Articles

Contribution from the Department of Chemistry,
University of California, Irvine, California 92717

Synthesis and Characterization of Vanadium-Containing Silsesquioxanes

Frank J. Feher* and John F. Walzer

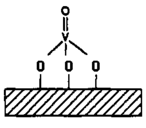
Received October 4, 1990

The reactions of $[(c\text{-}C_6H_{11})_7(Si_7O_9)(OH)_3]$ (**1**) with $VOCl_3$, $(n\text{-PrO})_3VO$, or $(Me_3SiCH_2)_3VO$ afford equilibrium mixtures of $[(c\text{-}C_6H_{11})_7(Si_7O_{12})VO]$ (**2**) and $[(c\text{-}C_6H_{11})_7(Si_7O_{12})VO]_2$ (**3**). Equilibrium mixtures of **2** and **3** are also obtained from the reactions of $[(c\text{-}C_6H_{11})_7(Si_7O_{12})V(C_5H_5N)]_2$ (**9a**) and $[(c\text{-}C_6H_{11})_7(Si_7O_{12})V(CH_3CN)]_2$ (**9b**) with molecular oxygen. The $\Delta H°$ and $\Delta S°$ for the dimerization of **2** to **3** are -25.2 ± 1.1 kJ/mol and -72 ± 1 J/(K mol), respectively. ^{51}V NMR data and comparisons of metrical data for **3** with that obtained from a single-crystal X-ray diffraction study of $(Ph_3SiO)_3VO$ (**4**) suggest that the instability of **2** relative to **3** results from poorer π-bonding between the vanadium ion and the silsesquioxane framework. The implications of these results on both the chemistry of silica-supported vanadium complexes and the utility of polyhedral oligometallasilsesquioxanes (POMSS) as models for silica-supported metal complexes are discussed. Compound **3** crystallizes as a CH_2Cl_2 solvate in the orthorhombic space group *Pbcn* with $a = 26.548$ (3) Å, $b = 22.436$ (3) Å, $c = 18.703$ (3) Å, $V = 11140$ (3) $Å^3$, and $Z = 4$. Compound **4** crystallizes as a benzene solvate in the triclinic space group $P\bar{1}$ with $a = 10.227$ (3) Å, $b = 13.175$ (3) Å, $c = 19.407$ (3) Å, $\alpha = 81.47$ (2)°, $\beta = 76.28$ (2)°, $\gamma = 73.44$ (2)°, $V = 2423.9$ (10) $Å^3$, and $Z = 2$.

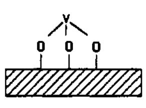
Introduction

Silica-supported vanadium complexes have recently attracted interest as catalysts for a variety of important transformations. Highly dispersed vanadium oxides, for example, have been investigated as possible catalysts for the oxidation of methane[1] and other hydrocarbons.[2] Lower valent vanadium surface complexes have been explored as possible catalysts for the polymerization of α-olefins.[3]

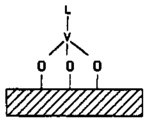
Like most heterogeneous catalysts, the identities of catalytically active species on silica-supported vanadium have remained elusive. We were, however, intrigued by the number of studies implicating "three-legged" surface complexes (e.g., I–IV) as important surface species.[2b,4] Unlike most other silica-supported catalysts, vanadium on silica is one of the few catalyst systems where three-legged complexes have been repeatedly implicated as predominant surface species.



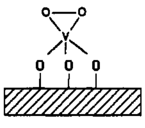
I



II



III

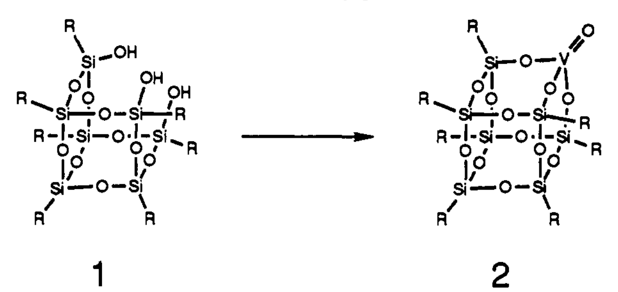


IV

Our recent development of a straightforward synthesis of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1**) provides an excellent structural model for trishydroxylated silica surface sites.[5] We were therefore eager to see if the chemistry of vanadium complexes derived from **1** could provide insight into the chemistry of silica-supported vanadium. In this paper we report our efforts to synthesize vanadium-containing polyhedral oligometallasilsesquioxanes (POMSS). The implications of our results on both the chemistry of silica-supported vanadium complexes and the utility of POMSS as models for silica-supported metal complexes will be discussed.

Results

Vanadium-Containing POMSS from 1 and Pentavalent Precursors. The reactions of **1** with $VOCl_3/NH_3$ (C_6H_6, 25 °C), $(n\text{-PrO})_3VO$ (C_6H_6, 25 °C), and $(Me_3SiCH_2)_3VO$ (C_6H_6, 80 °C) occur cleanly to give high yields of vanadium-containing silsesquioxanes. At room temperature and concentrations less than 0.05 mM (~20 mg/0.4 mL of $CDCl_3$ or C_6D_6), the ^{13}C NMR spectrum obtained on a typical reaction mixture exhibits three large resonances with relative integrated intensities of 3:3:1 for the ipso-carbons of the cyclohexyl groups. The same pattern is observed in the ^{29}Si NMR spectrum, except that one of the large (3 Si) resonances is broadened ($w_{1/2} = 29$ Hz) due to unresolved coupling and/or quadrupolar relaxation by the nearby vanadium nucleus (^{51}V, $I = {}^7/_2$, 99.76%). These results, and the presence of a single resonance at δ −676 ($w_{1/2} = 510$ Hz) in the ^{51}V NMR spectrum, strongly suggested that the expected C_{3v}-symmetric vanadate ester (i.e., **2**) was the only product from all three reactions, but all attempts to isolate **2** were unsuccessful. Instead, the highly crystalline product obtained in excellent yields after



1

2

(R = c-C_6H_{11})

---

[1] (a) Spencer, N. D.; Pereira, C. J. *J. Catal.* **1989**, *116*, 399-406. (b) Zhen, K. J.; Khan, M. M.; Mak, C. H.; Lewis, K. B.; Somorjai, G. A. *J. Catal.* **1985**, *94*, 501-7.

