Paramagnetic Vanadium Silyl Complexes: Synthesis, Structure, and Reactivity

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Vanadium silyl complexes of the type Cp(dmpe)VSiHRR′ are formed by reaction of Cp(dmpe)VMe (**1**) with RR′SiH$_2$ (**2**, R, R′ = Ph; **3**, R = Mes, R′ = H) in benzene at room temperature with concomitant release of CH$_4$ gas. These complexes are paramagnetic, with high-spin d^3 configurations, and exhibit broad ^{1}H NMR resonances. They possess three-legged piano-stool geometries, and each silicon atom adopts a tetrahedral structure with no agostic V$\cdots$HSi interaction. The V−Si bond length of **2** is 2.5629(8) Å, and the V−P bond lengths are 2.4613(8) and 2.4621(8) Å. A KIE value of 2.1 ± 0.1 was observed for the reaction of Cp(dmpe)VCH$_2$Ph (**4**) with Ph$_2$SiH$_2$/Ph$_2$SiD$_2$ at room temperature. The reaction of **2** with Ph$_2$SiHCl in benzene resulted in silyl group exchange to give Cp(dmpe)VSiClPh$_2$ (**5**) in 82% yield. A vanadium(III) silyl complex was obtained by oxidation of **5** with Ph$_3$CCl to give Cp(dmpe)V(Cl)SiClPh$_2$ (**6**). The V−Si and V−Cl bond lengths of **6** are 2.573(1) and 2.388(1) Å, respectively. The Si−Cl bond length of 2.160(1) Å is longer than those typically observed (ca. 2.023 Å). Reaction of **2** with CO afforded Cp(dmpe)V(CO)$_2$ (**7**) via homoleptic cleavage of the V−Si bond. The reaction of **5** with Li(Et$_2$O)$_3$B(C$_6$F$_5$)$_4$ generated what appears to be the silylene complex [Cp(dmpe)VSiPh$_2$]B(C$_6$F$_5$)$_4$, on the basis of elemental analysis.

Introduction

Since the synthesis of the first transition-metal silyl complex, CpFe(CO)$_2$SiMe$_3$, by Wilkinson and co-workers in 1956,[1] this area has undergone extensive development.[2] It is now widely appreciated that silyl complexes are important intermediates in a variety of transformations involving organosilanes. However, despite the importance of compounds with metal−silicon bonds in catalysis, only a few vanadium silyl complexes, such as (CO)$_5$VSiH$_3$, Cp$_2$V(SiCl$_3$)$_2$, and CpV(=N-*t*-Bu)(NH-*t*-Bu)Si-(SiMe$_3$)$_3$, have been reported, and very little is known about the chemistry of such compounds.[2,3] For example, compounds with vanadium−silicon bonds have not been structurally characterized by single-crystal X-ray crystallography.[2d] Undoubtedly, the paramagnetism associated with much of organometallic vanadium chemistry has contributed to the lack of progress in this area.

Common synthetic pathways to stable complexes containing a transition-metal−silicon bond involve oxidative addition or σ-bond metathesis of the Si−H bond of a hydrosilane.[2,4] For the application of such methods in the synthesis of vanadium silyl complexes, the vanadium hydrocarbyl derivatives Cp-(dmpe)VR, Cp(PMe$_3$)$_2$VR$_2$, and Cp(dmpe)V(CHCMe$_3$) (dmpe = 1,2-bis(dimethylphosphino)ethane; R = Me, ^{n}Bu, Ph), reported by Teuben and co-workers,[5] were targeted. As reported here, these compounds were used to prepare new vanadium−silicon-bonded complexes, which have been characterized by structural and reactivity studies.

Results and Discussion

Synthesis and Characterization of Vanadium Silyl Complexes. Treatment of a solution of Cp(dmpe)VMe (**1**) with 1 equiv of Ph$_2$SiH$_2$ in benzene at room temperature resulted in a dark red solution and the rapid release of CH$_4$ gas. Workup of this solution allowed for isolation of the vanadium silyl complex Cp(dmpe)VSiHPh$_2$ (**2**) in 74% yield as red-brown crystals (eq 1). In a similar manner, addition of 1 equiv of

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(2) For reviews on transition-metal silyl complexes, see: (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapter 10. (c) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 35. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (e) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95*, 1351. (f) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197.

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(4) (a) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (b) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702. (c) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357. (d) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428. (e) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (f) Sadow, A. D.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 803. (g) Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308. (h) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648.

