# The synthesis and characterization of $[IMesH]^+[(\eta^3-C_5H_5)V(N)Cl_2]^-$ : An anionic vanadium(v) complex with a terminal nitrido ligand<sup>†</sup>

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A series of new half-sandwich vanadium complexes have been prepared. The structures of two new anionic vanadium half-sandwich complexes,  $[CpVCl_3]^-$  and  $[CpV(N)Cl_2]^-$  are presented. <sup>15</sup>N isotopic labelling studies have been conducted to unambiguously assign the V=N infra red stretching frequencies of both a neutral and an anionic (cyclopentadienyl)vanadium nitrido complex. The influence of strongly  $\pi$ -basic coligands on the hapticity of the cyclopentadienyl ligands in half-sandwich complexes of vanadium is discussed.

### Introduction

The many interesting and useful physical properties displayed by transition-metal nitride compounds have provided the motivation for ongoing efforts to prepare and characterize new examples of such complexes.1 However, while many nitride complexes of the mid transition-metals (Groups 6, 7 and 8) have been prepared, relatively few examples of early transition-metal (Groups 4 and 5) nitride complexes have been studied. The principal reason for this disparity is that, while mid transition-metal nitride complexes are typically mononuclear and feature terminal nitrido ligands, in early transition metal systems, the highly polar  $M^{\delta+} \equiv N^{\delta-}$  terminal bonding mode combines a very nucleophilic nitrido group with an electron-deficient metal centre. There is, therefore, a strong tendency to form dimeric or oligomeric species with nitrides bridging two or three metal centres. For example, in the case of vanadium, several anionic vanadium nitride dimers have been reported. In these species the bridging unit may be a  $V_2(\mu_2-N)_2$  linkage; for instance,  $[\{[(Me_3Si)_2N]_2V\}_2(\mu_2-N)_2]^{-2}$ , prepared by Gambarotta et al. and  $[V((Me_3Si)N{CH_2CH_2N(SiMe_3)}_2)(\mu_2-N)]_2^{-,3}$  prepared by Cloke et al. Alternately, dimerization may occur through the interaction of two nucleophilic nitrido ligands with a bridging s-block metal cation; for instance,  $[Ar(Bu^{t})N]_{3}V = N^{-}Na^{+}]_{2}$  (Ar =  $3,5-Me_2C_6H_3$ ,<sup>4</sup> prepared by Cummins *et al.*, which is presumed to be dimeric with  $N \cdots Na^+ \cdots N$  bridging interactions by analogy to its structurally characterized niobium analogue.<sup>5</sup> The complexity of such dimeric and oligomeric species can make their characterization extremely difficult.6

However, complexes of early transition-metals with terminal nitrido ligands are very attractive synthetic targets. Crystallographic, vibrational, and theoretical studies of these systems will allow much greater insight into the nature and reactivity of metal-nitrogen multiple bonds; in particular, such highly polar  $M^{\delta \star} {\equiv} N^{\delta -}$  bonds may show useful and unusual reactivity towards unsaturated organic substrate molecules analogous to that observed for early transition-metal imido systems.<sup>7</sup>

At the present time there are no reported structures of a Group 4 metal complex with a truly terminal nitrido ligand, although a borane-capped nitrido complex of titanium has recently been reported.8 In addition, only three terminal nitrido complexes of Group 5 metals are currently included in the Cambridge Structural Database (CSD): two nitrido vanadium complexes: V(N)Cl<sub>2</sub>(pyridine)<sub>2</sub>;<sup>9</sup> and V(N)Cl<sub>2</sub>(quinuclidine)<sub>2</sub>;<sup>10</sup> together with one nitrido niobium complex, [Nb(N)(N[<sup>i</sup>Pr]Ar)<sub>3</sub>]<sup>-</sup>  $(N[Pr]Ar = isopropyl(3,5-dimethylphenyl)amide).^{11}$  The paucity of structurally characterized Group 5 metal complexes with terminal nitrido ligands prompted our interest in the synthesis of new vanadium complexes which display this unusual bondng motif. Furthermore, in view of the almost ubiquitous role that the cyclopentadienyl ligand (Cp) and its substituted derivatives play in early transition-metal chemistry, (cyclopentadienyl)vanadium nitride complexes are conspicuously absent from the literature. In fact, only three vanadium nitride species containing the pentamethylcyclopentadienyl ligand (Cp\*) have been reported to date, namely:  $[Cp*V(\mu_2-N)Cl]_2$ ;<sup>12</sup> the structurally related  $[Cp*V(\mu_2-N)(N_3)]_2$ ;<sup>13</sup> and  $[Cp*V(\mu_3-N)]_4$ ,<sup>14</sup> in all of which, the nitride ligands symmetrically bridge vanadium centres.

In order to prepare the target monomeric terminal nitrido complexes our strategy was to employ sterically demanding and strongly electron-donating ancillary N-heterocyclic carbene ligands to prevent the formation of dimers or oligomers. In this paper, we report the details of the syntheses of several new mono(cyclopentadienyl)vanadium complexes, two of which contain the CpV=N moiety (Scheme 1). <sup>15</sup>N isotopic labelling of these compounds has allowed the unambiguous assignment of the V=N infra red stretching frequencies of these complexes. Also presented is a discussion of the effects that strong  $\pi$ -electron donor coligands, such as nitrido or oxo, have on the hapticity of the cyclopentadienyl ligand in half-sandwich complexes of vanadium.

