$$2a + HX \xrightarrow[1\text{-}1.5\ h]{40\ ^\circ C} \underset{90\text{-}95\%}{(C_5Me_5)RuX_2(\eta^3\text{-}C_3H_5)} \qquad (4)$$

$$X = Br, I$$

The above results show that the Ru(IV) complexes **2** can be conveniently prepared from **1** by treatment with several allylic substrates. Furthermore, facile halogen exchange of **2** with HBr or HI provides a convenient preparation of **4** and **5**, which contain more reactive leaving groups and are useful in the syntheses of alkyl derivatives.[6] Since the starting Ru(III) complex **1** can be prepared simply by treating hydrated $RuCl_3$ with C_5Me_5H,[4] the present procedure has established a highly convenient and economical preparation of these ruthenium(IV)-allyl complexes.

The present reaction also generates keen mechanistic questions regarding the cleavage of C-Cl, C-Br, C-O, C-N, and C-S bonds by a Ru(III) precursor. As previously reported, the Ru(III) complex **1** undergoes reduction by alcohols in the presence of several phosphines or dienes to give Ru(II) complexes $(C_5Me_5)RuL_2Cl$ (**6**).[4] Furthermore, we have already found that **6** (L = CO, PPh_3) reacts with allylic chlorides to give **2**.[3] One explanation for the present route from **1** to **2** is the reduction of **1** to Ru(II) species by the alcohol, followed by the oxidative addition of the allylic compounds to the Ru(II) center. However, there are no known examples of oxidative addition of allylic alcohol derivatives, allylamine, or allyl sulfide to Ru(II) complexes. In all cases where C-O, C-N, and C-S bond cleavage occurs, *Ru-O, Ru-N, or Ru-S bond formation never was observed.* In the reaction with allyl bromide, the dichloro complex was **2a** formed mainly at the early stages of the reaction at lower temperature and the halogen exchange to **3** and **4** seemed the secondary reaction. The reaction with allyl phenyl sulfide was not accompanied by any oxidation of alcohol solvents; the reaction proceeded smoothly even in anhydrous CH_2Cl_2 and a quantitative formation of PhSSPh. All of these findings indicate an alternative mechanism that the reaction of **1** to **2** takes place with retention of the Ru(III) framework "$(C_5Me_5)RuCl_2$", which abstracts the allylic component homolytically from the allylic compounds. The resulting halo, hydroxy, thiyl, etc. radicals will abstract hydrogen from the alcohol solvent or will undergo dimerization. We are seeking experimental support for this homolytic pathway.[7]

Registry No. **1**, 96503-27-4; **2a**, 91083-13-5; **2b**, 91083-14-6; **2c**, 96503-23-0; **2d**, 96503-24-1; **3**, 96503-25-2; **4**, 91083-12-4; **5**, 96503-26-3; $H_2C{=}CHCH_2Cl$, 107-05-1; $H_2C{=}C(CH_3)CH_2Cl$, 563-47-3; $H_2C{=}C(C_6H_5)CH_2Cl$, 3360-52-9; $H_2C{=}CClCH_2Cl$, 78-88-6; $H_2C{=}CHCH_2OH$, 107-18-6; $H_2C{=}C(CH_3)CH_2OH$, 513-42-8; $H_2C{=}CHCH_2OAc$, 591-87-7; $H_2C{=}CHCH_2OCH_2Ph$, 14593-43-2; $H_2C{=}CHCH_2OPh$, 1746-13-0; $H_2C{=}CHCH_2NH_2$, 107-11-9; $H_2C{=}CHCH_2SPh$, 5296-64-0; $H_2C{=}C(CH_3)CH_2SPh$, 702-00-1; PhSSPh, 882-33-7; $H_2C{=}CHCH_2Br$, 106-95-6; 4-*tert*-butylcyclohexanol, 98-52-2; 4-*tert*-butylcyclohexanone, 98-53-3.

