Neutral and Cationic Vanadium(III) Alkyl and Allyl Complexes with a Cyclopentadienyl-amine Ancillary Ligand

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The (*N*,*N*-dimethylaminoethyl)cyclopentadienyl vanadium(III) complex $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2\text{-}NMe_2]VCl_2(PMe_3)$ (**1**), in which the pendant amine is coordinated to the metal center, was prepared by the reaction of $VCl_3(PMe_3)_2$ with $Li[C_5H_4(CH_2)_2NMe_2]$ in THF. Reaction of **1** with 2 equiv of MeLi yields $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]VMe_2(PMe_3)_2$ (**2**), in which the amine is released in favor of the binding of a second phosphine. Compound **2** reacts with $[PhNMe_2H]\text{-}[BPh_4]$ to form the ionic complex $\{[\eta^5,\eta^2\text{-}C_5H_4(CH_2)_2N(Me)CH_2]V(PMe_3)_2\}[BPh_4]$ (**3**), in which a methyl group of the pendant NMe_2 functionality is metalated, and 2 equiv of methane. Reaction of **1** with allylmagnesium chloride yields $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]V(\eta^3\text{-}C_3H_5)Cl(PMe_3)$ (**4**), in which the amine is released in favor of the η^3-bonding of the allyl ligand. Methylation of **4** to yield thermally labile $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]V(\eta^3\text{-}C_3H_5)Me(PMe_3)$ (**5**), followed by reaction with $[PhNMe_2H][BPh_4]$, gives protonation exclusively at the methyl group to yield the ionic allyl complex $\{[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(\eta^3\text{-}C_3H_5)(PMe_3)\}[BPh_4]$ (**6**) without concomitant NMe_2 metalation.

Introduction

Catalysts based on the group 5 metal vanadium have found application in the catalytic polymerization of alkenes, in particular in the preparation of ethene/propene and ethene/propene/diene copolymers.[1,2] As is the case for the extensive family of molecular catalysts based on the group 4 metals, this activity is likely to derive from the reactivity of electrophilic, probably cationic, metal alkyl species. It is therefore remarkable that thus far very little attention has been given to the synthesis and characterization of cationic vanadium alkyl complexes.[3] One of the possible reasons for this is that cationic early transition-metal alkyl species tend to be very reactive and/or thermally labile in the absence of (olefinic) substrates and that therefore their characterization is often based on (low temperature) solution NMR spectroscopy. As the most common oxidation states of vanadium in relevant organometallic complexes (2+, 3+, 4+) tend to yield paramagnetic species, this characterization method is distinctly less useful. In particular the complexes of V(III) (d^2, $S = 1$), the oxidation state implicated in many active vanadium-based polymerization catalyst systems,[4] are poorly accessible either by NMR or EPR spectroscopy. In this paper we describe the synthesis and characterization of cationic organometallic species of V(III) bearing an (*N*,*N*-dimethylaminoethyl)cyclopentadienyl ancillary ligand. This type of ligand has previously been found to be very useful in the chemistry of transition-metal organometallics.[5] The hard Lewis basic nature of the pendant amine functionality should have its greatest affinity for the relatively soft Lewis acidic V(III) center in its cationic derivatives, making it potentially very suitable for the stabilization of cationic V(III) alkyl species.

Results and Discussion

Synthesis of $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl_2(PMe_3)$ (1). Reaction of $VCl_3(PMe_3)_2$, generated in situ from $VCl_3(THF)_3$ and 2 equiv of PMe_3 in THF,[6] with 1 equiv of $Li[C_5H_4(CH_2)_2NMe_2]$,[7] followed by extraction with

