substitution patterns. Furthermore, the method represents a clear-cut example of the synthetically useful C–C bond formation via a homolytic process. It also demonstrates the obvious advantage of the polymer supported reagent over the corresponding low molecular weight one in the aspects of the product yield and reuse of the reagent, as well as the well-claimed simplicity of the procedure. C–C bond formations using polymer catalyst that has been hitherto reported have been very few.[19] The stereoselective homolytic carbocyclization may provide a new synthetic methodology. Studies on this line and the application to the natural product synthesis are now in progress.[20]

Registry No. 1a, 82918-70-5; **1b**, 82918-71-6; **1c**, 82918-72-7; **1d**, 82932-66-9; **1e**, 82918-73-8; **1f**, 73746-50-6; **2a**, 82918-74-9; **2b**, 82918-75-0; **2c**, 82918-76-1; **2d**, 82918-77-2; **2e**, 82918-78-3; **2f**, 82918-79-4; **3**, 82918-69-2; **4a**, 1679-49-8; **4b**, 16496-51-8; **4c**, 22530-99-0; **4d**, 82918-80-7; **4e**, 43142-60-5; **4f**, 82918-81-8; **6**, 82918-82-9; **7a**, 82918-83-0; **8a**, 10150-95-5; **8b**, 10150-96-6; Bu_3SnH, 688-73-3; $NaBH_4$, 16940-66-2.

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Tetrathiazyl Tetrakis(*F-tert*-butoxide)

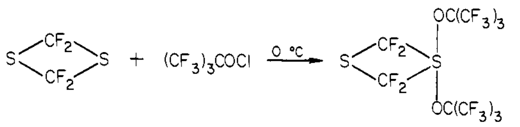
Gary L. Gard*[1] and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho
Moscow, Idaho 83843

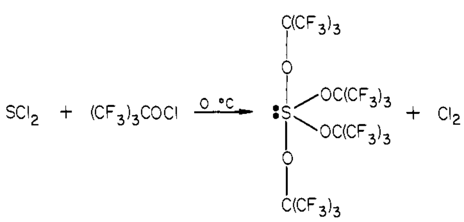
Received May 20, 1982

Extending our examination of the reactions of *F-tert*-butyl hypochlorite, we now report our studies with non-carbon-containing sulfur systems such as tetrasulfur tetranitride. Earlier we had demonstrated that $(CF_3)_3COCl$ can be caused to react with sulfur compounds in several ways,[2] e.g.

(a) oxidative addition



(b) oxidative displacement and oxidative addition



(c) oxidative displacement

$$CF_3S(O)Cl + (CF_3)_3COCl \xrightarrow{0\ ^\circ C} (CF_3)_3COS(O)CF_3 + Cl_2$$

The reactions of S_4N_4 are unusually diverse and continue to hold considerable fascination for the synthetic chemist. Tetrasulfur tetranitride appears to be susceptible to attack by free radicals to form S-tetrasubstituted or -disubstituted derivatives, e.g., with $(CF_3)_2NO \rightarrow N_4S_4(ON(CF_3)_2)_4$,[3,4] with $S_2O_6F_2 \rightarrow N_4S_4(OSO_2F)_2$,[5] where the latter contains the tetrathiazyl cation, $S_4N_4^{2+}$, or with $Cl_2 \rightarrow N_4S_4Cl_2$.[6]

Tetrasulfur tetranitride and *F-tert*-butyl hypochlorite react at 0 °C to form a white solid identified as $N_4S_4(OC(CF_3)_3)_4$ in 98% yield. After 8 or 9 h at 0 °C, the bright orange S_4N_4 is completely decolorized, and gaseous chlorine, which is recovered quantitatively, is visible in the reaction flask.

$$S_4N_4 + 4(CF_3)_3COCl \xrightarrow{0\ ^\circ C} N_4S_4(OC(CF_3)_3)_4 + 2\ Cl_2$$

If the reaction is carried out at 25 °C, small amounts of CF_3Cl and $(CF_3)_2CO$, which result from the decomposition of the hypochlorite, are also found in the vapor over the solid. The product was found to be insoluble or very slightly soluble in water, diethyl ether, carbon tetrachloride, and methylene chloride. It is soluble in CCl_3F and CCl_2FCF_2Cl and may be recrystallized from either one. In some runs a small amount of a yellow substance was formed upon contact with air.

Sublimation occurs at 70 °C at a pressure of 50 μm. In a sealed capillary, the sublimed solid melts at 161–162 °C accompanied by slight discoloration. The ^{19}F NMR spectrum contains a singlet at ϕ −70.7. In the mass spectrum, a parent ion is not observed, but an ion that may be assigned to $(M - OC(CF_3)_3)^+$ at *m/e* 889 is recorded. Other appropriate fragments are observed such as $S_4N_4^+$, $S_3N_3^+$, $S_2N_2^+$, and SN^+. This supports the retention of the eight-membered ring.

