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# Seven-Coordinate Titanium and Vanadium Carbonyls. Synthesis and X-ray Crystal Structures of [$t$-BuSi($CH_2PMe_2$)$_3$]Ti(CO)$_4$ and [$t$-BuSi($CH_2PMe_2$)$_3$]V(CO)$_3$H

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Reductive carbonylation of the tripod phosphine complexes [$t$-BuSi($CH_2PMe_2$)$_3$]$MCl_3$(thf), where M is Ti or V and thf is tetrahydrofuran, with sodium naphthalenide in thf under carbon monoxide gives the titanium(0) carbonyl [$t$-BuSi($CH_2PMe_2$)$_3$]Ti(CO)$_4$, **1**, and the vanadium(I) hydride [$t$-BuSi($CH_2PMe_2$)$_3$]V(CO)$_3$H, **2**. X-ray crystallographic studies of these two compounds reveal seven-coordinate 4:3 piano stool geometries, with slightly different orientations of the fourfold and threefold faces; the titanium and vanadium structures may also be described in terms of a face-capped trigonal prism and a face-capped octahedron, respectively. Important structural parameters are as follows: Ti–CO = 1.98 (1), 2.00 (1) Å; Ti–P = 2.612 (3), 2.632 (5) Å; C–Ti–C(cis) = 69.8 (5), 71.7 (5)°; C–Ti–C(trans) = 109.9 (5)°; V–CO = 1.852 (9), 1.862 (7) Å; V–P = 2.440 (2), 2.470 (2) Å; C–V–C(cis) = 82.0 (3)°; C–V–C(trans) = 96.9 (3)°. The chelating nature of the phosphine ligand lends these complexes unusual kinetic and oxidative stability. Spectroscopic data for **1** and **2** are discussed: in particular, the large downfield $^{13}C$ NMR chemical shift and low CO stretching force constant in **1** indicate that there is unusually strong Ti → CO $\pi$ back-donation.

## Introduction

Although binary carbonyls of virtually all of the transition elements are known, titanium is an exception since the 18-electron species $Ti(CO)_7$ has never been described and the hexacarbonyl $Ti(CO)_6$ is only stable in a matrix below 30 K.[1] The first substituted analogues of $Ti(CO)_7$ were prepared in 1981, when Wreford described the preparation of the capped octahedral species $Ti(CO)_2(PF_3)(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[2] and subsequently of $Ti(CO)_3(dmpe)_2$, and $Ti(CO)_3(depe)_2$ (depe = 1,2-bis(diethylphosphino)ethane).[3] More recently, Ellis has prepared the anionic cyclopentadienyl analogue [$NEt_4$][CpTi(CO)$_4$], which adopts a four-leg piano stool geometry in the solid state.[4,5] These complexes are of interest as rare examples of zerovalent titanium, but most are only marginally stable at room temperature and decompose over several hours even under an inert atmosphere.

For vanadium, the 17-electron carbonyl $V(CO)_6$ is well-known,[6] but the 18-electron hydride $VH(CO)_6$ is unstable and spontaneously eliminates $H_2$ and reduces to vanadium(0).[7] Substituted analogues of $VH(CO)_6$ such as $VH(CO)_4$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) have been described,[7-14] but again the thermal stability is generally poor and reductive elimination of $H_2$ occurs readily at room temperature. We now report the preparation of some seven-coordinate titanium(0) carbonyls and vanadium(I) hydrides containing the electron-donating tripod phosphine *tert*-butyltris((dimethylphosphino)methyl)silane, $t$-BuSi($CH_2PMe_2$)$_3$, that exhibit remarkable thermal and oxidative stability.

## Results and Discussion

**Preparation of Titanium(0) and Vanadium(I) Carbonyls.** We have recently described the preparation of the chelating phosphine *tert*-butyltris((dimethylphosphino)methyl)silane, $t$-BuSi($CH_2PMe_2$)$_3$, or "trimpsi".[15] This phosphine is similar to other electron-donating tripod ligands, such as $MeC(CH_2PEt_2)_3$,[16,17] $MeC(CH_2PMe_2)_3$,[18,19] and $MeSi(CH_2PMe_2)_3$,[20] that have been investigated recently but possesses in our experience the advantage of lending its complexes improved solubility and crystallinity. Reaction of $TiCl_3(thf)_3$ or $VCl_3(thf)_3$ with trimpsi in tetrahydrofuran gives the octahedral adducts (trimpsi)$TiCl_3$(thf) and (trimpsi)$VCl_3$(thf), which have been described elsewhere.[15]

The titanium complex (trimpsi)$TiCl_3$(thf) may be reductively carbonylated with 3 equiv of sodium naphthalenide in thf under carbon monoxide to give the red, diamagnetic titanium(0) carbonyl (trimpsi)Ti(CO)$_4$, **1**. The

$$\text{(trimpsi)TiCl}_3\text{(thf)} + 3\text{NaC}_{10}\text{H}_8 + 4\text{CO} \rightarrow \underset{\mathbf{1}}{\text{(trimpsi)Ti(CO)}_4} + 3\text{NaCl} + \text{thf} + 3\text{C}_{10}\text{H}_8$$

infrared spectrum of this complex shows three bands in the carbonyl region at 1915, 1820, and 1780 cm$^{-1}$ (Figure

