more difficult phosphine dissociation from the hydridoacyl compounds.

On the basis of the above observations, we believe that both the reductive elimination and the decarbonylation reactions of the complexes **2** proceed from a common unsaturated intermediate, **6**, formation of which is rate determing (Scheme I). Because the hydridoalkyl reductive elimination step in the decarbonylation process is irreversible, whereas the hydridoacyl reductive elimination is reversible, the decarbonylation process usually predominates. However, if the equilibrium is interrupted either by removal of the product aldehyde or the product Rh(I) complex, e.g., by oxidative addition of hydrogen as in the hydroformylation process, the hydridoacyl reductive elimination prevails.

We are currently actively pursuing further clarification of these reactions as well as studying other reactions of hydridoacylrhodium complexes, notably, hydroacylation.

Acknowledgment. I am grateful to Dr. S. S. Wreford for helpful discussions and to Mr. M. A. Cushing, Jr., for excellent technical assistance.

Registry No. 1, 36103-64-7; **2a**, 82555-25-7; **2b**, 82978-78-7; **2c**, 82963-16-4; **2d**, 82963-17-5; **3**, 83023-45-4; **4**, 36713-95-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; $(C_6H_5F)CHO$, 459-57-4; (MeO)CHO, 107-31-3; $[Rh(PMe_3)_4]Cl$, 70525-09-6.

Structure of $(C_5H_4CH_3)_2V_2S_5$ and Its Acetylene Addition Reaction

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Summary: Thermal rearrangement of $(C_5H_4CH_3)_2VS_5$ gives high yields of $(C_5H_4CH_3)_2V_2S_5$ (**1**) whose structure consists of equivalent $(C_5H_4CH_3)V$ units bridged by μ-S, μ-η^1-S_2, and μ-η^2-S_2 ligands.

It has previously been reported that $(C_5H_5)_2VS_5$ rearranges in refluxing benzene solutions to give a poorly soluble product analyzing as $[(C_5H_5)_2V_2S_5]_n$.[1] While the precursor complex has been structurally characterized as a pentasulfido chelate,[1,2] the nature of the bimetallic product, which can also be prepared by treatment of $(C_5H_5)V(CO)_4$ with sulfur,[3] remains a mystery. This problem attracted our attention because of its relevance to the coupling reactions we recently observed in our studies on the desulfurization of $(C_5H_4R)_2TiS_5$.[4,5] X-ray diffraction quality crystals of $[(C_5H_5)_2V_2S_5]_n$ have eluded us and others;[1] however, suitable single crystals of $[(C_5H_4CH_3)_2V_2S_5]_n$ (**1**) were easily grown from dichloromethane–methanol solutions.

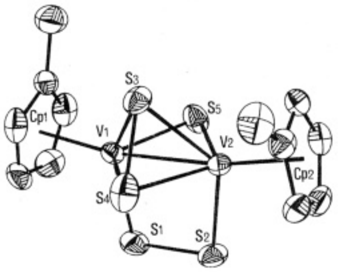

Figure 1. An ORTEP view of the $(C_5H_4CH_3)_2V_2S_5$ molecule showing the labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

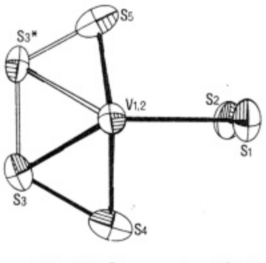

Figure 2. A view of the V_2S_5 core in $(C_5H_4CH_3)_2V_2S_5$ looking directly along the V1–V2 vector. In 19% of the molecules, S3* is present and S3 is absent. Thus, in the minority case, the S3*, S5 pair is the μ-η^2-S_2 ligand and S4 is a μ-S ligand.

