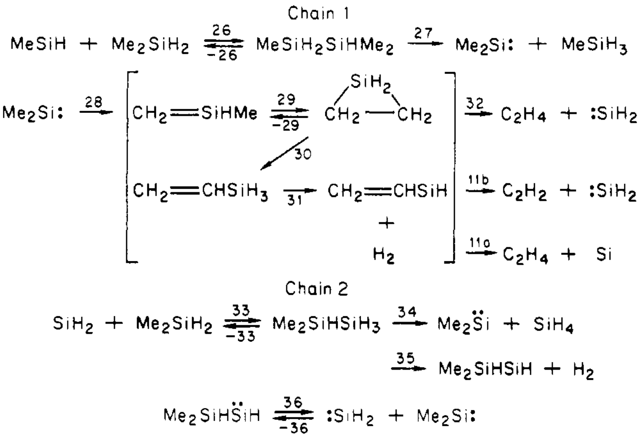
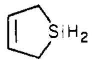
Table III. Kinetics of Some Silylene Reactions

reaction	log A, s^{-1}	E, kcal	how obtained
$CH_2{=}CH\ddot{Si}H \longrightarrow C_2H_2 + \ddot{Si}H_2$	15.0	49.6	modeling studies (VS)
$\longrightarrow C_2H_4 + \ddot{Si}$	15.0	50.6	modeling studies (VS)
$\ddot{Si}H_2 + \ddot{Si}H_2 \longrightarrow Si_2H_4$	11.9	0	kinetic molecular theory
$Si_2H_4 \longrightarrow 2\ddot{Si}H_2$	15.3	58.0	thermochemistry (DS, MS)
$Si_2H_4 \longrightarrow Si_2H_2 + H_2$	14.5	53.0	modeling studies (DS)
$ViSiH_2SiH_3 \longrightarrow ViSiH_2\ddot{Si}H + H_2$	15.45	55.3	modeling studies (VS)
n-$Pr\ddot{Si}H \longrightarrow C_3H_6 + \ddot{Si}H_2$	12.6	31 ± 5	see text
$\longrightarrow C_2H_4 + CH_2{=}SiH_2$	12.0	30.4 ± 5	see text
$\ddot{Si}H_2 + C_2H_4 \longrightarrow CH_2{=}CHSiH_3$	10.1	14.0	modeling studies (MS); thermochemistry (VS)

Scheme I



of silane, methylsilane, ethylene, and acetylene as products suggest the occurrence of the two coupled silylene chains shown in Scheme I. Subsequent decompositions of $MeSiH_3$ and SiH_4 promote chain branching in the system. As stated earlier the radical and silylene chains are not appreciably quenched by additions of trapping agents. This is undoubtedly a consequence of the high temperatures needed to investigate these reactions by our experimental technique (SPST, T(K) $\simeq$ 1150→1300 K). For example, we have found that the 1,3-butadiene–SiH_2



product decomposes fairly rapidly at temperatures around 1200 K. Further, the use of toluene as a free radical trap is relatively inefficient at these temperatures because toluene decomposes to H and benzyl radicals at rates that are *faster* than the primary processes of the reactant under our reaction conditions (30 toluene/1 reactant, $T > 1200$ K). Also, benzyl radicals, produced by trapping of more active radicals, can initiate chain decomposition of the reactant through hydridic H abstraction at these temperatures. Toluene should, therefore, not be used as a free radical trapping agent at temperatures much above 1200 K even in a shock tube.

In Table II we have summarized our observations on the overall decomposition kinetics for the group III silanes (various conditions). These kinetic parameters should be compared with those measured or estimated for the primary dissociation processes alone.

In Table III we summarize other kinetic data relative to secondary reactions of silylenes that we have been able to establish either completely or in part through our kinetic studies.

In conclusion, we would like to emphasize a point frequently overlooked. The kinetics of silane and silylene systems, like all kinetic systems, will vary significantly from one temperature and pressure regime to another. Full knowledge of the pertinent kinetics is therefore essential to even a qualitative understanding of these systems. Hopefully the kinetic data reported here will prove to be useful in this regard.

Acknowledgment. We are indebted to the Department of Energy for financial support of this work from Grant DE-FG02-80CS-83103.