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(1) For recent relevant reviews, see: (a) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (b) Hagen, H.; Boersma, J.; Van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(2) For recent work involving alkene polymerization by vanadium catalysts, see: (a) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *J. Mol. Catal. A* **2004**, *213*, 141. (b) Colamarco, E.; Milione, S.; Cuomo, C.; Grassi, A. *Macromol. Rapid Commun.* **2004**, *25*, 450. (c) Wang, W.; Yamada, J.; Fujiki, M.; Nomura, K.; *Catal. Commun.* **2003**, *4*, 159. (d) Sato, Y.; Nakayama, Y.; Yasuda, H. *J. Appl. Polym. Sci.* **2003**, *89*, 1659. (e) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583. (f) Milione, S.; Cavallo, G.; Tedesco, C.; Grassi, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1839. (g) Ruther, T.; Cavell, K. J.; Braussaud, N. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4684. (h) Bradley, S.; Camm, K. D.; Furtado, S. J.; Gott, A. L.; McGowan, P. C.; Podesta, T. J.; Thornton-Pett, M. *Organometallics* **2002**, *21*, 3443. (i) Reardon, D.; Guan, J.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R. *Organometallics* **2002**, *21*, 4309. (j) Kotov, V. V.; Avtomonov, E. V.; Sundermeyer, J.; Aitiola, E.; Repo, T.; Lemenovskii, D. A. *J. Organomet. Chem.* **2001**, *640*, 21.

(3) To our knowledge the V(IV) methyl complex $[Cp_2VMe(NCMe)]\text{-}[BPh_4]$ represents the only structurally characterized example: Choukroun, R.; Lorber, C.; Donnadieu, B. *Organometallics* **2002**, *21*, 1124.

(4) See for example: Ma, Y.; Reardon, D.; Gambarotta, S.; Yap, G.; Zahalka, H.; LeMay, C. *Organometallics* **1999**, *18*, 2773, and references therein.

(5) See: (a) Müller, C.; Vos, D.; Jutzi, P. *J. Organomet. Chem.* **2000**, *600*, 127. (b) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663. (c) Jutzi, P.; Siemeling, U *J. Organomet. Chem.* **1995**, *500*, 175, and references therein.

(6) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.

10.1021/om049660t CCC: $27.50

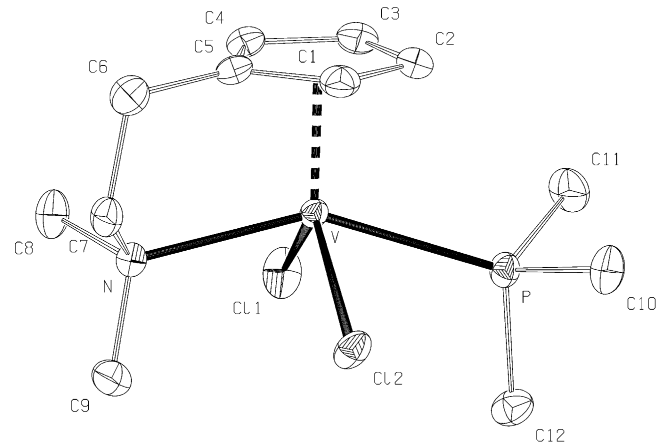

Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 1

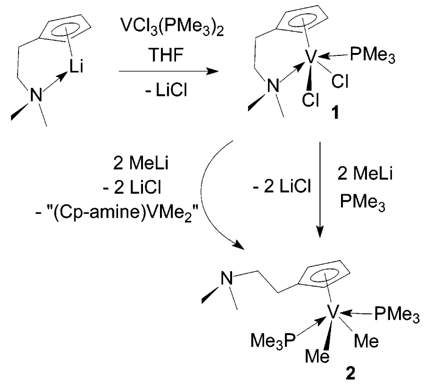

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

V−Cl(1)	2.3719(7)	V−C(1)	2.328(2)
V−Cl(2)	2.3947(7)	V−C(2)	2.306(2)
V−P	2.5145(8)	V−C(3)	2.298(2)
V−N	2.342(2)	V−C(4)	2.288(2)
V−Cg	1.968(1)	V−C(5)	2.299(2)
Cl(1)−V−Cl(2)	117.05(3)	Cl(2)−V−P	77.70(2)
P−V−N	149.40(5)	Cg−V−N	102.81(6)
Cl(1)−V−N	85.39(5)	Cg−V−P	107.64(4)
Cl(2)−V−N	84.55(5)	Cg−V−Cl(1)	122.68(4)
Cl(1)−V−P	80.88(3)	Cg−V−Cl(2)	120.17(4)

