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Investigation of a transition metal-assisted retro Diels–Alder reaction used in the synthesis of transition metal S_2O complexes

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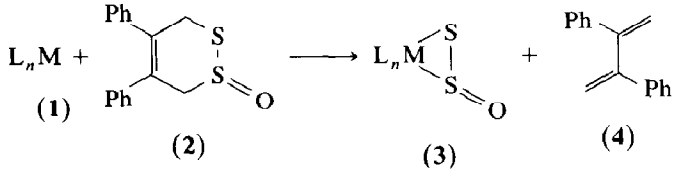
Abstract

Treatment of 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide with coordinatively unsaturated transition metal complexes resulted in the production of S_2O complexes and 2,3-diphenylbutadiene. A transition metal-assisted retro Diels–Alder mechanism has been proposed for this reaction. A series of IR and ^1H NMR experiments and MNDO calculations on 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide have been performed to gain additional information about this transformation.

Introduction

We recently reported a synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide (**2**) and its use in the synthesis of transition metal S_2O complexes [1]. Here, we provide full experimental details of an optimized synthesis of **2** and the S_2O complexes (**3**). At that time, we postulated that **2** served as a S_2O source via a transition metal-assisted retro Diels–Alder reaction. Two other examples of transition metal-assisted retro Diels–Alder reactions have been reported [2] and retro Diels–Alder reactions have been used to generate singlet oxygen and singlet sulfur [3,4]. Disulfur monoxide (S_2O) precursor (**2**) is stable for extended periods of time in the absence of coordinatively unsaturated transition-metal complexes and we were interested in the nature of the interaction between **2** and the metal which might initiate bond cleavage in **2**. Structures such as **5**, **6**, and **7** can be postulated as likely intermediates. We have performed additional infrared and ^1H NMR experiments to elucidate which of these intermediates, if any, may be present.



(1) (2) (3) (4)

(L$_n$M = Ir(diphos)$_2^+$Cl$^-$, CpMe$_n$Mn(CO)$_2$(thf), $n = 1, 5$)

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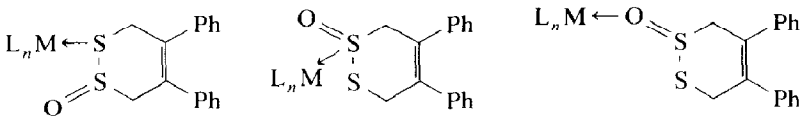
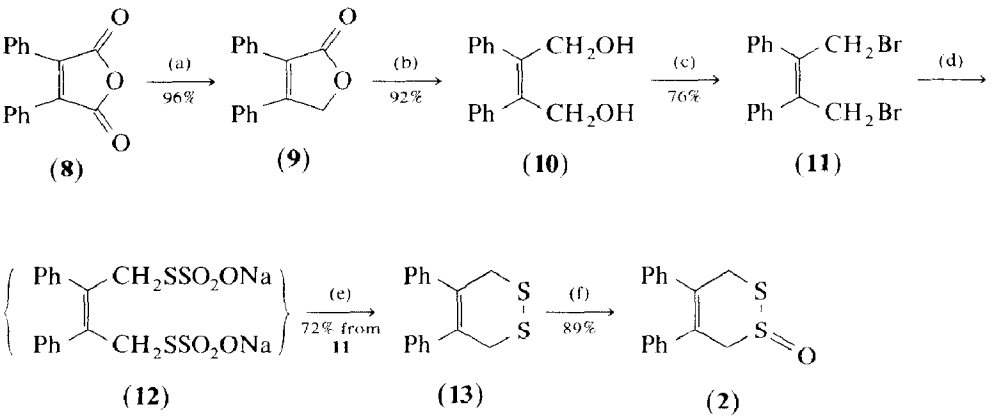


(5) (6) (7)

