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(CH₂CMe₃)₂(PMe₃) (14 electron, R = Me (2), Ph (3)) and CpV(CH(SiMe₃)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(CHCMe₃)₂(dmpe) (6), which has been structurally characterized. In contrast, 3 decomposes in the presence of excess PMe₃ through orthometalation of the aryl substituent to give the metallacycle complex CpV(=C=CH₂)(PMe₃) (7). In the absence of excess PMe₃ the (μ-alkyl)(μ-aryl) dimer [CpV(μ₂-CH₂CMe₂H₄)₂]₈ (8) is formed, with a short (2.313(2) Å) metal-metal distance. Reaction of CpV(Me)Cl(PMe₃)₂ (9) with n-BuLi produces the 1-butene complex CpV(=CH₂)(PMe₃) (10) through β-hydrogen abstraction and reductive elimination. Reactivity of the alkylidene complex 6 has been focused on the bis(cyclopentadienyl) systems Cp₂VX and Cp₂*VX (X = halide, alkyl, aryl, allyl, H; Cp* = τ-C₅H₅Me), although some homoleptic complexes, such as V[CH(SiMe₃)₂]₃ and VMes₃·THF (Mes = 2,4,6-trimethylphenyl)² have also been synthesized. Some of these complexes tend to have a paramagnetic high-spin d² (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 CpVCl₂(PMe₃)₂ (14) 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 and alkyne⁹ complexes. Both the observed thermolysis behavior of CpVMe₂(PMe₃) 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 conditions.
Results and Discussion

Synthesis. The 16-electron dialkyl complex CpVMes2(PMe3)2 acts in most of its reactivity as an electronically saturated system. The high-spin d5 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 CpVIII dialkyl complexes that are more electron deficient.

Reaction of CpVC12(PMe3)2 (1) with 2 mol of neopen-tyllithium in pentane or neophylmagnesium chloride (MgMe2Ph2C(CH3)2MgCl) in diethyl ether at −10 to 0 °C affords crystalline 14-electron complexes CpV(CH2CMes2R)2PMe3 (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 CMes and PMe3 protons at δ = 2.70 and ~4.72 ppm, respectively. Attempts at an X-ray structure determination of 2 were hampered by twinning problems.

Phosphine-free complexes are obtained when extremely large ligands are introduced. Reaction of 1 with 2 mol of LICH(SiMes3)2 produces the 12-electron species CpVCH(SiMes3)2PMe3 (4) as a green oil (eq 2). The absence of PMe3 ligands was established by the lack of characteristic PMe3 vibrations in the IR spectrum of 4. The 1H NMR spectrum shows the Cp and SiMes3 protons at δ 167.7 and 8.78 ppm, respectively, in a 5 to 36 ratio. Through an analogous procedure using NaN(SiMes3)2 the bis(amido) complex Cp-VIN(SiMes3)2L2 (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.

Thermolysis of CpV(CH2CMes2)2PMe3. 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 complexes13 are of the electrophilic ("Fischer") type, with the carbene moiety :C(R)X (R = OR, OR2) having Lewis-base type character toward the metal center.14 However, the intriguing complex (η3-C5Me5)V(C=C=ZrCp2)9a 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(CHOCH2)dmpe (6, eq 3).

\[
\text{CpV(CH2CMes2)2PMe3 + dmpe} \rightarrow \text{2} \\
\text{CpV(CHOCH2)dmpe + CMe3 + PMe3} \quad (3)
\]

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 Cp(V(CO)5)(=C(OR)Cp2)ZrCp16 and is indicative of a true alkylidene species. In the "bent metallacyclopentatriene" complex Cp(C5Me5)2Pd(CO)2 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(u-


to a metal in a relatively low oxidation state, yet still species.

