26, 110096-98-5; **27**, 110096-99-6; $[(\eta^5\text{-}C_5Me_5)OS(\eta^4\text{-}C_8H_{12})H]$, 100603-30-3; $[(\eta^5\text{-}C_5Me_5)OS(CO)_2Cl]$, 110097-00-2; $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})Cl]$, 110097-01-3; $[(\eta^5\text{-}C_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})Br]$, 110097-02-4; $[(\eta^5\text{-}({}_5H_4Me)Ru(\eta^4\text{-}C_8H_{12})I]$, 110097-03-5; 3-chloroprop-1-ene, 107-05-1; 3-chlorobut-1-ene, 563-52-0; 1-chloro-2-methylprop-2-ene, 563-47-3; 3,4-dichlorobut-1-ene, 760-23-6; *trans*-3-chloro-1-phenylprop-1-ene, 21087-29-6; 2,3-dichloroprop-1-ene, 78-88-6; 3-bromoprop-1-ene, 106-95-6; 1,4-dibromobut-2-ene, 6974-12-5; 2,3-dibromoprop-1-ene, 513-31-5; 3-iodoprop-1-ene, 556-56-9; 3,4-dichlorocyclobutene, 41326-64-1; 1-chloro-2-methylprop-1-ene, 513-37-1; 3-bromocyclohexene, 1521-51-3; cyclohexa-1,3-diene, 592-57-4.

Supplementary Material Available: Tables of anisotropic temperature factors, crystal data, and selected least-squares planes (3 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Paramagnetic Monocyclopentadienyl Hydrocarbyl and Borohydride Compounds of Vanadium(II) and Vanadium(III): Synthesis, Structure, and Reactivity

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Paramagnetic high-spin d^2 and d^3 monocyclopentadienyl vanadium hydrocarbyl complexes $CpV^{III}R_2(PMe_3)_2$ (R = Me, Ph) and $CpV^{II}R(dmpe)$ (R = Me, Pr, Ph) have been prepared from their corresponding halide precursors. From $CpV(Me)Cl(PMe_3)_2$, prepared by ligand exchange, the mixed hydrocarbyl complex $CpV(\eta^3\text{-}C_3H_5)Me(PMe_3)$ could be obtained. The V(II) borohydride complex $CpV(\eta^2\text{-}BH_4)dmpe$ is shown by EPR and solution magnetic measurements to have a low-spin ($S = {}^1/_2$) d^3 configuration. X-ray structures of CpVMe(dmpe) ($P2_12_12_1$, $a = 12.526$ (3) Å, $b = 9.285$ (2) Å, and $c = 12.772$ (3) Å at −158 °C, $Z = 4$) and $CpV(BH_4)dmpe$ ($P2_1/m$, $a = 8.198$ (2) Å, $b = 13.435$ (3) Å, $c = 13.987$ (4) Å, and $\beta = 102.09$ (1)° at −160 °C, $Z = 4$) have been determined. Several structural and electronic features are correlated to EHMO calculations. Both V(II) and V(III) alkyl compounds have been reacted with molecular hydrogen. Although catalytic activity in hydrogenation and isomerization of olefins has been observed, no stable V(III) hydrido species could be obtained, reductive elimination processes probably precluding their isolation. Reaction of $CpVMe_2(PMe_3)_2$ with H_2 generates active CpV fragments that can bind ligands like benzene and 2,3-dimethyl-1,3-butadiene.

Introduction

The organometallic chemistry of V(II) and V(III) has for a long time been centered around the metallocene derivatives $Cp_2V^{II}\cdot L$[2a–c] and $Cp_2V^{III}R$[2d–g] (Cp = $\eta^5\text{-}C_5H_5$). In recent years two main approaches to monocyclopentadienyl complexes of vanadium have been developed: elimination of CpK from $K[Cp_2V]$[3] and reaction of Cp_2Mg with $VCl_3\cdot 2PR_3$ to form $CpVCl_2(PR_3)_2$,[4] from which CpVCl(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) can be obtained by reduction.[5] Here we wish to report the synthesis of monocyclopentadienyl V(II) and V(III) alkyl, aryl, and borohydride complexes from their halide precursors (a preliminary report has been published[6]). The hydrogenolysis of these hydrocarbyl complexes was investigated as a possible route to the yet unknown paramagnetic CpV hydrides.

Table I. ^1H NMR Data for $CpVX_2(PMe_3)_2$[a]

X_2	$\delta(PMe_3)$	$\Delta\nu_{1/2}$,[b] Hz
Me_2[c] (3)	−4.1	780
Ph_2 (4)	−10.8	1200
MeCl[c] (5)	−9.1	1180
Cl_2 (1)	−16.9	1030
Br_2	−18.3	490
I_2	−19.6	520

[a] Data recorded at 200 MHz, 20 °C, in toluene-d_8, except 4 (360 MHz, 20 °C, benzene-d_6). Chemical shifts in parts per million relative to Me_4Si (δ 0) with downfield shifts positive. [b] Full width of half maximum. [c] In a range of ±300 ppm no α-alkyl protons could be observed.

Results and Discussion

Synthesis of Alkyl and Borohydride Complexes. The vanadium halide complexes $CpV^{III}Cl_2(PMe_3)_2$[4] (1) and

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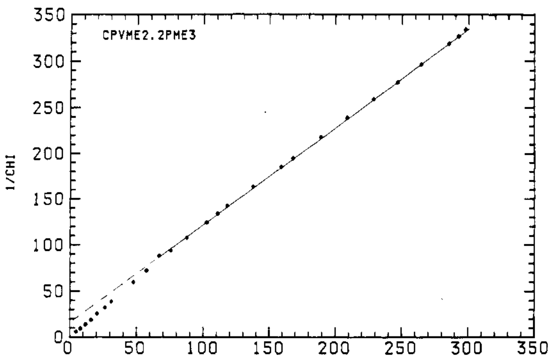

Figure 1. Plot of $1/\chi$ vs T for solid-state magnetic measurements on $\mathrm{CpVMe_2(PMe_3)_2}$ (3).

$\mathrm{CpV^{II}Cl(dmpe)}$[5] (2) are useful precursors for monocyclopentadienyl vanadium hydrocarbyl complexes. The synthesis of $\mathrm{CpV(\eta^3\text{-}C_3H_5)_2}$ by reaction of 1 with allyl Grignard was reported earlier.[7] It proved possible to prepare V(III) σ-bound hydrocarbyl complexes similarly (eq 1). Reaction

$$\mathrm{CpVCl_2(PMe_3)_2 + 2RM \xrightarrow[-30\,°C]{Et_2O} \underset{\mathbf{3,\,4}}{CpVR_2(PMe_3)_2} + 2MCl} \tag{1}$$

RM = MeLi, PhMgBr; R = Me (3), Ph (4)

of 1 with MeMgI produced a mixture of 3 and an iodine-containing compound (probably $\mathrm{CpV(Me)I(PMe_3)_2}$[8]), indicating halide exchange to give relatively inert V–I species. Compounds 3 and 4 are thermally quite stable (they can be handled at room temperature both in the solid state and in solution), though extremely air-sensitive. Thermolysis of 3 in the solid state (performed at 200 °C) or in solution (refluxing toluene) yields methane with only traces of ethane and ethylene. This indicates that proton abstraction from other ligands or from the solvent, and not reductive elimination, is the preferred decomposition pathway, comparable to the results found for the thermolysis of $\mathrm{Cp_2VMe_2}$.[9]

The compounds $\mathrm{CpVR_2(PMe_3)_2}$ are magnetically dilute d^2 high-spin ($S = 1$) complexes, as shown by solid-state magnetic measurements on 3. From 80 to 300 K the Curie–Weiss law is obeyed, with $\Theta = -14.0$ °C and $\mu_{\mathrm{eff}} = 2.74$ μ_{B}. Below 80 K the $1/\chi$ vs. T relation deviates from linearity (Figure 1). This behavior is normal for an $S = 1$ system with a small positive spin–orbit coupling constant.[10]

All paramagnetic high-spin d^2 complexes $\mathrm{CpVX_2(PMe_3)_2}$ show in the ^{1}H NMR spectrum a broad characteristic resonance for the $\mathrm{PMe_3}$ protons (Table I). Despite the broadness of the signals, the resonances of the various compounds are well-resolved and are useful in monitoring further reactions. Thus when equimolar amounts of 1 and 3 are dissolved in $\mathrm{C_6D_6}$, a ligand exchange reaction (eq 2)

$$\mathrm{CpVCl_2(PMe_3)_2 + CpVMe_2(PMe_3)_2 \xrightarrow[20\,°C]{C_6D_6} 2\underset{\mathbf{5}}{CpV(Me)Cl(PMe_3)_2}} \tag{2}$$

can be observed by NMR to proceed essentially to completion at 20 °C. The comproportionation product $\mathrm{CpV(Me)Cl(PMe_3)_2}$ (5) can be isolated as dark brown crystals. A thermodynamic bias for the dispersion of π-donor ligands has been observed before, e.g. in the $\mathrm{Cp_2TiX_2}$ system.[11] Reaction of 1 with 1 mol of MeLi at −30 °C yields equimolar amounts of 3 and starting material as the kinetic product, which at room temperature comproportionates to the thermodynamic product 5.

