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Alkylation and reductive dimerization of half-sandwich imido vanadium dichlorides ☆

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Abstract

The vanadium imido complex $ArNVCl_3$ (**2**) (Ar = 2,6-C_6H_3-$(^iPr)_2$) can be converted to the half-sandwich imido vanadium complex $CpV(NAr)Cl_2$ (**3**) by reaction with $CpSiMe_3$. Reaction of **3** and of CpV(N–*p*-tolyl)Cl_2 (**1**) with alkylating reagents did not allow the isolation of the pure dialkyl complexes but showed extensive reduction of vanadium. Reaction of **1** with $AlMe_3$ leads to the formation of a mixture of diamagnetic dimeric, imido-bridged complexes $(CpV)_2$(μ-N–*p*-tolyl$)_2$MeR (R = Me or Cl), which can be converted to the pure chloro compound [CpV(μ-N–*p*-tolyl)Cl$]_2$ (**4**) by reaction with HCl. Dimerization is prevented when the more bulky ArN ligand is used. Alkylation of **4** with MeLi proceeds cleanly to give the methyl compound [CpV(μ-N–*p*-tolyl)Me$]_2$ (**5**). The molecular structures of the formally vanadium(IV) complexes **4** and **5** have been obtained, showing a planar cyclovanadazene core with a vanadium–vanadium single bond and V–Cl and $V–C_{Me}$ bond lengths that are characteristic of V(V) compounds. Compound **5** reacts with CO by insertion in the V–C bond, but no reaction is observed with other small unsaturated molecules or Brønsted acids. The ^{51}V NMR chemical shifts of the new complexes are reported and compared with the chemical shifts of known imido vanadium complexes.

Keywords: Vanadium; Half-sandwich complexes; Imido complexes; Alkylation; Reduction

1. Introduction

Oxo and imido ligands are particularly suitable for stabilizing high oxidation state transition metal complexes because of their ability to participate in extensive ligand-to-metal π donation [1]. The imido ligand has the advantage that it contains an organic substituent through which the steric and electronic properties of the complex may be influenced. The use of imido ligands in vanadium(V) chemistry, mainly by Maatta and coworkers [2], Preuss and coworkers [3] and Horton and coworkers [4], has greatly expanded its organometallic chemistry and allowed the structural characterization of the first alkylvanadium(V) complex [4a].

Combination of a cyclopentadienyl ligand and an imido ligand on a Group 5 metal M results in the formation of half-sandwich imido fragments CpM(NR) (R = alkyl or aryl). These fragments are considered to have similar molecular orbitals, in both energy and shape, as the Group 4 metallocene fragments Cp_2M' [5]. This so-called isolobal relationship [6] (Fig. 1), which can also be extended to the non-cyclopentadienyl Group 6 metal fragments $(RN)_2M''$, has been confirmed by quantum-chemical calculations [5,7] and derives from the similarities between the symmetry properties of the frontier orbitals of the imido and cyclopentadienyl ligands. Although the isolobal analogy is, strictly speaking, structural, ligand substitution studies indicate that close similarities in reactivity exist for these fragments as well [8]. The relationship has been explored successfully for niobium versus zirconium by Gibson and coworkers. [5,8a–8e] but similar investigations for vanadium vs. titanium have not been reported, although suitable starting materials (i.e. cyclopentadienyl vanadium(V) imido dichlorides) are known [2,3b].

☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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We anticipated that thermally induced α-hydrogen abstraction in $CpV(NR)R'_2$ complexes containing alkyl groups lacking β-hydrogen atoms, which might be synthesized by simple salt-metathesis reactions, could provide a new synthetic route to d^0 vanadium alkylidenes. Although these species can be obtained by oxidative addition of carbene fragments to reduced vanadium complexes [9], the resulting phosphine-stabilized alkylidenes so far have proved to be inactive in olefin metathesis reactions. Indications have been obtained that phosphine-free imido vanadium alkylidenes [10] are more active in olefin metathesis reactions than the known d^0 or d^2 vanadium alkylidenes [9,11].

Here we present the synthesis of a half-sandwich vanadium(V) dichloride containing the bulky arylimido ligand ArN ($Ar = 2,6\text{-}C_6H_3\text{-}(^iPr)_2$) and the reactivity of half-sandwich arylimido vanadium dichlorides towards alkylating reagents. A special section is reserved for the reactivity towards trimethylaluminium, where reductive dimerization to half-sandwich imido vanadium(IV) complexes is observed. Similar reductive dimerizations in non-cyclopentadienyl vanadium imido systems have recently been reported by Preuss et al. [3e] and Floriani and coworkers [12]. Part of this investigation has been communicated previously [9].

2. Results and discussion

2.1. Synthesis of half-sandwich vanadium(V) imido dichlorides

Initial experiments on the alkylation of $CpV(N\text{-}p\text{-}tolyl)Cl_2$ (**1**) [2] and the available data on alkylation of $CpV(N\text{-}^tBu)(O\text{-}^tBu)Cl$ [3c] indicated that cyclopentadienyl vanadium(V) imido complexes containing relatively small imido ligands such as ^tBuN and *p*-tolylN have a strong tendency to undergo reductive dimerization upon attempted alkylation. The use of a more bulky imido ligand might prevent dimerization. In the imido chemistry of niobium and tantalum [5,8a–8e] the $2,6\text{-}C_6H_3\text{-}(^iPr)_2$ imido ligand has been used extensively and no dimerization has been reported to date.

In analogy with the established route to (phenylimido)vanadium complexes [2], $OVCl_3$ was reacted with $2,6\text{-}C_6H_3\text{-}(^iPr)_2$-isocyanate in refluxing octane (Eq. 1).

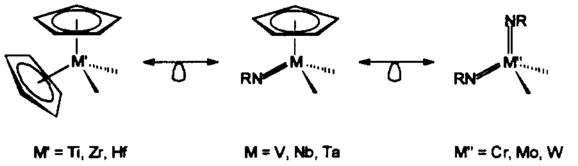
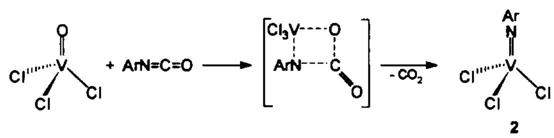


Fig. 1. Isolobal relationships in early transition metal cyclopentadienyl-imido systems.

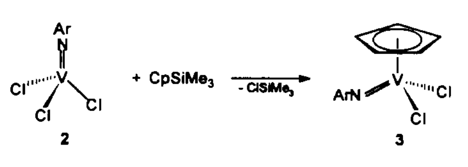


(1)

The initial brown color of the mixture changes slowly (hours) to green and gas evolution is observed. The arylimido complex $VCl_3(NAr)$ (**2**) can be isolated as a brown–green solid with a nearly quantitative yield. The compound decomposes quickly in air but can be stored under inert atmosphere indefinitely. The ^1H NMR spectrum shows the characteristic resonances for the ^iPr groups but shifted to lower field compared with the resonances in the starting isocyanate. Transfer of an RN fragment from isocyanates RNCO to metal oxo complexes is a common preparative method for metal imido complexes [13] and is postulated to occur through [2 + 2] cycloaddition of the metal oxo bond and the isocyanate (Eq. (1)) [14]. For vanadium, transfer was found to depend strongly on the nature of the R group. Transfer is easy for R = aryl [2] but fails for R = alkyl (i.e. $^tBu_3SiNCO$) [4a]. This transfer represents the first step in the condensation of isocyanates to carbodiimides, which has been found to be catalyzed by both vanadium oxide and imido complexes [15].

