a gauche-locked conformation, though a mixture of ae and ea conformers is likely. For **4**, the absence of cyclobutanol products and the high fragmentation yield are both consistent with dominance of the anti conformation expected on simple steric grounds. The lifetime of the gauche **3** is thus actually somewhat longer than that of the anti **4** in methanol and only very slightly shorter than that of **4** in heptane.[10]

It thus appears that shortening of lifetime in a gauche conformation is not realized in this system. The expectation of such was derived from the dependence of spin-orbit coupling terms on through-space distance.[1] We have previously[6] pointed out the gross similarity of lifetime for biradicals with zero, two, and four carbons between the termini. The present experiment reinforces the lack of dependence of lifetime on through-space interminal distance and further suggests that the hypothesis that τ(gauche) << τ(anti) for biradicals[2,3] at the very least lacks generality.

Acknowledgment. This work was supported by NSF Grants CHE 7915228 and 8213637 and by the Robert A. Welch Foundation (Grant AT-532). Flash kinetic work was done at the Center for Fast Kinetics Research at the University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas. The assistance of Dr. Steven Atherton is gratefully acknowledged. S.N.D. thanks Kurukshetra University (India) for granting study leave.

Registry No. 1, 92126-53-9; **2**, 6264-81-9; **3**, 92143-40-3; **4**, 80326-03-0; **6**, 92126-54-0; **7**, 92126-55-1; hydrogen, 1333-74-0.

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(9) Small, R. D.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *59*, 431.

(10) Somewhat longer lifetimes for **4** were reported in ref 3. Reexamination of the earlier data suggests that a cable ring caused some distortion of the temporal profile; when allowance is made for this, the earlier data are quite consistent with the present parameters. No qualitative conclusions of ref 3 need be altered thereby. Live and learn.

Rearrangement of $(C_5H_5)_2TiS_5$ Involving Migration of the Organic Fragment from Metal to Sulfur

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We report the discovery of a second structural isomer of Cp_2TiS_5 (Cp = η^5-C_5H_5) (**1**) the most heavily studied polysulfido chelate complex.[1] The structure of β-$C_{10}H_{10}S_5Ti$ spectacularly illustrates new bonding modes for organosulfur ligands and provides fresh insights into the pathways by which organic substrates add to sulfido ligands.

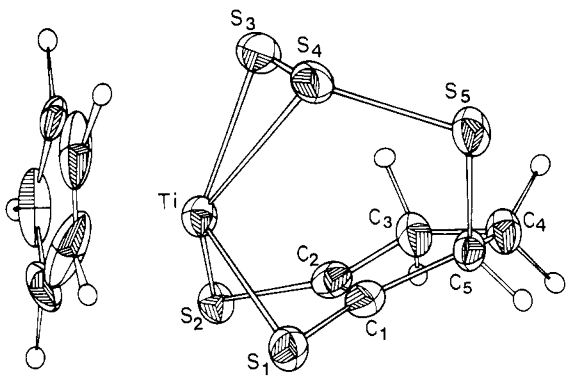

Figure 1. ORTEP plot of **2** with thermal ellipsoids drawn at 35% probability level.

Table I. Selected Bond Distances (Å) and Angles (deg) for One of the Two Molecules of **2** in the Asymmetric Unit[a]

Ti-S(1)	2.355 (3)	S(2)-C(2)	1.745 (9)
Ti-S(2)	2.358 (3)	S(1)-C(1)	1.738 (9)
Ti-S(3)	2.474 (3)	S(5)-C(5)	1.845 (9)
Ti-S(4)	2.537 (3)	S(1)-Ti-S(2)	90.8 (1)
Ti-C(1)	2.421 (8)	S(3)-Ti-S(4)	47.7 (1)
Ti-C(2)	2.483 (8)	Ti-S(3)-S(4)	67.8 (1)
Ti-Cp(av)	2.328	Ti-S(4)-S(5)	111.3 (1)
C(1)-C(2)	1.362 (11)	S(3)-S(4)-S(5)	112.8 (2)
S(3)-S(4)	2.025 (3)	C(5)-S(5)-S(4)	107.1 (3)
S(4)-S(5)	2.061 (3)		

[a] In comparing the two molecules in the asymmetric unit, it was found that no bond lengths differed significantly from the weighted mean values and the largest angular deviation was 0.7°.