Registry No. $CH_2{=}CHSiH_3$, 7291-09-0; C_2H_4, 74-85-1; $C_2H_5SiH_3$, 2814-79-1; $C_3H_7\ddot{Si}H$, 87640-43-5; $C_3H_7SiH_3$, 13154-66-0; $(CH_3)_2SiH_2$, 1111-74-6; CH_4, 74-82-8; $(CH_3)_3SiH$, 993-07-7; $C_2H_5Si(CH_3)_2H$, 758-21-4; C_3H_6, 115-07-1; $CH_2{=}CH\ddot{Si}H$, 78442-50-9; $\ddot{Si}H_2$, 13825-90-6; $C_2H_5\ddot{Si}H$, 81875-16-3; $CH_3\ddot{Si}H$, 55544-30-4; $CH_3SiH_2\cdot$, 24669-75-8; $\cdot CH_3$, 2229-07-4; $(CH_3)_2\ddot{Si}$, 6376-86-9; $(CH_3)_3Si\cdot$, 16571-41-8; $C_2H_5\ddot{Si}CH_3$, 87640-44-6; $(CH_3)_2SiH\cdot$, 24669-76-9; $\cdot C_2H_5$, 2025-56-1; $C_2H_5Si(CH_3)H\cdot$, 87640-45-7; Si_2H_4, 15435-77-5; silacyclopent-3-ene, 7049-25-4.

Preparation and Structure of $(\eta\text{-}C_5H_5)_2Ti(SC_6H_5)(SSSC_6H_5)$: The Product of a Sulfur Catenation Reaction

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Summary: The complex $Cp_2Ti(SH)_2$ was treated with 2 equiv of RS–imide, where imide = phthalimide and R = $CHMe_2$ and p-$C_6H_4CH_3$ and imide = succinimide and R = C_6H_5, to give the symmetrical disulfane $Cp_2Ti(SSR)_2$ when R = $CHMe_2$ and the unsymmetrical trisulfanes $Cp_2Ti(SR)(SSSR)$ when R = C_6H_5 and p-$C_6H_4CH_3$. The structure of the compound where R = C_6H_5 was determined and the TiSSSR linkage characterized.

Complexes containing cyclic polysulfane chelating ligands often have strongly preferred ring sizes.[2,3] For the complexes Cp_2MS_5, where M = Ti, Zr, and Hf, the ring size is six despite careful attempts to prepare smaller rings.[2] Thus, $Cp_2Ti(SH)_2$ reacts with sulfur-transfer reagents of the type imide–S_x–imide, where imide = phthalimide and

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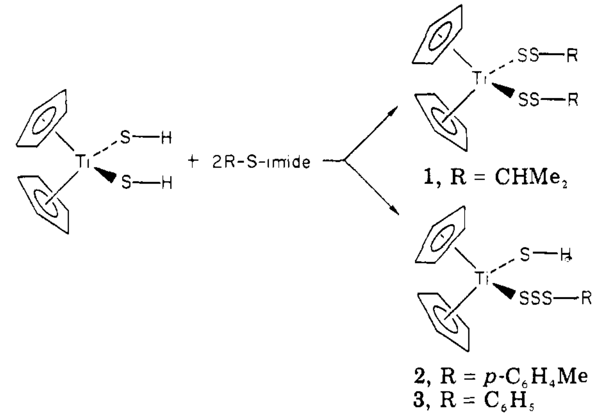
[1] (a) To whom correspondence concerning the preparations should be sent. (b) To whom correspondence concerning the X-ray structural determination should be sent.

[2] McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37–C39.

[3] Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 384–385.