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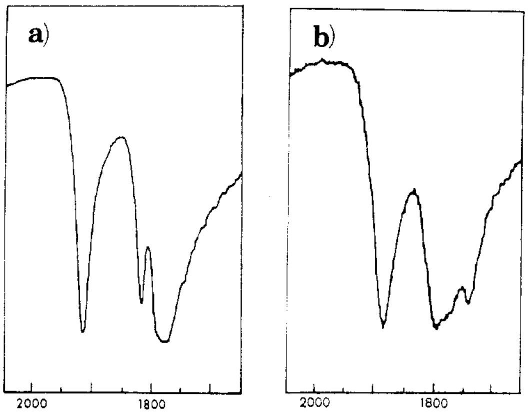

**Figure 1.** IR spectra of (a) (trimpsi)Ti(CO)$_4$ and (b) (trimpsi)V(CO)$_3$H as Nujol mulls.

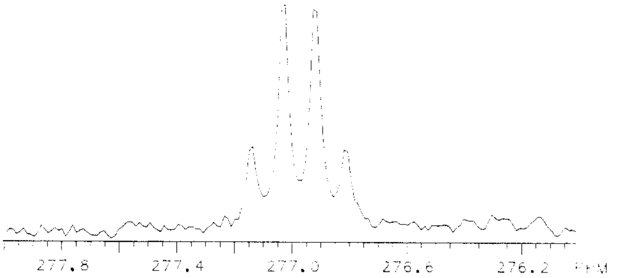

**Figure 2.** $^{13}C\{^1H\}$ NMR spectrum of $^{13}CO$-enriched (trimpsi)-Ti(CO)$_4$.

1) that are virtually identical in energy and intensity with those observed for the related titanium tetracarbonyl species [NEt$_4$][CpTi(CO)$_4$].[4] The $^{13}C$ NMR data indicate that all four carbonyl groups are equivalent down to −90 °C; the $^{13}C$ NMR chemical shift of $\delta$ 276.7 (Figure 2) is much farther downfield than commonly observed for metal carbonyls but is in fact typical of low-valent group 4 elements. For example, the $^{13}C$ chemical shifts of [NEt$_4$]-[CpTi(CO)$_4$],[4] [NEt$_4$][CpZr(CO)$_4$],[4] Ti(CO)$_3$(dmpe)$_2$,[3] and (C$_5$Me$_5$)$_2$Zr(CO)$_2$[21] are $\delta$ 289, 291, 284, and 264, respectively. The single phosphorus–carbon coupling constant of 8.2 Hz in 1 provides evidence that some fluxional process must be operating even at −90 °C; the $^1H$ and $^{31}P$ NMR data at room temperature are also consistent with a fluxional structure.

This titanium(0) complex, unlike previously known examples, is remarkably stable: it decomposes thermally under argon at ca. 190 °C and as a solid is unaffected by air for several hours.

The analogous reductive carbonylation of (trimpsi)-VCl$_3$(thf) with 4 equiv of sodium naphthalenide, followed by addition of triethylammonium chloride and crystallization from diethyl ether, gives the yellow vanadium(I) hydride (trimpsi)V(CO)$_3$H, 2. The hydride may be obtained in lower yield if NEt$_3$HCl is not added; in this case, the solvent, tetrahydrofuran, or adventitious water are the most likely sources of the hydride ligand. The infrared spectrum of 2 shows carbonyl bands at 1880 and 1785 cm$^{-1}$ and a hydride band at 1740 cm$^{-1}$ (Figure 1); the IR spectrum of the $^{13}CO$-labeled compound shows shifted bands at 1850 and 1760 cm$^{-1}$ and confirms the assignments of these peaks. The hydride signal in the $^1H$ NMR spectrum appears as a broad singlet at $\delta$ −5.59, fwhm = 105 Hz, that resolves into a quartet with $J_{PH}$ = 26 Hz upon $^{51}V$ decoupling (Figure 3). The $^{13}C$ NMR spectrum shows a 1:1:1:1:1:1:1:1 octet at $\delta$ 237.5, $J_{VC}$ = 114 Hz, while the $^{31}P\{^1H\}$ NMR spectrum consists of a similar octet with $J_{VP}$ = 180 Hz. The $^{51}V$ NMR spectrum consists of a quartet of doublets at $\delta$ −1583 with the same vanadium–phosporus coupling constant and a poorly resolved $J_{VH}$ coupling constant of ca. 12 Hz. These parameters indicate that 2 is fluxional at room temperature and match fairly closely with those reported for other vanadium hydrides: VH-(CO)$_4$(dmpe),[10] VH(CO)$_4$(dppe),[12] and VH(CO)$_3$[MeC-(CH$_2$PPh$_2$)$_3$][12] exhibit hydride $^1H$ NMR signals at $\delta$ −4.58, −5.03, and −5.06, while the $^{51}V$ NMR chemical shift of the latter compound is $\delta$ −1528. The only $^{13}C$ NMR data reported previously for vanadium carbonyls are shifts of $\delta$ 225.7, 225.3, 250.3, and 290.1 for [V(CO)$_6^-$],[22] [V(CO)$_5$-(NH$_3$)$^-$],[23] [VH(CO)$_5^{2-}$],[23] and [V(CO)$_5^{3-}$],[23] respectively.

$$(\mathrm{trimpsi})\mathrm{VCl_3(thf)} + 4\mathrm{NaC_{10}H_8} + 3\mathrm{CO} + \mathrm{NEt_3HCl} \rightarrow \underset{2}{(\mathrm{trimpsi})\mathrm{V(CO)_3H}} + 4\mathrm{NaCl} + \mathrm{thf} + 4\mathrm{C_{10}H_8} + \mathrm{NEt_3}$$

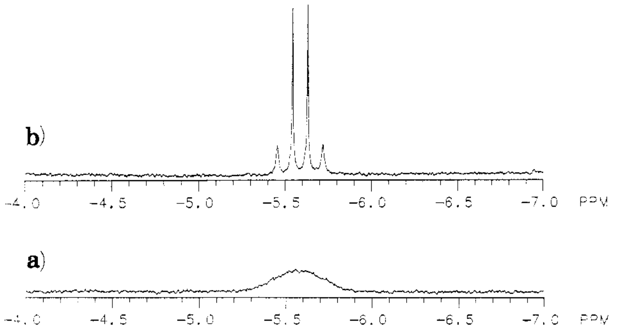

**Figure 3.** (a) $^1H$ NMR spectrum of (trimpsi)V(CO)$_3$H. (b) $^1H$ NMR spectrum of (trimpsi)V(CO)$_3$H with $^{51}V$ decoupling.

