ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 598 (2000) 150–159

Journal of Organometallic Chemistry

Reactions of transition-metal η^1-propargyl complexes with sulfur dioxide and sulfur trioxide: transition-metal–carbon bond cleaving reactions of the cycloadducts which yield 1,2-oxathiole-2-oxides and -2,2-dioxides

Allison L. Hurley, Mark E. Welker *,[1], Cynthia S. Day [2]

Department of Chemistry, Wake Forest University, PO Box 7486, Winston-Salem, NC 27109, USA

Received 24 September 1999; received in revised form 5 November 1999

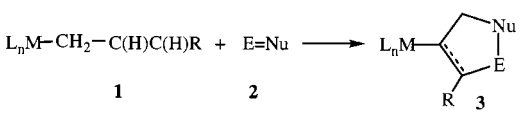
Abstract

The preparation of several cyclopentadienyl iron dicarbonyl and triphenylphosphine manganese tetracarbonyl η^1-2-alkynyl complexes are reported. The [3 + 2] cycloaddition reactions of these complexes with sulfur dioxide and sulfur trioxide yielded transition-metal substituted 1,2-oxathiolene-2-oxides and 1,2-oxathiolene-2,2-dioxides, respectively. One of the η^1-propargyl complex SO_3 cycloadducts has been characterized by X-ray crystallography. The transition metal can subsequently be cleaved from the oxathiole-oxide and dioxide containing complexes to produce a variety of new sulfur containing heterocycles. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Propargyl complexes; Alkynyl complexes; [3 + 2] Cycloaddition; Sulfur heterocycles

1. Introduction

Cycloaddition reactions between transition-metal η^1-2-alkynyl (**1**) and η^1-allyl complexes (**1**) and unsaturated electrophilic reagents (**2**) have been studied in detail for many years [1]. These [3 + 2] cycloaddition reactions have been shown to yield transition-metal substituted five-membered-ring heterocycles and carbacycles (**3**) [1].



We have also now reported a number of examples of these types of cycloaddition reactions [2]. We have been particularly interested in developing this chemistry as a new synthetic method for the preparation of unusual sulfur heterocycles. We are interested in five membered ring sulfur heterocycles as synthetic targets because of (1) their cancer chemopreventive effects since they function as glutathione *S*-transferase inducers [3]; and (2) a recent report that 1,2-dithiolanes and 1,2-dithianes look particularly promising as inhibitors of HIV type 1 replication [4]. 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.

In continuation of our efforts in this area, we report here the preparation of cyclopentadienyl iron dicarbonyl- and $(Ph_3P)(CO)_4$ manganese-η^1-alkynyl complexes and their reactions with SO_2 and SO_3. Demetallation reactions of these metal substituted cycloadducts are also reported.

2. Experimental

2.1. General

All nuclear magnetic resonance (NMR) were obtained using a Varian VXR-200 or Bruker AVANCE

* Corresponding author.
E-mail address: welker@wfu.edu (M.E. Welker)
[1] Henry Dreyfus Teacher–Scholar Awardee (1994–1999).
[2] Author to whom correspondence concerning X-ray crystallography should be addressed.

PII: S0022-328X(99)00693-2

300 FT NMR spectrometer. All absorptions are expressed in parts per million relative to residual undeuterated solvents. All infrared (IR) spectra were obtained using a Perkin–Elmer 1620 FT-IR spectrophotometer. All elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. High resolution mass spectral analyses (HRMS) were performed by the Duke University Center for Mass Spectrometry. Thin layer chromatography was carried out on 0.20 mm precoated polygram aluminum oxide plates or 0.25 mm precoated polygram SIL G/UV silica plates. Routine column chromatography was effected on alumina absorption (150 mesh, neutral), purchased from Aldrich or silica gel 60 purchased from VWR Scientific. Tetrahydrofuran was distilled from sodium–benzophenone under a nitrogen atmosphere immediately prior to use. Toluene and pentane were distilled from calcium hydride prior to use. All reactions were carried out under an atmosphere of dry nitrogen, unless otherwise noted. Cyclopentadienyl iron dicarbonyl dimer, manganese carbonyl dimer, and triphenyl phosphine were purchased from Strem Chemicals and used as received. $Mn(CO)_4[PPh_3]CH_2C{\equiv}CR$, (**4** R = Me, **5** R = Ph) [5] and $CpFe(CO)_2CH_2C{\equiv}CR$ (**6**, $R = CH_3$) [6] and (**7**, R = Ph) [6] were synthesized according to modified literature procedures via addition of a THF solution of the transition-metal anion to a THF solution of the appropriate 2-alkynyl tosylate. Literature procedures [5,6] typically use 2-alkynyl halides but the tosylates are more convenient to work with since they are solids, and have many times produced higher yields of propargyl complex.

2.2. 3-Cyclohex-(1′)-enyl-2-propyn-1-ol (9)

The boiling point and IR data for this compound but no experimental procedure or other characterization data have been reported previously [7]. 1-Ethynylcyclohexene (**8**) (3.00 g, 28.6 mmol) was dissolved in diethyl ether (125 ml) and cooled to −78°C. *n*-Butyllithium in hexane (12.4 ml, 2.5 M in hexane, 31.1 mmol) was added dropwise. The solution was allowed to stir at −78°C for 1.5 h and then paraformaldehyde (1.70 g, 56.5 mmol) was added. The reaction mixture was allowed to warm to 25°C overnight. The mixture was poured into saturated aq. NH_4Cl solution (125 ml) and then extracted with diethyl ether (3 × 50 ml). The ether extracts were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using 1:1 diethyl ether–pentane to yield a light yellow oil (3.17 g, 23.3 mmol, 82%). ^{1}H-NMR ($CDCl_3$): 6.09 (m, 1 H), 4.35 (s, 2 H), 2.07 (m, 4 H), 1.62–1.57 (m, 5 H). EI HRMS (*m*/*z*) Calc. for (M^+) ($C_9H_{12}O$) 136.0888, found 136.0894.

2.3. General procedure for the synthesis of substituted phenyl propargyl alcohols (10–12) [8]

The appropriate iodobenzene was dissolved in triethylamine (10–50 ml) and propargyl alcohol was added. The reaction mixture was deoxygenated thoroughly using nitrogen. $Pd(PPh_3)_2Cl_2$ (0.01 mol%) and CuI (0.02 mol%) were added and the resulting solution was allowed to stir for 2 h at 25°C. H_2O (20–40 ml) and ethyl acetate (20–40 ml) were added. The aqueous layer was extracted with ethyl acetate (2 × 20 ml). The organic extracts were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure. The crude products were purified by recrystallization or column chromatography on silica gel.

2.3.1. 3-(4-Methoxy)-phenyl-2-propyn-1-ol (10)

This compound has been prepared and characterized previously by an alternate procedure [9]. 4-Iodoanisole (5.00 g, 21.4 mmol), propargyl alcohol (1.25 ml, 21.4 mmol), $Pd(PPh_3)_2Cl_2$ (0.150 g, 0.214 mmol) and CuI (0.082 g, 0.428 mmol) were reacted using the above procedure to yield a crude product which was purified by column chromatography using silica gel (100% diethyl ether). The resulting off-white solid (3.40 g, 21.0 mmol, 98%) proved identical by spectroscopic comparison to the previously reported material [9].

