Chemistry of vanadium-carbon single and double bonds
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Chapter 5

Half-sandwich Imido Vanadium(V) and Niobium(V) Alkylidenes*

5.1 Introduction.

Although the first nucleophilic alkylidene complex of a transition metal was reported for tantalum as early as 1974, only one d₂ nucleophilic alkylidene and no d⁰ nucleophilic alkylidenes have been reported to date for the lightest of the group 5 metals, vanadium. A combination of the facts that traditionally nucleophilic alkylidenes have been synthesized almost exclusively via α-hydrogen abstraction and the low stability of d⁰ hydrocarbyl complexes of first-row transition metals beyond group 4 accounts for the existence of this void.

As has been shown in chapter 3, the combination of the strongly electron-donating cyclopentadienyl and arylimido ligands on d⁰ vanadium did not significantly improve the stability of alkyl derivatives towards reduction. In contrast, several stable d⁰ half-sandwich imido niobium alkyl complexes have been prepared through alkylation of the corresponding dichlorides. Thermal decomposition of the dibenzyl complex Cp*Nb(NAr)(CH₂Ph)₂ [Ar = 2,6-C₆H₃-(i-Pr)₂] in the presence of PMe₃ gave the structurally characterized d⁰ niobium alkylidene Cp*Nb(NAr)(PMe₃)(=CHPh) through α-hydrogen abstraction. Fortunately, d⁰ alkylidenes can also be prepared by methods which represent a formal two-electron oxidation of the metal, and therefore avoid the need to keep the metal in its highest oxidation state during preparation. The two best-studied methods in early transition metal chemistry are the transfer of an alkylidene group from easily synthesized and readily isolated phosphoranes (phosphorus ylides) to a reduced metal complex, and the ring-opening of 3,3-disubstituted cyclopropenes to give vinyl alkylidene complexes.

Alkylidene transfer from phosphoranes to reduced transition metal complexes has been reported for d² Cp₂Zr and Cp₂TaMe-systems, and recently for imido W(IV) complexes. The formation of nucleophilic alkylidenes is thought to favor loss of phosphine from the proposed intermediate phosphorane adducts. The first synthesis of isolable transition-metal vinyl alkylidene complexes from cyclopropenes was reported in 1989 by Binger et al. and involved the reaction of 3,3-disubstituted cyclopropenes with d² Cp₂Ti and Cp₂Zr precursors. Exlusive formation of the vinyl alkylidene

* Part of this chapter has been communicated: Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. Organometallics 1994, 13, 2922.
Cp₂Ti(PMe₃)(=CHCH=CR'R') was observed upon reaction of 3,3-diphenyl- and 3-methyl-3-phenylcyclopropene with Cp₂Ti(PMe₃)₂. More recently, this method has been used by Grubbs et al. to produce a range of vinyl alkylidene and carbene complexes of transition metals, including tungsten,⁵⁷ ruthenium⁵⁸ and rhenium.⁵⁹

Both the alkylidene transfer from phosphoranes and the ring-opening of 3,3-disubstituted cyclopropenes require reduced metal species with at least one labile ligand to allow introduction of an alkylidene fragment on the metal. In the preceding chapter the lability of one phosphine ligand of the half-sandwich vanadium imido d² complex CpV(NAr)(PMe₃)₂ was demonstrated by reaction with a number of π-acceptors L and oxidants to give complexes CpV(NAr)(PMe₃)L and mono(phoshine) d⁰ complexes, respectively. Similar reactivity has been reported for the half-sandwich imido niobium complex Cp*⁸Nb(NAr)(PMe₃)².⁶⁰

In this chapter reactions of CpM(NAr)(PMe₃)₂ (M = V, Nb) with phosphoranes and 3,3-disubstituted cyclopropenes will be described, as well as some aspects of the reactivity of the products of these reactions. Many of the experiments described have been performed on a small scale and were studied only by NMR spectroscopy, which renders these investigations a preliminary character.

5.2 Synthesis of half-sandwich imido vanadium(V) and niobium(V) alkylidene complexes.

The reaction of CpV(NAr)(PMe₃)₂ (1) with one equivalent of phosphorane RCH=PPh₃ (R = H, Me, Ph) proceeds under loss of PMe₃ and PPh₃ to produce the vanadium(V) alkylidenes CpV(NAr)(PMe₃)(=CHR) (2, R = H; 3, R = Me; 4, R = Ph) (eq 1).

Transfer of the alkylidene from phosphorus to vanadium is clear from the downfield shift of the alkylidene Hα and Cα resonances (Table I).⁶¹
Chapter 5: Half-sandwich imido vanadium(V) and niobium(V) alkylidenes.

### Table 1. Selected NMR spectroscopical data of the alkylidene part of CpV(NAr)(PMe₃)(=CHR) complexes.²

<table>
<thead>
<tr>
<th>compound</th>
<th>R</th>
<th>Hα</th>
<th>JHH</th>
<th>JPH</th>
<th>Cα</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>H</td>
<td>14.19/12.99</td>
<td>4.9/4.9 n = 1</td>
<td>9.8/6.6</td>
<td>c</td>
</tr>
<tr>
<td>3a</td>
<td>Me</td>
<td>15.00</td>
<td>b</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>3b</td>
<td>Me</td>
<td>13.32</td>
<td>9.5 n = 3</td>
<td>9.5</td>
<td>c</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>13.45</td>
<td></td>
<td>7.5</td>
<td>304d</td>
</tr>
</tbody>
</table>

² Spectra were acquired in benzene-d₆.  b Unresolved.  c Not observed.  d Δν₁/₂ = 600 Hz.

The CpV(NAr)PMe₃ part of the alkylidenes 2-4 shows the usual patterns in ¹H NMR spectroscopy, when compared with the compounds discussed in the preceding chapter, consistent with a mononuclear structure containing a four-coordinate chiral metal center. The cyclopentadienyl protons appear as a doublet, due to coupling with the vanadium bound phosphorus atom of the trimethylphosphine ligand. The i-Pr groups of the arylimido ligand give rise to a septet for the methine protons and two doublets at higher field for the methyl protons, which is consistent with a free rotating aryl group.

On the basis of the isolobal relationship between group 5 half-sandwich imido complexes and group 4 metallocene complexes the bonding of the alkylidene in 2-4 is expected to take place in the plane which bisects the Cpcentroid-V-N angle and contains the phosphorus atom. The p-orbital of the alkylidene ligand lies in this plane to allow interaction with the metallocene-like π-symmetry orbitals of the CpV(NAr) fragment. The alkylidene substituents will be oriented perpendicular to this plane. In case of two different alkylidene substituents two isomers (rotamers) are expected, one with the bigger substituent syn to the imido ligand, the other with the substituent trans. Throughout this chapter the terms syn and trans will be used to describe orientations of alkylidene substituents relative to the imido ligand.

The rate of formation and stability of the alkylidenes 2-4 is largely dependent on the nature and size of the alkylidene substituent R, as has been observed for the Cp₂TaMe system.² In case of R = H, reaction of the phosphorane with 1 is fast at 25 °C, with a conversion after 5 min of approximately 80% (Scheme 1). The stability of 2 under the reaction conditions is low, as 2 could not be observed by ¹H NMR spectroscopy after 1 h at 25 °C. The decomposition of 2 is accompanied by simultaneous formation of 1 and the ethene adduct CpV(NAr)(PMe₃)(η²-C₂H₄) (5) in a 1:1 ratio. When 1 is reacted with two equivalents of phosphorane H₂C=PH₃ complete conversion to 5 is observed. Complex 5 is stable for indefinite periods of time in a sealed NMR reaction tube, even at elevated temperatures, in the absence of light. Under the influence of light it slowly (days in daylight) decomposes to give free ethene and 1, which can be formed due to the presence of trimethylphosphine in the reaction mixture. It seems
therefore possible to catalyze the decomposition of $H_2C=PPh_3$ to ethene and $PPh_3$ with 3 under irradiation with light. Similar observations have been made in the Cp$_2$TaMe system.$^{6a}$ Attempts to isolate 5, thereby obtaining an alternative, fast procedure for its synthesis, initially failed due to the solubility of $PPh_3$ in the extraction solvent pentane. Addition of CuCl, a phosphine “sponge”,$^{62}$ resulted in the formation of the vanadium(IV)mono(chloride) complex CpV(NAr)(PMe$_3$)Cl (6) through a one electron oxidation process. Complex 6 could be isolated as orange crystals.$^{63}$

\[ \text{Scheme 1. Formation and decomposition of 2.} \]

The mechanism of decomposition of 2 in the presence of $H_2C=PPh_3$ is not clear. Determinations of the rate of decomposition, which could provide information about the mechanism, were hampered by the fact that 2 cannot be obtained pure, not even at low temperatures. Loss of trimethylphosphine from 2 followed by attack of $H_2C=PPh_3$ might lead to a vanadium bis(methylene) species, which is probably highly unstable and decomposes through coupling of the two methylene fragments to form ethene. Formation of ethene could also result from direct attack of the phosphorane on the methylene carbon, followed by coupling of the metal and phosphine bound methylene groups and elimination of $PPh_3$. Since in none of the phosphine displacement reactions discussed in chapter 4 substitution of the second phosphine was observed, the last explanation is probably the most plausible. However, investigations of the decomposition of relatively stable Cp$_2$Ta(CH$_3$)(CH$_2$) have shown that bimolecular decomposition by combination of two molecules of tantalum
methylidene is faster than decomposition through combination of \( \text{H}_2\text{C}=\text{PMe}_3 \) and one molecule of tantalum methylidene.\(^{64}\) Although a bimolecular decomposition involving two molecules of \( 2 \) seems unlikely on the basis of unfavorable steric interactions, it must be considered a possible pathway for the decomposition of \( 2 \).