**Table I. Crystallographic Data at 25 °C for (trimpsi)Ti(CO)$_4$, 1, and (trimpsi)V(CO)$_3$H, 2**

| | 1 | 2 |
|---|---|---|
| space group | $P6_3/m$ | $Pnma$ |
| $a$, Å | 18.173 (3) | 16.486 (9) |
| $b$, Å | 18.173 (3) | 13.556 (8) |
| $c$, Å | 13.365 (5) | 10.464 (4) |
| $V$, Å$^3$ | 3822 (3) | 2338 (3) |
| $Z$ | 6 | 4 |
| mol wt | 470.36 | 446.40 |
| $d_{calcd}$, g cm$^{-3}$ | 1.226 | 1.268 |
| $\mu_{calcd}$, cm$^{-1}$ | 5.80 | 6.74 |
| size, mm | 0.1 × 0.1 × 0.6 | 0.3 × 0.4 × 0.5 |
| diffractometer | Enraf-Nonius CAD-4 | |
| radiation | Mo K$\bar{\alpha}$, $\bar{\lambda}$, = 0.71073 Å | |
| monochromator | graphite crystal, $2\theta$ = 12° | |
| scan range, type | $2.0 \leq 2\theta \leq 46.0°$, $\omega/\theta$ | |
| scan speed, width | 3–16° min$^{-1}$, $\Delta\omega$ = 1.50 (1.00 + 0.35 tan $\theta$)° | |
| reflcns, total | 5303 | 1952 |
| reflcns, unique | 1643 | 1706 |
| reflcns, $I > 2.58\sigma(I)$ | 942 | 1104 |
| variables | 140 | 134 |
| $p$ factor | 0.020 | 0.030 |
| $R_F$ | 0.067 | 0.046 |
| $R_{wF}$ | 0.080 | 0.057 |

Unlike other known phosphine-substituted analogues of VH(CO)$_6$, 2 shows no tendency to reductively eliminate dihydrogen even after prolonged periods.

**X-ray Crystallographic Results for 1 and 2.** The titanium(0) carbonyl (trimpsi)Ti(CO)$_4$, 1, crystallizes in the hexagonal space group $P6_3/m$ (see Table I), and each

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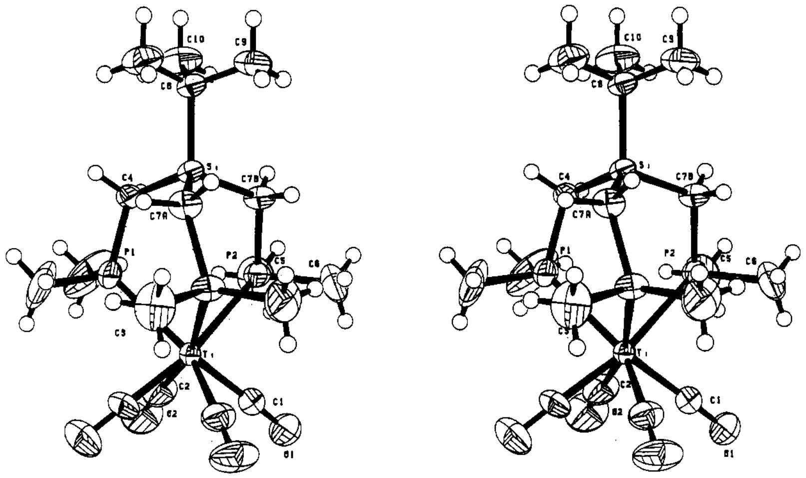