2.3.2. 3-(4-tert-Butyl)-phenyl-2-propyn-1-ol (11)

1-*tert*-Butyl-4-iodobenzene (1.00 g, 3.84 mmol), propargyl alcohol (0.223 ml, 3.84 mmol), $Pd(PPh_3)_2Cl_2$ (0.027 g, 0.038 mmol) and CuI (0.015 g, 0.077 mmol) were reacted using the above procedure to yield a crude product which was purified by column chromatography using silica gel (100% diethyl ether). The resulting product was a light yellow solid (0.615 g, 3.27 mmol, 85%): m.p. 94–95°C. ^{1}H-NMR ($CDCl_3$): 7.33 (m, 4 H), 4.47 (s, 2 H), 1.90 (br s, 1 H), 1.29 (s, 9 H). Anal. Calc. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.18; H, 8.54. EI HRMS (*m*/*z*) Calc. for M^+ ($C_{13}H_{16}O$), 188.1201, found 188.1203.

2.3.3. 3-(4-Nitro)-phenyl-2-propyn-1-ol (12)

This compound has been prepared in a much lower yield and characterized previously by an alternate procedure [10]. 1-Iodo-4-nitrobenzene (5.00 g, 20.1 mmol), propargyl alcohol (1.17 ml, 20.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.140 g, 0.200 mmol), and CuI (0.076 g, 0.400 mmol) were reacted using the above procedure to yield a crude product which was purified by recrystallization from ethyl acetate and pentane. The tan solid (3.18 g, 17.9 mmol, 89%) proved identical by spectroscopic comparison to the previously reported material [10].

2.4. 1-Tosyl-3-cyclohexenyl-2-propyne (13)

3-Cyclohex-1′-enyl-2-propyn-1-ol (**9**) (3.04 g, 22.3 mmol), *p*-toluene sulfonyl chloride (4.04 g, 21.2 mmol) and potassium hydroxide (6.26 g, 112 mmol) were reacted in a manner analogous to our previously reported procedure [2b] to yield the product (**13**) (5.66 g, 19.5 mmol, 92%) as a light yellow oil. ^{1}H-NMR ($CDCl_3$): 7.79 (d, $J = 8.1$ Hz, 2 H), 7.31 (d, $J = 8.1$ Hz, 2 H), 5.97 (m, 1 H), 4.81 (s, 2 H), 2.42 (s, 3 H), 2.02 (m, 2 H), 1.92 (m, 2 H), 1.53 (m, 4 H). FAB LRMS (m/z) Calc. for (MH^+) ($C_{16}H_{19}O_3S$): 291, found 291.

2.5. 1-Tosyl-3-(4-methoxy)phenyl-2-propyne (14)

3-(4-Methoxy)phenyl-2-propyn-1-ol (**10**) (3.56 g, 22.0 mmol), *p*-toluene sulfonyl chloride (3.97 g, 20.9 mmol), and potassium hydroxide (6.16 g, 110 mmol) were reacted in a manner analogous to our previously reported procedure [2b] to yield the product (**14**) (5.50 g, 17.4 mmol, 84%) as a white solid: m.p. 44–45°C. ^{1}H-NMR ($CDCl_3$): 7.83 (d, $J = 8.2$ Hz, 2 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 7.18 (d, $J = 8.7$ Hz, 2 H), 6.78 (d, $J = 8.7$ Hz, 2 H), 4.91 (s, 2 H), 3.78 (s, 3 H), 2.38 (s, 3 H). FAB LRMS (m/z) Calc. for (MH^+) ($C_{17}H_{17}O_4S$): 317, found 317.

2.6. 1-Tosyl-3-(4-tert-butyl)phenyl-2-propyne (15)

3-(4-*tert*-Butyl)phenyl-2-propyn-1-ol (**11**) (0.550 g, 2.92 mmol), *p*-toluene sulfonyl chloride (0.529 g, 2.77 mmol) and potassium hydroxide (0.819 g, 14.6 mmol) were reacted in a manner analogous to our previously reported procedure [2b] to yield the product (**15**) (0.649 g, 1.90 mmol, 68%) as a white solid: m.p. 83–84°C. ^{1}H-NMR ($CDCl_3$): 7.83 (d, $J = 8.1$ Hz, 2 H), 7.31–7.26 (m, 4 H), 7.16 (d, $J = 7.9$ Hz, 2 H), 4.93 (s, 2 H), 2.37 (s, 3 H), 1.28 (s, 9 H). Anal. Calc. for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.09; H, 6.59.

2.7. 1-Tosyl-3-(4-nitro)phenyl-2-propyne (16)

3-(4-Nitro)phenyl-2-propyn-1-ol (**12**) (3.18 g, 18.0 mmol), *p*-toluene sulfonyl chloride (3.25 g, 17.1 mmol), and potassium hydroxide (5.04 g, 89.8 mmol) were reacted in a manner analogous to our previously reported procedure [2b], except that the reaction mixture was allowed to stir overnight at 25°C to yield a yellow solid (**16**) (3.32 g, 10.0 mmol, 59%): m.p. 103–104°C. ^{1}H-NMR ($CDCl_3$): 8.14 (d, $J = 8.5$ Hz, 2 H), 7.84 (d, $J = 8.0$ Hz, 2 H), 7.40 (d, $J = 8.5$ Hz, 2 H), 7.33 (d, $J = 8.0$ Hz, 2 H), 4.94 (s, 2 H), 2.40 (s, 3 H). Anal. Calc. for $C_{16}H_{13}NO_5S$: C, 57.99; H, 3.95. Found: C, 57.71; H, 4.06.

2.8. Cyclopentadienyl(3-cyclohexenyl-2-propynyl)dicarbonyliron (18)

The iron anion was generated from $[CpFe(CO)_2]_2$ (3.68 g, 10.4 mmol) and was added to a THF solution of **13** (5.50 g, 18.9 mmol) using a procedure analogous to one we have reported previously [2b]. The product was obtained as a brown solid (**18**) (4.68 g, 15.8 mmol, 84%): m.p. 52–53°C. IR (NaCl): 2932, 2002, 1944 cm^{-1}. ^{1}H-NMR (C_6D_6): 6.10 (m, 1 H), 4.08 (s, 5 H), 2.25 (m, 2 H), 1.89 (m, 4 H), 1.41 (m, 4 H). ^{13}C-NMR (C_6D_6): 216.88, 130.55, 123.22, 98.51, 85.98, 53.61, 30.47, 25.88, 22.88, 22.08, −18.19. Anal. Calc. for $C_{16}H_{16}FeO_2$: C, 64.89; H, 5.45. Found: C, 64.18; H, 5.45.

