Vanadium(II) alkyls. Synthesis and X-ray crystal structures of *trans*-VMe$_2$(dmpe)$_2$ and *cis*-V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$

Robert J. Morris, Scott R. Wilson and Gregory S. Girolami

School of Chemical Sciences University of Illinois at Urbana-Champaign 505 South Mathews Avenue Urbana, IL 61801 (USA)

(Received April 8, 1993; in final form January 13, 1994)

Abstract

Treatment of the vanadium(II) tetrahydroborate complex *trans*-V(η^1-BH$_4$)$_2$(dmpe)$_2$ with (trimethylsilyl)methyllithium gives the new vanadium(II) alkyl *cis*-V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$, where dmpe is the chelating diphosphine 1,2-bis(dimethylphosphino)ethane. Interestingly, this complex could not be prepared from the chloride starting material VCl$_2$(dmpe)$_2$. The CH$_2$SiMe$_3$ complex has a magnetic moment of 3.8 μ_B, and has been characterized by ^{1}H NMR and EPR spectroscopy. The *cis* geometry of the CH$_2$SiMe$_3$ complex is somewhat unexpected, but in fact the structure can be rationalized on steric grounds. The X-ray crystal structure of *cis*-V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$ is described along with that of the related vanadium(II) alkyl complex *trans*-VMe$_2$(dmpe)$_2$. Comparisons of the bond distances and angles for VMe$_2$(dmpe)$_2$, V–C = 2.310(5) Å, V–P = 2.455(5) Å, and P–V–P = 83.5(2)° with those of V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$, V–C = 2.253(3) Å, V–P = 2.551(1) Å, and P–V–P = 79.37(3)° show differences due to the differing *trans* influences of alkyl and phosphine ligands, and due to steric crowding in latter molecule. The V–P bond distances also suggest that metal–phosphorus π-back bonding is important in these early transition metal systems. Crystal data for VMe$_2$(dmpe)$_2$ at 25°C: space group $P2_1/n$, with a = 9.041(1) Å, b = 12.815(2) Å, c = 9.905(2) Å, β = 93.20(1)°, V = 1145.8(5) Å^3, Z = 2, R_F = 0.106, and R_{wF} = 0.127 for 74 variables and 728 data for which $I > 2.58 \, \sigma(I)$; crystal data for V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$ at −75°C: space group $C2/c$, with a = 9.652(4) Å, b = 17.958(5) Å, c = 18.524(4) Å, β = 102.07(3)°, V = 3140(3) Å^3, Z = 4, R_F = 0.033, and R_{wF} = 0.032 for 231 variables and 1946 data for which $I > 2.58 \, \sigma(I)$.

Key words: Vanadium; Alkyls; Phosphine; Electron spin resonance; X-ray diffraction; Catalysis

1. Introduction

The chemistry of vanadium is of interest in many respects: for example, vanadium is an important constituent in certain Ziegler-Natta catalysts for the polymerization of alkenes [1–3], in catalysts for the selective oxidation of hydrocarbons [4–7], and in nitrogen-fixing systems including certain nitrogenase enzymes [2,8–16]. Much of the inorganic chemistry of vanadium has centered on the higher oxidation states, V^{III}, V^{IV}, and V^V [17]. In contrast, the chemistry of vanadium in its lower oxidation states has been much less intensively investigated, and in particular, the number of V^{II} coordination compounds is rather small [18–30].

With the exception of vanadocene and its derivatives, organovanadium(II) compounds are also quite rare. The first well-characterized vanadium(II) alkyl, VMe$_2$(dmpe)$_2$, was obtained via addition of methyllithium to the 1,2-bis(dimethylphosphino)ethane (dmpe) complex VCl$_2$(dmpe)$_2$ [18]. Since then, only two other σ-alkyls of V^{II} have been prepared: Teuben has reported that CpVCl(dmpe) can be treated with alkyllithium reagents to give CpVMe(dmpe) and CpV(n-Pr)(dmpe) [31,32]. There is one earlier report of a vanadium(II) alkyl: treatment of VCl$_3$(thf)$_3$ with 4 equiv of benzyllithium has been reported to give the peralkyl vanadate [Li(thf)]$_2$[V(CH$_2$Ph)$_4$] [33], although no spectroscopic or crystallographic data were obtained to support this formulation. The stoichiometry of this product must be viewed with caution, however; for example, several divalent aryl complexes originally thought to possess the stoichiometries Li$_2$[MAr$_4$] [34] and Li$_4$[MAr$_6$] (where M is V, Nb, or Ta) [34–37] have more recently been reformulated as benzyne complexes [38].

Correspondence to: Prof. G.S. Girolami.

We now describe the synthesis and characterization of the new divalent vanadium alkyl species cis-$V(CH_2SiMe_3)_2(dmpe)_2$, and report details of its crystal structure along with that of $trans$-$VMe_2(dmpe)_2$.

2. Results and discussion

2.1. Synthesis of vanadium (II) alkyls

Although treatment of $trans$-$VCl_2(dmpe)_2$ with 2 equiv of methyllithium gives the red-orange vanadium(II) alkyl $trans$-$VMe_2(dmpe)_2$ (1) [18] our attempts to prepare other vanadium(II) alkyls from $VCl_2(dmpe)_2$ have largely been disappointing. This situation resembles our experience with the titanium complex $TiCl_2(dmpe)_2$, which could not be alkylated to give halide-free products under any conditions [18,39]. Instead, we found that a much better starting material for the syntheses of titanium(II) alkyls was the tetrahydroborate complex $Ti(BH_4)_2(dmpe)_2$: the BH_4^- ligands in this complex can be cleanly replaced by addition of two equivalents of an alkyllithium reagent [39].

