

molecular spins are randomly oriented within the crystal lattice; after polymerization, they tend to align along the same direction with a ferromagnetic ordering of the molecular spins below T_c . Therefore, we prefer to speak of a molecular-based ferromagnet. Of course, this definition problem is a little bit byzantine and does not deserve much space. The choice is a matter of sensitivity. Our definition emphasizes the molecular approach.

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Supplementary Material Available: Tables SI-SV listing crystallographic data, atomic parameters, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atomic parameters, bond distances and angles involving hydrogen atoms, and least-squares planes and dihedral angles for $\text{MnCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ (8 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Vanadium-Promoted Reductive Coupling of CO and Facile Hydrogenation To Form *cis*-Disiloxyethylenes

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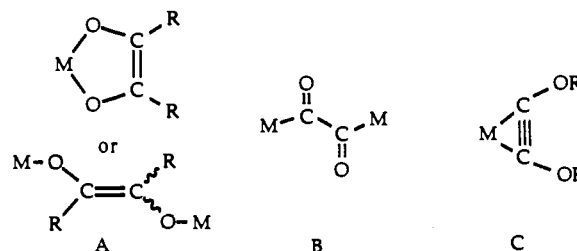
Abstract: Reaction of trimethylsilyl reagents with $\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]$ leads to reductive coupling of the two CO ligands to form a coordinated bis(trimethylsiloxy)acetylene ligand. When Me_3SiOTf was used, a novel six-coordinate, paramagnetic ($\mu_{\text{eff}} = 2.81 \mu_B$ at 20 K) $[\text{V}(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2]\text{OTf}$ complex was obtained, while addition of Me_3SiBr afforded diamagnetic $[\text{V}(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2\text{Br}]$, analogues of which are known in Nb and Ta chemistry. Both complexes were characterized in the solid state by single-crystal X-ray diffraction, and the latter was identified in solution by NMR spectroscopy. Significantly, these vanadium complexes react with hydrogen at room temperature and mild pressures in the absence of external catalysts to afford exclusively the *cis* isomer of bis(trimethylsiloxy)ethylene in good yield. In an experiment designed to investigate the mechanism of the reductive coupling reaction, vanadium carbyne species were prepared by addition of 1 equiv of a trialkyl- or triarylsilyl chloride to $\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]$. One such complex, $[\text{V}(\text{COSiPh}_3)(\text{CO})(\text{dmpe})_2]$, was crystallized and structurally characterized as the first unambiguous example of a vanadium carbyne complex. Carbynes of this kind are known to be intermediates in the reductive coupling of CO ligands in $[\text{M}(\text{CO})_2(\text{dmpe})_2\text{X}]$ compounds ($\text{M} = \text{Nb, Ta}$; $\text{X} = \text{halide, triflate}$). These results significantly extend the generality of CO reductive coupling chemistry to a first-row transition metal.

Introduction

There is considerable interest in the conversion of carbon monoxide and hydrogen to useful C2 oxygenates.¹⁻³ Modification of Fischer-Tropsch systems by changing operating conditions and catalysts can shift product distributions to favor oxygenate formation,⁴ but more promising are rhodium catalysts which produce mixtures of ethylene glycol and methanol at operating temperatures of 150–300 °C and pressures of 50–3000 atm.^{5,6}

Several homogeneous systems have been discovered that couple two CO molecules with the creation of a new carbon-carbon bond. Alkyl and hydride complexes of the group 4 transition metals react with CO to yield ene-diolate ligands bound to one or more metals (Chart I, product type A).⁷⁻⁹ Subsequent work revealed that complexes of the group 5,^{10,11} actinide,^{12,13} and lanthanide¹⁴⁻¹⁶

Chart I



metals behave similarly. Coupling of CO ligands to afford ene-diolate products is significantly influenced by the high metal-oxygen bond energies found for these oxophilic metals. Removal of the newly formed C2 oxygenates from these metal complexes has not yet been reported, presumably because of the inherently strong metal-oxygen bonds.¹⁷

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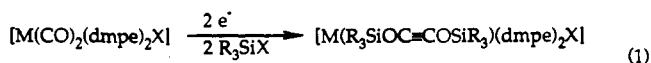
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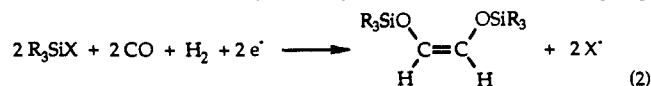
A different mode of reductive coupling has been found for rhodium porphyrin carbonyl complexes, in which dimetallic α -diketones (Chart I, product type B) are among the products.¹⁸ Use of the sterically encumbered ligand tetrakis(3,5-dimethylphenyl)porphyrin (TXP) allowed selective reaction of $[\text{Rh}(\text{TXP})_2]$ with CO under mild conditions to form $[(\text{TXP})\text{RhC}(\text{O})\text{C}(\text{O})\text{Rh}(\text{TXP})]$.¹⁹ Thermodynamic studies of the rhodium octaethylporphyrin analogues revealed the dimetallic α -diketone species to have relatively strong Rh-C acyl bonds, 54 ± 3 kcal/mol.²⁰

Work in our laboratory on the reductive coupling of CO has achieved C-C bond formation with the resulting organic species, formally an acetylene, bound to the metal center via both carbon atoms (Chart I, product type C). This transformation can be accomplished by addition of trialkylsilyl reagents to reduced group 5 metal dicarbonyl complexes, according to eq 1.^{21,22} In the



products, the oxygen atoms of the reductively coupled C2 moiety are bound to the silyl groups, thus utilizing the strong affinity of silicon for oxygen. Removal of the acetylene ligand from such a metal complex is not impeded by the occurrence of strong metal-oxygen bonds, as is the case for the enediolate complexes. Accordingly, we have recently demonstrated that the CO-derived acetylene ligand in $[\text{Ta}(\text{tBuMe}_2\text{SiOC}=\text{COSiMe}_2\text{tBu})(\text{dmpe})_2\text{Cl}]$ can be removed with its C-C bond intact by hydrogenation in the presence of cocatalysts to yield *cis*-bis(trialkylsiloxy)ethylenes.²³

Currently, we are interested in generating a catalytic system for the formation of C2-oxygenated olefins from CO and H₂, eq 2. In order to accomplish this goal, transition metal complexes were needed that not only would promote the reductive coupling



of CO but would also activate dihydrogen in order to facilitate release of the newly created acetylene as a disiloxyolefin or other hydrocarbon. Vanadium analogues of the Nb and Ta complexes described above were attractive candidates for several reasons. The smaller atomic radius of vanadium as compared to niobium or tantalum should bring the coordinated carbon atoms of the two CO ligands physically closer to one another, thus facilitating the coupling reaction.²⁴ In addition, it was anticipated that vanadium acetylene complexes would have a lower thermodynamic barrier to ligand release, because metal-carbon bond strengths generally increase down a group in the periodic table.²⁵ Finally, it was of interest to extend the scope of the reductive coupling reaction to a first-row transition metal, which are generally more kinetically labile and thus perhaps more amenable to catalytic chemistry.