Supplementary Material Available: Melting points, ^1H NMR data, and analyses for compounds **2c**, **2d**, **3**, and **5** (2 pages). Ordering information is given on any current masthead page.

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[6] Nagashima, H.; Yamaguchi, K.; Mukai, K.; Itoh, K. *J. Organomet. Chem.*, in press.

[7] According to this homolytic mechanism, **1** formally abstracts an allyl radical from the allylic compound. In other words, allylic compounds undergo homolytic substitution by **1** in releasing halo, hydroxy, or thiyl radicals. The transition metal-alkyl bond formation with an overall one-electron oxidation of the metal is usually initiated by halogen abstraction by the metal from organic halides, and the resulting alkyl radical was captured by another metal species to produce the metal-alkyl bond. The present oxidative allylation of **1** may be an unusual example involving the S_H pathway. For the leading references, see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 229-232. Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

Structure and Reactivity of $[CpFeS_2]_2$

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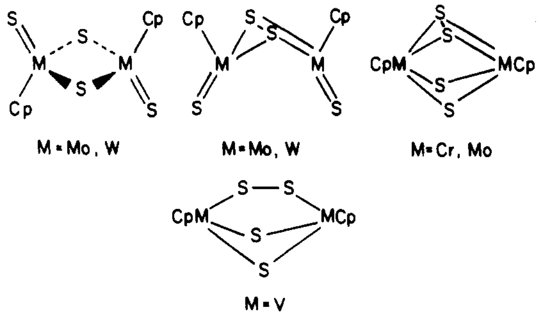
Summary: The complex $[CpFeS_2]_2$, IA (Cp = C_5H_5), which is the reported product of the photolytic reaction of elemental sulfur with $[CpFe(CO)_2]_2$, has been characterized by an X-ray diffraction study. The complex crystallizes in space group *Pbca* with a = 7.286 (1) Å, b = 17.468 (5) Å, and c = 19.472 (6) Å. The metal ions in IA are bridged by two mutually perpendicular disulfide ligands. In solution, IA is in equilibrium with a second isomer. The equilibrium mixture reacts with electrophiles such as methyl iodide and hexafluorobutyne. The reaction with the latter reagent results in two products, $(CpFeS)_2S_2C_2(CF_3)_2$, III, and $(CpFe)_2(S_2C_2(CF_3)_2)_2$, IV. Single crystals of IV crystallize in space group *C2/c* with a = 16.429 (3) Å, b = 10.134 (2) Å, c = 14.591 (2) Å, and β = 114.67 (2)°. Each butenedithiolate ligand in IV is bidentate with one bridging and one terminally coordinated sulfur donor.

Molybdenum dimers of oxidation states, V, IV, and III, which have in common the $Cp_2M_2S_4$ core, have been found to display unusual sulfur ligand-based reactivity.[2-4] Both the structure and reactivity of the M_2S_4 unit have been found to vary as a function of molybdenum ion oxidation state.[5] A variation in metal ion is an alternate way of changing the electronic and structural characteristics of the dimers. A comparison of the known complexes of chromium, molybdenum, tungsten, and vanadium with the $Cp_2M_2S_4$ formulation[6-8] (where Cp = $R_nC_5H_{5-n}$, n = 0, 1, or 5) reveal four different structural types in which the reactivities of the sulfur ligands vary significantly.



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[1] Sloan Fellow, 1981-1984. Camille and Henry Dreyfus Teacher Scholar, 1981-1986.

[2] Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

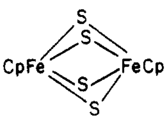
[3] Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L. Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

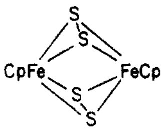
[4] Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

[5] DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429.

The report of the photolytic synthesis of two isomers of $Cp_2Fe_2S_4$,[9] I, provides an opportunity to compare the structure and reactions of this dimeric unit in a more electron-rich metal environment than is achieved with the vanadium and group 6 systems.