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Scheme 1 Preparation of complexes 1-4.

### **Results and discussion**

The work of Doherty *et al.* provides a convenient entry point for Cp\*VN chemistry; trimethylsilylazide oxidizes the vanadium(III) cluster,  $[Cp*V(\mu_2-Cl)_2]_3$ , to form the vanadium(v) nitride dimer,  $[Cp*V(\mu_2-N)Cl]_2$ , in high yield according to eqn (1):<sup>12</sup>

$$2[Cp*V(\mu_2-Cl)_2]_3+6Me_3SiN_3$$

$$\downarrow \qquad (1)$$

$$3[Cp*V(\mu_2-N)Cl]_2+6Me_3SiCl+6N_2$$

Later, Abernethy showed that sodium azide could also be similarly employed for the synthesis of this compound.<sup>15</sup>

Unfortunately, this synthetic method cannot be directly applied to CpV systems as the required 'CpVCl<sub>2</sub>' starting material is unsuitable, being both oligomeric, with very low solubility in organic solvents, and unstable with respect to disproportionation.<sup>16</sup> The stability of the CpVCl<sub>2</sub> moiety can be increased, however, by the coordination of an additional ligand that is both strongly electron-donating and sterically demanding. In this study, the N-heterocyclic carbene, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2ylidene (IMes), has been employed to form the synthetically useful CpVCl<sub>2</sub>(IMes) (1) complex, which has been further reacted to produce several other vanadium half-sandwich complexes including two containing the CpVN moiety.

An elegant method of preparing CpMCl(IMes) complexes by the reaction of a metallocene with 1,3-bis(2,4,6trimethylphenyl)imidazolium chloride (IMes·HCl) (eqn (2)), was developed independently by both Tilset *et al.* (M = Cr)<sup>17</sup> and Cowley *et al.* (M = Ni):<sup>18</sup>

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The synthesis of 1 was prepared by an analogous reaction from  $Cp_2VCl$  and IMes·HCl in refluxing THF (Scheme 1).

 $Cp_2M + IMes \cdot HCl \rightarrow CpMCl(IMes) + CpH$ 

Attempts to grow crystals of 1 suitable for X-ray diffraction studies, by layering the THF solution with hexanes, all resulted in the formation of an extremely air-sensitive olive brown powder. The <sup>1</sup>H NMR spectrum of this material (CDCl<sub>3</sub>) shows a number of broad resonances consistent with the spectrum of a paramagnetic complex. The assignments of these resonances were made on the basis of both their integrated intensities, and by comparison with the assignments made by Tilset et al. in the <sup>1</sup>H NMR spectra of the paramagnetic chromium complexes: CpCrCl(IMes); CpCrPh(IMes); and CpCrCl<sub>2</sub>(IMes).<sup>17</sup> Notable features of the <sup>1</sup>H NMR spectrum of 1 include a significant upfield shift of the protons of the imidazol-2-ylidene ring ( $\delta = -2.5$ ), and the far-downfield and very broad resonance of the Cp protons ( $\delta =$ 135,  $\Delta v_{1/2} = 140$  Hz). The paramagnetic nature of 1 was confirmed by an Evans method determination of its magnetic susceptibility  $(\mu_{\rm eff} = 2.71 \ \mu_{\rm B}, 291 \ {\rm K}, {\rm CDCl}_3 \text{ solution})^{19}$  which indicated the presence of two unpaired electrons in the complex.

Unfortunately, reproducible elemental analyses of this material were unobtainable due to its extreme sensitivity to both air and moisture. The identity of 1 was confirmed, however, by the addition of stoichiometric amounts of 4.0 M HCl(dioxane) to THF solutions at -35 °C, which resulted in the formation of [IMesH]<sup>+</sup>[CpVCl<sub>3</sub>]<sup>-</sup>, **2**, in approximately 60% yield (Scheme 1).

Layering of THF solutions of **2** with toluene resulted in the formation of pale yellow crystals, which were suitable for analysis by single crystal X-ray diffraction experiments. In addition to the cations and anions of **2**, these crystals also contained molecules of toluene within the lattice. The crystal structures of the constituent ions of **2** are shown in Fig. 1. The <sup>1</sup>H NMR spectrum of **2** displays broad resonances consistent with the expected paramagnetic nature of its vanadium(III) complex anion; the resonances of the protons belonging to the [IMesH]<sup>+</sup> are both broadened and shifted from their expected positions, while the much broader resonance for the Cp protons of the [CpVCl<sub>3</sub>]<sup>-</sup> is located far downfield at  $\delta$  150 ( $\Delta v_{1/2} = 120$  Hz). The magnetic susceptibility of **2** was determined



Fig. 1 ORTEP drawing of 2 with 50% probability ellipsoids for non-hydrogen atoms. Important distances (Å) and angles (°): V(1)–Cl(1) 2.352 (1); V(1)–Cl(2) 2.329 (1); V(1)–Cl(3) 2.318 (1); V(1)– $Cp_{cent}$  1.949 (7); Cl(1)–V(1)–Cl(2) 95.25 (4); Cl(1)–V(1)–Cl(3) 95.25 (4); Cl(2)–V(1)–Cl(3) 103.19 (4);  $Cp_{cent}$ –V(1)–Cl(1) 120.1 (2);  $Cp_{cent}$ –V(1)–Cl(2) 119.2 (2);  $Cp_{cent}$ –V(1)–Cl(3) 117.4 (2).

by the Evans method to be 2.87  $\mu_B$  (CDCl<sub>3</sub> solution at 291 K),<sup>19</sup> consistent with the expected presence of two unpaired electrons in the complex anion. Elemental analyses of crystals of **2** were in accord with its empirical formula:  $C_{26}H_{30}N_2Cl_3V$ .