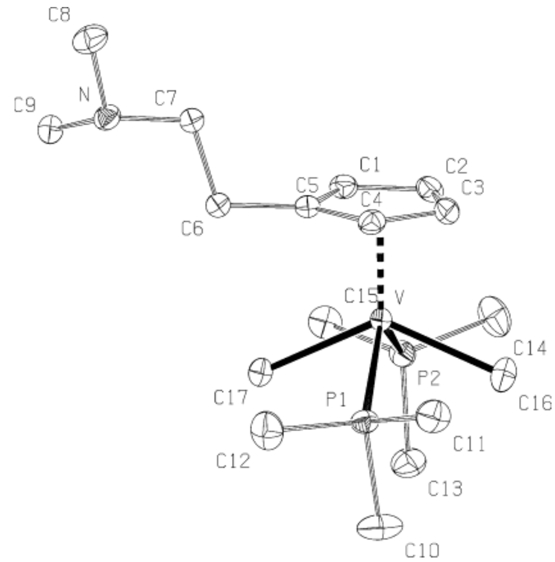

Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

V−P(1)	2.4829(4)	V−C(1)	2.313(1)
V−P(2)	2.4941(4)	V−C(2)	2.304(1)
V−C(16)	2.206(1)	V−C(3)	2.322(1)
V−C(17)	2.222(1)	V−C(4)	2.334(1)
V−Cg	1.9864(6)	V−C(5)	2.346(1)
P(1)−V−P(2)	124.58(1)	P(2)−V−C(17)	78.92(3)
C(16)−V−C(17)	131.05(5)	Cg−V−P(1)	116.64(2)
P(1)−V−C(16)	78.87(4)	Cg−V−P(2)	118.76(2)
P(1)−V−C(17)	79.39(3)	Cg−V−C(16)	113.49(4)
P(2)−V−C(16)	78.39(4)	Cg−V−C(17)	115.46(4)

diethyl ether and recrystallization from warm THF, gave $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl_2(PMe_3)$ (**1**, Scheme 1) as a purple crystalline solid in 83% isolated yield. The compound is paramagnetic (d^2, $S = 1$), as seen from the broad resonances in its ^1H NMR spectrum. Nevertheless, resonances that can be attributed to the PMe, NMe, and CH_2 protons are readily distinguished. A single-crystal X-ray structure determination (Figure 1, pertinent interatomic distances and angles in Table 1) shows that **1** has a four-legged piano-stool structure, with the coordinated amine and the PMe_3 ligand in *trans* geometry. In these respects its structure is comparable to that of $CpVCl_2(PMe_3)_2$[6] and $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2N(H)i\text{Pr}]VCl_2(PMe_3)$.[8] In the latter complex, the N−H bond of the coordinated secondary amine is eclipsed with one of the V−Cl bonds, and the sterically demanding *i*Pr group is pointing downward, minimizing steric hindrance. In **1**, the increased steric hindrance associated with eclipsing the N−C(8) bond with the V−Cl(1) bond results in a smaller Cl(1)−V−Cl(2) angle of 117.05(3)° and a longer V−N bond of 2.342(2) Å (versus 125.53(3)° and 2.290(2) Å in the complex with the secondary amine). The coordination of the NMe_2 functionality in **1** at the expense of the loss of one PMe_3 ligand contrasts with the noncoordination of the tertiary amine functionalities in the complexes $[\eta^5\text{-}C_5H_4(CH_2)_3NMe_2]VCl_2(PMe_3)_2$ and $[\eta^5\text{-}C_5H_4(CH_2)_2N(CH_2)_5]VCl_2(PMe_3)_2$, as observed by McGowan and co-workers.[2h] In the former complex this is likely to be caused by an unfavorable chelate ring size, in the latter possibly by a reduced ability to avoid steric interaction with the chloride ligands.