Compound **2** can be converted to the corresponding half-sandwich imido dichloride $CpV(NAr)Cl_2$ (**3**) by reaction with one equivalent of $CpSiMe_3$ (Eq. 2). Consistent with the presence of a more bulky imido substituent in **2**, the reaction proceeds slower than the corresponding reaction to give **1**. Attempts to synthesize **3** by reaction of **2** with sodium cyclopentadienide in tetrahydrofuran (THF) (reported as an alternative synthesis for **1** starting from *p*-$tolylNVCl_3$ [2]) gave mixtures of **2**, **3** and unidentified paramagnetic products. The ^1H NMR spectrum of **3** shows the expected singlet for the cyclopentadienyl ring protons. Complex **3** is markedly less air sensitive than **2**. It can be handled in air in the solid state for brief periods of time without decomposition.

The structures of **2** and **3** in the solid state have not been determined but the compounds can be assumed to be monomers based upon the absence of color changes upon dissolution in toluene [2]. Compound **3** is thought to be isostructural with the corresponding niobium complex $CpNb(NAr)Cl_2$, which was found to have a pseudotetrahedral geometry about the metal atom [5].



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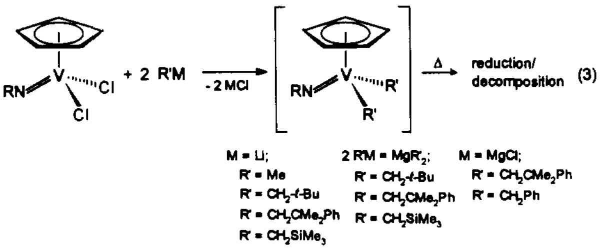


2.2. *Reactions of half-sandwich arylimido vanadium dichlorides with alkylating reagents*

Reaction of **1** and **3** with alkylating reagents containing alkyl groups lacking β-hydrogen atoms did not lead to the isolation of pure dialkyl complexes in any of the performed cases (Eq. 3).

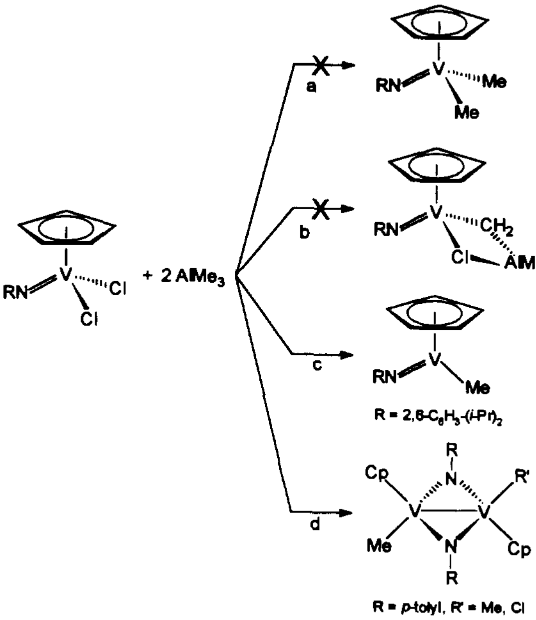
The reactions give complex oily mixtures of (partially) alkylated (as observed by ^1H NMR spectroscopy) and reduced–decomposed CpV(NR) fragments. The oily nature of the compounds prevented purification by standard inert handling techniques. Addition of PMe_3 to produce possibly more stable 18-electron derivatives $CpV(NR)R'_2PMe_3$ neither improved the selectivity of the alkylations nor allowed the isolation of alkylidene species that might be formed through α-hydrogen abstraction. Apparently, the cyclopentadienyl ligand in **1** and **3** does not significantly improve the stability of alkyl derivatives towards reduction, compared with *p*-tolylNVCl$_3$. Reaction of *p*-tolylNVCl$_3$ with $(Me_3SiCH_2)_2Mg$ allowed the isolation of a homologous series of (trimethylsilyl)methyl complexes *p*-tolylNV$(CH_2SiMe_3)_xCl_{3-x}$ ($x = 1$–3) [2]. Reaction of **3** with the mild alkylating reagent Me_4Sn did not proceed (benzene-d_6; 25 °C; 8 h).

2.3. *Reactions of half-sandwich arylimido vanadium dichlorides with AlMe$_3$*

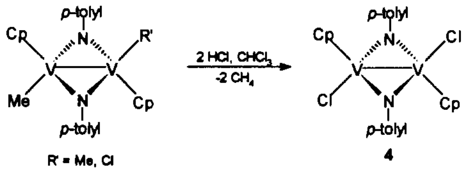
The reaction of Cp_2TiCl_2 with $AlMe_3$ is known to give two products, depending upon reaction conditions. With one equivalent of $AlMe_3$ in methylene chloride–pentane the mono methyl complex $Cp_2TiMeCl$ is formed [16]. From toluene, with two equivalents, the methylene-bridged complex $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ is obtained [17]. This last compound served as the starting point for titanocene alkylidene complexes in catalytic olefin metathesis chemistry [18]. Analogously, it is expected that reaction of $CpV(NR)Cl_2$ complexes **1** and **3** with two equivalents of $AlMe_3$ gives either $CpV(NR)Me_2$ or methylene-bridged complexes $CpV(NR)(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ (Scheme 1, routes a and b). Instead, reduction to half-sandwich imido V(IV) complexes is observed (Scheme 1, routes c and d). For **1** this reaction proceeds through formation of a mixture of (partially) methylated imido-bridged complexes [(CpV)$_2$(μ-N-*p*-tolyl)$_2$MeR′] (R′ = Me or Cl). For **3** this reaction gives methane and a paramagnetic (by NMR) product, tentatively formulated as CpV(NAr)Me on the basis of its high solubility in pentane and the almost complete absence of NMR resonances. Apparently, formation of dimers is prevented by the bulky imido substituent in the case of **3**.

The reaction leading to the mixture of imido-bridged dimers [(CpV)$_2$(μ-N-*p*-tolyl)$_2$MeR′] (R′ = Me or Cl) is best performed in a minimal amount of toluene with pure $AlMe_3$ added to **1**. The formation of a red precipitate and concomitant evolution of methane (^1H NMR spectroscopy) is observed. Generation of methane indicates the formation of methyl radicals, which may abstract hydrogen from for example the solvent or $AlMe_3$. The red precipitate can be isolated with a good yield. Recrystallization from toluene, THF, methylene chloride or chloroform gives block-shaped dark-red crystals which, although free of aluminum compounds, appears to be a mixture of fully and partially methylated imido-bridged dimers [19]. In order to obtain a pure compound the mixture of imido-bridged dimers [(CpV)$_2$(μ-N-*p*-tolyl)$_2$MeR′] (R′ = Me or Cl) was treated with a slight excess of hydrogen chloride, which leads to the quantitative formation of the parent chloro compound [CpV(μ-N–*p*-tolyl)Cl]$_2$ (**4**) (Eq. 4).

Complex **4** can be isolated as a virtually air-stable green crystalline material with a good yield. It is diamagnetic (by NMR spectroscopy). Reaction of **4** with a slight excess of MeLi in diethyl ether yields red [CpV(μ-N–*p*-tolyl)Me]$_2$ (**5**) (Eq. 5).



Scheme 1. Reaction pathways for reaction of $CpV(NR)Cl_2$ with two equivalents of $AlMe_3$.