2.9. Cyclopentadienyl(3-(4-methoxy)phenyl-2-propynyl)dicarbonyliron (19)

The iron anion was generated from $[CpFe(CO)_2]_2$ (3.26 g, 9.23 mmol) and was added to a THF solution of **14** (5.31 g, 16.8 mmol) using a procedure analogous to one we have reported previously [2b]. The product obtained was a dark red solid (**19**) (3.87 g, 12.0 mmol, 72%): m.p. 60–61°C. IR (NaCl): 2003, 1949, 1505, 1238, 827 cm^{-1}. ^{1}H-NMR (C_6D_6): 7.45 (d, $J = 8.0$ Hz, 2 H), 6.66 (d, $J = 8.2$ Hz, 2 H), 4.09 (s, 5 H), 3.21 (s, 3 H), 1.95 (s, 2 H). ^{13}C-NMR (C_6D_6): 216.88, 158.93, 132.63, 118.96, 114.30, 99.94, 85.99, 83.65, 54.70, −18.43. Anal. Calc. for $C_{17}H_{14}FeO_3$: C, 63.38; H, 4.38. Found: C, 63.18; H, 4.66.

2.10. Cyclopentadienyl(3-(4-tert-butyl)phenyl-2-propynyl)dicarbonyliron (20)

The iron anion was generated from $[CpFe(CO)_2]_2$ (0.355 g, 1.01 mmol) and was added to a THF solution of **15** (0.626 g, 1.83 mmol) using a procedure analogous to one we have reported previously [2b]. The product obtained was a dark red solid (**20**) (0.615 g, 1.77 mmol, 97%): m.p. 58–59°C. IR (NaCl): 2961, 2009, 1951, 825 cm^{-1}. ^{1}H-NMR (C_6D_6): 7.53 (d, $J = 8.4$ Hz, 2 H), 7.16 (d, $J = 8.4$ Hz, 2 H), 4.08 (s, 5 H), 1.93 (s, 2 H), 1.16 (s, 9 H). ^{13}C-NMR (C_6D_6): 216.78, 149.50, 131.11, 125.54, 123.80, 101.06, 85.94, 53.95, 34.52, 31.22, −18.55. Anal. Calc. for $C_{20}H_{20}FeO_2$: C, 68.98; H, 5.79. Found: C, 69.22; H, 5.99.

2.11. General procedure for the synthesis of manganese substituted 1,2-oxathiole-2-oxides [11]

The appropriate manganese propargyl complex (**4** or **5**) 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 manganese complex solution. The reaction mixture was allowed to warm to 25°C under nitrogen, to allow the evaporation of excess sulfur dioxide. The solvent was removed by rotary evaporation and the remaining solid was vacuum dried. The crude products were purified by recrystallization from CH_2Cl_2 and hexane.

2.11.1. Triphenylphosphine(4-(1-oxo-5-methyl-1,2-oxathiol-4-enyl))tetracarbonylmanganese (**21**)

Complex **4** (1.00 g, 2.07 mmol) was treated with SO_2 using the procedure outlined above to yield the product (**21**) (0.691 g, 1.26 mmol, 61%) as a light yellow solid. m.p. (dec.) 107–108°C (SO_2 loss). ^{1}H-NMR ($CDCl_3$): 7.45–7.32 (m, 15 H), 5.11 (d, $J = 16$ Hz, 1 H), 4.78 (d, $J = 16$ Hz, 1 H), 2.21 (s, 3 H). IR ($CDCl_3$): 3155, 2987, 2902, 2074 (s), 1989 (ssh), 1984 (s), 1979 (ssh) cm^{-1}. Anal. Calc. for $C_{26}H_{22}MnO_7PS$ ($M + H_2O$): C, 55.33; H, 3.93. Found: C, 55.83; H, 3.81. FAB MS (m/z) Calc. for $C_{26}H_{21}MnO_6PS$ ($M + H^+$): 547. Found: 547.

2.11.2. Triphenylphosphine(4-(1-oxo-5-phenyl-1,2-oxathiol-4-enyl))tetracarbonylmanganese (**22**)

Complex **5** (2.30 g, 4.23 mmol) was treated with SO_2 using the procedure outlined above to yield the product (**22**) (1.92 g, 3.16 mmol, 75%) as a light yellow solid: m.p. (dec.) 100–101°C (SO_2 loss). ^{1}H-NMR ($CDCl_3$): 7.51–7.24 (m, 20 H), 5.21 (d, $J = 14$ Hz, 1 H), 4.97 (d, $J = 14$ Hz, 1 H). FAB HRMS (m/z) Calc. for $C_{31}H_{23}O_6PSMn$ ($M + H^+$): 609.0333. Found: 609.0317.

2.12. Cyclopentadienyl(1-oxo-5-cyclohexenyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (**23**)

The iron alkynyl complex (**18**) (1.50 g, 5.07 mmol) was treated with SO_2 using a procedure analogous to one we have reported previously [2b]. The crude product was purified by recrystallization from CH_2Cl_2–pentane to yield a yellow solid (**23**) (1.39 g, 3.86 mmol, 76%): m.p. (dec.) 104–105°C. IR (NaCl): 2925, 2107, 1966, 1101, 876 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 5.80 (t, $J = 1.1$ Hz, 1 H), 5.35 (d, $J = 14.6$ Hz, 1 H), 5.00 (d, $J = 14.6$ Hz, 1 H), 4.93 (s, 5 H), 2.16 (m, 4 H), 1.66 (m, 4 H). ^{13}C-NMR ($CDCl_3$): 213.63, 213.38, 153.11, 148.81, 131.33, 131.07, 92.60, 85.35, 29.82, 25.62, 22.60, 21.63. Anal. Calc. for $C_{16}H_{16}FeO_4S$: C, 53.35; H, 4.48; Found: C, 52.67; H, 4.48. FAB HRMS (m/z) Calc. for ($M + H^+$) ($C_{16}H_{17}O_4FeS$), 361.0197; found 361.0195.

2.13. Cyclopentadienyl(1-oxo-5-(4-methoxy)phenyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (**24**)

The iron alkynyl complex (**19**) (1.50 g, 4.66 mmol) was treated with SO_2 using a procedure analogous to one we have reported previously [2b]. The crude product was purified by recrystallization from CH_2Cl_2–pentane to yield a red–brown solid (**24**) (1.21 g, 3.13 mmol, 67%): m.p. (dec.) 105–106°C. IR (NaCl): 2024, 1966, 1494, 1242, 1099, 895 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.31 (d, $J = 8.1$ Hz, 2 H), 6.94 (d, $J = 8.1$ Hz, 2 H), 5.51 (d, $J = 14.7$ Hz, 1 H), 5.13 (d, $J = 14.7$ Hz, 1 H), 4.75 (s, 5 H), 3.83 (s, 3 H). ^{13}C-NMR ($CDCl_3$): 213.50, 213.30, 159.60, 152.89, 150.31, 131.64, 125.84, 114.02, 92.77, 85.50, 55.30. Anal. Calc. for $C_{17}H_{14}FeO_5S$: C, 52.87; H, 3.65. Found: C, 52.69; H, 3.78.

