$= 52 \pm 1.7$ kJ·mol^{-1}) is ascribed to fast degenerate rearrangement of II and VII, respectively, rendering the lithium atoms in VII equivalent. "Chelatomers" of type VIII are likely intermediates in this process and can be formed from II and VII, respectively, by decoordination of two *trans*-NMe_2 groups followed by the conformational change and recoordination of the NMe_2 groups. At 290 K an exchange between II and VII ($\Delta G^{\ddagger}_{\text{II-VII}} = 64 \pm 2.1$ kJ·mol^{-1}, $\Delta G^{\ddagger}_{\text{VII-II}} = 63.5 \pm 2.5$ kJ·mol^{-1}) becomes apparent, which is possibly initiated by inversion at α-C.[17]

Acknowledgment. The X-ray data were kindly collected by A. J. M. Duisenberg. The investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: An ORTEP plot and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (4 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[17] Such a process would also account for part[16] of the temperature dependence of the NMe_2 signals (vide supra). One alternative mode of exchange, proceeding through a tetramer formed from II and VII, is rendered unlikely by the concentration independence of the coalescence temperatures.

An Organometallic Route to Binary Carbon Sulfides. The Structure of C_6S_{12}

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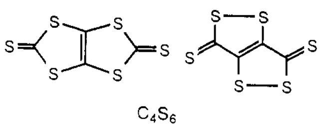
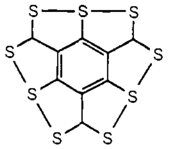
Given the great interest in sulfur nitrides,[1] the corresponding carbon sulfides could be expected to have a rich chemistry. In this report we describe the synthesis of two new carbon sulfides. Prior to our work five molecular carbon sulfides were known to be stable at room temperature: CS_2,[2] C_3S_2,[3] two isomers of C_4S_6,[4,5] and C_9S_9.[6]

S=C=S S=C=C=C=S

CS_2 C_3S_2



C_4S_6



C_9S_9

Our synthesis of carbon sulfides is predicated on two advances, the recent synthesis of salts of $C_3S_5^{2-}$ [7,8] and the ability of Cp_2Ti^{IV} compounds (Cp = C_5H_5) to serve as group-transfer agents.[9-11] Treatment of Cp_2TiCl_2 with 0.5 equiv of $(Et_4N)_2[Zn(C_3S_5)_2]$[7] in refluxing THF resulted in a color change from red to green. After 3 h the cooled solution was filtered through silica gel, concentrated, and diluted with hexane to afford black green crystals of $Cp_2TiC_3S_5$ (**1**) in 90% yield[12] (eq 1).

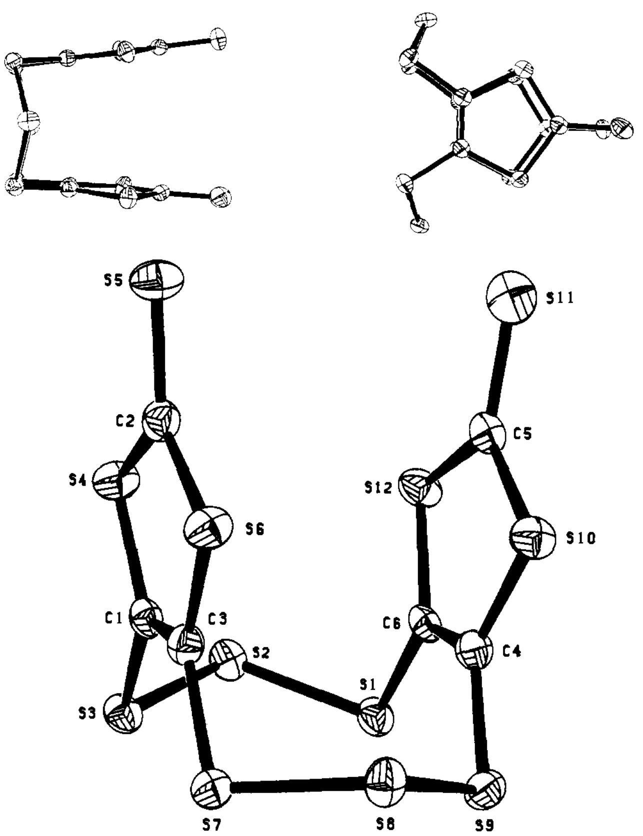
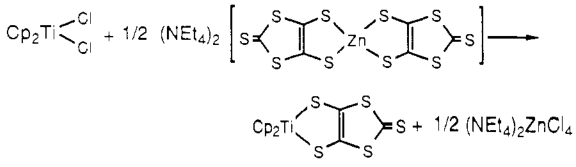


Figure 1. The structure of C_6S_{12} (**2**) with thermal ellipsoids drawn at the 35% level. Side and top views of the C_6S_{12} molecule are shown in the inset.