(4)

Table 1
Selected geometrical data for $[CpV(\mu\text{-N-}p\text{-tolyl})Cl]_2$ (**4**) and $[CpV(\mu\text{-N-}p\text{-tolyl})Me]_2$ (**5**).

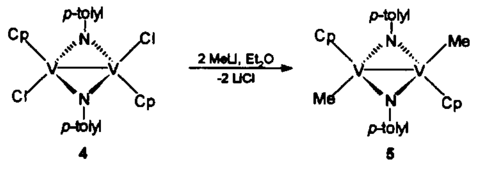
4		5	
Bond lengths (Å)			
V(1)–N(1)	1.850(2)	V(1)–N(1)	1.851(2)
V(1)–C(8)	2.260(5)	V(1)–C(8)	2.270(4)
V(1)–C(9)	2.290(4)	V(1)–C(9)	2.313(3)
V(1)–C(10)	2.302(4)	V(1)–C(10)	2.330(3)
V(1)–C(11)	2.284(4)	V(1)–C(11)	2.303(4)
V(1)–C(12)	2.257(5)	V(1)–C(12)	2.268(4)
V(1)–Cl(1)	2.2475(16)	V(1)–C(13)	2.090(4)
V(1)–V(1) [a]	2.5314(9)	V(1)–V(1) [a]	2.5095(6)
V(1)–N(1) [a]	1.850(3)	V(1)–N(1) [a]	1.849(3)
N(1)–C(1)	1.401(4)	N(1)–C(1)	1.406(4)
Bond angles (°)			
N(1)–V(1)–N(1) [a]	93.67(12)	N(1)–V(1)–N(1) [a]	94.58(11)
Cl(1)–V(1)–V(1) [a]	109.66(4)	C(13)–V(1)–V(1) [a]	106.96(9)
V(1)–N(1)–V(1) [a]	86.33(10)	V(1)–N(1)–V(1) [a]	85.42(10)
C(1)–N(1)–V(1)	135.8(2)	C(1)–N(1)–V(1)	136.7(2)

[a] Atoms generated by the symmetry operation: $-x, -y, -z$.

Recrystallization of **5** from dichloromethane–pentane produced red cubic crystals of pure **5**. Complex **5** is diamagnetic (by NMR spectroscopy) and displays a characteristic high field shifted resonance for the vanadium-bound methyl group at $\delta = -1.28$ ppm in the ^1H NMR spectrum. This resonance is very sharp and lacks the usual broadening caused by a combination of unresolved coupling to the $I = \frac{7}{2}$ vanadium nucleus and quadrupolar relaxation effects [3a,20]. In the ^{13}C NMR spectrum, however, no resonance of the vanadium-bound methyl group could be identified.

X-ray structure determinations were carried out for **4** and **5**. Both crystal structures involve the packing of two molecules in the unit cell. The asymmetric unit contains one half dimer molecule with no atom located at a special position. Both the crystal and the molecular structures of **4** and **5** are strictly comparable. The molecular structures of **4** and **5** are shown in Fig. 2; selected bond lengths and angles are given in Table 1.

The molecules have $\bar{1}$ symmetry (crystallographically imposed center of inversion) and consist of planar V_2N_2 cores with two η^5-Cp ligands and two methyl or chloride groups in a *trans* arrangement. The V–N distances in the V_2N_2 cores (1.850(2) and 1.850(3) Å in **4**; 1.851(2) and 1.849(3) Å in **5**) are moderately elongated compared with the V–N distances in terminal imido complexes (typically 1.60–1.68 Å) [1]. The V–V distances of 2.5314(9) and 2.5095(6) Å in **4** and **5** respectively lie in the range normal for a V–V single bond (2.200–2.733 Å) [21,22]. A vanadium–vanadium bond offers an explanation for the diamagnetism of this V(IV) derivative, although it could arise as well from superexchange of the two unpaired electrons through the bridging imido ligands. This last mechanism is observed in $[CpV(O\text{-}^tBu)(\mu\text{-N-}^tBu)]_2$, the first dinuclear V(IV) complex with bridging imido ligands reported [3c]. In this complex, which is also diamagnetic, the V–V distance of 2.907(3) Å was found to be too long to allow coupling of the unpaired electrons through a direct V–V bond [3d]. Since then, a number of organometallic V(IV) complexes containing a planar cyclodivanadazene core, including the tetra(alkyl) complexes $[(PhCH_2)_2V(\mu\text{-N-}p\text{-tolyl})]_2$ and $[(^tBu\text{-}CH_2)_2V(\mu\text{-N-}^tBu)]_2$ have been synthesized through several synthetic methods [3e,12,23]. Ab-initio calculations by Floriani and coworkers [12] on open-shell (V–V single bond) and closed-shell singlet states of the cyclodivanadazene core showed the former to be 45 kcal mol^{-1} more stable than the latter, supporting the idea that diamagnetism in these complexes is due to a regular V–V bond.



(5)

The bonding in the V_2N_2 cores of **4** and **5** was found to be similar to the bonding in the cyclodivanadazene cores of other imido-bridged dimeric vanadium alkyl or aryl compexes [3c,3e,12], with V–N bond distances ranging from 1.83 to 1.87 Å and V–V distances from 2.45 to 2.49 Å. The V–V bond in **4** is slightly longer (2.5314(9) Å), probably owing to the increased amount of valence electrons caused by the presence of both a cyclopentadienyl and a chloride ligand.

The V–Cl distance in **4** (2.2475(16) Å) equals the distances observed for $CpV(N\text{-}^tBu)Cl_2$ (2.223(8)–2.268(7) Å) [3b] or the alkoxide bridged dimer $[V(N\text{-}p\text{-tolyl})(\mu\text{-O-}2,6\text{-}C_6H_3Me_2)_2Cl]_2$ (2.240(1) Å) [2], which are V(V) complexes. It is significantly shorter than the V–Cl bond lengths in the V(III) dichloride $CpVCl_2(PMe_3)_2$ (2.401(1) and 2.405(1) Å) [24]. The V–C_{Me} bond distance in **5** (2.090(4) Å) comes very close to the V–C_{Me} distances observed in the vanadium(V) dimethyl complex $Li[(^tBu_3SiN)_2VMe_2]$ (2.057(8) and 2.043(5) Å) [4a] or the V–CH_2 bond lengths which were found in the V(IV) dimers $[(PhCH_2)_2V(\mu\text{-N-}p\text{-tolyl})]_2$ (2.065(2) and 2.082(3) Å) [12] and $[(^tBu\text{-}CH_2)(O\text{-}^tBu)V(\mu\text{-N-}^tBu)]_2$ (2.072(5)

Å) [3c]. Although formally V(IV), the observed V–Cl and V–C_{Me} distances indicate that **4** and **5** can be seen as V(V) complexes.

The formation of the mono(methyl) imido-bridged dimer $[(CpV)_2(\mu\text{-N-}p\text{-tolyl})_2MeCl]$ together with **5** in the reaction of **1** with $AlMe_3$ indicates that, in this system, reduction of V(V) to V(IV), followed by dimerization and (partial) substitution of the remaining chloride by methyl, is a more likely pathway than full alkylation of V(V) followed by homolytic splitting of a V–Me bond and dimerization of the resulting V(IV) methyl species. This mechanism contrasts with the observed formation of chloride-bridged dimers in the one electron reduction of *p*-tolylNVCl$_3$ with sodium [12] and of $CpV(N\text{–}^tBu)Cl_2$ with one equivalent of ^tBuLi [3c]. $AlMe_3$, however, might play an important role in the formation of imido bridged dimers, for instance by protecting the V–Cl bonds in a way reminiscent of the reagent of Tebbe et al. [17].