Accordingly, we have investigated whether the vanadium(II) tetrahydroborate complex $trans$-$V(\eta^1$-$BH_4)_2$-$(dmpe)_2$ [19] likewise serves as a better starting material than $VCl_2(dmpe)_2$ for the synthesis of vanadium(II) alkyls. Encouragingly, treatment of $V(BH_4)_2(dmpe)_2$ with methyllithium results in the clean replacement of the two unidentate BH_4^- groups to give the known complex $trans$-$VMe_2(dmpe)_2$ (1) in yields that are comparable to those obtained from $VCl_2(dmpe)_2$.

$$V(BH_4)_2(dmpe)_2 + 2 \text{ LiMe} \longrightarrow$$
$$trans\text{-}VMe_2(dmpe)_2 + 2 \text{ LiBH}_4$$

1
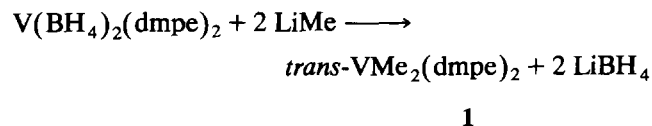
More interestingly, however, this starting material also provides an entry into the synthesis of new vanadium(II) alkyls. Interaction of $V(BH_4)_2(dmpe)_2$ with 2 equiv of (trimethylsilyl)methyllithium in diethyl ether at $-78°C$ leads to the green vanadium(II) alkyl cis-$V(CH_2SiMe_3)_2(dmpe)_2$ (2) in good yield. Although $VCl_2(dmpe)_2$ reacts with $LiCH_2SiMe_3$, the solutions obtained were red-brown instead of green, and no crystals of 2 could be obtained. It is not entirely clear why $V(BH_4)_2(dmpe)_2$ is a better starting material; the fact that the BH_4^- groups in this compound are unidentate [19] (and thus presumably weakly-bound) does not necessarily explain the synthetic superiority of BH_4^- as a leaving group in these alkylation reactions

$$V(BH_4)_2(dmpe)_2 + 2 \text{ LiCH}_2SiMe_3 \longrightarrow$$
$$cis\text{-}V(CH_2SiMe_3)_2(dmpe)_2 + 2 \text{ LiBH}_4$$

2
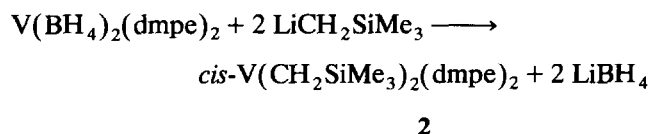
The ^1H NMR spectrum of 2 contains only one readily observable resonance, a broad peak at $\delta - 0.80$ (fwhm = 700 Hz), which is probably assignable to the methyl groups of the (trimethylsilyl)methyl ligands. This assignment is reasonable since in other vanadium(II) dmpe compounds such as $VCl_2(dmpe)_2$ [18] and $VMe_2(dmpe)_2$ [18] the dmpe resonances are shifted several tens of ppm from their diamagnetic positions. In the present case, the dmpe resonances are made more difficult to observe because they are split into several smaller components as a consequence of the low symmetry of 2.

The room temperature solution magnetic moment of this 15-electron species is 3.8 μ_B, which corresponds to three unpaired electrons. This conclusion is sup-
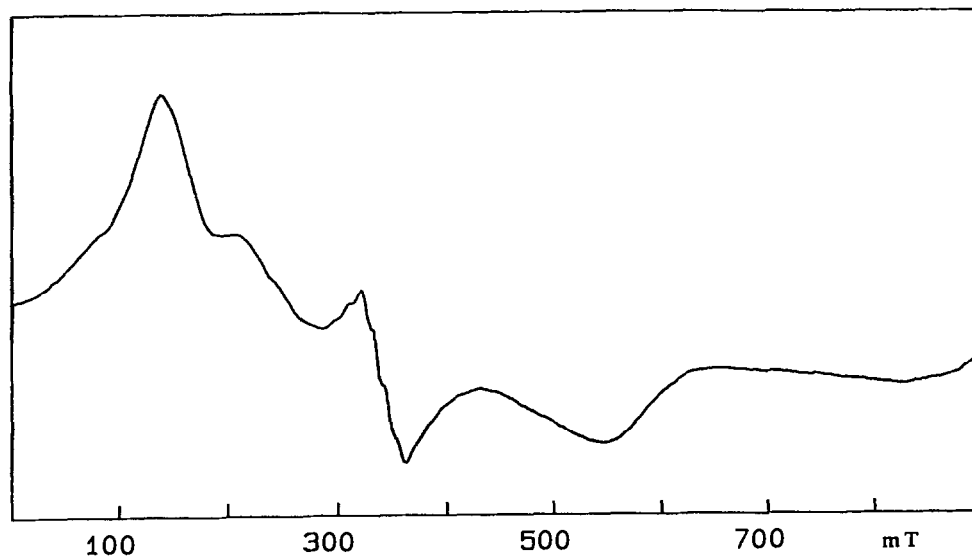

Fig. 1. X-band EPR spectrum of $V(CH_2SiMe_3)_2(dmpe)_2$ (2) in a frozen toluene glass at 110 K.

ported by the details of the EPR spectrum of **2**, which was measured in a toluene glass at liquid nitrogen temperature (Fig. 1). The spectrum contains a strong signal at *ca.* 140 mT and other features that are consistent with a rhombically distorted species with three unpaired electrons. The presence of hyperfine structure due to the I = 7/2 vanadium nucleus could be detected on the feature near 320m T (A_v = 0.064 cm^{-1}). The overall appearance of the spectrum is similar to those reported for the rhombically distorted S = 3/2 species *trans*-VCl$_2$(dmpe)$_2$ and *trans*-VMe$_2$(dmpe)$_2$ [18]. Note that EPR spectroscopy is not particularly effective in distinguishing *cis* and *trans* isomers when both are rhombically distorted. In the present case, both *cis*- and *trans*-VX$_2$(dmpe)$_2$ species are rhombically distorted with symmetry parameters (λ) near 0.1. Solutions of *cis*-V(CH$_2$SiMe$_3$)$_2$-(dmpe)$_2$ are green, and thus isomerization of this species to a *trans* geometry in solution appears unlikely.