2.14. Cyclopentadienyl(1-oxo-5-(4-tert-butyl)phenyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (**25**)

The iron alkynyl complex (**20**) (0.615 g, 1.77 mmol) was treated with SO_2 using a procedure analogous to one we have reported previously [2b]. The crude product was purified by recrystallization from CH_2Cl_2–pentane to yield a yellow solid (**25**) (0.484 g, 1.17 mmol, 67%): m.p. 59–60°C. IR (NaCl): 2961, 2023, 1973, 1109, 897 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.42 (d, $J = 8.3$ Hz, 2 H), 7.32 (d, $J = 8.0$ Hz, 2 H), 5.52 (d, $J = 14.8$ Hz, 1 H), 5.14 (d, $J = 14.8$ Hz, 1 H), 4.73 (s, 5 H), 1.33 (s, 9 H). ^{13}C-NMR ($CDCl_3$): 213.41, 213.29, 152.34, 151.34, 150.59, 130.51, 130.02, 125.47, 92.88, 85.54, 34.70, 31.33. Anal. Calc. for $C_{20}H_{20}FeO_4S$: C, 58.27; H, 4.89. Found: C, 58.54; H, 4.98.

2.15. General procedure for synthesis of 1,2-oxathiole-2-oxides (**26**–**28**) via cuprate demetallation

In a flame dried flask, CuI (three equivalents) was suspended in freshly distilled THF (5–10 ml) and the solution was purged thoroughly with nitrogen and cooled to −10°C. Methyllithium (1.5 M in Et_2O, six equivalents) was added slowly. The resulting solution was allowed to stir for 30 min at −10°C. In another flame dried flask, the appropriate iron complex was dissolved in THF (5–10 ml) and the solution was purged thoroughly with nitrogen and cooled to −10°C. The iron complex solution was added to the cuprate solution using a double ended needle. The reaction mixture was then allowed to stir at −10°C for 2 h. Saturated NH_4Cl solution (10–20 ml) was then added. The aqueous layer was extracted with diethyl ether (2 × 15 ml). The organic extracts were combined and dried with $MgSO_4$. The solvent was removed by rotary evaporation and the remaining oil or solid was

vacuum dried. The crude product was purified by column chromatography using silica gel at 0°C (jacketed column cooled by recirculating ice water) with diethyl ether–pentane (1:1).

2.15.1. 4-Methyl-5-cyclohexenyl-1,2-oxathiol-4-en-1-yl oxide (**26**)

Iron complex **23** (0.100 g, 0.278 mmol) was reacted with the cuprate formed from CuI (0.159 g, 0.833 mmol) and methyllithium (1.4 M in Et_2O, 1.19 ml, 1.67 mmol), using the above procedure to produce the crude product which was purified to yield a colorless oil (**26**) (0.012 g, 0.061 mmol, 22%). IR (NaCl): 2924, 1123, 971, 694 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 5.96 (m, 1 H), 5.46 (d, $J = 14.9$ Hz, 1 H), 4.99 (d, $J = 14.9$ Hz, 1 H), 2.17 (m, 4 H), 1.92 (s, 3 H), 1.65 (m, 4 H). ^{13}C-NMR ($CDCl_3$): 146.22, 137.20, 132.23, 127.01, 84.64, 28.55, 25.58, 22.39, 21.51, 11.23. Anal. Calc. for $C_{10}H_{14}O_2S$: C, 60.58; H, 7.12. Found: C, 60.84; H, 7.27.

2.15.2. 4-Methyl-5-(4-methoxy)phenyl-1,2-oxathiol-4-en-1-yl oxide (**27**)

Iron complex **24** (0.200 g, 0.518 mmol) was reacted with the cuprate formed from CuI (0.148 g, 0.777 mmol) and methyllithium (1.4 M in Et_2O, 1.11 ml, 1.55 mmol), using the above procedure to produce the crude product which was purified to yield an off-white solid (**27**) (0.027 g, 0.120 mmol, 23%): m.p. 74–75°C. IR (NaCl): 1602, 1501, 1246, 1116 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.36 (d, $J = 8.5$ Hz, 2 H), 6.94 (d, $J = 8.5$ Hz, 2 H), 5.58 (d, $J = 15$ Hz, 1 H), 5.14 (d, $J = 15$ Hz, 1 H), 3.82 (s, 3 H), 1.97 (s, 3 H). ^{13}C-NMR ($CDCl_3$): 160.08, 143.43, 139.10, 130.20, 120.72, 114.44, 84.68, 55.34, 11.04. Anal. Calc. for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 59.71; H, 5.54. EI HRMS (m/z) Calc. for M^+ ($C_{11}H_{12}O_3S$) 224.0507, found 224.0516.

2.15.3. 4-Methyl-5-(4-tert-butyl)phenyl-1,2-oxathiol-4-en-1-yl oxide (**28**)

Iron complex **25** (0.100 g, 0.243 mmol) was reacted with the cuprate formed from CuI (0.139 g, 0.728 mmol) and methyllithium (1.4 M in Et_2O, 1.04 ml, 1.46 mmol), using the above procedure to produce the crude product which was purified to yield an off-white solid (**28**) (0. 013 g, 0.052 mmol, 22.0%): m.p. 73–74°C. IR (NaCl): 2954, 1123, 963, 694 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.43 (d, $J = 8.6$ Hz, 2 H), 7.35 (d, $J = 8.3$ Hz, 2 H), 5.60 (d, $J = 15.0$ Hz, 1 H), 5.15 (d, $J = 15.1$ Hz, 1 H), 1.99 (s, 3 H), 1.31 (s, 9 H). ^{13}C-NMR ($CDCl_3$): 152.15, 143.91, 139.62, 128.55, 125.93, 125.61, 84.76, 34.75, 31.19, 11.08. Anal. Calc. for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 66.77; H, 7.25.

2.16. Cyclopentadienyl(2,2-dioxo-5-phenyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (**30**)

This compound was synthesized using two different procedures. Method A: Freshly distilled THF (0.280 ml, 3.50 mmol) was added to a flame dried flask and cooled to −78°C. SO_3 (0.280 g, 0.140 ml, 3.50 mmol) was added slowly to the cooled THF. This solution was allowed to stir at −78°C for 5 min. Cyclopentadienyl(3-phenyl-2-propynyl)dicarbonyliron (**7**) (1.00 g, 3.41 mmol) was dissolved in CH_2Cl_2 (15 ml) and the resulting solution was added dropwise by an addition funnel to the SO_3–THF solution. The reaction mixture was allowed to warm slowly to 25°C. Saturated $NaHCO_3$ solution (15 ml) was added. The aqueous layer was extracted with CH_2Cl_2 (2×10 ml). The organic extracts were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from CH_2Cl_2–pentane to yield a yellow solid (0.917 g, 2.46 mmol, 72%) which was identical by spectroscopic comparison to previously reported material [12]. Method B: Cyclopentadienyl(1-oxo-5-phenyl-1,2-oxathiol-4-en-4-yl)dicarbonyliron (0.050 g, 0.140 mmol) (**29**) [2b] was dissolved in CH_2Cl_2 (5 ml). The solution was purged thoroughly with nitrogen and then cooled to 0°C. *m*-Chloroperoxybenzoic acid (mCPBA) (60% pure, 0.040 g, 0.140 mmol) was dissolved in CH_2Cl_2 (5 ml) and added dropwise to the iron complex solution. The reaction mixture was allowed to warm to 25°C and stir for 3 h. The solution was then cooled to −78°C and filtered through a glass fritted funnel, which had been cooled in a CH_2Cl_2–dry ice bath. Recrystallization of the crude product from CH_2Cl_2–pentane afforded a yellow solid (0.043 g, 0.115 mmol, 83%) which was identical by spectroscopic comparison to previously reported material [12].