β-$C_{10}H_{10}S_5Ti$ (**2**) forms in 40% yield when solutions of **1** in rigorously dried and deoxygenated xylenes are heated at reflux for 24 h.[2] Compound **2** was separated from other soluble products by careful chromatography on 4% cross-linked polystyrene gel[3] and was easily obtained in analytically pure, crystalline form by hexane precipitation from dichloromethane solutions. The red color of **2** is deceptively similar to that of **1**. The ^1H NMR spectrum of **2** revealed the presence of one intact Cp group while the remaining resonances (5 H) were broad and complex, even at 360 MHz. Its ^{13}C NMR spectrum consisted of six resonances, two of which remain weak even with broad-band ^1H decoupling. Thermolysis of $(MeCp)_2TiS_5$ gave a complex mixture of products for reasons that became clear subsequent to the X-ray diffraction study on **2**.

The structure[4] of **2** is shown in Figure 1; the two crystallographically independent molecules in the asymmetric unit are quite similar. Chiral **2** consists of a CpTi moiety coordinated to four sulfur atoms of 1,2-dimercapto-3-(mercaptodithio)cyclopentene. The four coordinated sulfur atoms define a plane (±0.02 Å), 0.92 Å above which lies the titanium atom. The dithiolene is coordinated in an unusual manner as the Ti-C(dithiolene) distances are 2.42 and 2.48 Å which may be compared to the 2.32 Å Ti-C(Cp) distances (Table I).[5] As such **2** can be described as an example of an η^4-dithiolene complex. The η^2-attachment of the trisulfido group is unprecedented and the Ti-S(3) and Ti-S(4) distances indicate the absence of significant S to Ti π-bonding, unlike the case for **1**. The first examples of η^1-trisulfides have very recently been reported by Shaver and ourselves.[6,7] In the absence of S to Ti π-donation, **2** assumes a 16e configuration.

The mechanism for the rearrangement of **1** to **2** is undoubtedly complex and is probably related to the facile conversion of Cp_2VS_5 to $Cp_2V_2S_5$.[8,9] The short C$\cdots\beta$-S contacts, noted by Dahl and

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(1) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971. Steudel, R.; Straus, R. *J. Chem. Soc. Dalton Trans.* **1984**, 1775. Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149.

(2) Anal. C, H, S, Ti. ^1H NMR (200 MHz, $CDCl_3$) δ 6.42 (S, 5 H), 5.39 (m, 1 H), 3.27 (m, 1 H), 2.99 (7, 1 H), 2.75 (m, 1 H), 2.30 (m, 1 H); FD MS, *m/e* 338 (M^+); ^{13}C NMR (360 MHz, $CDCl_3$) δ 155.7, 142.2, 111.1, 59.4, 34.9, 32.3.

(3) Compound **2** and a number of related titanium sulfides are insufficiently robust to withstand adsorption chromatography on silica gel or alumina. Gel permeation chromatography using the less aggressive Sephadex SH-20 or, in this case, Biobeads X-4 is a more useful separation technique.

(4) A platy crystal (0.02 × 0.22 × 0.50 mm) was obtained by vapor diffusion of hexanes into a $C_2H_4Cl_2$ solution of **2**. Cell data: monoclinic, $P2_1/c$ (C^5_{2h}), $a = 18.60$ (2) Å, $b = 7.508$ (7) Å, $c = 18.66$ (1) Å, $\beta = 92.18$ (7)°, $Z = 8$, μ(Mo K$\bar{\alpha}$) = 13.98 cm^{-1}. 4757 unique intensities from the $\pm h+k+l$ quadrant having $2\theta < 50.0°$ (γ(Mo K$\bar{\alpha}$) = 0.71069 Å) were measured at 25 °C on a Syntex $P2_1$ four-circle diffractometer with graphite monochromator and were numerically corrected for absorption (min/max transmission factors, 0.738/9.792). 2197 reflections had $I > 2.58\ \sigma(I)$ and only these were used. The structure was solved by MULTAN-80 and refined by SHELX-76 to give $R = 0.054$ and $R_w = 0.046$, where non-hydrogen atoms were varied anisotropically, and hydrogens were fixed in calculated positions. The final difference Fourier map was featureless.

(5) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Radiochem.* **1979**, *22*, 303.