[2] (a) Jonson, B.; Rebenstorf, R.; Larsson, R.; Andersson, S. L. T. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3363-76. (b) Jonson, B.; Rebenstorf, R.; Larsson, R.; Andersson, S. L. T. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1897-1910. (c) Ohlman, G. *Z. Chem.* **1984**, *24*, 161-9. (d) Hanke, W.; Heise, K.; Jerschkewitz, H.-G.; Lischke, G.; Ohlmann, G.; Parlitz, B. *Z. Anorg. Allg. Chem.* **1978**, *438*, 176-94.

[3] (a) Karol, F. J.; Cann, K. J.; Wagner, B. E. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: New York, 1988; pp 149-61 and references sited therein. (b) Damyanov, D.; Velikova, M. *Eur. Polym. J.* **1979**, *15*, 1075-8. (c) Smith, W. E.; Zelmer, R. G. *J. Polym. Sci., Pt. A* **1963**, *1*, 2587-2600.

[4] (a) Horvath, B.; Strutz, J.; Geyer-Lippmann, J.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1981**, *483*, 205-218. (b) Horvath, B.; Strutz, J.; Geyer-Lippmann, J.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1981**, *483*, 193-204. (c) Horvath, B.; Strutz, J.; Geyer-Lippmann, J.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1981**, *483*, 181-92. (d) Roozeboom, F.; Fransen, T.; Mars, P.; Gellings, P. J. *Z. Anorg. Allg. Chem.* **1979**, *449*, 25-40. (e) Horvath, B.; Geyer, J.; Krauss, H. L. *Z. Anorg. Allg. Chem.* **1976**, *426*, 141-9. (f) Chien, J. C. W. *J. Am. Chem. Soc.* **1971**, *93*, 4675-84. (g) Vorobev, L. N.; Badalova, I. K.; Razikov, K. K. *Kinet. Katal.* (*Engl. Transl.*) **1982**, *23*, 94-8. (h) Pak, V. N. *Zh. Obshch. Khim.* (*Engl. Transl.*) **1975**, *45*, 920. (i) Gritscov, A. M.; Shvets, V. A.; Kazansky, V. B. *Chem. Phys. Lett.* **1975**, *35*, 511-12.

[5] Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741-8.

0020-1669/91/1330-1689$02.50/0

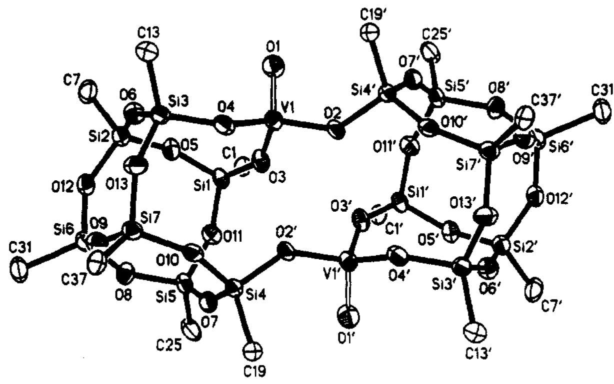
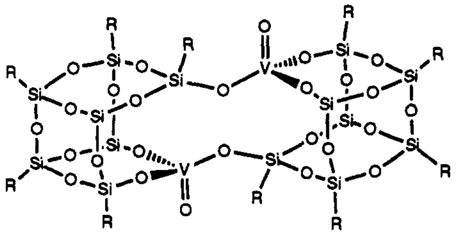


Figure 1. Perspective ORTEP plot of 3. For clarity, thermal ellipsoids are shown at 40% probability and only C atoms attached to Si are shown. Selected interatomic distances (Å) and angles (deg) are as follows: V1–O1, 1.564 (8); V1–O2, 1.772 (6); V1–O3, 1.737 (7); V1–O4, 1.746 (7); V1–O2′, 3.52 (1); Si1–O3, 1.645 (7); Si3–O4, 1.645 (7); Si4–O2′, 1.644 (7); Si–C_{av}, 1.845 (11); O1–V1–O2, 107.1 (4); O1–V1–O3, 108.9 (4); O1–V1–O4, 108.3 (4); O2–V1–O3, 113.7 (3); O2–V1–O4, 109.4 (3); O3–V1–O4, 109.3 (3); V1–O2–Si4′, 136.0 (4); V1–O3–Si1, 146.4 (5); V1–O4–Si3, 145.5 (5). Other Si–O distances vary from 1.599 to 1.644 Å. Other Si–O–Si and O–Si–O angles vary from 140.5 to 156.7 and 106.5 to 109.9°, respectively.

recrystallization from CH_2Cl_2 was an interesting dimeric vanadium-containing silsesquioxane (3).



3

The ORTEP plot of 3 is shown in Figure 1. The two silsesquioxane frameworks of 3 are crystallographically related by a 2-fold rotational axis. They are also perpendicularly bisected by a pseudo mirror plane of symmetry. The coordination environments around the two crystallographically related vanadium atoms are approximately tetrahedral, with bond distances and angles that are similar to those observed for monomeric $(Ph_3SiO)_3VO$ (vide supra). Interatomic Si–O distances and intrabond angles for atoms within the silsesquioxane framework are also normal.[6]

The isolation of 3 from solutions that appeared to contain only 2 (by NMR) was initially surprising, but the reason for this otherwise disturbing occurrence became clear when $CDCl_3$ solutions of 3 were examined by NMR spectroscopy. At ambient temperature and total vanadium concentrations less than 0.05 mM, all resonances in the ^{51}V, ^{13}C, and ^{29}Si NMR spectra were identical with those previously assigned to 2. At higher concentrations and/or lower temperatures, however, a new set of resonances with relative integrated intensities of 2:2:1:1:1 appeared in both the ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum (Figure 2). A new vanadate resonance also appeared at δ −710 ($w_{1/2}$ = 430 Hz) in the ^{51}V NMR spectrum. These resonances were clearly attributable to a C_{2h}-symmetric dimer such as 3, suggesting that the dimer dissociates in solution to give an equilibrium mixture of 2 and 3. This was confirmed by examining both the temperature dependence and concentration dependence of the equilibrium and further corroborated by a solution molecular weight measurement.

