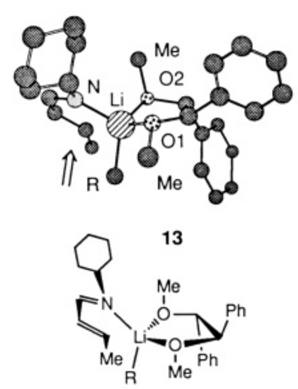

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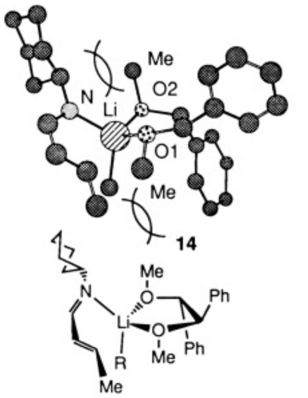

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asymmetric dihydroxylation of olefins recently developed.[11] We believe that the simple strategy of using a diether of a C_2 symmetric chiral diol as a stereocontrol catalyst provides a basis for further development of asymmetric reactions.[12]

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Transition-Metal-Mediated Thiosulfinate Ester Synthesis

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Unlike sulfur dioxide (SO_2), the coordination and organic reaction chemistry of disulfur monoxide (S_2O) has received little attention. A handful of transition-metal S_2O complexes have been synthesized via oxidation of the corresponding disulfur (S_2) complexes.[1] A few Diels–Alder reactions of simple dienes with S_2O have also been reported.[2] However, there were no reports of direct S_2O complex synthesis prior to our initial work.[3]

In order to undertake a detailed study of the chemistry of S_2O or S_2O complexes, a reliable source of S_2O or an S_2O equivalent was needed. Previously reported procedures for S_2O generation suitable for use in synthetic studies yielded mixtures of S_2O, SO_2, and SO.[2,4] We recently published a synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (**2**) which liberates S_2O via a transition-metal-assisted retro-Diels–Alder reaction.[3,5] Here we report further on the unusual reactivity of **2** and its utilization in the synthesis of cyclic thiosulfinate esters.

Scheme I

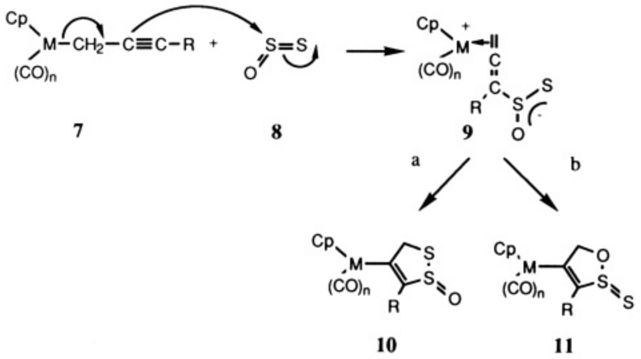
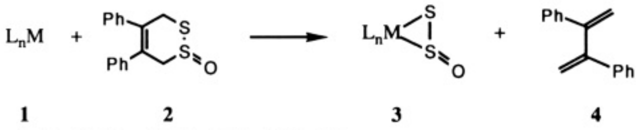


Table I. Cyclizations of 2-Alkynyl Complexes **12**

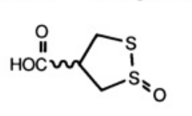
	M	*n*	*m*	R	yield, %
13a	Fe	5	2	CH_3	74
13b	Fe	5	2	Ph	81
13c	Fe	0	2	CH_3	71
13d	Fe	0	2	Ph	72
13e	Mo	0	3	CH_3	45[a]
13f	Mo	0	3	Ph	43[a]

[a] Greater than 90% based on recovered starting material.