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MesSiH$_3$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) to a benzene solution of **1** afforded Cp(dmpe)VSiH$_2$Mes (**3**) in 64% yield. Although these primary and secondary silanes readily gave vanadium silyl complexes, tertiary silanes, such as triphenylsilane and triethylsilane, did not react with **1** at room temperature in benzene over 1 day. Heating compound **1** with these tertiary silanes at 60 °C for 1 h resulted in decomposition. The V(II) silyl complexes **2** and **3** are soluble in aromatic solvents, and **3** is moderately soluble in pentane. These compounds are stable under an inert atmosphere at room temperature, both in the solid state and in solution. Heating a solution of **2** in benzene-d_6 at 100 °C for 13 h resulted in partial decomposition to intractable vanadium-containing products, including Ph$_2$SiH$_2$ and free dmpe.

$$ (1) $$

2: R, R' = Ph
3: R = H, R' = Mes
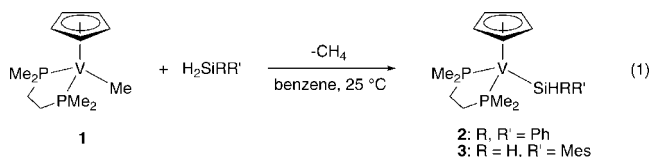
Reactions of the V(III) compounds Cp(PMe$_3$)$_2$VMe$_2$, Cp(PMe$_3$)V(CH$_2$CMe$_3$)$_2$, and Cp(dmpe)V(=CHCMe$_3$) with Ph$_2$SiH$_2$ did not proceed at room temperature, and heating the reaction mixtures at 60 °C resulted in decomposition of the starting materials. These results suggest that V(III) alkyl and alkylidene complexes may be less suitable as precursors to vanadium silyl complexes.

Complexes **2** and **3** exhibit broad ^{1}H NMR resonances, as expected for paramagnetic V(II) complexes.[5] For complex **2**, the chemical shifts for the P—*Me* groups of the dmpe ligand were observed at −3.32 ($\Delta\nu_{1/2}$ = 3800 Hz) and 24.36 ppm ($\Delta\nu_{1/2}$ = 3800 Hz), and overlapping resonances for the ethylene group appeared at 29.30 and 31.74 ppm. In addition, resonances for the silicon-bound Ph groups were observed at 5.08 ($\Delta\nu_{1/2}$ = 2000 Hz) and 11.11 ppm ($\Delta\nu_{1/2}$ = 870 Hz), while the hydrogen on the silicon atom was not observed. The ^{1}H NMR spectrum of **3** contained mesityl group resonances at 6.39 ppm ($\Delta\nu_{1/2}$ = 480 Hz, aromatic H), −6.25 ppm ($\Delta\nu_{1/2}$ = 500 Hz, *p*-Me), and −1.84 ppm (overlapping with peaks for the Me groups of dmpe, *o*-Me). The ^{1}H NMR signals for the Cp ligands were not observed; such resonances for similar CpV complexes are typically observed at very low field.[5,6] The infrared ν(SiH) stretching frequencies for **2** and **3** are observed at 1984 and 1991 cm^{-1}, respectively. These values are relatively low with respect to those of many other metal silyl derivatives[2d] but are in the range expected for metal complexes involving the more electropositive early transition metals. For example, Cp$_2$Ti(H)(SiHPh$_2$)(PMe$_3$)[4g] exhibits a ν(SiH) stretching frequency of 1924 cm^{-1}, and corresponding values for the tantalum silyls Cp$_2$Ta(H)(SiHMe$_2$)$_2$ and Cp$_2$Ta(SiH$_2$Me)(PMe$_3$) are 1985 and 1976 cm^{-1}, respectively.[4h]

The solution magnetic moments of compounds **2** (μ_{eff} = 3.3 μ_B) and **3** (μ_{eff} = 3.5 μ_B), determined by the Evans method,[7] are slightly lower than the calculated spin-only value for d^3 complexes (μ_{eff} = 3.8 μ_B). Nonetheless, these values strongly support the characterization of **2** and **3** as high-spin d^3 complexes.

(6) Köhler, F. H. *J. Organomet. Chem.* **1976**, *110*, 235.
(7) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872.
(8) The equilibrium constant K_{eq} was difficult to accurately determine from ^{1}H NMR data, due to the broadness of the resonances and overlapping of Si—H peaks; K_{eq} = [Cp(dmpe)VSiHPh$_2$][MesSiH$_3$]/[Cp(dmpe)-VSiH$_2$Mes][Ph$_2$SiH$_2$].
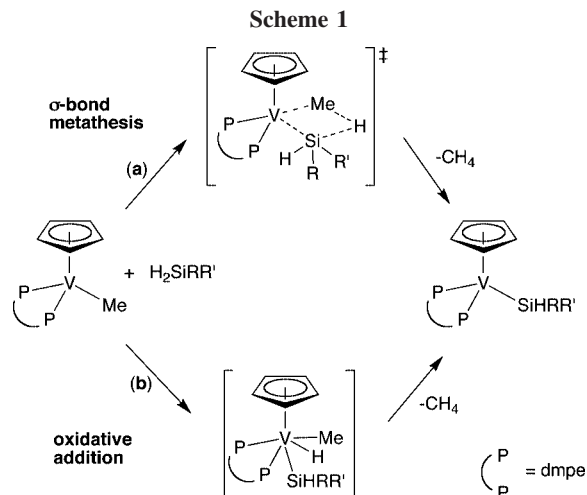
Scheme 1

