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(CH2CMe2R3)(PMe3)2 (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(CHCMes3)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(\(\sigma^2\)-CHCMe2CsH4)(PMe3)2 (7). In the absence of excess PMe3 the (μ-alkyl)2(μ-aryl) dimer CpV(μ2-CHCMe2CsH4)2 (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(\(\eta^2\)-CH2=CHEt)(PMe3)2 (10) through β-hydrogen abstraction and reductive elimination. Reactivity of the alkylidene complex 6 has been extended to the formation of the first imido complex of trivalent vanadium, CpV=NC(CMes)2=C(CMes)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: P21/a, a = 13.699(2) Å, b = 8.366(1) Å, c = 15.386(2) Å, \(\beta = 101.87(1)^\circ\), \(\alpha = 94.89(2)^\circ\), \(\gamma = 100.55(2)^\circ\), \(\gamma = 77.78(2)^\circ\), Z = 2. For 8: P21/c, a = 9.812(9) Å, b = 14.019(10) Å, c = 17.407(10) Å, \(\beta = 96.76(6)^\circ\), Z = 4. For 12: P1, a = 9.147(1) Å, b = 11.065(1) Å, c = 13.489(1) Å, \(\alpha = 71.95(1)^\circ\), \(\beta = 89.70(1)^\circ\), \(\gamma = 89.96(1)^\circ\), 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 Cp2VX and Cp2VX (X = halide, alkyl, aryl, alky, H, D; \(\text{Cp}^* = \text{Cp}^2\text{CMe}_3\)) though some homoleptic complexes, such as V(CH(SiMe3)2)2 and VMe3-THF (Mes = 2,4,6-trimethylphenyl) have also been synthesized. Some of the main trends 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 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 (11) has allowed the synthesis of a range of organometallic derivatives of V(III), V(II), and V(I) including allyl, alkyl, hydride, alkene, and alkyne complexes. Both the observed thermolysis behavior of CpVMe2(PMe3)2 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.
(ambient temperature) conditions. Products include the first vanadium alkylidene complex and new metallocyclic 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=Nmultiple bond. A part of this investigation has been communicated previously.\(^6\)

**Results and Discussion**

**Synthesis.** The 16-electron dialkyl complex CpVMe₂(PMe₃)₂ acts in most of its reactivity as an electronically saturated system. The high-spin d² configuration of its metal center leaves only half-filled orbitals accessible to reactants. This makes phosphine dissociation necessary for reactions with most substrates.\(^7\)\(^1\) Use of sterically more demanding alkyl groups, however, allows preparation of CpV(I) dialkyl complexes that are more electron deficient.

Reaction of CpVCl₂(PMe₃)₂ (1) with 2 mol of neopentyllithium in pentane or neopentylmagnesium chloride (Me₂PhCH₂Me₂MgCl) in diethyl ether at -10 to 0 °C affords crystalline 14-electron complexes CpV(CH₂CMe₂R)₂PMes₃ (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 PMes₃ 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 Li(H(SiMes)₂)₂ produces the 12-electron species CpV(CH(SiMes)₂)₂PMe₃ (eq 2).

\[
\begin{align*}
1 + 2 \text{M} \text{C} \text{H}_{2} \text{CMe}_{2} \text{R} + 2 \text{M} \text{Cl} + \text{PMes}_{3} & \rightarrow +2 \text{M} \text{Cl} + \text{PMe}_{3} \\
2: & \text{R} = \text{Me}, \text{M} = \text{Li} \\
3: & \text{R} = \text{Ph}, \text{M} = \text{MgCl}
\end{align*}
\]