THF solutions of 1 were reacted with equimolar amounts of  $NaN_3$  at reflux for 1.5 h, during which time bubbles of  $N_2$  were evolved, the olive solution turned dark blue/green and the solid NaN<sub>3</sub> was seen to dissolve. The proposed reaction, shown in Scheme 1, comprises of a metathesis reaction replacing a chloride ligand with azide, followed by a two-electron oxidation of the vanadium(III) centre to vanadium(v) with the concomitant twoelectron reduction of azide to nitride and dinitrogen gas. The THF was removed in vacuo and the solid residue extracted into toluene. Layering of these toluene solutions with hexanes resulted in the precipitation of an extremely air-sensitive blue/black powder 3, CpV(N)Cl(IMes). This compound decomposed when dissolved in CDCl<sub>3</sub>; NMR studies were, therefore, performed on solutions in THF-d<sub>8</sub>. The <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3** (THF-d<sub>8</sub>) indicate the presence of both an IMes and a Cp ligand in a 1:1 ratio; the resonances assigned to the IMes protons are very similar to those observed in the NMR spectra of other diamagnetic complexes featuring this ligand, while the Cp protons resonate at  $\delta$  4.53 and the Cp carbon nuclei at  $\delta$  123.0. The IR spectrum of freshly prepared samples of 3 in Nujol mull display a strong absorption at 945 cm<sup>-1</sup>, which we assign to the V $\equiv$ N stretching vibration based on the results of an <sup>15</sup>N labelling study (vide infra). Samples of 3 immediately hydrolyzed on exposure to air; perhaps, as a consequence of this reactivity, the elemental analyses of 3 poorly reflect the expected values.

Repeated attempts to grow X-ray quality crystals of **3** resulted in the formation of the blue/black powder described above. These failures led us to add an equimolar amount of 4.0 M HCl(dioxane) at -35 °C to THF solutions of **3** prepared *in situ* (Scheme 1). On warming to room temperature, the dark blue/green solution turned royal blue. After concentration *in vacuo* and layering with hexanes X-ray quality crystals of [IMes.H]<sup>+</sup>[CpV(N)Cl<sub>2</sub>]<sup>-</sup>, **4**, were formed in 56% yield based on the amount of Cp<sub>2</sub>VCl used. The Xray crystal structure of **4** is shown in Fig. 2. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of this compound show both resonances typical of an [IMesH]<sup>+</sup> cation and resonances due to the Cp ligand of the anion (<sup>1</sup>H:  $\delta$  5.93, <sup>13</sup>C:  $\delta$  125.9). Elemental analyses are in accord with the structure as determined by single-crystal X-ray diffraction. The IR spectrum of a freshly made Nujol mull of crystalline **4** shows a strong absorbance at 955 cm<sup>-1</sup>, which is assigned to the V $\equiv$ N



**Fig. 2** ORTEP drawing of **4** with 50% probability ellipsoids for non-hydrogen atoms. Important distances (Å) and angles (°): V(1)–N(3) 1.620(1); V(1)–Cl(1) 2.3375(7); V(1)–Cl(2) 2.3557(9); N(3)–V(1)–Cl(1) 103.33(4); N(3)–V(1)–Cl(2) 103.99(4); Cl(1)–V(1)–Cl(2) 95.87(1).

stretching vibration based on the results of the <sup>15</sup>N labelling study described below.

### V≡N stretching frequencies of 3 and 4

Infra red stretching frequencies of terminal V=N bonds have been reported from 1033 cm<sup>-1</sup>, in [V(N)Cl<sub>3</sub>]<sup>-,20</sup> to 960 cm<sup>-1</sup>, in V(N)Cl<sub>2</sub>(pyridine)<sub>2</sub>.<sup>9</sup> The IR spectra of **3** and **4** display characteristic strong absorptions at 945 and 955 cm<sup>-1</sup>, respectively. These frequencies are somewhat lower than those previously reported, but are in accord with the longer than expected V=N terminal bond observed in **4**. In order to determine unambiguously whether these absorbances are indeed V=N stretching frequencies, <sup>15</sup>N isotopic labelling studies were performed. The syntheses of **3** and **4** were repeated using sodium azide-1-<sup>15</sup>N (Na<sup>15</sup>N=NN & NaN=N<sup>15</sup>N). The products of these reactions were expected to contain an approximately 1 : 1 mixture of: **3** and CpV(<sup>15</sup>N)Cl(IMes) (**3a**); and **4** and [IMesH]<sup>+</sup>[CpV(<sup>15</sup>N)Cl<sub>2</sub>]<sup>-</sup> (**4a**), respectively. The IR spectra of the products of these reactions are shown in Fig. 3, together with the IR spectra of pure samples of **3** and **4**.



Fig. 3 IR spectra of: (a) 3; (b) 3 and 3a; (c) 4; and (d) 4 and 4a.

The IR spectrum of the sample containing a mixture of **3** and **3a** was almost identical to that containing **3** alone, the only observable difference being an additional sharp absorption at 915 cm<sup>-1</sup>. Similarly, compared to the IR spectrum of **4**, the spectrum of the sample containing **4** and **4a** displayed an additional single sharp absorption at 930 cm<sup>-1</sup>.