Two possible reaction pathways for the formation of **2** and **3** from the interaction of **1** with silanes are σ-bond metathesis (path a, Scheme 1) and oxidative addition followed by reductive elimination (path b). To further characterize the reaction mechanism of this process, a kinetic isotope effect (KIE) was obtained by measuring the relative rates of the reaction of Cp(dmpe)VCH$_2$Ph (**4**) with excess Ph$_2$SiH$_2$ and Ph$_2$SiD$_2$ in a 1:1 ratio. The benzyl complex **4** was found to undergo reactions analogous to those of **1**, but at a slower rate. With compound **4**, the release of toluene may be monitored by NMR spectroscopy, and this allows for the determination of a KIE. It was independently determined that toluene does not react with the product **2** under the reaction conditions. After a benzene-d_6 solution of **4** and Ph$_2$SiH$_2$/Ph$_2$SiD$_2$ was stirred for 24 h at 23 °C, the volatile components were vacuum-transferred to a J. Young NMR tube and the ratio of toluene/toluene-d was measured by ^{1}H NMR spectroscopy. The KIE observed for this reaction was 2.1 ± 0.1 (average of three runs). Whereas this value indicates that the Si—H bond is broken in a rate-determining step, it does not allow differentiation between the two mechanisms of Scheme 1.

The addition of 1 equiv of MesSiH$_3$ to a benzene-d_6 solution of **2** at room temperature resulted in an equilibrium mixture of **2**, **3**, Ph$_2$SiH$_2$, and MesSiH$_3$ ($K_{\text{eq}} \approx 0.6$, by ^{1}H NMR spectroscopy).[8] Cooling the reaction mixture in toluene-d_8 to −80 °C provided no evidence for reaction intermediates (such as oxidative addition products).

$$ (2) $$
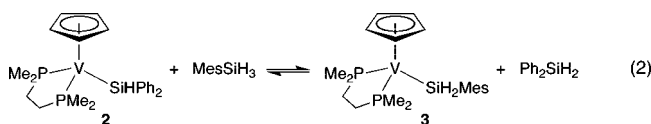
Vanadium complexes with a halogen-substituted silyl group are of interest as precursors to vanadium silylene complexes, via exchange of the halide for a noncoordinating ion, because this route has previously been used to obtain cationic silylene complexes of various transition metals.[9] Thus, an attempt was made to prepare Cp(dmpe)VSiClPh$_2$, by addition of 1 equiv of Ph$_2$SiHCl to a benzene solution of **1**. This resulted in a rapid color change of the solution to dark green; however, the product isolated from solution was Cp(dmpe)VCl, as determined by comparison of spectra with those previously reported by Teuben.[5] The silicon-containing product of this reaction is Ph$_2$SiHMe (ca. 90% from ^{1}H NMR spectroscopy). Reaction of **1** with Ph$_2$SiMeCl also gave Cp(dmpe)VCl, as well as Ph$_2$SiMe$_2$ (ca. 90% yield from ^{1}H NMR spectroscopy). The mechanisms

of these reactions are currently unknown, but possibilities include oxidative addition of the Si−Cl bond, followed by Si−Me reductive elimination, and a more concerted exchange of Me and Cl groups between the V and Si centers.

Fortunately, it proved possible to prepare Cp(dmpe)VSiClPh$_2$ (**5**) by an alternate procedure involving reaction of Ph$_2$SiHCl with **2** at room temperature (eq 3). This reaction afforded Ph$_2$SiH$_2$ and **5** in 82% yield as a dark brown solid. The structure of **5** is further supported by its reaction with LiAlH$_4$ in Et$_2$O/ benzene, which gave the expected product **2**, albeit in low yield (ca. 5% by ^{1}H NMR). Complex **5** was also obtained by the silyl-exchange reaction of **3** with Ph$_2$SiHCl, which gave MesSiH$_3$ and **5** in 83% yield. Monitoring this reaction by ^{1}H NMR spectroscopy provided no evidence for an equilibrium process, as observed in the related interconversion of **2** and **3** (vide supra).

(3)
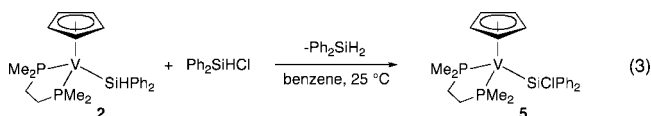
A vanadium(III) silyl complex was obtained by a one-electron oxidative addition to complex **5**. Addition of Ph$_3$CCl to a benzene solution of **5** gave complex **6**, Cp(dmpe)V(Cl)SiClPh$_2$, as a purple solid in 77% yield (eq 4). An additional product, observed by ^{1}H NMR spectroscopy, was trityl dimer.[10] The 16-electron complex **6** is paramagnetic and sparingly soluble in common organic solvents. However, pure samples were obtained by crystallization from benzene.

(4)
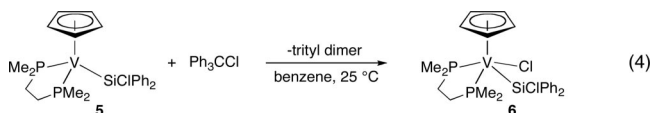
Molecular Structures of Vanadium Silyl Complexes. The structures of **2**, **3**, and **6** were determined by X-ray crystallography (Figures 1−3). To our knowledge, these are first examples of crystallographically determined structures for vanadium−silicon-bonded complexes.

