Relative Reactivity of the Metal−Amido versus Metal−Imido Bond in Linked Cp-Amido and Half-Sandwich Complexes of Vanadium

Marco W. Bouwkamp, Aurora A. Batinas, Peter T. Witte, Ton Hubregtse, Jeroen Dam, Auke Meetsma, Jan H. Teuben, and Bart Hessen*

Molecular Inorganic Chemistry Department, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Treatment of $(\eta^5\text{-}C_5H_4C_2H_4NR)V(N\text{-}t\text{-}Bu)Me$ (R = Me, i-Pr) and $CpV(N\text{-}p\text{-}Tol)(N\text{-}i\text{-}Pr_2)Me$ (Cp = $\eta^5\text{-}C_5H_5$) with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ results in formation of the corresponding cations, $[(\eta^5\text{-}C_5H_4C_2H_4NR)V(N\text{-}t\text{-}Bu)]^+$ and $[CpV(N\text{-}p\text{-}Tol)(N\text{-}i\text{-}Pr_2)]^+$. The latter could also be generated as its *N,N*-dimethylaniline adduct by treatment of the methyl complex with $[PhNMe_2H][BAr_4]$ (Ar = Ph, C_6F_5). Instead, the analogous reaction with the linked Cp-amido precursor results in protonation of the imido-nitrogen atom. Sequential cyclometalation of the amide substituents gave cationic imine complexes $[(\eta^5\text{-}C_5H_4C_2H_4NCR'_2)V(NH\text{-}t\text{-}Bu)]^+$ (R′ = H, Me) and methane. Reaction of cationic $[(\eta^5\text{-}C_5H_4C_2H_4NR)V(N\text{-}t\text{-}Bu)]^+$ with olefins affords the corresponding olefin adducts, whereas treatment with 1 or 2 equiv of 2-butyne results in insertion of the alkyne into the vanadium−nitrogen single bond, affording the mono- and bis-insertion products $[(\eta^5\text{-}C_5H_4C_2H_4N(i\text{-}Pr)C_2Me_2)V(N\text{-}t\text{-}Bu)]^+$ and $[(\eta^5\text{-}C_5H_4C_2H_4N(i\text{-}Pr)C_4Me_4)V(N\text{-}t\text{-}Bu)]^+$. The same reaction with the half-sandwich compound $[CpV(N\text{-}p\text{-}Tol)(N\text{-}i\text{-}Pr_2)]^+$ results in a paramagnetic compound that, upon alcoholysis, affords *sec*-butylidene-*p*-tolylamine, suggesting an initial [2+2] cycloaddition reaction. The difference in reactivity between the V−N bond versus the V=N bond was further studied using computational methods. Results were compared to the isoelectronic titanium system $CpTi(NH)(NH_2)$. These studies indicate that the kinetic product in each system is derived from a [2+2] cycloaddition reaction. For titanium, this was found as the thermodynamic product as well, whereas the insertion reaction was found to be thermodynamically more favorable in the case of vanadium.

Introduction

Group 4 and 5 imido complexes have been studied extensively as catalysts for the intermolecular hydroamination of alkynes with amines.[1,2] The most common mechanism proposed for this transformation involves a [2+2] cycloaddition of the unsaturated hydrocarbon with the metal−imido bond, followed by protonation of the resulting metallacycle with a primary amine, regenerating the metal imido catalyst.[3] Likewise, a similar mechanism in which the alkyne is reacting with the Ti=N bond is proposed for the half-sandwich titanium catalyst $CpTi(N\text{-}p\text{-}Tol)(NH\text{-}p\text{-}Tol)$ (Cp = $\eta^5\text{-}C_5H_5$).[4] However, for complexes of this type, i.e., complexes that have both a metal amido and a metal imido moiety, it is possible to invoke an alternative mechanism in which the alkyne reacts with the Ti−N bond, followed by protonation of the resulting aminoalkenyl ligand. This is similar to the mechanism proposed for group 3 and lanthanide-mediated intramolecular hydroamination/cyclization

reactions of ω-alkenylamines.[5] Recently this mechanism has also been postulated for the hydroamination reaction using the group 4 metal catalyst $\{\eta^5\text{-}C_5Me_4SiMe_2N(t\text{-}Bu)\}Zr(NMe_2)Cl$.[5d]

Our interest in the relative reactivity of the metal−amido and metal−imido bond was kindled by our observations in the chemistry of the linked Cp-amido vanadium imido cation $[(\eta^5\text{-}C_5H_4C_2H_4N\text{-}i\text{-}Pr)V(N\text{-}t\text{-}Bu)]^+$ (**2b**).[6] In our initial communication, which described the synthesis of the complex and its reactivity toward olefins, we reported the first adduct of simple olefins (ethylene and propylene) to a cationic d^0 metal center. However, no further reactivity with either the metal−amido or the metal−imido bond was observed. Here we report the reaction of cationic linked Cp-amido complexes and related half-sandwich complex $[CpV(N\text{-}p\text{-}Tol)(N\text{-}i\text{-}Pr_2)(BrC_6D_5)][MeB(C_6F_5)_3]$ (**10**) with alkynes, which gives evidence for both insertion and [2+2] cycloaddition chemistry.

Results and Discussion

Linked Cp-Amido Vanadium Imido Complexes. Vanadium chloride complexes, $(\eta^5\text{-}C_5H_4C_2H_4NR)V(N\text{-}t\text{-}Bu)Cl$ (R = Me, i-Pr), were obtained from the reaction of $t\text{-}BuNV(NMe_2)_2Cl$[6] with the ligand precursors $C_5H_5C_2H_4NHR$.[7] Treatment of a pentane solution of the chloride complexes with MeLi afforded the corresponding methyl complexes $(\eta^5\text{-}C_5H_4C_2H_4NR)V(N\text{-}t\text{-}$

* Corresponding author. E-mail: B.Hessen@rug.nl.

(1) For reviews on catalytic hydroamination reactions, see: (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Nobis, M.; Driessen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983. (c) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (d) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935. (e) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (f) Doye, S. *Synlett* **2004**, 1653. (g) Odom, A. L. *J. Chem. Soc., Dalton Trans.* **2005**, 225.

(2) For examples of group 5 hydroamination catalysts, see: (a) Anderson, L. L.; Schmidt, J. A. R.; Arnold, J.; Bergman, R. G. *Organometallics* **2006**, *25*, 3394. (b) Anderson, L. L.; Arnold, J.; Bergman, R. G. *Org. Lett.* **2004**, *6*, 2519. (c) Lorber, C.; Choukroun, R.; Vendier, L. *Organometallics* **2004**, *23*, 1845.
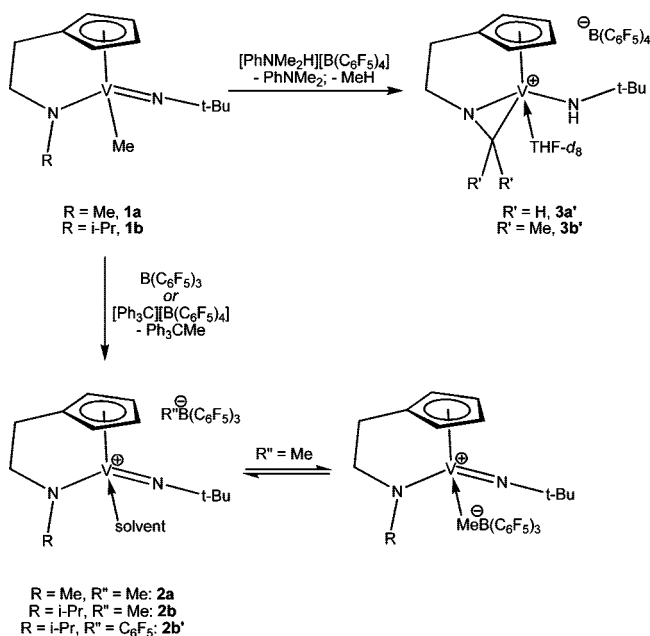
(3) Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305.

(4) Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 2923.

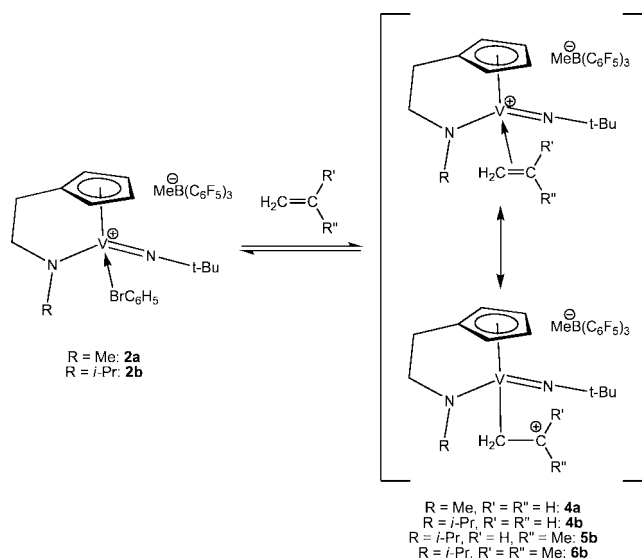(5) (a) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (b) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (c) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295. (d) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149.

(6) Witte, P. T.; Meetsma, A.; Hessen, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1997**, *119*, 10561.

Scheme 1

R = Me, **1a**
R = i-Pr, **1b**

R' = H, **3a'**
R' = Me, **3b'**

R = Me, R" = Me: **2a**
R = i-Pr, R" = Me: **2b**
R = i-Pr, R" = C$_6$F$_5$: **2b'**

Scheme 2

R = Me: **2a**
R = i-Pr: **2b**

R = Me, R' = R" = H: **4a**
R = i-Pr, R' = R" = H: **4b**
R = i-Pr, R' = H, R" = Me: **5b**
R = i-Pr, R' = R" = Me: **6b**

Table 1. Equilibrium Constants for Olefin Binding at 25 °C as Determined by ^{1}H NMR Spectroscopy

olefin adduct	^{13}C NMR shifts		K_{eq} (25 °C)
	=CH$_2$	=CRR'	
4a	101.3		99(10)
4b	103.3		100(10)
5b	92.7, 92.5	137.7, 135.4	44(4)
6b	84.8	177.5	23(2)

Bu)Me (R = Me, **1a**; R = i-Pr, **1b**), which could be used as convenient starting materials for cationic vanadium amido imido complexes. Addition of solutions of compounds **1a** and **1b** to B(C$_6$F$_5$)$_3$ resulted in the clean formation of ionic species [(η^5-C$_5$H$_4$C$_2$H$_4$NR)V(N-t-Bu)][MeB(C$_6$F$_5$)$_3$] (**2a,b** Scheme 1).[6] Depending on the solvent, the compound was obtained predominantly as a contact ion-pair or solvent-separated ion-pair, which was evident from the shifts observed in the ^{19}F fluorine NMR spectrum (amount of contact ion-pair observed for **2b**: bromobenzene-d_5, <10%; CD$_2$Cl$_2$, 22%; chlorobenzene-d_5, 33%; C$_2$D$_2$Cl$_4$, 66%; benzene-d_6, >90%).[8] Addition of a Lewis base, such as THF-d_8, results in clean formation of the corresponding THF adduct. The analogous solvent-separated ion-pair with the weakly coordinating anion [B(C$_6$F$_5$)$_4$]$^-$ (**2b'**, Scheme 1) could be prepared by treatment of compound **1b** with [Ph$_3$C]-[B(C$_6$F$_5$)$_4$]. The reaction of the methyl precursors with the borate reagent [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in THF-d_8 did not afford solvated or *N,N*-dimethylaniline-stabilized [(η^5-C$_5$H$_4$C$_2$H$_4$NR)V(N-t-Bu)] cations.[9] Instead, ^{1}H NMR spectroscopy indicated formation of [(η^5-C$_5$H$_4$C$_2$H$_4$NCR'$_2$)V(NH-t-Bu)(THF-d_8)][B(C$_6$F$_5$)$_4$] (R' = H: **3a'**; R' = Me: **3b'**), free *N,N*-dimethylaniline, and methane (Scheme 1). For **3a'**, two doublets were observed for the methylene protons of the aza-metallacyclopropane at δ 3.20 and 2.65 ppm (^{13}C NMR: δ 64.4, J_{CH} = 163 Hz), whereas two singlets corresponding to three protons each were observed at δ 1.72 and 1.42 ppm for the methyl substituents in **3b'**. In addition, resonances at δ 3.6 and 3.7 ppm were observed for the NH protons in **3a'** and **3b'**, respectively. Complex **2b'** is stable at room temperature in solution, suggesting that the formation of the linked Cp-imine complexes results from initial protonation of the *tert*-butylimido ligand, followed by methane elimination involving a ligand Me-group in the case of the formation of **3a'** and the i-Pr methine in the case of **3b'**, rather

than tautomerization of the [(η^5-C$_5$H$_4$C$_2$H$_4$NR)V(N-t-Bu)] cations. In a similar way, Nomura et al. reported the reaction of vanadium methyl (2,6-Me$_2$C$_6$H$_3$N)(t-Bu$_2$CN)$_2$VMe with aryl alcohols, which afforded complexes derived from protonation of an amide ligand, rather than of the methyl ligand, affording complexes of the type (2,6-Me$_2$C$_6$H$_3$N)(t-Bu$_2$CN)(OAr)VMe (Ar = aryl).[10] Cyclometalation reactions similar to the one observed here, involving alkyl-amide substituents, have been observed previously in the thermolysis of the tantalum compound (η^5-C$_5$Me$_5$)Ta(NMe$_2$)Me$_3$.[11]

Reaction of Cationic Linked Cp-Amido Vanadium Imido Complexes with Unsaturated Hydrocarbons. Addition of olefins to bromobenzene-d_5 solutions of cation **2b** resulted in a mixture of the starting material and the corresponding olefin adducts [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(CH$_2$CRR')][MeB-(C$_6$F$_5$)$_3$] (R = R' = H, **4b**; R = Me, R' = H, **5b**; R = R' = Me, **6b**; Scheme 2). In the case of propylene, two isomers were observed in virtually equimolar amounts. In a similar way, the ethylene adduct **4a** could be generated by addition of ethylene to a bromobenzene-d_5 solution of **2a**. As expected, equilibrium constants for the binding of the olefins at 25 °C (listed in Table 1) decrease with increasing number of methyl substituents on the olefin. However, there is virtually no effect of the substituent on the amide nitrogen (99(10) vs 100(10) for **4a** versus **4b**). Included in Table 1 are the ^{13}C chemical shifts for the coordinated olefins. From these data it is clear that the olefin is highly polarized, with a strong contribution of the canonical form in which the positive charge is located on the β-carbon

(7) (a) Sinnema, P. J.; Liekelema, K.; Staal, O. K. B.; Hessen, B.; Teuben, J. H. *J. Mol. Catal. A* **1997**, *128*, 143. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936.