Table I. Selected Bond Distances (Å) and Angles (Deg) for $(C_5H_4CH_3)_2V_2S_5$ (1)

(a) Bond Distances

V1–V2	2.658 (1)	V1–S5	2.267 (1)
V1–S1	2.316 (1)	V2–S5	2.263 (1)
V2–S2	2.315 (1)	V1–S3*	2.440 (6)
V1–S3	2.391 (2)	V2–S3*	2.414 (5)
V2–S3	2.401 (1)	S1–S2	2.023 (2)
V1–S4	2.348 (1)	S3–S4	1.956 (2)
V2–S4	2.353 (2)		

(b) Bond Angles

V1–S3–V2	67.4 (0)	V2–S4–S3	67.0 (1)
V1–S4–V2	68.9 (0)	S1–V1–V2	82.1 (0)
V1–S5–V2	71.9 (0)	S2–V2–V1	82.2 (0)
V1–S3*–V2	66.4 (1)	S3–V1–V2	56.5 (0)
V1–S1–S2	97.9 (1)	S3–V2–V1	56.1 (0)
V2–S2–S1	97.8 (1)	S4–V1–V2	55.7 (0)
V1–S3–S4	64.5 (1)	S4–V2–V1	55.5 (0)
V1–S4–S3	66.8 (1)	S5–V1–V2	54.0 (0)
V2–S3–S4	64.4 (1)	S5–V2–V1	54.1 (0)

$[(C_5H_4CH_3)_2V_2S_5]_n$ is easily prepared via the thermal rearrangement of $(C_5H_4CH_3)_2VS_5$ in refluxing toluene (7 mL/mmol of $(C_5H_4CH_3)_2VS_5$) (eq 1). After 3 h, the hot

$$(C_5H_4CH_3)_2VS_5 \xrightarrow[\text{PhCH}_3]{110\ ^\circ\text{C}} (C_5H_4CH_3)_2V_2S_5 \qquad (1)$$

toluene solution was filtered, concentrated, and cooled to −25 °C, giving analytically pure black crystals of **1** in 85% yield.[6]

The structure[7] of **1** is depicted in Figure 1, and a view of the V_2S_5 core is shown in Figure 2; important bond

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

(2) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416.

(3) Schunn, R. A.; Fritchie, C. J.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892.

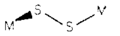
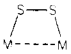
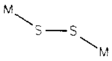
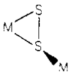
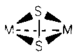
(4) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

(5) Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223.

(6) Anal. Calcd for $C_{12}H_{14}S_5V_2$ (1): C, 34.28; H, 3.36; S, 38.13; V, 24.23. Found: C, 34.28; H, 3.46; S, 38.03; V, 23.89. IR (mineral oil mull): 1067 (m), 1052 (m), 1034 (m), 931 (w), 917 (w), 889 (w), 815 (s), 602 (w), 566 (m), 534 (m), 469 (w), 430 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.59 (2 H, m), 6.38 (2 H, m), 2.38 (3 H, s). EI mass spectrum (70 eV), *m/e* (relative intensity): 420 (37, M^+), 356 (100, $C_{12}H_{14}S_3V_2^+$).

(7) $(C_5H_4CH_3)_2V_2S_5$ (1) crystallizes in the monoclinic space group $C2/c$ with $a = 12.703$ (5) Å, $b = 7.917$ (2) Å, $c = 31.30$ (1) Å, $\beta = 102.22$ (4)°, $V = 3075.9$ Å^3, $Z = 8$, and $\mu = 18.13$ cm^{-1} (Mo Kα, $\lambda = 0.71073$ Å). A total of 3057 reflections ($3° \le 2\theta \le 50°$) were collected on a Nicolet R3 diffractometer of which 2696 reflections were unique. Of these reflections, 2300 with $F_o \ge 2\sigma(F_o)$ were used in the subsequent solution and refinement. The final discrepancy factors are 4.63 and 4.22% for R_F and R_{wF}, respectively.

Table II. Bridging Disulfur Ligands Observed in Binuclear Cyclopentadienyl Complexes[a]

M_2S_2 geometry	descriptor	$(e^-/S)_{av}$	examples (ref)
	skew-μ-η^1	1	$(Cp''MoS_2)_2S_6$ (12)
	iso-μ-η^1	1	$(Cp''Cr)_2S_5$ (11)
	syn-μ-η^1	1–2	$(Cp'V)_2S_5$ $[CpFe(\mu\text{-}SEt)]_2S_2$ (13)
	anti-μ-η^1	2	$[CpMn(CO)_2]_2S_2$ (14)
	μ-η^1,η^2	2	$[Cp''MoS_2]_2S_6$ (12)
	μ-η^2	3	$(Cp'V)_2S_5$ $(Cp''Cr)_2S_5$ (11)