**Figure 4.** Stereoview of the molecular structure of (trimpsi)Ti(CO)$_4$.

**Table II. Atomic Coordinates for (trimpsi)Ti(CO)$_4$, 1, and (trimpsi)V(CO)$_3$H, 2**

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| | | 1 | |
| Ti | 0.1844 (1) | 0.3493 (1) | 0.25 |
| P1 | 0.0213 (3) | 0.2358 (3) | 0.25 |
| P2 | 0.1358 (2) | 0.4256 (2) | 0.1228 (2) |
| Si | −0.0272 (2) | 0.3781 (3) | 0.25 |
| O1 | 0.3463 (5) | 0.4429 (6) | 0.1114 (8) |
| O2 | 0.2038 (6) | 0.2170 (6) | 0.1140 (9) |
| C1 | 0.2866 (7) | 0.4101 (7) | 0.163 (1) |
| C2 | 0.1961 (7) | 0.2674 (7) | 0.163 (1) |
| C3 | −0.0123 (8) | 0.1642 (9) | 0.144 (1) |
| C4 | −0.0592 (10) | 0.266 (1) | 0.211 (1) |
| C5 | 0.1260 (8) | 0.3871 (8) | −0.0050 (9) |
| C6 | 0.2103 (7) | 0.5370 (6) | 0.101 (1) |
| C7A | 0.024 (1) | 0.404 (1) | 0.378 (2) |
| C7B | 0.050 (1) | 0.451 (1) | 0.159 (2) |
| C8 | −0.1235 (9) | 0.3923 (9) | 0.25 |
| C9 | −0.095 (1) | 0.486 (1) | 0.25 |
| C10 | −0.1781 (7) | 0.3511 (8) | 0.1595 (10) |
| | | 2 | |
| V | 0.24056 (7) | 0.75 | 0.2172 (1) |
| P1 | 0.2061 (1) | 0.75 | 0.4440 (2) |
| P2 | 0.3450 (1) | 0.6267 (1) | 0.2733 (2) |
| Si | 0.3900 (1) | 0.75 | 0.5142 (2) |
| O1 | 0.2686 (6) | 0.75 | −0.0668 (8) |
| O2 | 0.1280 (4) | 0.5830 (4) | 0.1373 (6) |
| C1 | 0.2614 (6) | 0.75 | 0.0433 (9) |
| C2 | 0.1715 (4) | 0.6472 (5) | 0.1713 (7) |
| C3 | 0.1440 (6) | 0.6500 (7) | 0.4969 (8) |
| C4 | 0.2850 (5) | 0.7064 (7) | 0.5647 (9) |
| C5 | 0.3085 (5) | 0.5033 (5) | 0.2998 (7) |
| C6 | 0.4205 (4) | 0.6022 (7) | 0.1550 (9) |
| C7A | 0.3857 (7) | 0.8744 (9) | 0.442 (1) |
| C7B | 0.4288 (8) | 0.661 (1) | 0.388 (1) |
| C8 | 0.4591 (4) | 0.75 | 0.6582 (7) |
| C9 | 0.5472 (5) | 0.75 | 0.6142 (8) |
| C10 | 0.4437 (4) | 0.6585 (5) | 0.7399 (6) |

**Table III. Important Bond Distances (Å) and Angles (deg) for (trimpsi)Ti(CO)$_4$, 1, and (trimpsi)V(CO)$_3$H, 2**

| 1 | | 2 | |
|---|---|---|---|
| | Bond Distances | | |
| Ti–C1 | 2.00 (1) | V–C1 | 1.852 (9) |
| Ti–C2 | 1.98 (1) | V–C2 | 1.862 (7) |
| Ti–P1 | 2.632 (5) | V–P1 | 2.440 (2) |
| Ti–P2 | 2.612 (3) | V–P2 | 2.470 (2) |
| C1–O1 | 1.16 (2) | C1–O1 | 1.16 (1) |
| C2–O2 | 1.19 (2) | C2–O2 | 1.182 (9) |
| Ti···Si | 4.132 (4) | V···Si | 3.967 (2) |
| | Bond Angles | | |
| C1–Ti–C1′ | 71.6 (5) | C1–V–C2 | 82.0 (3) |
| C2–Ti–C2′ | 71.7 (5) | | |
| C1–Ti–C2 | 69.8 (5) | | |
| C1–Ti–C2′ | 109.9 (5) | C2–V–C2′ | 96.9 (3) |
| P1–Ti–P2 | 82.5 (1) | P1–V–P2 | 86.04 (6) |
| P2–Ti–P2′ | 81.2 (1) | P2–V–P2′ | 85.13 (6) |
| C1–Ti–P1 | 143.7 (4) | C1–V–P1 | 177.2 (3) |
| C1–Ti–P2 | 78.1 (3) | C1–V–P2 | 96.0 (2) |
| C1–Ti–P2′ | 123.7 (3) | C2–V–P1 | 96.2 (2) |
| C2–Ti–P1 | 85.0 (3) | C2–V–P2 | 88.9 (2) |
| C2–Ti–P2 | 102.1 (4) | C2–V–P2′ | 173.5 (2) |
| C2–Ti–P2′ | 166.5 (4) | | |
| Ti–C1–O1 | 177.6 (9) | V–V1–O1 | 175.2 (9) |
| Ti–C2–O2 | 178 (1) | V–C2–O2 | 177.5 (6) |

molecule lies on a crystallographic mirror plane. A stereoview of the molecule is shown in Figure 4, while atomic positional parameters and selected bond lengths and angles are presented in Tables II and III. The overall geometry of 1 can be described as a 4:3 piano stool, with the carbonyl ligands and the phosphine occupying the fourfold and threefold faces, respectively. Alternatively, the coordination polyhedron can be described as a face-capped trigonal prism, with P1 capping the rectangular face formed by P2, P2′, C2, and C2′. It is of interest in this context to note that the structure of Ti(CO)$_2$(PF$_3$)(dmpe)$_2$ was described as a capped trigonal prism,[2] while Ti(CO)$_3$(dmpe)$_2$ was described as a capped octahedron.[3] As is usually the case in seven-coordination,[24] the geometric differences between the various coordination polyhedra are small, and doubtlessly the potential energy surface relating the different forms is relatively flat.

The tripod phosphine ligand exhibits a "twist" disorder, in which the PCH$_2$Si methylene carbon atoms adopt either a right- or left-handed conformation around the Ti···Si vector. The twisting of the pendant CH$_2$PMe$_2$ groups reduces the "bite" of the phosphine and optimizes bonding with the titanium center. This kind of disorder appears to be more common for trimpsi than for tripod phosphines such as MeC(CH$_2$PMe$_2$)$_3$ that have a smaller carbon atom, rather than the larger silicon, at the vertex of the tripod. This disorder is not resolvable in the PMe$_2$ methyl groups, which were successfully modeled as full-occupancy atoms with anisotropic thermal parameters and does not affect the accuracy of other aspects of the structural results.

