reactivity: we have only observed for 1 behavior of doubly bonded compound and never behavior of germylene $Mes_2Ge$ and phosphinidene ArP, as if the germanium–phosphorus connection was very weak.

**Registry No.** 1, 96481-35-5; 2, 96481-37-7; ArP(H)Li, 83115-13-3; 2,4,6-tri-*tert*-butylphenylphosphine, 83115-12-2; dimesityldifluorogermane, 96481-36-6.

**Supplementary Material Available:** A listing of the hydrogen atom positions (1 page); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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## Synthesis of a Stable Disulfur Monoxide Precursor and Trapping of Disulfur Monoxide with Transition-Metal Complexes

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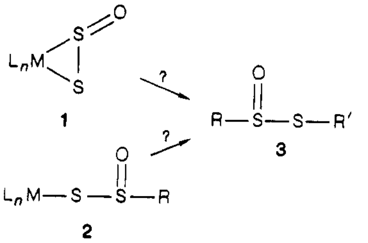
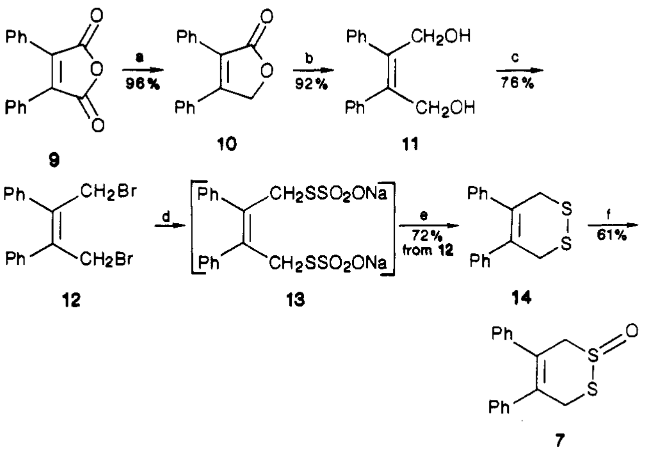
*Summary:* A five-step synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide starting from 2,3-diphenylmaleic anhydride is described. When the dithiin 1-oxide was treated with coordinatively unsaturated transition-metal complexes, a transition-metal disulfur monoxide complex and 2,3-diphenylbutadiene were isolated.

The ability of transition metals to stabilize small, reactive sulfur fragments such as sulfur monoxide (SO),[1] disulfur ($S_2$),[2] and trisulfur ($S_3$)[2b,3] offers chemists a chance to explore the reactivity of these molecules under mild, controlable conditions. Our goal within this active area of research is to synthesize transition-metal complexes containing the disulfur monoxide ($S_2O$) moiety in a variety of different bonding modes. Only two (1 and 2) of a variety of possibilities are shown below. Our hope is that the complexed $S_2O$ can be used as a template for the synthesis of thiosulfinate esters (3). The thiosulfinate esters (3) have shown interesting biological activities as antibacterials,[4] antifungals,[4] plant growth inhibitors,[5] and platelet aggregation inhibitors.[6]

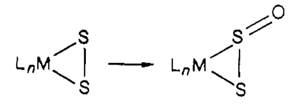


There are no reports in the literature of transition-metal $S_2O$ complexes obtained through the trapping of $S_2O$ and few reports of transition-metal $S_2O$ complexes 1 obtained through the oxidation of $S_2$ complexes 4.[1,2a,7] The reported mononuclear $S_2O$ complexes are presumed to contain $\eta^2$-$S_2O$ in all cases. Comparatively little is known about the reactivity of $S_2O$ in these complexes. Methylation on oxygen with methyl fluorosulfonate has been reported for an iridium complex.[7c] Reaction with triphenylphosphine and oxidation of complexed $S_2O$ have also been reported.[7b,e]

**Scheme I**[a]

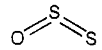


[a] (a) $LiAlH_4$, $Et_2O$, −20 °C. (b) $LiAlH_4$, $Et_2O$, −20 °C. (c) $PBr_3$, $C_6H_6$, 25–45 °C, 1 h. (d) $Na_2S_2O_3$, $THF/H_2O$, 1:1, reflux, 1.5 h; (e) $I_2$, reflux, 1 h. (f) mCPBA, $CH_2Cl_2$, 0–25 °C, 1 h.



4 1

In order to be able to trap $S_2O$ and study its reactivity, a method for clean, reproducible $S_2O$ generation is required. Free disulfur monoxide (5), structurally similar to sulfur dioxide (6),[8] is an extremely reactive molecule unless stored at very low pressures in the gas phase.[9] Disulfur monoxide has been produced in the past for synthetic purposes by the vacuum pyrolysis of $SOCl_2$ over $Ag_2S$ at 160 °C,[10] by pyrolysis of thiirane 1-oxide,[11] and by pyrolysis of a mixture of cupric oxide and sulfur.[11] All of these methods produce $S_2O$ which is contaminated to varying degrees with $SO_2$ and SO, making them impractical as $S_2O$ sources for transition-metal complex trapping studies. We set out to synthesize an air-stable, crystalline compound (7) which we hoped would yield $S_2O$ via a transition-metal-induced retro Diels–Alder reaction.[12]



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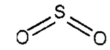

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(10) Schenk, P. W.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 61.