2.17. 5-Phenyl-1,2-oxathiol-4-en-1-yl dioxide (**31**)

Iron complex **30** (0.100 g, 0.268 mmol) was dissolved in CH_2Cl_2 (20 ml). The solution was purged thoroughly with nitrogen and cooled to −78°C. A 70% solution of $HClO_4$ (0.138 ml, 1.61 mmol) was added. The reaction mixture was allowed to stir at −78°C for 30 min. It was then was warmed to 25°C and was allowed to stir overnight. The solvent was removed under reduced pressure and the remaining solid was vacuum dried. The crude product was purified by chromatography on a silica gel prep plate (1 mm) using 100% diethyl ether to yield a tan solid (0.009 g, 0.046 mmol, 17%): m.p. 132–133°C. IR (NaCl): 1327, 1167, 1029, 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.67 (m, 2 H), 7.45 (m, 3 H), 6.92 (t, $J = 2.3$ Hz, 1 H), 5.12 (d, $J = 2.3$ Hz, 2 H). ^{13}C-NMR ($CDCl_3$): 138.17, 130.72, 129.33, 127.35, 126.72, 125.65,

69.96. Anal. Calc. for $C_9H_8O_3S$: C, 55.09; H, 4.11; Found: C, 55.46; H, 4.51.

2.18. 4-Methyl-5-phenyl-1,2-oxathiol-4-en-1-yl dioxide (32)

In a flame dried flask, CuCl (0.040 g, 0.402 mmol) and anhydrous LiCl (0.034 g, 0.804 mmol) were suspended in freshly distilled THF (5 ml). The solution was purged thoroughly with nitrogen and then cooled to −45°C. Methyllithium (1.4 M in Et_2O, 0.574 ml, 0.804 mmol) was added slowly and the resulting solution was allowed to stir for 30 min at −45°C [13]. In another flame dried flask, iron complex **30** (0.150 g, 0.402 mmol) was dissolved in THF (10 ml). The solution was purged thoroughly with nitrogen and cooled to −45°C. The iron complex solution was then added to the cuprate solution using a double ended needle. The reaction mixture was allowed to stir for 2 h at −45°C. Saturated NH_4Cl solution (20 ml) was added. The aqueous layer was extracted with diethyl ether (2 × 15 ml). The organic extracts were combined and dried with $MgSO_4$. The solvent was removed under reduced pressure and the remaining solid was vacuum dried. The crude product was purified by column chromatography using silica gel with 100% diethyl ether to yield an off-white solid (0.026 g, 0.124 mmol, 31%): m.p. 103–104°C. IR (NaCl): 1327, 1174, 978, 774, 753, 694, 622 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.45–7.50 (m, 5 H), 4.93 (s, 2 H), 2.02 (s, 3 H). ^{13}C-NMR ($CDCl_3$): 140.56, 131.40, 130.03, 129.14, 128.91, 125.76, 72.49, 13.01. Anal. Calc. for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79. Found: C, 56.60; H, 4.83.

Table 1
Crystal data and structure refinement for $Fe(CO)_2(C_5H_5)[SO_3C_3H_2(C_6H_5)]$

Empirical formula	$C_{16}H_{12}FeO_5S$
Formula weight	372.17
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P212121$-D_2^4 (no. 19)
Unit cell dimensions	
a (Å)	6.746(2)
b (Å)	13.300(2)
c (Å)	16.813(3)
V (Å^3)	1508.4(5)
Z	4
$D_{calc.}$ (g cm^{-3})	1.639
Absorption coefficient (mm^{-1}), transmission range	1.160, 0.688–1.000
$F(000)$	760
Crystal size (mm)	0.08 × 0.30 × 0.80
2θ Range for data collection	3.5–50.7
Limiting indices	$-1 \le h \le 8$, $-16 \le k \le 1$, $-1 \le l \le 20$
Reflections collected	2035
Independent reflections	1875 [$R_{int} = 0.037$]
Refinement method on F^2	Full-matrix least-squares
Data/parameters	1739/209
Goodness-of-fit on F^2	1.032
Final R indices	
[1301 data, $F_o > 4\sigma(F_o)$ data]	$R_1 = 0.053$, $wR_2 = 0.080$
[1739 data, $F_o 2 > 0$]	$R_1 = 0.077$, $wR_2 = 0.088$
[all 1875 data]	$R_1 = 0.094$, $wR_2 = 0.093$
Absolute structure parameter	−0.05(4)
Extinction coefficient	0.0023(6)
Largest difference peak and hole (e Å^{-3})	0.422 and −0.342

2.19. X-ray structure determination of cyclopentadienyl(2,2-dioxo-5-phenyl-1,2-oxathiol-4-en-4-yl)-dicarbonyliron (30)

Single crystals of $Fe(CO)_2(C_5H_5)[SO_3C_3H_2(C_6H_5)]$ are, at 293 K, orthorhombic, space group $P2_12_12_1$-D_2^4 (no. 19) with $a = 6.746(2)$ Å, $b = 13.300(2)$ Å, $c = 16.813(3)$ Å, $V = 1508.4(5)$ Å^3, and $Z = 4$ {$D_{calc.} = 1.639$ g cm^{-3}; μ (Mo–K_α) = 1.160 mm^{-1}}. Cell constants were obtained by least-squares analysis of 62 randomly selected reflections in the 2θ range 6–25°. A total of 1875 independent reflections having 2θ(Mo–K_α) < 50.7° (the equivalent of 0.8 limiting Cu–K_α sphere) were collected on a computer-controlled Bruker P4 autodiffractometer using ω scans and graphite-monochromated Mo–K_α radiation. The structure was solved using direct methods techniques with the Bruker SHELXTL-PC (version 5.0) software package. The resulting structural parameters have been refined to convergence (see Table 1) using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic hydrogen atoms. The hydrogen atoms were included in the structural model as fixed atoms (using idealized sp^3- or sp^2-hybridized geometry and C–H bond lengths of 0.97 and 0.93 Å) riding on their respective carbons with isotropic thermal parameters fixed at values 1.2 times the equivalent isotropic thermal parameter of their carbon atom.