The average Ti–C distance of 1.99 (1) Å is essentially identical with those of 1.986 (4) and 1.996 (6) Å in Ti(CO)$_3$(dmpe)$_2$[3] and [AsPh$_4$][CpTi(CO)$_4$],[4] and the carbonyl groups are essentialy linear, with Ti–C–O = 177.6 (9)° and 178 (1)°. Statistically, these Ti–C distances do not differ

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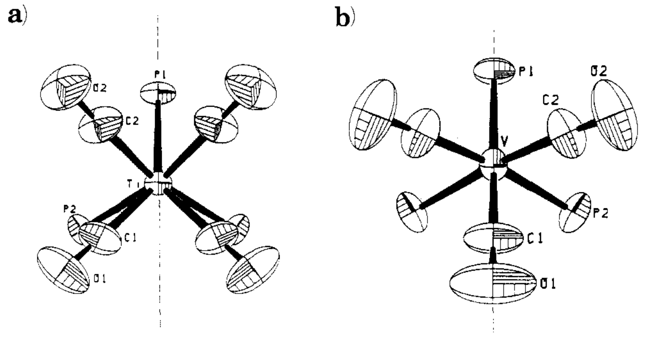

**Figure 5.** Relative orientation of the fourfold and threefold faces in (a) (trimpsi)Ti(CO)$_4$ and (b) (trimpsi)V(CO)$_3$H. Crystallographic mirror plane indicated by dashed line.

significantly from those of 2.03 (1) and 2.01 (1) Å in the titanium(II) carbonyls Cp$_2$Ti(CO)$_2$[25] and (C$_5$Me$_5$)$_2$Ti(CO)$_2$,[26] respectively, despite the lower oxidation state and larger covalent radius of titanium(0). The average Ti–P bond distance of 2.622 Å falls within the 2.545–2.633 Å range observed in Ti(CO)$_3$(dmpe)$_2$ and Ti(CO)$_2$(PF$_3$)(dmpe)$_2$; in fact all titanium–phosphine distances have been shown to fall in the range 2.58 ± 0.07 Å irrespective of oxidation state, spin state, or coordination number.[27] The P–Ti–P angles of 81.2 (1)° and 82.5 (1)° are normal for a chelating tripod phosphine.

A projection of the 4:3 piano stool geometry down the Ti···Si axis (Figure 5a) shows the relative orientation of the fourfold and threefold faces. Of the seven atoms in the inner coordination sphere, one phosphorus atom lies in the mirror plane, with the other two related by symmetry across the plane. The four carbonyl ligands are similarly arranged in mirror-related pairs. There are two different C–Ti–C angles, a "cis" angle averaging 71.0° and a "trans" angle of 109.9°.

The vanadium hydride (trimpsi)V(CO)$_3$H, **2**, crystallizes in the orthorhombic space group *Pnma* (see Table I) and also packs so that each molecule possesses crystallographically imposed mirror symmetry. A stereoview of **2** is shown in Figure 6, while atomic positional parameters and selected bond lengths and angles are presented in Tables II and III. The phosphine ligands again exhibit the "twist" disorder as found in **1**.

The overall geometry of **2** may be described as a 4:3 piano stool as observed for **1**, except that the relative orientation of the four- and threefold faces is different (Figure 5b). The fourfold face has rotated to bring one carbonyl group and the hydride (see below) into the mirror plane. Viewed down the V···Si axis, this rotation leads to staggered arrangement of the carbonyl and phosphine groups, while eclipsing the hydride and P1. The net effect of this orientation is to minimize nonbonded repulsions in the inner coordination sphere.

Given the nearly staggered arrangement of the carbonyl and phosphine groups, the geometry of **2** can perhaps be more accurately described as a capped octahedron, with the hydride ligand in the capping position. The interligand angles are most consistent with this view, with trans P–Ti–C angles of 177.2 (3)° and 173.5 (2)° within the distorted octahedron. Although the hydride ligand was not located in the electron density difference maps, it apparently caps the face defined by P1, C2, and C2′. Its position is shown by the P1–V–C2 and C2–V–C2′ angles around the capped face of 96.2 (2)° and 96.9 (3)°, which are larger than the other "cis" P–V–C and C–V–C angles of 88.9 (2)–96.0 (2)° and 82.0 (3)°, respectively.

The average V–C distance of 1.857 (8) Å in **2** is considerably shorter than that of 1.948 (9) Å in VH(CO)$_4$(dppe),[13] and this difference may be attributed to increased $\pi$ back-bonding in **2** due to the three electron-donating phosphorus substituents.[28] The average V–P distance of 2.455 Å is very similar to that of 2.466 (2) Å in VH(CO)$_4$(dppe).

