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α-, β-, and δ-Hydrogen Abstraction in the Thermolysis of Paramagnetic Vanadium(III) Dialkyl Complexes

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Electron deficient paramagnetic vanadium(III) dialkyls $CpV(CH_2CMe_2R)_2(PMe_3)$ (14 electron, R = Me (**2**), Ph (**3**)) and $CpV[CH(SiMe_3)_2]_2$ (12 electron, **4**) have been synthesized. At ambient temperature **2** decomposes through α-hydrogen abstraction to produce, in the presence of dmpe (1,2-bis(dimethylphosphino)ethane), the first vanadium alkylidene $CpV(CHCMe_3)dmpe$ (**6**), which has been structurally characterized. In contrast, **3** decomposes in the presence of excess PMe_3 through orthometalation of the aryl substituent to give the metallacycle complex $CpV(\sigma^2\text{-}CH_2CMe_2C_6H_4)(PMe_3)_2$ (**7**). In the absence of excess PMe_3 the $(\mu\text{-alkyl})_2(\mu\text{-aryl})_2$ dimer $[CpV(\mu^2\text{-}CH_2CMe_2C_6H_4)]_2$ (**8**) is formed, with a short (2.313(2) Å) metal–metal distance. Reaction of $CpV(Me)Cl(PMe_3)_2$ (**9**) with *n*-BuLi produces the 1-butene complex $CpV(\eta^2\text{-}CH_2{=}CHEt)(PMe_3)_2$ (**10**) through β-hydrogen abstraction and reductive elimination. Reactivity of the alkylidene complex **6** includes the formation of the first imido complex of trivalent vanadium, $CpV[{=}NC(CMe_3){=}C(CMe_3)H](dmpe)$ (**12**), with V═N = 1.707(2) Å and a *Z*-configuration around the C═C bond, in the reaction with *t*-BuCN. Crystallographic data for **6**: $P2_1/a$, a = 13.699(2) Å, b = 8.966(1) Å, c = 15.386(2) Å, β = 101.87(1)°, Z = 4. For **7**: $P\bar{1}$, a = 9.671(2) Å, b = 14.261(4) Å, c = 8.528(2) Å, α = 94.89(2)°, β = 100.55(2)°, γ = 77.78(2)°, Z = 2. For **8**: $P2_1/c$, a = 9.812(9) Å, b = 14.019(10) Å, c = 17.407(10) Å, β = 96.76(6)°, Z = 4. For **12**: $P\bar{1}$, a = 9.147(1) Å, b = 11.005(1) Å, c = 13.489(1) Å, α = 71.95(1)°, β = 89.70(1)°, γ = 69.56(1)°, Z = 2.

Introduction

The organometallic chemistry of trivalent vanadium has been relatively little studied. The main attention in this area has been focused on the bis(cyclopentadienyl) systems Cp_2VX and Cp^*_2VX (X = halide, alkyl, aryl, allyl, H, D; $Cp^* = \eta^5\text{-}C_5Me_5$),[1] although some homoleptic complexes, such as $V[CH(SiMe_3)_2]_3$[2] and $VMes_3{\cdot}THF$ (Mes = 2,4,6-trimethylphenyl)[3] have also been synthesized. Some of the main reasons for the slow development in this area of chemistry are the fact that many organometallic V(III) complexes tend to have a paramagnetic high-spin d^2 (S = 1) configuration, which is inaccessible even by ESR spectroscopy, and the thermolability of the V(III) hydrocarbyl derivatives.

The availability of the monocyclopentadienyl vanadium(III) dichloride complex $CpVCl_2(PMe_3)_2$ (**1**)[4] has allowed the synthesis of a range of organometallic derivatives of V(III), V(II), and V(I) including allyl,[5] alkyl,[6] hydride,[7] alkene,[8,9] and alkyne[9,10] complexes. Both the observed thermolysis behavior of $CpVMe_2(PMe_3)_2$[6] and the failure to isolate CpV dialkyl complexes with alkyl groups containing β-hydrogen atoms suggested that hydrogen abstraction processes are important in the thermolysis of V(III) alkyl complexes. As these processes are often involved in the formation of interesting species like metallacycles and alkylidene complexes, a more extensive study of V(III) dialkyls and their thermal decomposition processes seemed desirable. In this paper we describe the synthesis of 14-electron and 12-electron CpV(III) dialkyl species and their thermal decomposition under mild

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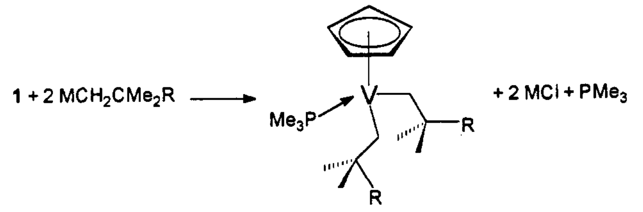
(ambient temperature) conditions. Products include the first vanadium alkylidene complex and new metallacyclic compounds. In the thermolysis of CpV(III) complexes, α-, β-, and δ-hydrogen abstractions were observed. The paper also describes some reactivity aspects of the new vanadium alkylidene species, including the formation of the first V(III) imido complex with a V–N multiple bond. A part of this investigation has been communicated previously.[6c]

Results and Discussion

Synthesis. The 16-electron dialkyl complex $CpVMe_2(PMe_3)_2$[6a,b] acts in most of its reactivity as an electronically saturated system. The high-spin d^2 configuration of its metal center leaves only half-filled orbitals accessible to reactants. This makes phosphine dissociation necessary for reactions with most substrates.[7,11] Use of sterically more demanding alkyl groups, however, allows preparation of CpV^{III} dialkyl complexes that are more electron deficient.

Reaction of $CpVCl_2(PMe_3)_2$ (1) with 2 mol of neopentyllithium in pentane or neophylmagnesium chloride (Me_2PhCCH_2MgCl) in diethyl ether at −10 to 0 °C affords crystalline 14-electron complexes $CpV(CH_2CMe_2R)_2PMe_3$ (R = Me, 2; Ph, 3; eq 1). The compounds are quite thermolabile, decomposing in solution at ambient temperature, and 3 even decomposing visibly at 0 °C. Though the compound is paramagnetic, the stoichiometry of the neopentyl complex 2 can be determined by ^1H NMR spectroscopy from the broad resonances of the CMe_3 and PMe_3 protons at δ −2.70 and −4.72 ppm, respectively. Attempts at an X-ray structure determination of 2 were hampered by twinning problems.

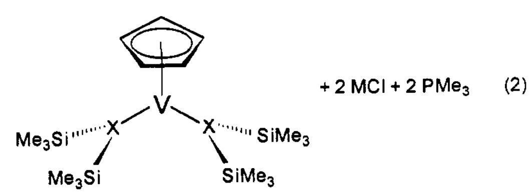


2: R = Me, M = Li

3: R = Ph, M = MgCl

(1)

Phosphine-free complexes are obtained when extremely large ligands are introduced. Reaction of 1 with 2 mol of $LiCH(SiMe_3)_2$ produces the 12-electron species $CpV[CH(SiMe_3)_2]_2$ (4) as a green oil (eq 2). The absence of PMe_3 ligands was established by the lack of characteristic PMe_3 vibrations in the IR spectrum of 4. The ^1H NMR spectrum shows the Cp and $SiMe_3$ protons at δ 167.7 and 8.78 ppm, respectively, in a 5 to 36 ratio. Through an analogous procedure using $NaN(SiMe_3)_2$ the bis(amido) complex $CpV[N(SiMe_3)_2]_2$ (5) was obtained as an orange brown solid with a melting point around room temperature (eq 2). This compound appears to be phosphine-free as well, according to the same criteria mentioned for 4.