2.4. *Reactivity of [CpV(μ-N-p-tolyl)Me]$_2$*

The majority of V(IV) hydrocarbyl complexes are bis(cyclopentadienyl) derivatives Cp_2VR_2 (R = alkyl or aryl) [25]. Their reactivity towards small molecules has hardly been studied. A reason for the lack of attention to this chemistry lies probably in the fact that V(IV) has the tendency to form paramagnetic complexes that are not easily identified by NMR spectroscopy, and that vanadium hydrocarbyl complexes tend to be thermally quite labile.

The compounds **4** and **5** form interesting starting materials for a study of the reactivity of (formally) vanadium(IV) hydrocarbyl complexes, since their diamagnetism allows observation of reaction processes by NMR spectroscopy, and their thermal stability is high. A major drawback is the low solubility of these complexes, even in rather polar solvents.

To explore the reactivity, the behavior of the methyl complex **5** towards a number of small molecules was investigated. The reactions were all performed on a micromolar scale in chloroform-d_1 at 25 °C and were followed by ^1H NMR spectroscopy.

Complex **5** failed to react with EtOH, MeCOOH, $MeSO_3H$, H_2O and $2,6\text{-}C_6H_3\text{–}(^iPr)_2NH_2$. Apparently, protonolysis of the V–Me bond with this range of acids does not take place, in contrast with the easy protonolysis of **5** by HCl. Likewise, no hydrogenolysis of **5** by H_2 could be observed upon stirring solutions of **5** under dihydrogen at 1 atm (25 °C).

The insertion chemistry of **5** is also rather limited; no insertion was observed for ^tBuCN, ethylene or acetylene, although this last reactant induces complete degradation of **5** to unknown products. Complex **5** does react with CO. Insertion of CO in the V–Me bonds and formation of η^2-acyl complexes is indicated by the broad resonance ($\Delta\nu_{1/2} = 300$ Hz) observed for the acyl carbon atoms at $\delta = 201$ ppm in the ^{13}C NMR spectrum of the reaction of **5** with ^{13}CO. Interpretation of the reaction behavior is complicated by the fact that each molecule of **5** contains two V–Me bonds, and that η^2-acyls can each take two positions relative to the Cp ring (Me pointing towards or away from Cp). Furthermore, the reaction is rather slow under CO at 1 atm, leaving unreacted starting material (about 25%) after 16 h, and is accompanied by degradation of the product mixture to unidentified species. Therefore a complete assignment of all resonances in the ^1H NMR spectrum could not be made.

Given the low activity of the methyl complex **5** towards Brønsted acids and small unsaturated molecules the synthesis of other V(IV) hydrocarbyl derivatives in this system was not persued, although exploratory experiments suggest that these can be prepared straightforwardly by salt metathesis of **4** and alkylating reagents such as alkyllithia.

2.5. *^{51}V NMR spectroscopy*

In case of diamagnetic vanadium complexes ^{51}V NMR spectroscopy can conveniently be used as a diagnostic tool for the electronic environment of the vanadium atom. As has been shown in [2,26] the ^{51}V chemical shifts in d^0 complexes follow the so-called "inverse halogen dependence", in which the nuclei become increasingly shielded as the electronegativity of the substituents is increased. The ^{51}V NMR spectroscopic data for the (arylimido) vanadium complexes described here and for a number of relevant V(IV) and V(V) complexes are collected in Table 2.

Electronically the $2,6\text{-}C_6H_3\text{–}(^iPr)_2$-imido ligand and the *p*-tolyl-imido ligand are similar, as can be judged from the relatively small downfield chemical shift (60–80 ppm) for **2** and **3** compared with V(N–*p*-tolyl)Cl$_3$ and **1** respectively. The aryl imido ligands are, however, considerably less electronegative than the alkyl imido

Table 2
^{51}V NMR spectroscopic data for selected complexes at 293 K

Complex	$\delta(^{51}V)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Reference
V(N–*p*-tolyl)Cl$_3$	305	500	[2]
CpV(N–*p*-tolyl)Cl$_2$ (**1**)	−240	790	[2]
$VCl_3[N\text{–}2,6\text{-}C_6H_3\text{–}(^iPr)_2]$ (**2**)	385	700	This work
$CpVCl_2[N\text{–}2,6\text{-}C_6H_3\text{–}(^iPr)_2]$ (**3**)	−183	875	This work
[CpV(μ-N–*p*-tolyl)Cl]$_2$ (**4**)	321	1950	This work
[CpV(μ-N–*p*-tolyl)Me]$_2$ (**5**)	674	950	This work
$CpV(N\text{–}^tBu)Cl_2$	−457	400	[3b]
$CpV(N\text{–}^tBu)(O\text{–}^tBu)Cl$	−763	400	[3b]
$[CpV(\mu\text{-N–}^tBu)(O\text{–}^tBu)]_2$	−251	570	[3c]
$V(N\text{–}^tBu)(O\text{–}^tBu)Cl_2$	−331	330	[27]
$[V(\mu\text{-N–}^tBu)(O\text{–}^tBu)(CH_2\text{–}^tBu)]_2$	1012	560	[3e]
$[V(\mu\text{-N–}^tBu)(CH_2\text{–}^tBu)_2]_2$	1474	156	[3e]

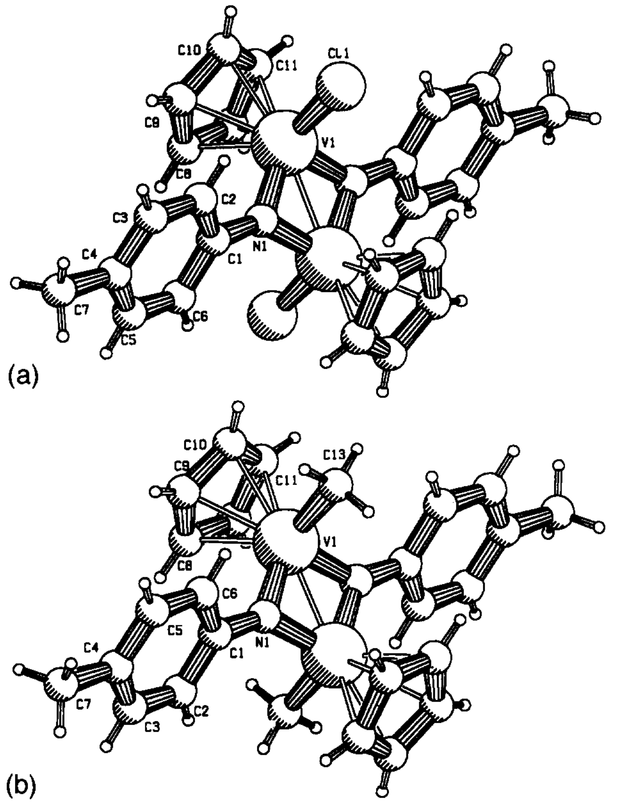


Fig. 2. Molecular structures of (a) [CpV(μ-N-*p*-tolyl)Cl]$_2$ (**4**) and (b) [CpV(μ-N-*p*-tolyl)Me]$_2$ (**5**).