5 can be used to prepare mixed hydrocarbyl complexes. With allyl Grignard $\mathrm{CpV(\eta^3\text{-}C_3H_5)Me(PMe_3)}$ (6) is formed, with an η^3-bound allyl ligand (as indicated by the IR absorption at 1510 cm^{-1} [3a,7]) and only one coordinated phosphine. In contrast to 3–5, this compound is thermally quite labile, decomposing in solution at 0 °C.

The IR spectra of the complexes $\mathrm{CpVR_2(PMe_3)_2}$ follow the pattern of Cp and $\mathrm{PMe_3}$ absorptions in $\mathrm{CpVX_2(PMe_3)_2}$ (X = Cl, Br),[4] with the characteristic Cp C–H out of plane deformation at slighly lower wavenumbers (797 cm^{-1} in 3, 810 cm^{-1} in 1). The methyl complexes show methyl C–H stretch vibrations at 2795 (3) and 2805 cm^{-1} (5) and V–C stretch vibrations at 600 and 615 cm^{-1}, respectively.

From CpVCl(dmpe) (2) V(II) σ-hydrocarbyl complexes can be prepared similarly to the V(III) complexes (eq 3).

$$\mathrm{CpVCl(dmpe) + RM \xrightarrow[-30\,°C]{Et_2O} \underset{\mathbf{7–9}}{CpVR(dmpe)} + MCl} \tag{3}$$

RM = MeLi, *i*-PrMgCl, PhLi;
R = Me (7), *n*-Pr (8), Ph (9)

Reaction of 2 with MeMgI results in exclusive formation of CpVI(dmpe), again demonstrating the facile halide exchange in this system and the relative inertness of the V–I bond. Complexes 7–9 are soluble in diethyl ether, THF, and aromatic solvents, but only 8 is pentane-soluble. They can be handled in solution and in the solid state at 0 °C.

The IR spectra of the CpVR(dmpe) complexes are all similar in their absorptions of the Cp and dmpe ligands, with a complicated dmpe pattern (including characteristic absorptions at 940 (vs), 730 (s), and 695 cm^{-1}) and a Cp C–H out of plane deformation absorption around 770 cm^{-1}, as found for other 15e V(II) complexes.[5] The alkyl complexes 7 and 8 show C–H stretch vibrations (at 2750 and 2740 cm^{-1}, respectively) at significantly lower frequencies than, e.g., in $\mathrm{Cp_2TiMe_2}$[12] or in high-valent transition-metal alkyl complexes.[13] They are comparable with those found for the low-valent complexes $\mathrm{M^{II}Me_2(dmpe)_2}$ (M = Ti, V).[14] Weakening of alkyl C–H bonds can occur through "agostic" CH···M interactions,[15] but it is not clear if this is the case in the complexes considered here. Further discussion on this point will follow below. The methyl complex exhibits a V–C stretch vibration at 540 cm^{-1}, which is 60 cm^{-1} lower than in the V(III) complex 3.

Like CpVCl(dmpe),[5] the hydrocarbyl derivatives are paramagnetic high-spin d^3 complexes ($S = {}^3/_2$) and they all show a similar resonance pattern for the Cp and dmpe ligands in the ^{1}H NMR spectra (Table II). Particularly noteworthy is the resolution of the diastereotopic methyl and methylene proton resonances of the dmpe ligands in 7–9. As was the case with 3, no resonances for the α-alkyl

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[8] ^{1}H NMR (200 MHz, toluene-d_8, 20 °C) of the crystalline product showed resonances at −3.5 ppm (from 3) and at −10.5 ppm, probably from $\mathrm{CpV(Me)I(PMe_3)_2}$. Elemental analysis showed that the product contained 11% weight of iodine. $\mathrm{CpVI_2(PMe_3)_2}$ has its resonance at −19.6 ppm.

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Table II. ^{1}**H NMR Data for CpVR(dmpe)**[a,b]

complex, R =	Cp	P–Me	P–CH$_2$	R
Cl (**2**)	250 (6000)	−25.5 (520)	7.9 (720)	
		2.5 (460)	17.0 (560)	
Me (**7**)	243 (4000)	−14 (400)	31.8	c
		19 (440)	34	
Pr (**8**)	238 (3800)	−12.4 (580)	33.5 (700)	−11.6 (γ-CH$_3$)
		17.6 (470)	37.7 (940)	−38.2 (1650, β-CH$_2$)
Ph[d] (**9**)	c	−11.3 (630)	33 (570)	c
		9.1 (570)	35	

[a] Data recorded at 200 MHz, 20 °C, in benzene-d_6, unless stated otherwise. [b] Shifts in parts per million relative to Me$_4$Si (δ 0), downfield shifts positive. Full widths at half maximum in parentheses (in Hz) except when hard to determine due to overlap with other signals. [c] Not observed. [d] Benzene-d_6 360 MHz, 21 °C.

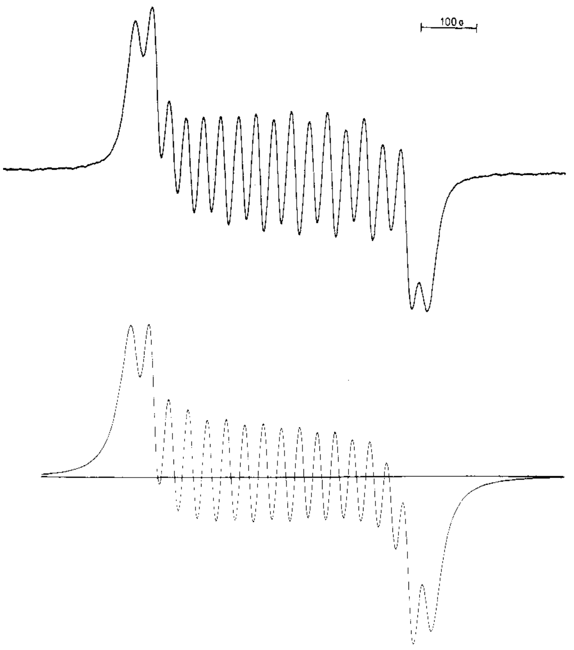

Figure 2. (a) EPR spectrum of CpV(BH$_4$)dmpe in toluene solution at 25 °C (above) and (b) calculated spectrum (below).

protons could be observed in a range of ±300 ppm. In the spectrum of the propyl complex **8** two new resonances at −38.2 (2 H) and −11.6 ppm (3 H, shoulder on a P–Me resonance) are observed, indicating the presence of an *n*-propyl group (for comparison, the spectrum of Cp$_2$V-*n*-C$_4$H$_9$ shows resonances for α, β and γ alkyl protons around 390, −45, and −5 ppm, relative to TMS, respectively[16]). This is remarkable, since the compound was prepared by using isopropyl Grignard. Evidently an isomerization of the alkyl group has occurred, probably via a hydride–olefin intermediate. Hydride–olefin complexes are well-known for the Cp$_2$M(H)(olefin) (M = Nb, Ta) system, where it is thermodynamically favored above the alkyl configuration.[17] The easy accessibility of a hydride–olefin configuration while the alkyl configuration is thermodynamically still the most stable indicates the possibility for the system to be active in the catalytic hydrogenation of olefins, which is indeed the case here (vide infra).

Thermolysis of **8** in the solid state (performed at 200 °C) yields a mixture of propene and propane (2:3), indicating both hydrogen abstraction an β-H elimination as thermal decomposition pathways (in contrast to, e.g., Cp*RuPr(PMe$_3$)$_2$, where clean β-H elimination occurs to form Cp*RuH(PMe$_3$)$_2$[18]). Under the same conditions **7** decomposes exclusively by hydrogen abstraction to form methane.