**The Nature of the Titanium–Carbonyl Interaction.** The unusual downfield $^{13}$C NMR chemical shifts of $\delta$ 275–300 for titanium(0) carbonyls indicate that the Ti–CO bonding in these complexes differs quantitatively from that in most transition-metal carbonyls. Some of the first $^{13}$C NMR studies of transition-metal carbonyls demonstrated that the $^{13}$C NMR chemical shift $\delta_{CO}$ is linearly related to the infrared stretching force constant $k$; specifically, downfield $^{13}$C NMR chemical shifts are correlated with small force constants.[29-31]

An analysis of the infrared stretching frequencies in (trimpsi)Ti(CO)$_4$ can be performed by using the "local-symmetry" concept as demonstrated for CpV(CO)$_4$.[32] For local $C_{4v}$ symmetry of the carbonyl ligands, three $\nu_{CO}$ frequencies are expected: $A_1$ (IR and Raman-active), $B_1$ (Raman-active only), and $E$ (IR and Raman-active). The bands at 1915 s, 1820 w, and 1780 vs cm$^{-1}$ in (trimpsi)Ti(CO)$_4$ may be assigned to these modes, respectively, with the IR-forbidden $B_1$ mode actually appearing as a weak band presumably because the local $C_{4v}$ symmetry is broken very slightly. This relaxation in the selection rules was also observed in CpV(CO)$_4$, but given the low IR intensity of the $B_1$ mode, the force constants calculated from the approximation that the local symmetry is $C_{4v}$ are expected to be relatively accurate.[32]

The **F** and **G** matrix method yields three secular equations from which the force constants $k$, $k_s$, and $k_d$ may be calculated, where $k_s$ and $k_d$ are the interaction force constants between carbonyl groups located across the side and the diagonal of the tetracarbonyl fragment, respectively.[33] The force constants obtained for (trimpsi)Ti(CO)$_4$ by this method are quite reasonable: $k$ = 1345, $k_s$ = 36, and $k_d$ = 65 N/m; by comparison, the analogous values deduced for CpV(CO)$_4$ are $k$ = 1556, $k_s$ = 31, and $k_d$ = 48 N/m. Most terminal carbonyl groups attached to transition metals have a principal stretching force constant $k$ of 1500–1750 N/m,[34] so the value of 1345 N/m for (trimp-

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(28) The X-ray crystal structure of VH(CO)$_4$(dppe)[13] revealed that the carbonyl and phosphine ligands describe a remarkably regular octahedron, with the hydride ligand assigned an *edge*-bridging position based on the electron density difference maps. However, we feel that the reported H–V–C and H–V–P angles of 57 (4)° and 38 (5)° are too small and chemically unreasonable. The authors state that VH(CO)$_4$(dppe) readily loses H$_2$ in solution, and that the X-ray crystal used had changed color from yellow to dark brown over the 5 months that preceded data collection. We suspect that either the hydride is disordered, or the X-ray data in fact describe the structure of the 17-electron species V(CO)$_4$(dppe); if the latter, some of the differences between this structure and that of **2**, especially the interligand angles and the V–C distances, are more readily interpretable in terms of a differing oxidation state.

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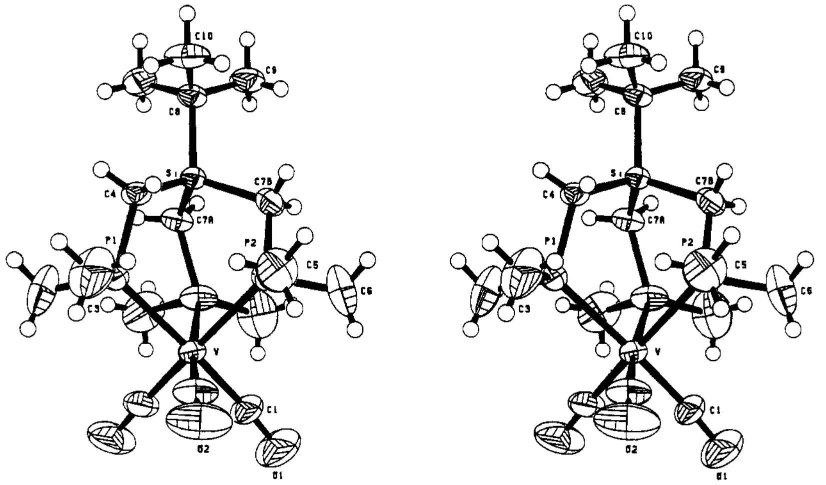

**Figure 6.** Stereoview of the molecular structure of (trimpsi)V(CO)$_3$H.

si)Ti(CO)$_4$ is indeed small, as expected from the correlation between $\delta_{CO}$ and $k$. We note here that the $\delta_{CO}$[35] and $k$[34] values for (trimpsi)Ti(CO)$_4$ are more typical of *bridging* carbonyls of the later transition elements.

Although the downfield $^{13}C$ chemical shift and the small force constant can be regarded as due to several effects, by far the most important factor is transition metal → carbonyl $\pi$ back-donation.[34,36,37] The titanium atom, with a low effective nuclear charge $Z_{eff}$ relative to later transition metals, is expected to have higher energy d orbitals which will more effectively engage in $\pi$ back-donation with the carbonyl ligands. The strongly electron-donating trimpsi ligand will also enhance this back-donation by increasing the electron density on titanium. We expect therefore that the carbonyl groups in (trimpsi)Ti(CO)$_4$ will be strongly bound but susceptible to electrophilic attack, and accordingly the reaction chemistry of this zerovalent titanium complex is under current investigation. These observations clearly demonstrate that Ti–CO bonds are *not* intrinsically weak as implied by the instability of Ti(CO)$_6$ and other titanium(0) carbonyls; in fact, carbon monoxide can be quite strongly bonded to group 4 metals given the proper ancillary ligands.[38]

## Experimental Section

All operations were conducted under vacuum or under argon. Solvents were distilled from sodium–benzophenone (diethyl ether, tetrahydrofuran) or sodium (toluene) immediately before use. The metal complex [$t$-BuSi(CH$_2$PMe$_2$)$_3$]MCl$_3$(thf), where M is Ti or V, were prepared as previously described. Sodium, naphthalene, and carbon monoxide were obtained commercially and used as received.

