

## Vanadium Complexes with N-Heterocyclic Vinylidene Ligands

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The preparation and the structural characterization of vanadium complexes with terminal and bridging N-heterocyclic vinylidene ligands is reported. The synthesis of the complexes was enabled by utilization of diazoolefins as ligand precursors. Structural data and theoretical results show that N-heterocyclic vinylidenes can act as 6e<sup>-</sup> donor ligands, leading to strong metal-carbon interactions.

N-Heterocyclic carbenes (NHCs) have found widespread applications in synthetic chemistry and in materials science.<sup>1–7</sup> Notably, they are employed as strong C-donor ligands for transition metal catalysts.<sup>8–13</sup> Vinylidene complexes are also involved in many transition-metal catalyzed processes.<sup>14–18</sup> In contrast to NHC ligands, vinylidenes are typically not spectator ligands. Most vinylidene complexes display Fischer-type characteristics, with an electrophilic carbene atom. Reactions with nucleophiles lead to an attack at C<sub>α</sub>. This type of reactivity is the basis for numerous applications of vinylidene complexes in synthetic organic chemistry.<sup>14–18</sup>

A formal structural merger between NHCs and vinylidenes gives N-heterocyclic vinylidenes (Figure 1a). This ligand class is largely unknown. Frogley and Hill have reported a tungsten complex, which can be described as a cationic N-heterocyclic vinylidene complex (Figure 1b, **A**).<sup>19</sup> However, the authors note that the structural data for this compound are more in line with the description as a tungsten carbyne complex featuring a pyridinium substituent (Figure 1b, **B**).

The difficulty to access metal complexes with N-heterocyclic vinylidene ligands is related to the fact that the standard synthetic procedures for making vinylidenes, which involve alkynes as ligand precursors,<sup>17,20,21</sup> cannot be employed. The N-heterocyclic vinylidene fragment has been incorporated into organophosphorus compounds by base-induced coupling of

N-heterocyclic olefins with phosphorus halides,<sup>22–24</sup> but a related strategy has yet to be realized with metal complexes.

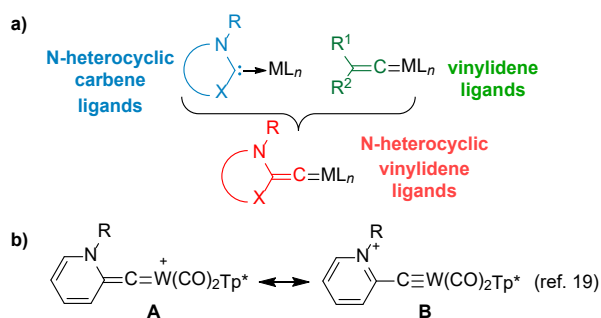


Figure 1 a) N-heterocyclic vinylidene ligands are obtained by a formal structural merger between N-heterocyclic carbene ligands and vinylidene ligands (X = NR, O, S, CR<sub>2</sub>). b) A cationic tungsten complex described by Frogley and Hill (ref. 19).

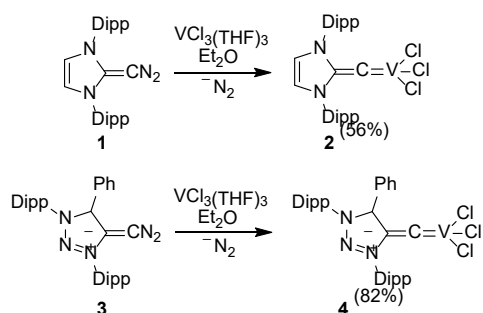
It is well established that diazo compounds are suited precursors for carbene complexes.<sup>25</sup> Vinylidene complexes are rarely made from diazo compounds,<sup>26</sup> because the corresponding precursors, diazoolefins, tend to lose dinitrogen at low temperatures.<sup>27,28</sup> Recently, we have shown that N-heterocyclic diazoolefins can be isolated on preparative scale.<sup>29</sup> Independently, the Hansmann group has reported that mesoionic N-heterocyclic diazoolefins are stable at room temperature.<sup>30,31</sup> These compounds appear to be ideal ligand precursors for N-heterocyclic vinylidenes. However, first studies with late transition metal complexes had shown that N-heterocyclic diazoolefins can bind to the metal center intact, that is without loss of dinitrogen.<sup>29</sup> Below, we demonstrate that neutral vinylidene complexes are obtained by combining N-heterocyclic diazoolefins with an early transition metal complex, VCl<sub>3</sub>(THF)<sub>3</sub>. Structural and theoretical analyses show that N-heterocyclic vinylidenes are unique C-donor ligands, with strong σ- and π-donor abilities.

