4 ppm absorption is in the range expected for the central carbon of the allene.²⁷ Complex 31 is presumably formed via $\text{S}_{\text{N}}2'$ attack on 23 with $\text{S}_{\text{N}}2'$ attack being favored due to the presence of the electron withdrawing benzyloxy substituent.



One other unexpected transformation was noted upon attempted purification of 32 by column chromatography on alumina. We isolated a material that was much more polar than expected. The infrared spectrum clearly showed an OH stretch, and the ^1H NMR spectrum contained a signal that exchanged with D_2O (δ 1.54, t, $J = 5.7$ Hz). There were also signals at 1.79 (d, $J = 5.7$ Hz, 3 H), 4.04 (dd, $J = 5.7, 2.7$ Hz, 2 H), and 6.35 (tq, $J = 9.3, 2.7$ Hz, 1 H). On the basis of this spectroscopic information, we had isolated an iron alkenyl complex (35) of either *E* or *Z* stereochemistry. Only one diastereomer had been isolated following chromatography. The ^1H NMR spectrum of the crude product prior to chromatography showed no evidence of 35. Nuclear Overhauser effect difference experiments⁷ were then performed to help elucidate the stereochemistry of the double bond in the product. Enhancement (3%) at the alkene hydrogen and the lack thereof at the methyl when the methylene was irradiated indicates *Z* stereochemistry in the product (35).



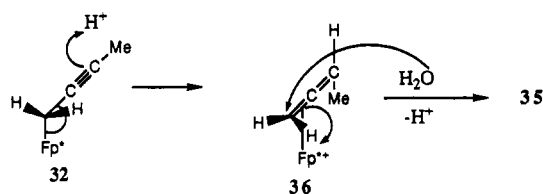
This alkenyl complex (35) is presumably formed via protonation on alumina followed by attack of water on the intermediate cationic allene complex (36). The stereochemistry of the product isolated here is analogous to that seen for nucleophilic attack on cationic $\text{CpFe}(\text{CO})_2(\text{allene})$ complexes.²⁸ Lichtenberg and Wojcicki reported isolating

Table II. Cyclizations of 2-Alkynyl Complexes with 37

alkynyl complex	product	M	n	m	R	% yield
32	42	Fe	5	2	CH_3	74
33	43	Fe	5	2	Ph	81
29	44	Fe	0	2	CH_3	70
28	45	Fe	0	2	Ph	72
30	46	Fe	0	2	$\text{C}(\text{CH}_3)=\text{CH}_2$	56
40	47	Mo	0	3	CH_3	45 ^a
41	48	Mo	0	3	Ph	43 ^a

^a >90% based on recovered alkynyl complex.

small amounts of similar hydration products of cyclopentadienylirion dicarbonyl 2-alkynyl complexes when they were allowed to stay on acid washed alumina for extended periods of time.^{28a} Rosenblum et al. have reported isolating metalloketones and aldehydes following aqueous acetone treatment of $\text{Fp}(\text{allene})$ cations.²⁹ The electron-donating pentamethylcyclopentadienyl ligand apparently makes 32 much more susceptible to electrophilic attack than its unsubstituted cyclopentadienyl counterpart (29). The desired 2-alkynyl complex (32) was



isolated following purification by sublimation rather than chromatography. This one-pot electrophilic/nucleophilic attack on 2-alkynyl complexes could serve as an alternate route to stereospecifically substituted iron alkenyl complexes.^{28,30}

Reaction of Transition-Metal 2-Alkynyl Complexes with 4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-Oxide (37). The 3+2 cycloaddition reaction to yield metallothiosulfinate esters (9) depicted in Scheme II requires disulfur monoxide (S_2O) or a disulfur monoxide equivalent for success. We have previously shown^{2,8,31} that 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (37) serves as a source of S_2O under mild reaction conditions. Dithiin 1-oxide (37) liberates S_2O via a transition-metal-assisted retro Diels-Alder reaction³² at 25 °C or below to form transition-metal S_2O complexes when it is treated with coordinatively unsaturated transition-metal complexes. Since all the 2-alkynyl complexes used in this study were coordinatively saturated, we suspected that we would have to heat 37 (to thermally liberate S_2O) in the presence of the 2-alkynyl complexes if we wanted to see 3+2 cycloaddition products. To our surprise, we found that all the 2-alkynyl complexes we had prepared (Table I) reacted with 37 in tetrahydrofuran at 25 °C to yield metallothio-