2.2. Crystallographic studies

Single crystals of *trans*-VMe$_2$(dmpe)$_2$ (**1**) and *cis*-V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$ (**2**) were grown by cooling saturated pentane solutions to −20°C. Compound **1** almost invariably crystallizes as thin flakes and on only one occasion were we able to obtain crystals suitable for

examination by X-ray crystallography. These crystals were generated according to the original recipe from VCl$_2$(dmpe)$_2$ [18]; to date, we have been unable to isolate single crystals of **1** via alkylation of V(BH$_4$)$_2$-(dmpe)$_2$. Crystals of **1** undergo a phase transition below room temperature that results in loss of crystallinity; as a result, the diffraction data were collected at 25°C.

The structural analyses show that crystals of **1** and **2** are composed of discrete monomers of *trans*-VMe$_2$-(dmpe)$_2$ and *cis*-V(CH$_2$SiMe$_3$)$_2$(dmpe)$_2$, respectively; views of these molecules are presented in Figs. 2 and 3. Molecules of **1** lie on centers of symmetry, while molecules of **2** lie on crystallographic C$_2$ axes that bisect the C(7)–V–C(7)′ angle. Crystal data are collected in Table 1 atomic coordinates for **1** and **2** are listed in Tables 2 and 3, and bond distances and angles for **1** and **2** are presented with estimated standard deviations in Tables 4 and 5. The molecular structures of **1** and **2** will be described in turn.

2.2.1. trans-VMe$_2$(dmpe)$_2$

In **1**, the vanadium center adopts a nearly ideal *trans*-octahedral geometry with the methyl groups in the axial positions and the dmpe ligands occupying the equatorial plane. The backbone carbon atoms of the dmpe ligands appear to be disordered in an unusual

TABLE 1. Crystal data for VMe$_2$(dmpe)$_2$ (**1**) and V(CH$_2$SiMe$_3$)$_2$(dmpe) (**2**)

	1	2
T, °C	25	−75
space gp	P2$_1$/n	C2/c
a, Å	9.041(1)	9.652(4)
b, Å	12.815(2)	17.958(5)
c, Å	9.905(2)	18.524(4)
β, °	93.20(1)	102.07(3)
V, Å^3	1145.8(5)	3140(3)
Z	2	4
d_{calcd}, g cm^{-3}	1.105	1.112
μ_{calcd}, cm^{-1}	6.85	5.87
size, mm	0.2 × 0.3 × 0.4	0.2 × 0.3 × 0.5
diffractometer	Enraf-Nonius CAD4	
radiation	Mo Kα, λ = 0.71073 Å	
monochromator	graphite crystal, 2θ = 12°	
scan range, type	2.0 ≤ 2θ ≤ 50°, ω/θ	
scan speed, width	2–16° min^{-1}, Δω = 1.50 (1.00 + 0.35 tan θ)°	
reflcns, total	2046	3118
reflcns, unique	1797	2762
reflcns, $I > 2.58\sigma(I)$	728	1946
R_i	0.020	0.018
R_F	0.106	0.033
R_{wF}	0.127	0.032
variables	74	231
p-factor	0.020	0.010
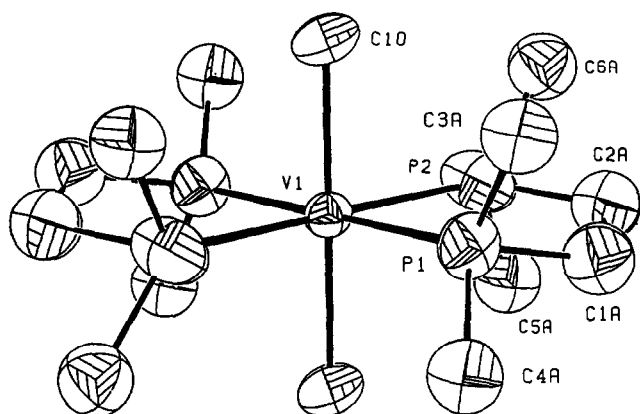
Fig. 2. Molecular structure of $VMe_2(dmpe)_2$ (1). The 35% probability density surfaces are shown.

TABLE 2. Atomic Coordinates for $trans$-$VMe_2(dmpe)_2$ (1)

	x	y	z
V(1)	0.0	0.0	0.0
P(1)	−0.1336(6)	0.1307(4)	0.1286(6)
P(2)	0.1413(8)	−0.0254(5)	0.2155(7)
C(1A)	−0.084(5)	0.106(4)	0.312(2)
C(2A)	0.063(5)	0.056(3)	0.352(3)
C(3A)	−0.086(5)	0.273(1)	0.129(5)
C(4A)	−0.341(1)	0.132(3)	0.120(5)
C(5A)	0.103(6)	−0.148(4)	0.311(8)
C(6A)	0.325(3)	0.024(4)	0.287(5)
C(1B)	−0.022(5)	0.172(4)	0.285(3)
C(2B)	0.093(5)	0.090(3)	0.321(4)
C(3B)	−0.282(4)	0.088(3)	0.241(4)
C(4B)	−0.143(5)	0.269(2)	0.067(5)
C(5B)	0.142(6)	−0.153(3)	0.308(8)
C(6B)	0.345(2)	0.004(4)	0.231(5)
C(10)	0.172(2)	0.125(1)	−0.053(2)

fashion. The model that gives the lower R factors is one in which the carbon atoms are disordered in a parallel fashion rather than the more common crossed pattern (see below). These two patterns predict different locations for the carbon atoms, and thus they should be distinguishable crystallographically (even if the partial occupancies of the carbon atom positions are near 50% as in the present case).
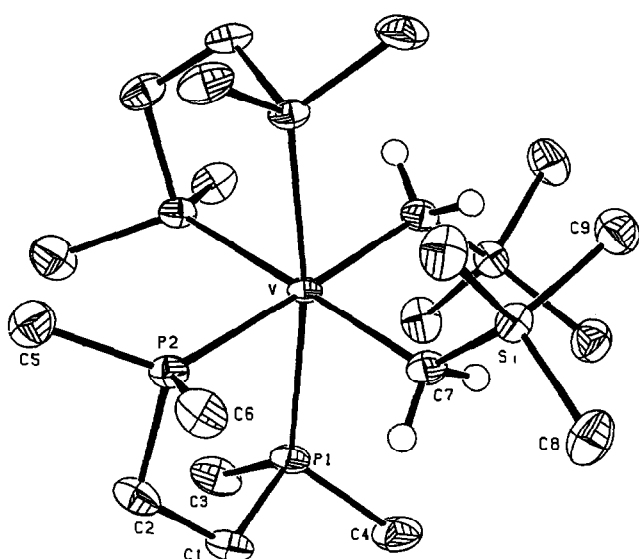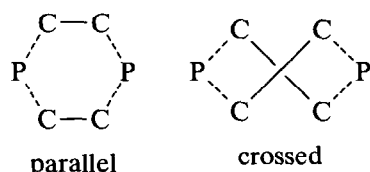