The iron isomers IA and IB have been synthesized from $[CpFe(CO)_2]_2$ and elemental sulfur in rather low yield (15%) by a procedure slightly modified from that reported by Gianotti and co-workers.[9,10] The previously proposed


IA


IB

structures for these isomers, shown above, required an unusually high formal oxidation state for iron in A and a violation of the 18-electron rule in B. It was therefore important to attempt to verify the structures by X-ray diffraction studies. Single crystals of A were grown from a dichloromethane/decane solvent mixture at low temperatures.[11] The complex crystallizes as discrete dimers of approximate C_{2v} symmetry with two bridging disulfide ligands. One of these is perpendicular to the metal–metal vector with both sulfur atoms bonding to both metals, while the second is parallel to the metal–metal vector with each sulfur atom bonding to only one iron in a planar Fe_2S_2 unit. These bonding modes have been classified previously as type III and type IIb, respectively.[12] The structure is unique in the series of $Cp_2M_2S_4$ dimers and provides the first example of a complex in which these two disulfide types bridge the same two metal ions. A perspective drawing and numbering scheme are shown in Figure 1, and selected bond distances and angles are summarized in Table I.

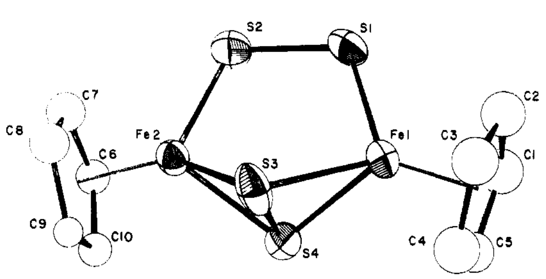


Figure 1. Perspective drawing and numbering scheme for $[CpFeS_2]_2$, IA. Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Bond Distances and Angles of Iron Dimers

distances, Å		angles, deg	
	A. $[CpFeS_2]_2$		
Fe1···Fe2	3.494	Fe1–S1–S2	111.1 (3)
Fe1–S1	2.107 (6)	Fe2–S2–S1	110.5 (3)
Fe1–S3	2.270 (6)	Fe2–S4–Fe1	101.7 (2)
Fe1–S4	2.250 (6)	Fe2–S3–Fe1	100.5 (2)
Fe2–S2	2.103 (6)		
Fe2–S3	2.275 (6)		
Fe2–S4	2.257 (6)		
S1–S2	1.999 (8)		
S3–S4	2.044 (8)		
	B. $[CpFeS_2C_2(CF_3)_2]_2$		
Fe1–Fe1′	2.657 (1)	Fe1–S1–Fe1′	74.0 (1)
Fe1–S1	2.163 (1)	Fe1–S1–C2	106.9 (1)
Fe1–S2	2.238 (1)	Fe1–S2–C3	104.7 (1)
Fe1–S1′	2.254 (2)	S1–Fe1–S2	88.5 (1)
S1–C2	1.756 (2)	S1–Fe1–S1′	103.4 (1)
S2–C3	1.707 (3)	S1–C2–C3	117.9 (2)
C2–C3	1.344 (4)	S2–C3–C2	122.0 (2)

The iron–iron distance of 3.49 Å precludes any metal–metal interaction. Despite this nonbonding distance between the formal iron(III) ions, the dimer is diamagnetic, suggesting an alternate ligand-based mechanism for electron pairing. A coupling mechanism which involves S–Fe pπ–dπ-bonding between each metal ion and a type IIb disulfide ligand has been proposed previously for the similarly bridged structure of $Cp_2Fe_2(\mu\text{-}S_2)(\mu\text{-}SR)_2$, II.[13] The Fe1–S1 and Fe2–S2 distances of IA are consistent with a similar π-bonding scheme. The distances are significantly shorter than the range normally observed for iron–sulfur single bonds (2.18–2.26 Å).[14] In contrast, the iron–sulfur distances of the type III ligand in IA are near the upper limit of this range. The S–S distance in the type IIb ligand, proposed to be involved in the delocalized π-bond, is also significantly shorter than that in the type III disulfide bridge. However both of the S–S distances lie within the range observed for other disulfide ligands and are consistent with S–S single bonding interactions.[12]