Synthesis of $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]VMe_2(PMe_3)_2$ (2). The cyclopentadienyl-amine vanadium(III) dichloride complex **1** is a convenient starting material for the synthesis of further derivatives. The reaction of **1** with 2 equiv of MeLi in diethyl ether, followed by extraction with and crystallization from pentane, afforded a red paramagnetic, highly air-sensitive crystalline compound in moderate yield. A single-crystal X-ray structure determination of the product (Figure 2, pertinent interatomic distances and angles in Table 2) revealed that this is the bis(trimethylphosphine) adduct of the vanadium(III) dimethyl derivative, $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]VMe_2(PMe_3)_2$ (**2**), in which the pendant amine functionality is not coordinated to the metal center. As the

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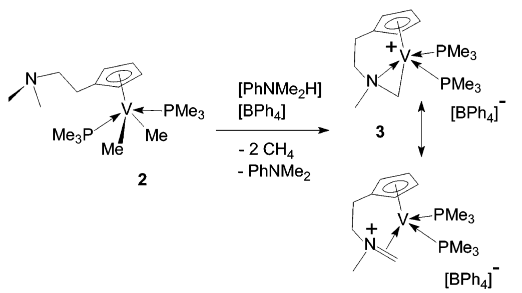
(7) Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287.

(8) Witte, P. T.; Meetsma, A.; Hessen, J. H. *Organometallics* **1999**, *18*, 2944. The detailed structural data can be found in the Supporting Information of the paper.

Scheme 2



starting material **1** contains only one PMe_3 ligand per vanadium, the low isolated yield (41%) of **2** and the presence of a significant amount of dark residue left after extraction are probably associated with redistribution of the phosphine ligands during synthesis, producing **2** in a maximum theoretical yield of 50%. This should be accompanied by the formation of "$[C_5H_4(CH_2)_2NMe_2]VMe_2$", the nature of which is as yet unclear (Scheme 2). Repeating the reaction between **1** and 2 equiv of MeLi with an added equivalent of PMe_3 afforded **2** in a significantly higher isolated yield of 83%. The structure of **2** reveals a normal four-legged piano-stool geometry, with V−P distances of 2.48−2.49 Å that are somewhat shorter than those in related dichloride complexes (2.50−2.52 Å)[2h,6,9] and with V−C(Me) distances of 2.20−2.22 Å. It is likely that the parent compound $CpVMe_2(PMe_3)_2$,[10] of which previous attempts at a crystal structure determination were unsuccessful, has a similar structure. The ^1H NMR spectrum of **2** is rather poorly resolved and does not provide much useful information. Its IR spectrum is informative in the sense that, in addition to the usual absorptions associated, for example, with coordinated PMe_3 (946, 1279, 1297 cm^{-1}), it shows C−H vibration bands at 2764 and 2799 cm^{-1} that are absent in **1** and that are likely to be associated with the NMe ν_{CH} of the noncoordinated $(CH_2)_2NMe_2$ group.[11] As such, these vibrations are useful probes for the behavior of the pendant amine functionality in paramagnetic complexes. The reason the metal center in **2** prefers coordination of a second monodentate phosphine to the pendant amine is perhaps more likely to be electronic rather than steric in nature. Vanadium(III) is not a particularly hard Lewis acid, and the replacement of the two electronegative chlorides in **1** by two methyls in **2** is likely to increase the covalent character of the bonding in the complex. This could lead to a preference for coordination of the soft Lewis base PMe_3 rather than the hard amine, despite its potentially chelating nature.

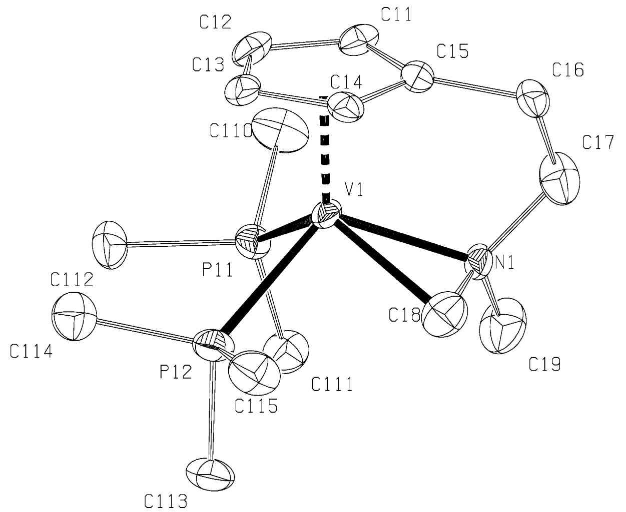


Figure 3. Molecular structure of the cation of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the anion have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Cation of 3