$L_nM = Ir(diphos)_2{}^+Cl^-$, $CpMn(CO)_2(thf)$

Thiosulfinate esters have shown biological activity as antibacterials,[6] antifungals,[6] antivirals,[7] plant growth regulators,[8] platelet aggregation inhibitors,[9] and tumor growth inhibitors.[10] Compounds containing this functional group have practical applications as alkene autoxidation inhibitors[11] and radioprotective agents.[12] Thiosulfinate esters of particular synthetic interest to us were analogues of the asparagusic acid *S*-oxides (**5**) (potent plant growth regulators)[8] and the brugeriols (**6**) (isolated from mangroves).[13] One possible route to compounds of this general type would be a (3 + 2) cycloaddition reaction between transition-metal 2-alkynyl complexes (**7**) and S_2O (**8**) (Scheme I). These complexes (**7**) have been shown to react in this manner with a variety of other small organic electrophiles.[14] If cyclization



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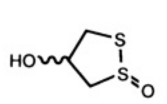

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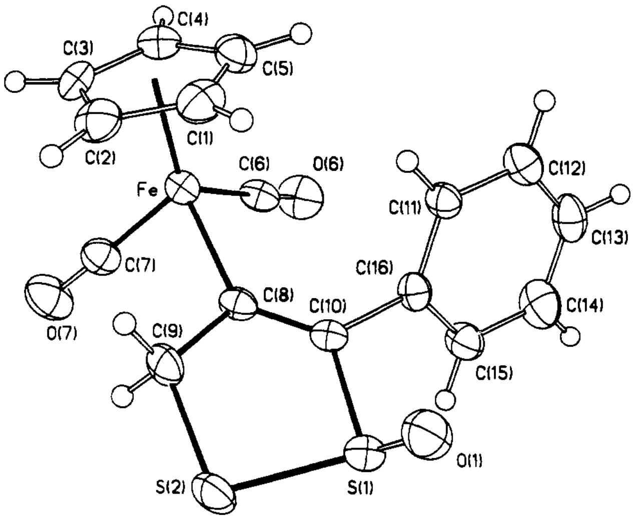
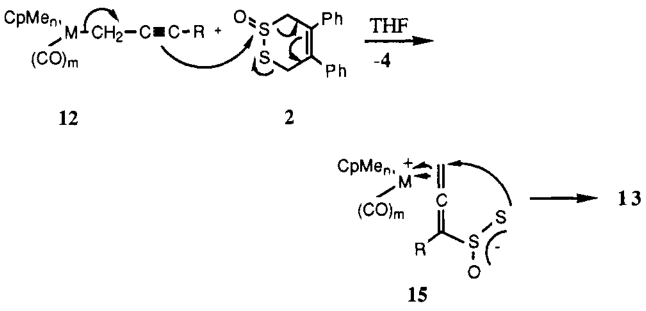


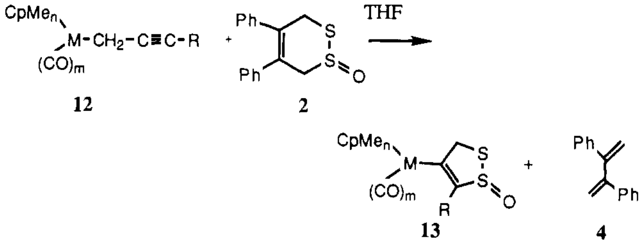
Figure 1. Molecular structure of **13d**. S(2) is disordered; a minor site S(2′) is omitted. Fe–CNT, 1.740 (7) Å; Fe–C(8), 2.008 (7) Å, C(8)–C(9), 1.503 (9) Å, C(9)–S(2), 1.823 (9) Å; S(1)–S(2), 2.082 (4) Å; S(1)–C(10), 1.824 (7) Å; C(8)–C(10), 1.330 (10) Å, S(1)–O(1), 1.456 (6) Å. CNT–Fe–C(6), 123.0 (3)°; CNT–Fe–C(7), 124.0 (3)°; CNT–Fe–C(8), 123.1 (3)°; C(9)–S(2)–S(1), 95.7 (3)°; S(2)–S(1)–C(10), 93.0 (2)°; S(2)–S(1)–O(1), 112.2 (3)°; C(10)–S(1)–O(1), 107.9 (3)°; S(1)–C(10)–C(8), 119.4 (5)°.

occurs with S_2O the proposed intermediate cationic allene complex (**9**) could close via sulfur (path a) or oxygen (path b). Control of the mode of cyclization should be effected by varying the electrophilicity of the metal M in **9**.