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)C₂H₄)ZrCP₃\(^{14}\) and is indicative of a true alkylidene species. In the "bent metallacyclopentatriene" complex CpV(C₂Me₅Ph₂)PMes₃ 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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to a metal in a relatively low oxidation state, yet still species. A metal center is conceivable, yielding an alkylidynehydride strongly distorted observed so far) and the upfield shift formally electronically unsaturated. In this kind of compound an oxidative addition of the C-H bond to the alkylidene a-hydrogen in the \( \text{H} \) NMR spectrum appears to be characteristics of alkylidene groups bound to the \( \text{C} \) atom (where the \( \text{C} \) atom is thermolyzed in the presence of excess \( \text{PMe}_3 \) the same mixture of two diamagnetic organometallic products, as observed by NMR. The \( \text{Cp} \) resonances in the \( \text{H} \) NMR spectrum suggest a 1:3 ratio for the two products. The minor product can be identified as the alkylidene species \( \text{CpV(CHCMe}_3\text{)(PMe}_3\text{)}_2 \) (6b): the resonance of the \( \text{Cp} \) protons at \( \delta \approx 4.98 \text{ ppm} \) shows the expected triplet structure from the coupling with the two phosphorus atoms (J(\( \text{VP} \)) = 2.8 Hz), the broad alkylidene proton resonance is observed at \( \delta \approx -5.7 \text{ ppm} \) and the \( \text{V} \) NMR spectrum shows a triplet at \( \delta \approx -1328 \text{ ppm} \) (J(\( \text{VP} \)) = 223 Hz). No coupling with phosphorus atoms is apparent on the \( \text{Cp} \) proton resonance of the major product. In the \( \text{V} \) NMR spectrum it exhibits a broad resonance at \( \delta \approx -22 \text{ ppm} \) (J(\( \text{VP} \)) = 5320 Hz). When 2 is thermolyzed in the presence of excess \( \text{PMe}_3 \) 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 \( \text{CpV(CH}_2\text{CMe}_2\text{Ph})_2\text{PMe}_3 \). The neophyl complex 3 decomposes readily in solution at ambient temperature. In the presence of excess \( \text{PMe}_3 \) a green paramagnetic crystalline solid is produced, which was characterized by X-ray diffraction as the metallacyclic complex \( \text{CpV(CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{PMe}_3)_2 \) (7, eq 4). The structure of 7 is shown in Figure 2, and pertinent bond distances and angles are given in Table II.

\[
\text{CpV(CH}_2\text{CMe}_2\text{Ph})_2\text{PMe}_3 + \text{PMe}_3 \rightarrow 3
\]

\[
\text{CpV(CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{PMe}_3)_2 + \text{PhCMMe}_2 \quad (4)
\]

The metal atom in 7 is to first approximation square pyramidal coordinated, with the \( \text{PMe}_3 \) ligands in cis position. The arrangement of the ligands in the basal

Figure 2. Molecular structure of \( \text{CpV(CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{PMe}_3)_2 \) (7). Thermal ellipsoids are drawn at the 50% probability level.

reactivity we have so far not observed any evidence for alkylidyne–hydride behavior.

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

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\[
\text{CpV(CH}_2\text{CMe}_2\text{Ph})_2\text{PMe}_3 + \text{PMe}_3 \rightarrow 3
\]

\[
\text{CpV(CH}_2\text{CMe}_2\text{C}_6\text{H}_4)(\text{PMe}_3)_2 + \text{PhCMMe}_2 \quad (4)
\]

The metal atom in 7 is to first approximation square pyramidal coordinated, with the \( \text{PMe}_3 \) ligands in cis position. The arrangement of the ligands in the basal

Figure 1. Molecular structure of \( \text{CpV(CHCMe}_3\text{)(PMe}_3\text{)}_2 \) (6). Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for \( \text{CpV(CHCMe}_3\text{)(PMe}_3\text{)}_2 \) (6).

<table>
<thead>
<tr>
<th>Distances/Angles</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>1.00(5)</td>
</tr>
<tr>
<td>C(12)–C(13)</td>
<td>1.510(4)</td>
</tr>
<tr>
<td>P(1)–V(1)</td>
<td>2.363(1)</td>
</tr>
<tr>
<td>P(2)–V(1)</td>
<td>2.363(1)</td>
</tr>
<tr>
<td>P(1)–V(1)–P(2)</td>
<td>79.48(5)</td>
</tr>
<tr>
<td>V(1)–C(12)–C(13)</td>
<td>173.3(3)</td>
</tr>
<tr>
<td>V(1)–C(12)–H(121)</td>
<td>113(3)</td>
</tr>
<tr>
<td>C(12)–C(13)–H(121)</td>
<td>91.5(1)</td>
</tr>
</tbody>
</table>