(2)

4: X = CH, M = Li

5: X = N, M = Na

Thermolysis of $CpV(CH_2CMe_3)_2PMe_3$. Thermolysis of bis(neopentyl) species is of interest because in some systems it leads through α-hydrogen abstraction to the formation of metal alkylidene species, thus providing a convenient way for the synthesis of nucleophilic carbene complexes.[12] This would be useful in the present system, as no nucleophilic alkylidenes of vanadium have been prepared previously. Known vanadium carbene complexes[13] are of the electrophilic ("Fischer") type, with the carbene moiety :C(R)X (R = H, alkyl; X = NR_2, OR) having Lewis-base type character toward the metal center.[14] However, the intriguing complex $(\eta^5\text{-}C_5Me_5)V[C_3P_3(CMe_3)_3]$ also appears to exhibit genuine V–C multiple bond type character.[15]

The bis(neopentyl) complex 2 decomposes in solution in various solvents (benzene, cyclohexane) at ambient temperature to form neopentane and a mixture of diamagnetic products (NMR). Thermolysis reactions on a preparative scale yielded only oily products. However, the thermolysis of 2 in the presence of 1 equiv of dmpe afforded an olive-green crystalline compound, which was identified as the alkylidene complex CpV(CHCMe₃)dmpe (6, eq 3).

$$\underset{\mathbf{2}}{CpV(CH_2CMe_3)_2PMe_3} + dmpe \rightarrow \underset{\mathbf{6}}{CpV(CHCMe_3)dmpe} + CMe_4 + PMe_3 \quad (3)$$

Compound 6 has been characterized by single crystal X-ray diffraction. Its structure is shown in Figure 1, and selected bond distances and angles are given in Table I. The complex has a typical monomeric three-legged piano-stool structure. The short V=C bond of 1.809(3) Å is significantly shorter than the 2.102(3) Å bond distance observed in the vanadium Fischer-carbene complex $CpV(CO)_3[{=}C(O)C_4H_6]ZrCp_2$[13a] and is indicative of a true alkylidene species. In the "bent metallacyclopentatriene" complex $CpV(C_4Me_2Ph_2)PMe_3$[9] the V—C distances are somewhat longer (1.883(3)/1.891(3) Å) than in the true alkylidene 6, reflecting the more ambivalent character of the bonding in the metallacyclopentatriene complexes. The alkylidene ligand in 6 is highly distorted, with a very obtuse V—C(12)—C(13) angle of 173.3(3)°. The alkylidene α-hydrogen atom is strongly bent toward the metal center, with V—C(12)—H(121) = 65(3)°. The observed V—H(121) distance of 1.66(5) Å is similar to the V—H distances found in the hydride-bridged dimer [CpV(μ-

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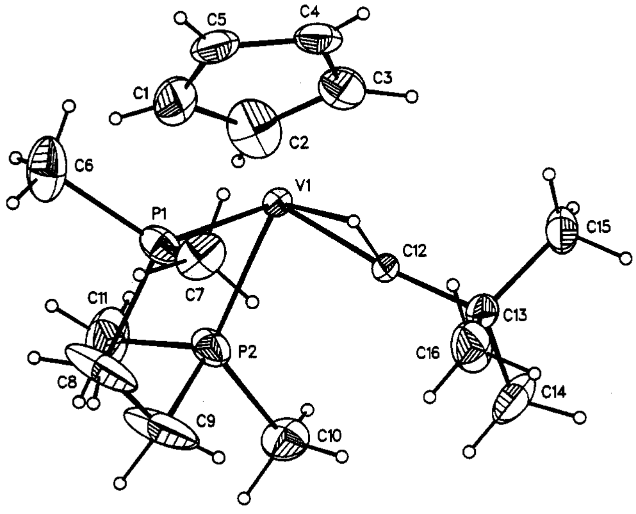

Figure 1. Molecular structure of CpV(CHCMe$_3$)dmpe (**6**). Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for CpV(CHCMe$_3$)dmpe (6)

V(1)–C(12)	1.809(3)	V(1)–C(1)	2.238(3)
V(1)–P(1)	2.363(1)	V(1)–C(2)	2.241(5)
V(1)–P(2)	2.331(1)	V(1)–C(3)	2.288(5)
V(1)–H(121)	1.66(5)	V(1)–C(4)	2.292(5)
C(12)–H(121)	1.00(5)	V(1)–C(5)	2.259(5)
C(12)–C(13)	1.510(4)	av (C–C)$_{Cp}$	1.403(7)
V(1)–C(12)–C(13)	173.3(3)	P(1)–V(1)–P(2)	79.48(5)
V(1)–C(12)–H(121)	65(3)	P(1)–V(1)–C(12)	99.4(1)
C(13)–C(12)–H(121)	113(3)	P(2)–V(1)–C(12)	91.5(1)

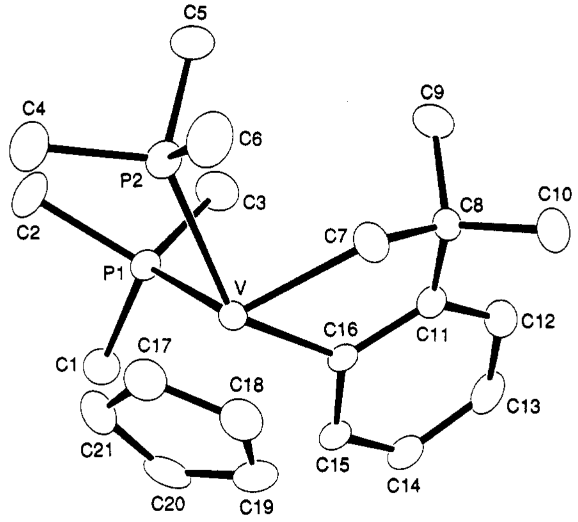

Figure 2. Molecular structure of CpV(σ^2-CH$_2$CMe$_2$-C$_6$H$_4$)(PMe$_3$)$_2$ (**7**). Thermal ellipsoids are drawn at the 50% probability level.

H)dmpe]$_2$ (1.64(4), 1.72(4) Å).[7] These structural features suggest a strong interaction between the alkylidene α-CH moiety and the metal center. This is also expressed in the diamagnetism of the compound, which is unusual for a V(III) complex with a formal 16 valence electron count (when extra electrons from the C—H bond are not included).

The ^{1}H NMR spectrum of **6** shows a triplet for the Cp protons due to a small (1.8 Hz) coupling to the dmpe phosphorus atoms. The resonance of the alkylidene proton is found at δ −7.76 ppm, strongly broadened by unresolved coupling to the ^{51}V nucleus ($I = {^7}/_2$). This broadening also precludes determination of the C–H coupling on the alkylidene carbon atom (δ 259.7 ppm) from the ^{13}C NMR spectrum **6**. Comparing the line widths in the ^{1}H coupled and decoupled ^{13}C NMR spectra at −90 °C (where the resonance is narrowed due to relaxation decoupling of the quadrupolar nucleus) suggests that the $^1J_{CH}$ coupling on the alkylidene carbon is ≤85 Hz. Another feature is the remarkably well-resolved ^{51}V NMR spectrum of **6**, with a triplet (J_{VP} = 329 Hz) at δ −285.4 ppm.