The magnitude of the differences between the wavenumbers of the original absorptions assigned to the V $\equiv$ N stretching frequencies of 3 and 4 and those of the new absorptions appearing in the spectra of the samples containing 3a and 4a are consistent with the difference in the reduced masses of the two atom pairs (*i.e.* V $\equiv$ <sup>14</sup>N and V $\equiv$ <sup>15</sup>N). These results thus serve to confirm the V $\equiv$ N stretching frequencies in 3 and 4 as 945 and 955 cm<sup>-1</sup>, respectively. The similarly between the stretching V $\equiv$ N vibrations of 3 and 4 indicates that the VN moiety must have a similar bonding mode in both complexes. These vibrational data, therefore, support the postulated monomeric structure of 3 shown in Scheme 1.

### X-ray structures

The ionic **2** is the first structurally characterized compound containing the complex anion,  $[CpVCl_3]^-$ , which has a three-legged piano stool structure (Fig. 1). The bond distances and angles within the  $[IMesH]^+$  cation in **2** are unremarkable being very similar to those observed in other ionic compounds featuring the  $[IMesH]^+$  cation, such as  $[IMesH]^+Cl^{-,21}$  The important bond distances and angles for the  $[CpVCl_3]^-$  anion are similar to those reported for the  $[(C_5H_4Me)VCl_3]^-$  anion as determined in the compound, tetramethyltetrathiafulvalenium (methyl-cyclopentadienyl)vanadium trichloride.<sup>22</sup>

The ionic compound **4**, illustrated in Fig. 2, is the first structurally characterized compound containing the complex anion,  $[CpV(N)Cl_2]^-$ . The monomeric nature of the anionic complex in **4** contrasts with many of the other structurally characterized vanadium nitride anions, which are dimeric.<sup>2,3,4</sup> In the case of **4**, the pseudo-octahedral coordination of the anion's vanadium centre and large steric bulk of the cation combine to prevent dimerization and so preserve the terminal nature of the anion's nitrido ligand.

A detailed view of this anion is given in Fig. 4. The V $\equiv$ N bond in 4 (1.620(1) Å) is longer than those observed in the two previously characterized complexes with terminal V $\equiv$ N bonds: 1.598(7) Å in V(N)Cl<sub>2</sub>(pyridine)<sub>2</sub>;<sup>9</sup> and 1.57(2) Å in V(N)Cl<sub>2</sub>(quinuclidine)<sub>2</sub>.<sup>10</sup>



Fig. 4 Crystallographically determined structure of  $[CpV(N)Cl_2]^-$  anion in 4, showing the asymmetrically bonded cyclopentadienyl ligand (hydrogen atoms have been omitted for clarity). Vanadium–carbon and carbon–carbon distances (Å): V(1)–C(22) 2.400(2); V(1)–C(23) 2.318(2); V(1)–C(24) 2.305(2); V(1)–C(25) 2.301(1); V(1)–C26 2.395(2); C(22)–C(23) 1.421(3); C(23)–C(24) 1.422(3); C(24)–C(25) 1.412(2); C(25)–C(26) 1.424(2); C(26)–C(22) 1.385(2).

The cyclopentadienyl ligand of the anionic complex in **4** does not adopt the usual eta-5 coordination mode. This is evidenced by several distinguishing structural features of the ligand. Firstly, the long V–C distances observed for the carbon atoms in the Cp ring located *trans* to the nitrido ligand (2.400(2) and 2.395(2) Å). Secondly, the C–C distances within the Cp ligand are asymmetric, the distance between the two carbon atoms positioned *trans* to the nitrido ligand, C(22)-C(26) 1.3852(2) Å, is shorter than the other observed C–C distances (all in the range 1.412–1.424 Å) indicating that the three carbon atoms that interact closely with the vanadium centre retain their delocalized C–C  $\pi$ -bonding (allyl), while the two more distant C atoms have developed a more localized C=C bonding character (alkene), as expected for an  $(\eta^3-C_5H_5)M$  system.<sup>23</sup> Finally, the Cp ligand is non-planar with an angle of 3.48° between the C(23)-C(24)-C(25) and C(25)-C(26)-C(22)-C(23) planes. Accordingly, [CpV(N)Cl<sub>2</sub>]<sup>-</sup> is best described as  $[(\eta^3-C_5H_5)V(N)Cl_2]^-$ .

## Ring-slippage in half-sandwich complexes of vanadium containing a strongly $\pi$ -basic ligand

At first sight, the eta-3 coordination of the Cp ligand in  $[CpV(N)Cl_2]^-$  is counterintuitive as the complex with the expected eta-5 Cp coordination,  $[(\eta^5-C_5H_5)V(N)Cl_2]^-$ , would be a 16electron species, while the observed  $[(\eta^3-C_5H_5)V(N)Cl_2]^-$  is a 14-electron species. However, apart from the carbyne ligand, the nitrido ligand is the strongest known  $\pi$ -electron donor.<sup>24</sup> Accordingly, the nitrido ligand has a very strong trans influence. In the case of  $[CpV(N)Cl_2]^-$ , there is competition for the same vanadium acceptor orbitals between the  $\pi$ -donor orbitals of both the nitrido ligand and those of the carbon atoms of the Cp ligand, which are trans to it. This competition accounts for both the slightly longer than expected  $V \equiv N$  bond in this complex as well as the loss of metal-carbon bonding between the vanadium centre and the two carbon atoms of the Cp ligand *trans* to the nitrido ligand. The eta-3 Cp coordination in [CpV(N)Cl<sub>2</sub>]<sup>-</sup> is, therefore, due to the presence of the strong *trans* influence of the nitrido coligand.