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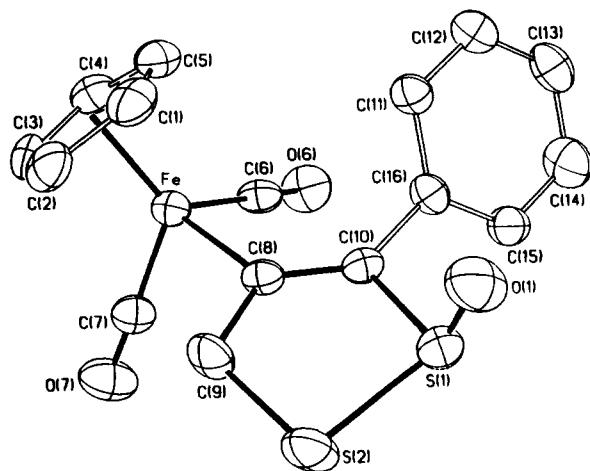


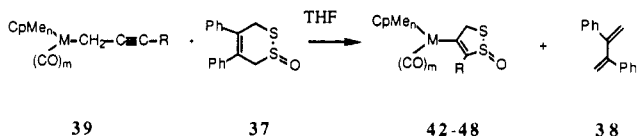
Figure 1. Molecular structure of 45.

Table III. Bond Lengths (Å)

Fe-C(1)	2.113 (8)	Fe-C(2)	2.107 (9)
Fe-C(3)	2.115 (8)	Fe-C(4)	2.107 (8)
Fe-C(5)	2.111 (8)	Fe-C(6)	1.783 (8)
Fe-C(7)	1.759 (8)	Fe-C(8)	2.008 (7)
S(1)-S(2)	2.082 (4)	S(1)-S(2')	1.930 (36)
S(1)-O(1)	1.456 (6)	S(1)-C(10)	1.824 (7)
S(2)-S(2')	0.765 (68)	S(2)-C(9)	1.823 (9)
S(2')-C(9)	1.779 (33)	C(1)-C(2)	1.399 (12)
C(1)-C(5)	1.395 (13)	C(2)-C(3)	1.406 (11)
C(3)-C(4)	1.407 (12)	C(4)-C(5)	1.415 (11)
C(6)-O(6)	1.133 (10)	C(7)-O(7)	1.138 (10)
C(8)-C(9)	1.503 (9)	C(8)-C(10)	1.330 (10)
C(10)-C(16)	1.496 (8)		

sulfinate esters (42-48) (Table II).

A trend in the relative rates of these cyclizations was observed that bears on a proposed mechanism for this reaction. Increased electron density at the metal center accelerated this reaction. Complexes 32 and 33 reacted completely with a slight excess of 37 within 2 h at 25 °C whereas it was most convenient to use 2 equiv of 37 to effect complete cyclization of 28-30 in 2 h. Reactions of molybdenum complexes 40 and 41 were only 50% complete after 24 h. Similar enhancements in cyclization rates have been reported in transition-metal 2-alkynyl/SO₂ cycloadditions¹¹ and in transition-metal allyl 3+2 cycloadditions^{1f,m} when CO was replaced by a phosphine. There was good mass balance in all reactions, and 2,3-diphenylbutadiene (38)²⁰ was isolated as the organic by-