parallel   crossed

Fig. 3. Molecular structure of $V(CH_2SiMe_3)_2(dmpe)_2$ (2). The 35% probability density surfaces are shown.

However, the conclusion that the parallel pattern represents the actual situation is only tentative, since the disordered model could only be refined successfully with constrained P–C and C–C distances.

Although the disorder of the dmpe backbone carbon atoms prevents a detailed discussion of their associated distances and angles, the internal core of atoms surrounding the vanadium center is static. The P(1)–V–P(2) bite angle described by the chelating dmpe ligands of 83.5(2)° is slightly outside the 78.6(2)–81.4(2)° range found in other structurally characterized vanadium dmpe complexes [18,19,41,42]. The P–V–C angles, which range from 88.0(5) to 92.0(5)°, describe a fairly ideal octahedron. The V–C distance of 2.310(5) Å is considerably longer than that of 2.219(3) Å in CpVMe(dmpe) [31,32]. This lengthening is best attributed to the trans influence of the two mutually $trans$ methyl groups in 1. [40*] The average V–P distance of 2.455(6) Å is somewhat shorter than the average V–P distance of 2.499(5) Å in $VCl_2(dmpe)_2$ [18]. Of the early first-row transition metal complexes with the stoichiometry $MX_2(dmpe)_2$ (M = Ti, V, Cr, and Mn, and X = Cl or Me), the present $VMe_2(dmpe)_2$ complex is the last to be structurally characterized. Table 6 presents some relevant bond distances for these divalent compounds.

2.2.2. cis-$V(CH_2SiMe_3)_2(dmpe)_2$

In 2, the vanadium center adopts a distorted cis-octahedral geometry. The P(1)–V–P(2) angle of 79.37(3)° described by the dmpe ligands in 2 is somewhat smaller

* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Atomic Coordinates for cis-V(CH₂SiMe₃)₂(dmpe)₂ (2)

	x	y	z
V	0.0	0.33086(4)	0.25
P(1)	0.14262(8)	0.31986(4)	0.14911(4)
P(2)	0.18165(8)	0.23258(4)	0.30625(4)
Si	0.19115(9)	0.47556(4)	0.37828(4)
C(1)	0.3105(3)	0.2745(2)	0.1914(2)
C(2)	0.2860(4)	0.2083(2)	0.2373(2)
C(3)	0.0861(5)	0.2608(3)	0.0676(2)
C(4)	0.2118(5)	0.4009(2)	0.1082(2)
C(5)	0.1465(5)	0.1385(2)	0.3364(3)
C(6)	0.3210(4)	0.2586(2)	0.3845(2)
C(7)	0.1640(3)	0.4178(2)	0.2946(2)
C(8)	0.3666(5)	0.5247(3)	0.3959(3)
C(9)	0.0539(5)	0.5509(2)	0.3706(2)
C(10)	0.1926(5)	0.4240(3)	0.4667(2)
H(1A)	0.365(3)	0.311(1)	0.224(1)
H(1B)	0.362(3)	0.260(1)	0.155(2)
H(2A)	0.369(3)	0.189(2)	0.262(2)
H(2B)	0.226(4)	0.170(2)	0.203(2)
H(3A)	−0.000(3)	0.277(2)	0.039(2)
H(3B)	0.152(4)	0.259(2)	0.042(2)
H(3C)	0.079(5)	0.208(2)	0.084(2)
H(4A)	0.138(3)	0.427(2)	0.076(2)
H(4B)	0.256(4)	0.436(2)	0.147(2)
H(4C)	0.277(3)	0.384(2)	0.084(2)
H(5A)	0.228(4)	0.110(2)	0.346(2)
H(5B)	0.104(4)	0.144(2)	0.377(2)
H(5C)	0.079(4)	0.117(2)	0.300(2)
H(6A)	0.367(3)	0.303(2)	0.375(2)
H(6B)	0.391(3)	0.222(2)	0.394(2)
H(6C)	0.283(3)	0.267(2)	0.425(2)
H(7A)	0.137(3)	0.455(2)	0.256(2)
H(7B)	0.260(3)	0.400(1)	0.294(1)
H(8A)	0.445(4)	0.488(2)	0.403(2)
H(8B)	0.380(4)	0.556(2)	0.432(2)
H(8C)	0.380(4)	0.551(2)	0.356(2)
H(9A)	−0.036(4)	0.534(2)	0.363(2)
H(9B)	0.055(4)	0.581(2)	0.334(2)
H(9C)	0.069(4)	0.581(2)	0.412(2)
H(10A)	0.128(4)	0.390(2)	0.464(2)
H(10B)	0.208(4)	0.452(2)	0.500(2)
H(10C)	0.282(4)	0.393(2)	0.479(2)

TABLE 4. Selected Bond Distances and Angles for trans-VMe₂(dmpe)₂, (1)

Distances (Å)			
V(1)-C(10)	2.310(5)	P(1)-C(3A)	1.87(2)
V(1)-P(1)	2.462(5)	P(1)-C(4A)	1.87(1)
V(1)-P(2)	2.448(7)	P(2)-C(5A)	1.88(6)
P(1)-C(1A)	1.87(2)	P(2)-C(6A)	1.87(3)
P(2)-C(2A)	1.88(4)	C(1A)-C(2A)	1.50(6)