In case of \( R = \text{Me} \), reaction of the phosphorane with \( 1 \) can easily be followed by \(^1\text{H} \) NMR spectroscopy at 25 °C. A 50% conversion is reached after 1.5 h, showing the exclusive formation of the rotamer with the most high-field shifted \( \text{H}_\alpha, 3\text{a} \). Over the course of the reaction the rate of formation of \( 3 \) decreases, probably due to build up of \( \text{PMe}_3 \), which can block coordination sites available for the phosphorane. Heating the reaction mixture results in an increased rate of formation of \( 3\text{a} \), but also increases the rate of isomerization of \( 3\text{a} \) to the other rotamer, \( 3\text{b} \). After 17 h at 50 °C a conversion to \( 3 \) is complete, and a 1:1 mixture of the two rotamers is formed. The ratio of the rotamers does not change after prolonged time at 50 °C.

Complex \( 3 \), which is the second known example of a terminal ethylidene complex,\(^{6a}\) is thermally stable in the reaction mixture in which it is formed for days at 50 °C. Attempts to isolate \( 3 \) failed due to decomposition upon removal of the organic volatiles \textit{in vacuo}. The ethene complex \( 5 \), which could be formed by a \( \beta \)-hydrogen abstraction, was not found as one of the decomposition products. The nature of the decomposition products has not been established yet.

In case of \( R = \text{Ph} \), reaction of the phosphorane with \( 1 \) is slow at 25 °C. In a sealed NMR tube a 70% conversion is reached after 20 h at 75 °C. Under a dynamic vacuum, to remove free \( \text{PMe}_3 \) that can block formation of 16 electron \( \text{CpV(NAr)}\text{PMe}_3 \) fragments, the rate of reaction is increased. Benzyldene complex \( 4 \) is thermally stable, showing no decomposition at 100 °C in solution for weeks. It could be isolated in good yield as red crystals after the side product \( \text{PPh}_3 \) had been removed by complexation with \( \text{CuCl} \).

The \(^1\text{H} \) NMR spectra of \( 4 \) show that only one rotamer of the benzyldene complex has been formed. The other rotamer is neither observed during formation nor after prolonged times in solution at 100 °C. In a 2D-NOESY spectrum of \( 4 \) an interaction between \( \text{H}_\alpha \) and the \( \text{Cp} \)-protons is observed, whereas nuclear Overhauser effects between this proton and the \( \text{i-Pr} \)-protons are absent, indicating a \textit{syn} arrangement of the benzyldene phenyl substituent. Comparison of the chemical shifts of \( \text{H}_\alpha \) of \( 3 \) and \( 4 \) indicates that a \textit{syn} arrangement of the alkylidene substituent relative to the imido group, as in \( 4 \), is also present in \( 3\text{b} \), the thermodynamically more stable rotamer of \( 3 \) (Table I).

To confirm the proposed arrangement of the alkylidene substituents an X-ray structure determination of \( 4 \) was carried out. The crystal structure of \( 4 \) involves the packing of 4 molecules in a monoclinic unit cell. The molecular structure of \( 4 \) is shown in Fig. 1. Selected bond lengths and angles are given in Table II.
Chapter 5: Half-sandwich imido vanadium(V) and niobium(V) alkylidenes.

Figure 1. Molecular structure of CpV[N=2,6-C₆H₃-(i-Pr)₂]₂(PMe₃) (=CHPh) (4), with adopted numbering scheme.

The molecular structure of 4 shows a slightly distorted tetrahedral geometry about the metal, similar to 1, with the anticipated syn arrangement of the alkylidene phenyl substituent and the imido group. All interligand angles are similar to those found in the structurally-characterized niobium analogue Cp*Nb(NAr)(PMe₃)(=CHPh), 4a whereas the differences in metal-ligand distances correlate well with the difference in ionic radii of V(V) and Nb(V) (e.g. V=C = 1.922(6) Å versus Nb=C = 2.026(4) Å). The V(1)-C(24)-C(25) angle of 136.9(4)° is indicative of an undistorted alkylidene ligand, which is in marked contrast with the very obtuse V=C-C angle of 173.3(3)° that was observed in the only other structurally-characterized 3d-metal alkylidene CpV(CH-t-Bu)dmpe. 2 This last complex, however, is a vanadium(III) alkylidene and has a highly distorted configuration of the alkylidene α-carbon. The alkylidene α-hydrogen is strongly bent back towards the metal center, resulting in a metal-hydride like V-Hₐ bond length (1.66(5) Å). The structure can be thought of as a "frozen" intermediate for the α-hydrogen transfer from an vanadium(III) alkylidene to an vanadium(V) alkylidyne-hydride species, explaining also the short vanadium-carbon "double" bond in this complex (1.809(3) Å). The tendency of vanadium to reach higher formal oxidation states by distortion of ligands is of course not present in the d⁰ alkylidene 4.

Another remarkable feature of the structure of 4 is the trend towards η³ coordination of the cyclopentadienyl moiety, as indicated by three short and two long V-C_Cp bond distances (C(19) and C(20), trans to the imido ligand). Similar observations have been made for several cyclopentadienyl imido complexes of group 5 metals. 66 The V-N distance of 1.679(5) Å in
this d⁰ vanadium imido complex lies just within the range of 1.60-1.68 Å reported as normal for V-N multiple bonds in V(IV) and V(V) systems.³

Table II. Selected geometrical data for CpV[N-2,6-C₆H₃-(i-Pr)₂](PMe₃)(=CHPh) (4).

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)-N(1)</td>
<td>1.679(5)</td>
<td></td>
</tr>
<tr>
<td>V(1)-P(1)</td>
<td>2.4010(19)</td>
<td></td>
</tr>
<tr>
<td>V(1)-C(24)</td>
<td>1.922(6)</td>
<td></td>
</tr>
<tr>
<td>V(1)-Cp centroid</td>
<td>1.990(3)</td>
<td></td>
</tr>
<tr>
<td>V(1)-C(19)</td>
<td>2.359(5)</td>
<td></td>
</tr>
<tr>
<td>V(1)-C(20)</td>
<td>2.362(5)</td>
<td></td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.397(7)</td>
<td></td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td>1.448(7)</td>
<td></td>
</tr>
<tr>
<td>C(24)-H(24)</td>
<td>0.951(7)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles (°)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)-N(1)-C(1)</td>
<td>169.5(4)</td>
<td></td>
</tr>
<tr>
<td>P(1)-V(1)-C(24)</td>
<td>87.62(17)</td>
<td></td>
</tr>
<tr>
<td>P(1)-V(1)-N(1)</td>
<td>99.24(15)</td>
<td></td>
</tr>
<tr>
<td>N(1)-V(1)-C(24)</td>
<td>105.1(2)</td>
<td></td>
</tr>
<tr>
<td>Cp centroid-V(1)-N(1)</td>
<td>126.96(16)</td>
<td></td>
</tr>
<tr>
<td>P(1)-V(1)-Cp centroid</td>
<td>113.12(9)</td>
<td></td>
</tr>
<tr>
<td>V(1)-C(24)-C(25)</td>
<td>136.9(4)</td>
<td></td>
</tr>
<tr>
<td>V(1)-C(24)-H(24)</td>
<td>113(3)</td>
<td></td>
</tr>
</tbody>
</table>

Attempts to prepare the niobium analogue of 4 failed. No reaction of CpNb(NAr)(PMe₃)₂ (7) and PhHC=PPh₃ was observed after 24 h at 75 °C.

In contrast, reaction of 7 and 3,3-disubstituted cyclopropenes does provide stable half-sandwich imido niobium alkylidenes. On the whole, ring-opening of 3,3-disubstituted cyclopropenes seems to be a more versatile method of synthesizing d⁰ alkylidenes than the transfer of an alkylidene group from a phosphorane to a transition metal. The reactions of 1 and 7 with one equivalent of 3,3-disubstituted cyclopropenes are summarized in Scheme 2.