IA can be converted to II, R = Me, in low yield by the stepwise addition of methyl iodide and methyllithium. The result suggests that in this electronic environment the type III ligand is more reactive toward electrophiles than the type IIb ligand. However definite conclusions on the relative reactivities of these two ligand types are not possible because of an isomerization of I in solution.[9] In tetrahydrofuran at room temperature, isomer A equilibrates with the second isomeric form B within 8–10 h. The room-temperature equilibrium ratio of 63% A and 37% B has been determined by NMR. This interconversion in solution has also hampered attempts to grow single crystals of the less thermodynamically stable isomer B.

An important difference between the reactivity of I and the previously reported disulfide-bridged iron dimer II involves their redox behavior. Oxidation of II occurs in two one-electron steps which are chemically reversible and

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(6) (a) Brunner, H.; Kauermann, H.; Meier, W.; Wachter, J. *J. Organomet. Chem.* **1984**, *263*, 183. (b) Brunner, J.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107. (c) Tyler, D. R.; Bruce, A. E. *Inorg. Chem.* **1984**, *23*, 3433.

(7) Rajan, O. A.; McKenna, M.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1984**, *3*, 831.

(8) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321.

(9) Chanaud, H.; Ducourant, A. M.; Giannotti, C. *J. Organomet. Chem.* **1980**, *190*, 201.

(10) $[CpFe(CO)_2]_2$ (1.55 g, 5.2 mmol) and elemental sulfur (0.57 g, 2.2 mmol) were dissolved in 1.3 L of toluene. The solution was purged with nitrogen for 15 min and then photolyzed with a Hanovia 450-W Hg arc lamp in a quartz vessel with a $CuSO_4$ filter for 1 h. The solvent was removed in vacuo, and the resulting green brown solid was eluted on an alumina column with dichloromethane. The dark green band $(CpFeS_2)_2CO$[9] was isolated, redissolved in toluene, purged with N_2, and photolyzed for 15 min with no $CuSO_4$ filter. Solvent was removed in vacuo, and the brown solid was chromatographed on alumina with 25% hexane in CH_2Cl_2. Isomer IA eluted first as a red brown band followed by the dark brown band of isomer IB; yield 15%. Isomers were identified by comparison of spectra with published data.

(11) Isomer A of $Cp_2Fe_2S_4$ crystallizes in space group *Pbca* with cell dimensions a = 7.286 (1) Å, b = 17.468 (5) Å, c = 19.472 (6) Å; V = 2478 (1) Å^3, Z = 8, ρ_{calcd} = 1.98 g/cm. Using a crystal of dimensions 0.05 × 0.05 × 0.70 mm, 2339 reflections were measured at values of $+h$, $\pm k$, and $+l$ to a maximum 2θ of 40°. These were averaged to 1158 independent reflections (R_{av} = 0.056). Full-matrix least-squares calculations on 79 variables using 529 observed reflections ($F_o > 6.0\sigma(F_o)$) converged with residuals of R = 0.047 and R_w = 0.056. Atomic parameters are included in the supplementary tables.

(12) Müller, A.; Enemark, J. *Coord. Chem. Rev.* **1982**, *46*, 245.

(13) Vergamini, P. J.; Ryan, R.; Kubas, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 1980.