V(1)−P(11)	2.515(1)	N(1)−C(19)	1.487(5)
V(1)−P(12)	2.472(1)	V(1)−C(11)	2.275(3)
V(1)−N(1)	2.072(3)	V(1)−C(12)	2.305(4)
V(1)−C(18)	2.121(4)	V(1)−C(13)	2.313(3)
N(1)−C(17)	1.488(5)	V(1)−C(14)	2.280(3)
N(1)−C(18)	1.387(5)	V(1)−C(15)	2.248(3)
P(11)−V(1)−P(12)	95.29(4)	N(1)−V(1)−C(18)	38.6(1)
P(11)−V(1)−N(1)	98.21(9)	V(1)−N(1)−C(17)	115.2(2)
P(11)−V(1)−C(18)	120.5(1)	V(1)−N(1)−C(18)	72.6(2)
P(12)−V(1)−N(1)	115.32(9)	V(1)−N(1)−C(19)	120.3(3)
P(12)−V(1)−C(18)	81.1(1)	V(1)−C(18)−N(1)	68.8(2)

Reaction of 2 with [PhNMe$_2$H][BPh$_4$]. In an attempt to generate a cationic V(III) monomethyl derivative from the dimethyl complex **2**, this compound was reacted with the Brønsted acid $[PhNMe_2H][BPh_4]$ in THF solvent. An experiment performed using a Toepler pump to determine the amount and nature of the gas evolved in this reaction showed a release of 1.9 equiv of methane per vanadium. This indicates that, in addition to simple protonation, a sequential reaction occurs as well. When the reaction was performed on a preparative scale, a dark red crystalline product was obtained by cooling a solution in THF. A single-crystal X-ray structure determination (Figure 3, pertinent interatomic distances and angles in Table 3) showed that the product is $\{[\eta^5,\eta^2\text{-}C_5H_4(CH_2)_2N(Me)CH_2]V(PMe_3)_2\}[BPh_4]$ (**3**), in which one of the NMe_2 methyl groups has been deprotonated (Scheme 2). The resulting NCH_2 moiety is η^2-bound to the metal center, with short V−C(18) and V−N distances of 2.121(4) and 2.072(3) Å respectively. For comparison, the V−Me distances in **2** are 2.20−2.22 Å and the V−N distance in **1** is 2.342(2) Å. The remarkably short $N-CH_2$ bond of 1.387(5) Å (relative to the other two N−C bonds of 1.48 Å) and the relatively small degree of pyramidalization of the N atom (the sum of the C−N−C angles is 348.2°, compared to 331.1° in the free amine of complex **2**) suggest that the V(I) η^2-iminium resonance state may be important in determining the overall structure of the cation of **3** (Scheme 2). In fact, the geometry of the cation strongly resembles that of the neutral V(I) ethene complex $CpV(\eta^2\text{-}C_2H_4)(PMe_3)_2$.[12] The relatively soft Lewis acidic character of the metal center is shown by the preference

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(10) (a) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946. (b) Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Huffman, J. C.; Jagner, S.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354.

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to bind the two phosphine ligands originally present in **2**, rather than the hard Lewis base THF that is used as a solvent.