Scheme I



x = 1 and 2, to give Cp_2TiS_5 in reasonable yields based on the sulfur present in the reaction, regardless of the reaction conditions.[2] "Blocked" sulfur-transfer reagents of the type RS_x–imide, where R = aryl or alkyl,[4] react with $CpW(CO)_3SH$ to give complexes of the type $CpW(CO)_3S_yR$, where y = 2 and 3.[5] However, these tungsten polysulfane compounds spontaneously lose sulfur to form the appropriate thiolato complexes where x = 1. Thus, it was of interest to study the reactions of $Cp_2Ti(SH)_2$ with "blocked" sulfur-transfer reagents. The product isolated is dependent on R and in the case where R = aryl and x = 1 a novel chain lengthening rearrangement occurs to give $Cp_2Ti(SR)(SSSR)$, a rare example of a trisulfano ligand.[6]

Treatment of $Cp_2Ti(SH)_2$ with 2RS–imide, where imide = phthalimide and R = $CHMe_2$ and p-$C_6H_4CH_3$ and imide = succinimide and R = C_6H_5, proceeds smoothly under N_2 in THF at 0 °C to give[11] complexes **1** (73%), **2** (67%), and **3** (61%) as purple solids that were stable to air for short periods (Scheme I). These were characterized satisfactorily by IR, NMR,[12] and mass spectroscopy and by elemental analysis. In contrast to the complexes $CpW(CO)_3S_xR$, where x = 2 and 3, there was no tendency for **1**–**3** to spontaneously desulfurize to give the thiolato complexes $Cp_2Ti(SR)_2$. However, complexes **1** and **3** decompose over the period of 3 days in aromatic solvents above 0 °C to produce mixtures of polysulfanes, RS_yR, for which y = 4 predominates when R = $CHMe_2$. The assignment of a symmetrical structure to **1** is based on the observation of resonances due to only one type of $CHMe_2$ group in the ^{13}C and ^1H spectra in a variety of solvents.[13] Thus, the isolation of **1** is consistent with the logic of the preparative route. The structure of **3** is shown in Figure 1 and is quite unexpected.[15]

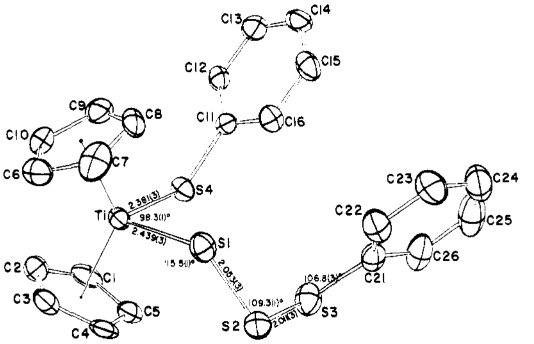


Figure 1. Perspective drawing of the solid-state structure of $Cp_2Ti(SPh)(SSSPh)$. The atoms are represented by thermal ellipsoids drawn to encompass 30% of their root-mean-square vibrational amplitudes.

Compound **3** is a monomer[16] with two η-C_5H_5 rings; however, the two SPh groups have been unsymmetrically incorporated as a SPh^- ligand and a $SSSPh^-$ ligand. The most unusual and important feature of **3** is the S_3 chain. Very few inorganic complexes containing a M–S_xR linkage have been structurally characterized for $x \geq 2$.[5,17,20] The immediate coordination sphere of **3** is similar to that of $Cp_2Ti(SPh)_2$ (**4**).[21,22] In **3** there is a difference in the two

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[4] These reagents have been used with great success to prepare unsymmetrical polysulfides: (a) Harpp, D. N.; Ash, D. K.; Back, T. G.; Gleason, J. G.; Orwig, B. A.; van Horn, W. F.; Snyder, J. P. *Tetrahedron Lett.* **1970**, 3551–3554. (b) Boustany, K. S.; Sullivan, A. B. *Ibid.* **1970**, 3547–3549. (c) Harpp, D. N.; Ash, D. K. *Int. J. Sulfur Chem., Part A* **1971**, *1*, 211–214. (d) Behforouz, M.; Kerwood, J. E. *J. Org. Chem.* **1969**, *34*, 51–55. (e) Abe, Y.; Nakabayaski, T.; Tsurugi, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1898–1899.

[5] Shaver, A.; Hartgerink, J.; Lai, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938–940.

[6] The IUPAC convention for linear polysulfur compounds is that they be named polysulfanes.[7,8] Thus, it is proposed[9] that ligands of the type SSR^- and $SSSR^-$ be called "alkyl (or aryl) disulfano" and "trisulfano", respectively. The term "perthiolato", as applied[10] to the ligands SSR^-, leaves no room for $SSSR^-$ and higher homologues. The use of "thiolato" rather than "monosulfano" or "sulfano" has been maintained. In addition, the SH^- ligand can be designated as "hydrosulfido" in order to differentiate it from SR^-, where R ≠ H.