Theoretical<sup>30,32</sup> and experimental studies<sup>33</sup> have provided evidence that N-heterocyclic vinylidenes display a triplet ground state. In analogy to Schrock-type carbenes, with alkylidene

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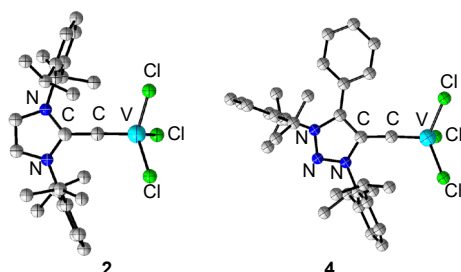
ligands in a triplet ground state,<sup>34</sup> we assumed that early transition metals would be suited for stabilizing N-heterocyclic vinylidenes.

Reaction of the imidazole-based diazoolefin **1**<sup>29</sup> with  $\text{VCl}_3(\text{THF})_3$  in  $\text{Et}_2\text{O}$  resulted in the formation of the vinylidene complex **2**, which could be isolated in 56% yield (Scheme 1, Dipp = 2,6- $\text{C}_6\text{H}_3\text{iPr}_2$ ). In a related fashion, the vinylidene complex **4** was obtained in 82% yield from the mesoionic diazoolefin **3**.<sup>31</sup> It is worth noting that the reaction proceeds equally well in the dark, indicating that light is not needed to promote cleavage of dinitrogen.



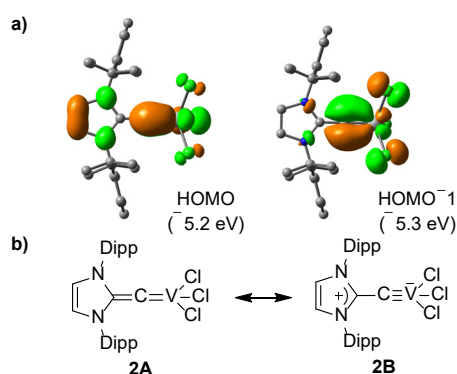
**Scheme 1** Synthesis of the vinylidene complexes **2** and **4**.

The products were characterized by multinuclear NMR spectroscopy and mass spectrometry. In addition, the structures in the solid state were analyzed by single crystal X-ray diffraction (XRD). In both cases, the N-heterocyclic vinylidene ligand is coordinated in a nearly linear fashion to the vanadium center (Figure 2). The V–C bond lengths (**2**: 1.706(2) Å; **4**: 1.704(2) Å) are in-between those found for vanadium alkylidene complexes (V–C ~ 1.79–1.92 Å)<sup>35</sup> and vanadium alkylidyne complexes (V–C ~ 1.68 Å).<sup>35–37</sup> The VC–C bonds have lengths of 1.412(3) Å (**2**) and 1.423(2) Å (**4**). These values are significantly larger than what was reported for the exocyclic C=CH<sub>2</sub> bonds of the corresponding N-heterocyclic olefins (1.331(8) and 1.361(1) Å).<sup>38,39</sup> Identification of the <sup>13</sup>C NMR signals of the C<sub>2</sub> group next to vanadium was hampered by coupling to <sup>51</sup>V. Only for **4**, we were able to detect a broad signal at 315 ppm when the sample was measured at 800 MHz ( $\text{CD}_2\text{Cl}_2$ ). We tentatively assign this signal to the metal-bound C atom. Using solid-state NMR spectroscopy, we were also able to record a <sup>51</sup>V NMR signal for **4**, with an isotropic shift at –1290 ppm.<sup>40</sup>



**Figure 2** Molecular structures of the vinylidene complexes **2** and **4** in the solid state. Hydrogen atoms and solvent molecules are not shown for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): **2**: V–C 1.706(2), VC–C 1.412(3), V–C–C 178.59(19); **4**: V–C 1.704(2), VC–C 1.423(2), V–C–C 177.04(14).

