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.

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

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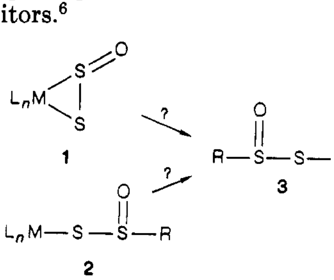
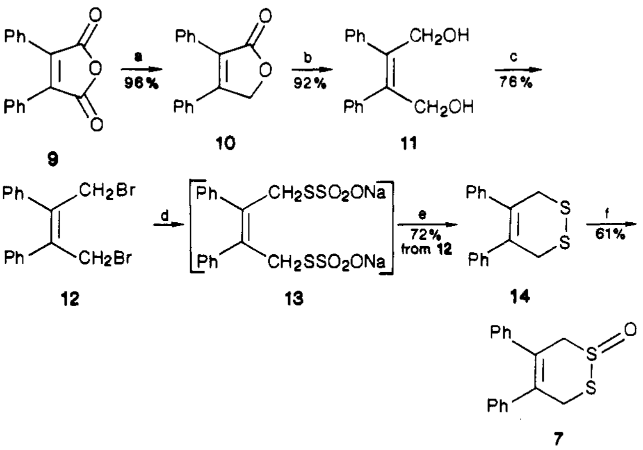
Summary: A five-step synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide starting from 2,3-diphenylmaleic anhydride is described. When the dithiin 1-oxide was treated with coordinatively unsaturated transition-metal complexes, a transition-metal disulfur monoxide complex and 2,3-diphenylbutadiene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

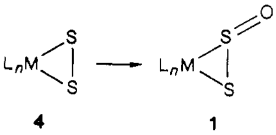
The ability of transition metals to stabilize small, reactive sulfur fragments such as sulfur monoxide (SO),[1] disulfur (S_2),[2] and trisulfur (S_3)[2b,3] offers chemists a chance to explore the reactivity of these molecules under mild, controlable conditions. Our goal within this active area of research 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 η^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]



^{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.



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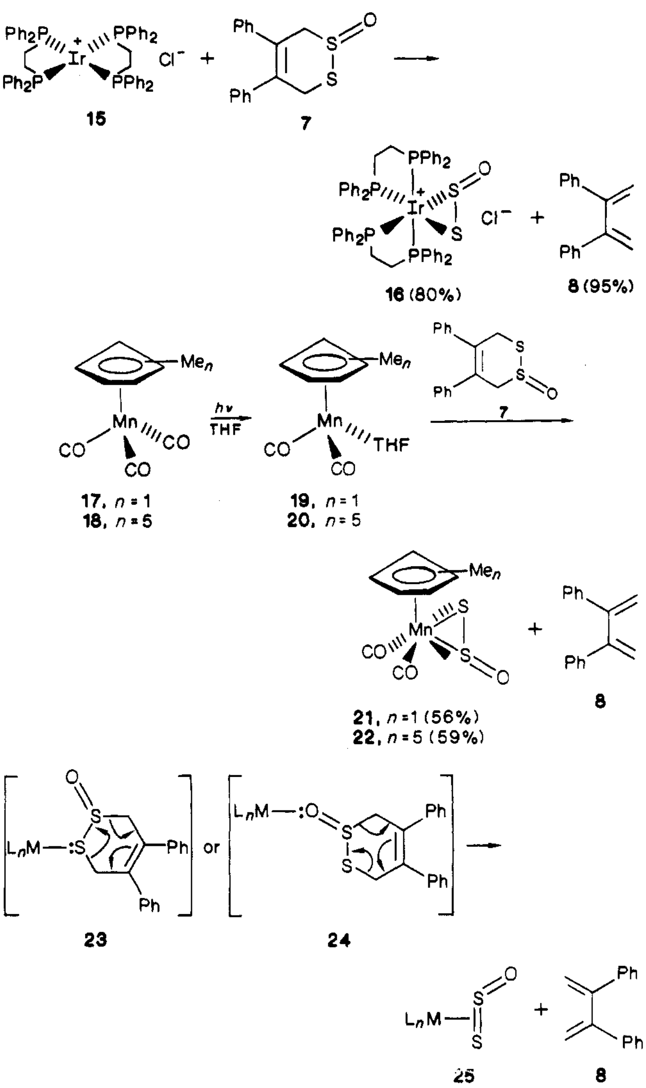
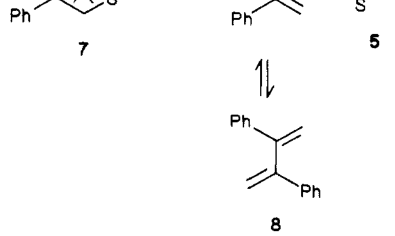
0276-7333/88/2307-1013$01.50/0

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 η^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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(12) Use of a retro Diels–Alder reaction for the production of singlet oxygen[12a] and singlet sulfur[12b] has been reported: (a) Wasserman, H. H.; Scheffer, J. R., Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991. (b) Ando, W.; Sonolse, H.; Akasaka, T. *Tetrahedron Lett.* **1987**, *28*, 6653.

(13) 2,3-Diphenylmaleic anhydride is commercially available (Aldrich Chemical Co.), but it can also be synthesized by a simple two-step procedure from benzyl cyanide: Weinberg, J. S.; Miller, A. *J. Org. Chem.* **1979**, *44*, 4722.

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(17) Allen, C. F. H.; Eliot, C. G.; Bell, A. *Can. J. Res., Sect. B* **1939**, *17*, 75.

(18) For one other example of a transition-metal-assisted retro Diels–Alder reaction see: (a) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1982**, *104*, 4484. (b) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.