The alkylidene a-hydrogen in the lH NMR spectrum appears to be frozen in an intermediate stage, and in its remarkably well-resolved 11V NMR spectrum of Ta(CHCMe3)(dpme)2.16 In the case of 6 the complex is shown at 60% probability level.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for CpV(CHCMe3)dmpe (6)

<table>
<thead>
<tr>
<th>Distance/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)-C(12)</td>
<td>1.809(3)</td>
</tr>
<tr>
<td>V(1)-P(1)</td>
<td>2.363(1)</td>
</tr>
<tr>
<td>V(1)-P(2)</td>
<td>2.331(1)</td>
</tr>
<tr>
<td>V(1)-H(121)</td>
<td>1.66(5)</td>
</tr>
<tr>
<td>C(12)-H(121)</td>
<td>1.05(5)</td>
</tr>
<tr>
<td>C(12)-C(12)</td>
<td>1.510(4)</td>
</tr>
<tr>
<td>P(1)-V(1)-P(2)</td>
<td>79.48(5)</td>
</tr>
<tr>
<td>P(1)-V(1)-C(12)</td>
<td>99.4(1)</td>
</tr>
<tr>
<td>C(13)-C(12)-H(121)</td>
<td>113(3)</td>
</tr>
<tr>
<td>P(2)-V(1)-C(12)</td>
<td>91.5(1)</td>
</tr>
</tbody>
</table>

The 1H NMR spectrum of 6 shows a triplet for the Cp resonances in the 1H NMR spectrum suggest a 1:3 ratio for the two products. The minor product can be identified as the alkylidene species CpV(CHCMe3)PMe3 (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 (JVP = 2.8 Hz), the broad alkylidene proton resonance is observed at δ ~5.7 ppm and the 11V NMR spectrum shows a triplet at δ ~1328 ppm (JVP = 223 Hz). No coupling with phosphorus atoms is apparent on the Cp proton resonance of the major product. In the 11V NMR spectrum it exhibits a broad resonance at δ ~22 ppm (Δν1/2 = 5320 Hz). When 2 is thermolysed in the presence of excess PMe3 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.

Thermalysis of CpV(CH2CMe3Ph)2PMe3. The neophyl complex 3 decomposes readily in solution at ambient temperature. In the presence of excess PMe3 a green paramagnetic crystalline solid is produced, which was characterized by X-ray diffraction as the metallacyclic complex CpV(η2-CH2CMe3C6H4)(PMe3)2 (7, eq 4). The structure of 7 is shown in Figure 2, and pertinent bond distances and angles are given in Table II.

CpV(CH2CMe3Ph)2PMe3 + PMe3 → 3
CpV(CH2CMe3C6H4)(PMe3)2 + PhCMe3 (4)

The metal atom in 7 is to first approximation square pyramidal, coordinated, with the PMe3 ligands in cis position. The arrangement of the ligands in the basal


(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.
The formation of this cyclometalated product indicates that in the CpVR(PMe3) system orthometalation of the aryl group in the bis(neophy1) complex is preferred for both dialkyl and Ph2VN(CH2CH2NEt2) complexes. The V-P distances of VM(C5H5)S2STHF

\[ 8.06 \text{ and } 8.02 \text{ A} \], respectively. The vanadium-aryl carbon bond length is somewhat longer (by 0.06 and 0.02 A, respectively) than the average vanadium-carbon bond lengths reported for VMes2THF3b and Ph2VN(C2H4NEt2)2.18 The V-P distances of 2.516(1)/2.544(1) A in this paramagnetic high-spin V(III) complex are significantly longer than those found in the diamagnetic low-spin alkyldene complex 6 and are comparable to those found in 16-electron high-spin complexes like CpV(q2-C2H4)(PMe2)2 and CpV(q4-CH2SiMe2Ph). 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.

Thermolysis of 3 in solution in the absence of extra PMe3 produces a brown solution from which red-brown crystals were obtained. The IR spectrum of this material PMe3 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 PMe3 (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(q2-CH2SiMe2Ph)2] (8, eq 5). The structure of 8 plane of the pyramid is somewhat twisted to allow suitable packing of the asymmetric σ2-CH3CMe2C6H4 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), respectively. The vanadium-aryl carbon bond length is somewhat longer (by 0.06 and 0.02 A, respectively) than the average vanadium-carbon bond lengths reported for VMes2THF3b and Ph2VN(C2H4NEt2)2.18 The V-P distances of 2.516(1)/2.544(1) A in this paramagnetic high-spin V(III) complex are significantly longer than those found in the diamagnetic low-spin alkyldene complex 6 and are comparable to those found in 16-electron high-spin complexes like CpV(q2-C2H4)(PMe2)2 and CpV(q4-CH2SiMe2Ph). 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.