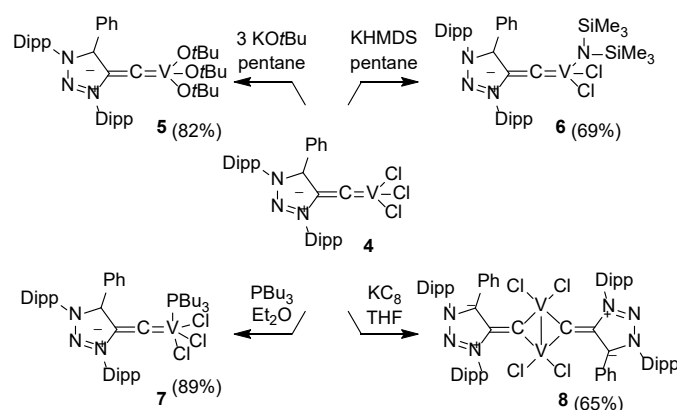
To shed light on the electronic structure of the vinylidene complexes, density functional calculations were performed at the BP86/def2-TZVP level of theory for **2** and **4**, as well as for the model compounds **2M** and **4M** (Me instead of aryl substituents at the heterocycle). The computational analyses revealed that the bonding situations for **2** and **4** are very similar (for details, see the Electronic Supplementary Information, ESI). Therefore, only **2** will be discussed in more detail. The HOMO and the HOMO–1 of **2** are centered on orthogonal  $\pi$ -bonding orbitals, indicating a triple bond character of the V–C bond (Figure 3a).



**Figure 3** a) Selected surface diagrams of the frontier orbitals of **2** (calculated at the BP86/def2-TZVP level). b) Leading resonance structures of **2**.

Natural bond orbital (NBO) analysis of **2** shows a filled V–C  $\sigma$  bond (1.96e) and partial occupancy of the V–C  $\pi$  bonds (1.89e and 1.71e). The Wiberg bond index (WBI) of the V–C bond is 2.1, and the bond order for the VC–C bond is 1.32 (Table S8). The calculations suggest that the bonding in **2** can be described by the mesomeric forms **2A** and **2B** (Figure 3b), and this description is supported by the crystallographic data.

Preliminary reactivity studies were performed with the vinylidene complex **4**, which was obtained in higher yield when compared to **2**. Reaction of **4** with  $\text{KOtBu}$  in pentane at RT resulted in a clean exchange of the three chloro ligands to give the alkoxy complex **5** in 82% yield (Scheme 2).

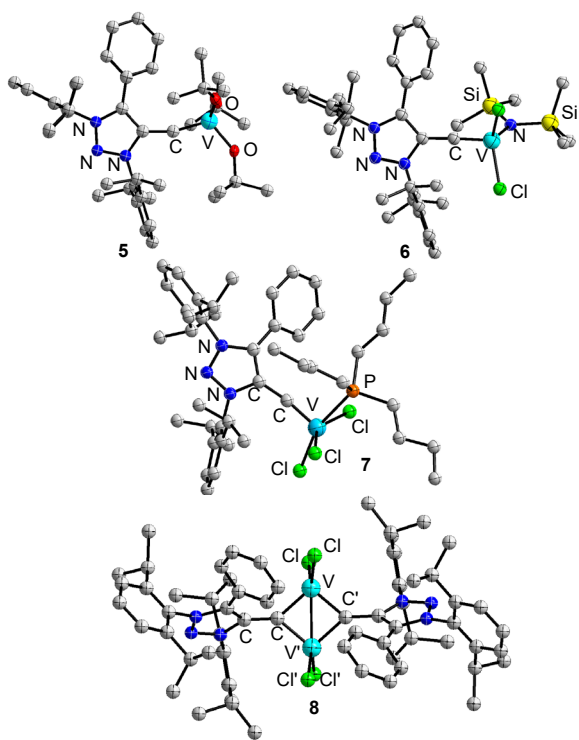


**Scheme 2** Synthesis of the vinylidene complexes **5**–**8**.

Ligand exchange was also observed in a reaction with potassium bis(trimethylsilyl)amide (KHMDS), which gave rise to amide complex **6** (Scheme 2). Only one chloro ligand was

exchanged, even when excess KHMDS was employed. Presumably, steric effects hamper substitution of the remaining chloro ligands. The metal-centered reactivity in reactions with alkoxides and amides is in contrast to what is found for Fischer-type vinylidene complexes of the late transition metals, where reactions with nucleophiles result in attack at the metal-bound carbon center.<sup>14–18</sup> The V center in **4** is still Lewis acidic, as shown by reaction of **4** with  $\text{PBu}_3$ , which gave the phosphine adduct **7** (Scheme 2).