Complex **2** possesses a three-legged piano-stool geometry with a V−Si bond length of 2.5629(8) Å, a value which falls between typical Ti−Si (ca. 2.69 Å) and Cr−Si (ca. 2.38 Å) bond lengths.[2d] The conformation about the Si atom is approximately tetrahedral, as defined by V−Si−H, V−Si−C1, and V−Si−C2 bond angles of 115(1), 116.93(8), and 117.55(8)°, respectively. The silicon-bound hydrogen atom was located from the Fourier difference map, and this allowed determination of a Si−H bond length of 1.46(3) Å. There is no evidence for an agostic interaction involving the Si−H bond, as indicated by the position of the silicon-bound hydrogen atom and by the presence of roughly similar V−Si–R angles (vide supra). The
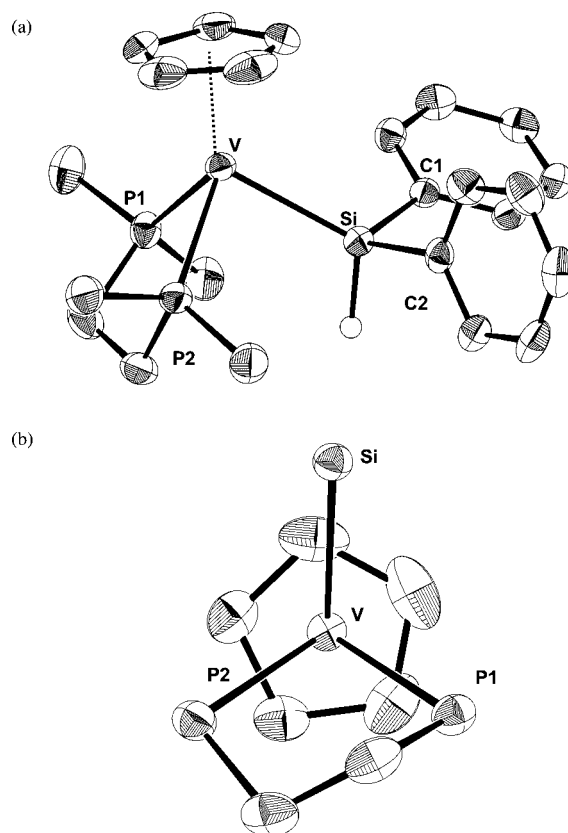
(9) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Grumbine, S. D.; Tilley, T. D.; Arnold, F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (c) Straus, D.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (d) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (e) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518. (f) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L.; Arnold, F. P. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (g) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 5495. (h) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4648. (i) Glaser, P. B.; Wanandi, P. W.; Tilley, T. D. *Organometallics* **2004**, *23*, 693. (j) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799.

(10) Lankamp, H.; Nauta, W. Th.; MacLean, C. *Tetrahedron Lett.* **1968**, *9*, 249.

Figure 1. ORTEP drawings of Cp(dmpe)VSiHPh$_2$ (**2**), with thermal ellipsoids drawn at the 50% probability level: (a) general view with hydrogen atoms, except for those on the silicon atom, omitted for clarity; (b) view along the V−Cp(centroid) axis with groups on the Si and P atoms removed for clarity. Selected bond distances (Å) and angles (deg): V−Si = 2.5629(8), V−P2 = 2.4621(8), V−P1 = 2.4613(8), Si−H = 1.45(3), Si−C1 = 1.915(2), Si−C2 = 1.913(2), V−Cp(centroid) = 1.946; P1−V−P2 = 81.68(3), P2−V−Si = 87.67(3), P1−V−Si = 92.82(3), V−Si−H = 115(1), V−Si−C1 = 116.93(8), V−Si−C2 = 117.55(8).

V−P distances of 2.4613(8) and 2.4621(8) Å are quite similar to those of Cp(dmpe)VMe (2.462(1) and 2.470(1) Å).[5] The average V−C(Cp) bond distance in **2** is slightly shorter than that of Cp(dmpe)VMe (2.279(3) vs 2.300(4) Å) but rather similar to the corresponding distance in vanadocene (average 2.260 Å).[11]

The structure of **3** is very similar to that of **2**. However, as shown by Newman projections, **2** is staggered about the V−Si bond, while **3** adopts a more eclipsed structure (Chart 1). The staggered nature of the bonding about the V−Si bond of **2** is described by a Cp(centroid)−V−Si−H torsion angle of 178(1)°. Note that there are two independent molecules (rotamers) in the unit cell of **3**, one of which is shown in Figure 2. The Cp(centroid)−V−Si−C torsion angles associated with these molecules are 2(1) and 134(1)°. The V−Si bond lengths observed for the two independent molecules in the unit cell are 2.576(2) and 2.577(2) Å. The Si−H bond lengths observed for **3** (average 1.42(3) Å) are similar to that found in **2**, and there is no interaction between this bond and the vanadium center.