The metalation of pendant ligand NMe_2 fragments via σ-bond metathesis with a metal hydride or alkyl functionality is not unprecedented.[13] It is nevertheless remarkable that this reaction is so efficient here, especially in a coordinating solvent like THF that potentially could block the coordination site required for σ-bond metathesis to proceed. When the reaction is performed in THF-d_8 in an NMR tube, no evidence was found for an intermediate with a lifetime at ambient temperature that would allow its observation by ^{1}H NMR. This suggests that, after initial protonation of one of the methyl groups of **2**, the subsequent ligand metalation is a fast reaction. Cyclopentadienyl-amine Ti(III) and Cr(III) systems have been shown to be highly active catalysts for alkene polymerization,[14] but their cationic monoalkyl species have not been extensively investigated. Interestingly, in the tetramethylcyclopentadienyl-amine chromium system, solids of composition {[Cp-amine]CrMe}[A] (A = $MeB(C_6F_5)_3$, $B[C_6H_3(CF_3)_2]_4$) were isolated, but were found to be catalytically inactive.[14c] The observations made here suggest that these ancillary ligands are not necessarily innocent after generation of the active catalyst species.

Cyclopentadienyl-amine Vanadium Allyl Complexes. Reaction of the dichloride **1** with 1 equiv of allylmagnesium chloride in diethyl ether, followed by extraction with pentane, afforded a red oil that separated from the solution upon cooling the concentrated pentane extract to −80 °C. Although this compound is again paramagnetic, showing a set of poorly resolved broad resonances in its ^{1}H NMR spectrum, useful information as to its nature can be obtained from the IR spectrum. An absorption at 1517 cm^{-1} indicates the presence of an η^3-allyl ligand.[15] In addition to the absorptions associated with PMe_3 (955, 1262, 1280 cm^{-1}), C−H absorptions are observed at 2766 and 2778 cm^{-1}, indicative of a noncoordinated NMe_2 group, as was seen for **2**. This suggests that the product may be formulated as $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]V(\eta^3\text{-}C_3H_5)Cl(PMe_3)$ (**4**, Scheme 3), in which a trihapto coordination of the allyl group is preferred over the intramolecular coordination of the pendant amine. On the basis of this formulation, compound **4** was obtained in 47% isolated yield. Subsequently, the allyl chloride complex **4** was reacted with MeLi in order to produce the allyl methyl complex **5** (Scheme 3). The product of this reaction is thermally labile, even at 0 °C. This low thermal stability is comparable to that of the allyl methyl complex $CpV(\eta^3\text{-}C_3H_5)Me(PMe_3)$ reported previously.[10b] Nevertheless, the compound could be precipitated as a brown-red oil in 48% crude yield by cooling a concentrated solution in pentane. This product was used in a subsequent reaction with the Brønsted acid $[PhNMe_2H][BPh_4]$ in THF solvent. Crystallization from THF afforded the ionic complex $\{[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(\eta^3\text{-}C_3H_5)(PMe_3)\}[BPh_4]$ (**6**, Scheme 3) as red crystals in 41% isolated yield. A single-crystal structure determination was complicated by a disorder problem: the complex appears to be present in the lattice in two different orientations, the minor fraction having a site occupancy factor of about 0.22 (as seen from a refinement including two separate metal atom positions). This is too low to allow for a separate refinement of the ligand environment of the minor fraction. Nevertheless, the observed non-hydrogen positions of the major fraction (Figure 4) are consistent with the formulation of **6** as given above. Additional support is obtained by elemental analysis (consistent with the proposed composition) and IR spectroscopy. The latter shows that the C−H absorption bands characteristic of a noncoordinating pendant amine (as in **2** and **4**) are now absent, indicating coordination of the amine, and also that an η^3-allyl absorption is present at 1523 cm^{-1}. Thus it appears that in the reaction of **5** with the Brønsted acid the protonation occurs preferentially at the methyl group. This was corroborated by an experiment on a vacuum line with Toepler pump that showed exclusively the forma-