[7] (a) Fehér, F.; Kraemer, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1953**, *8B*, 687. (b) Fehér, F.; Rempe, G. *Ibid.* **1953**, *8B*, 688. (c) Fehér, F.; Laue, W. *Ibid.* **1953**, *8B*, 687.

[8] Leoning, K. L. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3, pp 339–354.

[9] The use of this nomenclature is developed in: (a) Hartgerink, J. M.M.Sc. Thesis, McGill University, 1981. (b) Lai, R. D. Ph.D. Thesis, McGill University, 1981.

[10] Bhattacharya, S. N.; Senoff, C. V.; Walker, F. S. *Inorg. Chim. Acta* **1980**, *44*, L273–L274.

[11] The solvent was removed at 0 °C and the residue extracted with CS_2 at this temperature. The resulting solution was filtered and evaporated to dryness in vacuo. The residue was recrystallized from hot hexanes (**1**) and hot 1:1 hexanes–CH_2Cl_2 (**2**,**3**). The ^1H NMR spectra of the crude products taken before the CS_2 extraction were the same as those of the analytical samples[12] which indicates that no further reaction occurred during the workup. Anal. Calcd for $C_{16}H_{24}S_4Ti$ (**1**): C, 48.96; H, 6.16; S, 32.68. Found: C, 49.03; H, 6.05; S, 32.45. Anal. Calcd for $C_{24}H_{24}S_4Ti$ (**2**): C, 59.00; H, 4.95; S, 26.76. Found: C, 57.62; H, 4.95; S, 25.12. Anal. Calcd for $C_{22}H_{20}S_4Ti$ (**3**): C, 57.37; H, 4.38, S, 27.85. Found: C, 56.59; H, 4.12; S, 27.29.

[12] **1**: ^1H NMR ($CDCl_3$) δ 6.21 (s, C_5H_5), 3.06 (m, J = 6.7 Hz, CH), 1.28 (d, CH_3); ^{13}C NMR (C_6D_6) δ 113.17 (C_5H_5), 42.31 (CH), 23.14 (CH_3). **2**: ^1H NMR ($CDCl_3$) δ 7.57–7.03 (m, C_6H_4), 6.12 (s, C_5H_5), 2.35 (s, CH_3). **3**: ^1H NMR ($CDCl_3$) δ 7.2 (m, C_6H_5) 6.08 (s, C_5H_5).

[13] The chemical shift of groups attached to sulfur is usually dependent on the length of the sulfur chains in both organic compounds[14] and the complexes $CpW(CO)_3S_xR$, where x = 1–3.[9a] The methine resonance of $Cp_2Ti(SCHMe_2)_2$ appears at δ 3.65.

[14] Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1972**, 107–109.

[15] Only one slightly broadened resonance was observed for the methyl groups in the ^1H NMR spectrum of **2**. The chemical shift of the methyl group in p-tolyl polysulfanes is not sensitive to chain length.[5,9a] The structure of **2** was assigned by analogy to **3**.

[16] The crystal data for **3**: space group $P2_1/c$ (No. 14), a = 7.794 (5) Å, b = 14.664 (10) Å, c = 18.360 (10) Å, β = 101.90 (6)°, Z = 4, V = 2053.3 Å^3, d_{calcd} = 1.490 g cm^{-3}. A hemisphere of 3783 reflections measured on a Picker FACS-1 automated diffractometer yielded 1912 independent reflections. Of these 1209 with $I > 2\sigma(I)$ were used in the solution by direct methods and refinement by block-diagonal least squares. The final residuals were R_F = 0.0378 and R_{wF} = 0.0503. Hydrogen atoms were included in calculated positions.

[17] Examples include $CpW(CO)_3(S_2$-4-$C_6H_4Me)$ and cis-$(PPh_3)_2Pt(imide)(S_2CHMe_2)$, where imide = phthalimido.[5] Complexes that contain a M–S_3–M linkage include $[CpFe(CO)_2]_2(\mu$-$C_3)$[18] and $[(MeCp)_2Ti(\mu$-$S_3)]_2$.[19]

[18] El-Hinnawi, M. A.; Aruffo, A. A.; Santarsiero, B. D.; McAlister, D. R.; Schomaker, V. *Inorg. Chem.* **1983**, *22*, 1585–1590.