When **2** is reacted with LiBH$_4$ in THF, a green borohydride complex CpV(BH$_4$)dmpe (**10**) can be isolated. In the IR spectrum characteristic borohydride vibrations can be seen at 2380 (s), 2345 (s), 2255 (m), 1855 (br, m) and 1130 (s) cm^{-1}, but this does not allow immediate determination of the bonding mode as the pattern does not clearly conform to documented patterns for either η^2- or η^1-bound BH$_4$ groups.[19] The ^{1}H NMR spectrum of **10** differs considerably from those for the other CpVX(dmpe) complexes and is less well-resolved, with only one dmpe CH$_2$ resonance (1.3 ppm, $\Delta\nu_{1/2}$ = 256 Hz) and a dmpe CH$_3$ resonance at −12.9 ppm ($\Delta\nu_{1/2}$ = 600 Hz) with a shoulder on the downfield side. Solution magnetic measurements (Evans method[20]) show that **10** is in fact a low-spin d^3 complex with only one unpaired electron (μ_{eff} = 1.6 μ_B at 25 °C, while high-spin d^3 **7** has μ_{eff} = 3.6 μ_B as expected). The solution EPR spectrum of **10**, depicted in Figure 2a, confirms that this paramagnetic V(II) compound can be treated as an $S = {}^1/_2$ system. The hyperfine splitting pattern indicates that the unpaired electron interacts with the ^{51}V ($I = {}^7/_2$) nucleus and the two ^{31}P ($I = {}^1/_2$) nuclei of the dmpe ligand. Normally, under these circumstances one would expect to observe eight 1:2:1 triplets or a total of 24 hyperfine lines. However, in this case the fact that the isotropic ^{31}P hyperfine coupling constant is essentially half that for the ^{51}V nucleus leads to direct overlap of some of the internal hyperfine lines. This interpretation was confirmed by a computer simulation of the solution EPR spectrum (Figure 2b). The computed spectrum was calculated on the basis that $A(^{31}\text{P}) = {}^1/_2A(^{51}\text{V})$ = 31.8 G. The values for the corresponding isotropic parameters of g = 1.9858 and $A(^{51}\text{V})$ = 63.6 G were calculated from the magnetic field of the resolved vanadium hyperfine lines and the microwave frequency by using a modified form of the Breit–Rabi equation.[21] The rather large observed line widths in Figure 2a presumably arise from unresolved hyperfine coupling of the unpaired electron with the boron- and metal-coordinated hydrogen nuclei of the η^2-BH$_4$ ligand.[22] The hyperfine splitting pattern indicates that the

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(22) The EPR spectrum of **10** was also measured at 50 and −140 °C. When the solution sample was heated to 50 °C, the hyperfine lines broadened with concomitant reduction of their resolution. The corresponding frozen glass spectrum was recorded at −140 °C. Although the broadness in the resolved features in the spectrum prevents a clear determination of the principal components of the **g** and the ^{31}P and ^{51}V hyperfine tensors, the gross features of the spectrum are consistent with the nonaxial site symmetry about the paramagnetic V center in **10**. Although some hyperfine structure was partially resolved, no attempt was made to simulate this spectrum.

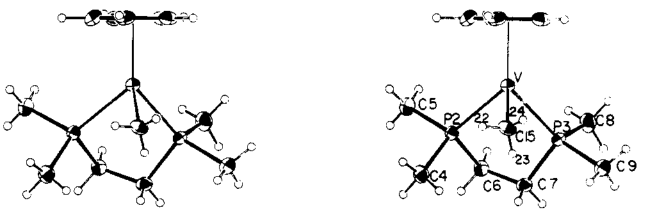

Figure 3. ORTEP stereo drawing of $CpVCH_3$(dmpe) showing atom labeling. Cyclopentadienyl carbons are C(10) through C(14). Methyl hydrogens only are indicated by small numbers.

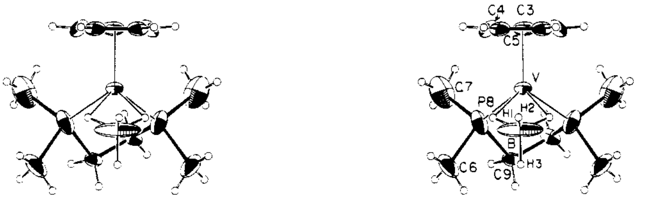

Figure 4. ORTEP stereo drawing of $CpV(BH_4)$dmpe showing atom labeling. C(3), V, B, H(2), and H(3) lie on a crystallographic mirror plane.

unpaired electron is delocalized in a molecular orbital that contains contributions from the V and P atoms. For paramagnetic transition-metal complexes with a less than half-filled d subshell, spin–orbit coupling reduces the isotropic g value below the free-electron value of 2.0023. For **10** a g value of 1.9858 is observed. The magnitude of $A(^{51}V)$ of 63.6 G falls within the range (60–75 G) observed for related d^1 Cp_2VL_2-type complexes,[23] in which the unpaired electron has been shown by theoretical[24] and EPR[23] studies to reside primarily in a metal-based orbital.

Attempts to remove BH_3 from the borohydride complex with Lewis bases in order to prepare a vanadium hydride failed. Even after prolonged reaction time no significant reaction with PMe_3 or NMe_3 had occurred.

X-ray Structure Determinations. X-ray structure determinations were carried out for the V(II) methyl (**7**) and borohydride (**10**) complexes. Their structures are depicted in Figures 3 and 4, respectively (bond lengths and angles in Tables III and IV). Both complexes are monomeric and show a three-legged piano-stool geometry. Despite this similarity, the compounds do not form isomorphous crystals.

Table III. Bond Distances (Å) and Angles (deg) for CpVMe(dmpe) (7) with Estimated Standard Deviations in Parentheses

	Bond Distances		
V–P(2)	2.4626 (12)	P(3)–C(8)	1.835 (4)
V–P(3)	2.4709 (12)	P(3)–C(9)	1.817 (4)
V–C(10)	2.300 (3)	C(6)–C(7)	1.531 (5)
V–C(11)	2.292 (4)	C(10)–C(11)	1.405 (5)
V–C(12)	2.298 (4)	C(10)–C(14)	1.403 (6)
V–C(13)	2.305 (4)	C(11)–C(12)	1.407 (6)
V–C(14)	2.303 (4)	C(12)–C(13)	1.416 (6)
V–C(15)	2.219 (4)	C(13)–C(14)	1.401 (6)
P(2)–C(4)	1.821 (4)	C(15)–H(22)	0.80 (6)
P(2)–C(5)	1.816 (4)	C(15)–H(23)	0.78 (5)
P(2)–C(6)	1.846 (4)	C(15)–H(24)	0.65 (6)
P(3)–C(7)	1.833 (4)	V–M[a]	1.964
	Bond Angles		
P(2)–V–P(3)	81.11 (4)	C(11)–C(12)–C(13)	107.6 (4)
P(2)–V–C(15)	92.67 (12)	C(12)–C(13)–C(14)	107.4 (4)
P(3)–V–C(15)	90.83 (12)	C(10)–C(14)–C(13)	108.7 (4)
V–P(2)–C(4)	120.16 (15)	V–C(15)–H(22)	105 (4)
V–P(2)–C(5)	119.43 (14)	V–C(15)–H(23)	122 (3)
V–P(2)–C(6)	107.95 (13)	V–C(15)–H(24)	105 (5)
V–P(3)–C(7)	106.70 (13)	H(22)–C(15)–H(23)	105 (5)
V–P(3)–C(8)	120.38 (16)	H(22)–C(15)–H(24)	117 (6)
V–P(3)–C(9)	121.36 (17)	H(23)–C(15)–H(24)	104 (6)
P(2)–C(6)–C(7)	108.31 (24)	M–V–C(15)	124.5
P(3)–C(7)–C(6)	110.78 (25)	M–V–P(2)	125.5
C(11)–C(10)–C(14)	107.6 (4)	M–V–P(3)	129.5
C(10)–C(11)–C(12)	108.4 (4)		

[a] M is the center of gravity of the C_5H_5 ring.

Table IV. Bond Distances (Å) and Angles (deg) for $CpV(BH_4)$dmpe (10) with Estimated Standard Deviations in Parentheses[a]

	Bond Distances		
V(1)–P(8)	2.3992 (15)	C(3)–C(4)	1.411 (6)
V(1)–C(3)	2.194 (6)	C(4)–C(5)	1.399 (6)
V(1)–C(4)	2.229 (4)	C(5)–C(5)′	1.380 (10)
V(1)–C(5)	2.288 (4)	C(9)–C(9a)′	1.516 (11)
V(1)–B(2)	2.254 (9)	V(1)–H(1)	1.78 (4)
P(8)–C(6)	1.825 (7)	B(2)–H(1)	1.17 (4)
P(8)–C(7)	1.810 (9)	B(2)–H(2)	1.12 (8)
P(8)–C(9)	1.919 (9)	B(2)–H(3)	1.11 (9)
P(8)–C(9a)	1.843 (9)		
	Bond Angles		
P(8)–V(1)–P(8)′	77.88 (7)	C(5)′–C(5)–C(4)	108.6 (5)
P(8)–V(1)–B(2)	104.33 (18)	P(8)–C(9)–C(9a)	107.8 (7)
V(1)–P(8)–C(6)	117.1 (3)	P(8)–V(1)–H(1)	121.2 (14)
V(1)–P(8)–C(7)	119.92 (26)	B(2)–V(1)–H(1)	31.0 (14)
V(1)–P(8)–C(9)	110.01 (27)	H(1)–V(1)–H(1)′	62 (3)
V(1)–P(8)–C(9a)	113.4 (3)	V(1)–B(2)–H(1)	51.7 (21)
C(6)–P(8)–C(7)	101.8 (4)	V(1)–B(2)–H(2)	123 (4)
C(6)–P(8)–C(9)	91.1 (4)	V(1)–B(2)–H(3)	125 (5)
C(6)–P(8)–C(9a)	110.3 (4)	H(1)–B(2)–H(1)′	103 (4)
C(7)–P(8)–C(9)	113.2 (4)	H(1)–B(2)–H(2)	112 (3)
C(7)–P(8)–C(9a)	91.0 (5)	H(1)–B(2)–H(3)	109 (3)
C(4)–C(3)–C(4)′	107.2 (6)	H(2)–B(2)–H(3)	112 (6)
C(3)–C(4)–C(5)	107.9 (4)	V(1)–H(1)–B(2)	97.3 (27)

[a] Prime indicates atom related by crystallographic mirror plane of symmetry.