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\[
\begin{align*}
\text{Table II. Selected Interatomic Distances (Å) and Angles (deg) for CpV(q2-CH2CMe2C6H4)(PMe3)}_2 (7) \\
V-P(1) & 2.516(1) & V-C(17) & 2.341(3) \\
V-P(2) & 2.544(1) & V-C(18) & 2.346(3) \\
V-C(7) & 2.194(3) & V-C(19) & 2.316(3) \\
V-C(16) & 2.170(3) & V-C(20) & 2.300(3) \\
C(7)-C(8) & 1.526(4) & V-C(21) & 2.320(4) \\
C(8)-C(11) & 1.521(4) & C(11)-C(12) & 1.388(4) \\
C(12)-C(13) & 1.383(5) & C(13)-C(14) & 1.376(3) \\
C(14)-C(15) & 1.381(5) & C(15)-C(16) & 1.412(4) \\
C(11)-C(16) & 1.418(4) & av (C-C) & 1.399(5) \\
\end{align*}
\]

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C(11)-C(16) & 1.418(4) & av (C-C) & 1.399(5) \\
\end{align*}
\]

The asterisk denotes an atom related by a center of symmetry.

\[
\begin{align*}
V(2)-V(2^*) & 2.213(3) & V(2)-C(16) & 2.330(5) \\
V(2)-C(21) & 2.213(3) & V(2)-C(17) & 2.330(5) \\
V(2)-C(21^*) & 2.276(5) & V(2)-C(18) & 2.349(6) \\
V(2)-C(30) & 2.209(6) & V(2)-C(19) & 2.342(5) \\
V(2)-C(30^*) & 2.212(6) & V(2)-C(20) & 2.335(5) \\
C(21)-C(21) & 1.387(7) & C(21)-C(26) & 1.417(7) \\
C(22)-C(22) & 1.391(8) & C(21)-C(26) & 1.417(7) \\
C(24)-C(25) & 1.356(9) & C(25)-C(26) & 1.397(9) \\
C(26)-C(27) & 1.506(8) & C(27)-C(30) & 1.543(7) \\
av (C-C) & 1.400(8) \\
\end{align*}
\]

Table III. Selected Interatomic Distances (Å) and Angles (deg) for CpV(q2-CH2CMe2C6H4)(PMe3)2 (8)*

\[
\begin{align*}
V(2)-V(2^*) & 2.313(2) & V(2)-C(16) & 2.327(5) \\
V(2)-C(21) & 2.213(3) & V(2)-C(17) & 2.330(5) \\
V(2)-C(21^*) & 2.276(5) & V(2)-C(18) & 2.349(6) \\
V(2)-C(30) & 2.209(6) & V(2)-C(19) & 2.342(5) \\
V(2)-C(30^*) & 2.212(6) & V(2)-C(20) & 2.335(5) \\
C(21)-C(21) & 1.387(7) & C(21)-C(26) & 1.417(7) \\
C(22)-C(22) & 1.391(8) & C(21)-C(26) & 1.417(7) \\
C(24)-C(25) & 1.356(9) & C(25)-C(26) & 1.397(9) \\
C(26)-C(27) & 1.506(8) & C(27)-C(30) & 1.543(7) \\
av (C-C) & 1.400(8) \\
\end{align*}
\]

* Data for one of the independent molecules in the unit cell only.

The unit cell contains two crystallographically independent molecules only. The asterisk denotes an atom related by a center of symmetry.

\[
2\text{CpV(CH2CMe2Ph)2PMe3} \rightarrow \]

\[
[\text{CpV(q2-CH2CMe2C6H4)}]_2 + 2\text{PhPMes} + 2\text{PMe3} \]

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.
(2.209(6) and 2.312(6) Å for the alkyl carbon C(30) and 2.213(6) and 2.276(6) Å for the aryl carbon C(21), respectively). The structure of 8 is strongly related to the (µ-alkyl)₄ complex [CPV(µ₂-C₅H₄)₂] reported by Jonas et al. A subtle difference is found in the bonding asymmetry of the bridging ligands: in 8 each µ² ligand has either two long or two short distances to the same V atom, whereas in [CPV(µ₂-C₅H₄)₂] each µ² ligand has two V atoms 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 contains @-CH bonds has been unsuccessful so far.