In the present paper we describe the synthesis and characterization of two different classes of (disiloxyacetylene)vanadium complexes, formed by reductive coupling of appropriate dicarbonyl precursors. The structure of one of these species departs substantially from the Nb and Ta analogues, and both classes react

with hydrogen at room temperature and mild pressures in the absence of cocatalysts to generate the desired free *cis*-bis(disiloxy)ethylenes. Furthermore, we have isolated several vanadium carbyne complexes, one of which has been structurally characterized, analogous to known intermediates on the reductive coupling pathway for the niobium and tantalum analogues.

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive compounds were carried out by standard Schlenk, vacuum, and drybox techniques. Pentane, diethyl ether, tetrahydrofuran (THF), and dimethoxyethane (DME) were distilled from sodium benzophenone/ketyl solutions. Tetrahydrofuran-*d*₈ was predried with potassium metal and distilled from Na/K alloy before use. Benzene-*d*₆ was dried by passage through a short column of alumina. Proton chemical shifts are referenced to residual solvent peaks (benzene-*d*₆, 7.15 ppm; THF-*d*₈, 1.73, 3.58 ppm). ³¹P chemical shifts are reported relative to external 85% phosphoric acid. ¹H NMR spectra were recorded on Varian XL300, Bruker AC250, and Bruker WM250 instruments. ³¹P NMR spectra were obtained with the XL300 instrument operating at 121 MHz. FTIR spectra were recorded on a Mattson Cygnus 100 Fourier transform instrument. GC/MS spectra were obtained by using a Hewlett-Packard Model 5971A system. $[\text{VCl}_2(\text{dmpe})_2]$ ²⁶ and *cis*-bis(trimethylsiloxy)ethylene²⁷ were prepared via literature procedures. Carbon monoxide (Matheson, Ultra High Purity 99.9%) was used as received. Hydrogen (Matheson, Purity 99.9995%) was dried by passage through a column (0.9 mm × 40 cm) of powdered activated 3-Å molecular sieves. Other reagents were obtained from commercial sources and used as received after degassing.

Na[V(CO)₂(dmpe)₂] (1). A 25-mL flask containing a solution of 0.256 g of $[\text{VCl}_2(\text{dmpe})_2]$ (0.606 mmol) in 15 mL of THF, sodium amalgam (0.100 g of Na in 16 g of Hg, 4.35 mmol of Na), and a stir bar was purged with CO and then left to stir rapidly under 10 psig of CO overnight. The cloudy red-orange solution was purged with argon and taken into the drybox. The solvent was removed under vacuum and the residue taken up in a minimal amount of THF (3–4 mL). Careful filtration through a fine-glass fritted funnel yielded a red solution, which was concentrated to about 1 mL. Addition of excess pentane (~20 mL) precipitated **1** as a bright yellow powder, which was collected by filtration and dried to yield 0.200 g of $[\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]]$ (77%). Compound **1** can also be obtained as a yellow microcrystalline solid by diffusion of pentane into a concentrated THF/pentane solution of **1** at room temperature. ¹H NMR (THF-*d*₆): δ 0.96 (6 H, s, CH₃), 1.27 (6 H, s, CH₃), 1.32 (6 H, d, CH₃, *J*_{HP} = 3 Hz), 1.41 (6 H, s, CH₃), 1.6–1.2 (8 H, br, CH₂). ³¹P{¹H} NMR (THF-*d*₆): δ 67.0 (br octet, *J*_{VP} = 350 Hz), 45.0 (br octet, *J*_{VP} = 350 Hz). FTIR (Nujol): 1612 (s), 1539 (s), 1419 (w), 1287 (w), 1272 (w), 972 (m), 878 (w), 679 (w), 629 (w) cm⁻¹. Anal. Calcd for C₁₄H₃₂NaO₂P₄V: C, 39.08; H, 7.50; N, 0.0; P, 28.80. Found: C, 38.53; H, 7.07; N, 0.0; P, 28.18.

[V(Me₃SiOC≡COSiMe₃)(dmpe)₂]OTf (2). To a stirred solution of 0.200 g of $[\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]]$ (0.465 mmol) in 15 mL of DME was injected 0.180 mL of Me₃SiOTf (0.930 mmol). The color of the solution rapidly changed from red to dark brown. Stirring was continued for 10 min, whereupon crystals of **2** began to form. The contents were transferred to a vial and chilled to -30 °C, which yielded 0.210 g of **2** as golden brown microcrystals (64%). FTIR (Nujol): 1500 (w), 1265 (s), 1148 (s), 1031 (m), 1020 (w), 941 (m), 899 (m), 844 (m), 721 (m), 638 (m) cm⁻¹. Anal. Calcd for C₂₁H₃₀F₃O₅P₄SSi₂V (2): C, 35.89; H, 7.17; N, 0.00; P, 17.63. Found: C, 36.05; H, 6.83; N, 0.00; P, 18.34.

[V(Me₃SiOC≡COSiMe₃)(dmpe)₂]Br (3). To a stirred solution of 0.060 g of $[\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]]$ (0.139 mmol) in 5 mL of DME was added 37 μ L of Me₃SiBr (2 equiv) by syringe, which caused a rapid color change from red to dark brown. After the mixture was stirred for 2 min, the solvent was removed and the product was extracted into 1–2 mL of pentane and cooled to -30 °C. Brown crystals of **3** (0.053 g, 60%) were collected after filtration and drying under vacuum. ¹H NMR (THF-*d*₆): δ 1.95 (8 H, br s, PCH₂), 1.35 (12 H, s, PCH₃), 1.22 (12 H, s, PCH₃), 0.20 (18 H, s, Si(CH₃)₃). ¹H NMR (C₆D₆): δ 1.92 (8 H, br s, PCH₂), 1.49 (12 H, s, PCH₃), 1.16 (12 H, s, PCH₃), 0.12 (18 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (C₆D₆): δ 31.1 (s), 20.3 (s), 18.3 (s), 2.4 (s). ³¹P{¹H} NMR (C₆D₆): δ 46 (br m, unresolved ⁵¹V coupling). FTIR (Nujol): 1631 (m), 1248 (m), 1114 (m), 993 (m), 938 (s), 855 (s), 723 (m), 694 (m), 631 (m) cm⁻¹. Anal. Calcd for C₃₀H₃₀BrO₂P₄Si₂V: C, 37.92; H, 7.96; N, 0.0; P, 19.56. Found: C, 38.28; H, 8.06; N, 0.0; P, 19.85.