In general, the reactions of 1 and 7 with 3,3-disubstituted cyclopropenes are characterized by the simultaneous formation of η²-cyclopropene adducts and vinyl alkylidenes through ring-opening of the cyclopropene. The η²-cyclopropene adducts can be converted to the vinyl alkylidenes by heating (75 °C). These reactivity patterns are similar to those observed for d² metallocene group 4 complexes⁸ and d² tungsten imido complexes¹⁰ in reaction with cyclopropenes. The relative rates of adduct and vinyl alkylidene formation depend on the metal. Vinyl alkylidene formation is much slower for niobium than for (smaller) vanadium, consistent with the observed rate dependence on the steric bulk of the ancillary ligands in the tungsten imido system.¹⁰ Although the mechanism of ring-opening of the cyclopropenes has not been determined, a metal-catalyzed rearrangement is indicated, as
uncatalyzed thermal ring-openings normally require higher temperatures than those reported here.$^67$

The reactions of 1 and 7 with one equivalent of 3,3-diethylcyclopropene were performed on an NMR scale only, due to unfavorable crystallization behavior of the resulting complexes (oils). Reactions of 1 and 7 with one equivalent of 3,3-diphenylcyclopropene on a preparative scale allowed the isolation of the $\eta^2$-cyclopropene adduct $\text{CpNb(NAr)(PMe}_3)(\eta^2$-CHCHCPh$_2$) (8b) and the vinyl alkylidene complexes $\text{CpM(NAr)(PMe}_3)(=\text{CHCH=CPh}_2)$ (10a, M = V; 10b, M = Nb) as solids in good yield.

The formation of $\eta^2$-cyclopropene adducts is indicated by the characteristic upfield shift of the olefinic protons (4-5 ppm), comparable to the upfield shift of ethylene protons upon formation of 5 (see chapter 4), and coupling of these protons with the vanadium bound phosphine ligand. Furthermore, the bonding mode of the cyclopropene ligand with the C=C axis in a plane containing the M-P vector which bisects the $\text{Cp}_{\text{centroid}}$-M-N angle causes the two olefinic protons to become inequivalent. The cyclopropene proton endo to the PMe$_3$ ligand is shifted more upfield than the exo proton, as can be concluded from the smaller phosphorus-hydrogen coupling constant for the latter.$^68$

In these $\eta^2$-cyclopropene complexes, syn and anti orientations of the cyclopropene substituents relative to the imido ligand, are equally likely on an electronic basis. As seen in alkylidene 4, syn orientation minimalizes the steric interactions of the $\pi$-acceptor substituents
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and the CpV(NAr)(PMe₃) fragment. Therefore, the major isomer of the 3,3-diethylcyclopropene complexes 9a and 9b was tentatively assigned syn, the minor anti. The syn:anti ratio was slightly higher for vanadium (3.6) than for niobium (2.7), possibly reflecting the greater steric crowding in the vanadium case. In contrast, only one isomer was observed (and isolated for niobium) in the 3,3-diphenylcyclopropene complexes 8a and 8b. In analogy with the tungsten imido η²-3,3-diphenylcyclopropene complexes described by Grubbs et al.,¹⁰ this isomer was assigned syn. The crystal structure of one of the tungsten 3,3-diphenylcyclopropene complexes reveals an alignment of the π-systems of the imido aryl substituent and one of the cyclopropene phenyl substituents,¹⁰ which might also account for the formation of only the syn isomer in the vanadium and niobium imido cases presented here.

The η²-cyclopropene complexes are stable at 25 °C, but not at higher temperatures. Higher temperatures, however, are needed for their formation at an appreciable rate. Slow ring-opening of the coordinated cyclopropene ligand to give vinylalkylidenes is observed at temperatures between 50 and 75 °C. Since the η²-cyclopropene and vinyl alkylidene complexes were found to have similar solubility characteristics this precluded isolation of pure cyclopropene adducts. However, in case of the niobium 3,3-diphenylcyclopropene complex 8b, ring-opening of the cyclopropene is slow relative to the formation of the adduct, thus allowing the isolation of the cyclopropene adduct.

The formation of the half-sandwich imido vanadium vinyl alkylidene complexes 10a and 11a is about 5-10 times as fast as the formation of the corresponding niobium complexes 10b and 11b. The compounds were observed as orange to red-brown solutions and isolated (10a and 10b) as orange or red powders. Coordination of the vinyl alkylidene moiety to vanadium and niobium was indicated by the downfield shifts of Hα and Cα,¹⁴ and the splitting of the Hα resonances by the phosphine ligand coordinated to the metal (Table III). In addition, a downfield shift of Hβ of the alkylidene moiety was also observed. The large coupling of Hα and Hβ is indicative of an s-trans arrangement of the double bonds of the vinyl alkylidene ligand. For the vanadium complexes coupling of phosphorus to Hβ is observed.

The assignment of the syn and anti rotamers in the vinyl alkylidene complexes was made by comparing the chemical shift of Hα with the chemical shift of the two rotamers of the ethylidene complex 3. The most low-field shifted resonance of each pair of rotamers was assigned to the syn rotamer. The ratio of rotamers did not deviate much from unity in any case, which is in agreement with the small size of the alkylidene vinyl substituents and the proposed s-trans arrangement of the double bonds in the vinyl alkylidene ligand.

The CpM(NAr)(PMe₃) parts of the molecules 10 and 11 display the usual spectroscopic features, which are consistent with a four-coordinate, chiral metal atom. The structures of these molecules are therefore expected to be similar to the structure of the vanadium benzylidene complex 4 (vide supra) or its niobium analogue.

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Cp*Nb(NAr)(PMe₃)(=CHPh).⁴ So far, no crystals of 10a or 10b suitable for an X-ray structure determination could be obtained.

Table III. Selected NMR spectroscopic data for the alkylidene part of vanadium and niobium vinyl alkylidene complexes.ᵃ

<table>
<thead>
<tr>
<th>vinyl alkylidene complex</th>
<th>Hα</th>
<th>Cα</th>
</tr>
</thead>
<tbody>
<tr>
<td>JCH</td>
<td>δ</td>
<td>JHH</td>
</tr>
<tr>
<td>syn-CpV(NAr)(PMe₃)(=CHCH=CPh₂) (10a)</td>
<td>14.44</td>
<td>15.0</td>
</tr>
<tr>
<td>anti-CpV(NAr)(PMe₃)(=CHCH=CPh₂) (10a)</td>
<td>13.03</td>
<td>13.7</td>
</tr>
<tr>
<td>syn-CpNb(NAr)(PMe₃)(=CHCH=CPh₂) (10b)</td>
<td>13.44</td>
<td>14.6</td>
</tr>
<tr>
<td>anti-CpNb(NAr)(PMe₃)(=CHCH=CPh₂) (10b)</td>
<td>11.97</td>
<td>13.9</td>
</tr>
<tr>
<td>syn-CpV(NAr)(PMe₃)(=CHCH=CEt₂) (11a)</td>
<td>14.97</td>
<td>14.3</td>
</tr>
<tr>
<td>anti-CpV(NAr)(PMe₃)(=CHCH=CEt₂) (11a)</td>
<td>13.42</td>
<td>13.7</td>
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<tr>
<td>syn-CpNb(NAr)(PMe₃)(=CHCH=CEt₂) (11a)</td>
<td>13.85</td>
<td>14.1</td>
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<tr>
<td>anti-CpNb(NAr)(PMe₃)(=CHCH=CEt₂) (11a)</td>
<td>12.23</td>
<td>13.6</td>
</tr>
</tbody>
</table>

ᵃ Spectra were acquired in benzene-d₆. b Not observed.

5.3 Reactivity of half-sandwich imido vanadium(V) and niobium(V) alkylidene complexes.

The main reasons for the development of early transition metal alkylidenes lie in the activity of these complexes as olefin metathesis catalysts and the possibility to gain more insight in the olefin metathesis reaction through well-defined complexes.⁶⁹ Therefore, the study of the reactivity of vanadium and niobium alkylidenes presented in this chapter has been limited to their activity in olefin metathesis and related reactions, with the exception of the reaction with elemental sulfur. Other interesting reactions, like the transformation of alkylidenes to Ziegler-Natta catalysts by addition of an electrophile,⁷⁰ have not been studied.

The availability of isostructural vinyl alkylidene complexes of vanadium and niobium allows, for the first time, a direct comparison of the activity of 3d and 4d metal alkylidenes in olefin metathesis reactions. The only other class of 3d transition metal alkylidenes consists of titanocene (vinyl)⁸ alkylidene complexes,⁷¹ but no stable zirconocene or hafnocene alkylidenes are known. Cp₂Zr(PPh₂Me)(=CH₂), obtained by transfer of a methyldiene group from a phosphorane to Cp₂Zr(PPh₂Me)₂, was reported unstable under the conditions under which it is formed,⁵ whereas Cp₂Zr(PMe₃)(=CHCH=CPh₂), obtained by ring-opening of 3,3-
diphenylcyclopropene in the presence of Cp₂Zr(PMe₃)(1-buten), was claimed without any experimental or spectroscopic detail.⁸

Before comparing the reactivity of the vinyl alkylidene complexes 10a and b, which consist of a mixture of rotamers, the activity in olefin metathesis and related reactions of benzylidene 4 (isolated as the syn rotamer) was studied. All reactions presented in this section were exploratory and performed on NMR scale.

Solutions of 4 in benzene-₁₄ do not react with 30-50 equivalents of norbornene over a temperature range of 25-100 °C (sealed NMR tube). Neither the formation of polynorbornene, nor vanadacyclobutanes nor decomposition of 4 was observed, even after reaction times of several weeks. The addition of two equivalents of AlCl₃, often used as a Lewis acid cocatalyst for oxo-alkylidene systems,¹²,⁷² to these solutions did not induce formation of polynorbornene. The ¹H NMR spectrum of 4 is unchanged by the addition of AlCl₃.