If, as we propose, it is the presence of the strongly  $\pi$ -basic nitrido ligand that causes the ring-slippage in  $[CpV(N)Cl_2]^{-}$  then other  $\pi$ -basic ligands with a strong *trans* influence should also induce similar effects in closely related  $(C_5R_5)V(A)Cl_2$  complexes  $(A = \text{strongly } \pi\text{-basic ligand})$ . This is, in fact, the case. Although not commented upon by the authors of the original papers, the structures of both CpV(O)Cl<sub>2</sub>,<sup>25</sup> and Cp\*V(O)Cl<sub>2</sub>,<sup>26</sup> reveal similar elongation of the V-C distances for the carbon atoms trans to the oxo ligand, the concomitant shortening of the distance between these two atoms, and non-planar ring systems (Table 1). In addition, DFT geometry optimizations without constraints using Gausian 03, Revision C.02,27 employing B3LYP functionals28 with 6-311G\*\* basis sets<sup>29</sup> not only show ring-slippage in these complexes but actually overstates this phenomenon (both the V-C distances for the carbon atons *trans* to the  $\pi$ -donor ligand and the bend in the Cp ligand) particularly for the nitrido complex of 4 (Table 1); this discrepancy may be due to the absence of any intermolecular interactions in the model systems. In view of their structural features, the (cyclopentadienyl)vanadium oxo complexes should also, properly, be regarded as  $(\eta^3-C_5H_5)V(O)Cl_2$ and  $(\eta^3 - C_5 Me_5)V(O)Cl_2$ .

Interestingly, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4**, recorded under ambient conditions, have singlet resonances attributable to the Cp ligand in the anion (<sup>1</sup>H: 5.71 ppm; <sup>13</sup>C: 129.1 ppm). The simplicity of the spectra is most likely due to rapid rotation of the cyclopentadienyl in solution at room temperature. It is worthy to note that both CpV(O)Cl<sub>2</sub> and Cp\*V(O)Cl<sub>2</sub> also display simple <sup>1</sup>H and <sup>13</sup>C NMR spectra under ambient conditions due, presumably, to similar fluxional behavior of the Cp and Cp\* ligands in these formally d° systems.<sup>25,26</sup>

	$[CpV(N)Cl_2]^-$		CpV(O)Cl <sub>2</sub>		Cp*V(O)Cl <sub>2</sub>	
	Experimental	Calculated	Experimental <sup>18</sup>	Calculated	Experimental <sup>19</sup>	Calculated
V(1)-C(22)	2.400 (2)	2.631	2.412 (2)	2.497	2.44 (1)	2.465
V(1)-C(23)	2.318 (2)	2.400	2.286 (2)	2.314	2.31 (1)	2.311
V(1)-C(24)	2.305 (2)	2.326	2.243 (2)	2.279	2.28 (1)	2.281
V(1)-C(25)	2.301(2)	2.399	2.264 (2)	2.314	2.28 (1)	2.311
V(1)-C(26)	2.395 (2)	2.631	2.402 (2)	2.497	2.42 (1)	2.464
C(22) - C(23)	1.421 (2)	1.431	1.420 (3)	1.447	1.46 (2)	1.434
C(23) - C(24)	1.422 (3)	1.415	1.409 (3)	1.424	1.43 (2)	1.414
C(24) - C(25)	1.412 (2)	1.415	1.400 (3)	1.424	1.43 (1)	1.414
C(25) - C(26)	1.424 (2)	1.431	1.429 (3)	1.448	1.42 (1)	1.434
C(26) - C(22)	1.385 (3)	1.394	1.382 (3)	1.401	1.38 (1)	1.392
Bend in Cp ligand	3.48	5.26	3.58	4.65	3.24	5.44

**Table 1** Experimental and calculated bond lengths (Å) in half-sandwich complexes of vanadium with  $\pi$ -donor coligands (e.s.d.'s are given in parentheses) and bend in cyclopentadienyl ligand (°). Carbon atoms are numbered with respect to those in 4. Unusual distances are highlighted in bold

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### Conclusions

N-heterocyclic carbenes have been used as coligands to stabilize highly reactive vanadium containing moieties. Furthermore, the addition of HCl(dioxane) has been shown to be a convenient method for the removal of N-heterocyclic carbene ligands from these vanadium complexes, resulting in the their replacement with chloride and the concomitant formation of ionic compounds comprised of imidazolium cations and anionic vanadium complexes. Ionic compounds containing the previously unknown complex anions [CpVCl<sub>3</sub>]<sup>-</sup> and [CpV(N)Cl<sub>2</sub>]<sup>-</sup> have been prepared by this method and structurally characterized. In addition, <sup>15</sup>N isotopic labelling studies of the nitrido vanadium complexes prepared has allowed the unambiguous assignment of the  $V \equiv N$  stretching frequencies in the infra red spectra of these complexes. Finally, the strong *trans* influence of  $\pi$ -donor ligands, such as nitrido and oxo, have been shown to induce ring-slippage in half-sandwich complexes of vanadium; the complexes [CpV(N)Cl<sub>2</sub>]<sup>-</sup>, CpV(O)Cl<sub>2</sub> and Cp\*V(O)Cl<sub>2</sub> should properly be referred to as  $[(\eta^3-C_5H_5)V(N)Cl_2]^-$ ,  $(\eta^3-C_5H_5)V(O)Cl_2$  and  $(\eta^3 - C_5 Me_5)V(O)Cl_2$ .