The geometry of the alkylidene moiety (the most strongly distorted observed so far) and the upfield shift of the alkylidene α-hydrogen in the ^{1}H NMR spectrum appear to be characteristics of alkylidene groups bound to a metal in a relatively low oxidation state, yet still formally electronically unsaturated. In this kind of compound an oxidative addition of the C–H bond to the metal center is conceivable, yielding an alkylidyne–hydride species. An equilibrium of this kind has been observed in Ta(CHCMe$_3$)(dpme)$_2$Cl.[16] In the case of **6** the complex appears to be frozen in an intermediate stage, and in its reactivity we have so far not observed any evidence for alkylidyne–hydride behavior.[17]

Thermolysis of **2** in the absence of dmpe produces a mixture of two diamagnetic organometallic products, as observed by NMR. The Cp resonances in the ^{1}H NMR spectrum suggest a 1:3 ratio for the two products. The minor product can be identified as the alkylidene species CpV(CHCMe$_3$)(PMe$_3$)$_2$ (**6b**): the resonance of the Cp protons at δ 4.98 ppm shows the expected triplet structure from the coupling with the two phosphorus atoms (J_{PH} = 2.8 Hz), the broad alkylidene proton resonance is observed at δ −5.7 ppm and the ^{51}V NMR spectrum shows a triplet at δ −1328 ppm (J_{VP} = 223 Hz). No coupling with phosphorus atoms is apparent on the Cp proton resonance of the major product. In the ^{51}V NMR spectrum it exhibits a broad resonance at δ −22 ppm ($\Delta\nu_{1/2}$ = 5320 Hz). When **2** is thermolyzed in the presence of excess PMe$_3$ the same mixture of oily diamagnetic organometallic products is obtained.

Although the major product in this reaction needs further characterization, present results suggest that in the thermolysis of **2** in the absence of chelating phosphines the monomeric alkylidene species is only formed as a minor product.

Thermolysis of CpV(CH$_2$CMe$_2$Ph)$_2$PMe$_3$. The neophyl complex **3** decomposes readily in solution at ambient temperature. In the presence of excess PMe$_3$ a green paramagnetic crystalline solid is produced, which was characterized by X-ray diffraction as the metallacyclic complex CpV(σ^2-CH$_2$CMe$_2$C$_6$H$_4$)(PMe$_3$)$_2$ (**7**, eq 4). The structure of **7** is shown in Figure 2, and pertinent bond distances and angles are given in Table II.

$$\underset{\mathbf{3}}{\mathrm{CpV(CH_2CMe_2Ph)_2PMe_3}} + \mathrm{PMe_3} \rightarrow \underset{\mathbf{7}}{\mathrm{CpV(CH_2CMe_2C_6H_4)(PMe_3)_2}} + \mathrm{PhCMe_3} \quad (4)$$

The metal atom in **7** is to first approximation square pyramidally coordinated, with the PMe$_3$ ligands in cis position. The arrangement of the ligands in the basal

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[17] Apart from the reagent mentioned in the text, **6** has been reacted with CO, butyne-2, and styrene oxide. No specific experiments to probe possible alkylidyne–hydride character in **6** have been performed.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for $CpV(\sigma^2\text{-}CH_2CMe_2C_6H_4)(PMe_3)_2$ (7)

V–P(1)	2.516(1)	V–C(17)	2.341(3)
V–P(2)	2.544(1)	V–C(18)	2.346(3)
V–C(7)	2.194(3)	V–C(19)	2.314(3)
V–C(16)	2.170(3)	V–C(20)	2.300(3)
C(7)–C(8)	1.526(4)	V–C(21)	2.320(4)
C(8)–C(11)	1.521(4)	C(11)–C(12)	1.388(4)
C(12)–C(13)	1.385(5)	C(13)–C(14)	1.376(5)
C(14)–C(15)	1.381(5)	C(15)–C(16)	1.412(4)
C(11)–C(16)	1.418(4)	av $(C–C)_{Cp}$	1.399(5)
av (P–C)	1.829(4)		
P(1)–V–P(2)	84.41(4)	C(7)–V–C(16)	74.6(1)
P(1)–V–C(7)	120.6(1)	C(7)–C(8)–C(11)	107.8(3)
P(1)–V–C(16)	79.25(8)	C(8)–C(11)–C(16)	116.6(3)
P(2)–V–C(7)	79.5(1)	V–C(16)–C(11)	118.1(2)
P(2)–V–C(16)	138.98(8)	V–C(16)–C(15)	127.2(2)
V–C(7)–C(8)	116.0(2)		

plane of the pyramid is somewhat twisted to allow suitable packing of the asymmetric $\sigma^2\text{-}CH_2CMe_2C_6H_4$ ligand. This ligand is a neophyl group metalated on the ortho position of the phenyl group. The V—C distances to the metal-bound aryl and alkyl carbon atoms are V—C(16) = 2.170(3) and V—C(7) = 2.194(3) Å, respectively. The vanadium—aryl carbon bond length is somewhat longer (by 0.06 and 0.02 Å, respectively) then the average vanadium—carbon bond lengths reported for $VMes_3{\cdot}THF$[3b] and $Ph_2VN(CH_2CH_2NEt_2)_2$.[18] The V—P distances of 2.516(1)/2.544(1) Å in this paramagnetic high-spin V(III) complex are significantly longer than those found in the diamagnetic low-spin alkylidene complex 6 and are comparable to those found in other 16-electron high-spin complexes like $CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2$ and $CpV[\eta^4\text{-}CH_2{=}CHC(Ph){=}C(Ph)Et]PMe_3$.[9]

The formation of this cyclometalated product indicates that in the $CpVR_2(PMe_3)$ system orthometalation of the aryl group in the bis(neophyl) complex is preferred over a possible α-hydrogen abstraction process. In other early transition metal systems like $M(CH_2CMe_2R)_2(NAr)_2$[19] (M = Mo, W; Ar = 2,6-C_6H_3-i-Pr_2) α-hydrogen abstraction occurs for R = Me and Ph, while in bis(phosphine)platinum dialkyl[20] complexes cyclometalation is preferred for both bis(neopentyl) and bis(neophyl) complexes. The latter is also observed in $Cp^*{}_2ThR_2$[21] complexes (R = CH_2CMe_3, CH_2SiMe_2Ph). Although no kinetic data on the thermal decomposition of 3 are available at present, in handling these materials the noticeably greater thermolability of 3 versus 2 can be observed.

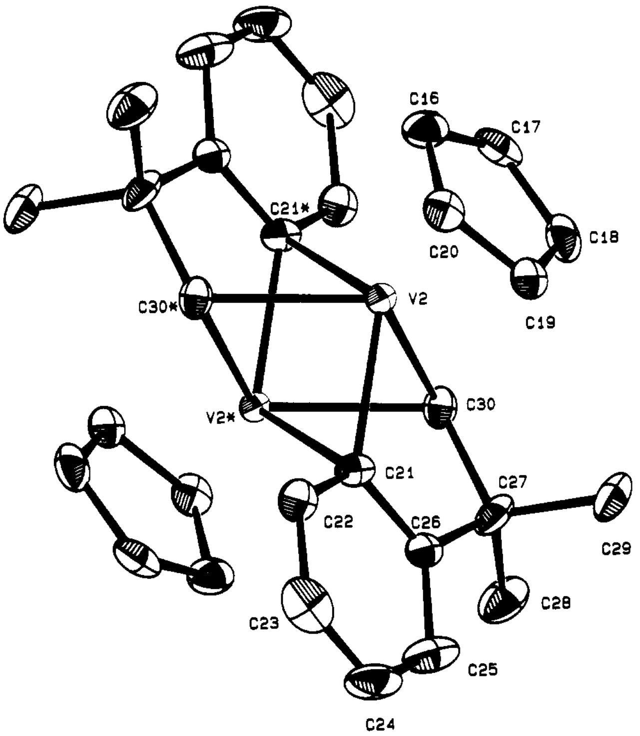

Figure 3. Molecular structure of $[CpV(\mu^2\text{-}CH_2CMe_2C_6H_4)]_2$ (8). Only one of the crystallographically independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[CpV(\mu^2\text{-}CH_2CMe_2C_6H_4)]_2$ (8)[a]