CpVMe(dmpe). The compound contains an η^2-dmpe ligand and a symmetrically bound η^5-C_5H_5 group (V–C(Cp) distances agree within 2σ). The V–P distances (2.4626, 2.4709 (12) Å) are slightly shorter than those in $VCl_2(dmpe)_2$ (average V–P = 2.498 (5) Å),[14] probably due to better π-back-donation into the phosphorus 3d orbitals. The V–C(Cp) are larger than those in vanadocene (average 2.300 (4) Å vs 2.260 (10) Å[25]). The V–CH_3 bond length (2.219 (4) Å) appears to be very long, comparable to the V–C distances in the vanadocene olefin adduct $Cp_2V(EtO_2CCH{=}CHCO_2Et)$ (2.186/2.213 (12) Å)[2c] and longer than any V–C σ-bond found so far.[26] This is probably due to the high spin ($S = {}^3/_2$) configuration of the vanadium d^3 center (vide infra). The methyl group does not show a strongly distorted geometry as found for example in the CH···M agostic complex $TiMe(Cl)_3$dmpe.[27] The V–C–H angles (105 (4)°, 122 (3)°, 105 (5)°) lie within a range of 3σ difference and provide no statistically significant evidence for CH_2···M agostic interactions (compare $Cp^*Ti(CH_2Ph)_3$[28]) either. A theoretical examination of this point will be described further on.

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CpV(BH$_4$)dmpe. The structure determination clearly shows that the BH$_4$ ligand in this complex is η^2-bound. Distances involving the BH$_4$ hydrogens exhibit the expected trend B–H(terminal) < B–H(bridge) < V–H. The V(μ-H)$_2$B unit is coplanar. Despite the overall similarity in geometry to 7, there are several differences. The average V–C(Cp) and V–P distances are considerably shorter than in the methyl complex (shorter by 0.063 Å (10σ difference) and 0.068 Å (34σ difference), respectively). We suggest that this decrease in bond length originates in the low-spin ($S = {}^1/_2$) configuration of the d^3 center in CpV(BH$_4$)dmpe, causing a general contraction of the metal covalent radius. This effect can be compared to that seen in the V–C distances in high-spin Cp$_2$V[25] and low-spin (2,4-dimethylpentadienyl)$_2$V,[29] which are on average 0.05 Å shorter in the low-spin complex. It is also remarkable that in the low-spin BH$_4$ complex the nonbonding V$\cdots$B distance is only 0.035 Å longer than the V–C single bond in the high-spin methyl complex. This contrasts with the much larger difference found, e.g., in the pair of compounds (C$_5$H$_4$Me)$_2$HfX$_2$ (X = Me,[30] η^2-BH$_4$[31]), which is 0.31 Å. This suggests that the long V–CH$_3$ bond in 7 is not exclusively due to the larger covalent radius of the high-spin d^3-metal center.

One other difference between the structures of 7 and 10 can be observed: the Cp ligand in the borohydride complex is rotated approximately 36° around the V–Cp centroid axis with respect to the orientation in the methyl complex. This causes a trans arrangement of the two dmpe P atoms and two Cp carbon atoms (C(5), C(5)′) in 10, which is absent in 7. In response to this arrangement these carbon atoms are significantly further away from the metal (on average 0.071 Å) than the other three. However, no distortion from planarity or any irregularity in the C–C distance of the Cp ligand is observed. Recently, several examples of such "trans-effect" distortions of the coordination of a Cp ligand have been observed, e.g., in *cis*-Cp*Re(CO)$_2$I$_2$.[32]

EHMO Calculations. Extended Hückel calculations[33] have been performed on the model system CpVMe(PH$_3$)$_2$ with geometrical parameters similar to those found in the X-ray structure of 7. For the high-spin d^3 state, the calculations indicate that the three unpaired electrons reside in MO's of which one is nonbonding and the other two (a′$_\pi$ and a″, CpVR(PH$_3$)$_2$ is of point group C_s) are slightly V–C antibonding. The Mulliken overlap populations for the three MO's are −0.020, −0.022, and −0.004 in order of decreasing orbital energy ϵ, on a total V–C overlap population of 0.229. This may also contribute to the relatively long V–C bond as found in the X-ray structure of 7. A slight destabilization of the a′$_\pi$ and a″ orbitals has also been observed in calculations on d^6 CpFe(CO)$_2$Me.[34]

Eisenstein and Jean[35] performed extensive EHMO calculations on the possibilities for CH$\cdots$M interactions in octahedral and tetrahedral Ti(IV) model systems. For the octahedral (H$_5$TiCH$_3$)$^{2-}$ significant stabilization occurred upon deviation of the Ti–C–H angle α from the tetrahedral value (the H–C–H angles were kept fixed at the tetrahedral value) (Figure 5a). Similar calculations for the high-spin CpVMe(PH$_3$)$_2$ system resulted in quite a different total energy vs α curve, with only a slight stabilization for $\alpha > 109°$ (Figure 5b) and the total energy minimum near $\alpha = 123°$. That the high-spin configuration of the metal is unfavorable for CH$_2\cdots$M interactions is demonstrated by calculations on the low-spin state (Figure 5c), where the total energy curve reaches a more pronounced minimum around $\alpha = 140°$. The calculations indicate that it is very well possible that CH$_2\cdots$M interactions occur in the CpVR(dmpe) system. However, it is still unclear to what extent the alkyl C–H bonds can be influenced by these interactions. The small but significant lowering of the alkyl C–H stretch vibration frequencies in 7 and 8 might be due to a weak CH$_2\cdots$M interaction, but it cannot be excluded that other electronic factors are responsible for this effect (e.g., the presence of electrons in high-energy metal-centered orbitals). (The monotonous increase in ν_{CH} in M(CH$_3$)$_2$(dmpe)$_2$ from 2750 to 2800 cm^{-1} on going from M = Ti to M = Mn,[14] which effectively corresponds to a progressive lowering of the energy of the metal centered orbitals, might indicate such a phenomenon.)

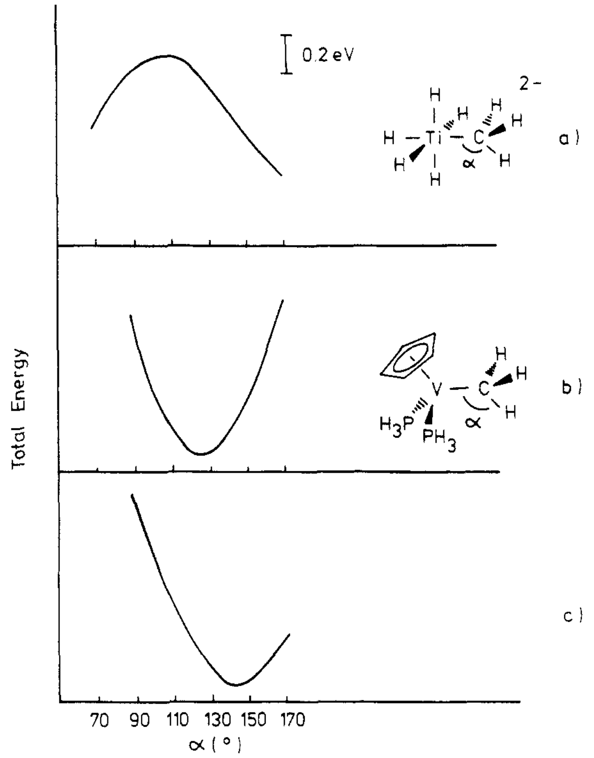

Figure 5. Total energy vs α curve from EHMO calculations on (a) H$_5$TiCH$_3$$^{2-}$ (from ref 35), (b) CpVCH$_3$(PH$_3$)$_2$ high-spin state, and (c) CpVCH$_3$(PH$_3$)$_2$ low-spin state.