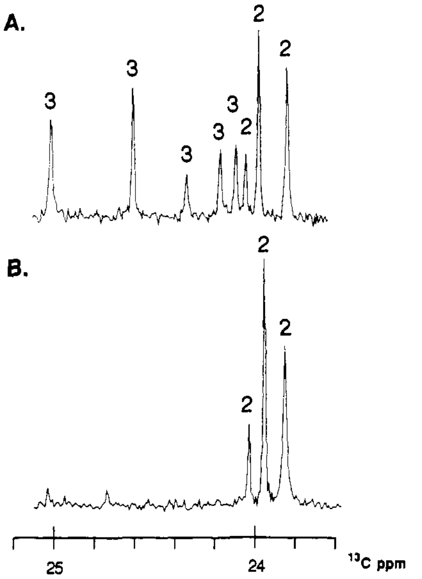


Figure 2. Methine (*C*H–Si) region of 125-MHz ^{13}C NMR spectra for 2 and 3 in toluene-d_8. The total vanadium concentration was 0.07 M, and spectra were recorded at (A) −20 °C and (B) 80 °C.

The concentration dependence (Figure 3A) of the ratio of [3] to [2] provides unambiguous support for a monomer/dimer equilibrium. A plot of [3] versus $[2]^2$ passes through the origin with a slope of K_{eq} (i.e., 5.10 M^{-1} in toluene-d_8 at 25 °C). An analysis of the temperature dependence of K_{eq} (Figure 3B) indicates that $\Delta H°$ and $\Delta S°$ for the dimerization reaction are −25.2 ± 1.1 kcal/mol and −72 ± 1 eu, respectively. The large $\Delta S°$ is consistent with a monomer/dimer equilibrium,[7] while the appreciable enthalpic preference for 3 explains why all attempts to isolate 2 afforded only 3. The equilibration of 2 and 3 is considerably slower than the ^1H, ^{13}C, and ^{29}Si NMR time scales because resonances for the two complexes exhibit no detectable exchange broadening up to 90 °C, but equilibration is complete within a matter of seconds at 25 °C. Cooling the solution to −30 °C (toluene-d_8) increases the half-life for approach to equilibrium to approximately 1 h.

Structural Comparisons: Why is a Dimer Preferred? The thermodynamic preference for 3 is somewhat surprising. Although the oligomerization of vanadate esters is well documented,[8] dimerization is normally driven by the tendency of electrophilic vanadium centers to increase their coordination numbers. This is clearly not the case for 3, however, because the distance between V1 and O2′ is more than 3.5 Å, which precludes the existence of any significant O→V dative bonding. The enthalpic preference for 3 must therefore be the consequence of some other energetically desirable feature that cannot be adequately accommodated by a monomeric structure such as 2. In order to identify this feature, it was desirable to compare metrical data for our vanadium-containing POMSS with structural data from other vanadate complexes. Since there were no structurally characterized four-coordinate vanadate triesters prior to the start of our work, a single-crystal X-ray diffraction study was performed on $(Ph_3SiO)_3V{=}O$ (4),[9] a more traditional model for silica-supported vanadates.

---

(6) (a) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931–6. (b) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288–9. (c) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638–40. (d) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850–2. (e) Feher, F. J.; Gonzales, S. L.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 3440–2. (f) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1990**, *29*, 1604–11. (g) Feher, F. J.; Budzichowski, T. A. *Organometallics* **1991**, *10*, 812–5. (h) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614–16.

(7) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13–20, footnote 21, and references cited therein.

(8) (a) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–62. (b) Rehder, D. *Z. Naturforsch.* **1977**, *32B*, 771–5. (c) Paulsen, K.; Rehder, D.; Thoennes, D. *Z. Naturforsch.* **1978**, *33A*, 834–9. (d) Tracey, A. S.; Gresser, M. J. *Can. J. Chem.* **1988**, *66*, 2570–4. (e) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013–9.

(9) Sekiguchi, S.; Kurihara, A. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1453–4.

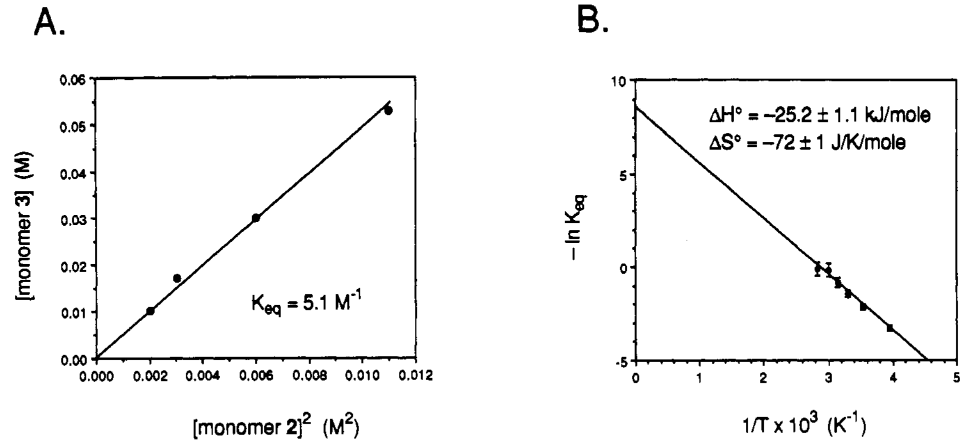


Figure 3. (A) Plot of [3] versus $[2]^2$ for the equilibrium mixture of 2 and 3 in toluene-d_8 at 25 °C. (B) Plot of $-\ln K_{eq}$ versus $1/T$ for the equilibrium of 2 and 3 in toluene-d_8.