### Experimental

### **General methods**

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line or dry box techniques. All solvents were degassed and dried using an MBraun Manual Solvent Purification System. Chlorobis(n<sup>5</sup>cyclopentadienyl)vanadium(III) was prepared by the reaction of vanadium trichlorode with (cyclopentadienyl)thallium as described by Manzer;<sup>30</sup> the (cyclopentadienyl)thallium used in this reaction was synthesized by the method of Nielson et al.31 Bis(2,4,6-trimethylphenyl)imidazium chloride was prepared as described by Tilset et al.17 All other chemicals were obtained commercially and used as received. <sup>1</sup>H and <sup>13</sup>C spectra were obtained using a JEOL 270 MHz spectrometer, operating at 270.0 and 67.5 MHz, respectively. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer Spectrum RX1 FT-IR spectrometer. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ, USA.

### Synthesis of CpVCl<sub>2</sub>(IMes) (1)

A mixture of  $(C_5H_5)_2$ VCl (0.45 g, 2.1 mmol) and IMes·HCl (0.71 g, 2.1 mmol) was dissolved in THF (100 mL) and heated to reflux for 1.5 h. The resultant olive green solution was allowed to cool then filtered to remove dark brown solid impurities. The volume was then reduced to 15 mL in vacuo. This solution was layered with hexane (50 mL) and set aside for 7 days, after which time an olive brown powder had formed. This was collected by filtration and washed with cold (0 °C) hexane. Yield 0.75 g, 73% based on vanadium. <sup>1</sup>H NMR (270 MHz, THF-d<sub>8</sub>):  $\delta$ -2.5 (br,  $\Delta v_{1/2}$  = 100 Hz, 2H, C=CH), 2.3 (br,  $\Delta v_{1/2} = 60$  Hz, 6H, *p*-CH<sub>3</sub>), 4.7 (br,  $\Delta v_{1/2} = 50$  Hz, 12H, *o*-CH<sub>3</sub>), 8.3 (br,  $\Delta v_{1/2} = 50$  Hz, 4H, Ar-H), 135 (br,  $\Delta v_{1/2} = 180$  Hz, 5H, C<sub>5</sub>H<sub>5</sub>). This material is extremely air-sensitive; samples of 1 left for several days in Schlenk flasks under an argon atmosphere acquired a bright green patina, while those exposed directly to air immediately turned dark green. Mp: 125 °C (dec). Reproducible elemental analyses were unobtainable, presumably due to decomposition of the samples during shipping due to its extreme air-sensitivity. The effective magnetic moment of 1 was determined to be 2.71 BM (based on a molecular formula of  $C_{26}H_{29}N_2Cl_2V$ ) by the Evans NMR method on a CDCl<sub>3</sub> solution at 291 K (using a 270 MHz instrument with a field strength of 6.34 Tesla).19

### Synthesis of [IMesH]<sup>+</sup>[CpVCl<sub>3</sub>]<sup>-</sup> (2)

A mixture of  $(C_5H_5)_2$  VCl (0.45 g, 2.1 mmol) and IMes·HCl (0.71 g, 2.1 mmol) was dissolved in THF (100 mL) and heated to reflux for 1.5 h. The resultant olive green solution was filtered to remove solid impurities, and cooled to -35 °C. 0.55 mL of 4.0 M HCl(dioxane) (2.2 mmol) were added drop-wise *via* a micro syringe. On warming to room temperature the solution turned yellow. This solution was reduced in volume to 10 mL *in vacuo*, layered with 50 mL of toluene and left to stand for 7 days. After this time large quantities of pale yellow crystals had formed. These were collected by filtration and washed with ice-cold THF (5 mL). Yield 0.50 g, 45% based on vanadium. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  2.0 (br,  $\Delta v_{1/2} = 50$  Hz, 12H, *o*-CH<sub>3</sub>), 2.8 (br,  $\Delta v_{1/2} = 50$  Hz, 6H, *p*-CH<sub>3</sub>), 6.6 ( $\Delta v_{1/2} = 55$  Hz, 4H, Ar-*H*), 7.4 ( $\Delta v_{1/2} = 65$  Hz, 2H, C=C*H*), 150 (br,  $\Delta v_{1/2} = 160$  Hz, 5H, C<sub>5</sub>H<sub>5</sub>), NCHCN resonance not observed.