(8) Horton, A. D.; De With, J.; Van der Linden, A. J.; Van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(9) An *N,N*-dimethylaniline adduct was prepared separately as a reference compound by treating compound **1a** with 1 equiv of *N,N*-dimethylaniline (see Experimental Section for details).

(10) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics* **2007**, *26*, 2579.

(11) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

Scheme 3

2b　　　　　**7b**　　　　　**8b**
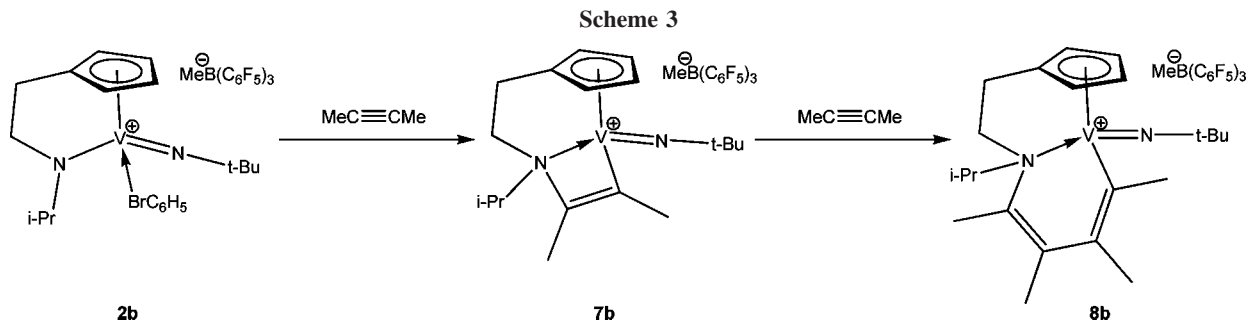
(Scheme 2).[12] In the case of the ethylene adducts **4a** and **4b**, only one resonance is observed in the ^{13}C NMR spectrum at δ 101.3 and 103.3 ppm, respectively, for the coordinated ethylene molecule, suggesting fast rotation around the metal−ethylene vector. Correspondingly, two resonances were observed for the coordinated ethylene molecule in the ^1H NMR spectrum of the reaction mixtures at δ 4.71 and 4.29 ppm for **4a** and δ 4.72 and 4.33 ppm for **4b**. The degree of polarization of the olefins increases with the number of methyl substituents on the distant carbon, as expected from the relative stability of the corresponding carbocations ($RCMe_2^+ > RCHMe^+ > RCH_2^+$) and from the steric bulk on this carbon atom (Scheme 2). In addition to the trend in ^{13}C NMR chemical shifts, the polarization of the olefin is manifested in a decrease in CH coupling constant for the α-carbon of the olefins with increasing number of methyl substituents on the olefin, suggesting increasing sp^3 character of the CH$_2$ group (**4b**, $J_{CH} = 164$ Hz; **5b**, $J_{CH} = 157$ and 159 Hz; **6b**, $J_{CH} = 156$ Hz).

Treatment of $[(\eta^5\text{-}C_5H_4C_2H_4N\text{-}i\text{-}Pr)V(N\text{-}t\text{-}Bu)(BrC_6D_5)]$-$[MeB(C_6F_5)_3]$ (**2b**) with a small excess (1.2 equiv) of 2-butyne did not result in the corresponding alkyne adduct. Instead, a mixture of two new complexes was obtained. ^1H NMR spectroscopy indicated the formation of $[(\eta^5\text{-}C_5H_4C_2H_4N(i\text{-}Pr)C_2Me_2)V(N\text{-}t\text{-}Bu)][MeB(C_6F_5)_3]$ (**7b**, major) and $[(\eta^5\text{-}C_5H_4C_2H_4N(i\text{-}Pr)C_4Me_4)V(N\text{-}t\text{-}Bu)][MeB(C_6F_5)_3]$ (**8b**, minor), resulting from an insertion reaction of the alkyne into the metal−nitrogen single bond (Scheme 3). Compound **8b** could be obtained exclusively by addition of additional alkyne to the reaction mixture. The ^1H NMR spectra of **7b** and **8b** show resonances for the *i*-Pr methine protons at 2.2 and 2.8 ppm, respectively. In complexes where the *i*-Pr amide is directly bound to vanadium and the *i*-Pr methine CH is directed toward the metal center, the methine protons are typically found at 5−6 ppm.[6] The upfield shifts observed for the mono- and bis-insertion products, **7b** and **8b**, are therefore a clear indication of an insertion reaction involving the V−N bond rather than a [2+2] cycloaddition reaction with the V=N bond. Unfortunately, the products could be isolated only as oils, despite numerous crystallization attempts, impeding full characterization.

Half-Sandwich Vanadium Imido Amido Complexes. As mentioned in the Introduction, Bergman and co-workers have reported the hydroamination reaction of alkynes with primary amines catalyzed by CpTi(N-*p*-Tol)(NH-*p*-Tol),[4] proposing a mechanism that involves a [2+2] cycloaddition reaction of the unsaturated hydrocarbon with the M=N bond and not an insertion reaction with the M−N bond as we observe here. Hence, we were interested in the reactivity of the nonlinked cationic vanadium system [CpV(N-*p*-Tol)(N-*i*-Pr$_2$)]$^+$. Vanadium
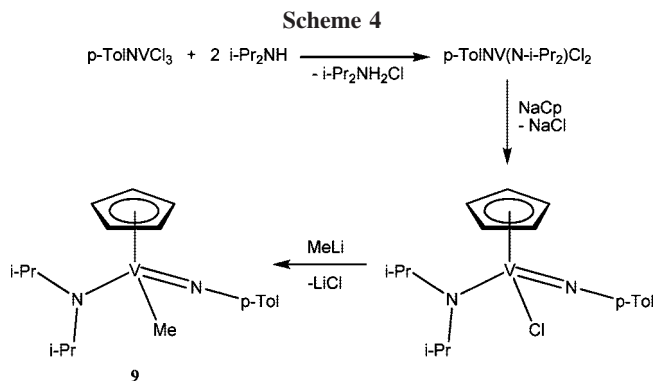
Scheme 4

chloride, CpV(N-*p*-Tol)(N-*i*-Pr$_2$)Cl, was prepared by addition of NaCp to *p*-TolNV(N-*i*-Pr$_2$)Cl$_2$, which was obtained from the addition of 2 equiv of di-isopropylamine to *p*-TolNVCl$_3$ (Scheme 4). This is different from the route reported for the *tert*-butylimido compound CpV(N-*t*-Bu)(NH-*t*-Bu)Cl, in which *t*-BuNVCl$_3$ was first converted to the half-sandwich compound CpV(N-*t*-Bu)Cl$_2$ and subsequently to CpV(N-*t*-Bu)(NH-*t*-Bu)Cl by the addition of 2 equiv of *tert*-butylamine.[13] However, reaction of CpV(N-*p*-Tol)Cl$_2$[14] with di-isopropylamine results in an intractable mixture of complexes, hence the choice of introducing the amide ligand prior to the cyclopentadienyl ligand. The vanadium methyl complex CpV(N-*p*-Tol)(N-*i*-Pr$_2$)Me (**9**, Scheme 4) was prepared by treatment of CpV(N-*p*-Tol)(N-*i*-Pr$_2$)Cl with methyllithium. The compound was obtained as reddish-brown crystals from pentane at −10 °C, which were suitable for a single-crystal X-ray analysis. An ORTEP representation is depicted in Figure 1; see Table 2 for pertinent bond lengths and angles. Included in Table 2 are the data for the crystal structure of the linked Cp-amido compound **1b**. The structure of **9** revealed a typical three-legged piano stool type geometry with bond distances and angles similar to the linked Cp-amide complex ($\eta^5\text{-}C_5H_4C_2H_4N\text{-}i\text{-}Pr)V(N\text{-}t\text{-}Bu)Me$ (**1b**).

Addition of B(C$_6$F$_5$)$_3$ to a solution of **9** in bromobenzene-*d*$_5$ generated a reddish-brown solution of the solvated solvent-separated ion-pair [CpV(N-*p*-Tol)(N-*i*-Pr$_2$)(BrC$_6$H$_5$)][MeB-(C$_6$F$_5$)$_3$] (**10**) and a small amount (<10%, based on ^{19}F NMR spectroscopy) of the contact ion-pair. The same solvated cation with the weakly coordinating [B(C$_6$F$_5$)$_4$] anion could be prepared by treatment of **9** with the borate reagent [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br (Scheme 5). In case of the reaction with the anilinium reagent, the corresponding *N,N*-dimethylaniline adduct [CpV(N-*p*-Tol)(N-*i*-Pr$_2$)(PhNMe$_2$)]-[B(C$_6$F$_5$)$_4$] (**11′**) was obtained cleanly. This is evident from the

(12) (a) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Stromberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750. (b) Vatamanu, M.; Stojcevic, G.; Baird, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 454.

(13) (a) Preuss, F.; Becker, H.; Hausler, H. J. *Z. Naturforsch.* **1987**, *42b*, 881. (b) Preuss, F.; Becker, H.; Wieland, T. *Z. Naturforsch.* **1990**, *45b*, 191.

(14) Buijink, J. K. F. Chemistry of vanadium-carbon single and double bonds. Ph.D. Thesis, University of Groningen, The Netherlands, 1995.
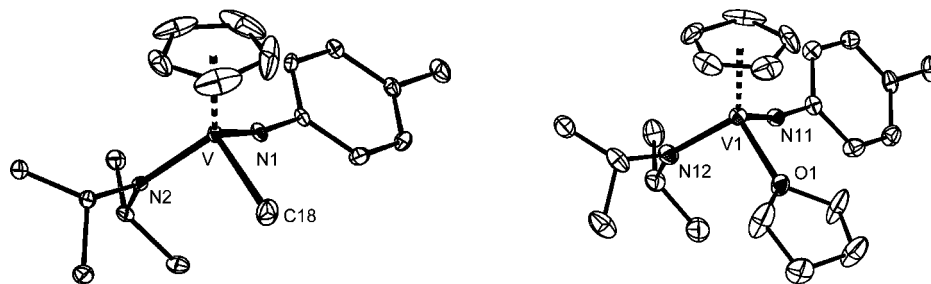
Figure 1. ORTEP representation of **9** and **12″** at the 30% probability level. Hydrogen atoms and the counterion of **12″** are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1b, 9, and 12″

	1b	9	12″
V−X^a	2.103(3)	2.122(5)	2.020(4)
V−N$_{imido}$	1.656(2)	1.666(2)	1.665(4)
V−N$_{amido}$	1.854(2)	1.851(2)	1.866(4)
V−Cp^b	1.9835(15)	2.006(2)	1.988(3)
V−N$_{imido}$−C$_{imido}$	175.61(18)	166.2(2)	165.3(4)
N$_{amido}$−V−X	86.10(11)	96.68(16)	98.96(18)
N$_{amido}$−V−N$_{imido}$	105.78(10)	103.02(11)	101.86(19)
N$_{imido}$−V−X	96.87(12)	98.54(15)	96.60(16)

^{a} X = C$_{Me}$ for **1b** and **9**; X = O1 for **12″**. ^{b} Centroid defined by the carbon atoms of the Cp ligand.

¹H NMR spectrum of the compound, which reveals, in addition to the resonances expected for the C_1-symmetric vanadium cation, two singlets for the diastereotopic methyl groups on the aniline nitrogen. It is remarkable that treatment of the Brønsted acidic borate reagent [PhNMe₂H][B(C₆F₅)₄] with **9** and **1b** affords products from two different types of reactivity. This might be explained by the increased basicity of the *tert*-butyl imido ligand, relative to the *p*-Tol imido ligand, a result of the electron-donating properties of the *tert*-butyl substituent. Nevertheless, it cannot be excluded that in the case of both reactions initial protonation occurs at the imido nitrogen, followed by methane elimination through either 1,2-elimination or β-H transfer to form a vanadium imido amido cation (**11′**) or a vanadium amido imine cation (**3a′,b′**), respectively.

As for the linked Cp-amido complexes, also their half-sandwich counterparts are obtained as oily substances. In contrast, the THF adduct [CpV(N-*p*-Tol)(N-*i*-Pr₂)(THF)][BPh₄] (**12″**) could be obtained as an orange, crystalline material. This compound was prepared from **9** and [PhNMe₂H][BPh₄] in THF solution. Single crystals were obtained by cooling a saturated THF solution. An ORTEP representation of the structure is presented in Figure 1 (see Table 2 for pertinent bond distances and angles). The metrical parameters of the compound are similar to the vanadium methyl starting material, **9**.