Benzylidene 4 does not react in a Wittig-type fashion with equimolar amounts of ketones or aldehydes in benzene-₁₄. In fact, it can be dissolved in acetone-₁₄ without decomposition.

Reaction of complex 4 is observed with an excess of elemental sulfur (eq 2). In an instantaneous reaction 4 is converted to the thiobenzaldehyde complex CpV(NAr)(PMe₃)(η²-S=CHPh) (12), which is stable in solution for days at 25 °C.

\[
\text{ArN}^+\text{V}^\cdot\cdot\cdot\text{PMe}_3 \quad \overset{S_8}{\rightarrow} \quad \text{ArN}^+\text{V}^\cdot\cdot\cdot\text{PMe}_3\text{S}^\cdot\cdot\cdot\text{Ph} \quad (2)
\]

The ¹H NMR spectrum of 12 shows a characteristic high-field shift of the thioaldehyde proton and the usual patterns for the CpV(NAr)(PMe₃) part of the spectrum, which are consistent with a four-coordinate, chiral metal center. The thioaldehyde function is thought to lie in a plane containing the V-P vector which bisects the Cp centroid-V-N angle, reflecting the metallocene-like character of half-sandwich imido vanadium complexes. The bonding is assumed to be similar to the bonding of the ketone functions in the acetone and diphenylketene complexes CpV(NAr)(PMe₃)(η²-O=CR₂) (R = Me, R₂ = CPh₂) presented in the preceding chapter. Only one of the four possible isomers of 12 (Ph syn or anti to imido, exo or endo to PMe₃) is obtained, as indicated by NMR spectroscopy. On the basis of steric arguments, formation of the syn,exo-isomer is most likely. Formation of thioaldehyde
complexes upon reaction of early-transition metal alkylidenes with elemental sulfur was observed before by Grubbs et al. for Cp₂Ti(PMe₃)(=CH₂).⁷³ Although the mechanism of the formation of 12 has not been investigated, one which involves the intermediacy of trimethylphosphine sulphide seems plausible, since the titanocene thioformaldehyde complex can also be obtained by reaction of the titanocene methylidene complex with triphenylphosphine sulphide.⁷⁶ Reaction of 4 with trimethylphosphine sulphide could occur through a [2+2] cycloaddition, reminiscent of the first step of olefin metathesis.

Benzene-d₆ solutions of the vinyl alkylidene complexes CpM(NAr)(PMe₃)(=CHCH=CPh₂) (10a, M = V; 10b, M = Nb) were allowed to react with norbornene, acetylene, benzaldehyde and elemental sulfur.

Like the vanadium benzylidene 4, the vanadium vinyl alkylidene 10a does not react with 50-100 equivalents of norbornene at 100 °C. Addition of one equivalent of AlMe₃, used instead of AlCl₃ because of its higher solubility in apolar solvents, at 25 °C gave no change in the ¹H NMR spectrum (except for an additional AlMe₃ resonance) and did not lead to ring-opening metathesis polymerization of norbornene. In contrast, the niobium vinyl alkylidene complex 10b shows slow ROMP of norbornene at 100 °C (50% conversion after 16 h), giving polynorbornene containing an approximately 7:3 ratio of trans and cis-vinylene bonds. The ratio cis:trans could be a reflection of the syn:anti ratio of the catalyst, or be completely accidental. Addition of one equivalent of AlMe₃ to solutions of 10b containing norbornene led to decomposition of the vinyl alkylidene and termination of ROMP of norbornene. In the ¹H NMR spectrum taken after the addition of AlMe₃, the vinylalkylidene resonances are absent, and numerous low-intensity resonances are found in the cyclopentadienyl region, indicating uncontrolled decomposition of 10b.

Similar differences in reactivity are observed in the reactions of 10a and 10b with acetylene. Whereas 10a does not react with acetylene at 1 atm at 70 °C, 10b immediately reacts with acetylene upon melting of a frozen benzene-d₆ solution under excess acetylene, producing a dark-red solution and a metallic-black insoluble precipitate, which was identified as trans-polyacetylene, by its characteristic IR spectrum (1014 cm⁻¹).⁷⁴ The ¹H NMR spectrum of the red-solution shows the presence of several new alkylidene species, but these disappear within hours at 25 °C, precluding full identification. A likely mechanism for the termination of polymerization of acetylene seems reaction of the alkylidene functions with the acidic protons of acetylene. Polymerization of acetylene by metal alkylidenes can be seen as ring-opening metathesis polymerization of an olefin with a very small ring. Living polymerization of acetylene by tungsten alkylidenes has been reported by Schrock et al.,⁷⁵ whereas polymerization of RC≡CR’ (R = H, R’ =H, Me, Ph; R = Me, R’ = Me) by Cp₂Ti(PMe₃)(=CHCH=CPH₂) was reported by Binger et al..⁷⁶ The niobium vinyl alkylidenes presented here might be excellent catalysts for the living polymerization of (substituted)
acetylenes, provided that their high, and probably uncontrolled, activity can be tempered, for instance by addition of Lewis bases to block free coordination sites temporarily.28

No reaction was observed between $^{10a}$ and benzaldehyde, while $^{10b}$ reacted in a fast, Wittig-type fashion with benzaldehyde to give the oxo compound CpNb(NAr)(PMe₃)=O (13) and a 1,3-diene (eq 3).

![Diagram](image)

Interpretation of the $^1$H NMR spectrum of this reaction is complicated by the presence of unknown ratios of several isomers of the 1,3-diene and apparent instability of 13. Although stable sulfides, selenides and tellurides are known in the Cp*Nb(NAr)(PMe₃) system,13b the corresponding niobium oxo complex has not been reported yet.

Both the vanadium and niobium vinyl alkylidenes react with excess elemental sulfur in benzene-$d_6$ to give the vinylthioaldehyde complexes CpM(NAr)(PMe₃)(η²-S=CHCH=CPh₂) (14a, M = V; 14b, M = Nb) (eq 4) quantitatively.

![Diagram](image)

The formation of thioaldehyde complexes 14 is indicated by the high-field shifts of both H$_α$ and H$_β$ of the former vinyl alkylidene moiety. In both cases only one of the possible 8 isomers is observed by NMR spectroscopy, presumably the syn,exo,s-trans-isomer. Both complexes show no sign of decomposition after 16 h at 25 °C in solution.
5.4 Discussion.

The successful formation of nucleophilic alkylidenes of vanadium and niobium by introduction of carbene fragments RCH: (R = alkyl, vinyl, aryl) depends on several factors. The reduced metal complexes CpM(NAr)L₂ used as starting materials need to have one labile ligand L which can be easily displaced by Π-acceptors. The rate of displacement of the second ligand L in CpM(NAr)L₂ and L in the alkylidene product CpM(NAr)(CHR)L should be much lower than the rate of displacement of the first ligand in the product forming step to avoid undesired side reactions. These side reactions are evident in the corresponding titanocene chemistry. For instance, the formation of Cp₂Ti(PMe₃)(=CHCH=CMMe₂) is accompanied by formation of a titanacyclopentane resulting from C,C-coupling of two η²-coordinated cyclopropenes on titanocene. Attempts to prepare titanocene alkylidene complexes by reaction of Cp₂Ti(PMe₃)₂ with phosphoranes RHC=PPh₃ (R = H, Me, Ph) failed. No alkylidenes could be detected by ¹H NMR spectroscopy, but instead fast decomposition of the starting materials was observed, leading to unidentified products.

The stability of the nucleophilic vanadium and niobium alkylidenes CpM(NAr)(CHR)L is dependent on the alkylidene substituent R and on the ease of displacement of L from the complex. Alkylidenes possessing substituents R that are capable to stabilize the alkylidene by resonance (e.g. vinyl, aryl) are much more stable than those possessing proton or alkyl substituents. Loss of L from the alkylidene opens up several decomposition pathways, for instance through bimolecular decomposition, as was found for Cp₂Ti(PMe₃)(=CH₂) or C-H activation of the solvent.

The activity of the vanadium alkylidenes CpV(NAr)(CHR)L in olefin metathesis like reactions appears to be low in comparison with their niobium analogues or the isolobal titanocene alkylidenes. The same factors that allow formation and isolation of stable nucleophilic vanadium alkylidenes also limit their usefulness for olefin metathesis reactions. Especially loss of phosphine from the 18 electron alkylidenes CpV(NAr)(CHR)PMe₃ (R = vinyl, phenyl), necessary to create electronically and sterically unsaturated CpV(NAr)(CHR) species capable of interacting with unsaturated substrates, was found non-occurring. A likely explanation for the tight bonding of the trimethylphosphine ligand in vanadium alkylidenes CpV(NAr)(CHR)PMe₃ and other vanadium Π-acceptor complexes (see chapter 4) might be found in the relatively small size of vanadium. Compared to the corresponding niobium ions the V⁺³ and V⁺⁵ ions are approximately 0.1 Å (or 15% relative to Nb) smaller. The difference between the sizes of V⁺⁵ and Ti⁺⁴ is of similar order. The small size of the central metal ion could result in a better overlap of the phosphine lone-pair and an empty frontier orbital of the CpM(NAr) fragment, and therefore in a tighter bond. On the other hand, a smaller central ion might also increase the relative steric hindrance between the CpM(NAr) fragment and incoming unsaturated substrates, thus preventing reaction.
More insight in the effects of size of the central metal ion in transition metal alkylidenes upon their activity in olefin metathesis reactions might be obtained by computational modelling studies, provided that the modelling packages used can handle differently sized transition metal ions. To date, no such studies have been reported.