V(2)–V(2*)	2.313(2)	V(2)–C(16)	2.327(5)
V(2)–C(21)	2.213(5)	V(2)–C(17)	2.330(5)
V(2)–C(21*)	2.276(5)	V(2)–C(18)	2.349(6)
V(2)–C(30)	2.209(6)	V(2)–C(19)	2.342(5)
V(2)–C(30*)	2.312(6)	V(2)–C(20)	2.335(5)
C(21)–C(22)	1.387(7)	C(21)–C(26)	1.417(7)
C(22)–C(23)	1.391(8)	C(23)–C(24)	1.379(9)
C(24)–C(25)	1.356(9)	C(25)–C(26)	1.390(7)
C(26)–C(27)	1.506(8)	C(27)–C(30)	1.543(7)
av $(C–C)_{Cp}$	1.400(8)		
C(21)–V(2)–C(21*)	118.0(1)	V(2)–C(21)–V(2*)	62.0(1)
C(21)–V(2)–C(30)	72.0(2)	V(2)–C(30)–V(2*)	61.5(1)
C(21)–V(2)–C(30*)	78.4(2)	V(2)–C(21)–C(22)	124.2(4)
C(21)–V(2*)–C(30)	79.3(2)	V(2)–C(21)–C(26)	116.1(4)
C(21)–V(2*)–C(30*)	69.0(2)	V(2)–C(21*)–C(22*)	117.3(3)
C(30)–V(2)–C(30*)	118.5(1)	V(2)–C(21*)–C(26*)	103.2(3)
C(22)–C(21)–C(26)	117.6(4)	V(2)–C(30)–C(27)	114.3(3)
C(21)–C(26)–C(27)	117.7(4)	V(2)–C(30*)–C(27*)	110.4(4)
C(26)–C(27)–C(30)	104.6(4)		

[a] Data for one of the independent molecules in the unit cell only. The asterisk denotes an atom related by a center of symmetry.

Thermolysis of 3 in solution in the absence of extra PMe_3 produces a brown solution from which red-brown crystals were obtained. The IR spectrum of this material indicates that the product, unlike 7, does not contain PMe_3 (e.g. lacking the characteristic strong δ P–Me vibration band around 950 cm^{-1}). X-ray diffraction showed that this product is a phosphine-free (μ-alkyl)$_2$(μ-aryl)$_2$ dimer $[CpV(\mu^2\text{-}CH_2CMe_2C_6H_4)]_2$ (8, eq 5). The structure of 8 is shown in Figure 3, and pertinent interatomic distances and angles are given in Table III.

$$\underset{3}{2CpV(CH_2CMe_2Ph)_2PMe_3} \rightarrow$$

$$\underset{8}{[CpV(\mu^2\text{-}CH_2CMe_2C_6H_4)]_2} + 2PhCMe_3 + 2PMe_3 \quad (5)$$

The unit cell contains two crystallographically independent molecules, that do not differ remarkably in their structure. Data are given for one of the two independent molecules only. The complex exhibits a short metal–metal distance of 2.313(2) Å, bridged by four carbon atoms of the two orthometalated neophyl groups. Each bridging carbon atom has one long and one short V–C distance

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(2.209(6) and 2.312(6) Å for the alkyl carbon C(30) and 2.213(5) and 2.276(5) Å for the aryl carbon C(21), respectively). The structure of **8** is strongly related to the (μ-alkyl)$_4$ complex $[\mathrm{CpV}(\mu^2\text{-}\mathrm{C_4H_8})]_2$ reported by Jonas et al.[22] A subtle difference is found in the bonding asymmetry of the bridging ligands: in **8** each μ^2 ligand has either two long or two short distances to the same V atom, whereas in $[\mathrm{CpV}(\mu^2\text{-}\mathrm{C_4H_8})]_2$ each μ^2 ligand has to one V atom one long and one short distance. The V–(μ-C)–V′ angles of 62.1(2) and 61.5(1)° are unusually acute. The backbone of the μ^2 organic ligand, C(21)–C(26)–C(27)–C(30), is slightly twisted (torsion angle −18.2(5)°).

The nature of the short V—V distance in this type of complex has recently been the subject of ab initio MO calculations,[23] which seem to suggest that this is not accompanied by the formation of a full V═V bond. Although no magnetic data on **8** are available at present, the broad, ill-resolved resonances observed in the ^{1}H NMR spectrum of **8** indicate that the species is paramagnetic.

Formation of $\mathrm{CpV}(\eta^2\text{-}\mathrm{CH_2{=}CHEt})(\mathrm{PMe_3})_2$. The synthesis of CpV(III) dialkyl species with aryl groups containing β-CH bonds has been unsuccessful so far. Reactions of **1** with ethyl Grignard reagents produce small amounts of the V(I) ethylene complex $\mathrm{CpV}(\eta^2\text{-}\mathrm{C_2H_4})(\mathrm{PMe_3})_2$,[8,9] or the V(II) compound $\mathrm{CpVCl(PMe_3)_2}$[24] when less than 2 equiv of Grignard reagent are used.[25] A likely explanation is that rapid β-hydrogen elimination takes place in the $\mathrm{CpVEt_2(PMe_3)_2}$ formed (note that in reaction of **1** with MeLi the substitution of the second Cl atom is faster than that of the first one[6b]), followed by reductive elimination of ethane to yield low-valent species.

This hypothesis was investigated by the reaction of the mixed methyl–chloride complex $\mathrm{CpV(Me)Cl(PMe_3)_2}$ (**9**)[6a,b] with *n*-BuLi. In a rapid reaction a green solution was formed from which the green V(I) 1-butene complex $\mathrm{CpV}(\eta^2\text{-}\mathrm{CH_2{=}CHEt})(\mathrm{PMe_3})_2$ (**10**) was obtained in a moderate yield (eq 6).

$$\underset{\mathbf{9}}{\mathrm{CpV(Me)Cl(PMe_3)_2}} + n\text{-BuLi} \rightarrow \underset{\mathbf{10}}{\mathrm{CpV}(\eta^2\text{-}\mathrm{CH_2{=}CHEt})(\mathrm{PMe_3})_2} + \mathrm{CH_4} + \mathrm{LiCl} \qquad (6)$$

The compound was characterized by elemental analysis and IR and ^{1}H NMR spectroscopy. When a solution of **10** in benzene-d_6 is exposed to CO, a rapid reaction forming free 1-butene and diamagnetic $\mathrm{CpV(CO)_2(PMe_3)_2}$[26] is observed (NMR, eq 7).

$$\underset{\mathbf{10}}{\mathrm{CpV}(\eta^2\text{-}\mathrm{CH_2{=}CHEt})(\mathrm{PMe_3})_2} + 2\mathrm{CO} \rightarrow \mathrm{CpV(CO)_2(PMe_3)_2} + \mathrm{CH_2{=}CHEt} \qquad (7)$$

Reactivity of V(III) Alkylidene Species. Transition metal alkylidene complexes exhibit a wide range of reactions with organic substrates, including important catalytic processes like ring-opening metathesis polymerization of cyclic olefins and olefin metathesis.[27] As the new vanadium(III) alkylidene complexes $\mathrm{CpV(CHCMe_3)dmpe}$ (**6**) and $\mathrm{CpV(CHCMe_3)(PMe_3)_2}$ (**6b**) are the first examples of nucleophilic alkylidenes for this element, and are rare examples of 3d-metal alkylidenes ($\mathrm{Cp_2Ti(CHR)PR'_3}$ forms the other available class[28]), some aspects of the reactivity of these complexes toward organic substrates have been studied.