ligands, as can be seen by comparing the ^{51}V chemical shifts of **1** and **3** with that of CpV(N–^{t}Bu)Cl$_2$. Compared with **1** the V resonance of the chloride containing aryl imido bridged dimer **4** appears about 560 ppm further downfield, while replacement of the chloride ligand by a σ-donating alkyl group in **5** adds another 350 ppm downfield, resulting in an overall downfield chemical shift of 910 ppm on going from **1** to **5**. An even larger downfield chemical shift of 1340 ppm is observed on going from the monomeric mono alkoxide V(N–^{t}Bu)(O–^{t}Bu)Cl$_2$ [27] to the imido bridged dimeric alkyl complex [V(μ-N–^{t}Bu)(O–^{t}Bu)(CH$_2$–^{t}Bu)]$_2$. These large downfield chemical shifts are not consistent with the ligand environments in these dimeric complexes and resulting deshielding [3e]. For instance, replacement of chloride by an alkyl ligand in V(N–*p*-tolyl)Cl$_3$ results in a downfield chemical shift of about 390 ppm [2]. The strong deshielding of the ^{51}V nuclei in imido-bridged dimers probably results from the V–V single bond, with each vanadium acting as a relatively strong σ donor. This view is supported by observations made for the imido-bridged dimer [CpV(μ-N–^{t}Bu)(O–^{t}Bu)]$_2$, where a V–V single bond is absent and a much smaller downfield chemical shift, compared with the systems discussed above, was observed. Further support is found in dimeric vanadium(IV)–sulfur compounds with strong V–V single bonds, which show large downfield chemical shifts compared with monomeric vanadium(V)–sulfur compounds [28].

The ^{51}V NMR spectroscopy resonances of the compounds described herein were all too broad (between 700 Hz for **2** and 1950 Hz for **5**) to allow resolution of vanadium–nitrogen spin coupling ($^1J_{^{51}\text{V}-^{14}\text{N}}$ values are typically around 100 Hz) [2,3a]. Line broadening in these complexes results from enhanced quadrupolar relaxation induced by lowering of symmetry, as can easily be seen by comparing the linewidths of OVCl$_3$ (23 Hz), containing the cylindrical vanadyl unit, and V(N–*p*-tolyl)Cl$_3$ (500 Hz), containing the planar (*p*-tolyl)imido group [2].

3. Conclusions

The half-sandwich imido vanadium dichloride CpVCl$_2$[N–2,6-C$_6$H$_3$–(^{i}Pr)$_2$], containing a sterically demanding aryl imido substituent can be prepared in good yield by sequential addition of the corresponding isocyanate and CpSiMe$_3$ to OVCl$_3$. Reactions of this complex and CpV(N–*p*-tolyl)Cl$_2$ with alkylating agents gave only impure mixtures of products, containing reduced metal species and in some cases small amounts of the anticipated V(V) dialkyl complexes. Half-sandwich (aryl)imido vanadium dichlorides seem therefore not to be good starting materials for the synthesis of d^0 vanadium alkylidenes by means of alkylation followed by α-hydrogen abstraction.

Reaction of the half-sandwich imido vanadium dichlorides with AlMe$_3$, expected to lead to vanadium analogues of the Tebbe et al. reagent, gave reductive dimerization, leading for CpV(N–*p*-tolyl)Cl$_2$ to a mixture of thermally stable diamagnetic imido-bridged complexes (CpV)$_2$(μ-N–*p*-tolyl)$_2$MeR′ (R′ = Cl or Me). Reaction with HCl converts the mixture to the pure chloro derivative [CpV(μ-N–*p*-tolyl)Cl]$_2$, which in turn produces the pure methyl complex [CpV(μ-N–*p*-tolyl)Me]$_2$ with MeLi. The molecular structures of these compounds show a planar cyclodivanadazene core with a vanadium–vanadium single bond and V–Cl and V–C$_{\text{Me}}$ bond lengths which are characteristic for V(V) compounds. Insertion of CO in V–Me bonds to produce vanadium acyls was the only productive reaction that could be observed for the imido-bridged methyl complex on reaction with a range of small molecules.

The observed large downfield ^{51}V NMR chemical shifts of the dimeric imido-bridged complexes compared to the shifts of monomeric species are in agreement with the presence of a vanadium–vanadium single bond.

The anticipated isolobal relationship between half-sandwich imido complexes of vanadium and titanocene derivatives is not evident in the reactivity of the dichlorides towards alkylating reagents.

4. Experimental details

All manipulations of air- and/or water-sensitive compounds were performed under nitrogen using standard high vacuum, Schlenk and glove-box techniques. NMR spectra were recorded on a Varian VXR-300 (^1H, 300 MHz; ^{13}C, 75.4 MHz; ^{51}V, 78.9 MHz) spectrometer in benzene-d_6 at 25 °C (unless stated otherwise). Chemical shifts are reported downfield from tetramethylsilane ($\delta = 0.00$ ppm; ^1H and ^{13}C) or $VOCl_3$ ($\delta = 0.00$ ppm; ^{51}V) positive. IR spectra were recorded on a Mattson-4020 Galaxy Fourier transform spectrophotometer from Nujol mulls between KBr discs. Elemental analyses were performed at the Microanalytical Department of the University of Groningen and are the average of at least two independent determinations.

THF, diethyl ether, pentane (mixed isomers) and toluene were distilled from Na–K alloy before use. Benzene-d_6 and toluene-d_8 were vacuum transferred from Na–K alloy. Dichloromethane, chloroform and chloroform-d_1 were dried over molecular sieves (4 Å). Octane, $OVCl_3$, 2,6-C_6H_3-(^{i}Pr)$_2$NCO (Aldrich), ethylene, acetylene, carbon monoxide (Ucar), $AlMe_3$ (Alfa), EtOH, MeCOOH, $MeSO_3H$, H_2O, 2,6-C_6H_3-(^{i}Pr)$_2$-NH_2, *p*-tolylNCO, Me_4Sn (Janssen) and ^{13}CO (MSD Isotopes) were used as received. $CpSiMe_3$ [29] and R_2Mg [30] (R=CH_2-^{t}Bu, CH_2CMe_2Ph or CH_2SiMe_3) were synthesized according to literature procedures. Grignard reagents and alkyllithia were prepared from the corresponding alkyl chlorides.

4.1. $VCl_3[N\text{-}2,6\text{-}C_6H_3\text{-}(^iPr)_3]$ (2)

A mixture of 2,6-C_6H_3-(^{i}Pr)$_2$NCO (9.11 g, 44.8 mmol) and $OVCl_3$ (4.2 ml, 7.8 g, 44.8 mmol) in 50 ml of octane was refluxed for 16 h. After cooling to 25 °C, the solvent was removed in vacuo and the resulting dark-green oil was stored at −50 °C for 16 h during which it solidified. 14.8 g (44.7 mmol; 99%) of product was isolated as a brown–green solid. ^1H NMR: δ 6.6 (m, 3H, NAr: $H_{m,p}$), 4.31 (sept, 2H, $^3J_{HH} = 6.8$ Hz, $C\mathit{H}Me_2$), 1.16 (d, 12H, $^3J_{HH} = 6.8$ Hz, $CH\mathit{Me}_2$) ppm. ^{13}C NMR ($CDCl_3$): δ 171.8 (br, NAr: C_{ipso}), 151.4 (NAr: C_o), 132.5 (NAr: C_p), 122.7 (NAr: C_m), 29.1 ($\mathit{C}HMe_2$), 24.1 ($CH\mathit{Me}_2$) ppm. ^{51}V NMR ($CDCl_3$): δ 385 ($\Delta\nu_{1/2} = 700$ Hz) ppm. IR: ν 2725(w), 2679(w), 1584(w), 1348(sh), 1304(w), 1263(w), 1230(w), 1178(w), 1143(w), 1097(w), 1060(w), 1043(w), 1020(w), 963(w), 933(w), 796(m), 752(m), 723(m), 534(w), 476(s), 411(m) cm^{-1}. Anal. Found: C, 42.70; H, 5.11; V, 15.46. $C_{12}H_{17}Cl_3NV$ Calc.: C, 43.33; H, 5.15; V, 15.32%.