For the borohydride complex 10, the low-spin configuration can be easily explained by MO considerations. Whereas the η^2-BH$_4^-$ ligand has an orbital capable of strong interaction with the CpV(PH$_3$)$_2^+$ fragment a″ LUMO, the CH$_3^-$ ligand has an orbital of that symmetry that is less suited for such an interaction. In Figure 6 the MO interaction digrams for the CpV(PH$_3$)$_2^+$ fragment with CH$_3^-$ and η^2-BH$_4^-$ ligands, as obtained from EHMO calculations, are shown (only a″ interactions are drawn explicitly). The weak a″ interaction in the methyl complex only slightly destabilizes the CpV(PH$_3$)$_2^+$ a″ LUMO, leading to an energy gap between the highest and lowest singly occupied MO's in high-spin CpVMe(PH$_3$)$_2$ of 0.98 eV. In the borohydride complex, due to the grater destabilization of the metal fragment LUMO, this separation is much larger (2.50 eV), thus enforcing spin pairing.

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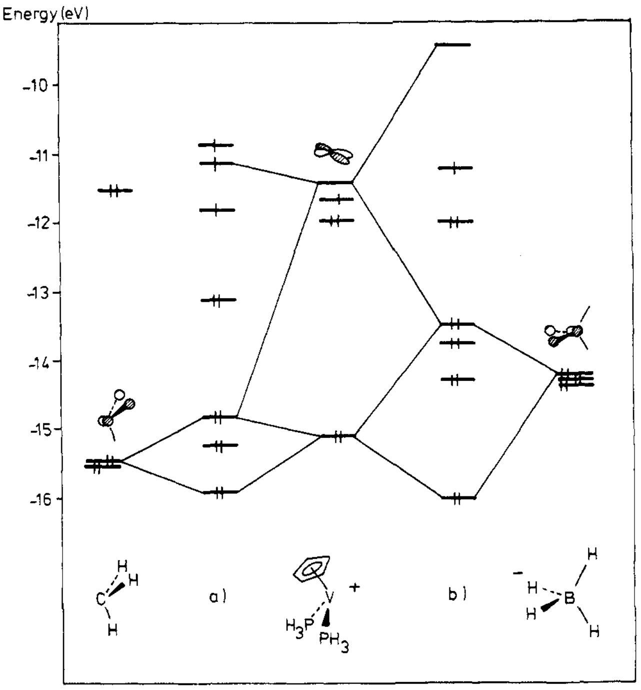

Figure 6. Orbital interaction diagrams for (a) $CpVCH_3(PH_3)_2$ and (b) $CpV(\eta^2-BH_4)(PH_3)_2$. Only the interactions of a″ symmetry are drawn explicitly.

Similar arguments predict diamagnetism for $Cp_2V(\eta^2-BH_4)$, as can be seen in the MO diagram for $Cp_2Nb(\eta^2-BH_4)$.[36] For Cp_2VBH_4 no magnetic measurements have been published, but the ^1H NMR suggests that the compound is diamagnetic.[37]

Apparently, the stabilization of two BH_4-orbitals is sufficient to compensate for the electron pairing energy, making the low-spin $CpV(\eta^2-BH_4)$dmpe complex more favorable than the high-spin η^1-BH_4 isomer. Interestingly, for the compound $CpRu(BH_4)(PR_3)_2$ one would predict an η^1-BH_4 ligand, like that found in $CH_3C(CH_2PPh_2)_3Cu(BH_4)$,[38] as the system has three more valence electrons than its vanadium analogue. Although the chemistry of the $CpRu(L_2)X$ system (L = CO, PR_3) is well-explored, the borohydride derivatives have not been reported so far.

Reactions with Molecular Hydrogen. In an inert solvent (pentane), $CpVMe_2(PMe_3)_2$ reacts with molecular hydrogen under uptake of 1 mol of H_2/mol of V, liberating 2 mol of methane/mol of V. Concomitantly, a black solid is formed. This compound has so far eluded characterization (it is NMR and EPR silent, gives an ill resolved IR spectrum, and could not be crystallized), but elemental analysis indicated the presence of only one phosphorus per V. This product will henceforth be reffered to as "X". For this reaction initial phosphine dissociation seems to be a prerequisite, as in the presence of excess PMe_3 under otherwise similar conditions no reaction takes place. From the X-ray structure of $CpVCl_2(PMe_3)_2$[4a] it can be seen that the compounds $CpVR_2(PMe_3)_2$ are sterically very crowded, with little accessibility of the metal atom. This necessitates phosphine dissociation[39] prior to reaction with most other substrate molecules. When **3** reacts with H_2 in benzene, again 1 mol of H_2 is consumed and 2 mol of methane are liberated, but a different product formation is observed: the triple-decker complex $CpV(C_6H_6)VCp$, earlier described by Duff, Jonas, et al.,[40] can be isolated (eq 4). This

Table V. Catalytic Hydrogenation and Isomerization of Olefins by 3 and 8 with Hydrogen[a]

cat. precursor, mmol	substr	alkane, mmol (mol/mol of V)	2-hexenes, mmol (mol/mol of V)
3,[b] 0.25	1-hexene	3.3 (13.2)	1.9 (7.6)
8, 0.26	1-hexene	2.2 (8.5)	1.1 (4.2)
3, 0.14	cyclohexene	0.7 (5.0)	
8, 0.10	cyclohexene	0.6 (6.0)	

[a] General reaction conditions are specified in the Experimental Section. [b] In this experiment some dimerization of the 1-hexene was also observed.

$$2CpVMe_2(PMe_3)_2 + 2H_2 + C_6H_6 \rightarrow CpV(C_6H_6)VCp + 4PMe_3 + 4CH_4 \quad (4)$$

indicates that unsaturated CpV^I fragments are generated in the reaction mixture that are capable of complexing other ligands that are present. Indeed, when the reaction is performed in 2,3-dimethyl-1,3-butadiene, the diene complex $CpV(C_6H_{10})\cdot PMe_3$ is produced (eq 5). With

$$CpVMe_2(PMe_3)_2 + H_2 + C_6H_{10} \rightarrow CpV(C_6H_{10})\cdot PMe_3 + PMe_3 + 2CH_4 \quad (5)$$

monoolefins (cyclohexene, 1-hexene) no olefin complexes could be isolated, but slow catalytic hydrogenation (and isomerization of the linear olefin) was observed (Table V), indicating both olefin complexation and the presence of active hydride intermediates. In addition some catalytic 1-hexene dimerization (about 2 mol/mol of V) was also observed. In these reactions "X" is slowly formed, disrupting the catalytic process, as "X" itself proved to be inactive under these circumstances.

Reaction of **3** with molecular hydrogen does not provide a suitable way of preparing stable vanadium hydrides, though it is likely that hydrido species are present as intermediates. It does however provide a means of generating active unsaturated CpV fragments. As such it resembles the $[Cp_2V]K$ system, which can liberate CpK^3, and $CpCr(allyl)_2$, which can generate CpCr fragments by easy elimination of 2,5-hexadiene.[41] In our case reductive elimination processes probably play an important role in precluding the isolation of CpV^{III} hydrides. That these processes can also be intermolecular is shown by the fact that reaction of **5** with H_2 yields $[CpV^{II}(Cl)PMe_3]_2$ as the only isolable product. The only V(III) paramagnetic hydride isolated so far is the sterically hindered bis(pentamethylcyclopentadienyl) compound $(C_5Me_5)_2VH$.[2g]

When the V(II) complex **8** reacts with H_2 in the presence of olefins, slow catalytic hydrogenation (and isomerization of the linear olefin) is observed. This probably occurs through hydride–olefin intermediates, already mentioned at the observed *i*-Pr to *n*-Pr rearrangement leading to **8**. Interestingly, unless dissociation of one leg of the bidentate phosphine ligand occurs, the M(alkyl) to M(H)(olefin) interconversion will have to be accompanied by spin pairing on the d^3-metal center, influencing the thermodynamic balance between the two configurations. In this respect it would be interesting to compare the perform-

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ances in the hydrogenations of a CpTi^{II}R(dmpe) d^2 system, where no spin pairing would be necessary.