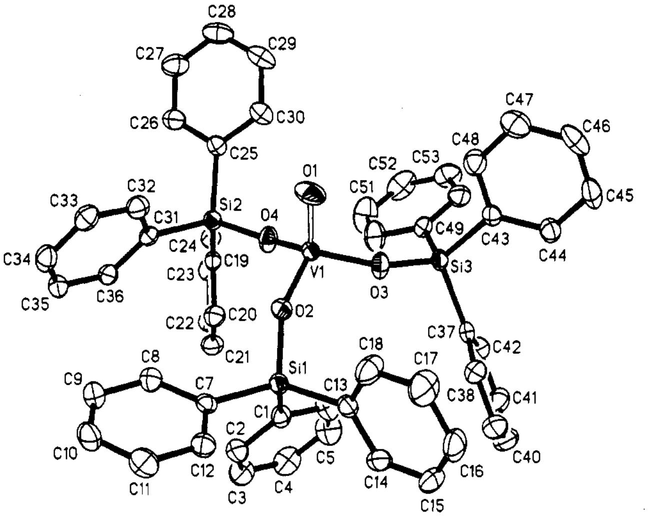


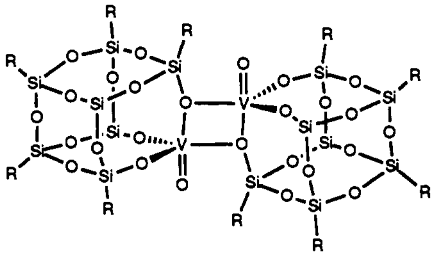
Figure 4. Perspective ORTEP plot of 4 with thermal ellipsoids plotted at 40% probability. Selected interatomic distances (Å) and angles (deg) are as follows: V1–O1, 1.572 (2); V1–O2, 1.743 (2); V1–O3, 1.745 (2); V1–O4, 1.739 (3); Si1–O2, 1.661 (2); Si2–O4, 1.650 (3); Si3–O3, 1.647 (2); Si–C_{av}, 1.862 (4); O1–V1–O2, 107.7 (1); O1–V1–O3, 109.9 (1); O1–V1–O4, 108.7 (1); O2–V1–O3, 111.6 (1); O2–V1–O4, 109.8 (1); O3–V1–O4, 109.2 (1); V1–O2–Si1, 146.5 (1); V1–O3–Si3, 161.8 (1); V1–O4–Si2, 155.5 (2).

The ORTEP plot of 4 is shown in Figure 4. The benzene solvate of 4 crystallizes as discrete monomers in the space group $P\bar{1}$, with a V–O double-bond length of 1.572 (2) Å and V–O single-bond lengths of 1.739 (3), 1.743 (2), and 1.745 (2) Å. The coordination geometry around V is nearly tetrahedral, with O–V–O interbond angles of 107.7 (1)–111.6 (1)°. As expected for alkoxide and siloxide complexes of electrophilic d^0 transition metals, the V–O–Si bond angles in 4 are also quite obtuse: V1–O2–Si1, 146.5 (1)°; V1–O4–Si2 155.5 (2)°; V1–O3–Si3, 161.8 (1)°.

A comparison of the structural data for 3 and 4 reveals a large number of structural similarities. Both complexes have approximately tetrahedral VO_4 moieties with comparable V–O distances and average interbond angles. The Si–O distances in 3 and 4 are also nearly equal. Superficially, it would therefore appear that the coordination environments around V in 3 and 4 are very similar. There is, however, one large structural difference that could have important chemical consequences: the average V–O–Si angle in 3 (143°) is 12° more acute than the average V–O–Si angle observed for 4 (155°). This difference could manifest itself in many ways, but the most obvious consequence should be a decrease in the extent of $O(p\pi) \rightarrow V(d\pi)$ bonding as the V–O–Si angle becomes more acute. This expectation, which is based on well-established principles from the chemistry of electrophilic d^0 transition metals,[10] is supported by trends in the ^{51}V chemical shifts for V=O moieties in 3, 4, and 2.

Like most NMR-active nuclei, chemical shifts for ^{51}V are dominated by paramagnetic contributions to the overall shielding (σ_{para}).[11] Many factors can influence the relative magnitude of these contributions, but for closely related compounds with the general formula VXZ_3 (X = O, N; Z = halide, alkyl, alkoxide, aryloxide), there is a definite trend toward higher field chemical shifts as purely σ-donating groups are replaced by ligands with better π-donating ability. The lower field ^{51}V chemical shift observed for 3 (δ −710) relative to 4 (δ −725) is consistent with the expectation that there is poorer π-donation from the siloxide groups to the electrophilic vanadium center as the average V–O–Si bond angle becomes more acute.[8,11] The occurrence of the ^{51}V resonance for 2 at even lower field (δ −676) clearly suggests that there is even poorer pπ–dπ overlap between the framework oxygen atoms and the d^0 vanadium center.[12]

The origin of the slight enthalpic instability of 2 relative to 3 thus appears to be the result of poorer π-donation from the silsesquioxane framework to the electrophilic vanadium center. By dimerizing, the vanadium ions are able to achieve more obtuse V–O–Si bond angles, which promotes much better π-bonding between vanadium and the siloxy groups. Another possible explanation for our observations is that a slight contraction of 3 occurred in solution to give siloxy-bridged dimer 5, the logical



5

---

(10) (a) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311–69 and references cited therein. (b) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, pp 335–64 and references cited therein. (c) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977–83.

(11) (a) Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33–83. (b) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

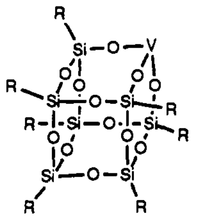
(12) (a) A reviewer has suggested that vanadium might not be different from silicon in its preference for obtuse Si–O–M (M = Si, V) angles in silsesquioxane frameworks. This simple view neglects the fact that empty d orbitals play fundamentally different roles in Si–O–Si and Si–O–M (M = transition metal) bonding. Despite plenty of folklore to the contrary, obtuse Si–O–Si bond angles are not due to pπ–dπ interactions.[12b] (b) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697–703 and references cited therein.

intermediate required for dissociation. This explanation is somewhat unusual because it requires different structures for the solid-state and solution-state dimers, but it could rationalize the 25.2 kJ/mol preference for a dimeric solution-state species on the basis of known vanadate and POMSS chemistry, rather than invoking relatively large differences in ligand → metal π-bonding between **2** and **3**. Although unusual, this possibility merited serious consideration because the cumulative effects of efficient crystal packing can have truly remarkable effects on the properties of some cyclohexyl-substituted silsesquioxanes, including **3**.[13]

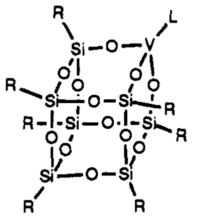
Despite the expectation that discrete, predominantly aliphatic molecules (e.g., **3**) should dissolve well in common organic solvents (i.e., "like dissolves like"), silsesquioxanes often exhibit strange and completely unpredictable solubility properties.[13] Dimer **3** is one such example. In the absence of CH_2Cl_2, **3** (and **2**) is so soluble in common organic solvents (e.g., C_6H_6, toluene, ether, THF, $CHCl_3$, CCl_4, pentane, hexane, etc.) that solutions containing more than 1 g/mL have steadfastly resisted crystallization, even after repeated attempts to induce crystallization by cooling (25 to −100 °C), seeding, and/or the addition of nonsolvents (e.g., CH_3CN). In the presence of traces of CH_2Cl_2, however, crystallization is extremely rapid and the solubility of **3** in these same solvents is reduced by more than 2 orders of magnitude. The CH_2Cl_2 solvate of **3**, which does not desolvate until well above 100 °C, is clearly a thermodynamic sink with very efficient crystal packing. Under such circumstances the chances that the solid-state structure is different from the most stable solution structure are maximized.