(1)

Solutions of **1** (1 g, 2.67 mmol) and S_2Cl_2 (0.216 mL, 2.67 mmol) each dissolved in 20 mL of CH_2Cl_2 were simultaneously added dropwise into 300 mL of stirred CH_2Cl_2 over a period of 6 h at room temperature. The resulting yellow-orange suspension was filtered, and the yellow solids were washed with CH_2Cl_2. The

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[8] The coordination chemistry and electronic properties of $C_3S_5^{2-}$ complexes have been the subject of recent work, see: Vincente, R.; Ribas, J.; Zanchini, C.; Gatteschi, D.; Legros, J.-P.; Faulmann, C.; Cassoux, P. *Z. Naturforsch.* **1988**, *43B*, 1137. Kim, H.; Kobayashi, A.; Sasaki, Y.; Kato, R.; Kobayashi, H. *Chem. Lett.* **1987**, 1799. Bousseau, M.; Valade, L.; Legros, J.-P.; Cassoux, P.; Garbauskas, M.; Interante, L. V. *J. Am. Chem. Soc.* **1986**, *108*, 1908. Alvarez, S.; Vicente, R.; Hoffmann *J. Am. Chem. Soc.* **1985**, *107*, 6253.

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[10] Dithiolene transfer: Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

[11] For conceptually related group transfers using Cp_2Zr^{IV}, see: Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

[12] $Cp_2TiC_3S_5$, **1**: ^{1}H NMR (−30 °C, $CDCl_3$) 6.16, 5.81 ppm. At 300 MHz the coalescence temperature is 35 °C. Anal. Calcd for $C_{13}H_{10}S_5Ti$: C, 41.72; H, 2.70. Found: C, 41.56; H, 2.61.

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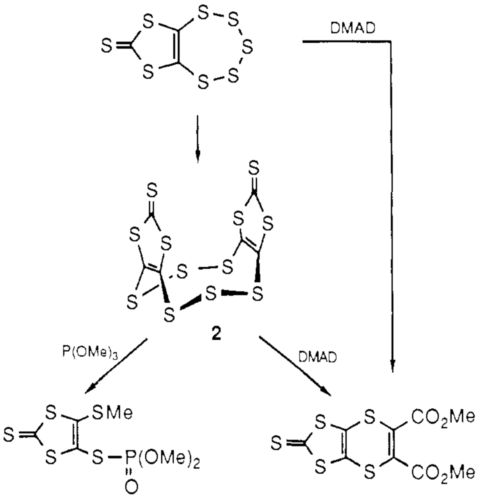
Scheme I



410 mg of yellow solids obtained in this way were examined by EI-MS and IR which indicated the absence of hydrocarbons (eq 2). The CH_2Cl_2 soluble portion of the reaction mixture was

$$\mathrm{Cp_2TiC_3S_5 + S_2Cl_2 \rightarrow Cp_2TiCl_2 + ``[C_3S_7]"} \qquad (2)$$

filtered through silica gel to remove Cp_2TiCl_2; concentration of this filtrate gave 120 mg of yellow crystalline solids identified as C_3S_8 by mass spectrometry, IR, and elemental analysis.[13]

Attempts to grow single crystals of C_3S_8 by slow evaporation of its CS_2 solutions gave well-formed orange prisms which proved to be C_6S_{12} (**2**).[14] This new compound is insoluble in all solvents tested; it can however be obtained in pure form directly from the reaction of $Cp_2TiC_3S_5$ with S_2Cl_2 by washing the resulting precipitate with CS_2. Solutions of C_3S_8 appear unstable with respect to S_8 and **2**. The EI mass spectrum of **2** does not show peaks for the parent ion, but the fragmentation pattern is distinct from that for C_3S_8. The IR spectra of C_3S_8 and **2** are also distinct, especially in the ν_{S-S} region below 510 cm^{-1}.

The molecular structure of C_6S_{12} is shown in Figure 1.[15] The molecule adopts a crown structure with approximate C_{2v} symmetry. The average S-S bond distances (2.061 Å) and S-S-S angles (106.8°) are very similar to the corresponding values for orthorhombic S_8.[16] The striking aspects of the structure are nearly eclipsed and mutually parallel (11.85°) C_3S_5 units with an interplanar distance of 3.88 Å for S(6) and S(10). The two C_3S_5 subunits are well suited for van der Waals' interaction since the electronegativities of carbon and sulfur are nearly the same.[17] The delocalized bonding in the C_3S_5 moieties should enhance the polarizability of its constituent atoms which in turn would strengthen this interaction. The structure of **2** and its formation from C_3S_8 indicate that the latter is a simple polysulfide derivative of the 1,3,2-dithiacyclopentenethione (Scheme I). Organic compounds with seven-membered 1,2-C_2S_5 rings are known.[18]

Preliminary studies have shown that C_6S_{12} is reactive. Treatment of dichloromethane suspensions of **2** with tributylphosphine followed by dimethylacetylenedicarboxylate (DMAD) gives $C_3S_5C_2(COOMe)_2$, isolated as pale yellow crystals.[19] Suspensions of C_6S_{12} in toluene dissolve upon addition of an excess of $P(OMe)_3$. After evaporation and recrystallization from toluene/ether we obtained the thiophosphonate[20] (Scheme I).