plane of the pyramid is somewhat twisted to allow suitable packing of the asymmetric \(\sigma^2\text{-CH}_3\text{CMe}_2\text{C}_6\text{H}_4\) 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) Å 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) than the average vanadium–carbon bond lengths reported for \(\text{VMe}_3\)THF\(_2\) and \(\text{Pb}_2\text{VN}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2\).\(^{18}\) 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 \(\text{CpV(q}_2\text{-C}_6\text{H}_4\text{)(PMe}_3\text{)}_2\) and \(\text{CpV(q}_4\text{-C}_6\text{H}_4\text{)}\text{Me}_3\text{Ph})\). 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 \(\text{PMe}_3\) produces a brown solution from which red-brown crystals were obtained. The IR spectrum of the product, unlike \(7\), does not contain \(\text{PMe}_3\) (e.g. lacking the characteristic strong \(\delta\) P–Me vibration band around 950 cm\(^{-1}\)). X-ray diffraction showed that this product is a phosphine-free (\(\mu\)-alkyl)\(_2\)(\(\mu\)-aryl)\(_2\) dimer \([\text{CpV(q}_2\text{-CH}_3\text{CMe}_2\text{C}_6\text{H}_4\text{H})_2]\) (8, eq 5). The structure of 8 is shown in Figure 3, and pertinent interatomic distances and angles are given in Table III.

\[
2\text{CpV(CH}_2\text{CMe}_2\text{Ph})_2\text{PMe}_3 \rightarrow 3
\]

\[\text{[CpV(q}_2\text{-CH}_3\text{CMe}_2\text{C}_6\text{H}_4\text{H})_2 + 2\text{PMe}_3 + 2\text{PMe}_3 (5)\]

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 othometalated 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-C₅H₅)]₂ reported by Jonas et al.²² 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-C₅H₅)]₂ each µ² 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 long or two short distances to the same V atom, whereas metal alkylidene complexes exhibit a wide range of.

Catalytic processes like ring-opening metathesis polymerization of cyclic olefins and olefin metathesis.²⁷ As the new vanadium(III) alkylidene complexes CPV(CMe₅)dmpe (6) and CPV(ChMe₅)(PMe₃)₂ (6b) are the first examples of nucleophilic alkylidenes for this element, and are rare examples of 3d-metal alkylidenes (CP₂Ti(CR)₅PR₃ forms the other available class²⁸), 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)=CHCMe₅]dmpe (12, eq 8).

CpV(ChMe₅)dmpe + Me₅CCŒN →
6
CpV(=NC(CMe₅))=CHCMe₅]dmpe (8)

This type of reaction has been observed before by Schrock and co-workers with (CMe₅)₂Ta(=CH(CMe₅)₂ and CpTa(=CHCMe₅)Cl.²⁹ 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 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)–Cp(V(dmpe) sterically 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=V 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(pentamethylcyclopentadienyl) systems CP₅V(NR) (R = Ph, 1.730(5) Å;²⁵ C₆Me₅H, 1.707(6) Å). The V–N=C(7) angle is


References

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(neo- 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 (Scheme I). When the bis(neo-penty1) complex 6 proved to be minimal, probably due to the combination of a relatively small metal center and the presence of a chelating diphenyl ligand.

Conclusions

In the thermolysis of paramagnetic monocyclopenta-
dienylvanadium(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[=NC(CMes)=CHCMe3]dmpe 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(neopenty1) 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 glovebox) or using vacuum line techniques. Gas uptakes were determined with a Töpler pump connected to a vacuum line. Solvents (diethyl ether, tetrahydrofuran (THF), toluene, pentane (mixed isomers), n-hexane, cyclohexane, benzene, and deuterated solvents except CDCl3) were distilled from Na/K alloy before use. NMR spectra were recorded on a Varian VXR-300 (1H, 300 MHz; 13C, 75.4 MHz; 51V, 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, 51V) positive. IR spectra were recorded on a Pye-Unicam SP3-800 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 Gronim-

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for CpV[=NC(CMes)=CHCMe3]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(12)  | 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) |

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.27e 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(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 diphenyl ligand.
were prepared according to published procedures. n-BuLi was gen. Values given are the average of at least two independent determinations.

were prepared according to an adapted literature using MeMgI instead of MeMgBr. Norbornene was distilled from sodium prior to use.