The properties of the three known $N_4S_4(R_f)_4$ (R_f = F, $(CF_3)_2NO$, $(CF_3)_3CO$) compounds are remarkably similar, e.g., $(M - R_f)^+$ is the largest *m/e*, and they are white crystals that sublime in vacuo and melt with decomposition or discoloration and are essentialy insoluble in all common organic solvents. While $N_4S_4(ON(CF_3)_2)_4$ does not appear to be even wetted by water, both $N_4S_4F_4$ and $N_4S_4(OC(CF_3)_3)_4$ are slowly attacked by water. The structure of the new tetrakis(*F-tert*-butoxide) is expected to be essentially identical with that of $N_4S_4(R_f)_4$ (R_f = F, $(CF_3)_2NO$) with the $(CF_3)_3CO$ groups bonded to the sulfur atoms. The S_4N_4 ring should be opened, slightly destroying any transannular interactions but retaining bond lengths associated with three coordinated sulfur and two coordinated nitrogen.

Thus, $(CF_3)_3COCl$ can be used as an excellent oxidative addition reagent for introducing *F-tert*-butoxy groups into cyclic lower valent sulfur compounds under sufficiently mild conditions to prevent ring opening.

Experimental Section. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a 5 cm stainless steel cell with KBr windows or as solids between KBr discs on a Perkin-Elmer 599 spectrometer. ^{19}F NMR spectra were recorded with a JEOL FX90Q spectrometer operating at 84.26 MHz. Chemical shifts are relative to CCl_3F. Mass spectra were measured with a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 25 eV. Elemental analyses were performed at the University of Idaho or by Beller Laboratories, Göttingen, West Germany.

F-tert-Butyl hypochlorite was synthesized by the literature method.[8] S_4N_4 was freshly recrystallized from benzene.

To S_4N_4 (0.105 g, 0.571 mmol) in a 50-mL Pyrex flask equipped with a Kontes Teflon stopcock and Teflon-coated stirring bar was added $(CF_3)_3COCl$ (1.053 g, 3.90 mmol). The mixture was stirred at 0 °C for 8–9 h. After the volatile materials were removed under vacuum, the white solid, $N_4S_4(OC(CF_3)_3)_4$, weighed 0.632 g (0.562 mmol) for a 98% yield. Chlorine (0.081 g; theoretical 0.081 g) was the only other product obtained. The infrared spectrum of $N_4S_4(OC(CF_3)_3)_4$ taken between KBr discs had bands at 1305 (sh), 1274 (br vs), 1250 (s), 1234 (sh), 1198 (m), 1188 (m), 1060 (vs), 998 (s), 979 (s), 778 (m), 754 (w), 745

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(w), 731 (ms), 714 (m), 599 (m), 570 (w), 548 (w), 535 (vw), 475 (m), 405 (w) cm^{-1}. The mass spectrum contained peaks at 889 (M - OC(CF$_3$)$_3$)$^+$, 419 (M - (OC(CF$_3$)$_3$)$_3$)$^+$, 197 ((CF$_3$)$_3$CO - 2F)$^+$, 184 S$_4$N$_4$$^+$, 147 ((CF$_3$)$_2$CO - F)$^+$, 138 S$_3N_3$$^+$, 128 ((CF$_3$)$_2$CO - 2F)$^+$, 97 (CF$_3$CO)$^+$, 92 S$_2N_2$$^+$, 69 CF$_3$$^+$, 46 SN$^+$.

Anal. Calcd for $C_{16}F_{36}N_4S_4O_4$: C, 17.09; N, 4.98; S, 11.41; F, 60.8. Found: C, 17.21; N, 5.17; S, 10.78; F, 62.3.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-8100156) for support of this research. We Thank Dr. Gary Knerr for mass and ^{19}F NMR spectral data.

Structure of *trans*-Bis(1,5-dithiacyclooctane)tetrachlorotin(IV): Evidence for an Intramolecular Interaction between a Remote Donor and a Coordinated Atom

Marilyn M. Olmstead, Keith A. Williams, and W. Kenneth Musker*

Department of Chemistry, University of California, Davis
Davis, California 95616

Received July 12, 1982

The observation of an intramolecular interaction between a remote electron-pair donor and a coordinated atom was recently reported by Stein and Taube in ruthenium complexes containing a monodentate 1,5-dithiacyclooctane (1,5-DTCO) ligand [(NH$_3$)$_5$Ru(1,5-DTCO)]$^{2+,3+}$.[1] The spectroscopic properties of the ruthenium(III) complex and the redox characteristics of the ruthenium(II) complex both reflected an involvement of the remote thioether group. Unfortunately, no crystals of these complexes could be obtained, and no other crystal studies of a complex having monodentate coordination of a normally bidentate ligand in which the remote donor could interact with the coordinated donor have been reported. In the course of our studies of the coordination properties of mesocyclic dithioethers, we isolated and determined the crystal structure of *trans*-SnCl$_4$(1,5-DTCO)$_2$. A relatively short nonbonded contact of 3.271 (3) Å between the two sulfur atoms was found. Since a similar interaction may be responsible for the unusual properties of the monodentate ruthenium complexes of 1,5-DTCO, we are reporting the structure of the tin(IV) complex at this time. The complex was prepared by combining equal volumes of about 5% solutions of 1,5-DTCO[2] and SnCl$_4$ in acetonitrile in a dry tube. The tube was lightly stoppered and set aside for several weeks at ambient temperature. The crystals deposited on the sides of the tube; far IR 367 (m) 312 (vs), 277 (m) cm^{-1}.