In summary we have developed a synthesis of two new carbon sulfides via the titanium-promoted transfer of 1,3,2-dithiacyclopentenethione groups. The new compounds have considerable synthetic potential as precursors to C-S polymers, coordination complexes, and new organosulfur compounds.

Acknowledgment. This research was supported by the National Science Foundation. We thank Jayantha Amarasekera for helpful comments and preliminary experiments.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond angles and distances (2 pages); tables of observed and calculated structures factors (9 pages). Ordering information is given on any masthead page.

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(13) C_3S_8: Anal. Calcd for C_3S_8: C, 12.33; S, 87.67. Anal. Calcd for C_3S_7: C, 13.83; S, 86.00. Found: C, 12.66; S, 86.16. EIMS 292 (M^+, 20), 256 (S_8^+, 7), 228 ($M^+ - 2S$, 77); IR $\nu_{C=S}$ = 1056 (vs), ν_{S-S} = 478, 464, 451 (m). The distinction between the S_7 and the S_8 formulations rests on the mass spectrometry; however, there are no established examples of $C_2(sp^2)S_4$ rings, but $C_2(sp^2)S_5$ rings are common. See ref 18.

(14) C_6S_{12}, **2**: Anal. Calcd for C_6S_{12}: C, 15.79; S, 84.21. Found: C, 16.16; S, 84.37. EIMS *m/e* (intensity) 328 ($M^+ - 4S$, 20), 292 ($C_3S_8^+$, 20), 256 (S_8^+, 17), 240 ($C_4S_6^+$, 65); IR (KI) $\nu_{C=S}$ = 1067, 1060 (vs), ν_{C-S} = 511, 505 (s), ν_{S-S} = 469, 448 cm^{-1} (m).

(15) X-ray crystallography of C_6S_{12}: orange-red crystal, 0.2 × 0.2 × 0.4 mm, orthorhombic, $P2_12_12_1$ (D_2 - No. 19); $a = 9.645$ (2) Å, $b = 7.933$ (2) Å, $c = 19.432$ (4) Å, $V = 1486.8$ (6) $Å^3$; $Z = 4$, $\rho_{calcd} = 2.040$ g/cm^3. Diffraction data: Syntex $P2_1$ automated four-circle diffractometer, Mo radiation ($K\alpha = 0.71073$ Å), no filters or attenuators, range $3.0 < 2\theta < 54.0°$ for $+h+k+l$ and $3.0 < 2\theta < 15.0°$ for $\pm h \pm k \pm l$, 2296 reflections consisting of 1911 unique data, 1588 of which were defined as observed ($I > \sigma(2.85I)$); corrected for anomalous dispersion, absorption, Lorentz and polarization effects. Least-squares refinement of 1588 independent reflections converged at $R = 0.028$ and $R_w = 0.032$.

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(19) Anal. Calcd for $C_9H_6O_4S_5$: C, 31.95; H, 1.78; S, 47.34. Found: C, 31.56; H, 1.69; S, 47.54. ^1H NMR ($CDCl_3$) 3.87 ppm; IR (KBr) $\nu_{C=S}$ = 1063 cm^{-1}; EIMS (70 eV) *m/e* 338 (M^+, 100).

(20) Anal. Calcd for $C_6H_9O_3PS_5$: C, 22.50; H, 2.81; S, 50.00. Found: C, 22.53; H, 2.81; S, 50.45. ^1H NMR ($CDCl_3$) 3.91 ppm (d, OCH_3, J(P,H) = 12.9 Hz), 2.54 (s, SCH_3); $^{31}P\{H\}$ NMR (CH_2Cl_2) 18.86 ppm (vs 85% H_3PO_4); IR (KBr) $\nu_{C=S}$ = 1063, $\nu_{P=O}$ = 1261 cm^{-1}; FD-MS (8 mA) *m/e* 320 (M^+, 100).

An ab Initio Investigation of the Double Proton Shift in Azophenine

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The automerization of 1,4-diamino-3,6-diimino-1,4-cyclohexadiene, **1a**, is an example of a degenerate double proton shift, as depicted in Figure 1. Based on kinetic and deuterium isotope effects on the rearrangement of the tetraphenyl derivative, azophenine (**1b**), Limbach et al.[1] initially suggested that both hydrogens move simultaneously in a single concerted step, i.e., **1** → $[4]^{\ddagger}$ → **1**. However, subsequent AM1 calculations by Dewar and Merz[2] disputed this mechanism, suggesting instead that classical automerization occurs through a two-step mechanism, i.e., **1** →

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