Complex **6** reacts with 1 mol of *t*-BuCN at 60 °C in benzene to form in a slow (65% conversion in 16 h) but quantitative reaction the imido complex $\mathrm{CpV[{=}NC(CMe_3){=}CHCMe_3]dmpe}$ (**12**, eq 8).

$$\underset{\mathbf{6}}{\mathrm{CpV(CHCMe_3)dmpe}} + \mathrm{Me_3CC{\equiv}N} \rightarrow \underset{\mathbf{12}}{\mathrm{CpV({=}NC(CMe_3){=}CHCMe_3]dmpe}} \qquad (8)$$

This type of reaction has been observed before by Schrock and co-workers with $\mathrm{(CMe_3CH_2)_3Ta({=}CHCMe_3)}$[29] and $\mathrm{CpTa({=}CHCMe_3)Cl_2}$.[30] In the reaction of **6**, the near exclusive formation (>95%) of one geometric isomer was observed by NMR. By X-ray diffraction the configuration around the C═C bond in **12** was found to be *Z* (vide infra). In the reactions involving Ta alkylidenes mixtures of *Z* and *E* isomers were obtained.[29,30] The reaction is likely to proceed through initial formation of a 2-azametallacyclobut-2-ene complex, followed by a ring-opening to yield the final product (Scheme I). The formation of *Z* or *E* products is determined by the sense of the rotation around the C—C bond in the ring-opening stage of the reaction. Formation of the *E* isomer involves turning the alkylidene *t*-Bu substituent toward the metal center, while the *Z* isomer is formed by rotating this substituent away from the metal. It is likely that in the case of **6** the relatively small metal center causes the (*t*-Bu)—CpV(dmpe) steric repulsion to prevail over the (*t*-Bu)—(*t*-Bu) repulsion in the ring-opening step, thus producing the *Z* isomer nearly exclusively.

The structure of **12** is shown in Figure 4, and pertinent interatomic distances and angles are given in Table IV. The compound represents the first example of a V(III) imido complex with a V—N multiple bond. The structure of the CpV(dmpe) moiety in **12** is generally comparable to that observed in the structure of the alkylidene complex **6**. The V—N distance of 1.707(2) Å is characteristic of V—N multiple bonding but is relatively long compared to most known V═N bonds in V(IV) or V(V) systems (usually 1.60–1.68 Å)[31] and similar to those found in the comparatively electron rich V(IV) bis(pentamethylcyclopentadienyl) systems $\mathrm{Cp^*_2V(NR)}$ (R = Ph, 1.730(5) Å;[32] $\mathrm{C_6Me_2H_3}$, 1.707(6) Å[33]). The V—N—C(7) angle is

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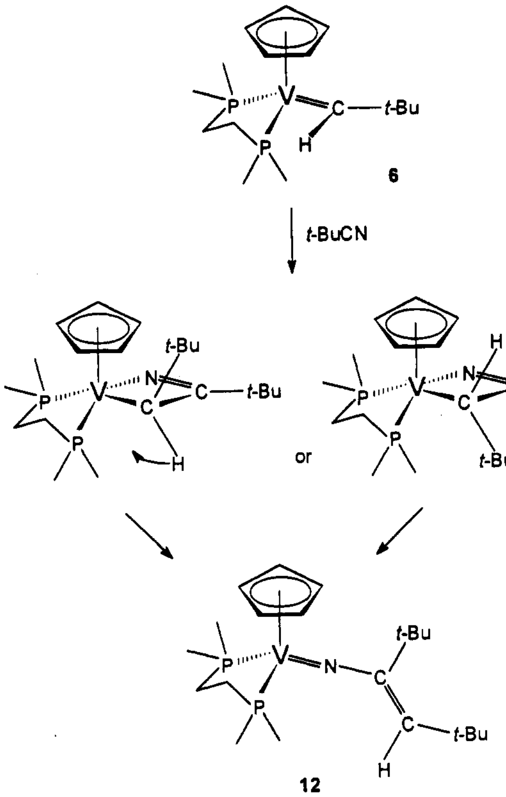
Scheme I



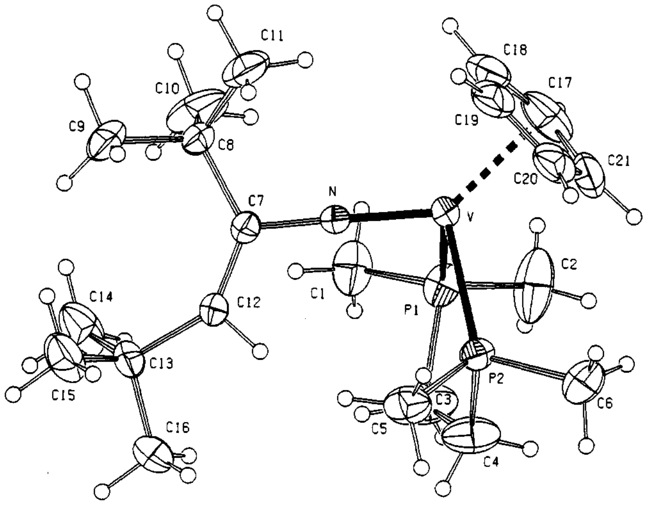


Figure 4. Molecular structure of CpV[$=$NC(CMe$_3$)$=$CHCMe$_3$]dmpe (12). Thermal ellipsoids are drawn at the 30% probability level.

172.5(2)°. The *t*-Bu substituents are clearly seen to have a *Z* geometry around the C$=$C bond. This geometry leads to a significant distortion, especially around C(12), as observed in the C(7)—C(12)—C(13) angle of 140.3(3)°.

One of the most interesting reactions catalyzed by transition metal alkylidene complexes is the ring-opening metathesis polymerization (ROMP) of cyclic olefins.[27a] The alkylidene complex 6 proved to be almost inactive as a ROMP catalyst: stirring 6 for 96 h with 75 equiv of norbornene (NBN) in benzene at 20 °C only produced a minor amount of poly(norbornene). When the bis(neopentyl) complex 2 was used in a similar experiment, significant polymerization activity was observed (24% of NBN recovered as poly-NBN). The poly-NBN produced had a *Z*:*E* ratio of 4.4:1 (as determined by ^{13}C NMR[34]). As 2 itself is not expected to be the active catalyst, the molecular weight distribution of the produced poly-NBN is expected to be broad, reflecting the formation of catalytically active species in the thermolysis of 2. It thus appears to be possible to catalyze ROMP of cyclic olefins with organovanadium species. The activity of the isolated alkylidene species 6 proved to be minimal, probably due to the combination of a relatively small metal center and the presence of a chelating diphosphine ligand.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for CpV[$=$NC(CMe$_3$)$=$CHCMe$_3$]dmpe (12)

V–P(1)	2.3467(12)	V–C(17)	2.289(6)
V–P(2)	2.3686(10)	V–C(18)	2.251(6)
V–N	1.707(2)	V–C(19)	2.239(4)
N–C(7)	1.387(4)	V–C(20)	2.253(4)
C(7)–C(12)	1.353(4)	V–C(21)	2.285(5)
C(7)–C(8)	1.545(4)	av (C–C)$_{Cp}$	1.374(8)
C(12)–C(13)	1.530(5)		
V–N–C(7)	172.46(19)	P(1)–V–P(2)	81.34(4)
N–C(7)–C(8)	113.5(2)	P(1)–V–N	90.57(7)
N–C(7)–C(12)	116.1(3)	P(2)–V–N	97.24(8)
C(8)–C(7)–C(12)	130.3(3)	C(7)–C(12)–C(13)	140.3(3)