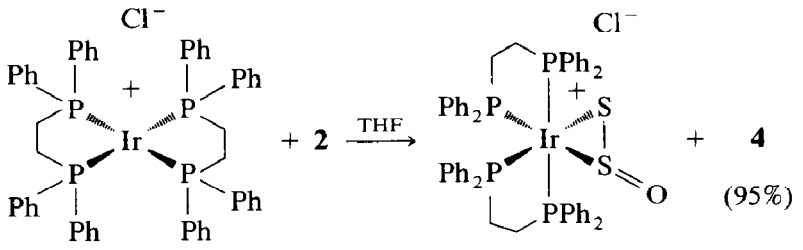
Results and discussion

Our synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide (**2**) (Scheme 1) begins with a stepwise reduction of 2,3-diphenylmaleic anhydride (**8**) [5] to yield (*Z*)-2,3-diphenyl-2-buten-1,4-diol (**10**) [6]. Direct reduction of **8** to **10** ($LiAlH_4$, Et_2O, reflux) resulted in isolation of **10** in only 41% yield. This is presumably due to C=C reduction competing with carboxylate anion reduction at elevated temperatures. Diol (**10**) was then treated with phosphorus tribomide to yield (*Z*)-1,4-dibromo-2,3-diphenyl-2-butene (**11**) [7]. This dibromide (**11**) was then treated with an excess of sodium thiosulfate which presumably reacted with **11** to form Bunte salt (**12**) [8]. The Bunte salt (**12**) was not isolated but was subjected to an oxidative workup to yield dithiin (**13**) [7]. Treatment of dithiin (**13**) with *m*-chloroperoxybenzoic acid yields dithiin-1-oxide (**2**) [7]. Neither dithiin (**13**) nor dithiin-1-oxide (**2**) are stable for extended periods of time in the presence of moisture, but both can be stored indefinitely in a desiccator. This scheme provides **2** on a 10–20 mmol scale in five steps in 43% overall yield.

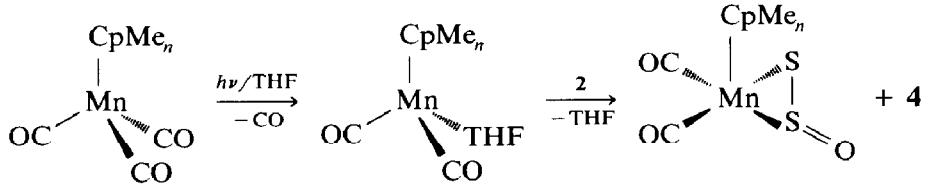


Scheme 1. (a) $LiAlH_4$, Et_2O, −20 °C; (b) $LiAlH_4$, Et_2O, −20 °C; (c) PBr_3, Et_2O, reflux; (d) $Na_2S_2O_3$, THF/H_2O, 1/1, reflux; (e) I_2, reflux; (f) mCPBA, CH_2Cl_2, 0–25 °C.

When **2** was added to a solution of the coordinatively unsaturated iridium complex (**14**) [9], a rapid reaction occurred to yield iridium S_2O complex (**15**) [10] and 2,3-diphenylbutadiene (**4**) [11]. Similarly, when manganese complexes (**18**) and (**19**) were treated with **2** reaction occurred to yield manganese S_2O complexes (**20**) and (**21**) [12].



(14) (80%) (15) (95%)



(16 $n = 1$, 17 $n = 5$) (18 $n = 1$, 19 $n = 5$) (20 $n = 1$ (56%), 21 $n = 5$ (59%))

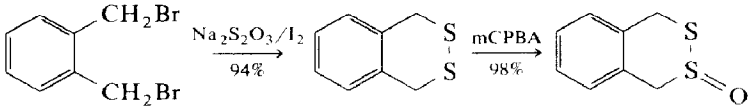
In order to gain additional information about the mechanism of these unusual transformations, we first performed a series of qualitative ^{1}H NMR experiments in which **2** was treated with equimolar amounts of "hard" and "soft" Lewis acids [13]. We reasoned that "hard" Lewis acids would bind at oxygen (**7**) and that "soft" Lewis acids could bind through the sulfenyl (**5**) or sulfinyl (**6**) sulfur. The results of similar experiments with sulfoxides have been reported [14]. Through these experiments we hoped to be able to differentiate the importance of intermediates such as **5** and **6** from **7** in the formation of S_2O complexes from **2**. The results of these experiments are presented in Table 1.