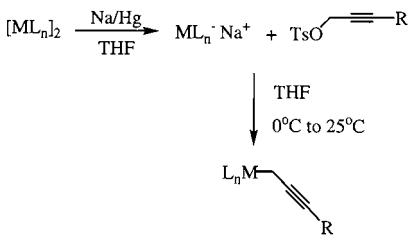
As a check on the correctness of the enantiomorphic description, the Flack parameter was varied during the final cycle of refinement; its final value was −0.05(4). Expected values are 0 (within three estimated SDs) for correct and +1 for inverted absolute structure.

All calculations were performed using the SHELXTL-PC (version 5.0) interactive software package (G. Sheldrick, Bruker-AXS, Madison, WI).

3. Results and discussion

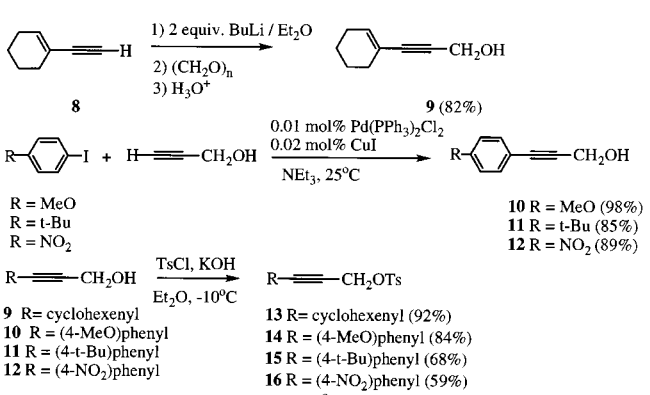
3.1. Preparation of alkynyl complexes

Simple substituted propargyl complexes of the form $Mn(CO)_4[PPh_3]CH_2CCR$ [5] and $CpFe(CO)_2CH_2CCR$ [6] where R = Me and Ph (**4**–**7**) were prepared by modifications of literature procedures. These complexes (**4**–**7**) were synthesized via addition of a THF solution of the transition-metal anion to a THF solution of the appropriate 2-alkynyl tosylate. Literature procedures [5,6] typically use 2-alkynyl halides but the tosylates are more convenient to work with since they are usually solids and many times produce higher yields of the propargyl complex [2b,e].

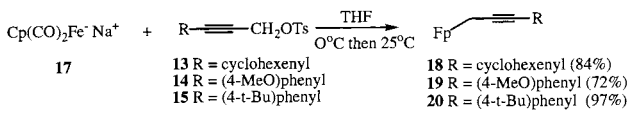


4 $L_nM = [PPh_3](CO)_4Mn$, R=CH_3, 62%
5 $L_nM = [PPh_3](CO)_4Mn$, R=Ph, 68%
6 $L_nM = Cp(CO)_2Fe$, R=CH_3, 70%
7 $L_nM = Cp(CO)_2Fe$, R=Ph, 66%

New cyclohexenyl substituted propargyl complex (**18**) and substituted phenyl propargyl complexes (**19**, **20**) were also easily prepared. 1-Ethynylcyclohexene (**8**) was deprotonated with butyl lithium and then condensed with paraformaldehyde to produce alcohol (**9**) (82%) [7]. Substituted phenyl propargyl alcohols (**10**–**12**) were prepared by Pd/Cu catalyzed cross coupling of the appropriate aromatic iodide with propargyl alcohol [6]. The substituted propargyl alcohols were then converted to tosylates (**13**–**16**) in high yield [2b,e]. The 4-nitrophenylpropynol (**12**) was the least nucleophilic, as expected, and required longer reaction times at higher temperature to get a good conversion to the tosylate (**16**).

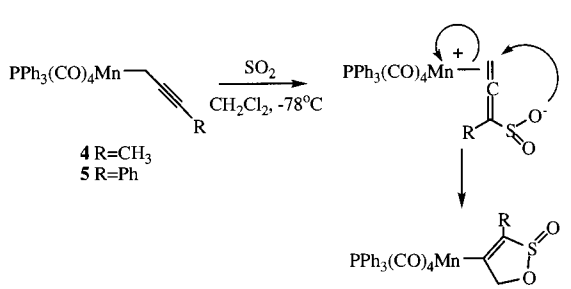


The alkynyl tosylates were then treated with the cyclopentadienyl iron dicarbonyl anion (**17**) (Fp = $CpFe(CO)_2$) to yield the iron alkynyl complexes (**18**–**20**) using a procedure analogous to one we have reported previously [2b]. When tosylate (**16**) was treated with the Fp anion, the tosylate (**16**) and $[CpFe(CO)_2]_2$ were recovered instead of the expected iron alkynyl complex. We suspected that electron transfer occurred between the iron anion (**17**) and the nitro group of the tosylate, inhibiting the expected S_N2 reaction. When the reaction was carried out in dioxane, which has a lower dielectric constant than THF, again the iron dimer and tosylate (**16**) were recovered with no observation of the desired product. Attempts to produce a nitrophenyl alkynyl complex by nitrating phenyl complex (**7**) with NO_2BF_4 were also unsuccessful.



3.2. Cycloaddition reactions of alkynyl complexes with sulfur dioxide and sulfur trioxide and subsequent demetallation reactions of the cycloadducts

Only one cyclization of a manganese tetracarbonyl triphenylphosphine alkynyl complex (**4**, **5** R = H) with SO_2 has been reported previously [11]. The alkynyl complexes (**4** and **5**) underwent a [3 + 2] cycloaddition with SO_2 at −78°C to produce the air-stable manganese substituted 1,2-oxathiole-2-oxides (**21** and **22**) in good yield. We were hopeful that these new complexes (**21** and **22**) would serve as precursors to a variety of new 1,2-oxathiole-2-oxides via demetallation reactions. Unfortunately, attempts at protonolysis (HCl, CH_2Cl_2, HBF_4, and Et_2O; −78 to 25°C), oxidative carboxylation (Ce(IV), CO, EtOH:CH_2Cl_2) and halogenolysis (I_2, CH_2Cl_2, 25°C), which have worked for us in the past on related iron complexes [2], resulted only in the decomposition of these manganese complexes. Organocuprate mediated demetallation conditions which have also worked on iron complexes for us in the past [2], resulted in the recovery of the unreacted complex **22** here.



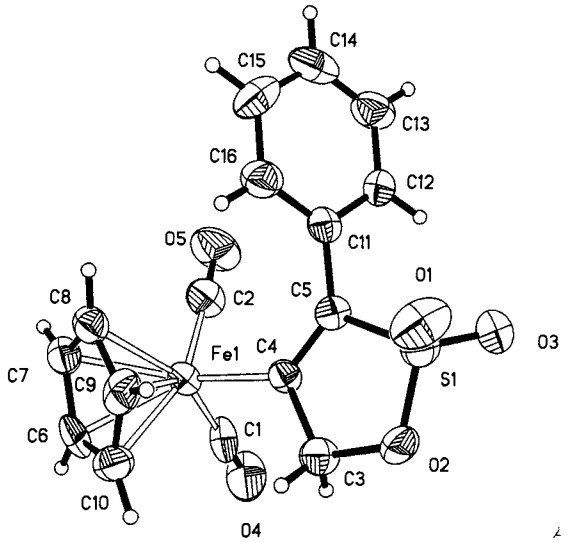


Fig. 1. Perspective drawing of the solid state structure for $Fe(CO_2)(C_5H_5)[SO_3C_3H_2(C_6H_5)]$ (**30**). All nonhydrogen atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of their electron density.