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

Formation of CPV(α²-CH₂=CHEt)(PMε₃)₂. The synthesis of CPV(III) dialky1 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 CPV(α²-C₆H₄)(PMε₃)₂ (20) or the V(II) compound CPVC(1)(PMε₃)₂ (21) when less than 2 equiv of Grignard reagent are used. A likely explanation is that rapid β-hydrogen elimination takes place in the CPVE(1)(PMε₃)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), followed by reductive elimination of ethane to yield low-valent species.

This hypothesis was investigated by the reaction of the mixed methyl-chloride complex CPV(Me)Cl(PMε₃₂) with n-BuLi. In a rapid reaction a green solution was formed from which the green V(I) 1-butene complex CPV(α²-CH₂=CHEt)(PMε₃)₂ (10) was obtained in a moderate yield (eq 6).

\[
\text{CPV(Me)Cl(PMε₃₂) + n-BuLi \rightarrow CPV(α²-CH₂=CHEt)(PMε₃)₂ + CH₄ + LiCl}
\]

The compound was characterized by elemental analysis and IR and ¹H NMR spectroscopy. When a solution of 10 in benzene-d₆ is exposed to CO, a rapid reaction forming free 1-butene and diamagnetic CPV(CO)₂(PMε₃)₂ is observed (NMR, eq 7).

\[
\text{CPV(α²-CH₂=CHEt)(PMε₃)₂ + 2CO \rightarrow CPV(CO)₂(PMε₃)₂ + CH₂=CHEt}
\]

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. As the new vanadium(III) alkylidene complexes CPV(CHMe₃)dmpe (6) and CPV(CHMe₃)(PMε₃)₂ (6b) are the first examples of nucleophilic alkylidenes for this element, and are rare examples of 3d-metal alkylidenes (CPV1(CHR)PR₃ forms the other available class), 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 CPV[=NC(CMe₃)=CHCMe₃]dmpe (12, eq 8).

\[
\text{CPV(CHMe₃)dmpe + Me₃CC=NN \rightarrow CPV(=NC(CHMe₃)=CHCMe₃)dmpe}
\]

This type of reaction has been observed before by Schrock and co-workers with (CHMe₂CH₂)₂Ta(=CHCMe₃) and CPV(=NC(CMe₃)=CHCMe₃)Cl, 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. 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 1). 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) and similar to those found in the comparatively electron rich V(IV) bis(pentamethyldiencyl) systems CP₅V(NR) (R = Ph, 1.750(5) Å, C₆H₅, 1.707(6) Å). The V-N-C(7) angle is

---

The alkylidene complex metathesis polymerization (ROMP) of cyclic transition metal alkylidene complexes is the ring-opening pentyl complex significant polymerization activity was observed (24% of minor amount of poly(norbomene). When the bis(neopenty1 norbornene (NBN) in benzene at 20 °C only produced a ROMP catalyst: stirring 6 for 96 h with 75 equiv of NBN recovered a ROMP catalyst.

A 2 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. 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(norbomene). When the bis(neopenty1) 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 13C NMR). 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.

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 CpVII 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(neophyl) 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 vacuum pump connected to a vacuum line. Solvents (diethyl ether, tetrahydrofuran (THF), toluene, pentane (mixed isomers), n-hexane, cyclohexane, benzene, and deuterated solvents except CDC13 were distilled from Na/K alloy before use. NMR spectra were recorded on a Varian VXR-300 (1H, 300 MHz; 13C, 75.4 MHz; 11V, 78.9 MHz) spectrometer in benzene-d6 at 20 °C (unless stated otherwise), chemical shifts in ppm, downfield from TMS (δ 0.00, 1H, 13C) or VOCl3 (δ 0.00, 11V) 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 Groningen.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for CpV[=NC(CMes)]=CHCMes]dmpe (12)