[V(COSiMe₂)(CO)(dmpe)₂] (4a) and [V(COSiMe₂tBu)(CO)(dmpe)₂] (4b). To a stirred solution of $[\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]]$ in THF was added

(17) Removal of a C2 oxygenate (as a ketone) from a CO-derived enediolate has been accomplished, but with concomitant cleavage of one of the C-O bonds to form a metal oxo species (see ref 10).

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1 equiv of R_3SiCl (or R_3SiOTf). The initially red solution quickly deepened in color. After the solution was allowed to stir for at least 15 min, the solvent was removed. Extraction of the product with pentane and removal of pentane under vacuum yielded **4a** or **4b** as red viscous oils, which were clearly present as judged by 1H and $^{31}P\{^1H\}$ NMR but contained varying amounts of *trans*- $[V(CO)_2(dmpe)_2]$ as determined by FTIR spectroscopy. Data for $[V(COSiMe_3)(CO)(dmpe)_2]$ (**4a**) follow. 1H NMR (C_6D_6): δ 1.69 (6 H, br, PCH_3), 1.37 (3 H, d, $J_{HP} = 5.1$ Hz, PCH_3), 1.30 (3 H, d, $J_{HP} = 3.9$ Hz, PCH_3), 1.26 (3 H, d, $J_{HP} = 4.8$ Hz, PCH_3), 1.12 (3 H, d, $J_{HP} = 2.4$ Hz, PCH_3), 0.87 (3 H, $J_{HP} = 2.7$ Hz, PCH_3), 0.62 (3 H, d, $J_{HP} = 3.0$, PCH_3) δ 0.30 (9 H, s, $SiCH_3$), 1.5–0.97, (8 H, br, PCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65–47 (br m, two overlapping signals), 21 (br octet, $J_{VP} = 210$ Hz), 33 (br octet, $J_{VP} = 280$ Hz). FTIR (Nujol): ν_{CO} 1790 cm^{-1} . Data for $[V(COSiMe_2^iBu)(CO)(dmpe)_2]$ (**4b**) follow. 1H NMR (C_6D_6): δ 1.70 (6 H, b, PCH_3), 1.36 (3 H, d, $J_{HP} = 5.1$ Hz, PCH_3), 1.31 (3 H, d, $J_{HP} = 3.9$ Hz, PCH_3), 1.23 (3 H, d, $J_{HP} = 4.5$ Hz, PCH_3), 1.13 (3 H, d, $J_{HP} = 2.1$ Hz, PCH_3), 0.94 (9 H, s, $SiC(CH_3)_3$), 0.89 (3 H, s, PCH_3), 0.63 (3 H, d, $J_{HP} = 3.0$ Hz, PCH_3), 0.35 (6 H, s, $SiCH_3$), 1.60–0.85 (8 H, br, PCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65–47 (br m, two overlapping signals), 35 (br octet, $J_{VP} = 300$ Hz), 23 (br octet, $J_{VP} = 160$ Hz). FTIR (Nujol): ν_{CO} 1790 cm^{-1} .

$[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**). To a stirred solution of 0.110 g of $Na[V(CO)_2(dmpe)_2]$ (0.256 mmol) in 20 mL of THF was added 0.069 g of Ph_3SiCl (0.234 mmol). The red color of the solution deepened over a 45-min period. The THF was removed under vacuum and the solid extract with 20 mL of pentane to yield 0.127 g of red orange **4c** (81%). 1H NMR (C_6D_6): δ 7.97 (6 H, m), 7.22 (9 H, m), 1.52 (3 H, d, $J_{HP} = 7.2$ Hz), 1.48 (3 H, d, $J_{HP} = 6.0$ Hz), 1.25 (3 H, d, $J_{HP} = 4.8$ Hz), 1.18 (3 H, d, $J_{HP} = 3.9$ Hz), 1.13 (3 H, d, $J_{HP} = 5.4$ Hz), 1.08 (3 H, d, $J_{HP} = 3.0$ Hz), 0.82 (3 H, d, $J_{HP} = 2.7$ Hz), 0.58 (3 H, d, $J_{HP} = 3.6$ Hz), 1.42–0.81 (8 H, br). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 67–50 (br m, two overlapping signals), 43–31 (br m), 28–20 (br m). FTIR (Nujol): 1753 (s), 1428 (w), 1288 (m), 1118 (m), 1105 (w), 929 (m), 922 (m), 822 (m), 714 (m), 698 (m), 634 (w), 512 (m) cm^{-1} . Anal. Calcd for $C_{32}H_{47}O_2P_4SiV$ (**4**): C, 57.65; H, 7.11; N, 0.0. Found: C, 57.36, H, 6.69, N, 0.0.

Magnetic Susceptibility Measurements. Solid-state magnetic susceptibility measurements of **2** (73.8 mg) were made between 5 and 300 K at a field of 156 kG by using a Quantum Design SQUID magnetometer. A plot of the magnetization of the sample vs field for data taken at 5 K was found to be linear up to 20 kG. The experimental moments were corrected for the magnetism of the Kel-F sample holder, and a diamagnetic correction of $74.9 \times 10^{-6} cm^3 mol^{-1}$, calculated from Pascal's constants,²⁸ was applied. Solution-phase magnetic measurements were made on a 0.0145 M solution of **2** in THF- d_6 and Me_4Si , with use of a capillary containing THF- d_6 and Me_4Si as the internal diamagnetic standard.^{29,30}

Hydrogenation Reactions. A known amount of either complex **2** or **3** was dissolved in either C_6D_6 or THF- d_6 along with a weighed quantity of $(\eta^5-C_5H_5)_2Fe$ as an internal standard. The solution was then loaded into a test tube equipped with a magnetic stir bar, which was then enclosed in a Parr Model 4763 pressure reactor. The vessel was pressurized to 100 psig with H_2 overnight, after which time an aliquot of the solution was withdrawn for 1H NMR analysis. Yields were determined by comparison of the integral of the methyl resonance of *cis*-bis(trimethylsilyloxy)ethylene with that of the cyclopentadienyl resonance of the ferrocene internal standard. Control experiments run in the absence of ferrocene showed similar yields by GC/MS analysis.

Collection and Reduction of X-ray Data. $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2]OTf$ (**2**). Brown crystals were grown by cooling a saturated solution of **2** in THF to $-30^\circ C$. A parallelepiped of dimensions $0.1 \times 0.2 \times 0.2$ mm was mounted on the end of a quartz fiber with silicon grease on a cold stage. Unit cell parameters and intensity data were obtained by methods standard in our laboratory,³¹ details of which are provided in Table I. The crystal was judged to be acceptable based on open counter ω -scans of several low-angle reflections ($\Delta\omega_{1/2} = 0.25^\circ$) and by axial photographs. Examination on the diffractometer revealed $2/m$ Laue symmetry and systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($l \neq 2n$), consistent with the space group $P2_1/c$ (C_{2h}^2 , No. 14). An analytical absorption correction was applied to the data. No decay correction was found to be necessary.