Compound **6** exhibits a four-legged piano-stool structure, as determined by X-ray crystallographic analysis. The bond length

(11) Rogers, R. D.; Atwood, J. L.; Foust, D.; Rausch, M. D. *J. Cryst. Mol. Struct.* **1981**, *11*, 183.

Chart 1

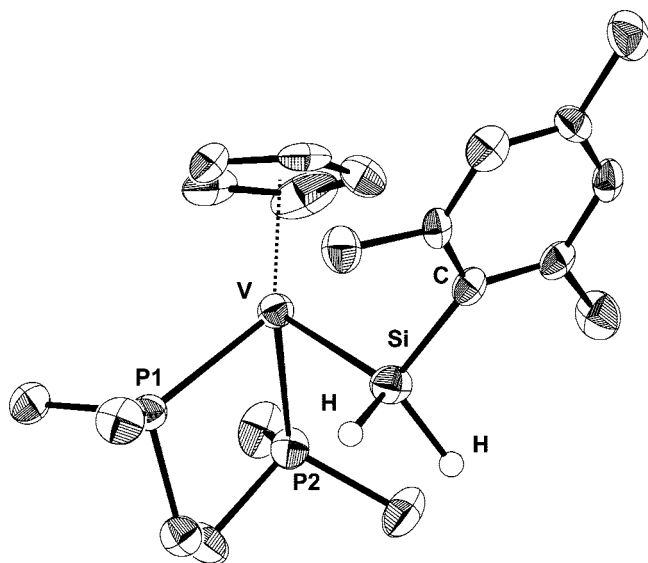(2.160(1) Å) is considerably longer than comparable values found in chlorosilanes (ca. 2.02 Å).[2d] This suggests that d-electron density at vanadium may be interacting, in a V→Si donor sense, with the Si−Cl σ* orbital.[12]

Reactions of Vanadium Silyl Complexes. Compounds **2** and **3** were examined as catalysts for the hydrosilation of 1-hexene, using Ph_2SiH_2 or $MesSiH_3$ as the silane in benzene-d_6 solution. In both cases, after 24 h at room temperature, no conversion was observed by ^{1}H NMR spectroscopy.

When CO gas (1 atm) was added to a benzene solution of **2** at room temperature, the solution color changed to dark green and eventually to dark orange. The resulting product, isolated in 94% yield by crystallization from a toluene−diethyl ether solvent mixture, was identified as the 18-electron dicarbonyl compound $Cp(dmpe)V(CO)_2$ (**7**). The byproducts of this reaction included Ph_2SiH_2 (60% by ^{1}H NMR spectroscopy), which would imply that the reaction proceeds by homolytic cleavage of the V−Si bond, to generate a V(I) species that is then trapped by carbon monoxide to form **7**. The resulting silyl radical presumably abstracts hydrogen from species present in the reaction mixture. Teuben has described a similar process, by which $Cp(PMe_3)_2VMe_2$ reacts with 1 atm of CO to afford $CpV(CO)_2(PMe_3)_2$ and acetone, presumably via an acyl intermediate.[5a] For comparison, we examined the reaction of $Cp(dmpe)VMe$ (**1**) with CO (1 atm), which gave **7** in 90% yield but no acetone by ^{1}H NMR spectroscopy. Characteristic [51]V and ^{31}P NMR chemical shifts for **7** were observed at −1229 ppm (t, J_{VP} = 30 Hz) and 78.81 ppm ($\Delta\nu_{1/2}$ = 2000 Hz), respectively.[13] The infrared spectrum of **7** exihibts CO stretching vibrations at 1830 and 1747 cm^{-1}. The structure of **7** was determined by X-ray crystallography (Figure 4).

Preliminary reactivity studies were designed to exploit the halide leaving groups in **5** and **6** in the synthesis of vanadium−silicon double bonds. In related work, Egorov and co-workers have reported the generation of Cp*$_2$V=SiMe$_2$, identified on

Figure 2. ORTEP drawing of one of the two independent molecules in the unit cell of $Cp(dmpe)VSiH_2Mes$ (**3**), with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, except for those bonded to the silicon atom, are omitted for clarity. Selected bond distances (Å) and angles (deg): V−Si = 2.576(2), 2.577(2), V−P1 = 2.441(2), 2.439(2), V−P2 = 2.465(2), 2.455(2), Si−H = 1.41(4), 1.38(4), 1.50(5), 1.43(5), Si−C = 1.909(5), 1.909(5), V−Cp(centroid) = 1.947, 1.941; P1−V−P2 = 80.95(5), 80.17(6), P2−V−Si = 92.95(6), 89.02(5), P1−V−Si = 99.76(6), 93.15(5), V−Si−H = 120(2), 117(2), 108(2), 118(2), V−Si−C1 = 126.0(2), 109.6(2).
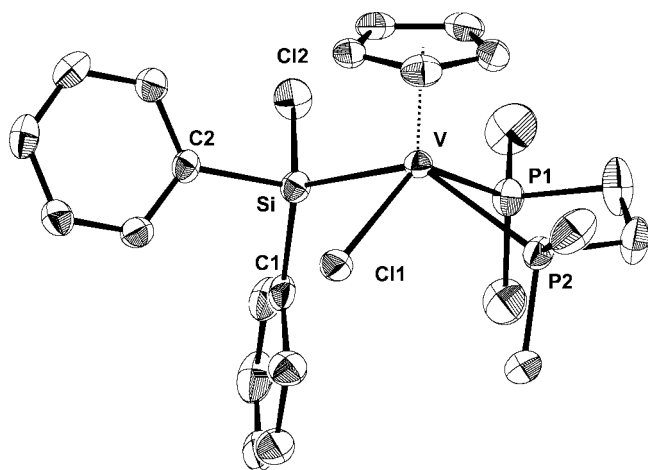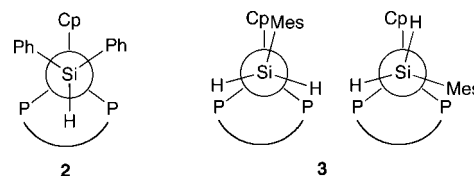