Conclusions

In the thermolysis of paramagnetic monocyclopentadienylvanadium(III) dialkyl complexes we have observed three different hydrogen abstraction processes. When alkyl groups with β-hydrogens are available, β-hydrogen abstraction is a very rapid process, precluding the isolation of dialkyl complexes even at low temperatures. In the absence of alkyl β-hydrogens CpV^{III} dialkyl complexes with a varying degree of electronic unsaturation (16, 14, and 12 valence electrons) can be isolated. α-Hydrogen abstraction is a process that readily occurs in these complexes, although in the bis(neophyl) complex 3 orthometalation of the aryl group is preferred. Thermolysis of the bis(neopentyl) complex 2 provides the first synthetic route to a genuine vanadium alkylidene complex. Characterization of the alkylidene complex 6 and the monomeric imido complex 12 shows that vanadium(III) can exhibit metal–nonmetal multiple bonding. Although no stable active catalyst has been isolated, we have obtained evidence that vanadium alkylidene species can be catalytically active in the ring-opening metathesis polymerization of norbornene.

Experimental Section

General Details. All manipulations were performed under nitrogen (using Schlenk techniques or a glovebox) or using vacuum line techniques. Gas uptakes were determined with a Töpler pump connected to a vacuum line.[35] Solvents (diethyl ether, tetrahydrofuran (THF), toluene, pentane (mixed isomers), *n*-hexane, cyclohexane, benzene, and deuterated solvents except CDCl$_3$) were distilled from Na/K alloy before use. NMR spectra were recorded on a Varian VXR-300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz; ^{51}V, 78.9 MHz) spectrometer in benzene-d_6 at 20 °C (unless stated otherwise), chemical shifts in ppm, downfield from TMS (δ 0.00, ^{1}H, ^{13}C) or VOCl$_3$ (δ 0.00, ^{51}V) positive. IR spectra were recorded on a Pye-Unicam SP3-300 or a Mattson-4020 Galaxy FT-IR spectrophotometer, from Nujol mulls between KBr disks (unless stated otherwise). Elemental analyses were performed at the Microanalytical Department of the University of Gronin-

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gen. Values given are the average of at least two independent determinations.

1,[4] 9,[6a,b] LiCH$_2$CMe$_3$,[29] LiCH(SiMe$_3$)$_2$,[36] and NaN(SiMe$_3$)$_2$[37] were prepared according to published procedures. *n*-BuLi was purchased from Janssen. Grignard reagents were prepared from the corresponding alkyl halides. Me$_3$CCN was vacuum transferred and stored over molecular sieves (4 Å). dmpe was prepared starting from Me$_2$P(S)P(S)Me$_2$ according to ref 38. PMe$_3$ was prepared according to an adapted literature procedure,[39] using MeMgI instead of MeMgBr. Norbornene was distilled from sodium prior to use.

CpV(CH$_2$CMe$_3$)$_2$PMe$_3$ (2). Onto a mixture of CpVCl$_2$(PMe$_3$)$_2$ (1, 0.99 g, 2.9 mmol) and Me$_3$CCH$_2$Li (0.46 g, 5.9 mmol) was condensed 20 mL of pentane. The mixture was thawed out and allowed to warm to 0 °C with stirring. After stirring for 1 h at 0 °C, the yellow-green mixture was filtrated. The residue was extracted twice with 10 mL of pentane (0 °C). Concentrating and cooling the combined filtrate and extracts to −80 °C yielded 0.53 g (1.6 mmol, 54%) of green crystalline 2. ^{1}H NMR: δ −2.70 ($\Delta\nu_{1/2}$ = 265 Hz, 18H, CMe$_3$), −4.72 ($\Delta\nu_{1/2}$ = 377 Hz, 9H, PMe$_3$). IR (cm^{-1}): 3090 (vw), 2735 (w), 2690 (vw), 1418 (m), 1350 (s), 1302 (w), 1282 (m), 1230 (m), 1207 (w), 1122 (w), 1098 (vw), 1061 (w), 1010 (m), 950 (vs), 941 (sh), 844 (w), 806 (s), 788 (vs), 760 (vw), 752 (vw), 728 (m), 665 (w), 562 (w), 534 (w), 477 (w), 456 (vw). Anal. Calcd for C$_{18}$H$_{36}$VP: C, 64.65; H, 10.72. Found: C, 64.40; H, 10.72.

CpV(CH$_2$CMe$_2$Ph)$_2$PMe$_3$ (3). At 20 °C, 5.8 mL of a 0.61 M solution of PhMe$_2$CCH$_2$MgCl in ether was added dropwise in 5 min to a suspension of 1 (0.601 g, 1.77 mmol) in 15 mL of ether. The mixture was then cooled to 0 °C and stirred for 30 min. The solvent was pumped off at 0 °C and the residue stripped of residual ether by addition of 5 mL of pentane (0 °C) which was subsequently pumped off. The mixture was extracted with 30 mL of pentane at 0 °C. Concentrating and cooling the extract to −30 °C produced 0.361 g (0.79 mmol, 44%) of green-brown needles of 3. IR (cm^{-1}): 3085 (w), 3055 (w), 3020 (w), 2780 (w), 2725 (vw), 1594 (mw), 1572 (vw), 1486 (m), 1437 (m), 1418 (mw), 1354 (mw), 1304 (w), 1283 (m), 1270 (mw), 1182 (m), 1161 (mw), 1113 (w), 1104 (w), 1078 (w), 1059 (w), 1030 (m), 1010 (s), 956 (vs), 900 (w), 853 (vw), 837 (w), 799 (vs), 760 (vs), 693 (vs), 662 (vw), 584 (mw), 560 (m), 472 (mw). Anal. Calcd for C$_{28}$H$_{40}$VP: C, 73.34; H, 8.79; V, 11.11. Found: C, 72.96; H, 8.78; V, 11.28.

CpV[CH(SiMe$_3$)$_2$]$_2$ (4). Onto a mixture of 1 (0.26 g, 0.77 mmol) and LiCH(SiMe$_3$)$_2$ (0.24 g, 1.44 mmol) was condensed 20 mL of ether. The mixture was thawed out and allowed to warm to 0 °C with stirring. After 2 h the solvent was pumped off from the green mixture at 0 °C. The residue was extracted twice with 30 mL of pentane (0 °C) after which the pentane was pumped off. The resultant emerald green oil was dried in vacuo at 0 °C, yielding 0.30 g (0.69 mmol, 90%) of 4. ^{1}H NMR: δ 167.7 ($\Delta\nu_{1/2}$ = 4750 Hz, 5H, Cp), 8.78 ($\Delta\nu_{1/2}$ = 230 Hz, 36H, SiMe$_3$). IR (neat, cm^{-1}): 3100 (vw), 2945 (m), 2890 (mw), 2800 (vw), 2750 (vw), 1424 (mw), 1280 (w), 1240 (s), 1020 (mw), 988 (m), 960 (w), 836 (vs), 797 (s), 765 (m), 730 (mw), 680 (mw), 664 (mw), 648 (mw), 600 (sh), 595 (mw), 472 (w).