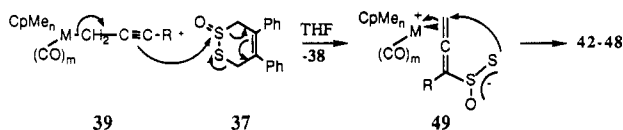


product in all cases. We saw no evidence for the production of the regioisomeric oxygen cyclization product (10) when achiral 2-alkynyl complexes were used. Complexes 42-48 are all air stable, crystalline, and chromatographable. Confirmation of proposed structure 45 comes from X-ray crystallographic data (see Figure 1). The sulfur-sulfur (2.082 Å) and sulfur-oxygen (1.456 Å) bond lengths are consistent with other limited crystallographic data available on thiosulfinate esters (see Tables III and IV for other crystallographic data).³³ Due to crowding on

Table IV. Bond Angles (deg)

C(1)-Fe-C(2)	38.7 (3)	C(1)-Fe-C(3)	64.6 (3)
C(2)-Fe-C(3)	38.9 (3)	C(1)-Fe-C(4)	65.1 (3)
C(2)-Fe-C(4)	65.6 (3)	C(3)-Fe-C(4)	38.9 (3)
C(1)-Fe-C(5)	38.6 (3)	C(2)-Fe-C(5)	65.2 (3)
C(3)-Fe-C(5)	65.0 (3)	C(4)-Fe-C(5)	39.2 (3)
C(1)-Fe-C(6)	126.1 (4)	C(2)-Fe-C(6)	158.3 (4)
C(3)-Fe-C(6)	128.1 (3)	C(4)-Fe-C(6)	94.6 (3)
C(5)-Fe-C(6)	93.9 (3)	C(1)-Fe-C(7)	140.2 (4)
C(2)-Fe-C(7)	102.6 (4)	C(3)-Fe-C(7)	90.4 (3)
C(4)-Fe-C(7)	114.7 (3)	C(5)-Fe-C(7)	153.4 (3)
C(6)-Fe-C(7)	93.6 (4)	C(1)-Fe-C(8)	89.8 (3)
C(2)-Fe-C(8)	101.0 (3)	C(3)-Fe-C(8)	138.6 (3)
C(4)-Fe-C(8)	153.3 (3)	C(5)-Fe-C(8)	114.7 (3)
C(6)-Fe-C(8)	93.1 (3)	C(7)-Fe-C(8)	90.3 (3)
S(2)-S(1)-S(2')	21.6 (20)	S(2)-S(1)-O(1)	112.2 (3)
S(2')-S(1)-O(1)	92.4 (19)	S(2)-S(1)-C(10)	93.0 (2)
S(2')-S(1)-C(10)	91.3 (11)	O(1)-S(1)-C(10)	107.9 (3)
S(1)-S(2)-S(2')	68.0 (28)	S(1)-S(2)-C(9)	95.7 (3)
S(2')-S(2)-C(9)	74.5 (25)	S(1)-S(2')-S(2)	90.5 (37)
S(1)-S(2')-C(9)	102.8 (18)	S(2)-S(2')-C(9)	81.0 (29)
Fe-C(1)-C(2)	70.4 (5)	Fe-C(1)-C(5)	70.6 (5)
C(2)-C(1)-C(5)	108.9 (7)	Fe-C(2)-C(1)	70.9 (5)
Fe-C(2)-C(3)	70.9 (5)	C(1)-C(2)-C(3)	107.4 (8)
C(2)-C(3)-C(2)	70.2 (5)	Fe-C(3)-C(4)	70.2 (5)
C(2)-C(3)-C(4)	108.6 (7)	Fe-C(4)-C(3)	70.8 (5)
Fe-C(4)-C(5)	70.5 (5)	C(3)-C(4)-C(5)	107.2 (7)
Fe-C(5)-C(1)	70.8 (5)	Fe-C(5)-C(4)	70.3 (4)
C(1)-C(5)-C(4)	107.9 (7)	Fe-C(6)-O(6)	175.2 (7)
Fe-C(7)-O(7)	178.1 (7)	Fe-C(8)-C(9)	114.2 (5)
Fe-C(8)-C(10)	129.5 (5)	C(9)-C(8)-C(10)	116.2 (6)
S(2)-C(9)-S(2')	24.5 (22)	S(2)-C(9)-C(8)	111.8 (5)
S(1)-C(9)-C(8)	107.5 (13)	Fe-C(10)-C(8)	119.4 (5)
S(1)-C(10)-C(16)	109.3 (4)	C(8)-C(10)-C(16)	131.1 (6)
C(10)-C(16)-C(11)	119.6 (3)	C(10)-C(16)-C(15)	120.3 (3)

Scheme III



the carbon-carbon double bond, the Fe-C(8)-C(10) and C(16)-C(10)-C(8) bond angles are large, 129.5 and 131.8°, respectively.