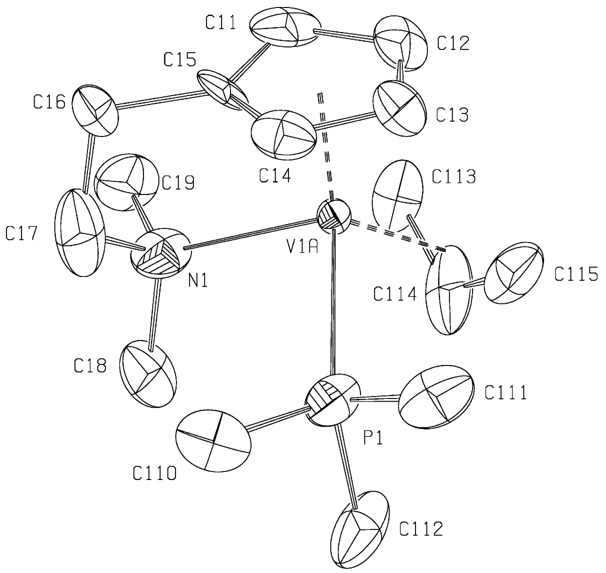
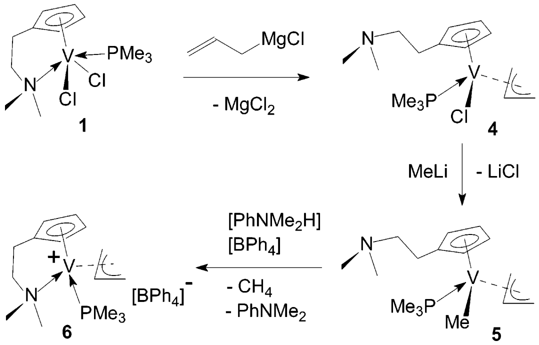


Figure 4. Molecular structure of the cation of **6** (majority orientation in the lattice). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the anion have been omitted for clarity.

Scheme 3



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(13) For an example of methyl metalation of a pendant dimethylaminoethyl functionality on a cyclopentadienyl group, see: Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720.

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tion of methane. After generation of the cationic species, the intramolecular coordination of the pendant amine is preferred over coordination of a THF molecule from the solvent.

Conclusions

From the chemistry of the (*N*,*N*-dimethylaminoethyl)cyclopentadienyl vanadium(III) complexes described here it can be seen that the affinity of the V(III) center for the pendant hard Lewis basic amine is only modest, despite its favorable orientation for chelation. In the neutral derivatives it can compete with PMe_3 only when electronegative chlorides are attached to the metal, and it is displaced by η^3 coordination of an allyl ligand. In the cationic derivatives the affinity for the amine is enhanced, and there it is preferred as ligand over the hard Lewis base THF that is used as the solvent. Metalation of the methyl substitents of the pendant amine upon generation of the monomethyl cation turned out to be remarkably easy, even in a potentially coordinating solvent like THF. This could present complications when the NMe_2 group is used in ancillary ligand systems for catalytic olefin polymerization. Nevertheless, the cationic allyl complex **6** appears to be stable toward ligand metalation at ambient temperature, suggesting that the stability of such cationic species is dependent on a more complex set of variables.

Making use of the (*N*,*N*-dimethylaminoethyl)cyclopentadienyl ligand, it thus proved possible to generate and characterize cationic V(III) hydrocarbyl species successfully. The isolated ionic complexes **3** and **6** described here are themselves not active in catalytic olefin polymerization.[16] Both are 16 valence electron species with an $S = 1$ configuration, rendering them unreactive toward Lewis basic substrates such as ethene without prior phosphine ligand dissociation. Nevertheless, it does show that cationic V(III) hydrocarbyl species can be readily and selectively generated from well-defined bis-hydrocarbyl precursors. Synthetic and catalytic studies on related phosphine-free systems are in progress.

Experimental Section

General Remarks. All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk or glovebox techniques. Pentane (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents (C_6D_6, C_4D_8O; Aldrich) were vacuum transferred from Na/K alloy prior to use. $VCl_3(THF)_3$ was prepared from VCl_3 (Merck) by continuous extraction with THF. PMe_3,[17] $Li[C_5H_4(CH_2)_2NMe_2]$,[7] and $[PhNMe_2H][BPh_4]$[18] were prepared via published procedures. ^1H NMR spectra were recorded on a Varian VXR-300 spectrometer in NMR tubes sealed with a Teflon (Young) stopcock. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrometer from Nujol mulls between KBr disks, unless mentioned otherwise. Elemental analyses were performed by Kolbe Analytical Laboratories, Mülheim a.d. Ruhr, Germany.