Hydroamination with Cationic Half-Sandwich Vanadium Imido Amido Complexes. Treatment of cation **10** with 1 equiv of 2-butyne resulted in a dark red reaction mixture. ¹H NMR spectroscopy revealed the formation of a paramagnetic compound. Attempts to isolate the paramagnetic vanadium cation were unsuccessful, but quenching the reaction mixture with methanol-*d₄* and analysis by GC-MS revealed the formation of partially deuterated *sec*-butylidene-*p*-tolylamine.[15] This suggests that the initially formed paramagnetic compound is the aza-allyl complex [CpV{*p*-TolNC(Me)CHMe}(Me₂CN-*i*-Pr)]⁺, the result of a [2+2] cycloaddition reaction of the alkyne with the V=N bond, followed by an intramolecular proton transfer
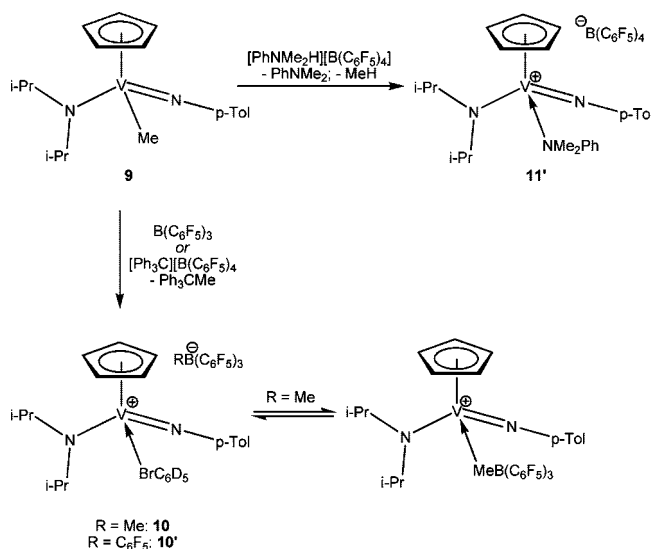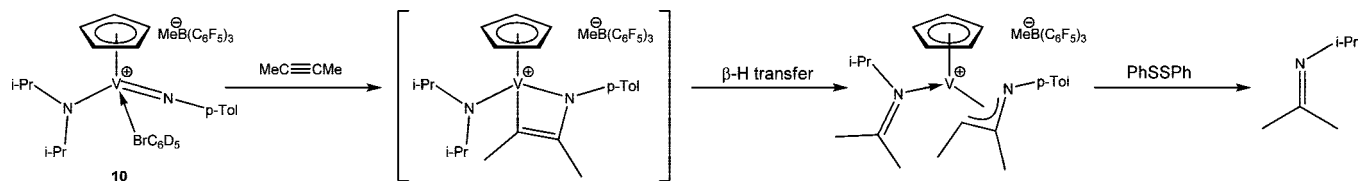
Scheme 5

reaction (Scheme 6). Formation of such a species is also supported by the observation that *N*-isopropylidene-isopropylamine is released upon addition of PhSSPh to a reaction mixture containing the paramagnetic species. Unfortunately the remainder of the reaction mixture is intractable. It is interesting to note that the initially formed reaction mixture in which the imine is still attached to the metal center is paramagnetic, whereas very similar species, [(η^5-C₅H₄C₂H₄NCR′₂)V(NH-*t*-Bu)][B(C₆F₅)₄] (**3a′,b′**), were found to be diamagnetic. As yet, we have no good explanation for these observations.
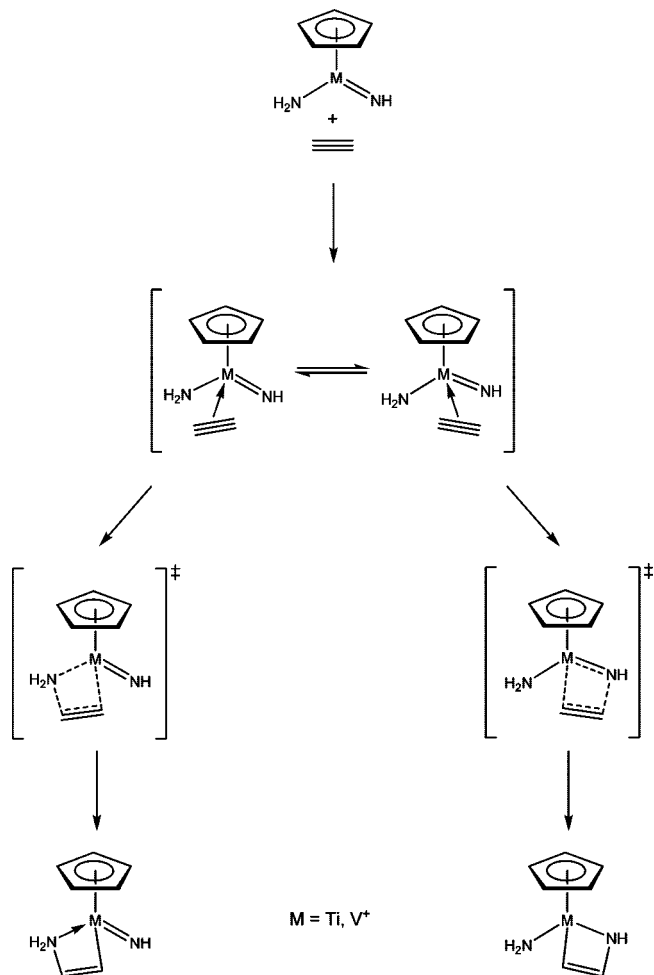
Despite the above-mentioned rearrangement to form a vanadium(III) species, [CpV(N-*i*-Pr₂)(N-*p*-tol)]⁺ could be used as a catalyst precursor in the hydroamination reaction of 2-butyne with *p*-toluidine by pretreatment of the vanadium cation with an excess of *p*-toluidine prior to the addition of the alkyne. This way, the di-isopropylamide cation is converted into the *p*-tolylamido cation [CpV(NH-*p*-Tol)(N-*p*-tol)(NH₂-*p*-Tol)]⁺ (**13′**), prohibiting the aforementioned β-hydrogen transfer from the *i*-Pr amido group to afford cationic vanadium(III) complexes. Nevertheless, the activity of the system is very low, especially compared to the activities observed for the isoelectronic titanium compound.[4] Using the procedure described above, 2-butyne and *p*-toluidine could be partially converted into *N*-isobutylidene-*p*-tolylamine at 80 °C. After 5 days and 24% conversion (determined by ¹H NMR spectroscopy), the reaction mixture had turned greenish-brown, indicating catalyst decomposition. Indeed, no further reaction was observed upon prolonged heating at 80 °C.

Computational Studies toward Alkyne Reactivity. The preference for the linked Cp-amido vanadium cation for insertion into the vanadium−amido bond differs remarkably from the

(15) *sec*-Butylidine-*p*-tolylamine-*dₙ* (*n* = 1−4) was observed. As yet, the reason for this distribution of isotopomers is not clear.

Scheme 6

Scheme 7

M = Ti, V⁺

proposed behavior of the isoelectronic Ti(IV) complexes described by Bergman and co-workers.[4] This prompted us to study the insertion and [2+2] cycloaddition reaction by means of computational methods (see Experimental Section for details). The reaction coordinate for the insertion and the cycloaddition reaction under investigation is summarized in Scheme 7. For computational ease, truncated versions of the molecules were studied in which the substituents on the imido and amido nitrogen have been replaced by hydrogen atoms. Also the effect of the counterion in the vanadium system has not been taken into account. Figure 2 shows the calculated Gibbs free energy diagram for both systems; see Table 3 for a summary of thermodynamic and kinetic parameters. Bergman and co-workers also studied the cycloaddition reaction of acetylene with $CpTi(NH)(NH_2)$ using computational methods, affording similar results.[16,17]

For vanadium, two different alkyne adducts were found with virtually identical energies: one with the hydrocarbon bound

parallel to the V≡N bond and one parallel to the V−N bond (the first being slightly lower in energy by 0.47 kcal/mol). The barrier for switching from one orientation of the alkyne ligand to the other is expected to be minute. A similar result was previously found for the olefin adduct $[(\eta^5\text{-}C_5H_4C_2H_4NH)V(NH)(\eta^2\text{-}C_2H_4)]^+$.[6] In the case of the corresponding titanium system, only one minimum was found, in which the acetylene was bound parallel to the Ti≡N bond.[18] The alkyne ligand in the calculated adducts is bound in an asymmetric fashion, similar to what was observed for the ethylene molecule in the calculated structure of the cation $[(\eta^5\text{-}C_5H_4C_2H_4NH)V(NH)(\eta^2\text{-}C_2H_4)]$.[6] The C≡C bonds in the alkyne ligands (M = Ti: 1.213 Å; M = V: 1.219 and 1.216 Å) are barely elongated upon coordinating to the metal center, as expected for binding to a d^0 metal center. The calculated distance of free acetylene is 1.203 Å.

Whereas binding of acetylene is slightly uphill ($\Delta G^0 = 1.35$ kcal/mol) in the case of titanium, the binding energies in the case of vanadium are −11.85 and −11.38 kcal/mol, depending on the orientation of the alkyne. Thermal corrections have been included in the calculations (see Experimental Section). The increased binding energy when going from titanium to vanadium can be explained by (a) the charge on the metal center[19] and (b) the small reorganization energy involved in the binding of the alkyne in the case of vanadium. The "naked" vanadium cation adopts a significantly pyramidalized structure (sum of the angles around V: 342.3°), whereas the neutral titanium analogue is virtually planar (sum of the angles around Ti: 360.0°). Accordingly, the Gibbs free energy associated with the geometrical change necessary for accommodating the substrate in the titanium case was calculated to be significantly higher than vanadium (12.08 kcal/mol for M = Ti versus 2.03 and 0.95 kcal/mol for M = V).[20]

For both metal complexes the kinetic product is calculated to be that originating from the [2+2] cycloaddition reaction. The energies of activation are 1.66 (M = Ti) and 2.82 (M = V) kcal/mol for the cycloaddition reaction and 10.06 (M = Ti) and 6.34 (M = V) kcal/mol for the insertion reaction. For titanium, the cycloaddition product is found to be the thermodynamic product as well, whereas the insertion product is the energetically preferred product in the case of $[CpV(NH)(NH_2)]^+$.

In addition to half-sandwich complexes of the type $[CpM(NH)(NH_2)]^{n+}$, the linked system $[(\eta^5\text{-}C_5H_5C_2\text{-}H_4NH)V(NH)]^+$ was studied (see Figure 3 and Table 3). Like

(16) Straub, B. F.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4632.

(17) The differences in energy can be explained by the use of different software packages (Gaussian03 vs Jaguar 4.0 Quantum Chemistry program package) and different basis sets for the metal center (LANL2DZ vs LACV3P**). See Experimental Section for a detailed description of the calculations used in this contribution.

(18) A geometry optimization starting with a structure in which the alkyne is bound parallel to the Ti−N bond results in the same geometry as found when starting with a structure in which the alkyne is bound parallel to the Ti≡N bond.

(19) Margl, P.; Deng, L.; Ziegler, T. *Organometallics* **1998**, *17*, 933.

(20) The distorted geometries of the $[CpM(NH)(NH_2)]^{n+}$ fragments are no local minima but originate from a single-point calculation of the fragments constructed from the corresponding alkyne adducts. A geometry optimization of these fragments relaxes to the naked cations $[CpM(NH)(NH_2)]^{n+}$.
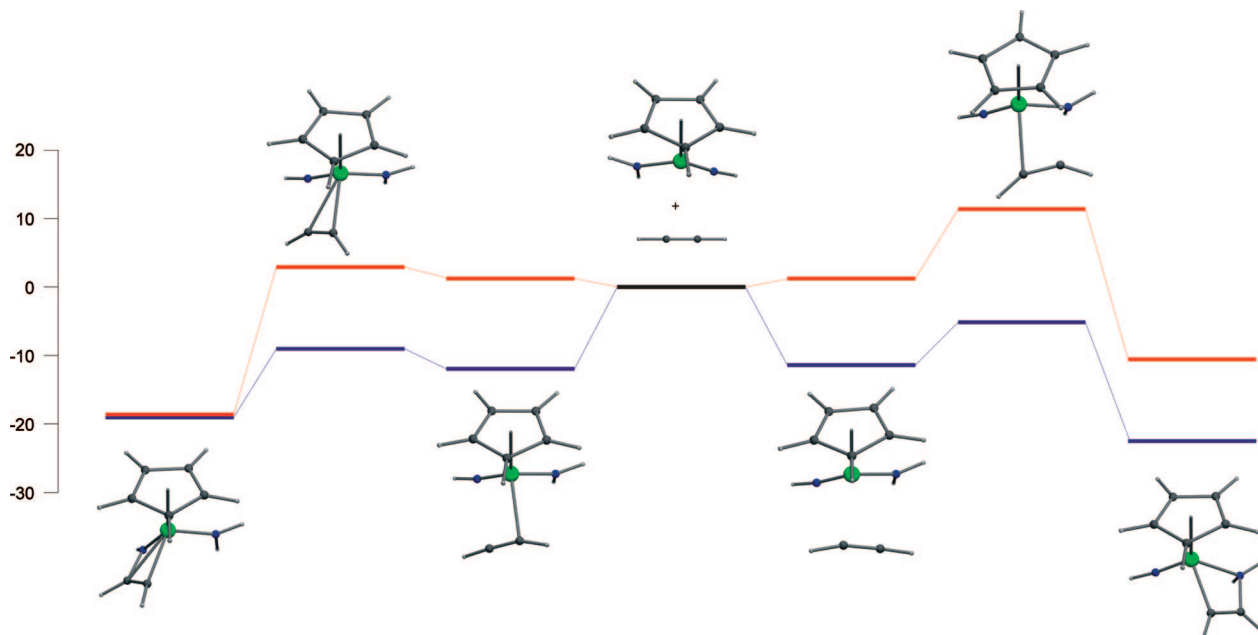
Figure 2. Calculated Gibbs free energy diagram for the insertion reaction of an alkyne into the M—N bond and the [2+2] cycloaddition reaction with the M=N bond in $[CpM(NH)(NH_2)]^{n+}$ (red: M = Ti, n = 0; blue: M = V, n = 1). Ball-and-stick representations of the stationary points for the vanadium reaction are shown.