These NMR tube experiments were monitored by following appearance of **4** and disappearance of **2**. These data suggest that when **2** is treated with a "soft" Lewis acid a rapid transition metal-assisted retro Diels–Alder reaction can be expected. However, when a "hard" Lewis acid is used the retro Diels–Alder reaction will be slow. Reaction may occur slowly through **7** or **7** may be in equilibrium with a small amount of **5** or **6** which undergo the retro Diels–Alder reaction. The fact that **2** is relatively stable in the presence of a "hard" Lewis acid may prove useful to us if we need to activate it toward nucleophilic attack.

Table 1

Relative rates of transition-metal assisted retro Diels–Alder reactions of **2**

2 + $Ir(diphos)_2^+ Cl^-$	(0.1 *M*/$CDCl_3$/25 °C)	complete reaction <1 min
2 + AgFOD	(0.1 *M*/$CDCl_3$/25 °C)	complete reaction <1 min
2 + $Eu(FOD)_3$	(0.1 *M*/$CDCl_3$/25 °C)	slow (5% reaction after 2 h, complete reaction after 48 h).
2 + CF_3CO_2H	(0.1 *M*/$CDCl_3$/25 °C)	slow, (14% reaction after 48 h).

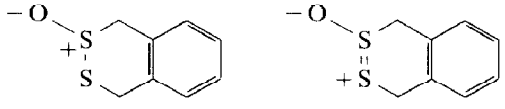


(22) (23) (24)

Scheme 2

Due to the fact that **2** reacted so rapidly with "soft" Lewis acids, we did not consider it a good candidate for detailed studies of the interactions of cyclic thiosulfinate esters with metals by IR and ^{1}H NMR. We instead chose to synthesize **24** (by a procedure analogous to that used to synthesize **2**, Scheme 2) as a model thiosulfinate ester for these studies [15].

Our NMR studies with **2** had allowed us to get some qualitative information about the rate of this retro Diels–Alder reaction but we needed more concrete information about the nature of the intermediates involved. For the infrared studies, we postulated again that "hard" Lewis acids would bind **24** through oxygen and that the SO stretching frequency would decrease when oxygen electron density is tied up in binding to the metal (**25**) [14a,c,d]. $Eu(FOD)_3$ has been shown to bind with acyclic thiosulfinate esters exclusively through oxygen previously [16]. "Soft" Lewis acids could bind through the sulfenyl (**5**) or sulfinyl (**6**) sulfur. Binding at the sulfinyl sulfur should result in a decrease in the observed SO stretching frequency for metals in low oxidation states with π-donor capability [14b]. However, binding at the sulfinyl sulfur should result in an increase in the observed SO stretching frequency for metals in high oxidation states due to decreased ability to back bond into S=O π^* [14a,c,d]. Binding at the sulfenyl sulfur should result in an observed increase in the SO stretching frequency due to a decreased contribution to the structure of **24** from a resonance contributor like **26**. The SO stretching frequencies for **24** and the adducts formed when treated with one equivalent of various Lewis acids are given in Table 2.