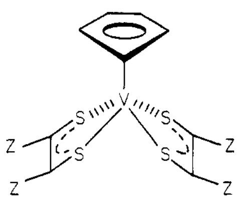
[a] $Cp = C_5H_5$; $Cp' = C_5H_4CH_3$; $Cp'' = C_5(CH_3)_5$

distances and angles are collected in Table I. The molecule is composed of two (methylcyclopentadienyl)vanadium fragments symmetrically bridged by three different types of sulfur ligands. The methylcyclopentadienyl ligands are inclined at an angle of 21° toward each other and away from the μ-η^1-S_2 ligand. The methyl groups are also positioned so as to minimize their interaction with this same sulfur ligand. The V(1)–V(2) bond distance of 2.658 Å is considerably longer than that observed for $(C_5H_5)_2V_2(CO)_5$ which is 2.46 Å.[8]

Bridging the two vanadium atoms are μ-S (S5), μ-η^1-S_2 (S1, S2), and μ-η^2-S_2 (S3, S4) ligands. The μ-S and μ-η^2-S_2 ligands are crystallographically disordered with regards to the position of S3 (81% occupancy) and S3* (19% occupancy),[9] these sites being related by the pseudomirror plane defined by V1, V2, S1, and S2. S1···S2 is parallel with the V1–V2 axis, and the V–S(1 or 2)–S(2 or 1) angles are close to 98°. While the S3–S4 distance of 1.956 (1) Å is the *shortest* observed for any disulfur ligand, this result is complicated by the disorder problem involving S3. In keeping with the bonding formalism developed to describe $Fe_2(\mu\text{-}S_2)(CO)_6$,[10] this μ-η^2-S_2 ligand functions as a net six-electron donor. It is intriguing that the S–S distance of 2.15 Å for the corresponding μ-η^2-S_2 ligand in $(C_5Me_5)_2Cr_2S_5$ is the *longest* S–S bond reported for any disulfur complex.[11] The V–S distances fall in the sequence 2.37 (μ-η^2-S_2), 2.32 (μ-η^1-S_2), and 2.27 Å (μ-S).

In order to appreciate the present results, it is instructive to review the bonding geometries observed for bridging disulfur ligands in related complexes. In Table II we summarize the disulfur ligation modes observed crystallographically for other binuclear cyclopentadienylmetal sulfides. The formal electron donor capability for the μ-S_2 ligands is strongly dependent on the conformation of the M_2S_2 unit.[15] The skewed μ-η^1-S_2 functions as a 1 e/S (pseudohalogen) ligand while maximum utilization of the donor capacity of bridging disulfur ligands involves the μ-η^2-S_2 unit. In the conversion of $(C_5H_4CH_3)_2VS_5$ to 1, the number of electrons donated to vanadium from five sulfur atoms increases from two, in the pentasulfido chelate, to ten–twelve in 1. This change dramatically illustrates the electronic variability of catenated sulfur ligands. Employing our electron-counting formalism, 1 is a 30–32-electron dimer. Aside from direct metal–metal bonding, additional electron donation may derive from the μ-sulfido ligand via π donation. Such an interaction would explain the short V–S(5) distances observed in 1.

As found for the dicyclopentadienyltitanium polysulfides,[4,5,16] 1 reacts with electrophilic acetylenes to give dithiolene complexes. Thus treatment of 1 with dimethyl acetylenedicarboxylate (4 equiv, THF solvent, 65 °C, 3 h) or hexafluoro-2-butyne (5 equiv, 1,2-$C_2H_4Cl_2$ solvent, 85 °C, 5 h, Carius tube) gave the intensely blue, very air-stable products (~25% yield based on S) which analyzed as $(C_5H_4CH_3)V(S_2C_2R_2)_2$ where R = CO_2CH_3 or CF_3. IR spectroscopy, mass spectrometry (70 eV electron impact and field desorption), and NMR spectroscopy confirm this formulation.[17] Based on these data and well-established literature precedents, we assign the structure depicted below for 2. This structure is closely related to those for $(C_5H_5)Ti(S_2C_2(CN)_2)_2^-$[18] and $(C_5H_5)W(S_2C_2(CF_3)_2)_2$,[19] which have been prepared from reactions involving *preformed* dithiolates ($R_2C_2S_2^{2-}$) or 1,2-dithietes ($R_2C_2S_2$). The *bimetallic* bis (dithiolene) $(C_5H_5)_2V_2(S_2C_2(CF_3)_2)_2$,[20] which can be prepared from the monometallic fragment $(C_5H_5)V(CO)_4$ and 1,2-bis(trifluoromethyl)dithiete, is not observed in appreciable quantities in the synthesis of 2.[21]