Figure 3. ORTEP drawing of $Cp(dmpe)V(Cl)SiClPh_2$ (**6**), with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the benzene molecule of crystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): V−Si = 2.574(2), V−P2 = 2.518(1), V−P1 = 2.480(1), Si−Cl = 2.160(1), V−Cl = 2.388(1), V−Cp(centroid) = 1.962; P1−V−P2 = 74.63(4), P1−V−Cl = 125.30(4), P2−V−Cl = 81.73(4), P1−V−Si = 83.67(4), P2−V−Si = 135.86(4), V−Si−Cl = 114.95(5), V−Si−C1 = 120.6(1), V−Si−C2 = 114.4(1).

of V−Si (2.573(1) Å) is within the range observed for the corresponding bond lengths in **2** and **3**. The Si−Cl bond length

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Figure 4. ORTEP drawing of $Cp(dmpe)V(CO)_2$ (**7**), with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V−C1 = 1.861(4), C1−O1 = 1.173(4), V−P1 = 2.393(1), V−Cp(centroid) = 1.922; C1−V−C1* = 72.9(2), P1−V−P1* = 74.84(5), P1−V−C1 = 77.7(1), P1−V−C1* = 120.6(1), V−C1−O1 = 177.4(3). Asterisks indicate symmetry-generated atoms.

Table 1. Crystallographic Data for Compounds 2, 3, 6, and 7

	2	3	6	7
formula	$C_{23}H_{32}P_2SiV$	$C_{20}H_{34}P_2SiV$	$C_{23}H_{31}Cl_2P_2SiV \cdot C_6H_6$	$C_{13}H_{21}O_2P_2V$
formula wt	449.46	415.44	597.46	322.18
cryst size (mm)	$0.30 \times 0.25 \times 0.25$	$0.20 \times 0.20 \times 0.10$	$0.30 \times 0.22 \times 0.15$	$0.15 \times 0.18 \times 0.09$
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$Pna2_1$	$P2_1/m$
a (Å)	10.1297(11)	15.365(6)	17.424(1)	7.024(2)
b (Å)	8.8751(10)	17.074(6)	9.4930(7)	13.185(4)
c (Å)	26.927(3)	17.199(7)	17.848(1)	8.438(2)
α (deg)	90	90	90	90
β (deg)	100.262(2)	90	90	101.602(4)
γ (deg)	90	90	90	90
V (Å^3)	2382.0(5)	4512(3)	2952.2(4)	765.5(4)
Z	4	8	4	2
D_{calcd} (g cm^{-3})	1.253	1.223	1.344	1.398
no. of indep rflns	13 628	23 691	16 012	3920
no. of params	248	449	316	85
R1 ($I > 2\sigma(I)$)	0.043	0.061	0.034	0.039
wR2 (all data)	0.078	0.108	0.054	0.079
goodness of fit	0.931	0.992	0.632	0.86

the basis of an ESR spectrum.[14] The reaction of KC_8 with **6** in C_6H_6 for 1 day at room temperature afforded a complex mixture.

The reaction of **5** with $Li(Et_2O)_3B(C_6F_5)_4$ in fluorobenzene led to a color change of the reaction mixture from dark red to dark green. Workup of the reaction mixture produced a dark green solid, which is insoluble in common organic solvents except PhF, and this compound exhibited no observable peaks by ^{1}H NMR spectroscopy (PhF/toluene-d_8 (1/5) cosolvent). Although little structural information could be obtained from spectroscopic methods, the combustion analysis is consistent with the formula $[Cp(dmpe)VSiPh_2][B(C_6F_5)_4]$ (**8**). Thus, we tentatively conclude that **8** is a paramagnetic, cationic silylene complex of vanadium.

Conclusion

This report describes the synthesis and characterization of new types of vanadium silyl complexes. These complexes are readily derived from the vanadium alkyl complexes Cp-(dmpe)VR (R = Me, CH_2Ph) in high yields. Given the ligand sets involved in these complexes, they are expected to be relatively electron-rich, and this is supported by the oxidation of **5** under mild conditions, to give the vanadium(III) silyl complex **6**. In general, spectroscopic features for these complexes suggest that they are similar to the related alkyl derivatives from which they are derived. Significantly, these studies have produced the first structural information for vanadium silyl complexes.