Microanalyses were performed by Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B instrument. The $^1$H NMR data were recorded on a Varian EM-390 instrument at 90 MHz or on a General Electric QE-300 at 300 MHz; $^{13}$C NMR data were acquired either on the latter instrument at 75.44 MHz or on a Nicolet NT-360 at 90.55 MHz. The $^{31}$P and $^{51}$V NMR data were recorded on a locally constructed instrument at 101.26 and 65.69 MHz. The $^1$H{$^{51}$V} NMR spectrum was recorded on a General Electric GN-300 instrument. Chemical shifts are reported in $\delta$ units (positive chemical shifts to higher frequency) relative to tetramethylsilane (TMS), H$_3$PO$_4$, or VOCl$_3$. Melting points were determined on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

**[*tert*-Butyltris((dimethylphosphino)methyl)silane]tetracarbonyltitanium(0).** To [$t$-BuSi(CH$_2$PMe$_2$)$_3$]TiCl$_3$(thf) (0.54 g, 1.00 mmol) in thf (25 mL) at −78 °C was added a solution of sodium naphthalenide (30 mL × 0.1 M, 3.00 mmol) in a Fischer–Porter bottle. The bottle was pressurized to 5 atm with carbon monoxide, and the solution was allowed to warm to room temperature. (Note: 5 atm is a convenient CO pressure for us, but the preparation may be conducted under 1 atm of CO with no appreciable decrease in yield.) After the solution was stirred for 6 h, the pressure bottle was vented, the red-brown solution was filtered and evaporated to dryness, and the excess naphthalene was removed by sublimation at 25 °C. The residue was extracted with toluene (3 × 50 mL), and the filtered extracts were combined, concentrated to ca. 25 mL, and cooled to −20 °C to give red prisms of the complex (the $^{13}$CO-labeled compound was prepared similarly under 1 atm of $^{13}$CO): yield 0.10 g (21%); mp 190 °C dec. IR (Nujol, cm$^{-1}$): 1915 s, 1820 w, 1780 vs br. IR (Nujol, cm$^{-1}$, $^{13}$CO labeled): 1880 s, 1782 w, 1745 vs. $^1$H NMR (C$_6$D$_6$, 25 °C): $\delta$ 1.02 (s, P*Me*$_2$), 0.53 (s, *t-Bu*Si), 0.01 ("q", "$J_{PH}$" = 2.8 Hz, Si*CH*$_2$P). $^{13}$C NMR (C$_7$D$_8$, −90 °C): $\delta$ 276.7 (q, $J_{PC}$ = 8.2 Hz, TiCO). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 25 °C, $^{13}$CO labeled): $\delta$ −10.8 (quintet, $J_{PC}$ = 8.2 Hz). Anal. Calcd for C$_{17}$H$_{33}$O$_4$P$_3$SiTi: C, 43.4; H, 7.07; Ti, 10.2. Found: C, 42.8; H, 7.54; Ti, 10.7.

**[*tert*-Butyltris((dimethylphosphino)methyl)silane]tricarbonylhydridovanadium(I).** To a solution of [$t$-BuSi(CH$_2$PMe$_2$)$_3$]VCl$_3$(thf) (0.54 g, 1.00 mmol) in thf (25 mL) at −78 °C was added sodium naphthalenide (40 mL × 0.10 M, 4.00 mmol) in a Fischer–Porter bottle. The bottle was pressurized to 5 atm with carbon monoxide, and the solution was allowed to warm to room temperature. (Note: as above, the preparation may be conducted under 1 atm of CO with no appreciable decrease in yield.) After the solution was stirred for 24 h, the pressure bottle was vented, triethylammonium chloride (0.14 g, 1.00 mmol) was added to the solution as a slurry in thf (5 mL), and stirring was continued for 6 h. The yellow-brown solution was filtered and evaporated to dryness. The excess naphthalene was removed by sublimation at 25 °C, and the residue was extracted with diethyl ether (3 × 25 mL). The solution was filtered, concentrated to ca. 25 mL, and cooled to −20 °C to give yellow crystals of the complex (the $^{13}$CO-labeled analogue was prepared similarly under 1 atm of $^{13}$CO): yield 0.25 g (56%); mp 244 °C dec. IR (Nujol, cm$^{-1}$): 1880s, 1785 vs br, 1740 m. IR (Nujol, cm$^{-1}$, $^{13}$CO labeled): 1850 vs, 1760 vs br. $^1$H NMR (C$_6$D$_6$, 25 °C): $\delta$ 1.17 (s, P*Me*$_2$), 0.58 (s, *t-Bu*Si), 0.12 (s, Si*CH*$_2$P), −5.59 (s, fwhm = 105 Hz, V*H*). $^1$H{$^{51}$V} NMR (C$_6$D$_6$, 25 °C): $\delta$ −5.59 (q, $J_{PH}$ = 26.5 Hz, V*H*). $^{13}$C NMR (C$_6$D$_6$, 25 °C): $\delta$ 237.5 (octet, $J_{VC}$ = 114 Hz, VCO). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 25 °C): $\delta$ 3.8 (octet, $J_{VP}$ = 180 Hz). $^{51}$V NMR (C$_6$D$_6$, 25 °C): $\delta$ −1583 (qd, $J_{VP}$ = 180 Hz, $J_{VH}$ = 12 Hz). $^{51}$V{$^1$H} NMR (C$_6$D$_6$, 25 °C, $^{13}$CO labeled): $\delta$−1583 (qq, $J_{VP}$ = 180 Hz, $J_{VC}$ = 114 Hz). Anal. Calcd for C$_{16}$H$_{34}$O$_3$P$_3$SiV: C, 43.1; H, 7.68; V,