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Acknowledgment. This research was supported by the National Science Foundation. Support for the NMR and mass spectral facilities comes from National Science Foundation (Grant NSF CHE 81-06781) and National Institute of Medical Sciences (Grant GM 27029).

Registry No. 1, 82978-84-5; 7 (R = CO_2CH_3), 82978-86-7; 2 (R = CF_3), 82978-87-8; $(C_5H_4CH_3)_2VS_5$, 82978-85-6; dimethyl acetylenedicarboxylate, 762-42-5; hexafluoro-2-butyne, 692-50-2.

Supplementary Material Available: A complete labeling scheme of $(C_5H_4CH_3)_2V_2S_5$, and tables of atom coordinates and

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(9) Site occupancy factor (sof) refinement for S3* with all other sof's fixed at 1.00 gave sof (S3*) = 0.18. Further refinement of the sof for both S3 and S3* with the constraint sof (S3*) = 1.00 – sof (S3) produced the reported fractional occupancies: S3 = 81%, S3* = 19%.

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(11) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765.

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(14) (a) Herberhold, M.; Reiner, D.; Zimmer-Gusser, B.; Schuberg, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 1281. (b) For a discussion of the related $Ru_2(NH_3)_{10}S_2^{4+}$ see: Elder, R. C.; Trkula, M. *Inorg. Chem.* **1977**, *16*, 1048.

(15) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

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(17) Anal. Calcd for $C_{14}H_7F_{12}S_4V$: C, 28.87; H, 1.21; S, 22.02; V, 8.75. Found: 28.96; H, 1.19; S, 21.37; V, 8.99. IR (mineral oil mull): 1230 (vs), 1178 (s), 1142 (s), 841 (m), 714 (m), 682 (w) cm^{-1}. ^1H NMR ($CDCl_3$) 5.77 (2 H, m), 5.49 (2 H, m), 2.29 (3 H, s). ^{19}F NMR ($CDCl_3$) at both +25 and –78 °C: 55.1 ppm upfield of internal $CFCl_3$. EI mass spectrum (70 eV), *m/e* (relative intensity): 582 (6, M^+), 563 (2, $C_{14}H_7F_{11}S_4V^+$), 356 (23, $C_{10}H_7F_6S_2V^+$), 168 (100, $C_6H_7F_2V^+$). Field desorption mass spectrum: *m/e* 582 (M^+). UV–vis (CH_2Cl_2): λ_{max} 583 nm (7200 L mol^{-1} cm^{-1}).

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(19) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1967**, *6*, 469.

(20) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587.

(21) Compound 1 reacts with P(*n*-Bu)$_3$ to give $(MeCp)_2V_2S_4$ whose structure and reactivity are currently under investigation.

temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Reactions of Trimethylchlorosilane with Various Nucleophiles in the Gas Phase Using the Flowing Afterglow Technique

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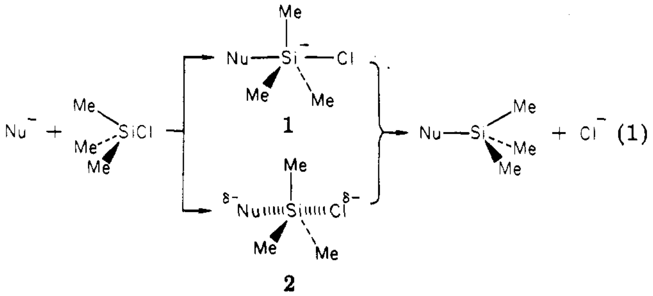
Summary: The reactivity of methyl iodide and trimethylchlorosilane with a number of different nucleophiles has been studied by using the flowing afterglow technique. The reactivity of various nucleophiles with methyl iodide generally varies with their basicity with the more basic nucleophiles reacting most rapidly. On the other hand, trimethylchlorosilane reacts with these nucleophiles in a very different manner; essentially it reacts either at the collision rate with nucleophiles giving exothermic reaction or not at all with nucleophiles giving endothermic reaction. Such results are consistent with a concerted nucleophilic substitution for methyl iodide and the intermediate formation of a pentacoordinate species for trimethylchlorosilane.