The activity of the phosphine containing vanadium alkylidenes in olefin metathesis reactions might be improved in several ways. Electronically and sterically more unsaturated vanadium alkylidenes could be obtained by addition of reagents capable of forming strong bonds with phosphines such as strong Lewis acids. Should the alkylidene phosphine complexes \( \text{CpV(NAr)(CHR)PMe}_3 \) be in equilibrium with the alkylidenes \( \text{CpV(NAr)(CHR)} \) than this might increase the amount of reactive alkylidene. Thus far, attempts in this direction using \( \text{AlCl}_3 \) or \( \text{AlMe}_3 \) did not improve the reactivity of vanadium alkylidenes in ROMP of norbornene. Changing the size and electronic properties of the phosphine, like has been done in tuning rhodium hydroformylation catalysts, is another possibility. So far, attempts to synthesize complexes containing bigger phosphines like \( \text{PPhMe}_2 \) (chapter 4) were not successful. Influencing the nature of the other ancillary ligands (imido, cyclopentadienyl) by replacing them by, for instance, alkoxides in the case of \( \text{Cp} \) and \( \text{oxo} \) in the case of imido, is a more drastic strategy, but one which creates more room to control steric and electronic properties of vanadium alkylidenes, provided they can be obtained by the same methodology used in this chapter. Another worthwhile strategy might be the synthesis of (reduced) vanadium complexes that do not contain phosphines. Given the fact that nitrogen containing substrates like pyridine are not capable of displacing \( \text{PMe}_3 \) from 1, complexes of the type \( \text{CpV(NAr)(N)}_2 \) (\( \text{N} = \) nitrogen containing donor ligand) might be good target molecules. Formation of bis(2,6-dimethylphenylisonitrile) complexes through magnesium reduction of metalloocene dichlorides in the presence of isonitrile has been reported for titanocene and zirconocene. Finally, vanadium alkylidenes \( \text{CpV(NAr)(CHR)} \) without any stabilizing ligand might be obtained in situ by reduction of \( \text{CpV(NAr)Cl}_2 \) in the presence of phosphoranes or 3,3-disubstituted cyclopropenes. This probably represents the most attractive and fast method for improving the reactivity of vanadium alkylidenes. Alkylidene transfer to tungsten has been reported upon reduction of bis(alkoxide) imido tungsten dichlorides in the presence of phosphoranes.

5.5 Concluding remarks.

The formation of nucleophilic half-sandwich imido vanadium and niobium alkylidenes has been approached by two methods. The first method involves transfer of an alkylidene group from phosphoranes \( \text{RHC=PPh}_3 \) (\( \text{R} = \text{H, Me, Ph} \)) to \( \text{CpM(NAr)(PMe}_3)_2 \) (\( \text{M} = \text{V, Nb} \)).

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The second method involves ring-opening of 3,3-disubstituted cyclopropenes to give vinyl alkylidenes in the presence of CpM(NAr)(PMe$_3$)$_2$ (M = V, Nb).

The first method works for vanadium in a limited number of cases (R = H, Me, Ph), although the full scope of this method still has to be determined. For niobium, no transfer of an alkylidene group from a phosphorane to the metal was observed.

The second method is more versatile, although limited by the availability of 3,3-disubstituted cyclopropenes, allowing the syntheses of both vanadium and niobium vinyl alkylidenes CpM(NAr)(PMe$_3$)(=CHCH=CR$_2$) (R = Ph, Et).

The low symmetry of the half-sandwich imido framework and the typical bonding mode of the alkylidene group by interaction of the alkylidene p-orbital with metallocene-like π-orbitals of the metal fragment give rise to the formation of two rotamers for each alkylidene (except R = H). This, and the low thermal stability of some of the alkylidenes formed has seriously hampered a fast evaluation of the field of nucleophilic d$^0$ vanadium and niobium alkylidenes. It was however possible to isolate a number in pure form and deduce from these general characteristics of complexes CpM(NAr)(PMe$_3$)(CHR) for help in interpreting less clear-cut mixtures.

The vanadium alkylidenes containing proton or alkyl substituents were found to be unstable. The methyldiene complex CpV(NAr)(PMe$_3$)(CH$_2$) decomposes rapidly through the formation of the ethylene complex CpV(NAr)(PMe$_3$)(η$^2$-C$_2$H$_4$) while the ethyldiene complex CpV(NAr)(PMe$_3$)(CHMe) is stable in solution but decomposes upon attempted isolation. The benzylidene complex CpV(NAr)(PMe$_3$)(CHPh) has excellent thermal stability and could be isolated in good yield as red crystals. The molecular structure of this vanadium alkylidene shows an undistorted alkylidene ligand, with a vanadium carbon bond length indicative of a regular vanadium-carbon double bond.

The formation of vinyl alkylidenes CpM(NAr)(PMe$_3$)(=CHCH=CR$_2$) by ring-opening of 3,3-disubstituted cyclopropenes is accompanied by the formation of the cyclopropene adducts CpV(NAr)(PMe$_3$)(η$^2$-CHCHR$_2$) (R = Et, Ph), which can be converted to the vinyl alkylidenes by heating. The 3,3-diphenylvinyl alkylidenes of niobium and vanadium, as well as the niobium 3,3-diphenyl cyclopropene adduct, could be isolated as solids in good yield.

An explorative study of the reactivity of vanadium and niobium vinyl alkylidenes was performed, comparing their activity in olefin metathesis reactions. It was shown that the vanadium alkylidene is much less reactive towards unsaturated substrates like norbornene, acetylene and benzaldehyde, than the niobium alkylidene. The last reacts with these molecules in a normal, Wittig-type fashion through [2+2] cycloadditions giving polynorbornene, polyacetylene and a niobium oxo species, respectively. However, the activity of vanadium and niobium alkylidenes towards elemental sulfur is comparable, giving rise to the formation of the η$^2$-thioaldehyde complex CpV(NAr)(PMe$_3$)(η$^2$-S=CHPh) and the η$^2$-
thio vinyl aldehyde complexes CpM(NAr)(PMe₃)(η²-S=CHCHCPh₂). Assuming a mechanism for this reaction which involves the intermediacy of trimethylphosphine sulfide, [2+2] cycloadditions seem also possible for vanadium alkylidenes.

An explanation for the lack of reactivity of the vanadium alkylidenes might be found in the relatively small size of the vanadium ion compared to the corresponding niobium ion. The smaller ion size could lead to increased Lewis acidity which might prevent dissociation of PMe₃, thus maintaining the electronic and coordinative saturation of the metal center in the vanadium alkylidene complexes CpV(NAr)(PMe₃)(CHR).

It has been shown that nucleophilic d⁰ vanadium alkylidenes are readily accessible in the half-sandwich imido system by transfer of an alkylidene group from a phosphorane to the metal and by ring-opening of 3,3-disubstituted cyclopropenes. Tuning of the system, which is possible in various ways, is needed to further develop the undoubtedly very interesting and surprising chemistry of nucleophilic vanadium alkylidenes.

5.6 Experimental.

General Considerations. All manipulations of air and/or water sensitive compounds were performed under nitrogen or argon (used only when specified) using standard high-vacuum, Schlenk and glove box techniques. NMR spectra were recorded on a Varian VXR-300 (300 MHz ¹H; 75.4 MHz ¹³C; 78.9 MHz ⁵¹V) spectrometer in benzene-d₆ (unless stated otherwise) at 25 °C. Chemical shifts are reported in ppm, downfield from TMS (δ 0.00, ¹H, ¹³C) or VOCl₃ (δ 0.00, ⁵¹V) positive. All coupling constants and line widths are reported in Hz. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer, from Nujol mulls between KBr-discs. Wavenumbers are reported in cm⁻¹. Elemental analyses were performed at the Microanalytical Department of the University of Groningen, and are the average of at least two independent determinations.

Materials. Tetrahydrofuran, benzene, pentane (mixed isomers) and toluene were distilled from Na/K alloy before use. Benzene-d₆ and toluene-d₈ were vacuum-transferred from Na/K alloy. Acetone-d₆ was dried over molecular sieves (4Å). Trimethylaluminum (Aldrich), benzaldehyde, ethylbromide, benzylbromide (Janssen), methylbromide, sulfur, copper(I)chloride, AlCl₃ (Merck) and acetylene (Ucar) were used as received. Norbornene was dried over Na, distilled and stored under argon. The phosphoranes used were synthesized by deprotonation of the corresponding phosphonium salts with an excess of NaNH₂ in refluxing THF. After filtering the solution the phosphoranes were recrystallized at -25 °C. Phosphonium salts were prepared by refluxing a 1:1 mixture of PPh₃ and alkylbromide in THF overnight. 3,3-diphenylcyclopropene was synthesized starting from 1,1-diphenylethene according to an internal laboratory procedure of the Max Planck Institut für
Kohlenforschung, Mühlheim, Germany obtained from Dr. S. Albus. 3,3-diethylcyclopropene was obtained as a gift from Dr. S. Albus. The procedures for the syntheses of 1 and 7 can be found in the preceding chapter.