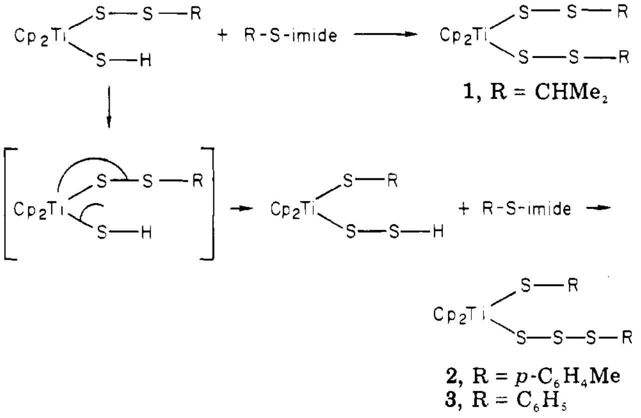
[19] Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620–5621.

[20] (a) Fackler, J. P., Jr.; Fetchin, J. A.; Fries, D. C. *J. Am. Chem. Soc.* **1972**, *94*, 7323–7333. (b) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301–469.

[21] Muller, E. G.; Watkins, S. F.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 73–89.

[22] Replacement of one SPh^- group in **4** by a $SSSPh^-$ moiety causes minor changes in the bond length and angles in the immediate coordination sphere of the metal atom.

Scheme II



1, R = CHMe$_2$

2, R = p-C$_6$H$_4$Me
3, R = C$_6$H$_5$

Ti-S distances (Ti-S1 = 2.439 (3) Å, Ti-S4 = 2.381 (3) Å), but this may not be entirely due to its unsymmetrical structure since similar asymmetry was observed for 4 and Cp$_2$V(SPh)$_2$.[21] The two S-S distances (S1-S2 = 2.053 (3) Å, S2-S3 = 2.011 (3) Å) are within the ranges observed for trisulfides,[23] and the variation between them is presumably a consequence of the different substituents terminating the S$_3$ chain.

The isolation of 3 is another example of the tendancy for chain growth in the Cp$_2$Ti system. The complex may be considered to be a model of a possible intermediate in the reactions that lead to Cp$_2$TiS$_5$ from unblocked sulfur transfer reagents. Scheme II depicts possible routes to 1-3 starting from Cp$_2$Ti(SSR)SH which is the most reasonable first product[25] from the reaction of Cp$_2$Ti(SH)$_2$ with 2 equiv of RS-imide. Aryl thiolate anions are much better leaving groups than alkyl ones[26] which may explain the difference between 1 and 2, 3. The formation of sulfur-sulfur bonds on transition-metal templates[18] would appear to be a promixing new area of study with potential applications to organosulfur chemistry.

Acknowledgment. This research was supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERCC), the Quebec Department of Education, and Imperial Oil Co. of Canada. Predoctoral fellowships awarded to J.M.M. by NSERCC and the Noranda Group of Companies are gratefully acknowledged. We thank Professor D. N. Harpp of McGill University for helpful discussions.

Registry No. 1, 87434-23-9; 2, 87434-24-0; 3, 87434-25-1; Cp$_2$Ti(SH)$_2$, 12170-34-2; 2-[(1-methylethyl)thio]-1*H*-isoindole-1,3(2*H*)-dione, 15199-26-5; 2-[(4-methylphenylthio]-1*H*-isoindole-1,3(2*H*)-dione, 15199-26-5; 1-(phenylthio)-2,5-pyrrolidinedione, 14204-24-1.

Supplementary Material Available: Tables of positional and thermal parameters, structure factors, and bond distances and angles with their estimated standard deviations for complex 3 (8 pages). Ordering information is given on any current masthead page.

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[23] The trans conformation, the SSS bond angle (109.3 (1)°), and the dihedral angles TiS1S2/S1S2S3 = 70.44 (8)° and S1S2S3/S2S3C21 = 78.98 (8)° are also within the ranges observed for trisulfides.[24]

[24] Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 3.