Angles (deg)			
C(10)-V(1)-C(10)'	180.0 a	P(1)-V(1)-P(1)'	180.0 a
P(1)-V(1)-C(10)	90.2(5)	P(1)-V(1)-P(2)	83.5(2)
P(1)-V(1)-C(10)'	89.8(5)	P(1)-V(1)-P(2)'	96.5(2)
P(2)-V(1)-C(10)	88.0(5)	P(2)-V(1)-P(2)'	180.0 a
P(2)-V(1)-C(10)'	92.0(5)		

a Crystallographically imposed.

result of the steric demands of the (trimethylsilyl)methyl groups. The average V–P distance of 2.551(1) Å is significantly longer than those in VCl₂(dmpe)₂ of 2.495(5) to 2.501(5) Å. Most likely, this lengthening is also the result of the steric crowding around the vanadium center. Furthermore, the V–P distances in 2 are essentially identical even though P(1) is trans to a phosphine and P(2) is trans to an alkyl. Normally, M–P distances trans to an alkyl group should be longer than M–P distances trans to phosphine ligands; evidently, the metal–phosphorus distances in 2 do not follow this general pattern because of the steric crowding.

The locations of the methylene hydrogen atoms of the CH₂SiMe₃ groups are of interest, since such hydrogen atoms often exhibit agostic [43] M ··· H–C interactions in molecules with low electron counts (the electron count of 2 is 15). All of the hydrogen atoms were located in the Fourier difference maps and their locations were refined without constraints. Interest-

than that of 83.5(2)° in 1 and is near the lower limit observed for such angles in other VX₂(dmpe)₂ complexes; the closing of this angle may be a consequence of the steric crowding in this molecule. Although the C(7)–V–C(7)' angle of 92.3(1)° is only slightly larger than the ideal angle of 90°, the crowding of the sterically demanding CH₂SiMe₃ groups is shown by the large P(1)–V–C(7)' angle of 103.34(8)°; the P(1)–V–P(1)' angle of 171.11(4)° is also consistent with the presence of steric repulsions between the dmpe ligands and the bulky alkyl groups.

The V–C distance of 2.253(3) Å is slightly longer than the Vᴵᴵ–C σ-bond distance of 2.219(3) Å in CpVMe(dmpe) [31,32]. This lengthening is probably a

TABLE 5. Selected Bond Distances and Angles for cis-V(CH₂SiMe₃)₂(dmpe)₂ (2)

Distances (Å)			
V-C(7)	2.253(3)	P(2)-C(2)	1.836(3)
V-P(1)	2.550(1)	P(2)-C(5)	1.833(4)
V-P(2)	2.552(1)	P(2)-C(6)	1.820(4)
C(7)-Si	1.838(2)	C(1)-C(2)	1.508(5)
P(1)-C(1)	1.836(3)	C(7)-H(7A)	0.97(3)
P(1)-C(3)	1.833(4)	C(7)-H(7B)	0.99(3)
P(1)-C(4)	1.830(4)		

Angles (deg)			
C(7)-V-C(7)'	92.3(1)	P(1)-V-P(2)	79.37(3)
P(1)-V-C(7)	82.92(8)	P(1)-V-P(2)'	94.43(3)
P(1)-V-C(7)'	103.34(8)	P(2)-V-P(2)'	92.47(3)
P(2)-V-C(7)	87.69(8)	V-C(7)-Si	131.7(2)
P(2)-V-C(7)'	177.27(8)	V-C(7)-H(7A)	98(2)
P(1)-V-P(1)'	171.11(4)	V-C(7)-H(7B)	111(2)

ingly, the V–C–H angles to the two methylene hydrogen atoms are significantly different: 98(2)° and 111(2)°; the former hydrogen atom lies 2.44(3) Å from the vanadium center. Although these distances and angles are suggestive of an incipient agostic interaction, we do not believe that such an interaction is present. In support of this view, the V–C–Si angle of 131.7(2)°, although somewhat larger than the *ca.* 120° angles typically seen [44], is much smaller than the *ca.* 150° value characteristic of authentic agostic complexes that contain CH_2SiMe_3 ligands [45–48]. Instead, the V–C–Si angle is large owing to the steric crowding, and correspondingly the methylene hydrogen atoms must "swing in" toward the vanadium atom to maintain the best tetrahedral geometry about the α-carbon center.

The *cis* configuration of 2 is somewhat surprising at first glance. The bulky alkyl groups would normally be expected to occupy mutually *trans* coordination sites to reduce the steric crowding around the vanadium center. In fact, of all first-row transition metal species with the stoichiometry $MX_2(dmpe)_2$, only the d^6 complexes *cis*-$Cr(CO)_2(dmpe)_2$ [49] and *cis*-$FeX_2(dmpe)_2$ (X = hydride, alkyl, aryl) adopt *cis* structures [18,50,51]. The *cis* geometry of 2 can be rationalized in terms of interligand repulsive forces [52]. In the *trans* geometry, any attempt to minimize repulsions between the alkyl and phosphine ligands by movement of the dmpe ligands away from one (trimethylsilyl)methyl group would only increase the steric interaction of the phosphines with the other alkyl group. In contrast, in the *cis* geometry the dmpe ligands are able to bend away from the large alkyl groups and minimize both alkyl–alkyl and alkyl–phosphine repulsions. Furthermore, the *cis* geometry allows the two alkyl ligands to adopt a type of "cog-wheel" arrangement: the $SiMe_3$ substituents (one of which is located above the C–V–C plane and one below) complement each other in filling the available

space. Other six coordinate complexes with two sterically demanding ligands are known that adopt structures in which the bulky ligands are mutually *cis*; one example is the uranium complex $UCl_2[N(SiMe_3)_2]_2$-(dme) (dme = 1,2-dimethoxyethane) [53].