(14) Vergamini, P. J.; Kubas, G. J. *Prog. Inorg. Chem.* **1976**, *21*, 261.

yield the monocation and dication, respectively.[15] The latter is unstable as a result of a labilization of the disulfide ligand, and dications of the type $[CpFe(SEt)(Solv)]_2^{2+}$ have been isolated. In contrast, each isomer of I undergoes an irreversible one-electron oxidation at a platinum electrode in acetonitrile.[16]

We thought it might be possible to isolate complexes derived from each of the isomeric forms of I by reacting the equilibrium mixture with a thiophilic alkyne (although such a reaction does not necessarily preclude sulfur ligand rearrangement).[8,17] The two products which have been isolated in rather low yield from the reaction with excess hexafluorobutyne at room temperature were found to be mono and bis adducts of composition $(CpFeS)_2S_2C_2(CF_3)_2$, III, and $[CpFeS_2C_2(CF_3)_2]_2$, IV, respectively.[18] The observation of differing extents of reaction of a metallosulfur complex with an activated alkyne is rather unusual. The compositions suggested the presence of one and two perfluorobutene-2,3-dithiolate ligands,[8,19] respectively, but the orientations of these ligands was unknown. An X-ray diffraction study of a single crystal of IV has therefore been undertaken.[20] The molecule has a crystallographically imposed twofold rotational axis perpendicular to the iron–iron vector, and the complex has C_{2v} symmetry. A perspective drawing and numbering scheme are shown in Figure 2, and selected bond distances and angles are listed in Table I.

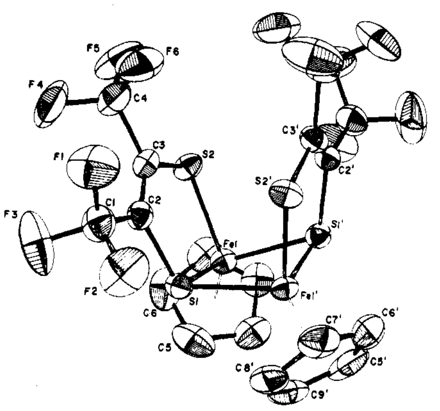

Figure 2. Perspective drawing and numbering scheme for $[CpFeS_2C_2(CF_3)_2]_2$, IV. Thermal ellipsoids are drawn at the 50% probability level.

Each dithiolate ligand contains one bridging and one terminally coordinated sulfur donor. The bonding mode is quite characteristic of other unsaturated, as well as saturated, dithiolates,[21-24] particularly in complexes which contain only this ligand type. The structure of one related cyclopentadienyl derivative has been reported previously.[25] As observed for related dimers,[21-24] the bridging sulfur atoms are asymmetrically bonded to the two iron atoms. For example, the Fe1–S1 distance, which is part of the $FeS_2C_2(CF_3)_2$ chelate ring, is significantly shorter than the Fe1′–S1 distance. A more unusual feature of the structure involves a particularly short intramolecular distance between S_2 in one planar chelate ring and an olefinic carbon in the other chelate; S2–C2′ = 3.181 (3) Å, compared to an expected S–C van der Waals distance in the range of 3.50–3.70 Å. In addition, the S2–C3′ distance of 3.456 (3) Å is somewhat shorter than expected on the basis of van der Waals radii. These short intramolecular contacts do not appear to be the result of inter- or intramolecular steric factors, and a charge-transfer interaction between the lone pair of S2 and the olefinic carbons of the electron-withdrawing alkenedithiolate ligand is therefore suggested.[26] As a possible consequence of the interaction between dithiolate ligands, the C2 to S1 distance within the chelate ring is longer than the C3–S2 bond and longer than C–S bonds in other perfluorobutenedithiolate complexes.[21,22]

The iron–iron distance in IV is suggestive of a M–M single bond.[27] However, we have been unsuccessful in obtaining an NMR spectrum for this complex, even after extensive recrystallization. Characterization of the magnetic properties of IV is the subject of further study. Since NMR data on IV are not available, we do not know whether the isomer with trans cyclopentadienyl ligands is also formed in this reaction.