4.2. $CpVCl_2[N\text{-}2,6\text{-}C_6H_3\text{-}(^iPr)_2]$ (3)

To a solution of **2** (7.50 g, 22.5 mmol) in 60 ml of CH_2Cl_2 was added $CpSiMe_3$ (3.12 g, 22.5 mmol). After stirring for 48 h at 40 °C the color of the mixture had changed from green to golden brown and the mixture was filtered. After removal of the solvent from the filtrate in vacuo, 15 ml of pentane was added to the residue and removed in vacuo, yielding 6.59 g (18.2 mmol; 81%) of product as a brown powder. ^1H NMR: δ 6.82 (d, 2H, $^3J_{HH} = 7$ Hz, NAr: H_m), 6.72 (t, 1H, $^3J_{HH} = 7$ Hz, NAr: H_p), 5.89 (s, 5H, Cp), 3.91 (sept, 2H, $^3J_{HH} = 6.8$ Hz, $C\mathit{H}Me_2$), 1.19 (d, 12H, $^3J_{HH} = 6.8$ Hz, $CH\mathit{Me}_2$) ppm, ^{13}C NMR: δ 159 (br, NAr: C_{ipso}), 150.5 (NAr: C_o), 129.3 (NAr: C_p), 122.8 (NAr: C_m), 116.6 (Cp) 28.2 ($\mathit{C}HMe_2$), 24.4 ($CH\mathit{Me}_2$) ppm. ^{51}V NMR: δ183 ($\Delta\nu_{1/2} = 875$ Hz) ppm. IR: ν 3113(w), 2725(w), 2681(w), 1579(m), 1558(w), 1357(sh), 1345(sh), 1321(w), 1300(w), 1248(w), 1224(w), 1168(w), 1157(w), 1140(w), 1109(w), 1093(w), 1053(w), 1026(m), 972(w), 931(w), 920(w), 856(m), 819(s), 800(s), 761(s), 738(m), 723(w), 563(w), 459(m), 430(m) cm^{-1}. Anal. Found: C, 55.14; H, 6.13; V, 14.23. $C_{17}H_{22}Cl_2NV$ Calc.: C, 56.37; H, 6.12; V, 14.06%.

4.3. General procedure for attempted syntheses of $CpV(NR)R'_2$

A solution of two equivalents of R′M (in diethyl ether or toluene) was added slowly (30 min) to a suspension of $CpV(NR)Cl_2$ in diethyl ether or toluene at −80 °C. The resulting mixture was allowed to warm to 25 °C while stirring. After removal of the solvent in vacuo, the oily residue was extracted with pentane. Concentrating and cooling of the extract sometimes gave waxy solids, in other cases the pentane was removed in vacuo to leave an oil. ^1H NMR spectra of the products were taken. In all cases numerous resonances in the cyclopentadienyl region (5–6 ppm) of low intensity compared with the resonance for the residual solvent protons were observed, indicating the formation of a number of alkylated V(V) products accompanied by formation of reduced–decomposed paramagnetic vanadium species.

4.4. $[(CpV)_2(\mu\text{-}N\text{-}p\text{-}tolyl)_2MeR']_2$ (R′ = Me (67%) and Cl (33%))

To a brown suspension of **1** (2.71 g, 9.3 mmol) in 20 ml of toluene, $AlMe_3$ (1.33 g, 18.6 mmol) was added. The resulting red–brown suspension was stirred for 16 h, after which 20 ml of pentane was added. The red–brown solid was isolated by filtration, washed with two portions of pentane (15 ml) and dried in vacuo (yield, 1.64 g (3.47 mmol, 75% based on vanadium) of dark-red powder). ^1H NMR ($CDCl_3$): δ 6.84 (AB q, 4H, $J_{AB} = 8.4$ Hz, $C_6\mathit{H}_4CH_3$), 5.88 (s, 5H, Cp), 2.37 (s, 3H, $C_6H_4C\mathit{H}_3$), −1.28 (s, 3H, *Me*) ppm; the resonances due to the complex with R′ = Cl appear as shoulders on the signals of the complex with R′ = Me, estimated $\Delta\delta = 0.01$ ppm. ^{13}C NMR ($CDCl_3$): δ 167 (NAr: C_{ipso}), 134 (NAr: C_p), 128.6 (NAr: C_o), 119.7 (NAr: C_m), 109.0 (C_p), 21.1 (C_6H_4Me) ppm; V–Me not observed. ^{51}V NMR ($CDCl_3$): δ 674 (s, $\Delta\nu_{1/2} = 950$ Hz) ppm. Anal. Found: C, 64.23; H, 6.50; V, 18.93; Cl, 2.80; Al, 4.2. $C_{26}H_{30}N_2V_2$ (67%)–$C_{25}H_{27}N_2V_2Cl$ (33%) Calc.: C, 64.40; H, 6.11; V, 21.27; Cl, 2.37; Al, 0.00%. These analytical data are compatible with a vanadium complex ratio given above plus some 10 wt.% $AlMe_3$. ^{1}H NMR (C_6D_6): δ −0.4 (s, Me) ppm.

4.5. *[CpV(μ-N-p-tolyl)Cl]$_2$ (4)*

To a red solution of the mixture described above (0.48 g, 1.01 mmol) in 30 ml of chloroform was added dropwise 4 ml of a 0.68 M HCl solution in diethyl ether (2.6 mmol) in 2 min. After stirring for 20 min at 25 °C the green solution was filtered and concentrated to approximately 20 ml. Cooling to −80 °C gave 0.34 g (0.66 mmol, 66%) of dark-green crystals. ^{1}H NMR ($CDCl_3$): δ 7.16 (AB q, 4H, $J_{AB} = 8.3$ Hz, $C_6H_4CH_3$), 5.88 (s, 5H, Cp), 2.44 (s, 3H, $C_6H_4CH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 167.1 (NAr: C_{ipso}), 137.4 (NAr: C_p),

