

## Coordination of Ethene and Propene to a Cationic $d^0$ Vanadium Center

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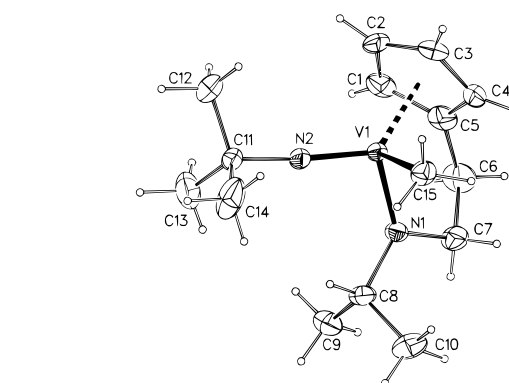
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The bonding of olefins to transition metals via the olefin  $\pi$ -system is usually described in terms of (olefin) $\pi$ -(M) $d$   $\sigma$ -donation and (M) $d$ -(olefin) $\pi^*$   $\pi$ -backdonation.<sup>1</sup> When the metal center has a  $d^0$  configuration the  $\pi$ -backdonation contribution to the bonding is lacking, and the metal-olefin interaction is expected to be relatively weak. Olefin adducts of  $d^0$ -metal centers are proposed as reaction intermediates in the catalytic olefin polymerization by electrophilic cationic group 4 metal alkyl species.<sup>2</sup> Although circumstantial evidence on the interaction of olefins with  $d^0$ -metal centers has been present for some time,<sup>3</sup> actual observation of the olefin adducts has been limited to one example of a cycloheptene adduct of a cationic W-alkylidene,<sup>4</sup> and two types of adducts (for Zr<sup>5</sup> and Y<sup>6</sup>) in which the olefin is held in proximity of the metal center by a covalent tether. Here we report the generation and NMR-spectroscopic characterization of adducts of simple olefins (ethene, propene) with a cationic  $d^0$  vanadium(V) metal center,  $\{[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})(\eta\text{-olefin})\}^+$ , as well as quantumchemical calculations on these new species.

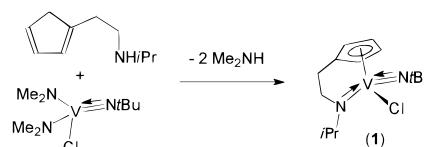
The vanadium(V) complex  $[\eta^5, \eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})\text{Cl}$  (**1**), with a linked Cp-amido ancillary ligand, was obtained by reaction of  $\text{C}_5\text{H}_5(\text{CH}_2)_2\text{NH-Pr}$ <sup>7</sup> with the vanadium imido complex  $(t\text{BuN})\text{V}(\text{NMe}_2)_2\text{Cl}$ <sup>8</sup> through dimethylamine elimination (Scheme 1). Reaction of **1** with MeLi yields the corresponding methyl derivative  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})\text{Me}$  (**2**), characterized by single crystal X-ray diffraction (Figure 1).

Reaction of the methyl complex **2** with the Lewis-acidic borane  $\text{B}(\text{C}_6\text{F}_5)_3$  produces the ionic species  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})[\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**3**), which was obtained analytically pure. In  $\text{C}_6\text{D}_6$  solvent **3** is present as a contact ion pair with substantial interaction between the methyl group of the anion and the cationic metal center.<sup>9</sup> In  $\text{C}_6\text{D}_5\text{Br}$  solvent the anion in **3** is displaced to give a solvated cationic species. In this solvated species and in Lewis-base adducts  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})(\text{L})^+$  ( $\text{L} = \text{THF, PMe}_3$ ) the exchange between coordinated base and excess free base is slow on the NMR timescale. The electronic and steric properties of the system may favor a dissociative rather than an associative displacement mechanism.

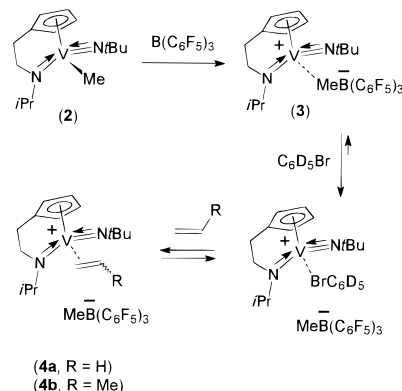


**Figure 1.** Molecular structure of **2**. Selected bond distances (Å) and angles (deg): V–N(1) = 1.854(2), V–N(2) = 1.656(2), V–C(15) = 2.103(3), V–N(2)–C(11) = 175.61(18), N(1)–V–C(15) = 96.10(11), N(1)–V–N(2) = 105.78(10), N(2)–V–C(15) = 96.87(12), V–N(1)–C(7) = 120.39(17), V–N(1)–C(8) = 125.09(18).

### Scheme 1



### Scheme 2



$[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ni-Pr}]\text{V}(\text{Nt-Bu})(\text{L})^+$  ( $\text{L} = \text{THF, PMe}_3$ ) the exchange between coordinated base and excess free base is slow on the NMR timescale. The electronic and steric properties of the system may favor a dissociative rather than an associative displacement mechanism.