CpV[N(SiMe$_3$)$_2$]$_2$ (5). At 0 °C, 4.3 mL of a 0.40 M solution of NaN(SiMe$_3$)$_2$ in ether was added dropwise to a suspension of 1 (0.28 g, 0.84 mmol) in 18 mL of ether. After stirring for 1 h the solvent was pumped off, and the orange-brown mixture was extracted with pentane. As even from the strongly concentrated extract no crystals could be obtained (−80 °C), the pentane was pumped off, leaving an orange-brown solid which becomes sticky above 0 °C. Yield: 0.17 g (0.44 mmol, 52%) of 5, spectroscopically pure. ^{1}H NMR: δ 153.6 ($\Delta\nu_{1/2}$ = 3050 Hz, 5H, Cp), 15.20 ($\Delta\nu_{1/2}$ = 268 Hz, 36H, SiMe$_3$). IR (neat, cm^{-1}): 2955 (m), 2900 (mw), 2860 (sh), 1432 (w), 1260 (sh), 1248 (s), 1182 (vw), 1011 (mw), 920 (vs), 879 (s), 845 (vs), 808 (s), 780 (m), 759 (mw), 683 (m), 657 (s), 630 (mw), 433 (w), 386 (w).

CpV(CHCMe$_3$)dmpe (6). A solution of CpV(CH$_2$CMe$_3$)$_2$PMe$_3$ (2, 0.24 g, 0.72 mmol) and 0.2 mL of dmpe in 12 mL of toluene was heated at 60 °C for 2^1/$_2$ h. The solvent was pumped off and the brown solid extracted with 30 mL of pentane. Concentrating and cooling the extract to −80 °C yielded 0.17 g (0.50 mmol, 69%) of olive-brown crystalline 6. ^{1}H NMR: δ 4.82 (t, J_{PH} = 1.8 Hz, 5H, Cp), 1.44 (m, 2H, PCH$_2$), 1.41 (ps t, 6H, PMe), 1.27 (m, 2H, PCH$_2$), 1.20 (s, 9H, CMe$_3$), 0.67 (ps t, 6H, PMe), −7.76 ($\Delta\nu_{1/2}$ = 780 Hz, 1H, V=CH−). ^{13}C NMR: δ 19.1 (q, 127 Hz, PMe), 27.3 (q, 126 Hz, PMe), 33.3 (t, 130 Hz, PCH$_2$), 33.6 (q, 126 Hz, C(CH_3)$_3$), 46.2 (br s, CMe$_3$), 89.1 (d, 170 Hz, Cp), 259.7 ($\Delta\nu_{1/2}$ = 780 Hz, V=C). ^{51}V NMR (21 °C): δ −285.4 (t, J_{PV} = 329 Hz). IR (cm^{-1}): 3090 (w), 2790 (vw), 1409 (m), 1342 (mw), 1283 (w), 1271 (m), 1248 (mw), 1180 (w), 1100 (mw), 1049 (w), 1000 (mw), 988 (mw), 921 (vs), 894 (mw), 880 (mw), 847 (vw), 822 (mw), 775 (s), 708 (mw), 676 (mw), 615 (mw), 610 (sh), 445 (w), 423 (w), 400 (w). Anal. Calcd for C$_{16}$H$_{31}$VP$_2$: C, 57.14; H, 9.29; V, 15.15. Found: C, 56.90; H, 9.22; V, 15.27.

CpV(CH$_2$CMe$_2$C$_6$H$_4$)(PMe$_3$)$_2$ (7). A solution of 3 (0.110 g, 0.24 mmol) in 3 mL of pentane, to which 0.5 mL of PMe$_3$ was added, was allowed to stand at 20 °C for 16 h, after which a greenish microcrystalline precipitate had formed. The mother liquor was decanted and the solid washed with cold (−80 °C) pentane. Yield: 0.053 g (0.133 mmol, 55%) of 7. IR (cm^{-1}): 3090 (vw), 3025 (m), 2775 (vw), 1560 (vw), 1418 (m), 1358 (w), 1340 (w), 1300 (mw), 1282 (m), 1009 (mw), 945 (vs), 817 (mw), 795 (s), 728 (s), 715 (m), 662 (w). Anal. Calcd for C$_{21}$H$_{35}$VP: C, 62.99; H, 8.81; V, 12.72. Found: C, 62.98; H, 8.84; V, 13.31.

[CpV(CH$_2$CMe$_2$C$_6$H$_4$)]$_2$ (8). A solution of 3 (0.227 g, 0.49 mmol) in 5 mL of cyclohexane was allowed to stand at 20 °C for 18 h. The solution was evacuated occasionally to pump off the PMe$_3$ released during the reaction. The solvent was pumped off and 4 mL of ether was added to the resultant red-brown oil. Slowly, small red-brown crystals of 8 precipitated. Yield: 0.065 g (0.13 mmol, 53%). IR (cm^{-1}): 3050 (vw), 3035 (w), 1566 (w), 1545 (vw), 1444 (m), 1367 (mw), 1351 (mw), 1274 (w), 1235 (m), 1087 (m), 1026 (sh), 1014 (m), 1000 (w), 792 (vs), 761 (s), 727 (mw), 560 (mw), 474 (mw). Anal. Calcd for C$_{30}$H$_{34}$V$_2$: C, 72.58; H, 6.90. Found: C, 71.52; H, 6.78. The carbon content was low due to the presence of an impurity of the PMe$_3$ complex 7.

CpV(CH$_2$=CHEt)(PMe$_3$)$_2$ (10). To a suspension of 9 (0.59 g, 1.85 mmol) in 20 mL of pentane was added dropwise at −80 °C 0.75 mL of a 2.5 M *n*-BuLi/hexane solution. The mixture was allowed to warm to 0 °C and stirred for an additional 1 h at this temperature. The green solution was subsequently filtered and concentrated. Cooling the solution to −80 °C produced green crystalline 10 (0.30 g, 0.93 mmol, 50%). ^{1}H NMR: δ 162 ($\Delta\nu_{1/2}$ = 2400 Hz, 5H, Cp), 13.75 ($\Delta\nu_{1/2}$ = 280 Hz, 18 H, PMe$_3$), −4.88 ($\Delta\nu_{1/2}$ = 75 Hz, 3H, CH$_2$=CHCH$_2$$CH_3$), −61 ($\Delta\nu_{1/2}$ = 1400 Hz, CH$_2$=CHCH_2CH$_3$). IR (cm^{-1}): 3095 (w), 1446 (m), 1421 (s), 1340 (w), 1298 (m), 1280 (s), 1221 (vw), 1149 (s), 1114 (sh), 1051 (vw), 1010 (m), 1003 (m), 950 (vs), 939 (vs), 885 (w), 862 (w), 835 (w), 821 (w), 792 (m), 769 (s), 715 (s), 661 (s), 543 (w). Anal. Calcd for C$_{15}$H$_{31}$P$_2$V: V, 15.71; C, 55.55; H, 9.63. Found: V, 16.01; C, 54.94; H, 9.53.