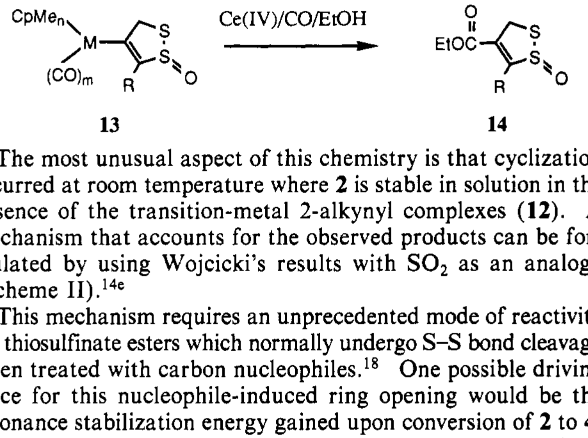
Scheme II



We have tested this idea by treating a variety of $CpMe_nM(CO)_mCH_2C{\equiv}CR$ complexes (**12**) with S_2O equivalent **2** (Table I). Cyclization proceeded cleanly at room temperature in tetrahydrofuran to yield metallothiosulfinate esters (**13**).[15] As expected, increased electron density at the metal center accelerated this reaction.[14g] Complexes **12a** and **12b** reacted completely with a slight excess of **2** within 2 h at room temperature, whereas it was most convenient to use 2 equiv of **2** to effect complete cyclization of **12c** and **12d** in 2 h. Reactions of molybdenum complexes **12e** and **12f** were only 50% complete after 24 h. There was good mass balance in all reactions, and 2,3-diphenylbutadiene (**4**) was isolated as the organic byproduct in all cases. We see no evidence for the production of the regioisomeric oxygen cyclization product (**11**). Complexes **13a–f** are all air stable, crystalline, and chromatographable. Confirmation of proposed structure **13d** 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.[16] Due to crowding on 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.



When these metallothiosulfinate esters (**13b–d,f**) were treated with ceric ammonium nitrate under 1 atm of CO in ethanol, CO insertion and iron–carbon bond cleavage occurred.[17] This produced the desired five-membered-ring thiosulfinate esters **14** in good yield (from **13c**, R = Me, 50%; from **13b 13d**, and **13f**, R = Ph, 66%, 75%, and 59%, respectively).



The most unusual aspect of this chemistry is that cyclization occurred at room temperature where **2** is stable in solution in the absence of the transition-metal 2-alkynyl complexes (**12**). A mechanism that accounts for the observed products can be formulated by using Wojcicki's results with SO_2 as an analogy (Scheme II).[14e]

This mechanism requires an unprecedented mode of reactivity for thiosulfinate esters which normally undergo S–S bond cleavage when treated with carbon nucleophiles.[18] One possible driving force for this nucleophile-induced ring opening would be the resonance stabilization energy gained upon conversion of **2** to **4**.

Our current efforts are centered around investigation of the reactivity of **2** with other organic as well as organometallic nucleophiles.

Acknowledgment is made to the North Carolina Board of Science and Technology, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 8817985) for support of this work. The Midwest Center for Mass Spectrometry, a National

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(15) General cyclization procedure: Iron propargyl complex **12d**[19] (0.200 g, 0.68 mmol) was dissolved in tetrahydrofuran (15 mL) and stirred under nitrogen at 25 °C. Dithiin 1-oxide **2** (0.390 g, 1.37 mmol) was dissolved in tetrahydrofuran (5 mL) and added dropwise to the propargyl complex. After 2 h at 25 °C, TLC analysis (silica gel, 20:1 petroleum ether/diethyl ether) showed complete disappearance of starting material (**12d**). The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel). Elution with petroleum ether yields 2,3-diphenylbutadiene (**4**), followed by elution with 10% ethanol in diethyl ether, which yields the metallothiosulfinate ester **13d** as a yellow-brown solid (0.182 g, 72%): mp 148 ° dec (acetone/petroleum ether).

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Science Foundation regional instrumentation facility (CHE 8211164), performed mass spectrometric analyses.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds and tables of thermal parameters, positional parameters, bond distances, and bond angles for **13d** (5 pages). Ordering information is given on any current masthead page.