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(38) We have learned that Prof. John Ellis and his research group at the University of Minnesota have prepared the tripod titanium carbonyl Ti(CO)$_4$[MeC(CH$_2$PMe$_2$)$_3$] by phosphine exchange from Ti(CO)$_5$(dmpe), and that it also exhibits remarkable thermal stability: Chi, K. M.; Frerichs, S. R.; Stein, B. K.; Blackburn, D. W.; Ellis, J. E. submitted for publication in *J. Am. Chem. Soc.*

11.4. Found: C, 43.5; H, 7.26; V, 10.0.

**Crystallographic Studies.** Single crystals of the titanium carbonyl (trimpsi)Ti(CO)$_4$ [or (trimpsi)V(CO)$_3$H; parameters listed in brackets from here on refer to this compound], grown from hot toluene, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 25 reflections, yielded the cell dimensions given in Table I.

Data were collected in one quadrant [octant] of reciprocal space $(\pm h,+k,+l)$ [$(+h,-k,+l)$] by using measurement parameters listed in Table I. Systematic absences for $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$ [$0kl$, $k + l \neq 2n$, and $hk0$, $h \neq 2$], were consistent with space groups $P6_3/m$ and $P6_3$ [$Pnma$ and $Pn2_1a$]. The centric space group was investigated initially, and this choice was subsequently confirmed after successful refinement and convergence of the centric model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. Absorption corrections were applied, the maximum and minimum transmission factors being 0.948 and 0.909 [0.836 and 0.790], respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged ($R_i = 0.028$) to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods using SHELX-86; correct positions for the titanium [vanadium], phosphorus, and silicon atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations revealed positions for the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where $w = 5.66/(\sigma(F_o)^2 + (pF_o)^2)$ [$w = 1.00/(\sigma(F_o)^2 + (pF_o)^2)$]. The analytical approximations to the scattering factors were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. Carbon atoms C4 and C7 were disordered across the mirror plane, and each was successfully modeled as two half-atoms. Due to the paucity of data, hydrogen atoms were included as fixed contributors in "idealized" positions (for methyl hydrogens, staggered with respect to the attached sp$^3$ Si or P atom) with C–H = 0.96 Å. In the final cycle of least squares, anisotropic thermal coefficients were refined for non-hydrogen atoms and a group isotropic thermal parameter was varied for the hydrogen atoms. [No evidence of the hydride attached to the vanadium atom was seen in the final difference maps.] Successful convergence was indicated by the maximum shift/error of 0.04[0.006] for the last cycle. Final refinement parameters are given in Table I. The final difference Fourier map had no significant features, and there were no apparent systematic errors among the final observed and calculated structure factors.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program for support of this research. We particularly wish to thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determinations and Prof. John Ellis of the University of Minnesota for communicating their results in ref 38 prior to publication.

**Registry No.** 1, 110512-29-3; 2, 110512-30-6; 3, 110512-31-7; [$t$-BuSi(CH$_2$PMe$_2$)$_3$]VCl$_3$, 110512-32-8.

**Supplementary Material Available:** Tables of hydrogen atom positions (S1) and anisotropic thermal parameters (S2) for (trimpsi)Ti(CO)$_4$ and (trimpsi)V(CO)$_3$H (2 pages); listings of final observed and calculated structure factors for (trimpsi)Ti(CO)$_4$ (S3) and (trimpsi)V(CO)$_3$H (S4) (9 pages). Ordering information is given on any current masthead page.

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# Cationic Alkylbis(cyclopentadienyl)titanium Complexes. Synthesis, Reactions with CO and *t*-BuNC, and the Structure of [Cp$_2$Ti{$\eta^2$-C(Me)N-*t*-Bu}(CN-*t*-Bu)]BPh$_4$·MeCN

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Cationic methylbis(cyclopentadienyl)titanium complexes [Cp$_2$TiMe(L)]BPh$_4$ (L = MeCN, *n*-PrCN, *t*-BuCN, PhCN, PMe$_3$, PMe$_2$Ph, PMePh$_2$, *n*-Bu$_3$P, pyridine) have been synthesized in high yields by reaction of Cp$_2$TiMeCl with L and sodium tetraphenylborate in polar solvents. A range of bis(indenyl)titanium complexes is similarly accessible. The complex [Cp$_2$TiMe(NCMe)]BPh$_4$ reacts with carbon monoxide to give [Cp$_2$Ti($\eta^2$-COMe)(NCMe)]BPh$_4$ in which the nitrile ligand is retained, while *tert*-butyl isocyanide displaces acetonitrile and inserts into the titanium–methyl bond to give [Cp$_2$Ti{C(N-*t*-Bu)Me}(CN-*t*-Bu)]BPh$_4$·MeCN (**18**) whose crystal structure was determined. The complex crystallizes in space group $P2_1/c$, $a = 13.212$ (10) Å, $b = 9.354$ (2) Å, $c = 33.951$ (4) Å, $\beta = 91.87$ (4)°, $V = 4193.3$ Å$^3$, $Z = 4$, and $D_{\text{calcd}} = 1.14$ g cm$^{-3}$. The iminoacyl ligand in **18** is $\eta^2$-coordinated, with Ti—C and Ti—N distances of 2.08 and 2.12 Å and a short C═N bond (1.24 Å).

## Introduction

Although the polymerization of olefins in the homogeneous phase by catalysts based on bis(cyclopentadienyl)titanium dihalide/aluminum alkyl halide systems has been known for over 30 years, the mechanism of this reaction has continued to attract attention.[1-5] An early suggestion by Breslow et al.[6] involved the intermediacy of electron-

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