Upon addition of ethene or propene to solutions of **3** in  $\text{C}_6\text{D}_5\text{-Br}$  at ambient temperature an equilibrium between the solvated cation of **3** and olefin adduct species is observed by NMR spectroscopy (Scheme 2). The nature of the ethene adduct **4a** is apparent from its NMR spectroscopic features.<sup>11</sup> The chemical shifts and coupling constants of the coordinated ethene (<sup>1</sup>H-NMR AA'BB', consistent with rapid rotation around the ethene-metal bond,  $\delta$  4.33, 4.72 ppm, <sup>13</sup>C-NMR  $\delta$  103.2 ppm,

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(8) Prepared by a comproportionation reaction between  $\text{Cl}_3\text{V}(\text{Nt-Bu})$  and  $(\text{Me}_2\text{N})_3\text{V}(\text{Nt-Bu})$ .

(9) A good indication for interaction of the  $\text{MeB}(\text{C}_6\text{F}_5)_3$  anion with the cationic metal center is found in the <sup>19</sup>F NMR data, where a  $\Delta\delta(p\text{F}-m\text{F})$  value larger than 3 ppm is indicative of significant interaction (ref 10). For **3**: ( $\text{C}_6\text{D}_6$ )  $\Delta\delta = 4.6$  ppm; ( $\text{C}_6\text{D}_5\text{Br}$ )  $\Delta\delta = 2.4$  ppm.

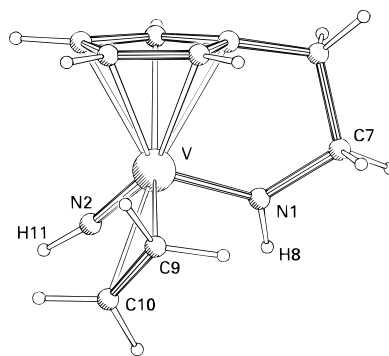
(10) Horton, A. D. *Organometallics* **1996**, *15*, 2675.

(11) For **4a**: <sup>1</sup>H NMR (500 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $-30^\circ\text{C}$ )  $\delta$  5.71, 5.61, 5.27, 5.02 (m, Cp), 5.34 (sept, 6.4 Hz, *i*-Pr CH), 4.72, 4.33 (m, =CH<sub>2</sub>), 4.61, 3.26 (m, NCH<sub>2</sub>), 2.70, 1.91 (m, CpCH<sub>2</sub>), 1.19 (br, BMe), 0.94 (*t*-Bu), 0.82 (d, 6.4 Hz, *i*-Pr Me), 0.59 (d, 6.7 Hz, *i*-Pr Me); <sup>13</sup>C NMR (125.7 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $-30^\circ\text{C}$ ):  $\delta$  149.3 (d,  $J_{\text{CF}} = 241$  Hz, *o*-CF), 141.9 (Cp C), 138.3 (d,  $J_{\text{CF}} = 244$  Hz, *p*-CF), 137.3 (d,  $J_{\text{CF}} = 248$  Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 109.6, 109.2, 103.1, 101.3 (4 CH of Cp), 103.2 (d,  $J_{\text{CH}} = 164$  Hz, =CH<sub>2</sub>), 76.3 (CH of *i*-Pr), 73.3 (NCH<sub>2</sub>), 29.5 (CpCH<sub>2</sub>), 31.1 (CH<sub>3</sub> of *t*-Bu), 22.6, 20.7 (2 CH<sub>3</sub> of *i*-Pr), 11.8 (br,  $\Delta\nu_{1/2} = 75$  Hz, B-Me),  $C_{\text{quat}}$  of *t*-Bu not observed.

$J_{\text{CH}} = 164.1$  Hz) relative to free ethene ( $^1\text{H}$   $\delta$  5.29 ppm,  $^{13}\text{C}$   $\delta$  123.9 ppm,  $J_{\text{CH}} = 159.6$  Hz) distinguish **4a** readily from a possible aza-metallacyclic structure, like the one found for (*t*-Bu<sub>3</sub>SiNH)(*t*-Bu<sub>3</sub>SiN)V[CH<sub>2</sub>CH<sub>2</sub>N(Si-*t*-Bu<sub>3</sub>)] with  $^1\text{H}$   $\delta$  3.22 ppm,  $^{13}\text{C}$   $\delta$  48.3 ppm,  $J_{\text{CH}} = 149$  Hz.<sup>12</sup> The propene adduct **4b** is formed as two isomers in nearly equimolar amounts, probably corresponding to two orientations of the methyl substituent. Comparison of the NMR characteristics<sup>13</sup> with those of free propene shows that the -CH= carbon resonance is shifted moderately downfield (+ 2.5 ppm), the =CH<sub>2</sub> carbon significantly upfield (-24 ppm), while the C-H and H-H coupling constants are relatively little affected. These changes correspond quite well with those observed for the structurally characterized 'tethered' d<sup>0</sup>-metal olefin adduct [Cp<sub>2</sub>Zr(OCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-CH=CH<sub>2</sub>)]<sup>+</sup>, where a substantial amount of olefin polarization was suggested.<sup>5</sup>

The olefin complexation is fully reversible, and **4** reverts to solvated **3** upon pumping off the olefin. As observed with other adducts in this system, the exchange between coordinated and free olefin is remarkably slow. An increase in temperature shifts the equilibrium more towards **3**, but a broadening of the  $^1\text{H}$ -NMR signals of the coordinated ethene is only seen at around 60 °C, suggesting a relatively strong bonding of the coordinated olefin.