2.2.3. Role of metal-phosphine π-back-bonding in early transition metal complexes

The structural data presented in Table 6 for the series of complexes $MX_2(dmpe)_2$, where M is Ti, V, Cr, and Mn, indicate that in all cases, the M–P distance in a $MMe_2(dmpe)_2$ complex is shorter than the M–P distance in the $MCl_2(dmpe)_2$ complex of the same metal. If M–P π-bonding were unimportant in these complexes, one would expect that the increased shielding (and corresponding reduced values of the effective nuclear charge Z_{eff}) induced by the methyl groups would expand the d-orbitals and would lead to longer M–P bond distances. Instead, the shielding of the nuclear charge by the inductive effect of the M–Me ligands raises the energies of the d-orbitals, which then more effectively π-back-bond with the dmpe ligands and shorten the M–P bonds. This view of the bonding is also consistent with the fact that the parameter Δ(M–P) as defined in Table 6 decreases from Ti to V to Cr. Therefore, it is not the number of d-electrons that is most important (as sometimes thought), but rather the energy of the d-electrons that dictates the amount of π-back-bonding. These results add strength to the view that early transition metals in their lower oxidation states are strong π-donors [54–59], and can engage in π-back-bonding even with normally poor π-acceptors such as trialkylphosphines [60*].

3. Experimental section

All operations were carried out in vacuum or under argon. Pentane and diethyl ether were distilled under nitrogen from sodium-benzophenone immediately before use. Halide-free methyllithium was obtained from Aldrich, while (trimethylsilyl)methyllithium [61] and $V(BH_4)_2(dmpe)_2$ [19] were prepared by literature procedures. Microanalyses were performed by Mr. Thomas McCarthy of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B infrared spectrometer as Nujol mulls between KBr plates. The ^1H NMR data were obtained on a Nicolet 360 MHz spectrometer or a General Electric 300 MHz spectrometer. The X-band EPR measurements were performed on a Bruker ESP-300 spectrometer. Magnetic moments were determined by a modification of Evans's method [62]. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

TABLE 6. Selected Bond Distances for $MX_2(dmpe)_2$ (M = Ti, V, Cr, and Mn) [a]

M	M–P in $MCl_2(dmpe)_2$	M–P in $MMe_2(dmpe)_2$	Δ(M–P) [b]	Ref.
Ti	2.586(5)	2.514(1)	0.072(5)	18,39
V	2.499(5)	2.455(6)	0.044(6)	18, c
Cr	2.369(3)	2.345(1)	0.024(3)	18
Mn	2.655(4) [d]	2.246(5)	0.409(5)	18,64

[a] Average M–P bond lengths are given in Å.
[b] Difference between M–P distance in $MCl_2(dmpe)_2$ and M–P distance in $MMe_2(dmpe)_2$.
[c] This work.
[d] This distance is for the bromide complex $MnBr_2(dmpe)_2$. The large difference between the Mn–P distance in this complex and that in $MnMe_2(dmpe)_2$ reflects the fact that these complexes have different spin states.

3.1. trans-Dimethylbis[1,2-bis(dimethylphosphino)ethane]vanadium(II) (1)

Methyllithium (4.6 ml of a 0.61 M solution, 2.8 mmol) was added to a $-78°C$ solution of $V(BH_4)_2$-$(dmpe)_2$ (0.52 g, 1.4 mmol) in diethyl ether (100 ml). The solution was stirred for 30 min at $-78°C$ and then for 1.5 h at 0°C. The solvent was removed under vacuum and the residue extracted with pentane (50 ml). The red extract was filtered, concentrated to *ca.* 15 ml, and cooled to $-20°C$ to give dark yellow crystals of the complex. Subsequent crops were obtained by concentration and cooling of the supernatant. Yield: 0.16 g (30%). Mp: 153°C (dec). This material was identified by a comparison of its infrared spectrum with that reported in the literature [18], IR (cm^{-1}): 2758m, 1420s, 1290s, 1275s, 1125m, 1100m, 1074m, 983m, 940s, 878s, 851m, 822s, 786w, 720s, 690s, 632s, 544m br, 435w, 412m, 338w.

3.2. cis-Bis[(trimethylsilyl)methyl)]bis[1,2-bis(dimethylphosphino)ethane]vanadium(II) (2)

To a cold $(-78°C)$ suspension of *trans*-$V(BH_4)_2$-$(dmpe)_2$ (0.41 g, 1.1 mmol) in diethyl ether (40 ml) was added $LiCH_2SiMe_3$ (3.6 ml of a 0.62 M solution in hexane, 2.3 mmol). The reaction mixture was warmed to 0°C and the green solution was stirred for 3 h. The solvent was removed in vacuum at 0°C and the green solid was extracted with cold (0°C) pentane (3 × 50 ml). The filtered extracts were combined, concentrated to *ca.* 100 ml and cooled to $-20°C$ to give dark green prisms of the product; additional crops of crystals were obtained from the supernatant. Yield: 0.23 g (50%). Mp: 117°C. Anal. Calcd. for $C_{20}H_{54}P_2Si_2V$: C, 45.7; H, 10.4; V, 9.69. Found: C, 42.8; H, 10.0; V, 10.6%. The low carbon analysis may be the result of carbide formation during combustion. IR (cm^{-1}): 2845s, 2832s, 2795s, 1422s, 1417s, 1296w sh, 1290m, 1275m, 1270m, 1250w, 1232s, 1223s, 1220s, 1128w, 1078w, 994w, 929vs, 918s, sh, 877s, 850vs, 812s, 805s, 727s, 710s, 678s, 659m, 647s, 628m, 477w, 447w, 432w, 378m.

3.3. Crystallographic studies

Details are given elsewhere [63]. Single crystals of $VMe_2(dmpe)_2$ (1) which were synthesized from the chloride complex $VCl_2(dmpe)_2$ and crystallized from pentane, were mounted in glass capillaries and a suitable crystal transferred to the diffractometer. [Single crystals of $V(CH_2SiMe_3)_2(dmpe)_2$ (2) also grown from pentane, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to $-75°C$ in a cold nitrogen gas stream on the diffractometer. Subsequent comments in brackets will refer to 2]. Standard peak search and indexing procedures gave rough cell dimensions, and the diffraction symmetry was confirmed by

inspection of the axial photographs. Least squares refinement using 25 reflections yielded the cell dimensions given in Table 1.