(25) (26)

When **24** was treated with Eu^{III} or CF_3CO_2H, the observed SO stretching frequency decreased as expected. This is consistent with binding through oxygen. When **24** was treated with AgFOD, the SO stretching frequency increased. This is

Table 2

SO stretching frequencies for **24** and adducts of **24**

		ν(SO) ($CDCl_3$, cm^{-1})
24		1070
24	$+CF_3CO_2H$	1027
24	$+Eu(FOD)_3$	1032
24	+AgFOD	1080
24	$+Ir(diphos)_2^+Cl^-$	1078

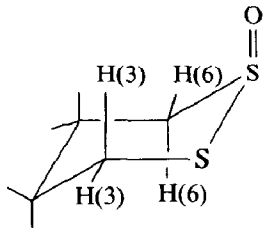
Table 3

Methylene proton chemical shifts (ppm) for **24** and adducts of **24**

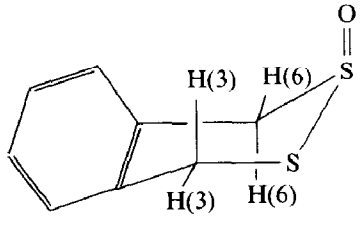
		$H(3)_{ax}$	$H(3)_{eq}$	$H(6)_{ax}$	$H(6)_{eq}$
24		4.37	3.94	4.21	4.32
24	+ $Eu(FOD)_3$	7.49	6.12	4.99	6.02
24	+ CF_3CO_2H	4.52	3.98	4.28	4.43
24	+ AgFOD	4.38	3.95	4.22	4.32
24	+ $Ir(diphos)_2^+ Cl^-$	4.30	3.93	4.18	4.29

consistent with binding through the sulfenyl sulfur. Finally, when $Ir(diphos)_2^+Cl^-$ was treated with **24** the SO stretching frequency increased as well. These infrared data are most consistent with involvement of an intermediate of structure **5** in the formation of **15**, **20**, and **21**.

Additional evidence for the modes of binding proposed for **24** above comes from ^1H NMR experiments. The results of these experiments are presented in Table 3.



(27)



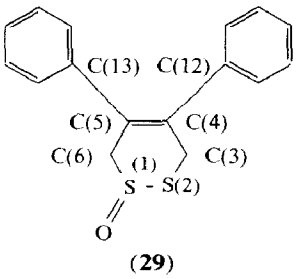
(28)

Assignment of H(3) and H(6) protons in **24** was made using standard homonuclear decoupling experiments and comparisons to the known compound, 4,4,5,5-tetramethyl-1,2-dithiane-1-oxide (**27**) [17]. This assumes that the dithiin ring in **24** will adopt a pseudo chair conformation (**28**) (similar to that **2** is predicted to adopt by MNDO calculations, see below). "Hard" Lewis acids $Eu(FOD)_3$ and CF_3CO_2H induce downfield shifts in $H(3)_{ax}$. Similar effects have been noted with shift reagents on other cyclic thiosulfinate esters [18]. "Soft" Lewis acid, AgFOD, has very little effect on the ^1H NMR spectrum of **24** whereas addition of $Ir(diphos)_2^+Cl^-$ to **24** actually induces a small upfield shift in all H(3) and H(6) protons. A similar upfield shift of methylene protons (3.69 to 3.60) was noted when dithiin (**13**) (which can only bind through sulfur) was treated with $Ir(diphos)_2^+Cl^-$.

Finally, MNDO calculations were performed on **2** in hopes of shedding additional light on its unusual reactivity. From these calculations, the 3,6-dihydro-1,2-dithiin-1-oxide ring is predicted to adopt a pseudo chair conformation with a C(3)–S(2)–S(1)–C(6) twist angle of −0.8°, and S(1)–S(2)–C(3)–C(4) and S(2)–S(1)–C(6)–C(5) twist angles of 5.7° and −5.4°, respectively. The phenyl groups are slightly offset from being coplanar (a C(12)–C(4)–C(5)–C(13) twist angle of 9°) and perpendicular to the 3,6-dihydro-1,2-dithiin-1-oxide ring. The C(6)–S(1) bond is predicted to be longer than the C(3)–S(2) bond. The C(3)–S(2) bond order is 0.98, however, the C(6)–S(1) bond order is only 0.87.