**Observation of CpV[N-2,6-C₆H₃-′-i-Pr)₂](PMe₃)(=CH₂) (2).** A mixture of 1 (15.0 mg, 0.034 mmol) and H₂C=PPh₃ (18.6 mg, 0.068 mmol) was dissolved in 0.5 mL of benzene- d₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken after 5 min at 25 °C showed a conversion of 80%: ¹H NMR δ 14.19 (dd, 1H, J₉Η = 9.8, J₉Η = 4.9, =CHH), 12.99 (dd, 1H, J₉Η = 6.6, J₉Η = 4.9, =CHH), 7.00 (m, 3H, NAr: Hₘ, Hₚ), 5.56 (d, 5H, J₉Η = 2.2, Cp), 4.70 (sept, 2H, J₉Η = 6.8, CHMe₂), 1.39 (d, 6H, J₉Η = 6.8, CHMe₂), 1.33 (d, 6H, J₉Η = 6.8, CHMe₂), 0.99 (d, 9H, J₉Η = 5.1, PMe₃).

**Observation of CpV[N-2,6-C₆H₃-′-i-Pr)₂](PMe₃)(=CHMe) (3).** A mixture of 1 (25.0 mg, 0.056 mmol) and MeHC=PPh₃ (16.0 mg, 0.056 mmol) was dissolved in 0.5 mL of benzene-d₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken after 17 h at 50 °C showed a conversion of 100%: ¹H NMR 3a δ 15.00 (unres. m, 1H, =CHMe), 7.00 (m, 3H, NAr: Hₘ, Hₚ), 5.49 (d, 5H, J₉Η = 2.6, Cp), 4.64 (sept, 2H, J₉Η = 6.6, CHMe₂), 3.10 (dd, 3H, J₉Η = 9.6, J₉Η = 9.6, =CHMe), 1.38 (d, 6H, J₉Η = 6.8, CHMe₂), 1.30 (d, 6H, J₉Η = 6.8, CHMe₂), 0.87 (d, 9H, J₉Η = 7.1, PMe₃); 3b δ 13.32 (mod. resolv. q, 1H, J₉Η = 9.5, J₉Η = 9.5, =CHMe), 7.00 (m, 3H, NAr: Hₘ, Hₚ), 5.50 (d, 5H, J₉Η = 2.6, Cp), 4.54 (sept, 2H, J₉Η = 6.6, CHMe₂), 3.66 (dd, 3H, J₉Η = 9.5, J₉Η = 9.5, =CHMe), 1.34 (d, 6H, J₉Η = 6.8, CHMe₂), 1.31 (d, 6H, J₉Η = 6.8, CHMe₂), 0.83 (d, 9H, J₉Η = 7.1, PMe₃). ⁵¹V NMR rotamer A δ -665 (d, J₉Π = 390); rotamer B δ -673 (d, J₉Π = 400). The ratio 3a:3b is 55:45.

CpV[N-2,6-C₆H₃-′-i-Pr)₂](PMe₃)(=CHPh) (4). A mixture of 1 (0.81 g, 1.82 mmol) and PhCH=PPh₃ (0.65 g, 1.82 mmol) in 20 mL of toluene was stirred at 70 °C for 16 h. Occasionally a vacuum was applied to remove PMe₃ liberated during reaction. After cooling to 25 °C solid CuCl (0.18 g, 1.82 mmol) was added and the resulting mixture was stirred at room temperature for 20 h. Removal of the solvent in vacuo gave a sticky, brown residue, which was extracted twice with 50 mL of pentane. Concentrating and cooling the combined extracts to -25 °C yielded 0.41 g (1.11 mmol, 61%) of red crystals in two crops: ¹H NMR δ 13.45 (d, 1H, J₉Π = 7.5, Hₐ), 7.65 (d, 2H, J₉Η = 7.9, Ph: Hₜ), 7.11 (t, 2H, J₉Η = 7.9, Ph: Hₚ), 7.00 (m, 3H, NAr: Hₘ, Hₚ, Ph: Hₜ), 6.83 (t, 1H, J₉Η = 7, NAr: Hₚ), 5.58 (d, 5H, J₉Π = 2.5, Cp), 4.27 (sept, 2H, J₉Η = 6.8, CHMe₂), 1.18 (d, 6H, J₉Η = 6.8, CHMe₂), 1.15 (d, 6H, J₉Η = 6.8, CHMe₂), 0.81 (d, 9H, J₉Π = 8.0, PMe₃); ¹³C NMR (toluene-d₈) δ 304 (Δν₁/₂ = 600, C₉), 148.5 (NAr: Cₚ), 144.8 (NAr: Cₙ), 137.8 (Ph: Cₚ), 127.8 (Ph: Cₙ), 126.4 (Ph: Cₚ), 125.1 (Ph: Cₘ), 123.1 (NAr: Cₚ), 122.5 (NAr: Cₙ), 101.4 (Cₚ), 26.8 (CHMe₂), 24.4 and
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24.1 (CHMe₂), 18.0 (d, JPC = 22.5, PMe₃); ⁵¹V NMR δ -630 (Δν₁/₂ = 1000); IR 2725(w), 2673(w), 1575(w), 1415(w), 1332(m), 1303(w), 1282(m), 1232(w), 1157(w), 1080(w), 1062(w), 1018(w), 952(s), 842(w), 819(w), 788(s), 756(s), 732(s), 723(s), 692(m). Anal. Calcd for C₂₇H₃₇NPV: C, 70.93; H, 8.16; V, 11.14. Found: C, 70.85; H, 8.11; V, 11.07.

Observation of CpV[N-2,6-C₆H₃-(i-Pr)₂](PMe₃)(η²-CHCHCPh₂) (8a). A mixture of 1 (22.0 mg, 0.050 mmol) and 3,3-diphenylcyclopropene (9.5 mg, 0.050 mmol) was dissolved in 0.5 mL of benzene-ᵈ₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken after 20 h at 50 °C showed a conversion of 100%: ¹H NMR δ 7.52 (m, 4H, Ph: Hₖ), 7.12 (m, 9H, Ph: Hₖ, Hₚ, NAr: Hₖ, Hₚ), 4.90 (d, 5H, JPH = 2.5, Cp), 4.00 (sept, 2H, JHH = 6.8, CHMe₂), 3.17 (dd, 1H, JHH = 12.0, JPH = 7.0, HĈ=CH exo), HC=ĈH endo not observed, 1.35 (d, 6H, JHH = 6.8, CHMe₂), 1.30 (d, 6H, JHH = 6.8, CHMe₂), 1.1 (d, 9H, JPH = 8, PMe₃). The product is obtained as a 40:60 mixture of 8a and 10a.

CpNb[N-2,6-C₆H₃-(i-Pr)₂](PMe₃)(η²-CHCHCPh₂) (8b). A mixture of 7 (0.19 g, 0.39 mmol) and 3,3-diphenylcyclopropene (0.08 g, 0.39 mmol) in 10 mL of toluene was stirred at 50 °C for 16 h. After cooling to 25 °C the solution was filtered and the solvent removed in vacuo. The residue was washed with 10 mL of cold pentane (0 °C) and dried in vacuo to give 0.20 g (0.33 mmol, 84%) of a beige powder: ¹H NMR δ 7.36 (m, 4H, Ph: Hₖ), 7.20 (m, 4H, Ph: Hₖ), 7.10 (m, 2H, Ph: Hₚ), 7.03 (m, 2H, NAr: Hₖ), 6.94 (m, 1H, NAr: Hₚ), 5.16 (d, 5H, JPH = 0.7, Cp), 3.96 (sept, 2H, JHH = 7.0, CHMe₂), 3.50 (dd, 1H, JHH = 8.8, JPH = 1.9, HĈ=ĈH exo), 2.84 (dd, 1H, JHH = 8.8, JPH = 8.8, HC=ĈH endo), 1.31 (d, 6H, JHH = 7.0, CHMe₂), 1.30 (d, 6H, JHH = 7.0, CHMe₂), 0.98 (d, 9H, JPH = 8.1, PMe₃); ¹³C NMR δ NAr: Cipso not observed, 153.6 and 148.6 (Ph: Cipso), 144.7 (NAr: Cₚ), 133.2, 128.5, 127.8, 126.3, 125.8, 124.6, 122.9, and 122.8 (Ph: Cₓ, Cₓ, Cₓ, Cₓ, NAr: Cₓ, Cₓ), 102.5 (Cp), 70.9 (dd, JCH = 150, JPH = 21, HC=ĈH exo), 64.5 (CPh₂), 61.9 (d, JCH = 150, HC=ĈH endo), 26.9 (CHMe₂), 24.8 and 24.5 (CHMe₂), 16.9 (d, JPC = 24.8, PMe₃). Anal. Calcd. for C₃₅H₄₃NPNb: C, 69.88; H, 7.20; Nb, 15.44. Found: C, 69.15; H, 7.19; Nb, 15.36.