Although a covalent, pentacoordinate intermediate is probably involved in many reactions of silicon compounds, most notably in reactions involving retention of configuration at silicon,[1,2] the question of whether such an *intermediate* (1) or a related *transition state* (2) is formed



in displacement reactions of chlorosilanes has been explored only rarely.[2,3] As a natural outgrowth of our studies of pentacoordinate silicon anions in the gas phase,[4] we have investigated this problem for S_N2 reactions by measuring the rates of reaction of a series of nucleophiles with both trimethylchlorosilane and methyl iodide. The response of these two halides to changes in the basicity of the nucleophiles is so dramatically different that we believe widely different mechanisms operate in the two systems. Indeed, the results are in full accord with the intervention of a pentacoordinate intermediate corresponding to 1 formed in each encounter between the chlorosilane and nucleophile.

Table I. Rate Constants for Reaction of Nucleophiles (Nu^-) with Methyl Iodide and Trimethylchlorosilane

Nu^-	proton affinity, kcal/mol	k_{CH_3I}, 10^{-10} cm^3 $molecule^{-1}$ s^{-1}	k_{Me_3SiCl}, 10^{-10} cm^3 $molecule^{-1}$ s^{-1}
H_2N^-	404	31	34
HO^-	391	30	28
F^-	371	26	21
H_2P^-	370	13	18
HS^-	353	8.9	21
NC^-	353	1.8	19
N_3^-	344	1.3	18
NSO^-	344 ± 5	0.28	20
NCO^-	344	0.13	21
Cl^-	333	2.1	5.7
NCS^-	325 ± 5	<0.002	<0.03

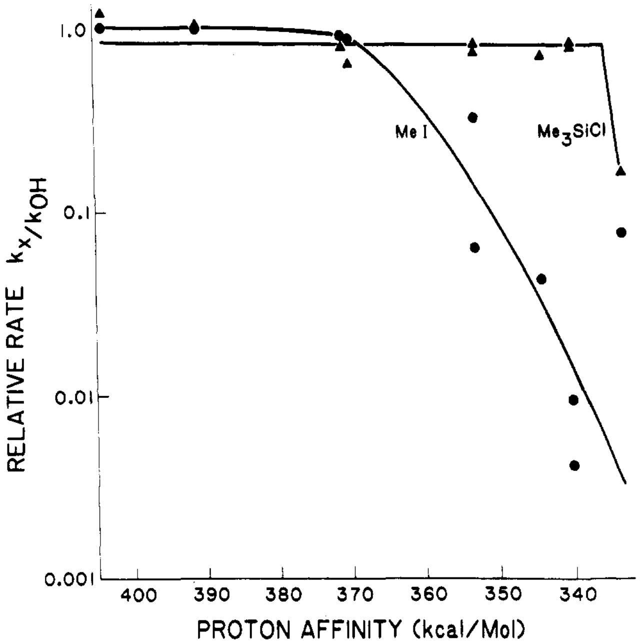


Figure 1. Relative rates of various nucleophiles reacting with methyl iodide and trimethylchlorosilane.

Our experiments were carried out in a flowing afterglow (FA) apparatus[5,6] in which H_2N^-, HO^-, F^-, and Cl^- are produced by electron impact on NH_3, N_2O/CH_4, NF_3, and CCl_4 in a helium stream (flow velocity 80 m/s, 0.3 torr of He) in a 100 × 8 cm stainless-steel tube. The tube is equipped with moveable and fixed inlets and terminates in a quadrupole mass filter detection system. Reaction rates are measured by adding the halides through the moveable inlet and measuring the decrease in reactant ion intensity as a function of reaction distance. Other nucleophiles are synthesized in the flow tube. All ions are allowed to reach thermal equilibrium with the helium buffer gas before reaction with halides commences.

The results are collected in Table I and displayed in Figure 1. Both trimethylchlorosilane and methyl iodide[7]

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