The net atomic charges (as compared to the sulfur atom) are polarized in **2** with S(2) being negative (−0.26) and S(1) positive (+0.78). The C(6)–C(5) distance (1.38

Å) is considerably shorter than the C(3)–C(4) distance (1.46 Å). The two hydrogens attached to C(6) have H–C(6)–S(1) bond angles of 98° and 100°.



(29)

On the basis of this theoretical and experimental work, we now postulate that **2** binds to "soft" transition metal complexes such as **14**, **18**, and **19** through the sulfenyl sulfur yielding an intermediate of structure **5**. Removal of electron density from sulfenyl sulfur S(2) upon binding should then accelerate cleavage of the weakest (C(6)–S(1)) carbon–sulfur bond. The differences in C(6)–C(5) and C(3)–C(4) bond lengths are consistent with the idea that the S(1)–C(6) bond breaks first and the H–C(6)–S(1) bond angles would suggest that C(6) more readily transforms into a sp^2 carbon. Transition metal initiation of this retro Diels–Alder reaction accounts for the isolated products **15**, **20**, **21**, and **4**.

Future efforts will be directed at investigation of the use of transition-metal S_2O complexes in thiosulfinate ester synthesis [19].

Experimental

General

All infrared spectra were recorded on Perkin Elmer 1330 or 1620 infrared spectrophotometers. Nuclear magnetic resonance spectra were obtained at 200 MHz on a Varian VXR-200. All ^1H NMR absorptions were expressed in parts per million (δ) relative to residual $CHCl_3$ in $CDCl_3$. Melting points were determined on a Mel–Temp melting point apparatus and were reported uncorrected. Combustion analyses were performed by Atlantic Microlab, Inc. 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. MNDO calculations were performed on a Digital Equipment Corporation VAX 11/780 using MOPAC version 3.10 and the MNDO Hamiltonian [20]. All bond distances, angles, and torsion angles were fully optimized (heat of formation on two successive RHF SCF cycles differed by less than 2 cal/mol) except those comprising the phenyl substituents. These groups were defined as planar, with bond angles of 120°, C–C distances of 1.39 Å, and C–H distances of 1.05 Å. The geometry of the phenyl groups with respect to their orientation to the 3,6-dihydro-1,2-dithiin-1-oxide ring was included in the optimization. Tables of interatomic distances, atomic charges, bond orders, and eigenvectors are available from the author upon request.

*3,4-Diphenyl-2(5H)-furanone (**9**).* Lithium aluminum hydride (0.758 g, 20.0 mmol) was added to diethyl ether (200 ml) with stirring. The solution was then cooled (−20°C) and 2,3-diphenylmaleic anhydride (**8**) [5] (5.00 g, 20.0 mmol) was

added in small portions. The solution was stirred for 0.75 h at −20 °C after which time TLC analysis (silica gel; 1/1 petroleum ether/diethyl ether) showed no unreacted 2,3-diphenylmaleic anhydride (**8**). Aqueous HCl (200 ml of a 1.2 *M* solution) was then added and an extraction (diethyl ether, 2 × 75 ml) was performed. The combined organic extracts were washed with water (50 ml) and dried ($MgSO_4$). Removal of solvent by rotary evaporation and high vacuum yielded (**9**) as a light yellow solid (4.60 g, 96%), sufficiently pure (> 90% by NMR) for further manipulations. Analytically pure material can be obtained by recrystallization from dichloromethane/petroleum ether; m.p. 114–116 °C, (lit. [6] 115–116 °C), IR (CH_2Cl_2, cm^{-1}): 1738, 1055, 1029, 950; ^1H NMR ($CDCl_3$): 7.49–7.28 (m, 10H), 5.16 (s, 2H).