The most unusual aspect of this chemistry is that cyclization occurred at room temperature, where 37 is stable in solution in the absence of the transition-metal 2-alkynyl complexes. A mechanism that accounts for the observed products and that is consistent with the observed relative rates of cyclization as well as MNDO calculations on the structure of 37^{3b} can be formulated with use of Wojcicki's results with SO₂ as an analogy (Scheme III).¹⁷

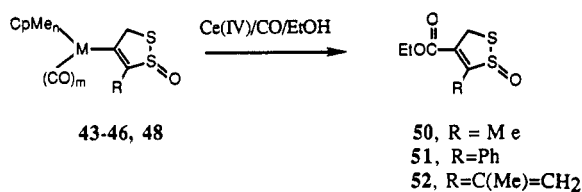
We propose that this cyclization reaction is initiated by nucleophilic attack of 2-alkynyl complexes (39) on 37 at the oxidized sulfur S(1) to form the cationic allene complex 49. Increased electron density on the metal should facilitate this nucleophilic attack. Nucleophilic attack on 37 would result in cleavage of the S(1)-C(6) and S(2)-C(3) bonds in 37 by a formal nucleophile-induced electrocyclic ring-opening reaction. This mechanism requires an unprecedented mode of reactivity for thiosulfinate esters, which normally undergo S-S bond cleavage when treated with carbon nucleophiles.³⁴ One possible driving force for this nucleophile-induced ring opening would be the resonance stabilization energy and relief of strain gained upon

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conversion of **37** to **38**. Our mechanism invokes an initial nucleophilic attack on the most electrophilic sulfur (S(1)) followed by cleavage of the weak S(1)–C(6) bond rather than the S(1)–S(2) bond. This is consistent with MNDO calculations on **37**, which predict a S(2)–C(3) bond order of 0.98 but a S(1)–C(6) bond order of only 0.87.^{8b}

Cleavage of the Metal–Carbon Bond in Metallo-thiosulfinate Esters (40). Synthesis of Cyclic Thiosulfinate Esters. As part of a general program aimed at synthesizing organosulfur compounds that may be useful as agricultural chemicals or pharmaceuticals, we needed to remove the cyclic thiosulfinate esters from the metal. Because of the known ease with which thiosulfinate esters undergo oxidation-induced rearrangements and disproportionations,³⁵ and the fact that most of the known methods for cleaving metal–carbon bonds in similar complexes are oxidative,³⁶ we approached the problem of how to remove the thiosulfinate ester from the metal with some caution. Indeed, attempts to cleave the metal–carbon bond in **46** with halogens (I₂, Br₂, NBS), copper (CuCl₂), and iron (FeCl₃) reagents under a variety of conditions led to the isolation of complex mixtures of products. However, when these metallothiosulfinate esters (**43–46** and **48**) were treated with ceric ammonium nitrate under 1 atm of CO in ethanol, CO insertion and iron–carbon bond cleavage occurred.²¹ This produced the desired five-membered-ring thiosulfinate esters **50–52**, in good yield (**50** from **44**, 48%;