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Distance Å</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V—P(1)</td>
<td>2.3467(12)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>V—P(2)</td>
<td>2.3856(10)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>V—C(17)</td>
<td>2.3856(10)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>V—C(18)</td>
<td>2.3856(10)</td>
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<tr>
<td>V—N</td>
<td>1.707(2)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>N—C(7)</td>
<td>1.387(4)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>C(7)—C(12)</td>
<td>1.353(4)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>C(7)—C(8)</td>
<td>1.545(4)</td>
<td>172.46(19)</td>
</tr>
<tr>
<td>C(12)—C(13)</td>
<td>1.530(5)</td>
<td>172.46(19)</td>
</tr>
</tbody>
</table>

were prepared according to published procedures. n-BuLi was starting from MelP(S)P(S)Me* according to ref 38. PMes was inferred and stored over molecular sieves (4A). dmpe was prepared from the corresponding alkyl halides. MesCCN was vacuum transferred and 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 filtered. The residue was extracted twice with 10 mL of ether by addition of 5 mL of pentane at 0 °C. The residue was extracted twice with 10 mL of pentane (0 °C), which was allowed to stand at 0 °C for 16 h, after which a greenish microcrystalline precipitate had formed. The mother liquor was decanted and the solid washed with cold (−20 °C) pentane. Yield: 0.053 g (0.133 mmol, 55%) of 4. 'H NMR: δ 5.62 (s, 1H, −CH−), 2.2 Hz, 5H, Cp), 1.87 (m, 2H, PCHn), 1.48 (m, 2H, PMe), 1.30 (m, 12H, 1,2,2,6,6-pentamethylpiperidin). IR (cm−1): 3095 (w), 2945 (vw), 2890 (vw), 2860 (vw), 2750 (vw), 1424 (mw), 1280 (w), 1240 (a), 1020 (mw), 988 (m), 960 (w), 836 (s), 797 (e), 765 (m), 730 (mw), 680 (mw), 644 (mw), 649 (mw), 676 (mw), 472 (mw). Anal. Calcd for C18H19VP: C, 75.34; H, 7.57; V, 11.11. Found: C, 72.96; H, 7.87; V, 11.38.

CpV(ChMe3)2Ph)2PMe3 (5). At 20 °C, 5.8 mL of a 0.61 M solution of PhMe2CH2Cl 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 90 min. The solvent was removed to −30 °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 (vw), 3020 (w), 2790 (vw), 2725 (vw), 1594 (mw), 1572 (vw), 1486 (m), 1457 (m), 1418 (mw), 1354 (mw), 1304 (w), 1285 (m), 1270 (mw), 1182 (mw), 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 (va), 693 (va), 662 (vw), 584 (mw), 660 (w), 472 (mw). Anal. Calcd for C26H22V2: C, 74.52; H, 6.82; V, 15.67. Found: C, 74.26; H, 6.87; V, 15.88.

CpV[Ch(Me)2CH2]2PMe3 (6). A solution of CpV(ChMe3)2PhPMe3 (2, 0.24 g, 0.72 mmol) and 0.2 mL of dmpe in 12 mL of toluene was heated at 80 °C for 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. 'H NMR: δ 8.42 (t, JFp = 1.8 Hz, 5H, Cp), 1.44 (m, 2H, PCH2), 1.41 (ps t, 6H, PMe), 1.27 (m, 2H, PCH2), 1.20 (a, 9H, CMes), 0.67 (ps t, 6H, PMe), −7.76 (Δν1/2 = 780 Hz, 1H, V = CH−). 31P NMR: δ 13.1 (q, 127 Hz, PMe), 27.3 (q, 126 Hz, PMe), 33.3 (t, 130 Hz, PCH3), 33.6 (q, 126 Hz, C(CH3)2), 46.2 (br s, CMes), 89.1 (d, 170 Hz, Cp), 258.7 (Δν1/2 = 780 Hz, V = C). 31V NMR (21°C): δ −285.4 (t, JFP = 329 Hz). IR (cm−1): 3090 (w), 2790 (vw), 1409 (m), 1342 (mw), 1283 (w), 1271 (m), 1248 (mw), 1180 (w), 1104 (w), 1049 (w), 1000 (mw), 988 (mw), 921 (w), 894 (mw), 880 (vw), 847 (vw), 822 (a, 775 (s), 708 (w), 676 (w), 615 (w), 610 (sh), 446 (w), 425 (w), 400 (w). Anal. Calcd for C26H23VP: C, 75.14; H, 9.28; V, 15.15. Found: C, 56.90; H, 9.22; V, 15.27.