Table 3. Pertinent Thermodynamic Parameters for Both the Insertion Reaction of an Alkyne into the M—N Bond and the [2+2] Cycloaddition Reaction with the M=N Bond in $[CpM(NH)(NH_2)]^{n+}$ (M = Ti, n = 0; M = V, n = 1) and $[(\eta^5-C_5H_5C_2H_4NH)V(NR)]^+$ (R = H, Me) (listed energies are in kcal/mol at 298 K)

	CpTi(NH)(NH$_2$)	$[CpV(NH)(NH_2)]^+$	$[(\eta^5-C_5H_5C_2H_4NH)V(NH)]^+$	$[(\eta^5-C_5H_5C_2H_4NH)V(NMe)]^+$
ΔG^0(insertion)	−11.82	−11.02	−7.45	−7.54
ΔG^0(cycloaddition)	−19.88	−7.19	−9.66	−4.09
$\Delta G^{\ddagger}$(insertion)	10.06	6.36	8.70	9.53
$\Delta G^{\ddagger}$(cycloaddition)	1.66	2.82	2.16	3.99
$\Delta G^{\ddagger}$(−insertion)	21.87	17.36	16.15	17.07
$\Delta G^{\ddagger}$(−cycloaddition)	21.55	10.01	11.82	8.08

in the titanium system, no local minimum was found for the adduct with the acetylene bound parallel to the metal-amido bond. More importantly, the insertion reaction is no longer thermodynamically favored in the linked Cp-amido system ($\Delta G^0_{insertion}$ = −7.45 kcal/mol; $\Delta G^0_{cycloaddition}$ = −9.66 kcal/mol). This can be explained by the increased steric bulk on the amide nitrogen by introducing the ethylene bridge. Indeed, when this effect is compensated for by introducing a methyl substituent on the imido ligand, the [2+2] cycloaddition reaction is again kinetically and the insertion reaction thermodynamically favored, similar to the parent system $[CpV(NH)(NH_2)]^+$ (Figure 3). These results illustrate the importance of the substituents on the relative reactivity of the M—N and M=N bond.

For the sake of completeness, we also considered a third potential reaction: [2+3] dipolar cycloaddition (Scheme 8). For both titanium and vanadium systems, including the linked Cp-amido vanadium cations, the product of such a [2+3] cycloaddition reaction is thermodynamically favored over those from the insertion and [2+2] cycloaddition reactions, especially when considering the triplet state of the product. However, calculations indicate that there is no single-step [2+3] dipolar cycloaddition path. Instead, the system first undergoes [2+2] cycloaddition as discussed above, and the addition product then rearranges to the formal [2+3] cycloaddition product in a separate step with higher activation energies. Thus, such a path does not seem to be relevant to the easy rearrangements observed in the present work (Table 4).

From experiment it is clear that in bromobenzene solution the vanadium cation exists as the corresponding bromobenzene

Scheme 8
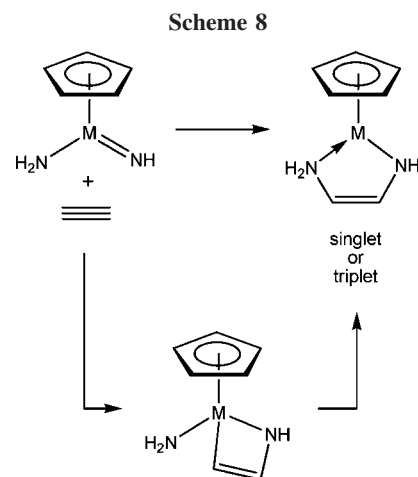
adduct. The binding energy for bromobenzene to the vanadium cation CpV(NH)(NH$_2$) was calculated to be −12.17 kcal/mol, slightly higher than the calculated binding energy for acetylene. The enthalpy contribution to the Gibbs free energy of binding, −24.96 kcal/mol, is slightly higher than the binding enthalpy calculated for the fluorobenzene adducts of d^0 scandocene cations[21] and the chlorobenzene adduct of $[(1,2-C_5H_3Me_2)_2ZrMe]^+$.[22] The V—Br—C angle of 109.2° found in

(21) Bouwkamp, M. W.; Budzelaar, P. H. M.; Gercama, J.; Del Hierro Morales, I.; De Wolf, J.; Meetsma, A.; Troyanov, S. I.; Teuben, J. H.; Hessen, B. *J. Am. Chem. Soc.* **2005**, *127*, 14310.
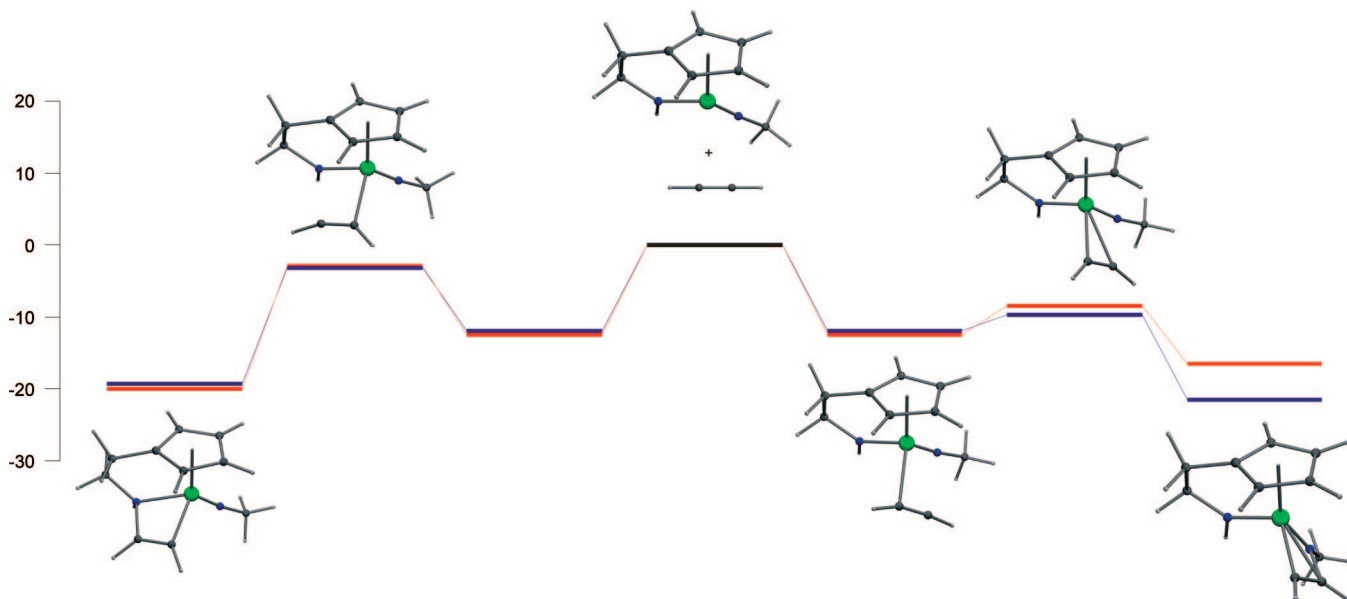
Figure 3. Calculated Gibbs free energy diagram for both the insertion reaction of an alkyne into the V−N bond and the [2+2] cycloaddition reaction with the V=N bond in [(η^5-C$_5$H$_4$C$_2$H$_4$NH)V(NR)]$^+$ (red: R = H; blue: R = Me). Ball-and-stick representations of the stationary points for [(η^5-C$_5$H$_4$C$_2$H$_4$NH)V(NMe)]$^+$ are shown.

Table 4. Pertinent Thermodynamic Parameters for the [2+3] Cycloaddition Reaction of an Alkyne with [CpM(NH)(NH$_2$)]$^{n+}$ (M = Ti, n = 0; M = V, n = 1) and [(η^5-C$_5$H$_5$C$_2$H$_4$NH)V(NR)]$^+$ (R = H, Me) (listed energies are in kcal/mol at 298 K)

	CpTi(NH)(NH$_2$)	[CpV(NH)(NH$_2$)]$^+$	[(η^5-C$_5$H$_5$C$_2$H$_4$NH)V(NH)]$^+$	[(η^5-C$_5$H$_5$C$_2$H$_4$NH)V(NMe)]$^+$
ΔG^0(2+3 singlet)	−2.49	−23.29	−23.27	−14.62
ΔG^0(2+3 triplet)	−18.98	−56.95	−49.91	−41.42
$\Delta G^{\ddagger}$(from metallacycle)	43.26	19.86	28.82	29.69

this study is very similar to the corresponding angle in the chlorobenzene adduct Cp$_2$Zr(ClC$_6$D$_5$)Me][B(C$_6$F$_5$)$_4$] (115.0-(1)°).[23] The binding energy of the solvent molecule might explain the poor productivity of the cationic vanadium catalyst in the hydroamination reaction, as the bromobenzene adduct might be regarded as a resting state of the catalyst, decreasing the effective concentration of the active species.

The differences in activation energies and thermodynamic preferences for the insertion and [2+2] cycloaddition reaction are very small. As a result, the outcome of the reaction of these types of metal imido amido complexes is likely to be highly susceptible to changes in the substituents on both the amido and imido ligands. Furthermore, the outcome of these reactions is predicted to be highly dependent on subsequent reactivity, such as the insertion of a second substrate molecule into the newly formed metal−carbon bond (formation of compound **8b**) or the cyclometalation of ligand substituents (formation of paramagnetic aza-allyl species).

Conclusions

Whereas a [2+2] cycloaddition-type mechanism is usually proposed for the hydroamination reaction catalyzed by group 4 and 5 metal complexes, we here present an example where insertion of an alkyne is observed into the V−N bond of a cationic amido imido vanadium complex. Computational studies have shown that half-sandwich amido imido complexes of titanium have a clear preference for [2+2] cycloaddition

reactions, whereas in the isoelectronic, cationic vanadium system the insertion into the vanadium−nitrogen single bond is thermodynamically favored. Nevertheless, the energy surface of the two reactions is relatively flat; hence the outcome of the reaction of metal amido imido complexes is most likely dictated by the steric and electronic effects of the substituents on the two nitrogen-based ligands and by the reactions subsequent to the initial insertion or cycloaddition reaction.

Experimental Section

General Considerations. All reactions and manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques. Reagents were purchased from commercial suppliers and used as received, unless stated otherwise. Deuterated solvents were dried over Na/K alloy prior to use (C$_6$D$_6$, THF-d_8) or degassed and stored over molecular sieves (4 Å) (C$_6$D$_5$Br, C$_6$D$_5$Cl, CD$_2$Cl$_2$, C$_2$D$_2$Cl$_4$). The compounds C$_5$H$_5$C$_2$H$_4$NHR (R = Me, *i*-Pr)[7] and *t*-BuNV(NMe$_2$)$_2$Cl[6] were prepared using literature procedures. ^{1}H, ^{19}F, and [51]V NMR spectra were recorded on a Varian Unity 500 or Varian Gemini 200 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent resonances as internal reference. ^{19}F NMR chemical shifts are reported in ppm relative to CFCl$_3$ and [51]V NNR chemical shifts to VOCl$_3$, which were both used as an external reference. Elemental analyses were performed at the analysis department at the University of Groningen. Reported values are the average of two independent determinations.

(η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-*t*-Bu)Cl. To a solution of 0.95 g (3.9 mmol) of *t*-BuNV(NMe$_2$)$_2$Cl in 20 mL of pentane was added 0.49 g (4.0 mmol) of C$_5$H$_5$C$_2$H$_4$NHMe. The brown solution was refluxed for 18 h, after which the color had changed to red. All volatiles were removed *in vacuo*, and the resulting solid was extracted twice

(22) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.

(23) Wu, F.; Dash, A. K.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 15360.

with pentane (10 mL). The pentane solution was concentrated and cooled to -20 °C, affording 0.80 g (2.9 mmol, 74%) of red crystals, identified as (η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-*t*-Bu)Cl. ^{1}H NMR (benzene-d_6, RT): δ 6.11 (m, 1H, Cp), 5.88 (m, 2H, Cp), 5.11 (m, 1H Cp), 4.60 (m, 1H, NCH$_2$), 4.01 (s, 3H, NMe), 3.20 (m, 1H, NCH$_2$), 2.46 (m, 1H, CpCH$_2$), 1.98 (m, 1H, CpCH$_2$), 1.19 (s, 9H, *t*-Bu). ^{13}C$\{^1$H$\}$ (benzene-d_6, RT): δ 137.5 (C$_{ipso}$ of Cp), 116.2, 111.7, 100.6, 99.6 (4 H, Cp CH), 81.6 (NMe), 61.6 (NCH$_2$), 30.9 (*t*-Bu Me), 28.3 (CpCH$_2$). ^{51}V NMR (benzene-d_6, RT): δ -679 ($\Delta\nu_{1/2}$ = 350). Anal. Calcd for C$_{12}$H$_{20}$N$_2$VCl: C, 51.72; H, 7.23; N, 10.05. Found: C, 51.28; H, 7.37; N, 9.99.