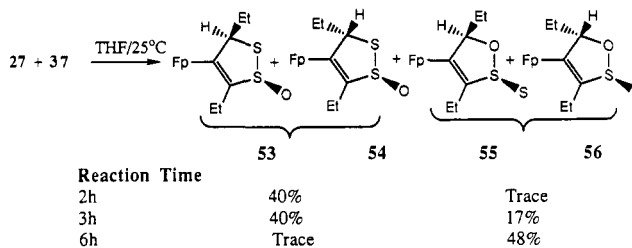


51 from **43**, **45**, and **48**, 66%, 72%, and 59%, respectively; **52** from **46**, 58%). These unsaturated cyclic thiosulfinate esters **50–52** have proven to be much less thermally stable than the saturated natural products **11** and **12**.³⁴ This may not be surprising, since some unsaturated acyclic thiosulfinate esters have been shown to be prone to intra- and intermolecular thermal rearrangements involving the double bond.³⁷

Reaction of Chiral, Racemic 2-Alkynyl Complexes with 37. To our knowledge, there are no reports of investigation of the diastereoselectivity of 3 + 2 cycloaddition reactions between chiral, racemic transition-metal 2-alkynyl complexes, and electrophiles. We were interested in exploring the diastereoselectivity of alkynyl complex/S₂O cycloadditions, and we wanted to get some information about the stabilities of these diastereomeric thiosulfinate esters **14** and **15** if they could be formed. Both the syn and anti diastereomers of the asparagusic acid *S*-oxides **11**^{3,38} and the brugerriols **12**^{4,39} have been isolated from plant sources. The question of whether both diastereomers are

actually present in the plants remains in doubt, however, since they were isolated with use of an acidic methanol extraction and the diastereomers of both **11** and **12** have been shown to be interconvertible in methanol.⁴⁰

Reaction of the chiral, racemic 2-alkynyl complex **27** with **37** was studied first because **27** had proven to be much more thermally stable than **26**. When **27** was allowed to react with **37** in tetrahydrofuran at 25 °C, the product mixture obtained (**53–56**) was dependent on reaction time. After a 2-h reaction time, we obtained a 1.3:1 mixture of two diastereomers (**54**:**53**; 40%) whose spectroscopic characteristics were consistent with the sulfur cyclized products **44–46** seen in the achiral cyclizations, plus a trace amount of two other complexes with spectroscopic characteristics most consistent with oxygen cyclized products (**55** and **56**). When the reaction time was increased to 3



h, **53/54** were still isolated (40%; 1.3:1, **54**:**53**) in addition to a larger amount of **55/56** (17%; 1.3:1, **55**:**56**). After a 6-h reaction time, **55/56** were the major products (48%; 1.3:1, **55**:**56**) and only a trace of **53/54** was seen in the crude product ¹H NMR spectrum.

The structures of the products of this cycloaddition (**53–56**) were determined with use of a variety of spectroscopic techniques. The IR spectrum of a mixture of **53** and **54** showed a strong SO stretch (1065 cm⁻¹), whereas **55/56** shows no strong absorption in the 1050–1100-cm⁻¹ range. Assignment of peaks in the ¹H NMR spectrum (C₆D₆) of a mixture of **53** and **54** to specific diastereomers **53** and **54** was based on spectral comparison to related metallothiosulfinate esters **42–48** and on the use of NMR shift reagents. The ¹H NMR spectrum of the kinetic products of this cyclization (**53/54**) showed absorptions for the methine protons at 4.75 ppm (**54**) and 4.42 ppm (**53**). Similar chemical shift differences (absorption at 4.8–4.9 ppm and 4.3–4.4 ppm) for the diastereotopic methylene protons, syn and anti to oxygen, were noted in complexes **44–46**. Assignment of the 4.75 ppm methine to the anti diastereomer (**54**) and the 4.42 ppm methine to the syn diastereomer (**53**) is also consistent with chemical shift differences noted in the diastereomers of the natural products **11** and **12** (protons syn to oxygen being 0.4–0.5 ppm more deshielded).^{3,4,39,40}

Addition of 0.4 equiv of the shift reagent Eu(FOD)₃ to the methyl esters of asparagusic acid *S*-oxides (**11**) has been shown to shift protons syn to oxygen downfield by up to 4 ppm and protons anti to oxygen downfield by a maximum of 1.5 ppm. When Eu(FOD)₃ (0.4 equiv) was added to the **53/54** mixture, the 4.75 ppm methine shifted downfield by 2.27 ppm, whereas the 4.42 ppm methine was shifted downfield by only 1.13 ppm. These shift reagent data are also consistent with assignment of the 4.75 ppm methine to the anti diastereomer (**54**) and the 4.42 ppm methine to the syn diastereomer (**53**).