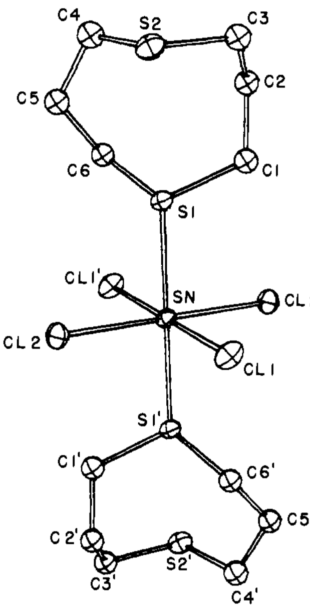

Figure 1. Perspective drawing of *trans*-SnCl$_4$(1,5-DTCO)$_2$ showing the atom numbering scheme.

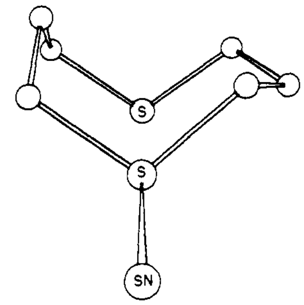

Figure 2. Drawing of one of the coordinated 1,5-DTCO rings showing the boat-chair conformation.

Table I. Bond Distances (Å) and Bond Angles (Deg) for *trans*-SnCl$_4$(1,5-DTCO)$_2$

Sn-Cl(1)	2.414 (1)	Cl(1)-Sn-Cl(2)	89.8 (1)
Sn-Cl(2)	2.428 (1)	Cl(1)-Sn-S(1)	84.1 (1)
Sn-S(1)	2.602 (1)	Cl(2)-Sn-S(1)	83.1 (1)
S(1)-C(1)	1.827 (3)	Sn-S(1)-C(1)	106.6 (1)
S(1)-C(6)	1.828 (3)	Sn-S(1)-C(6)	105.0 (1)
S(2)-C(2)	1.820 (3)	S(1)-C(1)-C(2)	115.7 (2)
S(2)-C(4)	1.821 (3)	S(1)-C(6)-C(5)	113.3 (2)
C(1)-C(2)	1.522 (4)	S(2)-C(3)-C(2)	115.7 (2)
C(2)-C(3)	1.526 (4)	S(2)-C(4)-C(5)	114.5 (2)
C(4)-C(5)	1.529 (4)	C(1)-S(1)-C(6)	105.3 (1)
C(5)-C(6)	1.533 (4)	C(1)-C(2)-C(3)	117.0 (2)
		C(3)-S(2)-C(4)	102.0 (1)
		C(4)-C(5)-C(6)	117.9 (2)

The bifunctional nature of the dithioether ligand naturally leads one to expect either a polymeric ligand-bridged structure, as in the glutaronitrile complex *cis*-SnCl$_4$[NC(CH$_2$)$_3$CN]$_2$[3] or *trans*-Ni(1,5-DTCO)Cl$_2$,[4] or a bidentate functionality, as in (Ph$_3$P)$_2$Pt(1,5-DTCO).[5] The discovery of a monodentate 1,5-DTCO in the tin complex was therefore somewhat of a surprise. The structure[6] of *trans*-SnCl$_4$(1,5-DTCO)$_2$ consists of isolated neutral molecules with no short intermolecular contacts. Two molecules are contained in the unit cell, and they are therefore

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(6) A pale yellow plate of SnCl$_4$(C$_6$S$_2$H$_{12}$)$_2$, M_r 557.08, was cut to dimensions 0.45 × 0.45 × 0.70 mm and mounted on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator. With Mo Kα radiation (λ 0.71069 Å) and with the crystal cooled to 140 K, crystal data are as follows: monoclinic, space group $P2_1/c$; a = 7.544 (2) Å, b = 13.401 (6) Å, c = 10.090 (2) Å; β = 99.55 (2)°; Z = 2; μ = 21.9 cm^{-1} (range of absorption correction factors 4.2-5.6). Data were collected to $2\theta_{max}$ of 50° with an ω scan technique. A total of 1753 unique data were collected of which 1607 had $I > 2.5\sigma(I)$. No absorption or extinction corrections were performed. Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. Computer programs were those of the SHELXTL, version 3, July 1981 package. The structure was solved by placing the tin atom at (0.0, 0.0, 0.0) and computing a Fourier map. With anisotropic thermal parameters for non-hydrogen atoms and with hydrogen atoms riding on the bonded carbon, R = 0.021, R_w = 0.027 in the final cycle of refinement (67 parameters). Atomic coordinates, thermal parameters, and structure factor tables are available as supplementary data.

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