(η^5-C$_5$H$_4$C$_2$H$_4$N-*i*-Pr)V(N-*t*-Bu)Cl. To a solution of 3.3 g (13 mmol) of *t*-BuNV(NMe$_2$)$_2$Cl in 100 mL of pentane was added 2.0 g (13 mmol) of C$_5$H$_5$C$_2$H$_4$NH-*i*-Pr. The brown solution was refluxed for 18 h, after which the color had changed to red. All volatiles were removed *in vacuo*, and the resulting solid was extracted twice with 50 mL of pentane. The pentane solution was concentrated and cooled to -20 °C, yielding 3.3 g (11 mmol, 83%) of red crystals, identified as (η^5-C$_5$H$_4$C$_2$H$_4$N-*i*-Pr)V(N-*t*-Bu)Cl. ^{1}H NMR (benzene-d_6, RT): δ 6.10 (m, 1H, Cp), 5.97 (m, 2H, Cp and CH of *i*-Pr), 5.87 (m, 1H, Cp), 5.13 (m, 1H, Cp), 4.66 (m, 1H, NCH$_2$), 3.25 (dd, 6 and 13 Hz, 1H, NCH$_2$), 2.47 (m, 1H, CpCH$_2$), 1.76 (m, 1H, CpCH$_2$), 1.19 (s, 9H, *t*-Bu), 1.01 (d, 7 Hz, 3H, *i*-Pr Me), 0.98 (d, 7 Hz, 3H, i-Pr Me). ^{13}C$\{^1$H$\}$ NMR (benzene-d_6, RT): δ 139.6 (C$_{ipso}$ of Cp), 115.1, 114.6, 100.5, 99.5 (4 CH of Cp), 72.3 (*i*-Pr CH), 70.5 (NCH$_2$), 30.0 (CpCH$_2$), 31.2 (*t*-Bu Me), 21.2, 20.5 (2 *i*-Pr Me), C$_q$ of *t*-Bu not observed. ^{51}V NMR (benzene-d_6, RT): δ -674 ($\Delta\nu_{1/2}$ = 360). IR: 652 (w), 810 (s), 837 (w), 876 (w), 1146 (w), 1169 (w), 1209 (s), 1225 (s), 1356 (s) cm^{-1}. Anal. Calcd for C$_{14}$H$_{24}$N$_2$VCl: C, 54.82; H, 7.89; N, 9.13; V, 16.61; Cl, 11.56. Found: C, 54.64; H, 7.92; N, 8.96; V, 16.45; Cl, 11.46.

(η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-*t*-Bu)Me (1a). To a solution of 1.2 g (4.2 mmol) of (η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-*t*-Bu)Cl in 30 mL of Et$_2$O was added 2.8 mL of 1.53 M MeLi in Et$_2$O (4.3 mmol). The solution was stirred for 0.5 h, after which all volatiles were removed *in vacuo*. The resulting oil was stripped by addition of 2 × 5 mL of pentane and removal *in vacuo*. Extraction with 2 × 10 mL of pentane and removal of the solvent afforded 0.89 g of the title compound as a red oil. ^{1}H NMR spectroscopy showed small amounts of impuries in the region of 0–4 ppm. ^{1}H NMR (bromobenzene-d_5, RT): δ 5.94 (br, 1H, Cp), 5.63 (br, 1H, Cp), 5.53 (br, 1H, Cp), 5.34 (br, 1H, Cp), 4.15 (m, 1H, NCH$_2$), 3.79 (s, 3H, NMe), 3.47 (m, 1H, NCH$_2$), 2.57 (m, 1H, CpCH$_2$), 2.40 (m, 1H, CpCH$_2$), 1.23 (s, 9H, *t*-Bu), 0.63 (br, $\Delta\nu_{1/2}$ = 12, 3H, VMe). ^{13}C$\{^1$H$\}$ NMR (bromobenzene-d_5, RT): δ 133.9 (C$_{ipso}$ of Cp), 114.7, 106.1, 102.3, 98.3 (4 CH of Cp), 78.6 (NMe), 58.9 (NCH$_2$), 32.2 (*t*-Bu Me), 29.1 (CpCH$_2$), C$_q$ of *p*-Tol and VMe were not located. ^{51}V NMR (bromobenzene-d_5, RT): δ -679 ($\Delta\nu_{1/2}$ = 700).

(η^5-C$_5$H$_4$C$_2$H$_4$N-*i*-Pr)V(N-*t*-Bu)Me (1b). To a solution of 1.1 g (3.7 mmol) of (η^5-C$_5$H$_4$C$_2$H$_4$N-*i*-Pr)V(N-*t*-Bu)Cl in 20 mL of pentane was added 4.5 mL of 0.88 M MeLi in Et$_2$O (4.0 mmol). The solution was stirred for 1 h, after which all volatile compounds were removed *in vacuo*. The resulting brown solid was extracted twice with 30 mL of pentane and concentrated to ~10 mL. Cooling to -60 °C yielded 0.50 g (1.8 mmol, 49%) of the title compound as red-brown, analytically pure crystals. ^{1}H NMR (benzene-d_6, RT): δ 5.83 (m, 1H, Cp), 5.50 (m, 1H, Cp), 5.41 (m, 2H, Cp), 5.29 (sept, 7 Hz, 1H, *i*-Pr CH), 4.13 (m, 1H, NCH$_2$), 3.30 (m, 1H, NCH$_2$), 2.50 (ddd, 3, 7, and 13 Hz, 1H, CpCH$_2$), 2.07 (m, 1H, CpCH$_2$), 1.25 (s, 9H, *t*-Bu), 1.15 (d, 7 Hz, 3H, *i*-Pr Me), 0.95 (d, 7 Hz, 3H, *i*-Pr Me), 0.69 (br, $\Delta\nu_{1/2}$ = 8, 3H, VMe). ^{13}C$\{^1$H$\}$ NMR (toluene-d_8, -70 °C): δ 132.9 (C$_{ipso}$ of Cp), 112.7, 107.5, 100.6, 94.1 (4 CH of Cp), 70.4 (C$_q$ of *t*-Bu), 67.1 (*i*-Pr CH), 66.5 (NCH$_2$), 29.4 (CpCH$_2$), 31.2 (*t*-Bu Me), 21.8, 20.7 (2 *i*-Pr Me), 17.7 (br, $\Delta\nu_{1/2}$ = 75, VMe). ^{13}C NMR (benzene-d_6, RT): δ 132.3 (s, C$_q$ of Cp), 113.0, 107.9, 100.9, 97.5 (d, 170, 172, 173, and 173 Hz, 4 CH of Cp), 67.5 (d, 142 Hz, *i*-Pr CH), 66.8 (t, 142 Hz, NCH$_2$),

31.6 (q, 126 Hz, *t*-Bu Me), 29.9 (t, 129 Hz, CpCH$_2$), 22.2 (q, 125 Hz, *i*-Pr Me), 21.1 (q, 125 Hz, *i*-Pr Me), 17 (v br, VMe). C$_q$ of *t*-Bu not observed. ^{51}V NMR (benzene-d_6, RT): δ -665 ($\Delta\nu_{1/2}$ = 320). IR: 656 (w), 667 (w), 689 (w), 814 (s), 851 (w), 868 (w), 957 (w), 990 (w), 1018 (w), 1036 (w), 1044 (w), 1071 (w), 1115 (w), 1148 (w), 1173 (w), 1213 (w), 1248 (s), 1333 (w), 1358 (s) cm^{-1}. Anal. Calcd for C$_{15}$H$_{27}$N$_2$V: C, 62.92; H, 9.50; N, 9.78; V, 17.79. Found: C, 62.66; H, 9.49; N, 9.80; V, 17.68.

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-*t*-Bu)][MeB(C$_6$F$_5$)$_3$] (2a). A solution of 17 mg (0.067 mmol) of **1a** in 0.1 mL of C$_6$D$_5$Br was added to a solution of 40 mg (0.078 mmol) of B(C$_5$F$_5$)$_3$ in 0.4 mL of C$_6$D$_5$Br. ^{1}H NMR spectroscopy showed full conversion to compound **2a**. The compound is mainly present as a solvent-separated ion-pair. ^{1}H NMR (bromobenzene-d_5, -30 °C): δ 6.04 (br, 1H, Cp), 5.44 (br, 1H, Cp), 5.33 (br, 1H, Cp), 5.08 (br, 1H, Cp), 4.44 (m, 1H, NCH$_2$), 3.87 (s, 3H, NMe), 3.61 (m, 1H, NCH$_2$), 2.48 (m, 1H, CpCH$_2$), 2.28 (m, 1H, CpCH$_2$), 0.92 (s, 9H, *t*-Bu). ^{13}C$\{^1$H$\}$ (bromobenzene-d_5, -30 °C): δ 143.0 (C$_{ipso}$ of Cp), 114.7, 108.1, 104.8, 104.1 (4 H of Cp), 84.9 (NMe), 79.2 (C$_q$ of *t*-Bu), 64.5 (NCH$_2$), 30.9 (*t*-Bu Me), 28.3 (CpCH$_2$). ^{51}V NMR (bromobenzene-d_5, -30 °C): δ -565 ($\Delta\nu_{1/2}$ = 7000).

[(η^5-C$_5$H$_4$C$_2$H$_4$N-*i*-Bu)V(N-*t*-Bu)][MeB(C$_6$F$_5$)$_3$] (2b). In 2 mL of pentane 43 mg (0.15 mmol) of **1b** was dissolved and slowly added to a stirred solution of 100 mg (0.19 mmol) of B(C$_6$F$_5$)$_3$ in 10 mL of pentane. The resulting suspension was stirred for an additional 5 min. After 10 min an orange precipitate had settled and the solution was decanted. The orange powder was washed three times with 5 mL of pentane and dried *in vacuo*. This yielded 97 mg (0.12 mmol, 81%) of compound **2b** as an analytically pure, orange powder. ^{1}H NMR (benzene-d_6, RT): of the contact ion-pair: δ 5.86 (br, 1H, Cp), 5.80 (sept, 6 Hz, 1H, *i*-Pr CH), 5.59 (br, 1H, Cp), 5.46 (br, 1H, Cp), 4.74 (m, 1H, NC$_2$), 4.52 (br, 1H, Cp), 2.98 (dd, 7 and 13 Hz, 1H, NCH$_2$), 2.28 (dd, 7 and 13 Hz, 1H, CpCH$_2$), 1.44 (m, 1H, CpCH$_2$), 0.84 (s, 9H, *t*-Bu), 0.63 (d, 6 Hz, 3H, *i*-Pr Me), 0.47 (d, 6 Hz, 3H, *i*-Pr Me), -0.20 (br, $\Delta\nu_{1/2}$ = 24 Hz, 3H, BMe). ^{13}C$\{^1$H$\}$ NMR (benzene-d_6, RT): δ 148.9 (d, J_{CF} = 242 Hz, C$_6$F$_5$), 142.9 (C$_{ipso}$ of Cp), 139.3 (d, J_{CF} = 240 Hz, C$_6$F$_5$), 137.6 (d, J_{CF} = 245 Hz, C$_6$F$_5$), 112.6, 112.3, 102.1, 100.9 (4 CH of Cp), 75.5 (*i*-Pr CH), 72.8 (NCH$_2$), 29.3 (CpCH$_2$), 30.5 (*t*-Bu Me), 21.3, 20.2 (2 *i*-Pr Me), C$_q$ of *t*-Bu and BMe not observed. ^{51}V NMR (benzene-d_6, RT): δ -514 ($\Delta\nu_{1/2}$ = 1600). ^{19}F NMR (benzene-d_6, RT): δ -133.6, -134.9^* (*o*-F), -162.2^*, -166.2 (*p*-F), -166.8^*, -168.7 (*m*-F). Resonances marked with an asterisk are from the contact ion-pair (>90%). ^{1}H NMR (bromobenzene-d_5, RT): δ 6.06 (br, 1H, Cp), 5.73 (sept, 6 Hz, 1H, *i*-Pr CH), 5.52 (br, 1H, Cp), 5.37 (br, 1H, Cp), 5.13 (br, 1H, Cp), 4.70 (m, 1H, NCH$_2$), 3.56 (dd, 7 and 13 Hz, 1H, NCH$_2$), 2.70 (dd, 6 and 13 Hz, 1H, CpCH$_2$), 2.09 (m, 1H, CpCH$_2$), 1.13 (br, $\Delta\nu_{1/2}$ = 25 Hz, 3H, BMe), 1.01 (s, 9H, *t*-Bu), 0.99 (shoulder, *i*-Pr Me), 0.76 (d, 6 Hz, 3H, *i*-Pr Me). ^{13}C$\{^1$H$\}$ NMR (bromobenzene-d_5, RT): δ 148.9 (d, J_{CF} = 239 Hz, C$_6$F$_5$), 143.2 (C$_{ipso}$ of Cp), 138.0 (d, J_{CF} = 241 Hz, C$_6$F$_5$), 136.0 (d, J_{CF} = 248 Hz, C$_6$F$_5$), 112.8, 110.8, 103.4, 103.0 (4 CH of Cp), 75.8 (*i*-Pr CH), 73.9 (NCH$_2$), 29.2 (CpCH$_2$), 30.7 (*t*-Bu Me), 22.3, 20.7 (2 *i*-Pr Me), 11.5 (br, $\Delta\nu_{1/2}$ ≈ 100 Hz, BMe), C$_q$ of *t*-Bu not observed. ^{51}V NMR (bromobenzene-d_5, RT): δ -544 ($\Delta\nu_{1/2}$ = 1300 Hz). ^{19}F NMR (bromobenzene-d_5, RT): δ -133.4, -134.5^* (*o*-F), -162.0^*, -165.7 (*p*-F), -166.3^*, -168.1 (*m*-F). Resonances marked with an asterisk are from the contact ion-pair (<10%). ^{19}F NMR (CD$_2$Cl$_2$, RT): δ -135.3^*, -135.8 (*o*-F), -163.3^*, -165.7 (*p*-F), -167.5^*, -168.5 (*m*-F). Resonances marked with an asterisk are of the contact ion-pair (20%). ^{19}F NMR (chlorobenzene-d_5, RT): δ -134.4 (overlap of solvent-separated and contact ion-pair) (*o*-F), -161.9^*, -164.9 (*p*-F), -166.2^*, -167.4 (*m*-F). Resonances marked with an asterisk are of the contact ion-pair (33%). ^{19}F NMR (C$_2$D$_2$Cl$_4$, RT): δ -134.9, -135.3^* (*o*-F), -162.4^*, -165.8 (*p*-F), -66.8^*, -168.4 (*m*-F). Resonances marked with an asterisk are of the contact ion-pair

(66%). Anal. Calcd for $C_{33}H_{27}BF_{15}N_2V$: C, 49.65; H, 3.41; N, 3.51; V, 6.38. Found: C, 49.78; H, 3.28; N, 3.40; V, 6.31.