Characterization of the ESR Spectrum of the Superoxide Anion in the Liquid Phase

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The anion radical O_2^-, which is of considerable importance in living matter,[3,4] has been shown to be moderately stable in low-temperature aprotic media.[5-8] Consequently, ESR studies on O_2^-[9-23] generally have been undertaken in frozen media containing aprotic solvent[9-19] or at low temperatures on various solid oxide surfaces.[20-23] For example, Bray et al.[9] studied the low-temperature ESR spectrum of O_2^- generated in aqueous dimethyl sulfoxide media by using pulse radiolysis followed by a rapid freezing method. The intensity of the two-line spectrum was found to be extremely temperature dependent, and the disappearance of the ESR lines at temperatures prior to melting of the solvent was attributed to line broadening resulting from fast relaxation. In contrast only brief reports at single temperatures are available on the solution phase O_2^- ESR spectrum.[24,25]

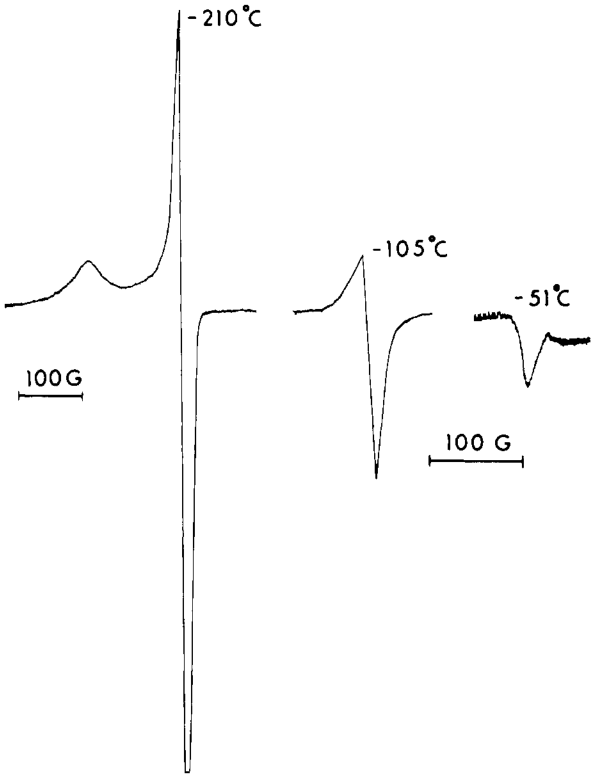

Figure 1. ESR spectra at various temperatures of the superoxide anion O_2^- generated by electrochemical reduction of molecular oxygen in butyronitrile containing 0.1 M Bu_4NClO_4.

This communication reports that ESR spectra of O_2^- can be obtained in solution at temperatures well above the melting point of aprotic solvents[26-28] such as butyronitrile (mp −112.0 °C) and propionitrile (mp −92.9 °C) and that frozen or solid-state media are not required for temperature-dependent studies.

Figure 1 shows the ESR spectra of electrochemically generated O_2^- in butyronitrile in the frozen solvent at −210 °C and in the liquid phase at −105 and −51 °C. Obviously it is possible to detect the ESR signal or O_2^- as high as 60 °C above the melting point (−112 °C) of butyronitrile. A similar study was undertaken in propionitrile, and the temperature dependence of the ESR signal amplitude in this solvent is shown in Figure 2 over a temperature range encompassing frozen solvent and the liquid phase. The temperature dependence is much greater than expected on the basis of the Curie law. For comparison purposes, Figure 2 also includes the temperature-dependent behavior of the well-known stable 4-hydroxy-2,2′,6,6′-tetramethylpiperidine-*N*-oxyl (TEMPOL) radical.

TEMPOL is a much larger molecule than O_2^- and has a much smaller *g*-factor anisotropy. Data for TEMPOL are in complete agreement with the Curie law.

The ESR spectra of O_2^- in frozen butyronitrile and propionitrile are characterized by $g_\parallel = 2.072$ (broad line) and $g_\perp = 2.009$ and are similar to the results reported in frozen solutions of dimethyl sulfoxide.[5] However, there are two unusual features of the solution ($g_{av} = 2.031$) spectra: (a) the signal height decreases sharply with

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