Fortunately, the possibility of a siloxy-bridged solution-state structure can be addressed by ^{29}Si NMR spectroscopy. Since the effects of both quadrupolar relaxation and *J*-coupling are generally cumulative,[14] the line widths of resonances for ^{29}Si nuclei nearest to vanadium should provide a semiquantitative measure of the number of vanadium nuclei attached to each siloxy group. In both **2** and its solution-state dimer, all resonances for ^{29}Si nuclei nearest to vanadium have line widths of approximately 29 Hz, strongly suggesting that the broadening in each case is the result of a single vanadium nucleus. Therefore, there is no reason to suspect that the structure of the solution-state dimer might be significantly different from that of **3**.

Vanadium-Containing POMSS from Trivalent Precursors. In addition to our efforts to synthesize high-valent V-containing silsesquioxanes, we have examined several possible routes to low-valent complexes such as **6** and **7**, which are POMSS analogues of V(III) complexes that have purportedly been identified on silica surfaces.[4] Unfortunately, from the standpoint of developing models for isolated silica-supported vanadium ions, all of our attempts to synthesize monomeric V(III)-containing POMSS afforded dimeric complexes.

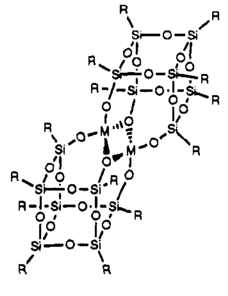


6

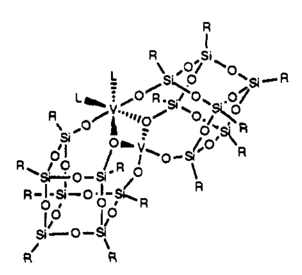


7

As we reported earlier,[6f] the reaction of **1** with a number of trivalent vanadium precursors produces moderate to high yields of dimeric siloxy-bridged complexes. In the absence of strongly coordinating ligands, the major product is **8** (M = V). This siloxy-bridged structure appears to be quite stable and has been observed with a number of different trivalent metal ions (e.g., **8** with M = Al,[6b] Ti,[6c] Ga,[6a] and Y[6b]). In the presence of strongly coordinating ligands, dimers such as **9** are observed, where one vanadium ion expands its coordination sphere by the addition of two ligands.



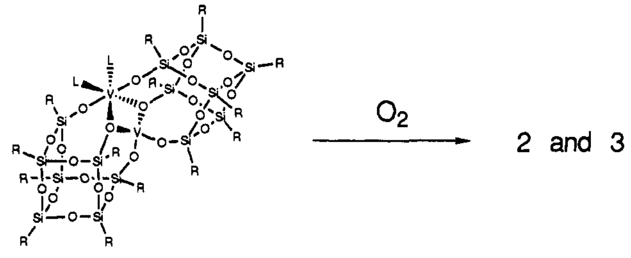
8 M = V



9

The syntheses and interesting magnetic properties of **9a** (L = pyridine) were recently described.[6f] A structurally similar bis(acetonitrile) adduct, **9b** (L = CH_3CN), can also be prepared from the reaction of **1** with $VCl_3(NMe_3)_2$, followed by recrystallization from CH_2Cl_2/MeCN. The molecular structure of **9b** was unambiguously established by a single-crystal X-ray diffraction study, but poor diffraction and disorder in several cyclohexyl rings prevented a satisfactory completion of the structure. The framework dimensions of **9b** are, however, very similar to those observed for **9a**, and the two V(III) centers in **9b** are antiferromagnetically coupled with approximately the same exchange constant observed for **9a**. A satisfactory simulation[6f] of the temperature-dependent molar susceptibility data for **9b** could be obtained by using the biquadratic Heisenberg Hamiltonian ($\mathcal{H} = -J\langle S_1 \cdot S_2\rangle + j\langle S_1 \cdot S_2\rangle^2$) for a exchange-coupled d^2–d^2 spin system. The "best-fit" *J*, *j*, TIP, and *g* values were −80 cm^{-1}, 1.1 cm^{-1}, 200 × 10^{-6} cgsu, and 1.95, respectively.

In contrast to **3**, trivalent siloxy-bridged dimers such as **8** and **9** show no evidence to suggest that dissociation to monomers (e.g., **6** or **7**) occurs in solution. Even in the presence of large excesses of coordinating ligands, the dimeric siloxy-bridged frameworks of **9a** and **9b** remain intact. Although the unexpected stability of these dimers greatly complicates their reaction chemistry, we have discovered that **9a** and **9b** can be cleanly oxidized to equilibrium mixtures of **2** and **3** by molecular oxygen.



9a L = pyridine
b MeCN

The reaction of a blue pentane solution of **9b** with dry oxygen proceeds rapidly at 25 °C to give an equilibrium mixture of **2** and **3**. The reaction is quantitative by NMR spectroscopy, and the products are identical in all respects with those obtained from the reactions of **1** with VOX_3 (X = Cl, OR, CH_2SiMe_3). A reaction performed by using ^{17}O-enriched dioxygen (11% $^{17}O_2$) produced a product mixture that exhibited large resonances in its ^{17}O NMR spectrum for the V═O groups in **2** (δ 1012, $w_{1/2}$ = 180 Hz) and **3** (δ 948, $w_{1/2}$ = 350 Hz), clearly indicating that the oxo groups in **2** and **3** originated from added dioxygen. The mechanism(s) by which this reaction occurs is (are) not known, but it is interesting to note that the oxidation also occurs rapidly and quantitatively in the solid state. Since siloxy-bridged divanadium units in **9b** are separated by more than 12 Å in the solid state, it is tempting to suggest that the reductive cleavage of O_2 is effected by adjacent V(III) ions. We do not, however, have any direct

---

[13] Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *373*, 153–63.

[14] Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley-Interscience: New York, 1981; Chapter 1.

[15] (a) Feher, F. J.; Budzichowski, T. A. Unpublished results. (b) Feher, F. J.; Walzer, J. F. Unpublished results.

evidence to support this suggestion.

Reactivity Studies on 2/3. The thermodynamic instability of **2** relative to **3** militates against its isolation, but at concentrations less than 0.05 mM and temperatures greater than 25 °C, **2** is the predominant V-containing species (>95%) in solution. It is therefore possible to study the chemistry of **2** (provided that it can be distinguished from the chemistry of **3**). We were particularly interested in exploring the possibility of using **2** as an oxidation catalyst because of its similarity to surface sites that have purportedly been identified on silica-supported vanadium oxide.[2,4] The results from our studies, which examined the reactivity of **2** (and/or **3**) toward a variety of "easily oxidizable" substrates, can be succinctly stated: neither **2** nor **3** shows any promise as an oxidation catalyst.