*(Z)-2,3-Diphenyl-2-buten-1,4-diol (**10**).* Lactone (**9**) (4.60 g, 19.5 mmol) was dissolved in diethyl ether (200 ml). The solution was then cooled to −20 °C and lithium aluminum hydride (1.11 g, 29.2 mmol) was added in small portions with stirring. The solution was maintained at −20 °C for 0.5 h then allowed to warm to room temperature over 1 h. After a workup analogous to that used for **9**, **10** was obtained as a light yellow solid (4.26 g, 92%) sufficiently pure (> 90% by NMR) for use in subsequent transformations. If desired this material can be purified by chromatography (silica gel, 230–400 mesh, diethyl ether), m.p. (CH_2Cl_2/petroleum ether) 85–87 °C, (lit. [6] 86.5–87.5 °C), IR ($CDCl_3$, cm^{-1}): 3360br, 3019, 2920, 1625, 1598, 1488, 1439, 1035, 1018, 985, 905; ^1H NMR ($CDCl_3$): 7.19–6.95 (m, 10H), 4.64 (s, 4H), 2.93 (br s, 2H).

*(Z)-1,4-Dibromo-2,3-diphenyl-2-butene (**11**).* Diol (**10**) (4.26 g, 17.9 mmol) was dissolved in diethyl ether (100 ml) and 10 drops of pyridine were added. A solution of phosphorus tribomide (1.7 ml, 17.9 mmol) in diethyl ether (20 ml) was then added to the diol solution at room temperature. After the PBr_3 addition was complete the solution was refluxed for 1 h. The solutition was then cooled in an ice bath and water (50 ml) was added. This aqueous layer was extracted (diethyl ether, 2 × 50 ml), the combined organic extracts were dried ($MgSO_4$) and the solvent removed by rotary evaporation and high vacuum to yield **11** (5.00 g, 76%) as a light yellow solid sufficiently pure (> 90% by NMR) for further manipulations. If desired this material can be purified by chromatography (silica gel, 230–400 mesh, 10/1 petroleum ether/diethyl ether). m.p. (CH_2Cl_2/petroleum ether) 98–100 °C, (lit. [7] 101–102 °C), IR (CH_2Cl_2, cm^{-1}): 3006, 1596, 1571, 1198, 1112, 1069, 1028; ^1H NMR ($CDCl_3$): 7.30–7.04 (m, 10H), 4.54 (s, 4H).

*4,5-Diphenyl-3,6-dihydro-1,2-dithiin (**13**).* Dibromide (**11**) (5.00 g, 13.7 mmol) was dissolved in tetrahydrofuran (30 ml). Water (30 ml) was then added along with sodium thiosulfate (5.40 g, 34.1 mmol). The solution was refluxed for 1.5 h after which time iodine (8.66 g, 34.1 mmol) was added in small portions. Reflux was maintained for 1 h after iodine addition. The solution was then cooled to room temperature and extracted with diethyl ether (2 × 50 ml). The combined organic extracts were washed with aqueous sodium bisulfite (2 × 50 ml) and water (50 ml) and finally dried ($MgSO_4$). The solvent was removed by rotary evaporation to yield a light brown oil which was chromatographed (silica gel, 230–400 mesh, 10/1 petroleum ether/diethyl ether) to yield dithiin (**13**) (2.64 g, 72%) as a light yellow solid; m.p. (CH_2Cl_2/petroleum ether) 99–100 °C, (lit. [7] 101–102 °C), IR (CH_2Cl_2, cm^{-1}) 1595, 1572, 1109, 1065, 1049, 1025; ^1H NMR ($CDCl_3$) 7.19–6.94 (m, 10H), 3.69 (s, 4H).