$[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]^{1/2}DME$ ($3^{1/2}DME$). Well-formed brown rectangular blocks of $3^{1/2}DME$ were grown by cooling a DME solution of **3** to $-30^\circ C$. A crystal (dimensions $0.4 \times 0.2 \times 0.2$ mm) suitable for X-ray analysis was obtained by cutting a larger spec-

Table I. Crystallographic Information for $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2]OTf$ (**2**), $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]^{1/2}DME$ ($3^{1/2}DME$), and $[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**)^a

	2	$3^{1/2}DME$	4c
<i>a</i> (Å)	9.212 (3)	11.181 (1)	9.270 (3)
<i>b</i> (Å)	31.607 (5)	11.475 (1)	26.262 (4)
<i>c</i> (Å)	12.382 (4)	15.574 (2)	14.861 (5)
α (deg)	90	103.35 (1)	90
β (deg)	96.46 (1)	90.59 (1)	98.31 (2)
γ (deg)	90	117.81 (1)	90
<i>V</i> (Å ³)	3582 (2)	1703.3 (4)	3580 (1)
temp (°C)	-78	-78	-78
<i>fw</i>	702.7	678.6	666.6
<i>Z</i>	4	2	4
ρ_{calc} (g cm ⁻³)	1.303	1.323	1.237
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
2θ limits (deg)	$3 \leq 2\theta \leq 48$	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 46$
data limits	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
μ (cm ⁻¹)	6.06	17.18	5.02
transmission factor range	0.91–0.95	N/A	0.92–0.93
total no. of data	7361	6476	5596
no. of unique data ^b	2943	4309	2989
no. of parameters	334	298	367
<i>R</i>	0.03	0.03	0.03
<i>R</i> ^c	0.056	0.037	0.066
<i>R</i> _w	0.063	0.044	0.089

^aData were collected on an Enraf-Nonius CAD-4F κ geometry diffractometer using Mo $K\alpha$ radiation. ^bObservation criterion: $I < 3\sigma(I)$. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^{1/2}]^{1/2}$, where $w = 1/\sigma^2(F)$, $\sigma^2(F) = [S^2(C + 4B) + (pF)^2] / (Lp \times 2F)^2$, *S* = scan rate, *C* = peak count, *B* = background count, *Lp* = Lorentz-polarization factor, and *p* = fudge factor.

imen with a razor blade on a cold stage and then mounted on a quartz fiber with grease. The crystal was judged to be acceptable based on open counter ω -scans of several low-angle reflections ($\Delta\omega_{1/2} = 0.22^\circ$) and by axial photographs. No decay or absorption corrections were applied to the data.

$[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**). Red crystals were grown by cooling a concentrated pentane solution of **4c** to $-30^\circ C$. A parallelepiped of **4c** (dimensions $0.25 \times 0.15 \times 0.15$ mm) was mounted on the end of a quartz fiber and its quality examined as described above ($\Delta\omega_{1/2} = 0.27^\circ$). Examination on the diffractometer revealed $2/m$ Laue symmetry and systematic absences $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$), consistent with the space group $P2_1/n$ (C_{2h}^2 , No. 14). An analytical absorption correction was applied to the data. No decay correction was found to be necessary.

Structure Solution and Refinement. $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2]OTf$ (**2**). The vanadium atom was located by direct methods. Remaining non-hydrogen atoms were revealed by subsequent least-squares refinements and differences Fourier maps. All non-hydrogen atoms were refined anisotropically, except for C31, C41, C31*, and C41*. These four carbon atoms, which comprise the methylene linkers of one of the dmpe ligands, were found to be disordered over two orientations. A model accounting for this disorder was introduced and refined. The relative occupancies were determined to be $2/3^{1/3}$. Hydrogen atoms were placed at calculated positions in the final refinement cycles (H atoms were not generated for C31, C41, C31*, and C41*). The largest residual peak in the final difference Fourier map was $0.526 e^-/\text{Å}^3$, located near the S atom of the triflate anion. A PLUTO diagram containing the full atomic labeling scheme (Figure S1) and final tables of positional and isotropic thermal parameters, tables of anisotropic temperature factors, and a table of calculated and observed structure factors can be found in supplementary material (Tables S1–S3, respectively).

$[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]^{1/2}DME$ ($3^{1/2}DME$). The vanadium atom was located by direct methods, and the remaining non-hydrogen atoms were revealed in subsequent series of least squares refinements and difference Fourier maps. All non-hydrogen atoms were refined anisotropically. H atoms were placed at calculated positions during the final refinement cycles. Largest residual peak in the difference Fourier map was $0.878 e^-/\text{Å}^3$, located near the oxygen atom of dimethoxyethane. A PLUTO diagram containing the full atomic labeling scheme (Figure S2) and final tables of positional and isotropic thermal parameters, tables of anisotropic temperature factors, and a table of calculated and observed structure factors are provided in the supplementary material (Tables S4–S6, respectively).

$[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**). The vanadium atom position was determined by direct methods, and the remaining non-hydrogen atoms

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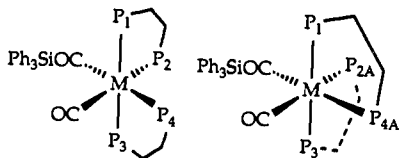
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Table II. Selected Bond Distances (Å) and Angles (deg) for $[V(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2]\text{OTf}$ (**2**) and $[V(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2\text{Br}]\cdot\frac{1}{2}\text{DME}$ (**3**) $\cdot\frac{1}{2}\text{DME}$ ^a