The new compounds reported here represent relatively rare examples of fully characterized paramagnetic silyl complexes[2,15] and, therefore, provide an opportunity to explore the chemistry of metal–silicon bonds in odd-electron systems. Future work in this laboratory will address this issue, and further attempts will be made to explore the synthesis and study of paramagnetic silylene complexes of vanadium.

Experimental Section

All manipulations were conducted under an N_2 atmosphere using standard Schlenk or glovebox techniques. In general, solvents were distilled from appropriate drying agents and were stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotope) were dried with appropriate drying agents and vacuum-transferred prior to use. The reagents Cp(dmpe)VCl, Cp(dmpe)VMe,[5] and dmpe[16] were prepared according to literature procedures. ^{1}H, ^{31}P, and ^{51}V NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.1 MHz (^{1}H) and 202.5 MHz (^{31}P) and on a Bruker AMX-400 spectrometer operating at 105.2 MHz (^{51}V). Chemical shifts are reported in ppm relative to an internal standard of C_6D_5H (7.15 ppm) (^{1}H), an external standard of 85% H_3PO_4 (^{31}P), or an external standard of $VOCl_3$ (^{51}V). Elemental analyses were perfomed by the Microanalytical Facility in the College of Chemistry at the University of California, Berkeley (C and H), and Desert Analytics, Inc. (V). Infrared spectra were recorded as KBr pellets on a Mattson FTIR 3000 instrument.

X-ray Data Collection. All single-crystal X-ray analyses were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made with a Bruker SMART OCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 69). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[17] All non-hydrogen atoms and hydrogen atoms on the silicon atoms of **2** and **3** were refined anisotropically. All other hydrogen atoms were placed using AFIX instructions. Details of data collections and refinments are given in Table 1 and in the CIF files given in the Supporting Information.

Synthesis of Cp(dmpe)VSiHPh$_2$ (2). Ph_2SiH_2 (0.078 g, 0.42 mmol) was added to a benzene solution of **1** (0.119 g, 0.423 mmol) at room temperature. After it was stirred for 1 h, the solution was filtered and then evaporated to dryness. The resulting solid was washed with pentane several times and then recrystallized from a mixed toluene (1 mL)−pentane (2 mL) solvent system at −30 °C in 74% yield as red-brown crystals. ^{1}H NMR (benzene-d_6): δ −3.32 (br, $\Delta\nu_{1/2}$ = 3800 Hz, 6H, P*Me*), 5.08 (br, $\Delta\nu_{1/2}$ = 2000 Hz, 4H, Si*Ph*$_2$), 11.11 (br, $\Delta\nu_{1/2}$ = 870 Hz, 6H, Si*Ph*$_2$), 24.36 (br, $\Delta\nu_{1/2}$ = 3800 Hz, 6H, P*Me*), 29.30 (br, 2H, PC*H*$_2$), 31.74 (br, 2H, PC*H*$_2$). IR (KBr pellet): ν(SiH) 1984 cm^{-1}. Anal. Calcd for $C_{23}H_{32}P_2SiV$: C, 61.46; H, 7.18. Found: C, 61.25; H, 7.32.

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Syntheisis of Cp(dmpe)VSiH₂Mes (3). MesSiH₃ (0.052 g, 0.35 mmol) was added to a solution of **1** (0.099 g, 0.35 mmol) in 5 mL of benzene, and the resulting solution was stirred for 2 h at room temperature. After filtration and removal of the solvent in vacuo, the resulting solid was washed several times with pentane. Recrystallization of the solution from a mixture of toluene (1 mL) and pentane (2 mL) at −30 °C gave pure **3** in 64% yield. ^{1}H NMR (benzene-d_6): δ −6.25 (br, $\Delta\nu_{1/2}$ = 500 Hz, 3H, *p*-Me), −2.50 (br, 6H, P*Me*), −1.84 (br, 6H, *o*-Mes), 6.39 (s, 2H, aromatic H on Mes group), 18.29 (br, $\Delta\nu_{1/2}$ = 3000 Hz, 6H, P*Me*), 25.19 (br, $\Delta\nu_{1/2}$ = 2700 Hz, 2H, PC*H*₂) 40.33 (br, $\Delta\nu_{1/2}$ = 2700 Hz, 2H, PC*H*₂). IR (KBr pellet): ν(SiH) 1991 cm^{-1}. Anal. Calcd for C₂₀H₃₄P₂SiV: C, 57.82; H, 8.25. Found: C, 57.99; H, 8.58.