Drastic conditions ($T > 250$ °C) are required for any observable reaction to occur between **2**/**3** and Me_3P, Ph_3P, norbornene, CO, or α-methylstyrene. Unfortunately, these "reactions" appear to result from decomposition of the starting material, rather than a reaction between the starting material and the substrate. For substrates that are kinetically stable toward dioxygen under 200 °C (e.g., CO, norbornene, toluene) the presence of added oxygen had no effect. The use of oxygen sources other than O_2 was not extensively explored because solutions of **2** and **3** are rapidly solvolyzed by hydroxylic reagents (e.g., hydroperoxides, alcohols, water) to give trisilanol **1** and complex mixtures of vanadium-containing products. In light of the reluctance of **2** (and **3**) to participate in oxo-transfer reactions and the instability of vanadium-containing silsesquioxanes toward solvolysis, there does not appear to be any immediate hope of effecting clean catalytic oxidation chemistry with either **2** or **3**.

Discussion and Conclusions

This paper has described our first attempts to use POMSS as models for monodisperse silica-supported vanadium catalysts. Of the three surface species that were targeted for modeling (i.e., I–III), one has been successfully synthesized. Vandate **2**, an analogue of silica-supported vanadium oxide with three strong metal-support interactions, can be prepared in dilute solution by the reaction of trisilanol **1** with a variety of vanadium precursors. Unfortunately, all attempts to isolate **2** afford **3**, a thermodynamically more stable dimer, which has been structurally characterized by a single-crystal X-ray diffraction study.

On the basis of X-ray crystallographic studies and ^{51}V NMR data, the instability of **2** relative to **3** appears to be a consequence of poorer π-donation from the siloxy groups of **1** to the vanadium ion in **2**. While unexpected, this result suggests one possible explanation for the inherently greater reactivity of many silica-supported d^0 transition-metal complexes relative to stoichiometrically similar alkoxide and/or siloxide complexes. The coordination of metal ions to a hydroxylated surface may increase their electrophilicity by forcing the ions to adopt pyramidalized geometries with acute M–O–Si bond angles. This suggestion is clearly consistent with the more general observation that sterically demanding alkoxide or siloxide ligands with relatively poor π-donating capabilities can lead to increased and/or unique reactivity relative to that observed for complexes possessing simpler alkoxide or strongly π-donating cyclopentadienyl ligands.[10,16]

We have also learned some of the limitations facing the use of POMSS as models for silica-supported complexes. In particular, it is apparent that the utility of our model will be limited by one of the problems afflicting all current solution models for heterogeneous catalysts—the tendency for highly reactive, low coordination number transition-metal complexes to oligomerize. Although trisilanol **1** can, in principle, reduce aggregation by occupying an entire hemisphere of coordination, it is neither bulky nor rigid enough to prevent the formation of siloxy-bridged dimers. This is well illustrated by the results of our efforts to synthesize **6** and **7**. The flexibility of silsesquioxane frameworks, which is clearly advantageous from the standpoint of developing a versatile model that can be used with any metal ion, can also accommodate the contortions necessary for highly reactive metal complexes to find alternative structures that reduce coordination unsaturation (and reactivity).

In spite of the limitations, incompletely condensed silsesquioxanes are still excellent models for hydroxylated silica surface sites. The utility of these models in the development of fundamental reaction chemistry relevant to silica surfaces has already been demonstrated.[6a] Forthcoming work from our laboratory will show that transition-metal-containing silsesquioxanes can exhibit reaction chemistry that is both different from that observed for simpler complexes containing conventional alkoxide ligands and reminiscent of the chemistry observed for silica-supported complexes.[6h,17]

Experimental Section

General experimental protocol and procedures for the synthesis of **1** are described in ref 5. ^1H NMR spectra were recorded at 500 MHz in $CDCl_3$ unless otherwise specified. $CDCl_3$ was vacuum-distilled (25 °C, 0.1 Torr) from CaH_2. C_6D_6 toluene-d_8, and THF-d_8 were vacuum-distilled (25 °C, 0.1 Torr) from sodium benzophenone ketyl. $VOCl_3$ (Aldrich Chemical Co. "Gold label") was vacuum-distilled (25 °C, 0.001 Torr), freeze–pump–thaw-degassed, and stored in a glass ampule sealed with a Teflon stopcock. ^{17}O-enriched oxygen gas (11% ^{17}O) was purchased from Cambridge Isotope Laboratory. $(Me_3SiCH_2)_3V{=}O$,[18a] $(n\text{-}PrO)_3V{=}O$,[18b] $(Me_3N)_2VCl_3$,[18c] and $(Ph_3SiO)_3V{=}O$[9] were prepared according to literature methods.

Preparation of 3. Method A: Reaction of $(n\text{-}PrO)_3V{=}O$ and Trisilanol 1. A 2-mL solution of $(n\text{-}PrO)_3V{=}O$ (248 mg, 1.06 mmol) in benzene was added with vigorous stirring to a suspension of **1** (1.00 g, 1.03 mmol) in benzene (20 mL). Complete dissolution of **1** occurs within a few minutes, but stirring was continued for 20 min to ensure complete reaction. Filtration through a fine sintered glass funnel and solvent removal in vacuo (25 °C, 0.001 Torr) afforded 1.003 g (98%) of **2**/**3** as a white amorphous foam. Crystallization of the crude mixture from a minimum amount of CH_2Cl_2 afforded large colorless crystals of **3** (970 mg, 94%). Crystalline samples prepared in this fashion contain only **3**. In solution, **3** exists in equilibrium with **2**. Analytical data for **3** are as follows. $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C): δ 24.74, 24.37, 24.30, 23.83, 23.74 (s, 2:2:1:1:1 for Si*C*H). $^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$, 23 °C): δ −64.51 ($w_{1/2}$ = 20 Hz), −64.75 ($w_{1/2}$ = 20 Hz), −68.16, −68.86, −69.51 (s, 2:1:1:1:2). $^{51}V\{^1H\}$ NMR (65.75 MHz, $CDCl_3$, 23 °C): δ −710 ($w_{1/2}$ = 427 Hz). MS (30 eV, 230 °C) [*m/e* (assignment, relative intensity)]: 954 ($M^+ - C_6H_{11}$, 100%). Anal. Calcd (found) for $C_{42}H_{77}O_{13}Si_7V$: C, 48.62 (49.10); H, 7.48 (7.55). Mp: 273–274 °C (desolvation occurs at ~120 °C). Analytical data for **2** are as follows. $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6. 23 °C): δ 23.67, 23.59, 23.45 (s, 1:3:3 for a for SiCH). $^{29}Si\{^1H\}$ NMR (99.4 MHz, $CDCl_3$, 23 °C): δ −63.51 ($w_{1/2}$ = 18 Hz), −68.48, −69.12 (s, 3:1:3). $^{51}V\{^1H\}$ NMR (65.75 MHz, $CDCl_3$, 23 °C): δ −676 ($w_{1/2}$ = 508 Hz). Characteristic, but unassignable, resonances for **2**/**3** in $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C): δ 28.0, 28.06, 27.93, 27.78, 27.76, 27.75, 27.69, 27.64, 27.61, 27.46, 27.43, 27.29, 27.27, 27.25, 27.23, 27.19, 27.16, 27.09, 26.97 (CH_2).