Experimental Section

General Remarks. All reactions were performed under purified dinitrogen by using Schlenk, glovebox, and vacuum line techniques. Solvents were distilled under dinitrogen from sodium (toluene) or sodium–potassium melts (benzene, THF, pentane, ether) before use. NMR solvents were dried on sodium–potassium alloy and vacuum transferred before use. PMe$_3$,[42] dmpe,[43] and **1**[4] were prepared according to published procedures. **2** was prepared according to a modification of the procedure given in the literature[5] and is described below. Salt-free MeLi was either purchased (Aldrich) or prepared from MeCl and Li sand in ether. Cyclohexene and 2,3-dimethyl-1,3-butadiene were vacuum transferred and stored over molecular sieves (4 Å). 1-Hexene was purified by column chromatography over alumina, degassed, and stored over molecular sieves (4 Å). Hydrogen gas of 99.9995% purity was used without further purification. IR spectra were recorded on Nujol mulls between KBr disks with a Pye-Unicam SP3-300 spectrophotometer. ^{1}H NMR spectra were recorded with Nicolet NT-200 and NT-360 spectrometers. The EPR spectra were recorded with an IBM/Bruker ER200D-SRC spectrometer. The wavelength frequency was measured with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer is calibrated by an internal NMR gaussmeter. The solution samples were prepared by vacuum transfer of toluene onto a few milligrams of the compound in a evacuable quartz tube. The temperature of the sample during the EPR measurements was controlled to within 1 °C by the instrument's variable-temperature control system. The computer program for the simulation of solution EPR spectra was provided to J.L.P. by H. Stokolosa, University of Kentucky. Gas chromatography was performed with a HP 7620A GC instrument using a Porapak Q packed column and a HP 3390 integrator. Magnetic susceptibility measurements on solid **3** were performed on a Faraday-type system (Oxford Instruments) equipped with a Mettler ME21 electronic vacuum microbalance. Elemental analyses were performed at the Microanalytical Department of the Groningen University. All data given are the average of at least two independent determinations.

Preparation of CpVR$_2$(PMe$_3$)$_2$ (R = Me (3), Ph (4)). A suspension of **1** (1.22 g, 3.60 mmol) in 23 mL of diethyl ether was cooled to −35 °C. In 25 min 4.6 mL of 1.56 M MeLi solution in diethyl ether was added dropwise. After the solution was stirred for 2 h while being warmed to −10 °C, the solvent was pumped off and the red solid extracted with 20 mL of pentane. Concentrating the extract and cooling to −76 °C yielded red crystalline **3** (0.92 g, 3.08 mmol, 85%). IR: 3100 (vw), 2795 (mw), 1438 (w), 1421 (mw), 1480 (w), 1300 (w), 1280 (m), 1115 (vw), 1010 (m), 948 (s), 935 (s sh), 840 (w), 785 (s), 715 (m), 662 (w), 600 (mw), 455 (w) cm^{-1}. Anal. Calcd: C, 52.35; H, 9.80, Found: C, 52.39; H, 9.82.

4 was prepared similarly by using PhMgBr is diethyl ether. In this case the product was recrystallized from diethyl ether to yield analytically pure material (41%). The IR spectrum shows Ph absorptions at 3040 (m), 1560 (mw), 1230 (w), and 705 (vs) cm^{-1}. Anal. Calcd: C, 65.40; H, 7.87; V, 12.06. Found: C, 65.23; H, 8.14; V, 12.01.

Preparation of CpV(Me)Cl(PMe$_3$)$_2$ (5). A mixture of solid **1** (0.793 g, 2.34 mmol) and **3** (0.740 g, 2.47 mmol) was dissolved in 40 mL of benzene and stirred for 14 h at room temperature. The solvent was pumped off and the black-brown solid extracted with hexane. Concentrating and cooling the extract to −76 °C yielded large black-brown crystals of **5** (1.132 g, 3.55 mmol, 76% calculated on **1**). Elemental analysis showed that the product contained 3 wt % of **1**. Anal. Calcd for $C_{12}H_{26}P_2VCl$: C, 45.23; H, 8.22; C, 11.12. Found: C, 45.06; H, 8.21; Cl, 11.57. This impurity could clearly be seen in the ^{1}H NMR spectrum.

Preparation of CpV(C$_3$H$_5$)Me(PMe$_3$) (6). **5** (0.75 g, 2.4 mmol) was dissolved in 20 mL of diethyl ether. At −50 °C 2.4 mL of a 1.0 M (allyl)MgCl solution in diethyl ether was syringed in dropwise. The solution was allowed to warm to −10 °C while being stirred. The solvent was pumped off and the solid dried in vacuo at −10 °C. Extraction with cold (−10 °C) pentane and cooling the extract to −80 °C yielded 0.43 g (1.7 mmol, 71%) of **6** as black-brown needles. ^{1}H NMR (90 MHz, C$_6$D$_6$, 21 °C): −3.0 ppm ($\Delta\nu_{1/2}$ = 390 Hz, P–Me). IR: 3070 (vw), 3045 (vw), 2790 (mw), 1507 (mw), 1420 (m), 1298 (w), 1278 (m), 1233 (vw), 1212 (w), 1010 (m), 947 (s), 936 (m sh), 840 (mw), 790 (vs), 720 (m), 661 (w) cm^{-1}. Anal. Calcd: C, 58.06; H, 8.93; V, 20.52. Found: C, 58.17; H, 8.90; V, 20.54.

Preparation of CpVCl(dmpe) (2). An amalgam was made of sodium sand (0.93 g, 40.5 mmol) and 8.5 mL of mercury. Subsequently 125 mL of THF and 14.00 g (41.3 mmol) of **1** were added, and the purple solution was stirred for 2 days at room temperature. The blue solution was decanted into another vessel, and the solvent was pumped off. The reddish solid was dissolved in 110 mL of toluene. dmpe (7.0 mL, 42.0 mmol) was added, and the solution turned green while being stirred for 30 min. The salt was allowed to settle whereafter the solution was filtered and cooled to −80 °C. In two crops (for the second crop 50 mL of pentane was added to the mother liquor) 8.36 g (27.7 mmol, 68%) of green crystalline **2** was obtained. This product was spectroscopically pure.

Preparation of CpVR(dmpe) (R = Me (7), Ph (9)). A suspension of **2** (0.783 g, 2.59 mmol) in 20 mL of diethyl ether was cooled to −35 °C. In 10 min 1.7 mL of a 1.56 M MeLi solution in diethyl ether was added dropwise. After the solution was stirred for 2 h while being warmed up to 0 °C, the white precipitate was allowed to settle. The brown solution was filtered at 0 °C and concentrated, after which 5 mL of pentane was added. Cooling the solution to −76 °C yielded 0.390 g (1.39 mmol, 53%) of **7** as black needles. IR: 3085 (vw), 2790 (vw), 2750 (w), 1415 (m), 1295 (w), 1282 (m), 1126 (vw), 1108 (w), 1074 (vw), 1001 (m), 940 (s), 925 (s sh), 887 (mw), 860 (vw), 828 (w), 780 (m), 766 (s), 756 (s), 727 (s), 698 (s), 640 (mw), 540 (w), 448 (mw), 435 (w) cm^{-1}. Anal. Calcd: C, 51.25; H, 8.60; V, 18.11. Found: C, 51.41; H, 8.71; V, 18.08.

9 was prepared similarly by using a PhLi solution, but due to the poor solubility of the product and the slow reaction rate it has not been possible to obtain analytically pure material. The compound could however be characterized spectroscopically. The IR spectrum shows Ph absorptions at 3030 (m), 1547 (mw), 1230 (w), and 700 (vs) cm^{-1}.

Preparation of CpVPr(dmpe) (8). To a suspension of **2** (0.209 g, 0.67 mmol) in 17 mL of diethyl ether, cooled to −20 °C, was added 0.52 mL of a 1.3 M solution of *i*-PrMgCl in diethyl ether dropwise in 5 min. The solution was stirred for 1.5 h while being warmed to 0 °C. The solvent was pumped off and the solid dried in vacuo at 0 °C. The mixture was extracted with 30 mL of pentane (0 °C). Concentrating the extract and cooling to −30 °C, later to −80 °C, yielded large dark brown crystals of **8** (0.128 g, 0.414 mmol, 62%). IR: 3090 (w), 2785 (mw), 2740 (mw), 1418 (s), 1290 (mw), 1272 (mw), 1108 (mw), 1075 (w), 1005 (m), 938 (vs), 935 (s sh), 883 (mw), 852 (w), 820 (w), 768 (vs), 760 (s), 723 (s), 698 (s), 640 (mw) cm^{-1}. Anal. Calcd: C, 54.37; H, 9.13; V, 16.47. Found: C, 54.07; H, 9.18; V, 16.53.

Preparation of CpV(BH$_4$)dmpe (10). Green **2** (0.500 g, 1.66 mmol) was suspended in THF (50 mL) at −30 °C and an excess of LiBH$_4$ (0.140 g, 6.7 mmol) was added over a period of 30 min. The solution was allowed to warm to room temperature and became green-brown to red-brown. The solvent was removed in vacuo, and the solid mixture was extracted with 40 mL of toluene. The green product was precipitated from the toluene extracts by addition of pentane. Recrystallization was effected by vapor diffusion of pentane into toluene solutions of **10** or by slow cooling of toluene solutions. IR: 3100 (w), 2380 (s, BH$_4$), 2345 (s, BH$_4$), 2255 (s, BH$_4$), 1855 (m, br, BH$_4$), 1420 (s), 1405 (sh), 1290 (m), 1275 (m), 1260 (m), 1130 (sh), 1120 (s), 1100 (sh), 995 (m), 935 (s), 910 (sh, m), 890 (m), 790 (br, m), 725 (m), 690 (m) cm^{-1}. ^{1}H NMR (360 MHz, 21 °C, C$_6$D$_6$): CH$_2$ 1.3 (256 Hz), Me −12.9 ppm (600 Hz with shoulder). Mass spectrum (EI): parent ion observed at *m/e* 281. Magnetic susceptibility (Evans method): 1.6 μ_B at 25 °C, C$_6$D$_6$ solution. Anal. Calcd: C, 47.01; H, 8.97. Found: C, 47.12; H, 9.02.