[25] As suggested by a reviewer, a similar rearrangement of Cp$_2$Ti-(SSR)$_2$ could lead to 2 and 3. No new complexes were detected upon the decomposition of 1.

[26] Field, L. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977.

Crystal and Molecular Structure of Cr(C$_6$H$_5$)$_3$(OC$_4$H$_8$)$_3$

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Summary: Although triphenyltris(tetrahydrofuran)chromium(III) is a classic "textbook" compound in the organometallic literature, its molecular structure has never been established unequivocally. In particular, the question of whether the compound has a cis(facial) or trans(meridional) configuration has remained unresolved. In this paper we show that the compound has a cis(facial) geometry, with three σ-bonded phenyl ligands.

Chromium-aryl complexes are among the very first organometallic compounds ever synthesized, chiefly as a result of Hein's pioneering work in the 1920s and 1930s.[1,2] The very interesting and widely studied reaction[2-5] of phenyl Grignard with chromium(III) halides shows a strong dependence on the choice of solvent, reaction temperature, and the particular stoichiometry of the reactants. While no recognizable product is obtained at room temperature in diethyl ether,[6] at low temperature a threefold excess of reducing agent produces a mixture of π-arene/chromium complexes.[7] However, in tetrahydrofuran the reaction leads to a σ-bonded complex, Cr(C$_6$H$_5$)$_3$(OC$_4$H$_8$)$_3$, a key intermediate of the above reaction.[8] Though the σ complex was made as early as 1957 during the extensive investigations by Zeiss and co-workers on the CrCl$_3$/PhMgBr/THF system, its molecular geometry has remained elusive. Over the years, it has been represented as having either a cis(facial)[9] or trans(meridional)[10] configuration. In solution, CrPh$_3$(THF)$_3$ selectively loses one molecule of THF,[12] and on this basis it has been suggested to have a trans structure.[4,13] A more interesting aspect of its chemical behavior is an unusual reaction whereby it irreversibly rearranges to π-arene/chromium compounds upon loss of solvated molecules either under heat, under reduced pressure, or on treatment with diethyl ether.[8] How this rearrangement is brought about is not clear; however, some speculations regarding possible mechanisms have been made.[3] We thus feel that it is important to establish the correct geometry of the parent complex, which would not only provide a more meaningful starting point for any proposed mechanism of the σ/π transformation but would also establish the geometry of a large

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[1] An excellent and comprehensive review of Hein's early work is given by Zeiss.[2]

[2] Zeiss, H. *ACS Monogr.* **1960,** *No. 147,* 380.

[3] Zeiss, H. H.; Sneeden, R. P. A. *Angew. Chem., Int. Ed. Engl.* **1967,** *6,* 435.

[4] Sneeden, R. P. A. "Organochromium Compounds"; Academic Press: New York, 1975.

[5] Cotton, F. A. *Chem. Rev.* **1955,** *55,* 551.

[6] Bennett, G. M.; Turner, E. E. *J. Chem. Soc.* **1914,** 1057.

[7] (a) Zeiss, H.; Tsutsui, M. *J. Am. Chem. Soc.* **1959,** *81,* 1367. (b) Zeiss, H.; Tsutsui, M. *Ibid.* **1957,** *79,* 3062. (c) Zeiss, H.; Herwig, W. *Ibid.* **1956,** *78,* 5959. (d) Zeiss, H.; Tsutsui, M. *Naturwissenschaften* **1957,** *44,* 420.

[8] (a) Herwig, W.; Zeiss, H. *J. Am. Chem. Soc.* **1957,** *79,* 6561. (b) Herwig, W.; Zeiss, H. *Ibid.* **1959,** *81,* 4798.

[9] See Figure 8.4 of ref 2.

[10] See, for example: (a) Scheme 1-1 (page 2) and structure 68 (page 139) of ref 4; (b) structure 9a (page 437) of ref 3; and (c) page 557 of ref 11.

[11] Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978.

[12] Hakle, J.; Stolze, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1964,** *19B,* 1081.

[13] Daly, J. J.; Sneeden, R. P. A. *J. Chem. Soc. A* **1967,** 736.

0276-7333/83/2302-1896$01.50/0