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(THF)(N-t-Bu)][MeB-(C$_6$F$_5$)$_3$]. A solution of 20 mg (0.07 mmol) of **1b** in 0.1 mL of C$_6$D$_5$Br was added to a solution of 10 mg (0.08 mmol) of B(C$_6$F$_5$)$_3$ in 0.4 mL of C$_6$D$_5$Br, and 6 μL (0.07 mmol) of THF was added subsequently by microsyringe. NMR showed clean conversion to the title compound. ^{1}H NMR (C$_6$D$_5$Br, RT): δ 6.12 (m, 1H, Cp), 5.89 (m, 1H, Cp), 5.64 (sept, 7 Hz, 1H, i-Pr CH), 5.37 (m, 1H, Cp), 5.02 (m, 1H, Cp), 4.93 (m, 1H, NCH$_2$), 3.48 (m, 1H, NCH$_2$), 3.42 (m, 2H, α-H of THF), 3.32 (m, 2H, α-H of THF), 2.75 (m, 1H, CpCH$_2$), 2.01 (m, 1H, CpCH$_2$), 1.52 (m, 4H, β-H of THF), 1.02 (s, 9H, t-Bu), 0.93 (d, 7 Hz, 3H, i-Pr Me), 0.73 (d, 7 Hz, 3H, i-Pr Me). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br, RT): δ 143.2 (C$_{ipso}$ of Cp), 112.4, 111.8 (2 CH of Cp), 102.7 (br, 2 CH of Cp), 80.8 (α-C of THF), 75.0 (i-Pr CH), 73.2 (NCH$_2$), 31.6 (t-Bu Me), 30.1 (CpCH$_2$), 26.5 (β-C of THF), 22.2, 22.0 (2 i-Pr Me), C$_q$ of t-Bu not observed. ^{51}V NMR (C$_6$D$_5$Br, RT): δ −567 (Δ$\nu_{1/2}$ = 940).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)][B(C$_6$F$_5$)$_4$] (2b′). A solution of 10.5 mg (0.037 mmol) of **1b** in 0.1 mL of C$_6$D$_5$Br was added to a suspension of 39 mg (0.042 mmol) of [Ph$_3$C][B(C$_6$F$_5$)$_4$] in 0.4 mL of C$_6$D$_5$Br. ^{1}H NMR spectroscopy revealed the formation of a species with an identical ^{1}H NMR spectrum to the solvent separated ion-pair, **2b**, and Ph$_3$CMe. ^{19}F NMR (bromobenzene-d_5, RT): δ −133.5 (o-F), −163.9 (p-F), 167.7 (m-F).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(PhNMe$_2$)]-[MeB(C$_6$F$_5$)$_3$]. The title compound was generated by the addition of an excess (5 equiv) of N,N-dimethylaniline to a bromobenzene-d_5 solution of **2b**. ^{1}H NMR (bromobenzene-d_5, RT): δ 7.22 (2H, o-CH of Ph), 7.04 (t, 7 Hz, 2H, m-CH of Ph), 5.88 (overlapping, 2H, Cp and i-Pr CH), 4.96 (overlapping, 2H, Cp and NCH$_2$), 4.65 (m, 1H, Cp), 3.93 (m, 1H, Cp), 3.38 (m, 1H, NCH$_2$), 2.82 (s, 3H, NMe), 2.59 (s, 3H, NMe), 2.50 (m, 1H, CpCH$_2$), 1.84 (m, 1H, CpCH$_2$), 1.08 (s, 9H, t-Bu), 0.96 (d, 7 Hz, 3H, i-Pr Me), 0.87 (d, 7 Hz, 3H, i-Pr Me), p-CH of Ph not located. ^{51}V NMR (C$_6$D$_5$Br, RT): δ −551 (Δ$\nu_{1/2}$ = 830).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$NCH$_2$)V(NH-t-Bu)(THF-d_8)]-[B(C$_6$F$_5$)$_4$] (3a′). Compound **3a′** was prepared in the same way as **3b′** (see below). ^{1}H NMR spectroscopy showed clean conversion to the title compound. ^{1}H NMR (THF-d_8, RT): δ 6.47 (br, 1H, Cp), 6.29 (br, 1H, Cp), 6.18 (br, 1H, NH), 5.88 (br, 1H, Cp), 5.75 (br, 1H, Cp), 4.08 (m, 1H, NCH$_2$), 3.62 (m, 1H, NCH$_2$), 3.20 (d, 9H, =CH$_2$), 2.65 (overlapping, CpCH$_2$ and =CH$_2$), 1.33 (s, 9H, t-Bu). ^{13}C NMR (THF-d_8, −90 °C): δ 139.6 (C$_{ipso}$ Cp), 118.1, 106.8, 105.0, 98.7 (4H of Cp), 79.0 (br, C$_q$ of t-Bu), 65.2 (t, 142 Hz, NCH$_2$), 64.4 (t, 163 Hz, =CH$_2$), 32.0 (t-Bu Me), 29.0 (CpCH$_2$). ^{51}V NMR (THF-d_8, RT): δ −563 (Δ$\nu_{1/2}$ = 470).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$NCMe$_2$)V(NH-t-Bu)(THF-d_8)]-[B(C$_6$F$_5$)$_4$] (3b′). A solution of 30 mg (0.011 mmol) of **2b** in 0.5 mL of THF-d_8 was added to 84 mg (0.011 mmol) of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. Gas evolution was observed immediately upon addition, and the color of the solution turned from brown to reddish-brown while the anilinium reagent dissolved. ^{1}H NMR spectroscopy showed clean conversion to the title compound and free N,N-dimethylaniline. ^{1}H NMR (THF-d_8, RT): δ 6.20 (m, 2H, Cp), 5.88 (m, 1H, Cp), 5.69 (m, 1H, Cp), 5.50 (br, 1H, NH), 4.04 (m, 2H, NCH$_2$), 2.78 (m, 1H, CpCH$_2$), 2.69 (m, 1H, CpCH$_2$), 1.99 (s, 3H, =CMe$_2$), 1.91 (s, 3H, =CMe$_2$), 1.38 (s, 9H, t-Bu). ^{13}C{^{1}H} NMR (THF-d_8, −50 °C): δ 140.0 (s, C$_{ipso}$ of Cp), 119.0 (d, 173 Hz, Cp CH), 107.6 (d, 176 Hz, Cp CH), 102.8 (d, 175 Hz, Cp CH), 98.7 (d, 173 Hz, Cp CH), 79.1 (br, Δ$\nu_{1/2}$ = 21 Hz, C$_q$ of t-Bu), 78.2 (s, =CMe$_2$), 60.0 (t, 140 Hz, NCH$_2$), 34.7 (q, 127 Hz, =CMe$_2$), 32.3 (q, 127 Hz, t-Bu Me), 31.4 (t, 129 Hz, CpCH$_2$), 25.6 (q, 125 Hz, =CMe$_2$). ^{51}V NMR (THF-d_8, RT): δ −354 (Δ$\nu_{1/2}$ = 1900).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$NMe)V(N-t-Bu)(C$_2$H$_4$)][MeB-(C$_6$F$_5$)$_3$] (4a). An NMR tube equipped with a Teflon (Young) valve was filled with 0.875 g of a 66 mM solution of **2a** in C$_6$D$_5$Br. The tube was connected to a vacuum line, frozen, and evacuated. Subsequently a calibrated volume of ethylene was condensed into the NMR tube, so that a pressure of approximately 1 bar was obtained after thawing the NMR tube. The tube was closed and thawed. After 1 h (to reach equilibrium) the sample was characterized by NMR spectroscopy. ^{1}H NMR (bromobenzene-d_5, RT): δ 5.74 (br, 1H, Cp), 5.52 (br, 1H, Cp), 5.22 (br, 1H, Cp), 4.96 (br, 1H, Cp) 4.71 (m, 2H, =CH$_2$), 4.54 (m, 1H, NCH$_2$), 4.29 (m, 2H, =CH$_2$), 3.79 (s, 3H, NMe), 3.63 (m, 1H, NCH$_2$), 2.48 (m, 1H, CpCH$_2$), 2.25 (m, 1H, CpCH$_2$), 0.91 (s, 9H, t-Bu). ^{13}C{^{1}H} NMR (bromobenzene-d_5, RT): δ 140.8 (C$_{ipso}$ of Cp), 108.0, 103.3, 101.5, 100.1 (4 CH of Cp) 101.3 (t, 165 Hz, =CH$_2$), 84.9 (NMe), 64.4 (NCH$_2$), 30.8 (t-Bu Me), 28.0 (CpCH$_2$), C$_q$ of t-Bu not observed. ^{51}V NMR (bromobenzene-d_5, −30 °C): δ −734 (Δ$\nu_{1/2}$ = 3500).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(C$_2$H$_4$)][MeB-(C$_6$F$_5$)$_3$] (4b). An NMR tube equipped with a Teflon (Young) valve was filled with 0.874 g of a 66 mM solution of **2b** in C$_6$D$_5$Br. The tube was connected to a high-vacuum line, frozen, and evacuated. Subsequently, a calibrated volume of ethene was condensed into the NMR tube, so that a pressure of approximately 1 bar was reached after the NMR tube was closed and thawed out. After 1 h (to reach equilibrium) the sample was characterized by NMR spectroscopy. ^{1}H NMR (bromobenzene-d_5, RT): free olefin: δ 5.29 (s); [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(C$_2$H$_4$)][MeB(C$_6$F$_5$)$_3$]: δ 5.71 (br, 1H, Cp), 5.61 (br, 1H, Cp), 5.34 (sept, 6 Hz, 1H, i-Pr CH), 5.27 (br, 1H, Cp), 5.02 (br, 1H, Cp), 4.72 (m, 2H, =CH$_2$), 4.61 (m, 1H, NCH$_2$), 4.33 (m, 2H, =CH$_2$), 3.26 (dd, 15 and 7 Hz, 1H, NCH$_2$), 2.70 (dd, 13 and 7 Hz, 1H, CpCH$_2$), 1.91 (m, 1H, CpCH$_2$), 0.94 (s, 9H, t-Bu), 0.82, 0.59 (d, 6 and 7 Hz, 2 i-Pr Me). ^{13}C NMR (bromobenzene-d_5, −30 °C), free olefin: δ 123.9 (t, 160 Hz); [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(C$_2$H$_4$)][MeB(C$_6$F$_5$)$_3$]: δ 141.9 (C$_{ipso}$ of Cp), 109.6, 109.2, 103.1, 101.3 (d, 173, 173, 179 and 181 Hz, 4 CH of Cp), 103.2 (d, 164 Hz, =CH$_2$), 76.3 (d, 143 Hz, i-Pr CH), 73.3 (t, 138 Hz, NCH$_2$), 29.5 (t, partial overlap, CpCH$_2$), 31.1 (q, 132 Hz, t-Bu Me), 22.6, 20.7 (q, 127 Hz, 2 i-Pr Me), C$_q$ of t-Bu not observed. ^{51}V NMR (bromobenzene-d_5, RT): δ −707 (Δ$\nu_{1/2}$ = 750 Hz).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(CH$_2$CHMe)]-[MeB(C$_6$F$_5$)$_3$] (5b). The same procedure was used as for **4b**. Only now the propene pressure after thawing the NMR tube was approximately 2 bar. Two isomers were formed (A and B) in a ~4:5 ratio. ^{1}H NMR (bromobenzene-d_5, −30 °C), free olefin: δ 5.71 (m, 1H, =CHMe CH), 5.00 (d, 17 Hz, 1H, =CH$_2$ cis-CH), 4.94 (d, 10 Hz, 1H, =CH$_2$ trans-CH), 1.58 (d, 6 Hz, 3H, Me); [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(CH$_2$CHMe)][MeB(C$_6$F$_5$)$_3$]: δ 6.26 (m, =CHMe^B), 6.01 (m, =CHMe^A), 5.98, 5.93, 5.55, 5.43, 5.40, 5.34, 5.30, 5.08 (m, Cp), 5.66, 5.42 (i-Pr CH), 4.65, 4.39 (m, NCH$_2$), 4.33 (d, 17 Hz, =CH$_2$ cis-CH^B), 4.01 (d, 17 Hz, =CH$_2$ cis-CH^A), 4.15 (d, 9 Hz, =CH$_2$ trans-CH^A), 3.65 (d, 8 Hz, =CH$_2$ trans-CH^B), 3.31, 3.16 (m, NCH$_2$), 2.58, 2.54 (m, CpCH$_2$), 1.99, 1.88 (m, CpCH$_2$), 1.32 (d, 5 Hz, =CHMe^A), 1.28 (d, 5 Hz, =CHMe^B), 0.98, 0.95 (s, t-Bu), 0.80, 0.72, 0.66, 0.56 (d, 6 Hz, i-Pr Me). ^{13}C NMR (bromobenzene-d_5, −30 °C), free olefin: 134.4 (d, 155 Hz, =CHMe), 116.8 (t, 153 Hz, =CH$_2$), 20.5 (q, overlap, Me); [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(CH$_2$CHMe)][MeB(C$_6$F$_5$)$_3$]: δ 142.2, 141.8 (s, 2 C$_{ipso}$ of Cp), 137.7, 135.4 (d, 157 and 159 Hz, 2 =CHMe), 111.2, 110.3, 109.6, 109.2, 102.4, 102.3, 101.3, 101.2 (d, 182, 177, 175, 173, 174, 174, 177, and 177 respectively, 8 CH of Cp), 92.7, 92.5 (t, 160 and 159 Hz, 2 =CH$_2$), 77.0, 76.4 (t, 2 NCH$_2$), 73.4, 72.7 (d, 2 i-Pr CH), 31.2, 30.9 (q, 127 and 128 Hz, 2 t-Bu Me), 29.7, 29.5 (2 CpCH$_2$), 23.4, 22.9, 22.8, 22.6 (4 i-Pr Me), 20.2, 20.1 (2 =CHMe), C$_q$ of t-Bu not observed. ^{51}V NMR (bromobenzene-d_5, RT): δ −646 and −650 (partial overlap).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)(CH$_2$CMe$_2$)]-[MeB(C$_6$F$_5$)$_3$] (6b). This compound was prepared similarly to compound **5b**. The reaction mixture was characterized using NMR spectroscopy. ^{1}H NMR (bromobenzene-d_5, −30 °C): δ 5.79 (br, 1H, Cp), 5.60 (overlapping, 2H, Cp and i-Pr CH), 5.26 (br, 1H, Cp), 4.99 (br, 1H, Cp), 4.54 (m, 1H, NCH$_2$), 3.76 (s, 1H, =CH$_2$), 3.69 (s, 1H, =CH$_2$), 3.24 (m, 1H, NCH$_2$), 2.60 (m, 1H, CpCH$_2$), 1.82 (m, 1H, CpCH$_2$), 1.72 (s, 3H, =CMe$_2$), 0.96 (s, 3H, =CMe$_2$), 0.94 (s, 9H, t-Bu), 0.87 (d, 7 Hz, 3H, i-Pr Me), 0.64 (d, 7 Hz, 3H, i-Pr). ^{13}C NMR (bromobenzene-d_5, −30 °C): δ 177.5 (s, =CMe$_2$), 142.3 (C$_{ipso}$ of Cp), 112.0, 110.7, 101.0, 101.4 (4 CH of Cp), 84.8 (t, 156 Hz, =CH$_2$), 76.5 (i-Pr CH), 72.7 (NCH$_2$), 30.9 (t-Bu Me), 29.9 (CpCH$_2$), 29.1, 29.0, 23.9, 19.2 (i-Pr Me and =CMe$_2$), C$_q$ of t-Bu not observed. ^{51}V NMR (bromobenzene-d_5, RT): δ −577 ($\Delta\nu_{1/2}$ = 860).