4,5-Diphenyl-3,6-dihydro-1,2-dithiin-1-oxide (2). Dithiin (**13**) (2.40 g, 8.87 mmol) was dissolved in freshly distilled dichloromethane (50 ml) and the solution was cooled (0 °C). *m*-Chloroperoxybenzoic acid (85%, 1.80 g, 8.87 mmol) was also dissolved in dichloromethane (15 ml) and added to the dithiin (**13**) solution dropwise. After the addition of the mCPBA the solution was allowed to warm to 25 °C and stir 1 h. The solution was then cooled to −45 °C and the precipitated *m*-chlorobenzoic acid byproduct removed by vacuum filtration. The solvent was then removed by rotary evaporation to yield a light yellow solid. This crude product was triturated once with diethyl ether (10 ml) at 0 °C to remove the last traces of mCBA. After trituration, dithiin-1-oxide (**2**) was obtained as a white solid (2.25 g, 89%); m.p. (CH_2Cl_2/petroleum ether) 125–127 °C, (lit. [7] 126–127 °C), IR ($CDCl_3$, cm^{-1}): 3059, 3022, 2915, 1596, 1436, 1131, 1068vs, 1031; ^1H NMR ($CDCl_3$): 7.22–7.02 (m, 10H), 4.48 (d, *J* 14Hz, 1H), 4.25 (d, *J* 13Hz, 1H), 3.70 (d, *J* 14Hz, 1H), 3.67 (d, *J* 13Hz, 1H).

Ir(diphos)$_2$(S$_2$O)Cl (15) [10]. 4,5-Diphenyl-3,6-dihydro-1,2-dithiin-1-oxide (**2**) (0.028 g, 0.098 mmol) was dissolved in dichloromethane (10 ml) and the solution was degassed with nitrogen. Ir(diphos)$_2$Cl (**14**) [9] (0.100 g, 0.098 mmol) was then added under nitrogen. The color of the solution rapidly changed from orange to yellow. The solution was allowed to stir at 25 °C for 1 h, then the solvent was removed by rotary evaporation. The crude product was triturated with diethyl ether (2 × 5 ml) to remove 2,3-diphenylbutadiene (**4**) (0.019 g, 95%) (identified by spectral comparison to an authentic sample) [11] from **15** (0.086 g, 80%); m.p. (CH_2Cl_2/petroleum ether) 200–202 °C, IR (CH_2Cl_2, cm^{-1}): 1601, 1570, 1155, 1093, 1042vs, 999; ^1H NMR ($CDCl_3$): 7.82–6.79 (m, 36H), 6.45–6.18 (m, 4H), 2.80–2.00 (m, br, 8H).

MeCpMn(CO)$_2$(S$_2$O) (20). Methylcyclopentadienylmanganese tricarbonyl (**16**) (Strem Chemical Co.) (0.148 g, 0.68 mmol) was dissolved in tetrahydrofuran (150 ml) and photolyzed (Hanovia 450W Photochemical Reactor w/quartz filter) for 1.5 h. Dithiin-1-oxide (**2**) (0.195 g, 0.68 mmol) was then added under nitrogen. The red color of the solution slowly darkened and the solution was allowed to stir for 2 h at 25 °C. The solvent was then removed by rotary evaporation and the crude product purified by column chromatography (silica gel). Elution with 1/1 CH_2Cl_2/petroleum ether yielded **4** and a trace amount of a green Mn disulfur complex [12]. Elution with tetrahydrofuran yielded **20** (0.101 g, 56%) as a red solid: m.p. (CH_2Cl_2/petroleum ether) 106–107 °C, IR ($CDCl_3$, cm^{-1}): 2010, 1972, 1051; ^1H NMR ($CDCl_3$): 5.00 (s, br, 2H), 4.72 (s, br, 2H), 1.95 (s, br, 3H); Anal. Found: C, 35.82; H, 2.68, S, 23.44. $C_8H_7MnS_2O_3$ calcd.: C, 35.56; H, 2.61; S, 23.69%.