2				3 $\cdot\frac{1}{2}\text{DME}$			
V-P1	2.501 (2)	V-P3	2.483 (2)	V-P1	2.417 (1)	V-P3	2.407 (1)
V-P2	2.539 (2)	V-P4	2.498 (2)	V-P2	2.423 (1)	V-P4	2.416 (1)
V-C1	1.939 (7)	V-C2	1.962 (7)	V-C1	1.995 (4)	V-C2	1.988 (4)
C1-C2	1.348 (9)			C1-C1	1.295 (5)	V-Br	2.6917 (7)
C1-O1	1.366 (7)	C2-O2	1.375 (8)	C1-O1	1.379 (4)	C2-O2	1.382 (4)
Si1-O1	1.672 (5)	Si2-O2	1.663 (5)	Si1-O1	1.662 (3)	Si2-O2	1.661 (3)
P1-V-P2	78.55 (7)	P1-V-P3	91.83 (8)	P1-V-P2	80.54 (4)	P1-V-P3	96.51 (4)
P1-V-P4	163.95 (9)	P2-V-P4	91.58 (8)	P1-V-P4	167.96 (4)	P2-V-P4	99.07 (4)
P2-V-P3	111.10 (8)	P3-V-P4	79.85 (8)	P2-V-P3	164.58 (4)	P3-V-P4	80.66 (4)
P1-V-C1	103.5 (2)	P1-V-C2	98.4 (2)	P1-V-C1	104.1 (1)	P1-V-C2	87.9 (1)
P2-V-C1	156.6 (2)	P2-V-C2	116.2 (2)	P2-V-C1	116.2 (1)	P2-V-C2	79.9 (1)
P3-V-C1	92.2 (2)	P3-V-C2	132.6 (2)	P3-V-C1	79.2 (1)	P3-V-C2	115.2 (1)
				P1-V-Br	84.13 (3)	P2-V-Br	81.89 (3)
				P3-V-Br	82.76 (3)	P4-V-Br	83.90 (3)
C1-V-C2	40.4 (3)	V-C1-C2	70.7 (4)	C1-V-C2	38.0 (1)	V-C1-C2	70.7 (2)
V-C1-O1	154.0 (5)	V-C2-O2	163.2 (5)	V-C1-O1	148.9 (3)	V-C2-O2	149.0 (3)
C1-O1-Si1	127.7 (4)	C2-O2-Si2	123.0 (5)	C1-O1-Si1	135.5 (2)	C2-O2-Si2	132.7 (2)
bond type	min	max	mean	min	max	mean	
P-CH ₃	1.781 (9)	1.828 (9)	1.808	1.817 (4)	1.836 (4)	1.825	
P-CH ₂	1.828 (8)	1.91 (2)	1.861	1.848 (4)	1.856 (4)	1.852	
CH ₂ -CH ₂	1.49 (2)	1.60 (3)	1.54	1.529 (6)	1.533 (6)	1.531	
Si-CH ₃	1.83 (1)	1.856 (9)	1.844	1.845 (5)	1.856 (5)	1.851	

^aSee Figure 1 for atom-labeling scheme. Standard deviations in the last significant figure(s) are given in parentheses.

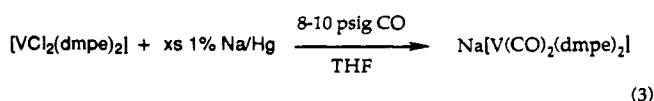
were located in subsequent series of least-squares refinements and difference Fourier maps. An interesting disorder of the dmpe ligands, corresponding to two optical isomers of the complex, was resolved and modeled. In this model, P1-P2 and P3-P4 represent two dmpe ligands at two-thirds occupancy, while the other isomer is comprised of P1-P4A and P3-P2A dmpe ligands at one-third occupancy (see diagram below).



P1 and P3 were refined at full occupancy, since these phosphorus atoms are part of both sets of dmpe ligands, while the P2/P2A and P4/P4A pairs were refined at $\frac{2}{3}$ / $\frac{1}{3}$ occupancy. All dmpe methyl and methylene carbon atoms were located and refined isotopically at either two-thirds or one-third occupancy. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions for the final refinement cycles (H atoms were not generated for dmpe methyl or methylene groups). A PLUTO diagram containing the full atomic labeling scheme (Figure S3) and final tables of positional and isotropic thermal parameters, tables of anisotropic temperature factors, and a table of calculated and observed structure factors are supplied as supplementary material (Tables S7-S9, respectively).

Results and Discussion

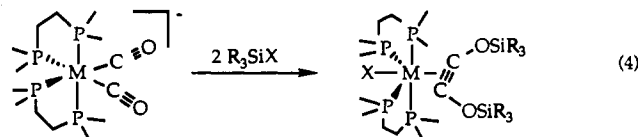
Formation of $\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]$ (1**).** In 1987 the synthesis and structural characterization of *trans*- $[\text{V}(\text{CO})_2(\text{dmpe})_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) was reported.³² Preparation of this 17-electron species was accomplished by reduction of $[\text{VCl}_2(\text{dmpe})_2]$ with excess 1% Na/Hg under 5 atm of CO. We have found that, by allowing the reaction to proceed to longer times, one can isolate the anionic vanadium complex $\text{Na}[\text{V}(\text{CO})_2(\text{dmpe})_2]$ (**1**) in good yield (eq 3). Reduction of *trans*- $[\text{V}(\text{CO})_2(\text{dmpe})_2]$ with excess 1% Na/Hg also afforded **1**.



A pair of intense CO stretching bands at 1612 and 1539 cm^{-1} in the FTIR (Nujol) spectrum of **1** is indicative of the expected³³

rearrangement to *cis* stereochemistry. The energies of these bands reflect the electron-rich character of the low-valent vanadium center. Similar low-frequency bands appear in the FTIR spectra of $\text{Na}[\text{Ta}(\text{CO})_2(\text{dmpe})_2]$ (1663 and 1561 cm^{-1} in KBr) and (*n*-hexyl)₄N $[\text{Ta}(\text{CO})_2(\text{dmpe})_2]$ (1705 and 1614 cm^{-1} in KBr), the latter having been structurally characterized by X-ray diffraction.³⁴ The ¹H and ³¹P{¹H} NMR spectra of **1** in THF-*d*₈ are also consistent with a *cis* disposition of dmpe ligands and are very similar to corresponding spectra of $\text{Na}[\text{Ta}(\text{CO})_2(\text{dmpe})_2]$ and (*n*-hexyl)₄N $[\text{Ta}(\text{CO})_2(\text{dmpe})_2]$. The large V-P coupling constant of 350 Hz in the ³¹P{¹H} spectrum of **1** is similar to that recently reported for *cis*- $\text{Na}[\text{V}(\text{N}_2)_2(\text{dmpe})_2]$ ($J_{\text{VP}} = 316 \text{ Hz}$).³⁵

Reductive Coupling of Two CO Ligands To Form $[\text{V}(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2]\text{OTf}$ (2**).** Previous mechanistic studies have shown that the first intermediate in the reductive coupling reaction (eq 1) is a highly reduced tantalum or niobium dicarbonyl anion.³⁶ Addition of 2 equiv of trialkylsilyl halide to such a species afforded the disiloxyacetylene complex, as shown in eq 4. In a



similar manner, when 2 equiv of Me_3SiOTf was added to a red DME solution of **1**, a dark brown solution was immediately generated from which golden brown crystals of **2** could be isolated. The absence of CO stretching bands in the FTIR spectrum of this complex is consistent with reductive coupling of the two carbonyl ligands. Unlike the previously investigated $[\text{M}(\text{R}_3\text{SiOC}\equiv\text{COSiR}_3)(\text{dmpe})_2\text{X}]$ (M = Ta, Nb; X = halide, OTf) species,²² however, this extremely air- and water-sensitive compound displays no resonances in its ¹H or ³¹P{¹H} NMR spectra. Such behavior suggested that the complex is paramagnetic and that perhaps the triflate counterion is not bound to the vanadium center.