Determination of K_{eq}. Equilibrium constants (K_{eq}) were determined from ^{1}H NMR spectra of the reaction mixture of olefin adduct and free olefin at 25 °C. The ratio olefin adduct:solvent-separated ion-pair was determined by careful integration of well-separated resonances of both complexes (mostly resonances corresponding to the Cp moiety or the C$_2$H$_4$ bridge). In order to have reliable data, spectra were measured with a 25 s delay between transients. The concentration of free olefin was also determined by integration of its resonances in the ^{1}H NMR spectrum. The value for K_{eq} was calculated using the formula K_{eq} = [olefin adduct] × [C$_6$D$_5$Br] × [ion-pair]$^{-1}$ × [olefin]$^{-1}$.

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N(i-Pr)C$_2$Me$_2$)V(N-t-Bu)][MeB-(C$_6$F$_5$)$_3$] (7b). A solution of 10 mg (0.035 mmol) of (η^5-C$_5$H$_4$C$_2$H$_4$N-i-Pr)V(N-t-Bu)Me in 0.1 mL of C$_6$D$_5$Br was added to a solution of 23 mg (0.045 mmol) of B(C$_6$F$_5$)$_3$ in 0.4 mL of C$_6$D$_5$Br. This solution was transferred into an NMR tube equipped with a Teflon Young valve. The tube was connected to a high-vacuum line, frozen in liquid nitrogen, and evacuated. Subsequently, 1.2 equiv of 2-butyne was condensed into the NMR tube, which was then closed, thawed out, and kept at 0 °C for 10 min. ^{1}H NMR spectroscopy showed complete conversion to the title compound, a small amount of **8b** (see below), and traces of unidentified impurities. ^{1}H NMR (bromobenzene-d_5, −30 °C): δ 6.53 (br, Cp), 5.71 (br, Cp), 5.27 (br, Cp), 4.99 (br, Cp), 2.86 (m, NCH$_2$), 2.65 (m, NCH$_2$), 2.37 (m, CpCH$_2$), 2.21 (m, i-Pr CH), 2.00 (m, CpCH$_2$), 1.84 (s, CMe), 1.16 (s, CMe), 1.03 (s, t-Bu Me), 0.63 (br, i-Pr Me), 0.23 (br, i-Pr Me). ^{13}C{^{1}H} NMR (bromobenzene-d_5, −30 °C): δ 132.9 (C$_{ipso}$ of Cp), 122.3 (CMe), 120.6, 110.2, 104.0, 95.1 (4 × Cp CH), 78.9 (C$_q$ of t-Bu), 58.7, 56.6 (i-Pr CH and NCH$_2$), 31.5 (t-Bu Me), 26.3, 24.2, 23.0, 21.3, 5.0 (2 × i-Pr Me, 2 × CMe and CpCH$_2$). ^{51}V NMR (bromobenzene-d_5, −30 °C): δ −181 ($\Delta\nu_{1/2}$ = 8900).

Generation of [(η^5-C$_5$H$_4$C$_2$H$_4$N(i-Pr)C$_4$Me$_4$)V(N-t-Bu)][MeB-(C$_6$F$_5$)$_3$] (8b). Into the NMR tube used for the generation of **8a**, described above, an additional 2 equiv of 2-butyne was added. The tube, after thawing, was kept at room temperature for 30 min. ^{1}H NMR spectroscopy showed complete conversion to the title compound (with retention of the trace impurities). ^{1}H NMR (bromobenzene-d_5, −30 °C): δ 5.56 (br, Cp), 5.1 (br, Cp), 5.27 (br, Cp), 5.09 (br, Cp), 2.83 (overlapping, i-Pr CH and NCH$_2$), 2.37 (m, NCH$_2$), 2.16 (m, CpCH$_2$), 1.96 (m, CpCH$_2$), 2.16 (s, CMe), 1.39 (s, CMe), 1.35 (s, CMe), 1.31 (s, CMe), 1.03 (s, t-Bu Me), 0.75 (br, i-Pr Me), 0.60 (br, i-Pr Me). ^{13}C{^{1}H} NMR (bromobenzene-d_5, −30 °C): δ 135.1, 133.0, 129.2, 114.0 (C$_{ipso}$ of Cp and 3 × CMe), 113.8, 108.5, 105.4, 97.4 (4 × Cp CH), 77.5 (br, C$_q$ of t-Bu), 66.6 (i-Pr CH), 59.0 (NCH$_2$), 31.1 (t-Bu Me), 26.0 (CpCH$_2$), 30.6, 22.1, 20.8, 20.1, 18.9, 18.4 (2 × i-Pr Me, 4 × CMe). ^{51}V NMR (bromobenzene-d_5, −30 °C): δ −436 ($\Delta\nu_{1/2}$ = 8100).

p-TolNV(N-i-Pr$_2$)Cl$_2$. To a suspension of 2.46 g (9.37 mmol) of p-TolNVCl$_3$ in 50 mL of ether was added 2.85 mL (28.1 mmol) of HN-i-Pr$_2$ in 5 min. The suspension was stirred for 18 h at room temperature, after which all volatiles were removed *in vacuo*.

Pentane (5 mL) was added twice and pumped off to remove residual volatiles. Extraction of the red solid with 50 mL of pentane, followed by concentrating and cooling the extract to −25 °C, afforded 2.09 g (6.39 mmol, 68%) of p-TolNV(N-i-Pr$_2$)Cl$_2$ as a red powder. ^{1}H NMR (benzene-d_6, RT): δ 7.26 (d, 8 Hz, 2H, p-Tol CH), 6.58 (d, 9 Hz, 2H, p-Tol CH), 5.89 (sept 6 Hz, 1H, i-Pr CH), 3.01 (br, 1H, i-Pr CH), 1.88 (s, 3H, p-Tol Me), 1.31 (d, 6 Hz, 6H, i-Pr Me), 0.87 (d, 6 Hz, 6H, i-Pr Me). ^{13}C NMR (benzene-d_6, RT): δ 138.6 (s, p-Tol C$_{ipso}$), 129.2 (d, 160 Hz, p-Tol CH), 126.3 (d, 163,2 p-Tol CH), 61.2 (d, 138 Hz, i-Pr CH), 55.7 (d, 130 Hz, i-Pr CH), 28.5 (q, 128 Hz, i-Pr Me), 21.2 (q, 127, p-Tol Me), 18.8 (q, 127 Hz, i-Pr Me), C$_q$ of p-Tol was not observed. ^{51}V NMR (benzene-d_6, RT): δ −67 (t, $J_{V−N}$ = 96). Anal. Calcd for C$_{13}$H$_{21}$N$_2$VCl: C, 47.73; H, 6.47; N, 8.56. Found: C, 47.27; H, 6.42; N, 8.24.

CpV(N-p-Tol)(N-i-Pr$_2$)Cl. Toluene (30 mL) was condensed onto a mixture of 0.536 g (1.64 mmol) of p-TolNV(N-i-Pr$_2$)Cl$_2$ and 0.146 g (1.66 mmol) of CpNa. The mixture was stirred for 3 h at −40 °C and one night at room temperature, after which all volatiles were removed *in vacuo*. The red solid was extracted with pentane (2 × 30 mL). Concentration of the red solution to 10 mL and slow cooling to −25 °C afforded 0.47 g (1.26 mmol, 77%) of red crystals identified as CpV(N-p-Tol)(N-i-Pr$_2$)Cl. ^{1}H NMR (benzene-d_6, RT): δ 7.19 (d, 8 Hz, 2H, p-Tol CH), 6.78 (d, 8 Hz, 2H, p-Tol CH), 5.83 (s, 5H, Cp), 4.96 (sept, 7 Hz, 1H, i-Pr CH), 3.33 (sept, 6 Hz, 1H, i-Pr CH), 2.03 (s, 3H, p-Tol Me), 1.85 (d, 7 Hz, 3H, i-Pr Me), 1.25 (d, 7 Hz, 3H, i-Pr Me), 1.04 (d, 7 Hz, 3H, i-Pr Me), 0.74 (d, 6 Hz, 3H, i-Pr Me). ^{13}C{^{1}H} NMR (benzene-d_6, RT): δ 136.0 (p-Tol C$_{ipso}$), 129.2 (p-Tol CH), 125.1 (p-Tol CH), 108.6 (Cp), 65.0 (i-Pr CH), 58.5 (i-Pr CH), 31.1 (i-Pr Me), 27.4 (i-Pr Me), 21.2 (p-Tol Me), 19.4 (i-Pr Me), 17.6 (i-Pr Me), C$_q$ of p-Tol was not observed. ^{51}V NMR (benzene-d_6, RT): δ −591 ($\Delta\nu_{1/2}$ = 400). Anal. Calcd for C$_{18}$H$_{26}$N$_2$VCl: C, 60.59; H, 7.35; N, 7.85; Cl, 9.94. Found: C, 60.45; H, 7.44; N, 7.87; Cl, 10.14.

CpV(N-p-Tol)(N-i-Pr$_2$)Me (9). A 1.6 M ether solution of MeLi (2.2 mL, 1.6 M in ether, 3.5 mmol) was added to a cooled (−40 °C) solution of 1.18 g (3.31 mmol) of CpV(N-p-Tol)(N-i-Pr$_2$)Cl in 50 mL of ether. The reaction mixture was stirred for 20 min at −10 °C, resulting in a color change from red to orange, after which the volatiles were removed *in vacuo*. Pentane was added and removed *in vacuo* to remove residual ether. Extraction with 30 mL of cold pentane and removal of the solvent *in vacuo* yielded 0.81 g (2.41 mmol, 73%) of yellow crystals of **9**. During the entire workup procedure, the compound was kept at −10 °C. ^{1}H NMR (THF-d_8, RT): δ 7.00 (d, 9 Hz, 2H, p-Tol CH), 6.94 (d, 9 Hz, 2H, p-Tol CH), 5.72 (s, 5H, Cp), 4.57 (sept, 6 Hz, 1H, i-Pr CH), 3.43 (br, 1H, i-Pr CH), 2.28 (s, 3H, p-Tol Me), 1.62 (d, 6 Hz, 3H, i-Pr Me), 1.40 (d, 7 Hz, 3H, i-Pr Me), 1.08 (d, 7 Hz, 3H, i-Pr Me), 0.92 (d, 7 Hz, 3H, i-Pr Me), 0.4 (s, VMe). ^{13}C{^{1}H} NMR (benzene-d_6, RT): δ 135.2 (C$_{ipso}$ of p-Tol), 130.5 (p-Tol CH), 126.2 (p-Tol CH), 107.6 (Cp), 63.4 (i-Pr CH), 56.4 (i-Pr CH), 33.3 (i-Pr Me), 28.2 (i-Pr Me), 22.2 (p-Tol Me), 21.8 (i-Pr Me), 20.3 (i-Pr Me), V-Me not observed. ^{51}V NMR (benzene-d_6, RT): δ −600 ($\Delta\nu_{1/2}$ = 320). Anal. Calcd for C$_{19}$H$_{29}$N$_2$V: C, 67.84; H, 8.69; N, 8.33; V, 15.14. Found: C, 67.65; H, 9.03; N, 8.27; V, 15.09.