A bridging configuration for the dithiolate ligand in the monoadduct III which is similar to that observed for IV is tentatively proposed on the basis of ^1H and ^{19}F NMR data which show the presence of inequivalent Cp and CF_3 groups.[18] We have so far been unsuccessful in obtaining a single crystal of III. Our initial studies have established a versatility in both the structural forms and the reactivities of the $Cp_2Fe_2S_4$ systems, and this work appears to provide an entry into new types of organometallic iron sulfur complexes.

Acknowledgment. Support from the National Institutes of Health and from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. M.R.D. is grateful for a fellowship from the John Simon Guggenheim Foundation, 1984–1985.

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(15) Kubas, G. J.; Vergamini, P. J.; Eastman, M. P.; Prater, K. B. *J. Organomet. Chem.* **1976**, *117*, 71.

(16) Isomer IA undergoes an irreversible oxidation at 0.56 V vs. SCE in acetonitrile/0.1 M $(n\text{-}Bu)_4NBF_4$ (scan rate = 100 mV/s). Isomer IB undergoes an irreversible oxidation at 0.66 V vs. SCE under similar conditions. Coulometric measurements on the oxidations of A and B yielded *n* values of 1.0 for each isomer. An irreversible reduction is observed at −1.18 V vs. SCE for A and at −1.20 V for B. Current amplitudes suggest that these may be two-electron processes.

(17) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.

(18) Excess hexafluorobutyne (5 equiv) was reacted with an equilibrium mixture of I in dichloromethane at 25 °C for 5 days. After removal of solvent, the product was chromatographed on an alumina column eluted with a 50:50 mixture of hexane–dichloromethane. The second and third green bands are the bis adduct IV and mono adduct III, respectively. III: yield 9%; ^1H NMR ($CDCl_3$) δ 4.93, 5.04 (2 s); ^{19}F NMR ($CDCl_3$) −53.92, −56.04 ppm (2 q) (referenced to CF_3CO_2H at −78.50 ppm); MS, *m/e* 532 (P), 467 (P − Cp), 347 ($CpFeS_2C_2(CF_3)_2$), 185 ($CpFeS_2$(base)). IV: yield 8%; MS, *m/e* 694 (P), 347 ($CpFeS_2C_2(CF_3)_2$(base)); IR (Nujol) 1529 cm^1 ($\nu_{C=C}$); NMR spectra of IV are not observed.

(19) Krespan, C. G.; McKusick, B. C. *J. Am. Chem. Soc.* **1961**, *83*, 3434.

(20) IV was crystallized from dichloromethane/hexane in space group *C*2/*c*. A crystal of this compound (0.12 × 0.14 × 0.08 mm) was used as a test crystal in the evaluation of diffractometers, and two complete data sets were collected: cell dimensions (Nonius and [Nicolet]) a = 16.429 (3) [16.452 (4)] Å, b = 10.134 (2) Å, [10.121 (3)] Å, c = 14.591 (2) [14.599 (4)] Å, β = 114.67 (2)° [114.70 (2)°]; V = 2205.6 (5) [2208.5 (9)] Å^3, Z = 4, ρ_{calcd} = 2.08 g/cm^3. Of 5115 [6678] reflections at values of $h, \pm k, \pm l$ [$h, k, \pm l$] in the range $3.0 \leq 2\theta \leq 55°$ [45°], 1902 [1450] reflections were observed ($F_o > 6\sigma(F_o)$). The structure was solved by direct methods. Full-matrix least-squares refinement on 179 [163] variables converged with residuals of R = 0.027 [0.038] and R_w = 0.041 [0.047]. The resulting structures were identical within error. Final tables and drawings are based on the Nonius data. Atomic parameters and tables of observed and calculated structure factors are included in the supplementary material.

(21) Enemark, J.; Lipscomb, W. N. *Inorg. Chem.* 1965, *4*, 1729.

(22) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295.