X-ray analysis of a single crystal of the triflate salt of the $[\text{V}(\text{Me}_3\text{SiOC}\equiv\text{COSiMe}_3)(\text{dmpe})_2]^+$ cation revealed the structure displayed in Figure 1. Selected bond distances and angles are given in Table II. As anticipated, the triflate ion is not coord-

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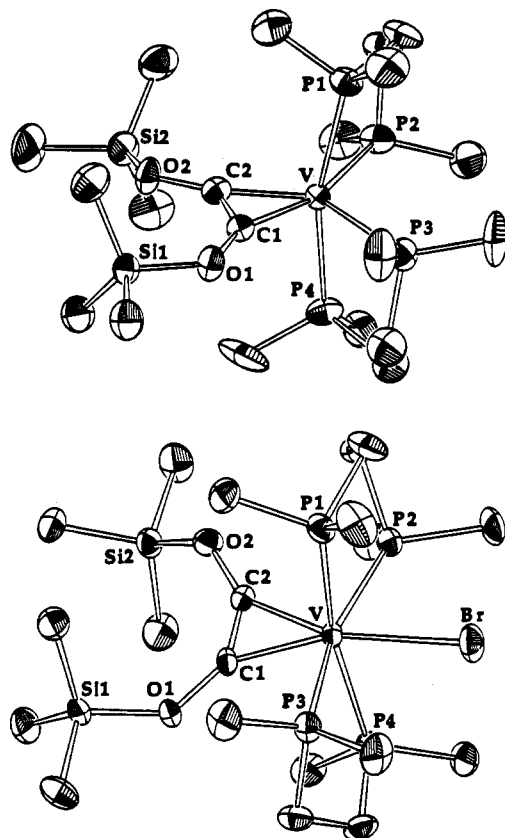


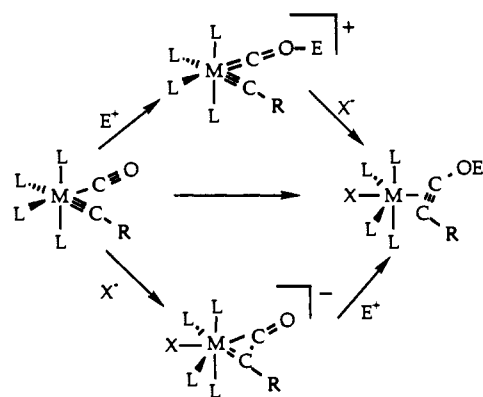
Figure 1. Structural diagrams of **2** (top) and $3 \cdot 1/2$ DME (bottom) showing the 50% probability thermal ellipsoids. The triflate counterion of **2**, the DME solvate of **3**, and the hydrogen atoms of both molecules have been omitted for clarity.

dinated. The phosphorus atoms and the midpoint of the acetylene ligand describe a distorted trigonal bipyramid, with angles of 136.3° and 112.6° between vectors connecting the vanadium atom with the midpoint of the C–C bond and either P2 or P3, respectively. The short C–C distance of 1.348 (9) is within the range for the coordinated 4-electron-donating acetylene ligands in $[M(R_3SiOC\equiv COSiR_3)(dmpe)_2X]$ ($M = Nb, Ta$) complexes reported previously.^{22,36} A comparable C–C acetylene distance occurs in $[(\eta^5-C_5H_5)V(PhC\equiv CPh)(PMe_3)_2]$, 1.328 (3) Å,³⁷ whereas a much shorter value of 1.287 (4) Å is observed for the 2-electron-donating acetylene in $[(\eta^5-C_5H_5)_2V(MeO_2CC\equiv CCO_2Me)]$.³⁸

In the solid state, **2** exhibits a magnetic moment of $2.81 \mu_B$ at 20 K, characteristic of the spin-only value for a complex having two unpaired electrons.²⁸ At higher temperatures, however, the moment decreases uniformly, reaching a value of $2.32 \mu_B$ at 300 K. A comparable value of $2.44 \mu_B$ at 294 K was also determined by an NMR measurement^{29,30} in THF- d_8 solution. We presently have no explanation for this interesting behavior, which is clearly not a solid-state phenomenon. Further work is in progress to address this question. As discussed previously,³⁶ the coupled ligand in **2** can be written either as a 4-electron-donating acetylene bonded to a V(I) center or as a (metallocyclopropene)vanadium(III) complex. In either case, the compound is expected to have two unpaired electrons.³⁹

Although the details of the critical C–C bond forming step in CO- and CNR-carbyne coupling reactions are currently unknown, nucleophilic attack by halide, acetate, or triflate to form an η^2 -ketenyl species is a distinct possibility (Scheme I, lower pathway).^{36,40} Alternatively, electrophilic attack on the CO ligand

Scheme I



could lead to a carbene-carbyne species, followed by coupling of the two carbon atoms and trapping of the acetylene complex with halide (Scheme I, upper pathway). Compound **2** is unique in demonstrating that the reductively coupled product need not have a Lewis base coordinated in the position trans to the newly created acetylene. This result alone, however, does not rule out the possibility that triflate ion coordinates to vanadium at some point during the C–C bond forming process. Kinetic measurements are planned to evaluate this possibility.

Reductive Coupling of Two CO Ligands To Form $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]$ (3**).** Addition of 2 equiv of Me_3SiBr to the red DME solution of **1** immediately caused a rapid color change to brown. Removal of the solvent and extraction into pentane followed by chilling to $-30^\circ C$ yielded **3** as a brown crystalline compound. As with complex **2**, this material displayed no CO stretches in its FTIR spectrum, but the complex has readily discernible, characteristic 1H and $^{31}P\{^1H\}$ NMR spectral features. The NMR spectra are fully consistent with the assignment as $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2Br]$ (**3**), by comparison to previously characterized $[M(Me_3SiOC\equiv COSiMe_3)(dmpe)_2X]$ ($M = Nb, Ta$) complexes.^{22,36} This new vanadium analogue could also be produced quantitatively by addition of 1.1 equiv of nBu_4NBr to a THF- d_8 solution of **2**. The molecular structure of the complex, determined in an X-ray crystallographic study, is depicted in Figure 1.

The geometry at the vanadium center in **3** is very similar to that observed for other seven-coordinate niobium and tantalum acetylene complexes prepared by reductive coupling of carbon monoxide ligands.³⁶ The presence of the bromide ligand in **3** results in a shortening of the V–P bond distances by 0.09 Å compared to the values in **2**. This bond length diminution is counterintuitive to what might be expected from raising the coordination number and is presumably the result of an increase in π -back-bonding from vanadium to phosphorus. The bromide ligand in **3** also effects a noticeable decrease of 0.05 Å in the C–C bond length of the coordinated acetylene compared to its value in **2**. This change is also manifest by the increase of 130 cm^{-1} in the ν_{CC} stretching mode in the FTIR spectrum of **2**, which occurs at 1500 cm^{-1} compared to the value of 1630 cm^{-1} in compound **3**. A slight increase of 0.04 Å in the corresponding V–C distances is also observed. The P2–V–P3 bond angle of $111.10(8)^\circ$ in **2** is increased by 53.5° to accommodate the bromide ligand in **3**, while there is little difference in the P1–V–P4 angles of the two complexes.