Table 3
Crystallographic data for **4** and **5**

	4	**5**
Crystal data		
Formula	$C_{24}H_{24}Cl_2N_2V_2$	$C_{26}H_{30}N_2V_2$
Formula weight	513.26	472.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	7.6853(6)	7.6777(4)
b (Å)	14.1080(13)	14.4427(5)
c (Å)	10.6747(14)	10.6511(7)
β (°)	96.670(9)	95.267(5)
V (Å^3)	1149.6(2)	1176.08(11)
Z	2	2
D_{calc} (g cm^{-3})	1.4827(3)	1.3340(1)
F(000) (electrons)	524	492
μ (cm^{-1})	10.3 (Mo Kα)	68.4 (Cu Kα)
Crystal size (mm)	0.2 × 0.3 × 0.5	0.2 × 0.3 × 0.4
Data collection		
T (K)	295	295
θ_{min} (°); θ_{max} (°)	1.44; 27.5	3.07; 75.0
Wavelength (Å)	0.71073 (Mo Kα; Zr-filtered)	1.54184 (Cu Kα; Ni filtered)
Scan type	ω–2θ	ω–2θ
$\Delta\omega$ (°)	$0.90 + 0.35 \tan\theta$	$0.68 + 0.14 \tan\theta$
Horizontal aperture (mm); vertical aperture (mm)	3.01; 5.00	2.82; 6.00
X-ray exposure time (h)	52	43
Linear instability (%)	2	2
Reference reflections	$\bar{2}31$, $\bar{2}25$, $\bar{3}02$	$\bar{2}02$, $0\bar{2}3$, $\bar{3}02$
Data set	−9:9, 0:18, −13:13	−9:8, −18:0, −13:13
Number of total data	3712	5355
Number of total unique data	2629 ($R_{int} = 0.102$)	2429 ($R_{int} = 0.027$)
DIFABS correction range	0.849, 1.435	0.608, 2.145
Refinement		
Number of parameters refined	137	138
Final wR_2 [a]	0.131	0.113
Final R_1 [b]	0.052 (1525 $F_o > 4\sigma(F_o)$)	0.041 (1689 $F_o > 4\sigma(F_o)$)
Goodness of fit	0.95	1.05
Weighting scheme [c]	$1/[\sigma^2(F^2) + (0.0672P)^2]$	$1/[\sigma^2(F^2) + (0.0564P)^2 + 0.15P]$
$(\Delta/\sigma)_{av}$; $(\Delta/\sigma)_{max}$	0.000; 0.000	0.000; 0.003
Minimum and maximum residual density (electrons Å^{-3})	−0.31; 0.34	−0.52; 0.29

[a] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[b] $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$.
[c] $P = (\max(F_o^2 0) + 2F_c^2)/3$.

128.9 (NAr: C_o), 121.8 (NAr: C_m), 111.9 (Cp), 21.3 (C_6H_4Me) ppm. ^{51}V NMR ($CDCl_3$): δ 321 (s, $\Delta\nu_{1/2} = 1950$ Hz) ppm. Anal. Found: C, 55.12; H, 4.70; V, 19.64. $C_{24}H_{24}N_2Cl_2V_2$ Calc.: C, 56.16; H, 4.71; V, 19.85%.

4.6. *[CpV(μ-N-p-tolyl)Me]$_2$ (5)*

To a green suspension of **4** (0.50 g, 0.97 mmol) was added 1.0 ml of a 1.98 M MeLi solution in diethyl ether (1.98 mmol) at 25 °C in 5 min. After stirring at 25 °C for 30 min the solvent was removed in vacuo, leaving a dark-red residue. Extraction with 4 × 20 ml of toluene, removal of the solvent in vacuo and washing of the residue with 10 ml of pentane gave 0.26 g (0.55 mmol; 57%) of a red solid. ^{1}H NMR ($CDCl_3$): δ 6.84 (AB q, 4H, $J_{AB} = 8.4$ Hz, $C_6H_4CH_3$), 5.88 (s, 5H, Cp), 2.37 (s, 3H, $C_6H_4CH_3$), −1.28 (s, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ 167 (NAr: C_{ipso}), 134 (NAr: C_p), 128.6 (NAr: C_o), 119.7 (NAr: C_m), 109.0 (Cp), 21.1 (C_6H_4Me) ppm; V–Me not observed. ^{51}V NMR ($CDCl_3$): δ 674 (s, $\Delta\nu_{1/2} = 950$ Hz) ppm. Anal. Found: C, 65.56; H, 6.35; V, 21.37. $C_{26}H_{30}N_2V_2$ Calc.: C, 66.10; H, 6.40; V, 21.57%.

4.7. *Exploration of the reactivity of [CpV(μ-N-p-tolyl)Me]$_2$ (5)*

All reactions were performed with a 42 mM stock solution of **4a** in chloroform-d_1. Liquid reactants (two equivalents) were added with a syringe to 0.5 ml of the stock solution in a 5 mm NMR tube fitted with a septum. Gaseous reactants (1 atm) were allowed to react with 0.5 ml of the stock solution in a 10 ml vessel equipped with a Young tap. The resulting chloroform-d_1 solution was transferred to a 5 mm NMR tube after 16 h. NMR spectra were recorded after 16 h reaction time at 25 °C.

4.8. *X-ray structure determinations of 4 and 5*

Pertinent crystal data and data collection parameters can be found in Table 3. Crystals suitable for X-ray diffraction were grown for both **4** and **5** by slow cooling (3 °C h^{-1}) of saturated dichloromethane solutions from 25 to −25 °C, followed by slow diffusion of pentane at this temperature. Suitable crystals of **4** and **5** were sealed in Lindemann-glass capillaries and mounted on an Enraf–Nonius CAD4-F diffractometer on a sealed tube. Accurate unit-cell parameters and an orientation matrix were determined by a least-squares refinement of the setting angles of 25 well-centered reflections (SET4 [31]) in the range $7.5° < \theta < 14.6°$ and $13.10° < \theta < 27.0°$ for **4** and **5** respectively. The unit-cell parameters were checked for the presence of higher lattice symmetry [32]. Data were corrected for Lorentz and polarization effects and for the observed linear instability of the reference reflections. An empirical absorption–extinction correction (DIFABS [33]) was applied for both compounds. The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92 [34]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93 [35]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms, respectively. Neutral scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography* [36]. Geometrical calculations and illustrations were performed with PLATON [37]; all calculations were performed on a DEC 5000 cluster.

5. Supplementary material available

Further details of the structure determinations, including atomic coordinates, bond lengths and angles and thermal parameters for **4** (15 pages), **5** (15 pages) and the compound described in [19] (23 pages) are available from the authors.

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References and notes

[1] W.A. Nugent and J.M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.

[2] D.D. Devore, J.D. Lichtenhan, F. Takusagawa and E.A. Maatta, *J. Am. Chem. Soc., 109* (1987) 7408.

[3] (a) F. Preuss and H. Becker, *Z. Naturforsch., 41b* (1986) 185; (b) F. Preuss, H. Becker and H.-J. Häusler, *Z. Naturforsch., 42b* (1987) 881; (c) F. Preuss, H. Becker, J. Kaub and W.S. Sheldrick, *Z. Naturforsch., 43b* (1988) 1195; (d) F. Preuss, H. Becker and T. Wieland, *Z. Naturforsch., 45b* (1990) 191; (e) F. Preuss, G. Overhoff, H. Becker, H.-J. Häusler, W. Frank and G. Reiß, *Z. Anorg. Allg. Chem., 619* (1993) 1827.

[4] (a) J. de With, A.D. Horton and A.G. Orpen, *Organometallics, 9* (1990) 2207; (b) J. de With and A.D. Horton, *Angew. Chem., Int. Edn. Engl., 32* (1993) 903; (c) J. de With, A.D. Horton and A.G. Orpen, *Organometallics, 12* (1993) 1493.

[5] D.N. Williams, J.P. Mitchell, A.D. Poole, U. Siemeling, W. Clegg, D.C.R. Hockless, P.A. O'Neill and V.C. Gibson, *J. Chem. Soc., Dalton Trans.*, (1992) 739.

[6] R. Hoffman, *Angew. Chem., Int. Edn. Engl., 21* (1982) 711.

[7] D.S. Williams, M.H. Schofield and R.R. Schrock, *Organometallics, 12* (1993) 4560.