CpV[NC(CMe$_3$)=CHCMe$_3$]dmpe (12). A solution of 6 (0.196 g, 0.585 mmol) and Me$_3$CCN (70 μL, 0.63 mmol) in 8 mL of benzene was stirred at 60 °C for 4 days. After evaporation of the solvent, the solid was extracted twice with 7 mL of pentane. Cooling the extract to −30 °C yielded 0.140 g of green crystalline 12 in two crops (0.33 mmol, 57%). ^{1}H NMR: δ 5.62 (s, 1H, =CH−), 4.90 (t, J_{PH} = 2.2 Hz, 5H, Cp), 1.87 (m, 2H, PCH$_2$), 1.48 (ps t, 6H, PMe), 1.30 (s, 9H, CMe$_3$), 1.24 (s, 9H, CMe$_3$), 1.10 (m, 2H, PCH$_2$), 0.57 (ps t, 6H, PMe). ^{13}C NMR (cyclohexane-d_{12}, 20 °C): δ 18.7 (br q, 126 Hz, all PMe), 31.3 (s, CMe$_3$), 31.9 (s, CMe$_3$), 32.1 (q, 128 Hz, CMe_3), 32.5 (t, 126 Hz, PCH$_2$), 34.0 (q, 126 Hz, CMe_3), 92.7 (d, 172 Hz, Cp), 128.1 (d, 145 Hz, =CH−), C—N not observed. ^{51}V NMR: δ −64.4 (t, J_{PV} = 269 Hz). IR (cm^{-1}): 3100 (vw), 1532 (mw), 1420 (m), 1364 (vw), 1356 (m), 1290 (mw), 1277 (m), 1256 (s), 1213 (s), 1200 (sh), 1180 (s), 1107 (mw), 1064 (vw), 1034 (w),

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Table V. Crystallographic Data for 6, 7, 8, and 12

	6	7	8	12
formula	$C_{16}H_{31}P_2V$	$C_{21}H_{35}P_2V$	$C_{30}H_{34}V_2$	$C_{21}H_{40}NP_2V$
fw	336.31	400.40	496.48	419.44
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	13.699(2)	9.671(2)	9.812(9)	9.147(1)
b, Å	8.966(1)	14.261(4)	14.019(10)	11.005(1)
c, Å	15.386(2)	8.528(2)	17.407(10)	13.489(1)
α, deg		94.89(2)		71.93(1)
β, deg	101.87(1)	110.55(2)	96.76(6)	89.70(1)
γ, deg		77.78(2)		69.56(1)
V, Å^3	1849.4(4)	1076.3(5)	2378(3)	1201.5(2)
Z	4	2	4	2
d_{calcd}, g cm^{-3}	1.208	1.24	1.39	1.159
F(000), e	720	428	1040	452
μ(Mo Kα), cm^{-1}	6.8	5.93	7.76	5.3
cryst size, mm	0.10 × 0.12 × 0.14	0.30 × 0.30 × 0.15	0.11 × 0.11 × 0.30	0.25 × 0.38 × 0.38
T, K	130	150	150	300
θ limits, deg	$1.35 \le \theta \le 27.0$	$1.75 \le \theta \le 25.0$	$1.75 \le \theta \le 25.0$	$1.6 \le \theta \le 27.5$
no. of data collcd	5025	4029	4646	6723
no. of unique data	4029	3782	4377	5498
no. of rflns obsd	2651	2515	2543	4027
no. of params refined	276	357	425	260
R(*F*)	0.053	0.033	0.045	0.047
$R_w(F)$	0.050	0.037	0.054	0.051
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$

1009 (w), 991 (mw), 932 (vs), 902 (vw), 889 (mw), 856 (vw), 825 (m), 785 (s), 754 (w), 739 (vw), 723 (s), 691 (s), 652 (w), 624 (s), 575 (vw), 446 (w).

Preparation of Poly(norbornene) with 6 and 2. 6 (39 mg, 0.12 mmol) or 2 (94 mg, 0.28 mmol) was dissolved in 3 mL of 3.04 M (9.12 mmol) norbornene in benzene. The solution was stirred for 96 h at 20 °C and then poured into 15 mL of methanol with vigorous stirring. The precipitated polymer was filtered off and dried in vacuo. Yields: 10 mg (0.11 mmol, 1%) and 210 mg (2.23 mmol, 24%) of poly(norbornene) for 6 and 2, respectively.

X-ray Structure Determinations of 6, 7, 8, and 12. Pertinent crystal data and data collection parameters can be found in Table V. Crystals suitable for X-ray diffraction were grown as follows: 6, by cooling a pentane solution from +20 to −25 °C at 3 °C/h (twinned crystal plates, from which a suitable single crystal fragment was cut); 7, directly from a synthetic procedure as described above; 8, by diffusion of pentane vapor into a toluene solution at ambient temperature; 12, by cooling a pentane solution from 0 to −30 °C in 2 h.

For 6 a crystal was transferred by inert atmosphere handling techniques directly into the cold nitrogen stream mounted on an Enraf-Nonius CAD-4F diffractometer. Lattice parameters were determined from the angular settings of 22 reflections in the range 12.90° < θ < 18.59°. The space group was derived from the observed systematic absences and checked for the presence of higher metrical symmetry.[40] The monitoring of three standard reflections during the data collection showed no significant decay of the crystal. The net intensities of the data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86)[41] and refined on *F* by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Difference Fourier synthesis gave 28 hydrogen atoms (including the alkylidene α-H), and the remaining hydrogen atoms were initially included in calculated positions. These were refined riding on their carrier atom with a C–H distance of 1.0 Å. In the final difference Fourier the highest residuals were 1.24 and 0.73 e/Å^3, each located near a phosphorus site. Neutral scattering factors are those of ref 42, corrected for anomalous dispersion.[43] All calculations were carried out on a CDC-Cyber 170/760 with the program packages XTAL,[44] EUCLID[45] (calculation of geometric data), and ORTEP[46] (preparation of illustrations).

For 7 a crystal was sealed in a thin-walled capillary and mounted on a Rigaku AFC6R diffractometer, equipped with a 12-kW rotating anode generator. Lattice parameters were obtained from the setting angles of 25 reflections in the range 19.25° < θ < 24.35°. The monitoring of three standard reflections during data collection showed no significant decay of the crystal. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRIL)[47] and refined on *F* by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located from a difference Fourier map and refined with isotropic temperature factors. Atomic scattering factors and anomalous dispersion corrections were taken from ref 48. A final difference Fourier map showed maximum and minimum residual densities of +0.36 and −0.22 e/Å^3, respectively. All calculations were carried out with the TEXSAN program system,[49] and illustrations were drawn with ORTEP.[46]

For 8 a crystal was sealed in a thin-walled capillary and mounted on a Rigaku AFC6R diffractometer, equipped with a 12-kW rotating anode generator. Lattice parameters were obtained from the setting angles of 20 reflections in the range 19.7° < θ < 20.0°. The monitoring of three standard reflections during data collection showed no significant decay of the crystal. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRIL)[47] and refined on *F* by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located from a difference Fourier map and refined with isotropic temperature factors. Atomic scattering factors and anomalous dispersion corrections were taken from ref 48. A final difference Fourier map showed maximum and minimum residual densities of +0.45 and −0.43 e/Å^3, respectively. All calculations were carried out with the TEXSAN program system,[49] and illustrations were drawn with ORTEP.[46]

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For **12** a crystal was sealed in a thin-walled capillary and mounted on an Enraf-Nonius TurboCAD4 diffractometer equipped with a rotating anode generator. Lattice parameters were obtained from the setting angles of 25 reflections in the range $11.0° < \theta < 14.0°$. The monitoring of three standard reflections during the data collection showed a 5% linear decay of the intensity, for which a correction was applied. Intensity data were corrected for Lorentz and polarization effects and absorption (DIFABS,[50] corrections 0.75:1.10). The structure was solved by direct methods (SHELXS86)[41] and refined by full-matrix least-squares techniques on F by SHELX76.[51] Hydrogen atoms were accounted for at calculated positions with three common isotropic thermal parameters. A final difference Fourier map showed maximum and minimum residual densities of +0.59 and −0.42 e/Å^3, respectively. Neutral scattering factors are those of ref 42, corrected for anomalous dispersion.[43] Derived geometry calculations and the thermal motion ellipsoid plot were done with PLATON.[52] All calculations were carried out on a DEC5000/ULTRIX system.

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Supplementary Material Available: Textual presentation of the full details of structure determinations and tables of positional and thermal parameters and bond distances and angles for **6**, **7**, **8**, and **12** (40 pages). Ordering information is given on any current masthead page.

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