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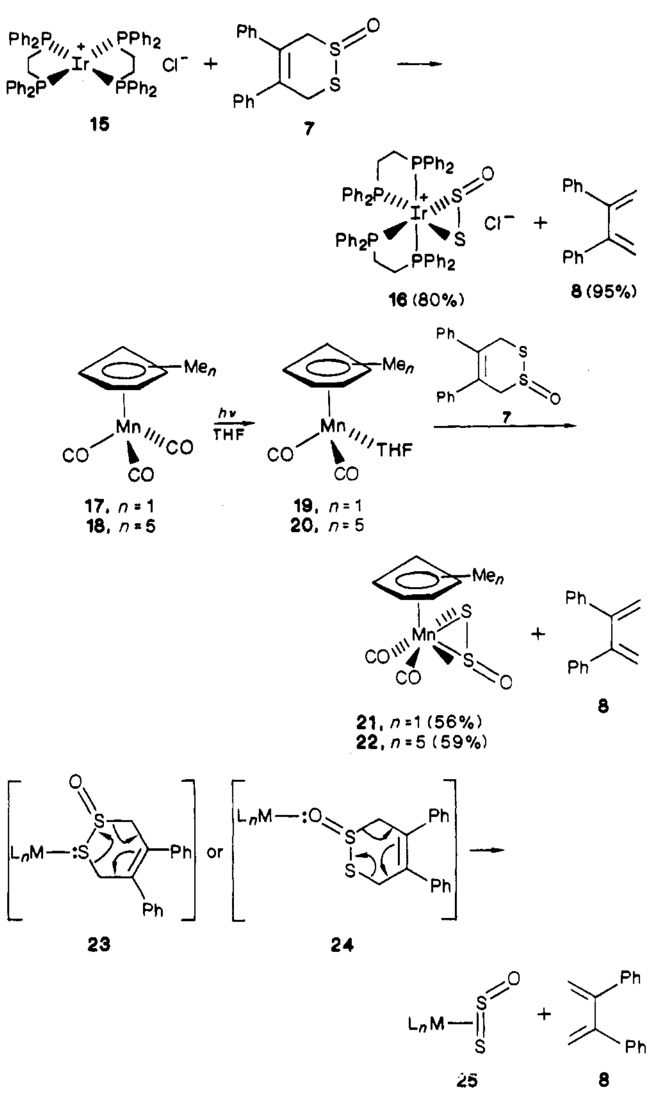
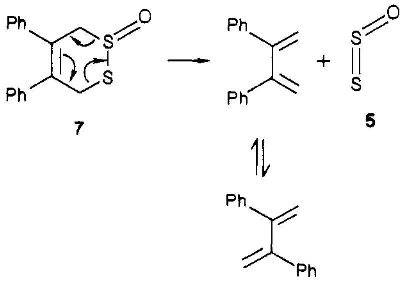
0276-7333/88/2307-1013$01.50/0

Scheme II



4,5-Diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (7) has been synthesized once previously in five steps (2% overall yield) and was reported to "decompose on drying in vacuo at 80 °C".[11] This decomposition presumably yielded $S_2O$ (5) and 2,3-diphenylbutadiene (8).



Our synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (7) (Scheme I) begins with a stepwise reduction of 2,3-diphenylmaleic anhydride (9)[13] to yield (Z)-2,3-diphenyl-2-butene-1,4-diol (11).[14] Diol (11) was then treated with $PBr_3$ to yield (Z)-1,4-dibromo-2,3-diphenyl-2-butene (12).[11] Dibromide (12) was then treated with an excess of sodium thiosulfate which presumably reacted to form the Bunte salt (13).[15] This Bunte salt (13) was not isolated but was subjected to an oxidative workup ($I_2$) to yield 4,5-diphenyl-3,6-dihydro-1,2-dithiin (14).[11] Dithiin (14) was then oxidized (mCPBA) to 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (7).[11] This scheme provided dithiin 1-oxide (7) on a 10-mmol scale in five steps in 30% overall yield. This synthesis is potentially modifiable in that the phenyl substituents could be replaced by sterically larger or smaller substituents to accelerate or inhibit $S_2O$ liberation.

With a likely $S_2O$ precursor in hand, we sought to test the feasibility of using a transition-metal complex to both induce liberation of $S_2O$ and trap the $S_2O$ after liberation (Scheme II). When dithiin 1-oxide (7) was added to a solution of the coordinatively unsaturated iridium complex 15,[16] a rapid reaction occurred to yield the iridium $S_2O$ complex 16 and 2,3-diphenylbutadiene (8) (identified by spectral comparison to an authentic sample).[17] Iridium $S_2O$ complex 16 was identical by spectroscopic comparison with the complex synthesized previously by oxidation of the corresponding $S_2$ complex.[7b,e] We have also treated $Me_nCpMn(CO)_2(THF)$ ($n$ = 1, 19; $n$ = 5, 20) with dithiin 1-oxide (7) to yield the red $Me_nCpMn(CO)_2(S_2O)$ complexes ($n$ = 1, 21; $n$ = 5, 22). All spectroscopic characteristics of these manganese $S_2O$ complexes were analogous to those reported previously for the $\eta^2$-$S_2O$ complex 22, synthesized by oxidation of the $S_2$ complex and characterized crystallographically.[2a] We propose that these reactions are transition-metal-assisted retro Diels–Alder reactions, proceeding through intermediates such as 23 or 24 where the dithiin 1-oxide (7) serves as a two-electron-donor ligand prior to bond cleavage.[18]

Future efforts will be directed toward the synthesis of $S_2O$ complexes containing $S_2O$ in other bonding modes and applications of transition-metal $S_2O$ complexes in the synthesis of thiosulfinate esters.

**Acknowledgment.** This investigation was supported by the Research Corp., the North Carolina Board of Science and Technology, and a NIH New Basic Research Support Grant (2SO7RR07230-02) administered by Wake Forest University. We thank Professor Daniel F. Harvey for a helpful early discussion of this work.

**Supplementary Material Available:** Complete experimental details for the syntheses of 7 and 16 (4 pages). Ordering information is given on any current masthead page.

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