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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.²⁶

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 26 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 (MULTAN),²⁴ 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, and illustrations were drawn with ORTEP.²⁶

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

<table>
<thead>
<tr>
<th>6</th>
<th>7</th>
<th>8</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Formula} )</td>
<td>( \text{C}_2\text{H}_3\text{P}_2\text{V} )</td>
<td>( \text{C}_2\text{H}_3\text{P}_2\text{V} )</td>
<td>( \text{C}_2\text{H}_3\text{V}_2 )</td>
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<tr>
<td>( f_w )</td>
<td>336.31</td>
<td>400.40</td>
<td>496.48</td>
</tr>
<tr>
<td>( \text{Crystal System} )</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>( \text{Space Group} )</td>
<td>( P_2_1_1/a )</td>
<td>( P_2_1_1 )</td>
<td>( P_2_1_1 )</td>
</tr>
<tr>
<td>( a, \AA )</td>
<td>13.699(2)</td>
<td>9.812(9)</td>
<td>9.147(1)</td>
</tr>
<tr>
<td>( b, \AA )</td>
<td>9.866(1)</td>
<td>14.261(4)</td>
<td>14.019(10)</td>
</tr>
<tr>
<td>( c, \AA )</td>
<td>15.386(2)</td>
<td>8.528(2)</td>
<td>17.407(10)</td>
</tr>
<tr>
<td>( \alpha, \text{deg} )</td>
<td>101.87(1)</td>
<td>94.89(2)</td>
<td>96.76(6)</td>
</tr>
<tr>
<td>( \beta, \text{deg} )</td>
<td>110.53(2)</td>
<td>96.76(6)</td>
<td>89.70(1)</td>
</tr>
<tr>
<td>( \gamma, \text{deg} )</td>
<td>77.78(2)</td>
<td>69.56(1)</td>
<td>71.93(1)</td>
</tr>
<tr>
<td>( R(F) )</td>
<td>1849.4(4)</td>
<td>1076.3(5)</td>
<td>2378(3)</td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>( \text{Crystal size, mm} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a, \text{mm} )</td>
<td>1.208</td>
<td>1.24</td>
<td>1.39</td>
</tr>
<tr>
<td>( b, \text{mm} )</td>
<td>720</td>
<td>428</td>
<td>1040</td>
</tr>
<tr>
<td>( c, \text{mm} )</td>
<td>6.8</td>
<td>5.93</td>
<td>7.76</td>
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<tr>
<td>( T, \text{K} )</td>
<td>130</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>( \theta \text{ limits, deg} )</td>
<td>1.35 ≤ θ ≤ 27.0</td>
<td>1.75 ≤ θ ≤ 25.0</td>
<td>1.75 ≤ θ ≤ 25.0</td>
</tr>
<tr>
<td>( \text{No. of data collected} )</td>
<td>5025</td>
<td>4029</td>
<td>4646</td>
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<tr>
<td>( \text{Wavelength, Å} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Mo (Kα)} )</td>
<td>0.71069</td>
<td>0.71070</td>
<td>0.71070</td>
</tr>
<tr>
<td>( \text{Crystal size, mm} )</td>
<td>0.73</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>( \text{Cell parameter, Å} )</td>
<td>1.010 × 0.12 × 0.14</td>
<td>0.30 × 0.30 × 0.15</td>
<td>0.11 × 0.11 × 0.30</td>
</tr>
<tr>
<td>( \text{Unit cell volume, Å}^3 )</td>
<td>963</td>
<td>963</td>
<td>963</td>
</tr>
</tbody>
</table>


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° < θ < 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, corrections 0.75:1.10). The structure was solved by direct methods (SHELXI) 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 e/Å³, 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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