Reaction of 2 with MeMgI. To a suspension of **2** (0.898 g, 2.98 mmol) in 20 mL of diethyl ether was added 2.0 mL of a 1.47 M solution of MeMgI in diethyl ether dropwise at −30 °C. After

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[42] Basolo, F. *Inorg. Synth.* **1976**, *16*, 153.

[43] Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 185.

the mixture was stirred for 1.5 h, during which the mixture was allowed to warm to 0 °C, the solvent was pumped off. Extraction with 80 mL of toluene and cooling to −80 °C yielded 0.573 g (1.46 mmol, 49%) of CpVI(dmpe) as greenish-blue crystals. The yield was not optimized. Anal. Calcd: C, 33.61; H, 5.39; V, 12.96; I, 32.28. Found: C, 33.84; H, 5.46; V, 12.96; I, 31.91.

Reactions of 3 with H_2 in Benzene and Pentane. A solution of **3** (0.124 g, 0.415 mmol) in benzene was stirred under 1.26 mmol of H_2 for 14 h at room temperature. A brownish solution with a green precipitate of $(CpV)_2(C_6H_6)$ had formed. The gas was pumped off quantitatively by using a Toepler pump. Oxidation of residual H_2 over CuO at 300 °C (the water thus formed was collected in a cold trap of −70 °C) showed that 0.47 mmol of H_2, 1.1 (±0.1) mol/mol of V, had been consumed and that 0.86 mmol of methane, 2.1 (±0.1) mol/mol of V, had been produced. An analogous procedure for the reaction in pentane gave a H_2 uptake of 1.1 (±0.1) mol/mol of V and a production of 1.8 (±0.1) mol of methane/mol of V.

Preparation of $(CpV)_2(C_6H_6)$. **3** (1.12 g, 3.75 mmol) was dissolved in 50 mL of benzene. The solution was frozen in liquid nitrogen and the N_2 atmosphere replaced by 1 atm of hydrogen. The solution was thawed out and stirred for 15 h at room temperature. The solvent was filtered off, and the green precipitate was washed with pentane, yielding 0.30 g (0.97 mmol, 52%) of $(CpV)_2(C_6H_6)$. MS: parent ion (*m/e* 310 (M^+)) observed, as are the fragment ions $CpVC_6H_6^+$ (*m/e* 194), CpV^+ (*m/e* 116) and $C_6H_6^+$ (*m/e* 78). IR: 3080 (vw), 3055 (vw), 1417 (w), 1358 (m), 1105 (m), 1050 (vw), 998 (s), 933 (s), 838 (vw), 790 (w), 768 (vs), 675 (w) cm^{-1}.

Preparation of $CpV(C_6H_{10})\cdot PMe_3$. **3** (0.215 g, 0.72 mmol) was dissolved in 3.5 mL of 2,3-dimethyl-1,3-butadiene. The solution was frozen in liquid nitrogen: then the N_2 atmosphere was replaced by 1 atm of hydrogen. The solution was thawed out and stirred for 2 days at room temperature. The solvent was pumped off and the green residue extracted with 10 mL of pentane. Concentrating and cooling of the extract to −80 °C yielded dark green crystalline $CpV(C_6H_{10})\cdot PMe_3$ (0.075 g, 0.27 mmol, 38%). ^1H NMR (200 MHz, C_6D_6, 20 °C): 176 ($\Delta\nu_{1/2}$ = 4700 Hz, Cp), 26.2 ($\Delta\nu_{1/2}$ = 340 Hz, 6 H, diene-Me), 1.6 ppm ($\Delta\nu_{1/2}$ = 195 Hz, 9 H, PMe_3). IR: 3090 (w), 3005 (m), 2715 (vw), 1485 (w), 1448 (s), 1433 (s), 1415 (s), 1295 (mw), 1276 (s), 1237 (mw), 1185 (vw), 1119 (mw), 1010 (s), 1004 (sh), 945 (vs), 904 (w), 880 (vw), 848 (w), 815 (mw), 780 (vs), 724 (s), 667 (mw), 583 (mw) cm^{-1}. Anal. Calcd: C, 61.31; H, 8.82; V, 18.57. Found: C, 61.18; H, 8.74; V, 18.67.

Catalytic Hydrogenation and Isomerization of Olefins. Small amounts (<0.30 mmol) of catalyst precursor (**3**, **8**) were dissolved in 1–3 mL of the olefin (cyclohexene, 1-hexene) in flasks of 170-mL volume. The solutions were frozen in liquid nitrogen; then the flasks were evacuated. After the solution was thawed out, H_2 (approximately 7 mmol) was admitted and the mixtures were stirred at room temperature for 2 days. The volatile components were then collected in a cold trap and analyzed by GC, using internal standards (cyclohexane, hexane, 1-hexene) for quantitative determinations.

Molecular Orbital Calculations. Calculations were of the extended Hückel type[33,44] with weighted H_{ij}'s.[45] H_{ii}'s for V were obtained from a charge-iterative calculation on $CpVMe(PH_3)_2$ with quadratic charge dependence on V. Extended Hückel parameters H_{ii} used are (in eV) as follows: V 3d, −11.24; V 4s, −9.75; V 4p, −6.33; P 3s, −18.6; P 3p, −14.0; P 3d, −7.0; B 2s, −15.2; B 2p, −8.5; C 2s, −21.4; C 2p, −11.4; H 1s, −13.6. Used Slater orbital exponents: V 3d, 4.750 (0.45578) +1.500 (0.75164); V 4s, 1.20; V 4p, 0.75; P 3s, 1.75; P 3p, 1.60; P 3d, 1.40; B 2s, 1.30; B 2p, 1.30; C 2s, 1.625; C 2p, 1.625; H 1s, 1.30. Geometrical parameters for the $CpV(PH_3)_2$ fragment include the following: V–C(Cp), 2.293 Å; V–P, 2.47 Å; C–C, 1.40 Å; C–H, 0.90 Å; P–H, 1.40 Å, Cp(centroid)–V–P, 126°; for the methyl system, V–C, 2.219 Å; C–H, 1.00 Å; Cp(centroid)–V–C, 126°; for the borohydride system, V–H, 1.84 Å; B–H, 1.16 Å; V–B, 2.254 Å; H–B–H, 109.5°.

Table VI. Crystal Data for CpVX(dmpe) (X = CH_3 and BH_4)

	7	10
formula	$C_{12}H_{24}P_2V$	$C_{11}H_{25}BP_2V$
color of cryst	brown/yellow	black
cryst dimens, mm	0.21 × 0.21 × 0.26	0.18 × 0.18 × 0.24
space group	$P2_12_12_1$	$P2_1/m$
cell dimens	at −158 °C; 28 reflctns	at −160 °C; 24 reflctns
a, Å	12.526 (3)	8.198 (2)
b, Å	9.285 (2)	13.435 (3)
c, Å	12.772 (3)	13.987 (4)
β, deg		102.09 (1)
molecules/cell	4	4
V, $Å^3$	1485.40	1506.48
d(calcd), g/cm^3	1.26	1.24
wavelength, Å	0.71069	0.71069
mol wt	281.21	281.02
linear abs coeff, cm^{-1}	8.3	8.2
no. of unique reflctns	1958	2792
no. with $F > 3.00\sigma(F)$	1797	2200
final residuals for $F > 3\sigma(F)$		
R(*F*)	0.0323	0.0595
$R_w(F)$	0.0349	0.0637
goodness of fit for the last cycle	0.802	1.321
max Δ/σ for the last cycle	0.05	0.05

Crystallography. $CpVCH_3(dmpe)$. A brownish yellow crystal grown from Et_2O/pentane was affixed to a glass fiber and transferred to the goniostat by using standard inert atmosphere handling techniques.[46] The sample was then cooled to −158 °C for characterization and data collection using a graphite-monochromated radiation and a diffractometer of local construction. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with orthorhombic symmetry and systematic absences of *h*00, *h* = 2*n* + 1, 0*k*0, *k* = 2*n* + 1, and 00*l*, *l* = 2*n* + 1, placing it in the acentric space group $P2_12_12_1$. Subsequent solution and refinement of the structure confirmed this choice. Data were collected (Table VI) for +*h*,+*k*,+*l* in the range 6° ≤ 2*θ* ≤ 55° and processed in the usual manner. The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least-squares methods. All atoms were located and refined (isotropic for H; anisotropic for V, C, P). Both the structures as given in the following tables and its enantiomorph were refined while the reported coordinates gave slightly lower residuals; these were not significantly lower to verify the absolute configuration for the crystal chosen. Because of the small size and low absorption coefficient of the sample, no absorption correction was deemed necessary. A final difference Fourier was featureless, the largest peak being 0.21 e/$Å^3$.