Mp: 150 °C (dec). Elemental analysis calculated (%) for  $C_{26}H_{30}N_2Cl_3V$ : C, 59.16; H, 5.73; N, 5.31; Cl, 20.15. Found: C,

59.43; H, 6.00; N 5.15; Cl 20.85. The effective magnetic moment of **2** was determined to be 2.78 BM (based on a unit formula of  $C_{26}H_{30}N_2Cl_3V$ ) by the Evans NMR method on a CDCl<sub>3</sub> solution at 291 K (using a 270 MHz instrument with a field strength of 6.34 Tesla).<sup>19</sup>

### Synthesis of CpV(N)Cl(IMes) (3)

A mixture of  $(C_5H_5)_2$ VCl (0.45 g, 2.1 mmol) and IMes·HCl (0.71 g, 2.1 mmol) was dissolved in THF (100 mL) and heated to reflux for 1.5 h. The resultant olive green solution was filtered to remove dark solid impurities, and NaN<sub>3</sub> (0.14 g, 2.1 mmol) added. The mixture was then stirred for 3 h at 60 °C, during which time the solid NaN<sub>3</sub> dissolved, bubbles of N<sub>2</sub> were evolved, and the solution turned dark blue. The solution was reduced in volume to 25 mL in vacuo, filtered to remove solid NaCl, and layered with 50 mL of hexane. A dark blue/black powder precipitated on standing for 3 days. This was collected via filtration and washed with ice-cold THF (5 mL). Yield 0.55 g, 58% based on vanadium. <sup>1</sup>H NMR (270 MHz, THF-d<sub>8</sub>): δ 2.30 (s, 12H, *o*-CH<sub>3</sub>), 2.40 (s, 6H, p-CH<sub>3</sub>), 4.53 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 7.03 (s, 4H, Ar-H), 6.31 (s, 2H, C=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (67.5 MHz, THF-d<sub>8</sub>):  $\delta$  16.2 (s, *o*-CH<sub>3</sub>), 19.5 (s, p-CH3), 105.1 (s, C<sub>5</sub>H<sub>5</sub>), 123.0 (s, NC=CN), 124.0 (s, Ar-C3,5), 130.4 (s, Ar-C4), 133.8 (s, Ar-C2,6), 139.2 (s, Ar-C1), NCN resonance not observed. Mp: 110 °C (dec). IR (Nujol) v =945 cm<sup>-1</sup> (s sharp) (V $\equiv$ N). Elemental analysis calculated (%) for C<sub>26</sub>H<sub>29</sub>N<sub>3</sub>ClV: C, 66.45; H, 6.22; N, 8.94; Cl, 7.54. Found: C, 64.90; H, 6.08; N 8.62; Cl 8.75.

### Synthesis of [IMesH]<sup>+</sup>[CpV(N)Cl<sub>2</sub>]<sup>-</sup> (4)

A mixture of  $(C_5H_5)_2$ VCl (0.45 g, 2.1 mmol) and IMes·HCl (0.71 g, 2.1 mmol) was dissolved in THF (100 mL) and heated to reflux for 1.5 h. The resultant olive green solution was filtered to remove dark insoluble impurities, and NaN<sub>3</sub> (0.14 g, 2.1 mmol) added. The mixture was then stirred for 3 h at 60 °C during which the solid NaN<sub>3</sub> was seen to dissolve, bubbles of  $N_2$  were evolved, and the solution turned dark blue. The resultant dark blue solution was filtered and then cooled to -35 °C. 4.0 M HCl in 1,4-dioxane (0.53 mL, 2.1 mmol) was added drop-wise via a micro syringe. The solution quickly turned green and was allowed to warm to room temperature then stirred for a further 1 h. The solution was reduced in volume to 20 mL in vacuo then layered with hexanes (20 mL) and set aside at -25 °C for 7 days. During this time, green crystals formed. These were collected by filtration, washed with ice-cold THF (1.0 mL) and dried under a stream of argon. Yield: 0.81 g, 76% based on vanadium. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  2.16 (s, 12H, o-CH<sub>3</sub>), 2.34 (s, 6H, p-CH<sub>3</sub>), 5.93 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 7.01 (s, 4H, Ar-H), 7.14 (s, 2H, C=CH), 9.95 (s, 1H, NCHCN). <sup>13</sup>C{<sup>1</sup>H} NMR (67.5 MHz, CDCl<sub>3</sub>):  $\delta$  18.2 (s, *o*-CH<sub>3</sub>), 21.5 (s, *p*-CH<sub>3</sub>), 125.9 (s, NC=CN), 128.1 (s, C<sub>5</sub>H<sub>5</sub>), 130.2 (s, Ar-C3,5), 134.4 (s, Ar-C2,6), 135.4 (s, Ar-C4), 141.9 (s, Ar-C1), NCHN resonance not observed. Mp: 270 °C (dec). IR (Nujol)  $v = 955 \text{ cm}^{-1}$  (s sharp)  $(V \equiv N)$ . Elemental analysis calculated (%) for  $C_{26}H_{30}N_3Cl_2V$ : C, 61.67; H, 5.97; N, 8.30; Cl, 14.00. Found: C, 61.05; H, 5.80; N, 8.15; Cl 14.50.

	2	4
Chemical Formula	$C_{21}H_{25}N_2 \cdot C_5H_5Cl_3V$	$C_{21}H_{25}N_2 \cdot C_5H_5Cl_2NV_1$
Crystal habit	Block	Prism
Crystal system	C2/c	$P\overline{1}$
Space group	Monoclinic	Triclinic
a/Å	29.542 (5)	8.3520 (17)
b/Å	14.710 (5)	8.7980 (18)
c/Å	14.792 (5)	18.550 (4)
α (°)	_	79.78 (3)
β(°)	94.190 (5)	89.34 (3)
$\gamma$ (°)	_	72.16 (3)
$V/Å^3$	6411 (3)	1275.6 (5)
Ζ	8	2
$D_{\rm calcd}/{\rm g~cm^{-1}}$	1.094	1.318
M	527.81	506.39
<i>F</i> (000)	2192	528
$\mu$ Mo-K $\alpha$ /mm <sup>-1</sup>	0.573	0.62
$\Theta_{\rm max}/^{\circ}$	27.49	30.0
No. reflections measured	12353	7456
No. unique reflections	7233	7433
R <sub>int</sub>	0.047	0.023
R	0.069	0.035
$wR_2$	0.183	0.100
S	1.08	0.94
No. parameters	295	290
Largest diffraction peak and hole/e $Å^{-3}$	0.51, -0.36	1.06, -0.39