The molecular structures of **5**, **6** and **7** in the crystal are depicted in Figure 4. Compared to its precursor **4**, complex **5** displays a longer V–C bond (1.739(2) Å) and a shorter VC–C bond (1.402(3) Å). The differences can be explained by the reduced Lewis acidity of the  $\text{V}(\text{OtBu})_3$  fragment compared to  $\text{VCl}_3$ . It is also worth noting that the vinylidene ligand in **5** is bound in a bent fashion, with a C–C–V angle of 164.0(2)°. The geometric parameters of the vinylidene ligands in the complexes **6** and **7**, on the other hand, are similar to what was observed for **4**.



**Figure 4** Molecular structures of the vinylidene complexes **5–7** in the solid state. Hydrogen atoms and solvent molecules are not shown for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): **5**: V–C 1.739(2), VC–C 1.402(3), V–C–C 164.0(2); **6**: V–C 1.705(2), VC–C 1.417(3), V–C–C 172.95(19); **7**: V–C 1.703(5), VC–C 1.424(7), V–C–C 171.6(4); **8**: V–C 1.905(2), VC–C 1.419(2), V–V 2.471(1).

Next, we examined the reactivity of **4** towards the Brønsted acid  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (1 equiv.).<sup>41</sup> Analysis of the reaction mixture by NMR spectroscopy showed only very minor conversion (RT, 1 h,  $\text{CD}_2\text{Cl}_2$ ). A lack of reactivity was likewise noted in attempted reactions of **4** with  $\text{CS}_2$ , phenyl azide, *N,N'*-di-*tert*-butylcarbodiimide, and norbornene using similar conditions.

Upon reduction of **4** with  $\text{KC}_8$  in THF, we were able to isolate the dinuclear complex **8** (Scheme 2). A crystallographic analysis of **8** showed that the two V atoms are connected by two bridging vinylidene ligands. The V–C bond lengths in **8**, 1.9045(16) Å and 1.8991(16) Å, are significantly longer than what was found for the terminal vinylidene complexes. The two V atoms are 2.4706(5) Å apart from each other, suggesting the presence of a V–V single bond.<sup>42</sup> This description is supported by the fact that the dinuclear V(IV) complex **8** is diamagnetic, and by results of density functional calculations. The HOMO of **8M** (all aryl substituents are simplified as methyl groups) corresponds to a  $\sigma$ -bonding orbital between the V atoms (ESI, Figure S46). The WBI value for this bond is 0.88 (ESI, Table S8). Furthermore, the calculations indicate that the V–C bonds have partial double bond character.

To conclude: we have shown that vanadium complexes with N-heterocyclic vinylidene ligands are obtained in reactions of diazoolefins with  $\text{VCl}_3(\text{THF})_3$ . The results of crystallographic analyses reveal very short V–C bonds, with bond lengths close to what is found for vanadium alkylidyne complexes. The unique electronic nature of N-heterocyclic vinylidene ligands was corroborated by results of density functional calculations, which show a partial triple bond character for the V–C bond. With isolation of the dinuclear complex **8**, we demonstrate that N-heterocyclic vinylidenes can also act as bridging ligands. Preliminary studies indicate a low intrinsic reactivity of metal-bound N-heterocyclic vinylidenes. This finding suggests that N-heterocyclic vinylidenes might find applications as new types of spectator ligands.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgments

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## Author contributions

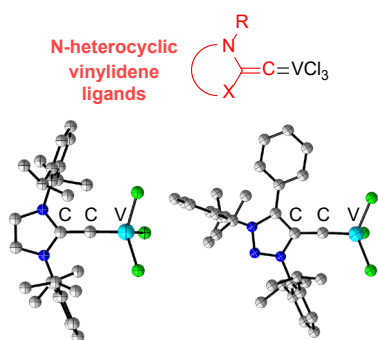
B.K., P.V. and K.S. initiated the study, B.K. performed the experiments and analyzed the data, Z.D. performed the density functional calculations, P.V. synthesized compound **1**, F.F.-T. and R.S. collected and processed the X-ray data, L.P. performed the solid-state NMR measurements, and B.K., Z.D. and K.S. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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## Graphic for the TOC:



Vanadium complexes with N-heterocyclic vinylidene ligands are reported. The vinylidenes can act as  $6e^-$  donor ligands, leading to strong metal-carbon interactions.