The results of the structure determination are displayed in Tables III and VII and Figure 3. There is no evidence for disorder in any part of the structure. Refined C–H distances range from 0.65 (6) to 1.00 (5) Å and average 0.88 Å.

$CpV(BH_4)(dmpe)$. A suitable crystal was located and transferred to the goniostat by using standard inert atmosphere handling techniques and cooled to −160 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to one of the monoclinic space groups $P2_1$ or $P2_1/m$. Data were collected in the usual manner[46] using a continuous *θ*–2*θ* scan with fixed backgrounds. Characteristics of the crystal and the data collection[46] (6° ≤ 2*θ* ≤ 45°), processing, and refinement appear in Table VI. $CpV(BH_4)(dmpe)$ crystallizes from toluene in a unit cell containing two independent molecules. Initial attempts to solve the structure using either direct methods (MULTAN78) or Patterson techniques led to partial solutions in which one molecule ("molecule 1") was moderately well-resolved, but the

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(44) A Fortran 5 version of the program ICON 8 by J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann (Cornell University, Ithaca, NY) was used.

(45) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(46) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table VII. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $CpVCH_3(dmpe)$

atom	x	y	z	B_{iso}, Å^2
V(1)	1655.3 (4)	784 (1)	4132.5 (5)	14
P(2)	3518 (1)	−56 (1)	4045 (1)	14
P(3)	2428 (1)	2802 (1)	3124 (1)	15
C(4)	4387 (4)	117 (5)	5181 (3)	23
C(5)	3794 (4)	−1895 (4)	3643 (3)	21
C(6)	4226 (3)	1059 (4)	3071 (3)	17
C(7)	3883 (3)	2628 (4)	3221 (3)	18
C(8)	2240 (4)	2905 (5)	1701 (3)	23
C(9)	2228 (4)	4661 (5)	3522 (4)	23
C(10)	−174 (3)	618 (4)	4029 (3)	20
C(11)	252 (3)	274 (4)	3042 (3)	21
C(12)	867 (3)	−987 (5)	3142 (3)	24
C(13)	819 (3)	−1425 (4)	4203 (4)	25
C(14)	178 (3)	−433 (4)	4739 (3)	21
C(15)	1931 (3)	1956 (5)	5623 (3)	19
H(1)	419 (4)	−44 (5)	568 (4)	24 (10)
H(2)	515 (4)	−11 (5)	502 (4)	29 (10)
H(3)	437 (4)	99 (7)	542 (4)	40 (13)
H(4)	350 (4)	−254 (5)	412 (4)	27 (9)
H(5)	354 (3)	−207 (5)	298 (3)	20 (9)
H(6)	445 (4)	−208 (5)	363 (4)	27 (10)
H(7)	497 (4)	90 (5)	319 (3)	25 (9)
H(8)	405 (3)	73 (4)	240 (3)	3 (6)
H(9)	421 (3)	329 (3)	275 (3)	8 (7)
H(10)	407 (3)	292 (4)	382 (3)	9 (7)
H(11)	265 (3)	369 (5)	143 (3)	21 (9)
H(12)	240 (4)	205 (6)	139 (4)	36 (12)
H(13)	155 (4)	308 (5)	154 (3)	22 (9)
H(14)	242 (3)	476 (5)	422 (3)	20 (9)
H(15)	257 (4)	522 (6)	320 (4)	26 (11)
H(16)	153 (4)	497 (5)	338 (4)	30 (10)
H(17)	−58 (4)	133 (5)	418 (4)	35 (11)
H(18)	13 (4)	73 (5)	244 (4)	24 (9)
H(19)	110 (5)	−146 (7)	270 (4)	48 (15)
H(20)	116 (3)	−224 (5)	451 (3)	22 (9)
H(21)	0 (4)	−53 (6)	537 (4)	34 (11)
H(22)	210 (5)	135 (7)	603 (5)	47 (15)
H(23)	237 (4)	255 (5)	567 (3)	22 (9)
H(24)	149 (5)	230 (7)	572 (5)	40 (15)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

image of the second was quite confused. Initial attempts to find a model for refinement of these two molecules were unsatisfactory, with the residuals falling to only 0.15, and many of the geometric parameters obviously incorrect. When characterization and data collection using two new crystals gave results (space group and F_0) wholly consistent with the above, S.J. reconsidered the abundance of peaks in the region of the second molecule (molecule 2). This led to the discovery that molecule 2 occupies a position with vanadium only 0.70 Å from (and one phosphorus exactly on) the mirror plane at $y = {}^1/_4$, with the result that two disordered half-weight molecules overlap considerably. (See supplementary material for a figure .) Molecule 1 is bisected by the mirror plane at $y = {}^1/_4$ and shows "ring pucker" disorder common to the $Me_2PCH_2CH_2PMe_2$ ligand. The disorder is well-resolved, with two positions (C(9) and C(9a)) located for the crystallographically unique ring carbon. The hydrogens associated with boron (as well as all hydrogens on carbon—including C(9) and C(9a)) were readily located and refined for molecule 1. The boron was modeled in a single position on the crystallographic mirror plane, but the large apparent vibrational amplitude perpendicular to the mirror plane suggests some disorder into two slightly out of plane positions. The off-plane location is probably correlated with the two different dmpe "ring-pucker" forms. In spite of the disorder, the overall residuals are quite low. The final refinement model included hydrogens in fixed, idealized positions (d(C–H) = 0.95 Å) on molecule 2. An inspection of the data indicated that corrections for the effects of extinction and absorption were unnecessary. While the structural details of molecule 2 agree (to within 3σ) with those of molecule 1, the results and discussion will employ only data from the more accurately determined molecule 1 (Tables IV and VIII and Figure 4). Additional details, including parameters for molecule 2, are available as supplementary material.

Table VIII. Fractional Coordinates[a,b] and Isotropic Thermal Parameters[c] for $CpV(BH_4)dmpe$

atoms	x	y	z	B_{iso}, Å^2
V(1)	4032 (1)	2500*	4500 (1)	19
B(2)	5334 (11)	2500*	6088 (6)	75
C(3)	1879 (7)	2500*	3267 (4)	29
C(4)	1730 (5)	1655 (4)	3842 (3)	29
C(5)	1495 (5)	1987 (4)	4752 (3)	26
C(6)	7239 (8)	643 (6)	4540 (8)	63
C(7)	4607 (12)	441 (6)	2894 (6)	64
P(8)	5645 (2)	1378 (1)	3736 (1)	38
C(9)	7320 (13)	2100 (7)	3249 (7)	22
C(9a)	6519 (13)	3038 (8)	2761 (8)	26
H(1)	496 (5)	318 (3)	557 (3)	30 (10)
H(2)	466 (10)	250*	671 (6)	62 (21)
H(3)	671 (12)	250*	636 (6)	68 (22)
H(4)	207 (8)	250*	267 (5)	31 (15)
H(5)	170 (6)	103 (4)	365 (3)	28 (10)
H(6)	131 (5)	163 (3)	520 (3)	26 (10)
H(7)	674 (7)	24 (5)	485 (4)	53 (15)
H(8)	787 (9)	29 (5)	423 (5)	72 (19)
H(9)	812 (15)	103 (9)	506 (8)	173 (45)
H(10)	408 (8)	−2 (5)	329 (5)	65 (17)
H(11)	379 (8)	74 (5)	242 (4)	49 (15)
H(12)	524 (8)	20 (5)	256 (5)	63 (17)
H(13)	829 (9)	221 (5)	378 (5)	11 (16)
H(14)	763 (14)	159 (10)	279 (10)	0 (29)
H(15)	571 (8)	287 (4)	217 (5)	6 (14)
H(16)	730 (12)	341 (7)	254 (6)	57 (17)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are ×10. [b] Parameters marked by an asterisk (*) were not varied. [c] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

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Supplementary Material Available: Tables of solid-state magnetic susceptibility data for $CpVMe_2(PMe_3)_2$, anisotropic thermal parameters, positional and thermal parameters, and bond lengths and angles for the second (disordered) molecule in the unit cell of $CpV(BH_4)$ dmpe (8 pages); listings of observed and calculated structure factors for CpVX(dmpe) (X = CH_3 and BH_4) (18 pages). Ordering information is given on any current masthead page.