Observation of CpV[N-2,6-C₆H₃-(i-Pr)₂](PMe₃)(η²-CHCHCEt₂) (9a). A mixture of 1 (24.0 mg, 0.054 mmol) and 3,3-diethylcyclopropene (5.2 mg, 0.054 mmol) was dissolved in 0.5 mL of benzene-d₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken after 2 h at 50 °C showed a conversion of 44%, after an additional 1.5 h at 75 °C 100% conversion is reached: ¹H NMR δ 7.11 (m, 2H, NAr: Hₖ, syn and anti), 6.92 (m, 1H, NAr: Hₚ, syn and anti), 5.40 (d, 5H, JPH = 2.4, Cp, syn), 5.18 (d, 5H, JPH = 2.4, Cp, anti), 4.52 (sept, 2H, JHH = 7.0, CHMe₂, anti), 3.93 (sept, 2H, JHH = 7.0, CHMe₂, syn), 3.2 (m, 1H, HC=ĈH exo, syn and anti), 2.25 (m, 1H, HC=ĈH endo, syn and anti).
Observation of CpNb[N-2,6-C₆H₃-(i-Pr)₂]_2(PMe₃)(η^2-CHCHCEt₂) (9b). A mixture of 7 (31.0 mg, 0.064 mmol) and 3,3-diethylcyclopropene (6.0 mg, 0.064 mmol) was dissolved in 0.5 mL of benzene-d₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A $^1$H NMR spectrum taken after 72 h at 25 °C showed a conversion of 100%: $^1$H NMR $\delta$ 7.04 (m, 2H, NAr: H$_p$, syn and anti), 5.62 (s, 5H, Cp, syn), 13.03 (dd, 1H, J$_{HH}$ = 13.7, J$_{PH}$ = 7.0, =CHCH, syn), 7.74; V, 9.10. Found: C, 73.86; H, 7.64; V, 9.85.

CpV[N-2,6-C₆H₃-(i-Pr)₂]_2(PMe₃)(=CHCH=CPh₂) (10a). A mixture of 1 (0.37 g, 0.83 mmol) and 3,3-diphenylcyclopropene (0.16 g, 0.83 mmol) in 20 mL of toluene was stirred at 75 °C for 40 h. After cooling to 25 °C the solution was filtered and the solvent removed in vacuo. The residue was washed with 20 mL of pentane and dried in vacuo to give 0.50 g (0.48 mmol, 58%) of a red powder: $^1$H NMR $\delta$ 14.44 (dd, 1H, J$_{HH}$ = 15.0, J$_{PH}$ = 10, =CHCH, syn), 13.03 (dd, 1H, J$_{HH}$ = 13.7, J$_{PH}$ = 7.0, =CHCH, anti), 9.63 (dd, 1H, J$_{HH}$ = 13.7, J$_{PH}$ = 4.0, =CHCH, anti), 8.66 (dd, 1H, J$_{HH}$ = 15.0, J$_{PH}$ = 3.4, =CHCH, syn), 7.53 (d, 4H, J$_{HH}$ = 8.0, Ph: H$_o$, syn and anti), 7.1 (m, 9H, NAr: H$_m$, H$_p$, Ph: H$_m$, H$_p$, syn and anti), 5.62 (s, 5H, Cp, syn), 5.42 (s, 5H, Cp, anti), 4.54 (sept, 2H, J$_{HH}$ = 6.9, CHMe₂, anti), 4.39 (sept, 2H, J$_{HH}$ = 6.9, CHMe₂, syn), 1.25 (d, 6H, J$_{HH}$ = 6.9, CHMe₂, syn and anti), 1.18 (d, 6H, J$_{HH}$ = 6.9, CHMe₂, syn), 0.90 (d, 9H, J$_{PH}$ = 7.9, PMe₃, anti), 0.80 (d, 9H, J$_{PH}$ = 8.2, PMe₃, syn). $^{13}$C NMR C$_\alpha$ not observed $\delta$ 146.5, 146.4, 145.1, 142.1, 142.0, 141.9, 131.5, 131.4, 131.3, 131.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 126.7, 126.6, 125.9, 123.5, 123.4, 122.8, and 122.6 (NAr and Ph C), 101.7 (Cp, syn), 101.5 (Cp, anti), 27.6 (CHMe₂, syn), 27.3 (CHMe₂, anti), 25.0 (CHMe₂, syn), 24.6 (CHMe₂, anti), 24.4 (CHMe₂, anti), 23.7 (CHMe₂, syn), 18.5 (d, J$_{PC}$ = 23.3, PMe₃, anti), 18.4 (d, J$_{PC}$ = 23.7, PMe₃, syn). $^{51}$V NMR $\delta$ -571 ($\Delta\nu_{1/2}$ = 1400, anti), -582 ($\Delta\nu_{1/2}$ = 1600, syn). The ratio syn:anti is 6:4. Anal. Calcd for C$_{35}$H$_{43}$NPV: C, 75.12; H, 7.74; V, 9.10. Found: C, 73.86; H, 7.64; V, 9.85.

CpNb[N-2,6-C₆H₃-(i-Pr)₂]_2(PMe₃)(=CHCH=CPh₂) (10b). A mixture of 7 (0.78 g, 1.61 mmol) and 3,3-diphenylcyclopropene (0.31 g, 1.61 mmol) in 25 mL of toluene was stirred at 75 °C for 10 d. After cooling to 25 °C the solution was filtered and the solvent removed in vacuo. The residue was washed with 10 mL of pentane and dried in vacuo to give 0.50 g (0.83 mmol, 52%) of an orange powder: $^1$H NMR $\delta$ 13.44 (d, 1H, J$_{HH}$ = 14.6, =CHCH,
Observation of Cpx[N-2,6-C₆H₃-(i-Pr)₂][PMe₃] (=CHCH=C Et₂) (11a). A mixture of 1 (24.0 mg, 0.054 mmol) and 3,3-diethylcyclopropene (5.2 mg, 0.054 mmol) was dissolved in 0.5 mL of benzene-δ₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken was taken after 3 d at 75 °C: ¹H NMR δ 14.97 (dd, 1H, JHH = 14.3, JPH = 9.0, =CHCH, syn), 13.42 (dd, 1H, JHH = 13.7, JPH = 11.0, =CHCH, anti), 8.59 (dd, 1H, JHH = 13.7, JPH = 3.8, =CHCH, anti), 7.71 (dd, 1H, JHH = 14.3, JPH = 3.3, =CHCH, syn), 7.56 (dd, 1H, JHH = 8.0, Ph: Hₕ, syn), 5.77 (d, 5H, Cp, syn), 4.68 (sept, 2H, JHH = 6.9, CHMe₂, anti), 4.55 (sept, 2H, JHH = 6.9, CHMe₂, syn), 2.35 (overlapping q, 4H, CH₂CH₃, syn and anti), 1.42 (d, 6H, JHH = 6.8, CHMe₂, anti), 1.33 (d, 6H, JHH = 6.8, CHMe₂, anti), 1.31 (d, 6H, JHH = 6.9, CHMe₂, syn), 1.23 (d, 6H, JHH = 6.9, CHMe₂, syn), 1.08 (overlapping t, 6H, CH₂CH₃, syn and anti), 0.93 (d, 9H, JPH = 7.9, PMe₃, anti), 0.87 (d, 9H, JPH = 7.9, PMe₃, syn). ⁵¹V NMR δ -571 (Δν₁/₂ = 1400, anti), -582 (Δν₁/₂ = 1600, syn). The ratio syn:anti is 1:1.

Observation of CpxNb[N-2,6-C₆H₃-(i-Pr)₂][PMe₃] (=CHCH=C Et₂) (11b). A mixture of 7 (31.0 mg, 0.064 mmol) and 3,3-diethylcyclopropene (6.0 mg, 0.064 mmol) was dissolved in 0.5 mL of benzene-δ₆ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A ¹H NMR spectrum taken after 72 h at 25 °C shown by 9 days at 75 °C showed a conversion of 100%: ¹H NMR δ 13.85 (d, 1H, JHH = 14.1, =CHCH, syn), 12.23 (d, 1H, JHH = 13.6, =CHCH, anti), 8.37 (d, 1H, JHH = 13.6, =CHCH, anti), 7.47 (d, 1H, JHH = 14.1, =CHCH, syn), 7.16 (m, 2H, NAr: Hₚ, syn and anti), 7.02 (m, 1H, NAr: Hₚ, syn and anti), 5.77 (s, 5H, Cp, syn), 5.48 (s, 5H, Cp, anti), 4.47 (sept, 2H, JHH = 6.9, CHMe₂, syn), 3.85 (sept, 2H, JHH = 6.9, CHMe₂, anti), 2.25 (overlapping q, 4H, CH₂CH₃, syn and anti), 1.40

Chapter 5: Half-sandwich imido vanadium(V) and niobium(V) alkylidenes.

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Chapter 5: Half-sandwich imidovanadium(V) and niobium(V) alkylidenes.