Table 2
Bond lengths in crystalline $Fe(CO)_2(C_5H_5)[SO_3C_3H_2(C_6H_5)]$ [a]

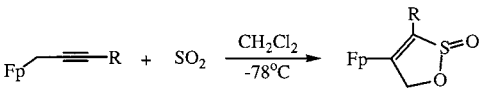
Type [b]	Length (Å)	Type [b]	Length (Å)
Fe1–C1	1.761(10)	Fe1–C6	2.085(8)
Fe1–C2	1.741(8)	Fe1–C7	2.086(8)
		Fe1–C8	2.110(8)
Fe1–C4	1.963(7)	Fe1–C9	2.100(8)
		Fe1–C10	2.073(8)
S1–O1	1.423(6)	Fe1–Cpg [c]	1.719(–)
S1–O3	1.427(6)		
S1–O2	1.575(5)	S1–C5	1.736(7)
O2–C3	1.450(8)	O4–C1	1.117(9)
		O5–C2	1.154(8)
C3–C4	1.484(10)	C6–C7	1.373(10)
C5–C11	1.478(10)	C6–C10	1.407(11)
		C7–C8	1.411(11)
C4–C5	1.356(9)	C8–C9	1.394(11)
		C9–C10	1.414(11)
C11–C16	1.376(11)	C13–C14	1.355(13)
C11–C12	1.394(10)	C14–C15	1.376(12)
C12–C13	1.361(10)	C15–C16	1.382(10)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Fig. 1.

[c] The symbol Cpg is used to represent the center of gravity for the 5-membered cyclopentadienyl ring; this value is therefore listed without an estimated standard deviation.

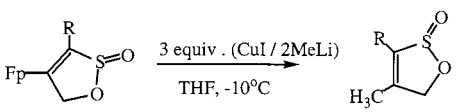
The transition-metal mediated [3 + 2] cycloadditions of the iron alkynyl complexes (**18**–**20**) with sulfur dioxide were performed under conditions analogous to prior work [2b,6b]. All the alkynyl complexes (**18**–**20**) cyclized to produce iron substituted 1,2-oxathiole-2-oxides (**23**–**25**) in good yield.



18 R = cyclohexenyl
19 R = (4-MeO)phenyl
20 R = (4-t-Bu)phenyl

23 R = cyclohexenyl, 76%
24 R = (4-MeO)phenyl, 67%
25 R = (4-t-Bu)phenyl, 67%

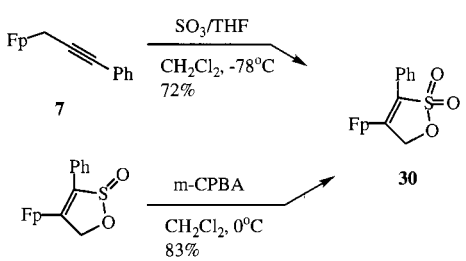
Treatment of **23** with perchloric acid, for the purpose of replacing the iron–ligand set with a proton, produced a complicated mixture of products, none of which resembled the desired product. Reaction of iron complex (**24**) with three equivalents of the highly THF soluble methyl cuprate [13] generated from copper(I) chloride, lithium chloride, and methyl lithium only produced a 14% yield of 1,2-oxathiole-2-oxide (**27**). Treatment of iron complex (**24**) with three equivalents of the standard methyl cuprate generated from copper(I) iodide and methyl lithium produced **27** in 23% yield. Similarly, when iron complexes **23** and **25** were treated with three equivalents of the same methyl cuprate, **26** and **28** were both isolated in 22% yield. Isolated yields of demetallated cycloadducts were probably diminished to some extent by competitive ring opening reactions of **26**–**28** that these nucleophilic conditions might induce [14].



23 R = cyclohexenyl
24 R = (4-MeO)phenyl
25 R = (4-t-Bu)phenyl

26 R = cyclohexenyl (22%)
27 R = (4-MeO)phenyl (23%)
28 R = (4-t-Bu)phenyl (22%)

In the early 1970s, Wojcicki [12a,b] and Roustan [12c] independently reported the [3 + 2] cycloaddition of the iron complex (**7**) with the SO_3–dioxane adduct to produce **30** in 66% yield. We found that sulfur trioxide, which had been precomplexed with THF, worked similarly as expected. Metal substituted 1,2-oxathiole-2,2-dioxide (**30**) can also be prepared by *m*-chloroperoxybenzoic acid (mCPBA) oxidation of the monoxide (**29**) [2b]. In practice this later route was more convenient for us because of the extreme moisture sensitivity of sulfur trioxide.



Iron sultone (**30**) was characterized by single crystal X-ray crystallography. The molecular structure of compound **30** is shown in Fig. 1. Table 1 contains crystal data and structure refinement information. Tables 2 and 3 contain selected bond lengths and angles of **30**.

The average Fe–C(carbonyl) distance and the average Fe–Cp centroid distance are both in agreement with those previously observed in similar complexes [2e,13]. The average Fe–C_{vinyl} bond length is 1.963 (4) Å, which is similar to values reported for other Fp complexes containing a sulfur which is γ to iron [2e,15]. The average C=C bond distance in the sultone ring is 1.356(9) Å, which is similar to the one we found previously in a related iron substituted 1,2-oxathiole-2-oxide (1.301(6) Å) [2b].

Wojcicki had reported that sultone (**30**) was much more stable to acid than related iron complexes [12b]. They report recovery of unreacted **30** from 1 h of exposure to HCl saturated CH_2Cl_2 at 25°C, conditions which would decompose the sultines reported here. We found that when iron sultone (**30**) was treated with perchloric acid, sultone (**31**) could be isolated in 17% yield. Likewise, we found that the use of copper(I) chloride and two equivalents of lithium chloride to produce a more THF soluble dimethylcuprate [13] produced sultone (**32**) in 31% yield.