Vanadium Carbyne Complexes, Intermediates on the Reductive Coupling Pathway. In the generalized mechanism for the reductive coupling of two CO, two CNR, or CO/CNR ligands coordinated to group 5 or 6 transition metals, carbyne complexes have been shown to be essential intermediates.^{34,41–45} In a similar reaction,

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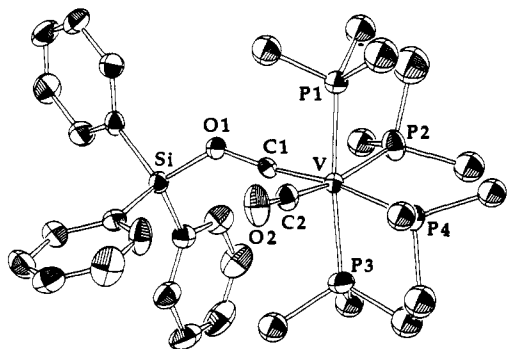
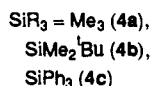
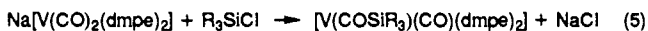


Figure 2. Structural diagram of **4c** showing the 40% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

addition of 1 equiv of R_3SiCl or R_3SiOTf to $Na[V(CO)_2(dmpe)_2]$ in THF generated the first characterized carbyne complexes of vanadium (eq 5).^{46–48} Compounds **4a** and **4b** were isolated as



red, pentane-soluble oils with characteristic 1H and $^{31}P\{^1H\}$ NMR spectral features; however, FTIR spectroscopy revealed significant quantities of the contaminating electron-transfer product, *trans*- $[V(CO)_2(dmpe)_2]$. Unfortunately, this complex could not be separated from the desired carbyne species. A crystalline vanadium carbyne analogue, $[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**), was obtained in the reaction of **1** with Ph_3SiCl , however. This compound was isolated free of contaminating *trans*- $[V(CO)_2(dmpe)_2]$, as ascertained by infrared and elemental analyses.

The 1H and $^{31}P\{^1H\}$ NMR spectra of **4a–c** indicate a static, *cis* carbonyl–carbyne structure in solution. In their infrared spectra, compounds **4a** and **4b** both display a single CO stretching band at 1790 cm^{-1} , while complex **4c** contains a single CO stretch at 1753 cm^{-1} . Comparable low ν_{CO} stretches were observed for the previously prepared $[M(COSi^iPr_3)(CO)(dmpe)_2]$ species, the CO stretches of which occur at 1781 and 1775 cm^{-1} for Nb and Ta, respectively.³⁴

The molecular structure of **4c** is shown in Figure 2. The V–C bond length to the carbyne ligand, $1.754(8)\text{ \AA}$, is the shortest discovered to date and characteristic of a vanadium–carbon triple bond. The shortest V–C distance reported previously, $1.809(3)\text{ \AA}$, occurred in $[CpV(CH^iBu)(dmpe)]$.⁴⁹ The hydrogen atom of the carbyne ligand forms a bridge to the vanadium atom in this complex, which could be described either as a vanadium(III) alkylidene or a vanadium(V) alkylidyne hydride. Longer vanadium–carbon distances of $1.849(3)$ ⁵⁰ and $2.102(3)\text{ \AA}$ ⁵¹ occur in two other vanadium carbene complexes that have been structurally characterized.

The geometry at vanadium in **4c** is approximately octahedral, with an average vanadium–phosphorus distance of 2.401 \AA . The V–P bond trans to the carbyne ligand is longer by $>0.1\text{ \AA}$ than the other three V–P bonds, reflecting the strong trans influence of the carbyne ligand. Atoms C1 and C2 of the carbyne and carbonyl ligands, respectively, are separated by a distance of 2.52

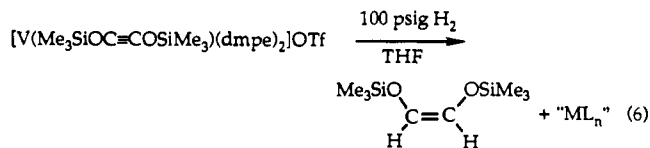
Table III. Selected Bond Distances (\AA) and Angles (deg) for $[V(COSiPh_3)(CO)(dmpe)_2]$ (**4c**)^{a,b}

V–P1	2.347 (3)	V–P2	2.394 (5)		
V–P3	2.365 (3)	V–P4	2.497 (4)		
V–C1	1.754 (8)	V–C2	1.89 (1)		
C1–O1	1.356 (9)	C2–O2	1.18 (1)		
Si–O1	1.649 (6)				
P1–V–P2	79.2 (2)	P1–V–P3	174.5 (1)	P1–V–P4	98.8 (1)
P2–V–P3	96.5 (2)	P2–V–P4	99.2 (2)	P3–V–P4	78.5 (1)
P1–V–C1	86.5 (3)	P1–V–C2	89.6 (3)	P2–V–C1	92.7 (3)
P2–V–C2	168.8 (3)	P3–V–C1	97.1 (3)	P3–V–C2	94.6 (3)
P4–V–C1	167.7 (3)	P4–V–C2	81.5 (3)	C1–V–C2	87.5 (4)
V–C1–O1	170.7 (7)	V–C2–O2	177.7 (8)	C1–O1–Si	132.4 (6)
bond type		min	max	mean	
P–CH ₃		1.80 (2)	1.92 (2)	1.86	
P–CH ₂		1.81 (2)	1.92 (2)	1.86	
CH ₂ –CH ₂		1.45 (2)	1.61 (3)	1.53	
Si–C		1.853 (9)	1.866 (9)	1.857	
C–C (aromatic)		1.35 (1)	1.42 (1)	1.38	

^aSee Figure 2 for atom-labeling scheme. Standard deviations in the last significant figure(s) are given in parentheses. ^bDistances and angles listed involving the dmpe ligands are reported for the set refined at two-thirds occupancy.

(2) \AA , indicating the lack of any incipient C–C bond formation. The V–C1–O1 angle is $170.7(7)^\circ$, nearly linear as expected for a carbyne ligand. The C1–O1–Si angle of $132.4(6)^\circ$ deviates from the expected 120° value, most likely due to the steric bulk of the $SiPh_3$ group.