Synthesis of Cp(dmpe)VCH₂Ph (4). A suspension of Cp(dmpe)VCl (0.808 g, 2.68 mmol) in 30 mL of diethyl ether was cooled to −30 °C, and 1.4 mL of a 2.0 M PhCH₂MgBr solution in THF was added dropwise. The reaction solution was warmed to 0 °C and stirred for 2 h. The solution was filtered and concentrated to ca. 5 mL, and then 5 mL of pentane was added. Concentration and cooling (−30 °C) of the resulting solution gave **4** in 38% yield. ^{1}H NMR (benzene-d_6): δ −12.57 (br, 6H, P*Me*), 3.77 (br, 3H, *Ph*), 11.25 (br, 6H, P*Me*), 14.23 (br, 2H, *Ph*), 15.83 (br, 2H, PC*H*₂), 31.45 (br, 2H, PC*H*₂). Anal. Calcd for C₁₈H₂₈P₂V: C, 60.51; H, 7.90. Found: C, 60.23; H, 8.16.

Reaction of Cp(dmpe)VCH₂Ph with Silanes. A 1:1 solution of Ph₂SiH₂/Ph₂SiD₂ (0.085 mL, 2.0 M solution) was added to a solution of **4** (0.020 g, 0.056 mmol) in benzene-d_6 (1 mL). After 24 h, the volatile components were transferred into a J. Young NMR tube by trap-to-trap distillation. The ratio of toluene to toluene-*d* was determined by the integration of resonances in ^{1}H NMR spectra.

Synthesis of Cp(dmpe)VSiPh₂Cl (5). Ph₂SiHCl (0.110 g, 0.504 mmol) was added to a benzene solution (3 mL) of **2** (0.200 g, 0.445 mmol). After the mixture was stirred for 20 h at room temperature, the resulting solution was filtered and then the solvent was removed in vacuo. The resulting solid was washed several times with pentane (3 × 2 mL). Recrystallization from a toluene (1 mL)−pentane (2 mL) solvent mixture at −30 °C gave Cp(dmpe)VSiPh₂Cl in 82% as a red-purple solid. ^{1}H NMR (benzene-d_6): δ −5.72 (br, 6H, P*Me*), 2.36 (br, 4H, Si*Ph*₂), 8.01 (br, 2H, Si*Ph*₂), 9.70 (br, 4H, Si*Ph*₂), 26.19 (br, 6H, P*Me*), 30.00 (br, 4H, PC*H*₂). Anal. Calcd for C₂₃H₃₁ClP₂SiV: C, 57.09; H, 6.46. Found: C, 56.75; H, 6.43.

Synthesis of Cp(dmpe)V(Cl)SiPh₂Cl (6). Ph₃CCl (0.054 g, 0.19 mmol) was added to a benzene solution (4 mL) of **4** (0.093 g, 0.19 mol), and color of the resulting solution immediately changed to purple. The solution was then stirred for 2 h at room temperature and filtered, and the solvent was removed in vacuo. The resulting solid was washed with pentane (3 mL) several times and dried under reduced pressure to give **6** in 77% yield as purple crystals. Anal. Calcd for C₂₃H₃₁Cl₂P₂SiV: C, 53.19; H, 6.02. Found: C, 52.84; H, 6.20.

Cp(dmpe)V(CO)₂ (7). CO gas (1 atm) was admitted into a Schlenk tube containing a solution of **2** (0.113 g, 0.251 mmol) in benzene (5 mL). After the reaction mixture was stirred for 24 h, a precipitate was filtered followed by drying under vacuo. After the resulting solid was washed several times by pentane (3 × 2 mL), it was dried under reduced pressure and then crystallized from a mixture of toluene (1 mL) and Et₂O (3 mL). The product (**7**; 0.076 g, 0.24 mmol) was obtained in 94% yield as yellow crystals. ^{1}H NMR (benzene-d_6): δ 0.87 (br, 10H, overlapping P*Me* and PC*H*₂ resonances), 1.14 (br, 6H, P*Me*), 4.49 (br, 5H, Cp). ^{13}C{^{1}H} NMR (benzene-d_6): δ 19.03, 19.96, 29.78, 87.86; ^{31}P{^{1}H} NMR (benzene-d_6): δ 78.8. ^{51}V NMR (benzene-d_6): δ −1229.2 (t, $^1J_{VP}$ = 208 Hz). IR (KBr pellet): ν(CO) 1830, 1747 cm^{-1}. Anal. Calcd for C₁₃H₂₁O₂P₂V: C, 48.46; H, 6.57. Found: C, 48.80; H, 6.30.

Reaction of 5 with Li(Et₂O)₃B(C₆F₅)₄. To a solution of **5** (0.104 g, 0.215 mmol) in fluorobenzene (5 mL) was added Li(Et₂O)₃B(C₆F₅)₄ (0.188 g, 0.207 mmol). The reaction mixture was stirred for 3 h at room temperature, and then the solution was filtered. The volatile components were removed under reduced pressure to leave an oily foam. This solid was washed with pentane (3 × 2 mL) and toluene (3 × 2 mL), and drying under vacuum resulted in a dark green solid in 62% yield. Anal. Calcd for C₄₇H₃₁BF₂₀P₂SiV: C, 50.07; H, 2.77; V, 4.52. Found: C, 49.73; H, 3.15; V, 4.54.

Supporting Information Available: CIF files giving crystallographic data for **2**, **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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