Assignment of structures **55** and **56** to the thermodynamic products of this cyclization is consistent with the IR data (no SO absorption), chromatographic character-

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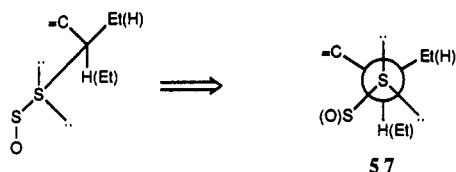
(38) Yanagawa, H.; Kato, T.; Kitahara, Y.; Takahashi, N. *Plant Cell Physiol.* **1973**, *14*, 791.

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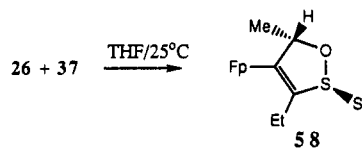
istics R_f 0.45 (silica gel, diethyl ether) for 55/56 as compared to R_f 0.40 for 53/54, and ^1H NMR data. A significant deshielding of the methine protons was noted in these oxygen cyclized products 55/56, with the methines of 56 and 55 seen at 5.42 and 5.02 ppm, respectively. These chemical shifts are consistent with those observed in other unsaturated sultines.^{17,41} Assignment of the most deshielded methine to the anti diastereomer (56) is based on analogy to 54 and the natural products (11 and 12). When $\text{Eu}(\text{FOD})_3$ (0.4 equiv) was added to 55/56, the methine absorptions for 55 and 56 shifted downfield by 1.3 and 3.1 ppm, respectively.

Introduction of a substituent on the carbon next to the nonoxidized sulfur in these thiosulfinate esters (53/54) has obviously affected their stability. We assume that this is a conformational effect similar to those seen in other cyclic thiosulfinate esters⁴² where interactions between the sulfur lone pairs and the substituent (57) are responsible for the

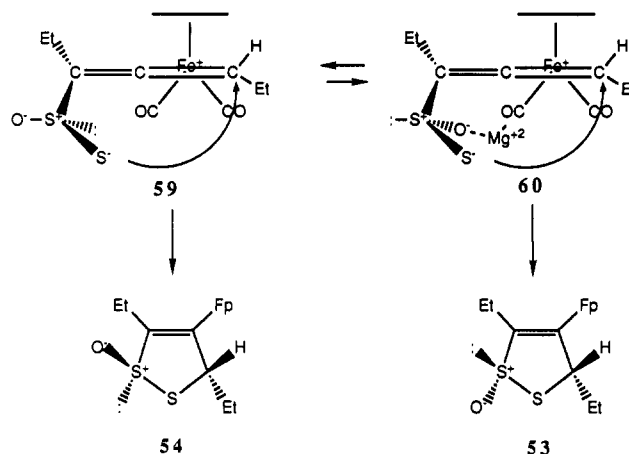


instability of 53/54. This assumption is consistent with the fact that we saw no evidence for the oxygen cyclized regioisomer when achiral alkynyl complexes were used in the cyclization. Complex 45 showed no visible decomposition or isomerization by ^1H NMR spectroscopy after 24 h in CDCl_3 . Also, when 45 was treated with 37 for 19 h in THF at 25 °C, it (45) was recovered unaffected. A mixture of 54/53 (1.4:1) after being stirring overnight in THF contained a mixture of 54/53 and 56/55 (1.7:1), indicating that this isomerization occurs thermally in the absence of other reagents.

Attempts to react 26 with 37 to yield cyclized products met with little success, presumably due to the instability of 26 at the temperatures required for reasonable cyclization rates. A very small amount (6%) of a cyclized product (58) with spectroscopic data most consistent with an oxygen cyclized product (58) was isolated.