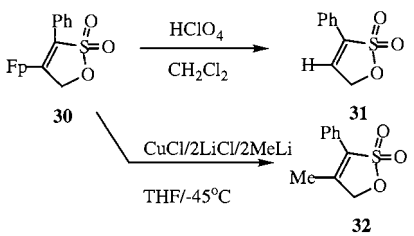


Table 3
Bond angles in crystalline $Fe(CO)_2(C_5H_5)[SO_3C_3H_2(C_6H_5)]$ [a]

Type [b]	Angle (°)	Type [b]	Angle (°)
C2–Fe1–C1	91.8(4)	C2–Fe1–C4	94.6(4)
C1–Fe1–C4	91.5(3)	C2–Fe1–C10	158.5(4)
C4–Fe1–C7	148.5(3)	C1–Fe1–C10	99.9(4)
C2–Fe1–C9	131.0(4)	C4–Fe1–C10	103.0(3)
C1–Fe1–C9	137.1(4)	C2–Fe1–C6	122.6(4)
C4–Fe1–C9	87.2(3)	C1–Fe1–C6	92.3(3)
C2–Fe1–C8	96.6(4)	C4–Fe1–C6	142.4(3)
C1–Fe1–C8	156.8(3)	C2–Fe1–C7	92.4(4)
C4–Fe1–C8	109.3(3)	C1–Fe1–C7	119.0(3)
O1–S1–O3	116.5(4)	O1–S1–C5	111.7(4)
O1–S1–O2	108.2(4)	O3–S1–C5	113.7(3)
O3–S1–O2	108.2(4)	O2–S1–C5	96.4(3)
C3–O2–S1	111.3(4)	O4–C1–Fe1	178.9(8)
O5–C2–Fe1	175.9(8)	O2–C3–C4	110.9(6)
C4–C5–C11	131.4(7)	C5–C4–C3	110.2(6)
C4–C5–S1	110.9(6)	C5–C4–Fe1	131.8(6)
C11–C5–S1	117.7(6)	C3–C4–Fe1	117.9(5)
C16–C11–C5	121.5(7)	C12–C11–C5	119.8(7)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Fig. 1.

4. Summary

In summary, we have extended metal alkynyl–SO_2 [3 + 2] cyclization reactions to produce new manganese and iron substituted 1,2-oxathiole-2-oxides. The iron substituted heterocycles can be demetallated but the manganese complexes could not. We also report the first crystal structure of a metal substituted 1,2-oxathiole-2,2-dioxide and the first demetallation reactions of this family of complexes. We will report on the biological activity of these new heterocycles in due course.

5. Supplementary material

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 **30** have been deposited at the Cambridge Crystallographic Data Centre (CCDC no. 136602).

Acknowledgements

We thank the NIH NIGMS and the Camille and Henry Dreyfus Foundation (Henry Dreyfus Teacher–Scholar Award to M.E. Welker, 1994–1999) for their support. Low resolution mass spectra were obtained on an instrument purchased with the partial support of NSF (CHE-9007366). The Duke University Center for Mass Spectrometry performed high resolution mass spectral analyses.

References

[1] For reviews of transition-metal mediated [3 + 2] cycloadditions see: (a) M.E. Welker, Chem. Rev. 92 (1992) 97. (b) D.M.T. Chan, in: B.M. Trost (Ed.), Comprehensive Organic Syntheses, vol. 5, Pergamon, New York, 1991, p. 271. (c) A. Wojcicki, Coord. Chem. Rev. 105 (1990) 35. (d) M. Rosenblum, J. Organomet. Chem. 300 (1986) 191.

[2] (a) B.L. Hayes, M.E. Welker, Organometallics 17 (1998) 5534. (b) A.L. Hurley, M.E. Welker, C.S. Day, Organometallics 17 (1998) 2832. (c) H.L. Stokes, L.M. Ni, J.A. Belot, M.E. Welker, J. Organomet. Chem. 487 (1995) 95. (d) L.M. Ni, J.A. Belot, M.E. Welker, Tetrahedron Lett. 33 (1992) 177. (e) M.E. Raseta, R.K. Mishra, S.A. Cawood, M.E. Welker, A.L. Rheingold, Organometallics 10 (1991) 2936. (f) M.E. Raseta, S.A. Cawood, M.E. Welker, A.L. Rheingold, J. Am. Chem. Soc. 111 (1989) 8268.

[3] T.W. Kensler, J.D. Groopman, T.R. Sutter, T.J. Curphey, B.D. Roebuck, Chem. Res. Toxicol. 12 (1999) 113.

[4] (a) M. Huang, A. Maynard, J.A. Turpin, L. Graham, G.M. Janini, D.G. Covell, W.G. Rice, J. Med. Chem. 41 (1998) 1371. (b) W.G. Rice, D.C. Baker, C.A. Schaeffer, L. Graham, M. Bu, S. Terpening, D. Clanton, R. Schultz, J.P. Bader, R.W. Buckheit, L. Field, P.K. Singh, J.A. Turpin, Antimicrob. Agents Chemother. 41 (1997) 419. For a review see: W.G. Rice, J.A. Turpin, Rev. Med. Virol. 6 (1996) 187.

[5] J.P. Williams, A. Wojcicki, Inorg. Chem. 16 (1977) 3116.
[6] (a) J.L. Roustan, P. Cadiot, C.R. Acad. Sci. 268 (1969) 734. (b) J.E. Thomasson, P.W. Robinson, D.A. Ross, A. Wojcicki, Inorg. Chem. 10 (1971) 2130.
[7] R. Baudouy, F. Delbecq, F. Gore, Tetrahedron 36 (1980) 189.
[8] (a) Z.Y. Yang, D.J. Burton, Tetrahedron 31 (1990) 1369. (b) Y. Kondo, S. Kojima, T. Sakamoto, J. Org. Chem. 62 (1997) 6507.
[9] D.H. Wadsworth, S.M. Geer, M.R. Detty, J. Org. Chem. 52 (1987) 3662.
[10] M.A. Harris, I. McMillan, J.H.C. Nayler, N.F. Osborne, M.J. Pearson, R. Southgate, J. Chem. Soc. Perkin Trans. I (1976) 1612.
[11] W.D. Bannister, B.L. Booth, R.L. Haszeldine, P.L. Loader, J. Chem. Soc. A (1971) 930.
[12] (a) D.W. Lichtenberg, A. Wojcicki, J. Organomet. Chem. 33 (1971) C77. (b) D.W. Lichtenberg, A. Wojcicki, Inorg. Chim. Acta 7 (1973) 311. (c) J.L. Roustan, J.Y. Merour, J. Benaim, C. Charrier, Acad. Sci. Ser. C 274 (1972) 537.
[13] R.K. Dieter, R.R. Sharma, W. Ryan, Tetrahedron Lett. 38 (1997) 783.
[14] (a) R.M.J. Liskamp, H.J.M. Zeegers, H.C.J. Ottenheijm, J. Org. Chem. 46 (1981) 5408. (b) F. Jung, N.K. Sharma, T. Durst, J. Am. Chem. Soc. 95 (1973) 3420. (c) D.N. Harpp, S.M. Vines, J.P. Montillier, T.H. Chan, J. Org. Chem. 41 (1976) 3987. (d) T.G. Squires, C.G. Venier, B.A. Hodgson, L.W. Chang, F.A. Davis, T.W. Panunto, J. Org. Chem. 46 (1981) 2373.
[15] D.A. Ross, J.E. Thomasson, A. Wojcicki, M.R. Churchill, J. Wormald, J. Am. Chem. Soc. 92 (1970) 1795.