Method B: Reaction of $(Me_3SiCH_2)_3V{=}O$ and Trisilanol 1. A solution of $(Me_3SiCH_2)_3V{=}O$ (14 mg, 0.043 mmol) and **1** (41 mg, 0.042 mmol) in C_6D_6 (0.5 mL) was heated (80 °C) in a 5-mm NMR tube. The reaction is complete within 1.5 h (by ^{13}C NMR spectroscopy) and produces an equilibrium mixture of **2** and **3**, which is identical in all respects with that obtained from method A.

Method C: Reaction of $VOCl_3$ and Trisilanol 1. $VOCl_3$ (10 mL, 1.06 mmol) was added with vigorous stirring to a suspension of **1** (1.00 g, 1.03 mmol) in benzene. Immediately after the addition of $VOCl_3$, anhydrous ammonia was bubbled through the solution for 15 min. Filtration

---

(16) (a) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056–72. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423–35 and references cited therein. (c) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424–35. (d) Chamberlin, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471–8 and references cited therein. (e) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987–98 and references cited therein. (f) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981–7 and references cited therein.

(17) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.*, in press.

(18) (a) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 533. (b) Pauling, H.; Andrews, D. A.; Hindley, N. C. *Helv. Chim. Acta* **1976**, *59*, 1233. (c) Casey, A. T.; Clark, R. J. H.; Pidgeon, K. J. *Inorg. Synth.* **1973**, *13*, 179.

Table I. Crystallographic Data for 3 and 4

compd	3	4
chem formula	$C_{84}H_{154}O_{26}Si_{14}V_2 \cdot CH_2Cl_2$	$C_{54}H_{45}O_4Si_3V \cdot 0.5C_6H_6$
mol wt	2160.1	932.2
space group	*Pbcn* (No. 60)	$P\bar{1}$
a, Å	26.548 (3)	10.227 (3)
b, Å	22.436 (3)	13.175 (3)
c, Å	18.703 (3)	19.407 (3)
α, deg		81.47 (2)
β, deg		76.28 (2)
γ, deg		73.44 (2)
V, Å^3	11140 (3)	2423.9 (10)
d_{calcd}, g/cm^3	1.288	1.277
Z	4	2
λ	0.71073	0.71073
μ, cm^{-1}	4.20	3.14
final *R*, %	11.4	5.52
final R_w, %	11.6	5.72
GOF	1.79	1.41
temp, °C	−115	−95

through a fine sintered glass frit (to remove NH_4Cl) and evaporation of the solvent (25 °C, 0.001 Torr) afforded an off-white amorphous foam. Extraction of the foam with pentane, filtration through a plug, and evaporation of the solvent (25 °C, 0.001 Torr) afford 916 mg (86%) of **2**/**3** as an amorphous white foam. Crystallization of the mixture from a minimum amount of CH_2Cl_2 afforded large colorless crystals of **3**, which were identical in all respects with those obtained by using method A.

Concentration Dependence of the 2/3 Equilibrium: Determination of K_{eq}. A solution of **3** (77.5 mg) in freshly vacuum-distilled toluene-d_8 (283 mg) was prepared in a 5-mm NMR tube. The sample was allowed to thermally equilibrate in the NMR probe (25 °C, 20 min), and then a ^{13}C NMR spectrum (3000 transients) was acquired. The relative concentrations of monomer and dimer were calculated from the integrated intensities of resonances for the methine carbons (*C*H–Si) of **2** and **3**, respectively. (The solution volumes were determined later by measuring the mass of pure solvent necessary to occupy the same volume in the NMR tube.) An additional 189.4 mg of toluene-d_8 was added, and then a second ^{13}C NMR spectrum (3000 transients) was acquired after thermal equilibration (25 °C, 20 min). This process was repeated twice to give a total of four ^{13}C NMR spectra. From these data, K_{eq} for the dimerization of **2** to **3** was determined to 5.10 M^{-1} from a plot of [**3**] versus [**2**]^2 (Figure 3A).

Determination of $\Delta H°$ and $\Delta S°$ for the Dimerization of 2 to 3. A solution of **3** (26.8 mg) in freshly vacuum-distilled toluene-d_8 (465 mg) was prepared in a 5-mm NMR tube. (The solution volume was determined later by measuring the mass of pure solvent necessary to occupy the same volume in the NMR tube.) The sample was allowed to thermally equilibrate in the NMR probe (80 °C, 20 min), and then a ^{13}C NMR spectrum (3000 transient) was acquired. The relative concentrations of monomer and dimer were calculated from the integrated intensities of resonances for the methine carbons (*C*H–Si) of **2** and **3**, respectively. Spectra were similarly recorded at 60, 45, 30, 10, and −20 °C. (A 2-h equilibration period was required at −20 °C due to the slow rate of the equilibration reaction at this temperature.) From these data, $\Delta H°$ and $\Delta S°$ were determined to be −25.2 ± 1.1 kJ/mol and −72 ± 1 J/(K mol), respectively, from a linear "least-squares" fit of $-\ln K_{eq}$ versus $1/T$ data ($-\ln K_{eq} = \Delta H°/RT - \Delta S°/R$) (Figure 3B).