Removal of the Coupled Ligand from Vanadium as *cis*-Bis(trimethylsiloxy)ethylene. Release of the newly created C–C bonded ligand in the tantalum complex $[Ta(R_3SiOC\equiv COSiR_3)(dmpe)_2X]$ ($R_3Si = Me_3Si, ^iBuMe_2Si$) could be accomplished by hydrogenation with either H_2 or H_2/CO only in the presence of $[Rh(PPh_3)_3Cl]$ or Pd/C as an external hydrogenation catalyst.²³ It was therefore of considerable interest to determine whether the 16-electron complex $[V(Me_3SiOC\equiv COSiMe_3)(dmpe)_2]OTf$ (**2**) would react with hydrogen to generate *cis*-bis(trimethylsiloxy)ethylene without the need for an external catalyst. Indeed, stirring a THF- d_8 solution of **2** at room temperature overnight in the presence of 100 psig of H_2 resulted in the formation of *cis*-bis(trimethylsiloxy)ethylene in 60% yield (eq 6). Identification of the product as *cis*-bis(trimethylsiloxy)ethylene was made by comparison of its 1H NMR and GC/MS spectra with those of an authentic sample.²⁷ No evidence was found for the presence of the *trans* isomer in the reaction mixture.



The only other product detected by 1H NMR spectroscopy in the hydrogenation reaction was $Me_3SiOSiMe_3$. Hexamethyldisiloxane could arise either by hydrolysis of the starting vanadium complex or of *cis*-bis(trimethylsiloxy)ethylene in the presence of traces of water. Addition of 1 equiv of H_2O to a solution of **2** in THF- d_8 immediately afforded hexamethyldisiloxane as well as a 4% yield of *cis*-bis(trimethylsiloxy)ethylene.^{52–55} As with the hydrogenation, no dmpe metal complexes were detected by NMR spectroscopy at the end of the reaction.²³ Reaction of **2** in THF with 3 equiv of aqueous HCl yielded $[V(CO)_2(dmpe)_2Cl]$;³² under the same conditions, $[Ta(HOC\equiv COH)(H)(dmpe)_2Cl]Cl$ forms from $[Ta(Me_3SiOC\equiv COSiMe_3)-$

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(dmpe)₂Cl].²³ *cis*-Bis(trimethylsiloxy)ethylene was also found to react with excess water in THF-*d*₈ on a much slower time scale (20 min to 24 h) to form first trimethylsilanol (by ¹H NMR and GC/MS analysis) and eventually hexamethyldisiloxane. Similar problems with hydrolysis occurred in isolating the free olefin from hydrogenation of [Ta(Me₃SiOC≡COSiMe₃)(dmpe)₂Cl], which were partly solved by use of the more sterically encumbered ¹BuMe₂Si derivative.²³

Interestingly, subjecting the electronically saturated [V-(Me₃SiOC≡COSiMe₃)(dmpe)₂Br] (**3**) complex to the same hydrogenation conditions as described above for compound **2** also gave *cis*-bis(trimethylsiloxy)ethylene, in 41% yield. No metal-dmpe-containing species was observed by NMR spectroscopy, and the other organic product was hexamethyldisiloxane. Dissociation of the bromide ligand from **3** would afford the same 16-electron species as in **2**, which could then react with dihydrogen in the absence of an external catalyst. No diminution in the yield of olefin was observed when the reaction of **3** with H₂ was run in the less polar solvent C₆D₆, rather than THF-*d*₈, in contrast to what one might expect for rate-limiting loss of bromide ion. In a separate experiment, no free olefin was detected when [Ta-(Me₃SiOC≡COSiMe₃)(dmpe)₂Cl] was subjected to the same hydrogenation conditions; only starting material was observed in the ¹H NMR spectrum. As was found with **2**, addition of 1 equiv of H₂O to **3** in THF-*d*₈ yielded predominantly hexamethyldisiloxane and a small amount (4%) of free olefin.

Summary and Prospectus. The present study has significantly extended the generality of the CO reductive coupling reaction to a first-row transition metal, vanadium. Reductive coupling of the CO ligands in Na[V(CO)₂(dmpe)₂] has afforded both the un-

precedented 16-electron, six-coordinate and the more commonly encountered 18-electron, seven-coordinate bis(trialkylsiloxy)-acetylene complexes. These acetylene complexes react directly with hydrogen at ambient temperature and modest pressures to yield *cis*-disiloxyethylene. Furthermore, we have structurally characterized the first unambiguous example of a vanadium carbyne complex. Such species are believed to be key intermediates in the formation of CO-derived acetylene complexes by reductive coupling. Current work is directed toward the incorporation of other ligands into the coordination sphere of the 16-electron acetylene complex to promote further insertion and functionalization of the original CO ligands. In this regard we have recently found that complex **2** reacts with 1 equiv of CO to yield *cis*-[V(Me₃SiOC≡COSiMe₃)(CO)(dmpe)₂]OTf.⁵⁶ We are also exploring the reactivity of Na[V(CO)₂(dmpe)₂] with carbon-centered electrophiles in attempts to generate the analogous dialkoxyacetylene complexes.

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Supplementary Material Available: PLUTO diagrams containing the complete atom-labeling schemes and tables of positional and isotropic thermal parameters and anisotropic temperature factors for **2-4c** (15 pages); tables of observed and calculated structure factors for **2-4c** (72 pages). Ordering information is given on any current masthead page.

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Crown Ether Alcohols as Bifunctional Ligands for Simultaneous Cation Complexation and Anion Solvation

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Abstract: Structural modification of crown ethers by attachment of one or more pendant hydroxyl groups offers the potential for anion solvation as well as cation complexation by the ligand. Molecular structures have been determined for LiNCS complexes of two dibenzo-14-crown-4 alcohols and a dibenzo-14-crown-4 diol as well as a LiNO₃ complex for one of the alcohols. Crystal structures for these four complexes show intracomplex "scorpion-like" and intercomplex "head-to-tail" hydrogen bonding of the crown ether hydroxyl groups with the anions. These complexes provide the first demonstration of the exploitation of structurally modified crown ethers as bifunctional ligands for simultaneous anion solvation and cation complexation.

Introduction

Cyclic polyethers (crown ethers) are selective complexing agents for alkali-metal cations.¹⁻⁴ They are utilized to extract alkali-metal cations from aqueous solutions into hydrophobic, nonpolar organic solvents⁵⁻¹⁶ and to carry these cations selectively through solvent-polymeric^{17,18} and liquid membranes.^{19,20} For such extractions and membrane processes, the identity of the anion that must be concomitantly transported into the organic medium is very important. Extraction efficiency and membrane transport rates are favorable for large and highly polarizable organic anions,

such as picrate,^{5-10,19,20} tetraphenylborate,¹¹ and dipicrylamine.¹² Large inorganic anions, such as permanganate,⁵ perchlorate,¹²

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