(23) Bravard, D. C.; Newton, W. E.; Enemark, J. H.; Yamanouchi, K.; Huneke, J. T. *Inorg. Chem.* **1982**, *21*, 3795.

(24) (a) Costa, T.; Dorfman, J. R.; Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 4091. (b) Snow, M. R.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 249. (c) Dorfman, J.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3179.

(25) $[CpFe(S_2C_6H_4)]_2$ was found to have an analogous structure. However, the structure could only be refined to R_w = 0.14 and accurate bond distances were not determined: Sellman, D.; Unger, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1438.

(26) This is in contrast to an apparent repulsive interaction between perfluorobutenedithiolate chelate rings observed in a cobalt dimer $Co_2C_8S_8(CF_3)_8$ (see ref 21).

(27) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7472.

Registry No. IA, 96688-96-9; II, 96688-97-0; III, 96688-98-1; IV, 96688-99-2; $(\text{CpFeS}_2)_2\text{CO}$, 75071-60-2; $[\text{CpFe(CO)}_2]_2$, 12154-95-9; hexafluorobutyne, 692-50-2; sulfur, 7704-34-9.

Supplementary Material Available: Tables of conditions and parameters for the X-ray diffraction studies, positional and thermal parameters, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Organosilane High Polymers: Thermochromic Behavior in Solution

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Summary: Aliphatically substituted polydiorganosilylenes display reversible thermochromic behavior in solution with a bathochromic shift occurring with decreasing temperature. Solutions of polymers $(\text{RMeSi})_n$, R = *n*-propyl and *n*-hexyl, and poly(di-*n*-propylsilylene) show gradual bathochromic shifts of 16–25 nm from 92 to −67 °C. In polymers containing long di-*n*-alkyl substituents (*n*-alkyl = *n*-butyl, *n*-pentyl, and *n*-hexyl) the principal absorption band disappears as the temperature is lowered and a new band appears at 354 nm, giving a total red shift of up to 44 nm. The temperature dependence of the UV absorption maxima is thought to be due to conformational changes occurring along the polymer backbone with temperature.

Organopolysilenes, because of their remarkable long wavelength absorption spectra,[1] offer a unique opportunity[2] to observe the dependence of electronic transition energy on backbone conformation. These polymers display an intense UV absorption band, described as a delocalized $\sigma \rightarrow \sigma^*$ or a $\sigma \rightarrow 3d$ transition, in the mid-UV region. The position of the band ($\lambda_{\max}$) and its absorptivity per Si–Si bond ($\epsilon_{\text{Si-Si}}$) increase regularly with increasing chain length, finally becoming constant for very long chains. The absorption maxima *at room temperature* (λ_{maxRT}) exhibit a red shift with increasing size of the alkyl substituent with λ_{maxRT} in the range from 305 to 326 nm. The variation of λ_{maxRT} with substituent bulk has been attributed to conformational changes about the polysilane skeletal framework[1] induced by interactions between adjacent Si-bound substituents, which alter the overlap between geminal or 1,3 Si–Si σ orbitals and change the orbital energies.[3,4]

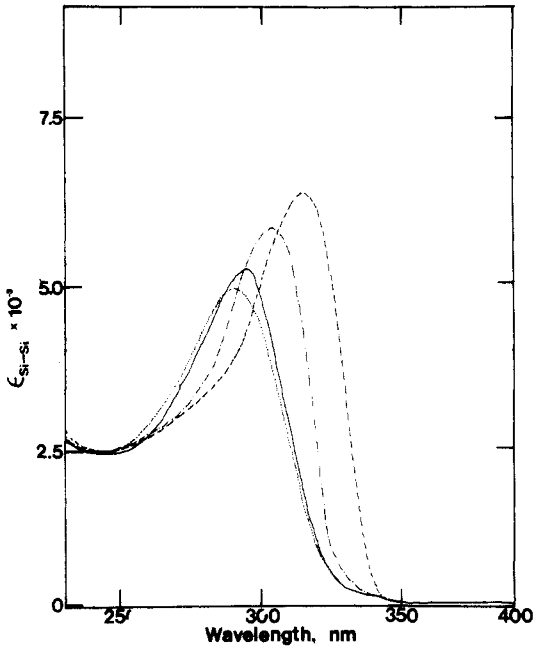

Figure 1. UV spectrum of a 0.0035% solution of $(n\text{-HexMeSi})_n$ in isooctane: (···), 92 °C; (—), 24 °C; (-·-), −17 °C; (- - -), −67 °C.