### Crystallography

Diffraction data for 2 were collected at 153 K with a Nonius Kappa CCD diffractometer, those for 4 were collected at 120 K with a Bruker SMART diffractometer, both using Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . The structures were solved by direct methods (2 SHELX-97;<sup>32</sup> 4 SIR92<sup>33</sup>) and refined with full-matrix leastsquares technique on F<sup>2</sup> (2 SHELXL-97;<sup>32</sup> 4 CRYSTALS<sup>34</sup>). The hydrogen atoms were included in geometrically calculated positions riding on the concerned atoms and refined with thermal parameters tied to that of the riding atom. The crystal lattice of 2 contained a badly disordered solvent molecule which could not be unambiguosly identified. The SQUEEZE35 subroutine of PLATON<sup>36</sup> software was therefore applied to create new reflection data where contributions from the disordered solvent were removed from the original data but were included in the structure factor calculations. The details of crystallographic data and structure refinement parameters for 2 and 4 are summarized in Table 2.

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### References

- 1 The Chemistry of Transition Metal Carbides and Nitrides, ed. S. T. Oyama, Blackie Academic and Professional, Glasgow, 1996.
- 2 J.-I. Song and S. Gambarotta, *Chem.-Eur. J.*, 1996, **2**, 1258.
- 3 G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock and F. G. N. Cloke, J. Am. Chem. Soc., 1999, **121**, 10444.
- 4 J. K. Brask, M. G. Fickes, P. Sangtrirutnugul, V. Dura-Vila, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 2001, 1676.
- 5 M. G. Fickes, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1993.
- 6 A. Abarca, M. V. Galakhov, J. Gracia, A. Martin, M. Mena, J.-M. Probet, P. P. Sarasa and C. Yélamos, *Chem.-Eur. J.*, 2003, **9**, 2337.
- 7 N. Hazari and P. Mountford, Acc. Chem. Res., 2005, 38, 839.
- 8 A.-M. Fuller, W. Clegg, R. W. Harrington, D. L. Hughes and S. J. Lancaster, *Chem. Commun.*, 2008, 5776.
- 9 W. Willing, R. Christophersen, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem., 1987, 555, 16.
- 10 S. C. Critchlow, M. E. Lerchen, R. C. Smith and N. M. Doherty, J. Am. Chem. Soc., 1988, 110, 8071.
- 11 D. J. Mindiola, K. Meyer, J.-P. F. Cherry, T. A. Baker and C. C. Cummins, *Organometallics*, 2000, **19**, 1622.
- 12 T. S. Haddad, A. Aistars, J. W. Ziller and N. M. Doherty, Organometallics, 1993, 12, 2420.
- 13 M. Herberhold, A.-M. Dietel, A. Goller and W. Milius, Z. Anorg. Allg. Chem., 2003, 629, 871.
- 14 C. D. Abernethy, F. Bottomley, A. Decken and T. S. Cameron, Organometallics, 1996, 15, 1758.
- 15 C. D. Abernethy, Ph.D. Dissertation, University of New Brunswick, Fredericton, NB, Canada, 1997.
- 16 J. Nieman, J. H. Teuben, J. C. Huffman and K. G. Caulton, J. Organomet. Chem., 1983, 255, 193.
- 17 M. H. Voges, C. Rømming and M. Tilset, Organometallics, 1999, 18, 529.
- 18 C. D. Abernethy, A. H. Cowley and R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3.
- 19 (a) D. F. Evans, J. Chem. Soc., 1959, 2003; (b) S. K. Sur, J. Mag. Reson., 1989, 169; (c) H. D. Grant, J. Chem. Educ., 1995, 72, 39.
- 20 K. D. Scherfise and K. Dehnicke, Z. Anorg. Allg. Chem., 1986, 538, 119.
- 21 A. J. Arduengo, III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson and H. A. Craig, J. Am. Chem. Soc., 1995, 117, 572.

- 22 D. B. Morse, T. B. Rauchfuss and S. R. Wilson, J. Am. Chem. Soc., 1988, 110, 2646.
- 23 J. M. O'Connor and C. P. Casey, Chem. Rev., 1987, 87, 307.
- 24 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1981, 20, 413.
   25 C. Stoll, I.-A. Lorenz, H. Noth and T. Z. Seifert, *Naturforsh., B: Chem.Sci.*, 1998, 53, 153.
- 26 F. Bottomley, J. Darkwa, L. Sutin and P. S. White, Organometallics, 1986, 5, 2165.
- 27 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pompelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzales, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 03 (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.
- 28 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 284
- 29 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., 1980, 72, 650.
- 30 L. E. Manzer, Inorg. Synth., 1990, 28, 260.
- 31 A. J. Nielson, C. E. F. Richard and J. M. Smith, *Inorg. Synth.*, 1986, 24, 97.
- 32 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 33 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, G. and M. Camalli, J. Appl. Cryst., 1994, 27, 435.
- 34 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.
- 35 P. v. d. Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 194.
- 36 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.