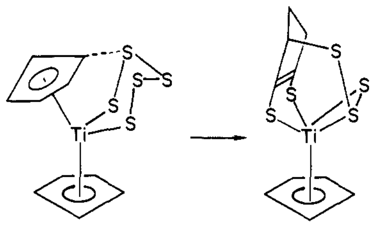
(6) Shaver, A.; McCall, J. M.; Bird, P. H.; Ansari, N. *Organometallics* **1983**, *2*, 1894.

(7) Giolando, D. M.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 487.

(8) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.

(9) Muller, K. G.; Peterson, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.

co-workers[9] in their crystallographic characterization of **1**, provides a structural basis for the initiation of the rearrangement process, i.e., C···S bond formation concomitant with lysis of S(2)-S(1) (eq 1).

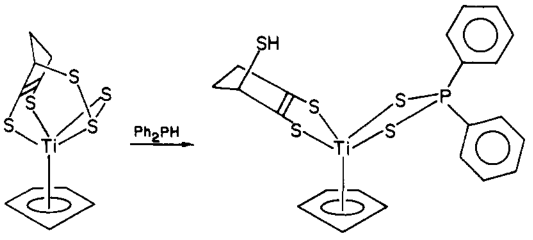


(1)

1 2

Two aspects of this reaction are particularly significant independent of the finer mechanistic details. First, the transformation provides a precedent for the *migration of* a *π-complexed organic fragment to inorganic sulfur ligands*. An associated feature of the rearrangement is that hydrogen migration accompanies the sulfiding of the C_5H_5 fragment. It is very likely that this rearrangement occurs intramolecularly.

Compound **2** cleanly adds Ph_2PH[10] to give a single diastereoisomer wherein each of the S–S bonds has been disconnected.[11] The structure of the product was assigned on the basis of NMR spectroscopy, particularly crucial was the D_2O-exchangeable doublet at 2.24 ppm attributable to the SH substituent, which we suggest is endo (eq 2).



(2)

2 3

In summary, the thermally induced rearrangement of Cp_2TiS_5 gives a novel organosulfur complex via migration of an organic ligand to coordinated sulfur atoms. Conceivably similar but more facile metal-to-sulfur migrations occur in previously reported "additions" of organic substrates to sulfido ligands.[12,13]

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Registry No. 1, 12116-82-4; **2**, 92126-84-6; **3**, 92126-85-7.

Supplementary Material Available: Structure factor tables, positional the thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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(10) For the related reaction of an η^2-S_2OCH_3 ligand, see: Hoots, J. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1226.

(11) Anal. C, H, P, S, Ti. ^1H NMR (90 MHz, $CDCl_3$) δ 7.5 (m, 10 H), 6.4 (s, 5 H), 4.3 (q, 1 H), 3.1 (m, 2 H), 2.2 (d, 1 H), 2.0 (q, 2 H). ^1H NMR (200 MHz, $CDCl_3$, D_2O shake) δ 7.5 (m, 10 H), 6.4 (s, 5 H), 4.3 (t, 1 H), 3.1 (m, 2 H), 2.0 (q, 2 H). ^{13}C NMR (360 MHz, $CDCl_3$) δ 145.5, 145.2, 137.1 (d, J_{PC} = 74.16 Hz), 129.65 (d, J_{PC} = 12.11 Hz), 128.41 (d, J_{PC} = 13.04 Hz), 47. 697, 37.0, 33.0. $^{31}P\{^1H\}$ NMR (250 HMz, CH_2Cl_2) δ 66.05 relative to H_3PO_4 as external standard.

(12) (a) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. D.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329 and references therein. (b) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139. (c) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. A recent study on the reaction of $CH_3O_2CCCCO_2CH_3$ with 1,4-$[(MeCp)_2Ti]_2S_4$ establishes an insertion mechanism: Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L., unpublished results.

(13) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

Hapalindoles: New Alkaloids from the Blue-Green Alga *Hapalosiphon fontinalis*

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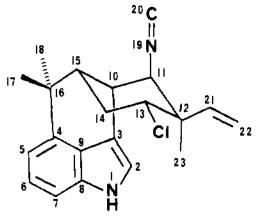
Hapalosiphon intricatus has been reported to produce an extracellular substance that inhibits the growth of another blue-green alga, an *Anabaena* sp.[1] A similar antialgal response has been reported for *H. fontinalis* toward *A. oscillarioides*.[2] In neither case has the active principle been identified.[3] In our work *H. fontinalis* was isolated from soil samples collected in the Marshall Islands in 1981. The lipophilic extract of the cultured alga showed antialgal and antimycotic activities.