Me$_5$CpMn(CO)$_2$(S$_2$O) (21) [12]. Pentamethylcyclopentadienylmanganese tricarbonyl (**17**) (Strem Chemical Co.) (0.110 g, 0.40 mmol) was dissolved in tetrahydrofuran (200 ml) and photolyzed using a procedure analogous to that described for **20**. Dithiin-1-oxide (**2**) (0.114 g, 0.40 mmol) was then added under nitrogen and the solution color changed from dark red to dark orange. The solution was allowed to stir at 25 °C for 2 h and then worked up and isolated by a procedure analogous to that used for **20** above to yield **21** as a red solid (0.077 g, 59%); m.p. (CH_2Cl_2/petroleum ether) 146–150 °C, (lit. [12] 140–145 °C); IR ($CDCl_3$, cm^{-1}): 2018, 1968, 1049; ^1H NMR ($CDCl_3$): 1.78 (s, br, 15H).

1,4-Dihydro-2,3-benzodithiin (23) [21]. α,α'-Dibromo-*o*-xylene (**22**) (Aldrich Chemical Co.) (5.00 g, 18.9 mmol) was dissolved in tetrahydrofuran/water (1/1,

200 ml). Sodium thiosulfate (6.29 g, 39.8 mmol) was added and the solution refluxed (1.5 h). Iodine (10.10 g, 39.8 mmol) was introduced and the reflux was maintained for an additional 1 h. After cooling, the solution was extracted with diethyl ether (2 × 75 ml) and the organic extracts then washed with aqueous sodium bisulfite (75 ml) and water (75 ml). The extracts were then dried ($MgSO_4$) and the solvent removed by rotary evaporation and high vacuum to yield **23** as light yellow crystals (2.98 g, 94%). If desired this material can be recrystallized from methanol. m.p. 76–78°C (lit. [19] 77–78°C) IR (CH_2Cl_2, cm^{-1}): 3001, 2960, 2880, 1568, 1385, 1148, 1093, 942, 838; ^1H NMR ($CDCl_3$): 7.26–7.13 (m, 2H), 7.13–7.03 (m, 2H), 4.07 (s, 4H).

1,4-Dihydro-2,3-benzodithiin-2-oxide (24) [15]. 1,4-Dihydro-2,3-benzodithiin (**23**) (2.98 g, 17.7 mmol) was dissolved in dichloromethane (50 ml) and the solution cooled to 0°C. *m*-Chloroperoxybenzoic acid (85%, 3.59 g, 17.7 mmol) was dissolved in dichloromethane (25 ml) and added to **23** dropwise. The mixture was then allowed to stir at 0°C for 1 h and 1 h at 25°C. The solution was then cooled to −45°C to precipitate the *m*-chlorobenzoic acid byproduct and filtered while cold. Removal of the solvent by rotary evaporation and trituration with cold diethyl ether (10 ml) yielded **24** as a light brown solid (3.23 g, 98%); m.p. 123–125°C (lit. [15] 128–129°C). If desired this material can be recrystallized from methanol. IR ($CDCl_3$, cm^{-1}): 3055, 3016, 2900, 1421, 1402, 1169, 1112, 1054vs; ^1H NMR ($CDCl_3$) 7.53–7.35 (m, 4H), 4.37 (d, *J* 14Hz, 1H), 4.32 (d, *J* 13Hz, 1H), 4.21 (d, *J* 13Hz, 1H), 3.94 (d, *J* 14Hz, 1H).

Typical experimental procedure for ^1H NMR experiments with 2

2 (0.020 g, 0.069 mmol) was dissolved in $CDCl_3$ (0.6 ml) in a standard 5 mm NMR tube. Toluene (10 μl, 0.094 mmol) was added as an internal standard followed by CF_3CO_2H (6 μl, 0.078 mmol). The reaction was monitored periodically for the appearance of 2,3-diphenylbutadiene (**4**).

Typical experimental procedure for IR and ^1H NMR experiments with 24

24 (0.020 g, 0.109 mmol) was dissolved in $CDCl_3$ (0.5 ml) in a standard 5 mm NMR tube. CF_3CO_2H (9 μl, 0.117 mmol) was added and the NMR tube was shaken vigorously. ^1H NMR spectra were recorded immediately thereafter and samples for IR spectra were taken directly from the NMR tube.

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