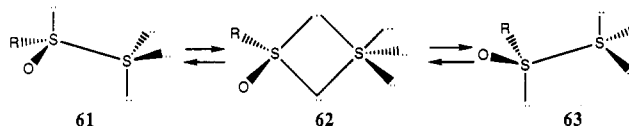


Proposed Cyclization Mechanism and How To Alter the Stereochemical Outcome of the Cyclization. To attempt to account for the lack of diastereoselectivity observed in the cyclization of 27 with 37 and to look for a way to improve diastereoselectivity, we need to postulate a mechanism for the cycloaddition. We will assume that these cycloadditions proceed through cationic allene complex intermediates 59 and 60. These intermediates (59 and 60) are analogous to those reported previously in alkynyl complex cycloadditions.¹ 59 and 60 should exist predominantly in the conformations shown, which place the substituent on the carbon that was α to iron away from the bulky cyclopentadienyl ligand. This has been shown to be the preferred conformation for related cationic $\text{CpFe}(\text{CO})_2(\text{alkene})$ complexes.⁴³ Rotation of the allene



around the metal-alkene bond (a process that is rapid for the related tetramethylallene complex)^{25c} would have no effect on the stereochemical outcome of the cycloaddition reaction. If 1,2-shifts of the iron on the allene occurred, this would yield complexes that could not undergo cyclization to yield five-membered-ring products.

Proposed intermediates 59 and 60, as well as 49, mentioned earlier, are chiral sulfonic acid anions, a class of compounds with almost completely unexplored reaction chemistry.⁴⁴ We would anticipate that 59 and 60 would be interconvertible via a thermal racemization mechanism (61–63) reported for thiosulfinate esters.⁴⁵



There would appear to be little steric or electronic bias to favor either 59 or 60 at equilibrium. We hoped to be able to influence the position of this equilibrium by adding a divalent Lewis acid to coordinate the thiosulfonic acid anion oxygen and a metal carbonyl oxygen, thus favoring intermediate 60.⁴⁶ When MgBr_2 was added to the cyclization reaction, syn product 53 (predicted from this model) became the major product (2:1) and the chemical yield improved (95%). The Lewis acid in this case may also be serving to activate 37 toward nucleophilic attack. Addition of ZnCl_2 or SnCl_2 to the reaction between 27 and 37 resulted in rapid decomposition of 37 and recovery of 27. We are in a precarious situation attempting to control the stereochemical outcome of this cyclization reaction with Lewis acids because we have previously shown that 37 is very unstable in the presence of soft Lewis acids.^{8b} Fortunately, MgBr_2 does not decompose 37 at a rate faster than 27 reacts with 37.

Conclusions. We have demonstrated that metallo-thiosulfinate esters can be formed via a formal 3 + 2 cycloaddition between transition-metal 2-alkynyl complexes and 37. This cyclization reaction presumably involves an unprecedented carbon-sulfur rather than sulfur-sulfur bond cleavage when thiosulfinate ester 37 is attacked by a nucleophile. The metal-carbon bond in the metallo-thiosulfinate esters can be cleaved to yield unsaturated

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(46) For related examples of metal carbonyl binding, see: Ozin, G. A.; Gil, C. *Chem. Rev.* 1989, 89, 1749.

(41) King, J. F.; de Mayo, P.; McIntosh, C. L.; Piers, K.; Smith, D. J. *H. Can. J. Chem.* 1970, 48, 3704.

(42) Juaristi, E.; Cruz-Sanchez, J. S. *J. Org. Chem.* 1988, 53, 3334 and references therein.

cyclic thiosulfinate esters. The 3 + 2 cycloaddition reactions between chiral, racemic 2-alkynyl complexes and **37** did not prove to be highly diastereoselective; however, recent work in our laboratory suggests that 3 + 2 cycloaddition reactions between transition-metal allyl complexes and **37** will yield saturated metallothiosulfinate esters in a highly diastereoselective reaction. We will report the results of that study in the future.

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Supplementary Material Available: Listings of thermal parameters and positional parameters for **45** (2 pages); a table of structure factors (10 pages). Ordering information is given on any current masthead page.