Survey of reactivity of 4. Acetone, benzaldehyde: Solutions of 4 (10 mg, 0.022 mmol) in 0.4 mL of benzene-$d_6$ were placed in a 5 mm NMR tube fitted with a septum. One equivalent of acetone or benzaldehyde was added with a syringe. $^1$H NMR spectra were acquired after 30 min at 25 °C. No changes in the spectrum of 4 were observed in both cases. Acetone-$d_6$: Alkylidene 4 (10 mg, 0.022 mmol) was dissolved in 0.4 mL of acetone-$d_6$, giving a red solution: $^1$H NMR δ 13.35 (d, 1H, $J_{PH} = 7.5$, H$_{α}$), 7.36 (d, 2H, $J_{HH} = 8.2$, Ph: H$_o$), 7.03 (t, 2H, $J_{HH} = 7.9$, Ph: H$_m$), 6.8 (m, 4H, NAr: H$_m$, H$_p$, Ph: H$_p$), 5.73 (d, 5H, $J_{PH} = 2.4$, Cp), 4.15 (sept, 2H, $J_{HH} = 6.8$, C$_2$HMe$_2$), 1.29 (d, 9H, $J_{PH} = 8.8$, PMe$_3$), 1.09 (d, 6H, $J_{HH} = 6.8$, CHMe$_2$). Norbornene: A solution of 4 (8 mg, 0.018 mmol) and norbornene (88 mg, 0.93 mmol) in 0.4 mL of benzene-$d_6$ was placed in a 5 mm NMR tube. The tube was sealed and kept at 100 °C after an initial $^1$H NMR spectrum had been taken. No polynorbornene could be observed after 24 h. The spectra of 4 and norbornene were unchanged.

Observation of CpV[N-2,6-C$_6$H$_3$-(i-Pr)$_2$](PMe$_3$)(η$_2$-S=CHPh) (12). A mixture of 4 (24.0 mg, 0.052 mmol) and S$_8$ (5 mg, 0.16 mmol) was dissolved in 0.5 mL of benzene-$d_6$ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A $^1$H NMR spectrum taken after 5 min at 25 °C showed a conversion of 100%: $^1$H NMR δ 7.68 (d, 2H, $J_{HH} = 7.7$, Ph: H$_o$), 7.28 (t, 2H, $J_{HH} = 7.7$, Ph: H$_m$), 7.04 (t, 1H, $J_{HH} = 7.2$, Ph: H$_p$), 6.86 (m, 3H, NAr: H$_m$, H$_p$), 5.72 (s, 1H, S=CHPh), 5.19 (d, 5H, $J_{PH} = 2.5$, Cp), 3.70 (sept, 2H, $J_{HH} = 6.8$, CHMe$_2$), 1.23 (d, 6H, $J_{HH} = 6.8$, CHMe$_2$), 1.15 (d, 6H, $J_{HH} = 6.8$, CHMe$_2$), 1.09 (d, 9H, $J_{PH} = 8.8$, PMe$_3$); $^{13}$C NMR δ NAr: C$_{ipso}$ not observed, 153.8 (NAr: C$_o$), 147.3 (Ph: C$_{ipso}$), 127.9 (Ph: C$_o$), 124.6 (Ph: C$_p$, NAr: C$_p$), 124.4 (Ph: C$_m$), 123.3 (NAr: C$_m$), 104.6 (Cp), 26.7 (CHMe$_2$), 25.5 and 24.4 (CHMe$_2$), 16.9 (d, $J_{PC} = 24.0$, PMe$_3$); $^{51}$V NMR δ -878 (d, $J_{PV} = 190$).

Survey of reactivity of 10a. Benzaldehyde: A solutions of 10a (11 mg, 0.02 mmol) in 0.5 mL of benzene-$d_6$ was placed in a 5 mm NMR tube fitted with a septum. One equivalent of benzaldehyde was added with a syringe. A $^1$H NMR spectrum was acquired after 30 min at 25 °C. No changes in the spectrum of 10a were observed. Acetylene: A solution of 10a (11 mg, 0.02 mmol) in 0.5 mL of benzene-$d_6$ was placed in a 10 mL flask fitted with a Young tap. The solution was cooled to -10 °C, and the atmosphere replaced by 1 atm of acetylene. Next, the solution was kept at 65 °C. After 3 h the still clear, red solution was transferred to a 5 mm NMR tube. No changes in the spectrum of 10a were observed. Norbornene: A solution of 10a (11 mg, 0.02 mmol) and norbornene (60 mg, 0.64 mmol) in 0.4 mL of
benzene-$d_6$ was placed in a 5 mm NMR tube. The tube was sealed and kept at 100 °C after an initial $^1$H NMR spectrum had been taken. No polynorbornene could be observed after 24 h. The spectra of 10a and norbornene were unchanged.

**Survey of reactivity of 10b. Benzaldehyde:** A solution of 10b (11 mg, 0.018 mmol) in 0.5 mL of benzene-$d_6$ was placed in a 5 mm NMR tube fitted with a septum. One equivalent of benzaldehyde was added with a syringe. A $^1$H NMR spectrum was acquired after 30 min at 25 °C, showing a complicated mixture of several CpNb(NAr) fragments, free PMe$_3$, traces of benzaldehyde and several isomers of PhCH=CHCH=CPh$_2$ ($\delta$ 6.6-5.7 ppm, overlapping multiplets. No 10b could be observed. *Acetylene:* A solution of 10b (10 mg, 0.016 mmol) in 0.5 mL of benzene-$d_6$ was placed in a 10 mL flask fitted with a Young tap. The solution was cooled to -10 °C, and the atmosphere replaced by 1 atm of acetylene. Upon warming to room temperature the color of the solution changed from orange to dark red and the formation of a black, metallic shining precipitate was observed. After 3 h at 25 °C the red solution was transferred to a 5 mm NMR tube; several new resonances in the vinyl alkylidene region were observed (doublets at $\delta$ 13.4, 17, 13.14, 13.08, 11.95, 11.6, 11.54, 11.52, 8.85, 8.80, 8.68, 8.6, 8.45, 8.1). A small amount of 10b was still present (< 10%). An IR spectrum of the black solid was taken after washing with pentane and drying in vacuo: IR 1014. *Norbornene:* A solution of 10b (11 mg, 0.018 mmol) and norbornene (100 mg, 1.06 mmol) in 0.4 mL of benzene-$d_6$ was placed in a 5 mm NMR tube. The tube was sealed and kept at 100 °C after an initial $^1$H NMR spectrum had been taken. After 16 h about 50% of the polynorbornene was converted to polynorbornene containing a 7:3 mixture of trans and cis vinylene bonds. The $^1$H NMR spectrum of polynorbornene was identical to that reported in literature.

**Observation of CpM[N-2,6-C$_6$H$_3$-(i-Pr)$_2$](PMe$_3$)(\eta^2-S=CHCH=CPh$_2$) (14a, M = V; 14b, M = Nb).** A mixture of 10a (12.0 mg, 0.021 mmol) and S$_8$ (5 mg, 0.16 mmol) was dissolved in 0.5 mL of benzene-$d_6$ and placed in a 5 mm NMR tube. The tube was cooled to -196 °C and sealed. A $^1$H NMR spectrum taken after 5 min at 25 °C showed a conversion of 100% to 14a: $^1$H NMR $\delta$ 7.67 (d, 2H, $J_{HH}$ = 7.2, Ph: H$_o$), 7.49 (d, 2H, $J_{HH}$ = 7.3, Ph': H$_o$), 7.0 (m, 4H, Ph and Ph': H$_m$), 6.85 (m, 6H, NAr: H$_p$, H$_p'$; Ph and Ph': H$_p'$, S=CHCH), 5.43 (d, 5H, $J_{PH} = 2.4$, Cp), 5.38 (d, 1H, $J_{HH} = 10.3$, S=CHCH), 3.54 (sept, 2H, $J_{PH} = 8.8$, PMe$_3$), 0.90 (d, 6H, $J_{HH} = 6.8$, CHMe$_2$). A similar procedure using 10b (16.0 mg, 0.027 mmol) and S$_8$ (5 mg, 0.16 mmol) gave 14b: $^1$H NMR $\delta$ 7.55 (m, 4H, Ph and Ph': H$_o$), 7.22 (m, 4H, Ph and Ph': H$_m$), 7.04 (m, 2H, Ph and Ph': H$_p'$), 6.88 (m, 3H, NAr: H$_p$, H$_p'$), 5.94 (d, 1H, $J_{HH} = 12.3$, S=CHCH), 5.76 (d, 5H, $J_{PH} = 1.8$, Cp), 4.80 (dd, 1H, $J_{HH} = 12.3$, $J_{PH} = 8.0$, S=CHCH), 3.53 (sept, 2H, $J_{HH}$
= 6.8, CHMe₂), 1.26 (d, 6H, J²HH = 6.8, CHMe₂), 1.01 (d, 9H, J³PH = 8.8, PMe₃), 0.78 (d, 6H, J²HH = 6.8, CHMe₂).

**Table 4. Crystallographic Data for 4.**

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ᵃ Reﬁned by least-squares on F²(SHELXL-93). ᵇ P = (Max(F₀, 0) + 2F²)/3.

**References and notes.**