Recently a temperature-dependent change of the UV spectrum has been observed for films of poly(di-*n*-hexylsilylene)[5,6] and attributed to crystallization of the side chains in the solid.[5] We have now examined the UV spectra of solutions of several polysilylenes as a function of temperature and find that striking and unprecedented thermochromic changes in the UV absorption also occur in solution.

Three distinct types of thermochromic behavior have been observed for poly(dialkylsilylenes). The first is exemplified by poly(*n*-propylmethylsilylene), **1**, poly(*n*-hexylmethylsilylene), **2**, and poly(di-*n*-propylsilylene), **3** [λ_{maxRT} 305 (**1**), 306 (**2**), and 310 nm (**3**)].[7] In these polymers, $\lambda_{\max}$ undergoes a continuous bathochromic shift of 25 nm for **1**, 16 nm for **2**, and 22 nm for **3** (Figure 1) on cooling from 92 to −67 °C. We believe this thermochromism is probably due to a continuously increasing relative population of trans conformation in the polymer backbone with cooling.[8,9]

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(1) (a) Trefonas, P. III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823. (b) West, R. In "Ultrastructure Processing of Ceramics, Glass and Composites"; Hench, L., Ulrich D. R., eds. Wiley: New York, 1984; Chapter 19. (c) Miller R. D.; Hofer, D.; Willson, C. G.; West, R.; Trefonas, P. In "Materials for Microlithography"; Thompson, L., Willson, C. G., Frechet, J. M. J., Eds.; American Chemical Society: Washington, D.C., 1984; ACS *Symp. Ser. No.* 266, p 293.

(2) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387.

(3) It has been shown that the energies of the delocalized $\sigma_{\text{Si-Si}}$ HOMO in tetrasilane and pentasilane vary with molecular conformation: Bock, H.; Ensslin, W.; Feher, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668.

(4) Full relaxation, empirical force field calculations for poly(dimethylsilylene) reveal that this polymer adopts the gauche conformation in the ground state. However, if the VDW radii of the methyl groups are increased to simulate increasing substituent bulk, the trans conformation becomes increasingly preferred. Damewood, J. R.; West, R., unpublished results.

(5) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N., submitted for publication in *J. Am. Chem. Soc.*

(6) Harrah, L. A.; Zeigler J. M. *J. Polym. Sci., Polym. Lett. Ed.*, in press.

(7) All polymers used (except **1**, $\bar{M}_w = 3.0 \times 10^4$, and **6**, $\bar{M}_w = 4.0 \times 10^4$) are of high molecular weight, with $\bar{M}_w$ in excess of 5.0×10^5. Ultraviolet spectra were taken in isooctane for **1–3**, hexane for **4–1**, and methylcyclohexane for **7**.

(8) Conformations of polymers in solution are frequently temperature dependent; see: Elias, H.-G. In "Macromolecules"; Plenum Press: New York, 1976; Chapter 4.

(9) A qualitative LCAO model predicts that the $\sigma_{\text{Si-Si}}$ HOMO–LUMO energy separation will be smaller in the trans conformation than the gauche. The UV absorption would therefore be expected to red shift with increasing trans population in the polymer backbone. These predictions have been confirmed by MNDO calculations on tetrasilabutane and by molecular mechanics calculations on **6**. Damewood, J. R., unpublished results.

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