Solution Molecular Weight Determination for 2/3. The average molecular weight of solution of **2**/**3** was determined by using the method described by Signer. A sample of **3** (53.1 mg) was weighed into one arm of an isopiestic molecular weight apparatus,[19] and pentane was added to bring the volume to 0.623 mL. The tris-trimethylsilylated derivative **1**, $(C_6H_{11})_7Si_7O_9(OTMS)_3$ (50.5 mg, 0.424 mmol), was added as a standard to the other arm of the apparatus, and then pentane was added to bring the volume of this arm to 1.445 mL. After 45 days, the volumes of both arms had stabilized; the arm containing **2**/**3** had 0.995 mL of solution, while the arm containing the standard had 1.095 mL of solution. Assuming that both solutions behave as "ideal solutions", the number-average molecular weight for solutes in the pentane solution of **2**/**3** was 1465, which corresponds to a 1.4:1 mixture of **2** and **3**. This is in excellent agreement with the monomer:dimer ratio of 1.3:1, which is expected from the K_{eq} measured in toluene at 25 °C (Figure 3A).

Synthesis of 9b. Solid $VCl_3[N(CH_3)_3]_2$ (344.0 mg, 0.1.249 mmol) was added to a solution of trisilanol **1** (1.250 mg, 1.283 mmol) in benzene (120 mL) containing 10% (v/v) Et_3N. The mixture was stirred for 15 min at 25 °C, and then solvent was removed in vacuo (25 °C, 10^{-3} Torr) to leave a blue residue, which was extracted with pentane and filtered to remove Et_3NHCl. Evaporation of the volatiles (25 °C, 10^{-3} Torr) left a dark blue solid (presumably **9** with L = Et_3N),[6f] which was reacted with acetonitrile by carefully layering acetonitrile (75 mL) over a concentrated benzene solution (15 mL) of the blue solid. The large blue/green pleochroic crystals, which formed at the benzene/acetonitrile interface, rapidly desolvated upon filtration to afford 823 mg (62%) of **9b** as a deep blue powder. Anal. Calcd (found after benzene desolvation in vacuo) for $C_{88}H_{160}N_2O_{24}Si_{14}V_2$: C, 49.73 (49.66); H, 7.59 (7.41). Mp: 221–22 °C dec. Crystallographic data for **9b**: Well-formed but poorly diffracting crystals were obtained by the slow diffusion of CH_3CN into a benzene solution of **9b**. The benzene solvate of **9b** crystallizes in a monoclinic space group ($P2_1$ or $P2_1/m$) with a = 13.439 (3) Å, b = 30.306 (9) Å, c = 29.887 (4), β = 95.88 (1)°, and Z = 4. The structure was solved by using direct methods (SHELXTL PLUS) in the space group $P2_1$. All non-hydrogen atoms could be located by using a series of difference-Fourier syntheses, but the poor quality of the diffraction data gives $R_F \sim 16\%$. The silsesquioxane framework appears to be 2-fold rotationally symmetric about the V–V vector, which is parallel to the *y* axis. This strongly suggests that the correct space group may be $P2_1/m$, but repeated attempts to solve the structure in $P2_1/m$ have been uniformly unsuccessful.

Oxidation of 9b with $^{17}O_2$. (a) A (blue) solution of **9b** (100 mg, 0.047 mmol) in pentane (5 mL) was stirred under an atmosphere of dry oxygen (11% ^{17}O) until the solution was colorless. Filtration and solvent evaporation (25 °C, 10^{-3} Torr) afforded 94 mg (96%) of produce **2**/**3**. (b) Solid **9b** (100 mg, 0.047 mmol) was exposed to an atmosphere of dry oxygen (11% ^{17}O) until the solid was white.

In both cases, ^{13}C NMR spectra of the product mixtures were indistinguishable from spectra of authentic **2**/**3**. ^{17}O NMR for ^{17}O-enriched **2** and **3** (67.8 MHz, C_6D_6/C_6H_6, 23 °C): δ 1012 ($w_{1/2}$ = 180 Hz) for **2** and δ 948 ($w_{1/2}$ = 350 Hz) for **3**.

X-ray Diffraction Study of 3. Crystals suitable for an X-ray diffraction study were obtained by crystallization from CH_2Cl_2. Crystal data for $\mathbf{3}\cdot CH_2Cl_2$ [$C_{84}H_{154}O_{26}Si_{14}V_2 \cdot CH_2Cl_2$ (fw 2160.1)] are as follows: orthorhombic *Pbcn*, a = 26.548 (3) Å, b = 22.436 (3) Å, c = 18.703 (3) Å, V = 11140 (3) Å^3, D_{calc} = 1.288 g/cm^3 (Z = 4). A total of 6213 unique reflections with $4.0 \le 2\theta \le 45.0°$ were collected on a Nicolet R3m/V diffractometer at −115 °C with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS). Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for Si, O, C, V, Cl) led to convergence with a final *R* factor of 11.4% for 528 variables refined against 5267 data with $|F_o| > 2.0\sigma(|F_o|)$. Crystallographic data for **3** are summarized in Table I. All other details regarding the crystal structure are reported in the supplementary material.

X-ray Diffraction Study of 4. Crystals suitable for an X-ray diffraction study were obtained by crystallization from benzene. Crystal data for $\mathbf{4}\cdot 0.5C_6H_6$ [$C_{54}H_{45}O_4Si_3V \cdot 0.5C_6H_6$ (fw 932.2)] are as follows: triclinic $P\bar{1}$, a = 10.227 (3) Å, b = 13.175 (3) Å, c = 19.407 (3) Å, α = 81.47 (2)°, β = 76.28 (2)°, γ = 73.44 (2)°, V = 2423.9 (10) Å^3, D_{calc} = 1.277 g/cm^3 (Z = 2). A total of 6234 unique reflections with $4.0 \le 2\theta \le 45.0°$ were collected on a Nicolet R3m/V diffractometer at −95 °C with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS). Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for Si, O, C, V) led to convergence with a final *R* factor of 5.52% for 583 variables refined against 6234 data with $|F_o| > 2.0\sigma(|F_o|)$. Crystallographic data for **3** are summarized in Table I. All other details regarding the crystal structure are reported in the supplementary material.

Acknowledgment. These studies were supported by the National Science Foundation (Grants CHE-8703016 and CHE-9011593) and an NSF Presidential Young Investigator Award (Grant CHE-8657262). Acknowledgement is also made to the Chevron Research Co. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Research Fellowship. We also thank Mr. Rusty L. Blanski for technical assistance and Dr. Joseph W. Ziller for assisting with the crystallographic study on **4**.

Supplementary Material Available: X-ray crystal data for **3** and **4**, including text discussing experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (20 pages); listings of calculated and observed structure factors for **3** and **4** (46 pages). Ordering information is given on any current masthead page.

---

(19) Clark, E. P. *Ind. Eng. Chem. Anal. Ed.* **1941**, *13*, 820.