[8] (a) U. Siemeling and V.C. Gibson, *J. Organomet. Chem., 426* (1992) C25; (b) A.D. Poole, V.C. Gibson and W. Clegg, *J. Chem. Soc., Chem. Commun.*, (1992) 237; (c) P.W. Dyer, V.C. Gibson, J.A.K. Howard, B. Whittle and C. Wilson, *J. Chem. Soc., Chem. Commun.*, (1992) 1666; (d) J.K. Cockcroft, V.C. Gibson, J.A.K. Howard, A.D. Poole, U. Siemeling and C. Wilson, *J. Chem. Soc., Chem. Commun.*, (1992) 1668; (e) U. Siemeling and V.C. Gibson, *J. Chem. Soc., Chem. Commun.*, (1992) 1670; (f) D.S. Williams, M.H. Schofield, J.T. Anhaus and R.R. Schrock, *J. Am. Chem. Soc., 112* (1990) 6728; (g) N. Meijboom, C.J. Schaverien and A.G. Orpen, *Organometallics, 9* (1990) 774; (g) A.D. Poole, D.N. Williams, A.M. Kenwright, V.C. Gibson, W. Clegg, D.C.R. Hockless and P.A. O'Neil, *Organometallics, 12* (1993) 2549.

[9] J.-K.F. Buijink, J.H. Teuben, H. Kooijman and A.L. Spek, *Organometallics, 13* (1994) 2922.

[10] J.-K.F. Buijink, A. Meetsma, and J.H. Teuben, *Organometallics, 12* (1993) 2004.

[11] B. Hessen, J.-K.F. Buijink, A. Meetsma, J.H. Teuben, G. Helgesson, M. Håkansson, S. Jagner and A.L. Spek, *Organometallics, 12* (1993) 2268.

[12] G.A. Solan, G.P. Cozzi, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics, 13* (1994) 2572.

[13] (a) I.S. Lolomnikov, Yu.D. Koreshkov, T.S. Lobeeva and M.E. Volpin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1971) 2065; (b) S.F. Pedersen and R.R. Schrock, *J. Am. Chem. Soc., 104* (1982) 7483; (c) A.J. Nielson, *Inorg. Synth., 24* (1986) 194; (d) L.K. Johnson, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc., 115* (1993) 8130.

[14] P. Jernakoff, G.L. Geoffroy, A.L. Rheingold and S.J. Geib, *J. Chem. Soc., Chem. Commun.*, (1987) 1610.

[15] K.R. Birdwhistell, T. Boucher, M. Ensminger, S. Harris, M. Johnson and S. Toporek, *Organometallics, 12* (1993) 1023.

[16] K. Claus and H. Bestian, *Justus Liebigs Ann. Chem., 654* (1962) 8.

[17] F.N. Tebbe, G.W. Parshall and G.S. Reddy, *J. Am. Chem. Soc., 100* (1978) 3611.

[18] (a) F.N. Tebbe, G.W. Parshall and D.W. Ovenall, *J. Am. Chem. Soc., 101* (1979) 5074; (b) K.C. Ott, J.B. Lee and R.H. Grubbs, *J. Am. Chem. Soc., 104* (1982) 2942; (c) D.A. Strauss and R.H. Grubbs, *Organometallics, 1* (1982) 1658; (d) J.B. Lee, K.C. Ott and R.H. Grubbs, *J. Am. Chem. Soc., 104* (1982) 7491; (e) L.R. Gilliom and R.H. Grubbs, *J. Am. Chem. Soc., 108* (1986) 733; (f) J.D. Meinhart, E.V. Anslyn and R.H. Grubbs, *Organometallics*, 8 (1989) 583.

[19] A single crystal containing a mixture of $[(CpV)_2(\mu\text{-N-}p\text{-tolyl})_2MeR']$ (R' = Me or Cl) was studied by A. Meetsma. The structure of this complex was similar to those of **4** and **5** (vide supra). The crystal belongs to the monoclinic space group $P2_1/c$ (No. 14), with $a = 7.605(1)$ Å, $b = 14.307(2)$ Å, $c = 10.407(1)$ Å, $\beta = 93.734(8)°$, $V = 1129.9(2)$ Å^3, $Z = 2$, 3148 reflections measured, 2460 unique reflections, 130 K, Mo Kα radiation and $1.42° < \theta < 27.0°$. The structure was solved by automated Patterson methods (DIRDIF-92). A strong residual peak in the difference Fourier map in the neighborhood of the Me group was interpreted as an indication for the presence of a chlorine compound analog. Site occupancy factor refinement showed a population of 16.7% of Cl compound in the asymmetric unit. Refinement on F converged at $R = 0.045$, $wR = 0.057$ and $S = 1.395$. As a result of the mixing of Me and Cl groups in the measured crystal the observed bond lengths V–Me (2.24(3) Å) and V–Cl (2.11(4) Å) are unreliable.

[20] F. Preuss and L. Ogger, *Z. Naturforsch., 37b* (1982) 957.

[21] F.A. Cotton and M.J. Millar, *J. Am. Chem. Soc., 99* (1977) 7886.

[22] H. Vahrenkamp, *Chem. Ber., 111* (1978) 3472.

[23] J. Ruiz, M. Vivanco, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics, 12* (1993) 1811.

[24] J. Nieman, J.H. Teuben, J.C. Huffman and K.G. Caulton, *J. Organomet. Chem., 255* (1983) 193.

[25] (a) H.J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta, 4* (1970) 651; (b) F.W. Siegert and H.J. de Liefde Meijer, *Recl. Trav. Chim. Pays-Bas, 89* (1970) 764; (c) G.A. Razuvaev, V.N. Latyaeva, L.I. Vishinskaya, V. Cherkasov, S.P. Korneva and N.N. Spiridonova, *J. Organomet. Chem., 129* (1979) 169; (d) D.F. Foust, M.D. Rausch and E. Samuel, *J. Organomet. Chem., 193* (1980) 209; (e) A.G. Evans, J.C. Evans, D.J.C. Espley, P.H. Morgan and J.J. Mortimer, *J. Chem. Soc., Dalton Trans.*, (1978) 57.

[26] (a) D. Rehder, *Z. Naturforsch., 32b* (1977) 771; (b) W. Priebsch and D. Rehder, *Inorg. Chem., 24* (1985) 3058.

[27] F. Preuss, W. Towae, V. Kruppa and E. Fuchslocher, *Z. Naturforsch., 39b* (1984) 1510.

[28] (a) M. Herberhold and M. Kuhnlein, *New J. Chem.*, (1988) 357; (b) C.M. Bolinger, T.B. Rauchfuss and A.L. Rheingold, *J. Am. Chem. Soc., 105* (1983) 6321.

[29] C.S. Kraihanzel and M.L. Losee, *J. Am. Chem. Soc., 90* (1968) 4701.

[30] R.A. Andersen and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1977) 809.

[31] J.L. de Boer and A.J.M. Duisenberg, *Acta Crystallogr., Sect. A, 40* (1984) C410.

[32] A.L. Spek, *J. Appl. Crystallogr., 21* (1988) 578.

[33] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

[34] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits and C. Smykalla, The DIRDIF program system, *Tech. Rep.*, 1992 (Crystallography Laboratory, University of Nijmegen, Netherlands).

[35] G.M. Sheldrick, *SHELXL-93 Program for crystal structure refinement*, University of Göttingen, Göttingen, 1993.

[36] A.J.C. Wilson (ed.), *International Tables for Crystallography*, Vol. C, Kluwer, Dordrecht, 1992.

[37] A.L. Spek, *Acta Crystallogr., Sect. A, 46* (1990) C34.