CpV(CHMe3)2C6H5 (PMes2)3 (7). A solution of 3 (0.110 g, 0.24 mmol in 5 mL of pentane, to which 0.5 mL of PMes2 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 (−20 °C) pentane. Yield: 0.065 g (0.133 mmol, 55%) of 7. IR (cm−1): 3090 (w), 3025 (vw), 2775 (vw), 1560 (vw), 1418 (m), 1358 (w), 1340 (w), 1300 (mw), 1282 (w), 1099 (w), 945 (vw), 817 (mw), 785 (a), 728 (e), 715 (m), 662 (w). Anal. Calcd for C26H23VP: C, 72.58; H, 6.84; V, 15.38. Found: C, 72.52; H, 6.87. The carbon content was low due to the presence of an impurity of the PMes complex 7.

CpV(CPh2)(CHMe3)PMe3 (8). A solution of 1 (0.110 g, 0.24 mmol) in 10 mL of toluene was heated at 80 °C for 2 h. The solution was evaporated occasionally to pump off the PMes 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), 1666 (w), 1545 (vw), 1444 (m), 1387 (mw), 1351 (mw), 1274 (w), 1235 (w), 1087 (w), 1026 (sh), 1014 (m), 1000 (w), 792 (w), 761 (s), 727 (m), 560 (w), 474 (mw). Anal. Calcd for C26H23VP: C, 72.58; H, 6.90. Found: C, 71.82; H, 6.78. The carbon content was low due to the presence of an impurity of the PMes complex 7.

CpV[Cp2(Me)2CH2]2PMe3 (9). A solution of 1 (0.28 g, 0.55 mmol) in 20 mL of ether was added dropwise to a suspension of 1 (0.50 mmol, 69%) in 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 20 mL of pentane. The mixture was thawed out and allowed to warm to 0 °C with stirring. After stirring for 1 h the solvent 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. 31P NMR: δ 185.3 (Δν1/2 = 9300 Hz, 5H, Cp), 15.20 (Δν1/2 = 289 Hz, 1H, PMes). IR (cm−1): 2965 (m), 2900 (mw), 2890 (sh), 1492 (w), 1290 (sh), 1248 (s), 1192 (wv), 1011 (mw), 920 (vs), 877 (va), 835 (w), 736 (m), 720 (w).
Table V. Crystallographic Data for 6, 7, 8, and 12

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>12</th>
</tr>
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<tbody>
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<td>F(000), e</td>
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<td>0.11 x 0.11 x 0.30</td>
<td>0.25 x 0.38 x 0.38</td>
</tr>
<tr>
<td>T, K</td>
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<td>150</td>
<td>150</td>
<td>300</td>
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<td>1.75 ≤ θ ≤ 25.0</td>
<td>1.75 ≤ θ ≤ 25.0</td>
<td>1.6 ≤ θ ≤ 27.5</td>
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<td>5498</td>
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<td>no. of params refined</td>
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<td>0.033</td>
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<tr>
<td>R_{w}(F)</td>
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<td>0.054</td>
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<tr>
<td>w</td>
<td>1/σ(^2)(F)</td>
<td>1/σ(^2)(F)</td>
<td>1/σ(^2)(F)</td>
<td>1/σ(^2)(F)</td>
</tr>
</tbody>
</table>

Preparation of Poly(norbornene) with 6 and 7. 6 (39 mg, 0.12 mmol) or 7 (94 mg, 0.28 mmol) was dissolved in 5 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 7, 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 °C 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 Etraf-Nomius CAD-4 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. The monitoring of three standard reflections during the data collection showed no significant decay of the crystal. Intensity data were corrected for Lorentz and polarization effects. 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 and illustrations were drawn with ORTEP.

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 2θ 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) 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 and illustrations were drawn with ORTEP.

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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 $11.0^\circ < \theta < 14.0^\circ$. 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, corrections 0.75:1.10). The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques on $F$ by SHELX. 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 $-0.42 \text{ e/Å}^2$, respectively. Neutral scattering factors are those of ref 42, corrected for anomalous dispersion. Derived geometry calculations and the thermal motion ellipsoid plot were done with PLATON. All calculations were carried out on a DEC5000/ULTRIX system.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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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