Data were collected in one quadrant of reciprocal space $(\pm h, +k, +l)$ using the measurement parameters listed in Table 1. [For 2, data were collected in one quadrant $(\pm h, +k, +l)$ for $h + k = 2n + 1$ over the range $2.0 < 2\theta < 12.0°$ and $(+h, -k, \pm l)$ for $h + k = 2n$ over the range $2.0 < 2\theta < 50°$]. Systematic absences for h0l $(h + l \neq 2n)$ and 0k0 $(k \neq 2n)$ were consistent only with space group $P2_1/n$. [For 2, the systematic absences hkl $(h + k \neq 2n)$ and h0l $(l \neq 2n)$ were consistent with space groups Cc and $C2/c$. The average values of the normalized structure factors and the successful refinement of the proposed model established that the correct choice of space group was the centric group $C2/c$]. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum factors being 0.886 and 0.860 (0.808 and 0.728). Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(l)$ were used in the least squares refinement.

The structure was solved using Patterson (SHELXS-86) and unweighted difference Fourier methods. The correct position for the vanadium atom was deduced from a vector map, and partial structure expansion gave positions for the vanadium-bound phosphorus and carbon atoms. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining disordered non-hydrogen atoms. [For 2, the structure was solved by direct methods (SHELXS-86) and correct positions for the vanadium, phosphorus, and silicon atoms were deduced from a vector map. Subsequent least-squares refinement and difference Fourier calculations revealed positions for all the remaining atoms]. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 3.11/(\sigma(F_o)^2 + pF_o^2)$ [for 2, $w = 0.79/(\sigma(F_o)^2 + pF_o^2)$]. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, anisotropic thermal coefficients were refined for the vanadium, phosphorus, and C(10) atoms, and a common group isotropic thermal parameter was refined for the remaining carbon atoms. The carbon atoms of the dmpe ligands were disordered, and a two-site model best fit the data. The P–C and C(1)–C(2) distances were constrained to common variables,

which converged to 1.88(1) and 1.50(3) Å, respectively, and the disordered "A" positions converged with an occupancy factor of 0.51(2). [For 2, anisotropic thermal coefficients were refined for the nonhydrogen atoms; hydrogen atoms were located in the difference Fourier maps and their locations were independently refined with individual isotropic thermal parameters]. Successful convergence was indicated by the maximum shift/error of 0.009 [0.004] for the last cycle. Final refinement parameters are given in Table 1. The largest peaks in the final difference Fourier difference map (-0.85 e Å^{-3}) were located in the vicinity of the dmpe ligand and possibly indicate that additional disorder is present. A final analysis of variance between observed and calculated structure factors showed an inverse dependence on sin θ. [For 2, the final difference Fourier map had no significant features (the largest peak in the final difference Fourier difference map was -0.39 e Å^{-3}), and a final analysis of variance between observed and calculated structure factors showed no apparent systematic errors].

Although the room temperature disorder model for 1 was not satisfactory in all respects, it was the best of several models tested. Attempts to collect data from a crystal mounted with Paratone-N oil under a nitrogen cold stream at $-50°C$ to $-100°C$ were unsuccessful, and there was some evidence to suggest that the crystals undergo a phase transition in this temperature range.

Tables of thermal parameters, and bond distances and angles, and final observed and calculated structure factors for $VMe_2(dmpe)_2$ and $V(CH_2SiMe_3)_2(dmpe)_2$ are available from G.S.G. and will be deposited in the Cambridge Crystallographic Data Center.

Acknowledgments

References and notes

1 J. Boor, Ziegler-Natta Catalysts and Polymerizations, Academic Press, New York, 1979.
2 P.D. Gavens, M. Bottrill, J.W. Kelland and J. McMeeking, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), Comprehensive Organometallic Chemistry, Pergamon, New York, 1982, Vol. 3, pp. 475–547.
3 P.D. Smith, J.L. Martin, J.C. Huffman, R.L. Bansemer and K.G. Caulton, Inorg. Chem., 24 (1985) 2997.
4 M.S. Wainwright and N.R. Foster, Catal. Rev.-Sci. Eng., 19 (1979) 211.
5 R.Y. Saleh and I.W. Wachs, Appl. Catal., 31 (1987) 87.
6 G. Centi, F. Trifiro, J.R. Ebner and V.M. Franchetti, Chem. Rev., 88 (1988) 55.
7 M.A. Pepera, J.L. Callahan, M.J. Desmond, E.C. Milberger, P.R. Blum and N.J. Bremer, J. Am. Chem. Soc., 107 (1985) 4883.
8 N.D. Chasteen, Vanadium in Biological Systems, Kluwer, Dordrecht, 1990.
9 D. Rehder, Angew. Chem., Int. Ed. Engl., 30 (1991) 148.
10 R. Wever and K. Kustin, Adv. Inorg. Chem., 35 (1990) 81.
11 J.R. Dilworth and R.L. Richards in G. Wilkinson, F.G.A. Stone, E.W. Abel, (eds.), Comprehensive Organometallic Chemistry, Pergamon, New York, 1982, Vol. 8, 1073–1106.
12 R.A. Henderson, G.J. Leigh and C.J. Pickett, Adv. Inorg. Chem. Radiochem., 27 (1983) 197.
13 J. Chatt, L.M. da Camera Pina and R.L. Richards, New Trends in the Chemistry of Nitrogen Fixation, Academic Press, New York, 1980.
14 J.J.H. Edema, A. Meetsma and S. Gambarotta, J. Am. Chem. Soc., 111 (1989) 6878.
15 C. Woitha and D. Rehder, Angew. Chem., Int. Ed. Engl., 29 (1990) 1438.
16 D. Rehder, C. Woitha, W. Priebsch and H. Gailus, J. Chem. Soc., Chem. Commun., (1992) 364.
17 L.V. Boas, J.C. Pessoa, in G. Wilkinson, R.D. Gillard and J.A. McCleverty, (eds.), Comprehensive Coordination Chemistry, Pergamon, New York, 1987 Vol. 3, pp. 456–583.
18 G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 1339.
19 J.A. Jensen and G.S. Girolami, Inorg. Chem., 28 (1989) 2107.
20 F.A. Cotton, G.E. Lewis and G.N. Mott, Inorg. Chem., 22 (1983) 560.
21 F.A. Cotton and M. Millar, J. Am. Chem. Soc., 99 (1977) 7886.
22 F.A. Cotton, M.P. Diebold and I. Shim, Inorg. Chem., 24 (1985) 1510.
23 D. Dapporto, F. Mani and C. Mealli, Inorg. Chem., 17 (1978) 1323.
24 F.A. Cotton, S.A. Duraj and W.J. Roth, Inorg. Chem., 24 (1985) 913.
25 F.A. Cotton, L.R. Falvello, R. Llusar, E. Libby, C.A. Murillo and W. Schwotzer, Inorg. Chem., 25 (1986) 3423.
26 C.E. Holloway and M. Melnick, J. Organomet. Chem., 304 (1986) 41.
27 M.J. Scott, W.C.A. Wilisch and W.A. Armstrong, J. Am. Chem. Soc., 112 (1990) 2429.
28 H. Oumous, C. Lecompte, J. Protas, J.L. Poucet, J.M. Barbe and R. Guilard, J. Chem. Soc., Dalton Trans., (1984) 2677.
29 J.J.H. Edema, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W.J.J. Smeets and A.L. Spek, Inorg. Chem., 29 (1990) 1302.
30 R.J. Bouma, J.H. Teuben, W.R. Beukema, R.L. Bansemer, J.C. Huffman and K.G. Caulton, Inorg. Chem., 23 (1984) 2715.
31 B. Hessen, J.H. Teuben, T.H. Lemmen, J.C. Huffman and K.G. Caulton, Organometallics, 4 (1985) 946.
32 B. Hessen, T.H. Lemmen, H.J.G. Luttikhedde, J.H. Teuben, J.L. Peterson, J.C. Huffman, S. Jagner and K.G. Caulton, Organometallics, 6 (1987) 2354.
33 K. Jakob, Z. Chem., 18 (1978) 227.
34 W. Seidel, P. Scholz and G. Kreisel, Z. Anorg. Allg. Chem., 458 (1979) 263.