An edaphic form of *Hapalosiphon fontinalis* (Ag.) Bornet (Stigonemataceae), strain number V-3-1, was isolated by repeated subculture on solidified media.[4] The alga was cultured in 25-L glass bottles containing an inorganic medium[5] modified by replacing citrate buffer with 3 mM 3-morpholinopropanesulfonic acid (pH 7) and by supplementing the medium with a comprehensive minor and trace element mixture.[6] Cultures were illuminated continuously at an incident intensity of 330 μEinstein m^{-2} s^{-1} from banks of cool-white fluorescent tubes. Cultures were vigorously aerated with 1% CO_2 in air and incubated at 24 ± 1 °C. The alga was harvested by filtration; yields typically were 0.4–0.5-g dry weight of cells per liter of culture. The freeze-dried alga (360 g) was extracted with 1:1 *i*-PrOH/CH_2Cl_2 and the oily extract (15.1 g) was subjected to gel filtration on Sephadex LH-20 with 1:1 *i*-PrOH/CH_2Cl_2 and rapid chromatography on silica gel (TLC grade) with hexane, 1:1 hexane/CH_2Cl_2, CH_2Cl_2, CH_2Cl_2/EtOAc, EtOAc, and EtOAc/EtOH. The fraction that was eluted with 1:1 hexane/CH_2Cl_2 was purified by HPLC on Whatman Partisil with 1:1 hexane/CH_2Cl_2 to give 2.1 g (0.58%) of hapalindole A (**1**), mp 160–167 °C dec and $[\alpha]^{25}{}_D$ −78° (CH_2Cl_2, *c* 1.2) after crystallization from hexane/CH_2Cl_2 and sublimation at 125 °C (0.1 mm). Hapalindole A was responsible for most of the antialgal and antimycotic activity of *H. fontinalis*.



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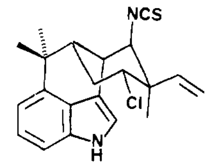

2

Compound **1** exhibited a UV spectrum [λ_{max} (ϵ) 222 (38 000), 280 (7000), 291 nm (5800)] typical of an indole and IR and ^{13}C NMR peaks [ν_{max} 2145 cm^{-1}; $\delta_{^{13}C}$ 157.40] characteristic of an isonitrile. A molecular formula of $C_{21}H_{23}N_2Cl$ could be deduced for the alkaloid from detailed analyses of the ^1H and ^{13}C NMR spectra (Table I) and a high-resolution EI mass spectrum (M^+ observed at *m/z* 338.1595; mmu error 4.6).[7]

The indole system appeared to be 3,4-disubstituted since the

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(1) Srivastava, P. N. "Taxonomy and Biology of Blue-Green Algae"; Desikachary, T. V., Ed.; University of Madras: Madras, India, 1972, pp 391–392.

(2) Zzvarzina, N. B. *Vestn. Akad. Nauk Kaz. SSR* **1969**, *5*, 69.

(3) Recently a chlorine-containing algicide, cyanobacterin, which inhibits the growth of *Synechococcus*, has been isolated from *Scytonema hofmanni*. (a) Mason, C. P.; Edwards, K. R.; Carlson, R. E.; Pignatello, J.; Gleason, F. K.; Wood, J. M. *Science (Washington, D.C.)* **1982**, *215*, 400. (b) Jong, T.-T.; Willard, P. G.; Porwoll, J. P. *J. Org. Chem.* **1984**, *49*, 735.

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(5) Allen, M. B. *Arch. Mikrobiol.* **1952**, *17*, 34.

(6) O'Flaherty, L. M.; Phinney, H. K. *J. Phycol.* **1970**, *6*, 95.

(7) The EI MS of **1** does not show an ion peak for loss of HCN from the molecular ion. In the mass spectra of isonitriles, the M–HCN ion peak is generally very intense. The characteristic 3:1 isotopic cluster is observed at *m/z* 338,340 for the chlorine-containing molecular ion.

0002-7863/84/1506-6456$01.50/0