Generation of [CpV(N-p-Tol)(N-i-Pr$_2$)][MeB(C$_6$F$_5$)$_3$] (10). To a solution of 29 mg (0.057 mmol) of B(C$_6$F$_5$)$_3$ in C$_6$D$_5$Br was added slowly a solution of 14 mg (0.042 mmol) of **9** in C$_6$D$_5$Br. The mixture was transferred to an NMR tube. ^{19}F NMR indicated the formation of a small amount of the contact ion-pair (<5%), the ^{1}H NMR data of which will not be described here. ^{1}H NMR (bromobenzene-d_5, RT): δ 6.92 (overlapping doublets, 4H p-Tol CH), 5.72 (s, 5H Cp), 5.11 (sept, 7 Hz, 1H, i-Pr CH), 3.50 (sept, 6 Hz, 1H, i-Pr CH), 2.19 (s, 3H, p-Tol Me), 1.51 (d, 6 Hz, 3H, i-Pr Me), 1.15 (br s., 3H, B-Me), 1.12 (d, 6 Hz, 3H, i-Pr Me), 0.92 (d, 6 Hz, 3H, i-Pr Me), 0.84 (d, 7 Hz, 3H, i-Pr Me). ^{13}C{^{1}H} NMR (bromobenzene-d_5, RT): δ 148.7 (d, J_{CF} = 241 Hz, o-C$_6$F$_5$), 140.0

(C_{ipso} p-Tol), 137.4 (d, J_{CF} = 249 Hz, p-C_6F_5), 136.6 (d, J_{CF} = 246 Hz, m-C_6F_5), 129.6 (p-Tol CH, overlap with solvent), 125.3 (p-Tol CH), 110.1 (Cp), 70.2 (i-Pr CH), 62.2 (i-Pr CH), 32.2 (i-Pr Me), 26.7 (i-Pr Me), 21.2 (i-Pr Me), 20.2 (p-Tol Me), 20.2 (i-Pr Me). B−Me resonance was not observed. ^{19}F NMR (bromobenzene-d_5, RT): δ −132.5 (d, 21 Hz, o-F), −132.8* (o-F), −160.3* (p-F), −164.1 (t, 21 Hz, p-F), −164.7* (m-F), −166.6 (t, 20 Hz, m-F). Resonances marked with an asterisk are from the contact ion-pair (<5%). ^{51}V NMR (bromobenzene-d_5, RT): δ −397 ($\Delta\nu_{1/2}$ = 2500).

Generation of [CpV(N-p-Tol)(N-i-Pr$_2$)][B(C$_6$F$_5$)$_4$] (10′). To a solution of 11 mg (0.034 mmol) of **9** in 0.6 mL of C_6D_5Br was added 31 mg (0.034 mmol) of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. ^{1}H NMR spectroscopy indicated formation **10′** and Ph$_3$CMe. ^{1}H NMR (bomobenzene-d_5, RT): δ 7.16−6.92 (overlapping, 13H, p-Tol and Ph$_3$CMe), 5.72 (s, 5H, Cp), 5.11 (sept, 7 Hz, 1H, i-Pr CH), 3.50 (sept, 7 Hz, 1H, i-Pr CH), 2.20 (s, 3H, p-Tol Me), 2.04 (s, 3H, Ph$_3$CMe Me), 1.50 (d, 6 Hz, 3H, i-Pr Me), 1.12 (d, 7 Hz, 3H, i-Pr Me), 0.91 (d, 6 Hz, 3H, i-Pr Me), 0.84 (d, 7 Hz, 3H, i-Pr Me). ^{13}C{^{1}H} NMR (bromobenzene-d_5, RT): δ 149.2 (C_{ipso} of p-Tol), 148.1 (d, J_{CF} = 238.78 Hz, B(C$_6$F$_5$)$_4$), 140.0 (C_{ipso} of p-Tol), 138.6 (d, J_{CF} = 239 Hz, B(C$_6$F$_5$)$_4$), 136.1 (d, J_{CF} = 239 Hz, B(C$_6$F$_5$)$_4$), 128.7 (p-Tol CH), 127.8 (p-Tol CH), 125.9 (Ph$_3$CMe Ph), 125.3 (Ph$_3$CMe Ph), 110.0 (Cp), 70.3 (i-Pr CH), 62.2 (i-Pr CH), 32.3 (i-Pr Me), 30.5 (i-Pr Me), 26.8 (i-Pr Me), 25.6 (Ph$_3$CMe Me), 21.3 (p-Tol Me), 20.2 (i-Pr Me). ^{19}F NMR (bromobenzene-d_5, RT): δ −132.2 (o-F), −162.4 (p-F), −166.3 (m-F).

Generation of [CpV(N-p-Tol)(N-i-Pr$_2$)(PhNMe$_2$)][B(C$_6$F$_5$)$_4$] (11′). [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (48 mg, 0.059 mmol) was added to a solution of **9** (20 mg, 0.059 mmol) in C_6D_5Br (0.5 mL) at room temperature. Gas evolution was observed. After 20 min the reaction was complete and the solution turned from reddish-brown to intense red. ^{1}H NMR (bromobenzene-d_5, RT): δ 7.2−7.0 (m, 6H, PhNMe$_2$ CH and p-Tol CH, overlap with solvent), 6.89 (d, 8 Hz, 2H, p-Tol CH), 5.34 (5H Cp), 4.88 (sept, 6 Hz, 1H, i-Pr CH), 3.52 (sept, 6 Hz 1H, i-Pr CH), 2.81 (s, 3H, NMe), 2.56 (s, 3H, NMe), 2.25 (s, 3H p-Tol Me), 1.78 (d, 7 Hz, 3H, i-Pr Me), 0.98 (d, 6 Hz, 6H, i-Pr Me), 0.93 (d, 6 Hz, i-Pr Me). ^{13}C{^{1}H} NMR (bromobenzene-d_5, RT): δ 151.5 (C_{ipso} of p-Tol), 148.7 (d, J_{CF} = 241 Hz, B(C$_6$F$_5$)$_4$), 139.8 (C_{ipso} of p-Tol), 135.7 (t, J_{CF} = 238 Hz, B(C$_6$F$_5$)$_4$), 130.0, 127.0, 125.9 (p-Tol CH and Ar of PhNMe$_2$), 119.5 (p-Tol CH), 110.0 (Cp), 68.7 (i-Pr CH), 61.5 (i-Pr CH), 58.5 and 50.0 (PhNMe_2), 32.1 (i-Pr Me), 26.5 (i-Pr Me), 21.4 (p-Tol Me), 21.3 (i-Pr Me), 20.6 (i-Pr Me). Two PhNMe$_2$ arene signals not observed. ^{19}F NMR (bromobenzene-d_5, RT): δ −132.3 (o-F), −162.4 (t, 21 Hz, p-F), −166.3 (m-F).

[CpV(N-p-Tol)(N-i-Pr$_2$)(THF)][BPh$_4$] (12″). THF (5 mL) was added to a mixture of **9** (0.20 g, 0.60 mmol) and [PhNMe$_2$H][BPh$_4$] (0.40 g, 0.91 mmol), resulting in gas evolution. After 3 h the THF was evaporated under reduced pressure, and the crude product was washed with pentane (2 × 3 mL). The reaction mixture was redisolved in 5 mL of THF and warmed to 80 °C. Cooling to room temperature yielded 0.23 g (0.32 mmol, 54%) of orange crystals of the title compound. ^{1}H NMR (THF-d_8, RT): δ 7.34−7.30 (br m, 8H, o-CH BPh$_4$), 7.22 (d, 8 Hz, 2H, p-Tol CH), 7.15 (d, 8 Hz, 2H, p-Tol CH), 6.89 (t, 7 Hz, 8H m-CH BPh$_4$), 6.71 (t, 7 Hz, 4H p-CH BPh$_4$), 6.18 (s, 5H, Cp), 5.38 (sept, 6 Hz, 1H, i-Pr CH), 3.90 (sept, 6 Hz, 1H, i-Pr CH), 2.38 (s, 3H, p-Tol Me), 1.83 (d, 6 Hz, 3H, i-Pr Me), 1.34 (d, 7 Hz, 3H, i-Pr Me), 1.28 (d, 6 Hz, 3H, i-Pr Me), 1.10 (d, 7 Hz, 3H i-Pr Me). ^{13}C{^{1}H} NMR (benzene-d_6, RT): δ 166.4 (q, J_{CB} = 50 Hz, C, PhB), 140.9 (C_{ipso} of p-Tol), 138.3 (CH, PhB), 131.4 (p-Tol CH), 127.5 (p-Tol CH), 126.7 (CH, PhB), 122.9 (CH, PhB), 118.1 (C_{ipso} of p-Tol), 112.2 (Cp), 70.0 (i-Pr CH), 67.4 (THF), 61.0 (i-Pr CH), 31.2 (i-Pr Me), 27.4 (i-Pr Me), 25.6 (THF), 21.9 (i-Pr Me), 20.5 (p-Tol Me), 20.3 (i-Pr Me). Anal. Calcd for $C_{46}H_{54}N_2VBO$: C, 77.45; H, 7.52; N, 3.92. Found: C, 77.58; H, 7.48; N, 3.77.

Reaction of [CpV(N-i-Pr$_2$)(N-p-Tol)][MeB(C$_6$F$_5$)$_3$] with MeC-CMe. Compound **10** was generated by addition of bromobenzene-d_5 (0.5 mL) to a mixture of 6.5 mg (0.019 mmol) of **9** and 9.9 mg (0.019 mmol) of B(C$_6$F$_5$)$_3$. The solution was attached to a vacuum line and frozen in liquid nitrogen. Via a calibrated gas bulb, 4.2 mmHg (9.4 mL, 0.021 mmol) of 2-butyne was added. The tube was thawed and the reaction mixture was analyzed by ^{1}H NMR spectroscopy, revealing formation of a paramagnetic compound. ^{1}H NMR (bromobenzene-d_5, RT): δ 73.3 (br, $\Delta\nu_{1/2}$ = 3500 Hz), 57.4 (br, $\Delta\nu_{1/2}$ = 4000 Hz), 30.4 (br, $\Delta\nu_{1/2}$ = 120 Hz), −15.5 (br, $\Delta\nu_{1/2}$ = 340 Hz). ^{19}F NMR (bromobenzene-d_5, 25 °C): δ −130.0 (br, o-C_6F_5), −163.0 (br, p-C_6F_5), −164.6 (br, m-C_6F_5). The resulting solution was treated with methanol-d_4 and analyzed by GC-MS analysis, revealing the formation of *sec*-butylidene-p-tolylamine-d_n (n = 1−4).

Generation of [CpV(N-p-Tol)(NH-p-Tol)(NH$_2$-p-Tol)][B(C$_6$-F$_5$)$_4$] (13′). In an NMR tube, p-toluidine (0.08 g, 0.77 mmol) was added to a freshly prepared solution of **10′** (0.08 mmol) in 0.6 mL of C_6D_5Br. After 1 h at ambient temperature the solvent and volatiles were removed *in vacuo* and the remaining residue was washed with pentane (2 × 0.5 mL). Removal of residual pentane gave a red oil, which was identified as the title compound. ^{1}H NMR (bromobenzene-d_5, RT): δ 12.77 (br s, 1H, NH), 7.14−7.06 (m, 15H Ph$_3$CMe), 6.87 (d, 7 Hz, free p-toluidine), 6.86 (d, 6 Hz, 4H, p-Tol), 6.76 (d, 6 Hz, 4H p-Tol), 6.41 (d, 6 Hz, free p-toluidine) 5.68 (s, 5H, Cp), 2.17 (br s, 6H, p-Tol Me), 2.13 (s, free p-toluidine), 2.04 (s, 3H CH$_3$, Ph$_3$CMe). ^{13}C{^{1}H} NMR (bromobenzene-d_5, −25 °C): δ 148.9 (C_{ipso} Ph$_3$CMe), 145.5 (C_{ipso} p-Tol), 148.6 (d, J_{CF} = 241.19 Hz, o-C_6F_5), 143.8 (C_{ipso} p-Tol), 143.6 (C_{ipso} p-toluidine), 138.1 (overlapping doublets 243 and 234 Hz, p-C_6F_5 and m-C_6F_5), 131.2 (p-Tol CH, overlapping with the solvent), 129.7 (p-toluidine CH), 129.6 (p-Tol CH, overlap with solvent), 128.8 (p-Tol CH), 128.7 (Ph$_3$CMe CH), 127.8 (C_{ipso} p-toluidine), 127.7 (Ph$_3$CMe CH), 127.2 (C_{ipso} p-Tol), 126.6 (C_{ipso} p-Tol), 126.5 (p-Tol CH, overlapping with solvent), 125.9 (Ph$_3$CMe CH), 125.1 (br, C_{ipso} C_6F_5), 116.4 (p-Tol CH), 115.2 (p-toluidine CH), 110.3 (Cp), 52.5 (Ph$_3$CMe), 30.5 (Ph$_3$CMe), 21.6 (br, p-Tol Me), 20.5 (p-toluidine Me), 20.4 (p-Tol Me). ^{19}F NMR (bromobenzene-d_5, RT): δ −133.4 (br, o-C_6F_5), −163.5 (t, 20 Hz, p-C_6F_5), −166.5 (t, 20 Hz, m-C_6F_5).

Hydroamination Experiment. Bromobenzene-d_5 (0.4 mL) was added to a mixture of 5.1 mg (0.016 mmol) of **9** and 12.0 mg (0.015 mmol) of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. After 2 h the starting material had disappeared and ^{1}H NMR spectroscopy showed clean conversion to **11′**. To the reaction mixture was added 32.1 mg (0.300 mmol) of p-TolNH$_2$, and the reaction mixture was warmed for 2.5 h at 50 °C, resulting in disappearance of the di-isopropylamido cation and formation of free *N,N*-dimethylaniline, di-isopropylamine, and **13′**. Addition of 97 mmHg (56.5 mL, 0.295 mmol) of 2-butyne and warming to 80 °C resulted in partial conversion of the two substrates (24%, as determined by ^{1}H NMR spectroscopy) and formation of *N*-isobutylidene-p-tolylamine over a period of 5 days.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*; Gaussian, Inc.: Pittsburgh, PA, 2003.

No further conversion of the reactants was observed upon prolonged heating at 80 °C for 3 more days.

Computational Method. All calculations were performed using the Gaussian03 package.[24] Geometries for all stationary points and transition states were optimized using the B3LYP level of theory, with the 6-311G basis set for C, H, and N and LANL2DZ for the metal centers. Each calculation was followed by a single point calculation using 6-311G** (C, H, and N) and LANL2DZ (Ti and V) to obtain reliable energies, and a vibrational analysis using 6-311G (C, H, and N) and LANL2DZ (Ti and V) to extract thermal corrections (enthalpy and entropy); free energies mentioned in the text are for the gas phase, 298.15 K, 1 bar. No attempts were made to correct for solvent effects or (in the case of V) for the presence of a counterion.

Supporting Information Available: Crystallographic data for compounds **9** and **12″**, coordinates for optimized structures, and complete overview of the thermodynamic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8003306