35 M.M. Olmstead, P.P. Power and S.C. Shoner, *Organometallics, 7* (1988) 1380.

36 B. Sarry and P. Velling, *Z. Anorg. Allg. Chem., 426* (1976) 107.

37 F.N. Tebbe, *J. Am. Chem. Soc., 95* (1973) 5823.

38 R.A. Bartlett, P.P. Power and S.C. Shoner, *J. Am. Chem. Soc., 110* (1988) 1966.

39 J.A. Jensen, S.R. Wilson, A.J. Schultz and G.S. Girolami, *J. Am. Chem. Soc., 109* (1987) 8094.

40 It is unlikely that the V–C bond in **1** only appears long owing to the presence of small amounts of chloride groups occupying the axial positions in the crystal used for data collection, microanalytical data for samples of **1** prepared by alkylation of $VCl_2(dmpe)_2$ show that less than 0.2% chloride is present.

41 F.J. Wells, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *Polyhedron, 6* (1987) 1351.

42 S.J. Anderson, F.J. Wells, G. Wilkinson, B. Hussain and M.B. Hursthouse, *Polyhedron, 7* (1988) 2615.

43 M. Brookhart and M.L.H. Green, *Prog. Inorg. Chem., 36* (1988) 1.

44 A.R. Hermes, R.J. Morris and G.S. Girolami, *Organometallics, 7* (1988) 2372.

45 J.W. Bruno, T.J. Marks and V.W. Day, *J. Organomet. Chem., 250* (1983) 237.

46 J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz and J.M. Williams, *J. Am. Chem. Soc., 108* (1986) 40.

47 C.M. Fendrick, L.D. Schertz, V.W. Day and T.J. Marks, *Organometallics, 7* (1988) 1828.

48 K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc., 109* (1987) 3195.

49 J.E. Salt, G.S. Girolami, G. Wilkinson, M. Motevalli, M. Thorn-ton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* (1985) 685.

50 D.H. Gerlach, W.G. Peet and E.L. Muetterties, *J. Am. Chem. Soc., 94* (1972) 4545.

51 S.D. Ittel, C.A. Tolman, A.D. English and J.P. Jesson, *J. Am. Chem. Soc., 100* (1978) 7577.

52 D.L. Kepert, *Prog. Inorg. Chem., 23* (1977) 1.

53 L.G. McCullough, H.W. Turner, R.A. Andersen, A. Zalkin and D.H. Templeton, *Inorg. Chem., 20* (1981) 2869.

54 T.G. Gardner and G.S. Girolami, *Organometallics, 6* (1987) 2551.

55 T.G. Gardner and G.S. Girolami, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1693.

56 R.J. Morris and G.S. Girolami, *Inorg. Chem., 29* (1990) 4167.

57 J.C. Dodson and H. Taube, *Inorg. Chem., 28* (1989) 1310.

58 M. Casarin, E. Ciliberto, A. Gulino and I. Fragala, *Organometallics, 8* (1989) 900.

59 G.T. Palmer, F. Basolo, L.B. Kool and M.D. Rausch, *J. Am. Chem. Soc., 108* (1986) 4417.

60 For an alternative view of the electronic structure and bonding in $TiCl_2(dmpe)_2$ and $TiMe_2(dmpe)_2$ based on *ab initio* molecular orbital calculations, see: C.Q. Simpson, II, M.B. Hall and M.F. Guest, *J. Am. Chem. Soc., 113* (1991) 2898.

61 H.L. Lewis and T.L. Brown, *J. Am. Chem. Soc., 92* (1970) 4664.

62 D.F. Evans, G.V. Fazakerley and R.F. Phillips, *J. Chem. Soc. A,* (1971) 1931.

63 J.A. Jensen, S.R. Wilson and G.S. Girolami, *J. Am. Chem. Soc., 110* (1988) 4977.

64 G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Am. Chem. Soc., 105* (1983) 6752.