Quantumchemical calculations (DFT/B3LYP)<sup>14</sup> were performed on the model system [C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NH]V(NH)(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup> of which the optimized geometry is shown in Figure 2. In the lowest energy conformation the olefin is oriented parallel to the metal-imido bond (although the orientation parallel to the metal-amido bond is only 1.2 kcal mol<sup>-1</sup> higher in energy). The ethene molecule is bound asymmetrically, with V-C(ethene) distances of 2.43 and 2.54 Å, d(C-C) = 1.36 Å (free ethene 1.33 Å), and the closest C...N(imido) distance 2.63 Å. The 'naked' [C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NH]V(NH)<sup>+</sup>-fragment was found to be nearly as pyramidal as in the ethene adduct, and the calculated ethene bonding energy remarkably large (31 kcal mol<sup>-1</sup>). This may be due to the small reorganisation energy of the organo-



**Figure 2.** Optimized calculated geometry for [C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NH]V(NH)-(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup>. Selected distances (Å) and angles (deg): V-C(9) = 2.43, V-C(10) = 2.54, C(9)-C(10) = 1.36, V-N(1) = 1.82, V-N(2) = 1.64, V-N(2)-H(11) = 171.1, N(1)-V-N(2) = 103.9, V-N(1)-C(7) = 125.6, V-N(1)-H(8) = 120.3.

metallic fragment needed to accommodate the ethene. A strong pyramidity combined with a relatively strong olefin binding energy was also found in DFT calculations on the 'constrained geometry' olefin polymerisation catalyst model system, [C<sub>5</sub>H<sub>4</sub>(SiH<sub>2</sub>)NH]ZrCH<sub>3</sub><sup>+</sup> when compared to metallocene-type systems.<sup>2c,15</sup>

The two remarkable features of the cationic (Cp-amido)V-(imido)(olefin) system studied are a) the slow exchange between coordinated and free olefin, and b) the reluctance to form a vanada-aza-cyclobutene type product. Both features are likely to stem from the 'constrained geometry' imposed by the linked Cp-amido ancillary ligand. The strong bonding of the olefin seems to be related to the preference of the (Cp-amido)V(imido)-cation for a pyramidally distorted structure. The lack of observation of the metalla-azacycle may have thermodynamic rather than kinetic reasons. In the 'unconstrained' (imido)<sub>2</sub>V-(amido) system<sup>12</sup> the metallacycle is observed, but with rapid reversibility even at low temperatures. Due to the Cp-amido link in **4**, the Cp(centroid)-V-N(amido) angle may not be able to open up sufficiently to compensate for the expected small C-V-N angle in the metalla-aza-cyclobutane, shifting the equilibrium towards the olefin adduct.

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**Supporting Information Available:** Experimental details and spectroscopic and analytical data of the reported compounds; Details of the structure determination of **2** including lists of positional and thermal parameters and bond distances and angles; details of the calculations and optimized Z-matrices for [C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NH]V(NH)<sup>+</sup> and its ethene adduct (**2** conformations) (28 pages). See any current masthead page for ordering and Internet access instructions.

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(13) For **4b** (C<sub>6</sub>D<sub>5</sub>Br, -30 °C) coordinated propene, two isomers  $^1\text{H}$  NMR  $\delta$  4.15, 4.01 and 3.65, 4.33 (CH<sub>2</sub>), 6.02 and 6.27 (CH),  $^3J_{\text{HH}} = 8.3$  and 8.3 Hz (*cis*), 17.3 and 16.8 Hz (*trans*);  $^{13}\text{C}$  NMR  $\delta$  92.7 and 92.5 (CH<sub>2</sub>,  $J_{\text{CH}} = 157.1$  and 158.6 Hz), 137.7 and 135.4 (CH,  $J_{\text{CH}} = 158.5$  and 158.6 Hz). For free propene (C<sub>6</sub>D<sub>5</sub>Br, -30 °C)  $^1\text{H}$  NMR  $\delta$  4.94, 5.00 (CH<sub>2</sub>), 5.71 (CH),  $^3J_{\text{HH}} = 9.9$  Hz (*cis*), 17.0 Hz (*trans*);  $^{13}\text{C}$  NMR  $\delta$  116.8 (CH<sub>2</sub>,  $J_{\text{CH}} = 155.8$  Hz), 134.4 (CH,  $J_{\text{CH}} = 152.7$  Hz).

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