Synthesis of $[\eta^5,\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl_2(PMe_3)$ (1). PMe_3 (2 mL, 20.5 mmol) was added at ambient temperature to a suspension of $VCl_3(THF)_3$ (4.20 g, 11.2 mmol) in 25 mL of THF. The resulting brown solution was stirred for 1 h and then cooled to −80 °C, after which $Li[C_5H_4(CH_2)_2NMe_2]$ (1.683 g, 11.76 mmol) was added. The mixture was allowed to warm to ambient temperature, during which the color changed via red to deep purple. After stirring for 72 h the volatiles were removed in vacuo and remaining THF was removed by stirring the mixture twice with 15 mL of diethyl ether, which was subsequently pumped off. The residue was repeatedly extracted with 50 mL of diethyl ether. The solvent was then removed in vacuo and the residue was dissolved in 10 mL of hot THF. Gradually cooling to −60 °C yielded 2.08 g of a purple crystalline solid. Subsequent recrystallization of the material left in the mother liquor from THF/pentane resulted in another portion of 1.03 g of material. The combined yield of the title compound was 3.11 g (9.31 mmol, 83%). IR (Nujol/KBr): 3103 (vw), 1422 (mw), 1330 (w), 1294 (w), 1276 (mw), 1260 (m), 1239 (w), 1208 (w), 1166 (vw), 1114 (w), 1096 (w), 1076 (w), 1060 (mw), 1044 (mw), 1022 (s), 1004 (m), 944 (s), 918 (m), 877 (vw), 825 (m), 807 (s), 779 (mw), 726 (m), 696 (w), 665 (w), 627 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 17 ($\Delta\nu_{1/2} = 710$ Hz, CH_2), 1 ($\Delta\nu_{1/2} = 1070$ Hz, NMe_2), −15 ($\Delta\nu_{1/2} = 1080$ Hz, CH_2), −21 ($\Delta\nu_{1/2} = 1280$ Hz, PMe_3). Anal. Calcd for $C_{12}H_{23}Cl_2NPV$: C, 43.12; H, 6.94; N, 4.19. Found: C, 43.27; H, 6.90; N, 4.54.

Synthesis of $[\eta^5\text{-}C_5H_4(CH_2)_2NMe_2]VMe_2(PMe_3)_2$ (2). (a) Without Added PMe_3. Methyllithium (7.66 mmol, as a 1.6 M solution in diethyl ether) was added to a solution of **1** (1.28 g, 3.83 mmol) in 30 mL of diethyl ether, cooled to −80 °C. After addition, the mixture was allowed to warm to −10 °C, after which it was stirred at this temperature for 2 h. The volatiles were removed in vacuo, and residual ether was removed by stirring the mixture twice with a portion of cold (0 °C) pentane, which was subsequently pumped off. The solid was extracted repeatedly with cold pentane, leaving a dark residue. Concentration and cooling of the extract to −30 °C yielded 0.70 g of the title compound as red crystals (1.90 mmol, 41%).

(b) With Added PMe_3. The procedure was followed as described above (using 0.49 g, 1.47 mmol of **1** in 15 mL of diethyl ether, and 2.92 mmol of MeLi), with the difference that, before adding the MeLi solution, first 0.14 mL (1.47 mmol) of PMe_3 was added to the solution of **1**. Via the same workup procedure, 0.45 g (1.22 mmol, 83%) of red crystalline **2** was obtained. IR (Nujol/KBr): 3088 (w), 2799 (mw), 2764 (w), 1422 (mw), 1297 (mw), 1279 (s), 1214 (w), 1168 (w), 1129 (w), 1097 (w), 1042 (m), 1018 (vw), 946 (vs), 859 (vw), 840 (m), 785 (s), 718 (s), 665 (w) cm^{-1}.^1H NMR (300 MHz, C_6D_6, 20 °C): δ 5 ($\Delta\nu_{1/2} = 380$ Hz, with shoulder, NMe_2+CH_2), −4.5 ($\Delta\nu_{1/2} = 1090$ Hz, PMe_3). Anal. Calcd for $C_{17}H_{38}NP_2V$: C, 55.28; H, 10.37; N, 3.79. Found: C, 55.18; H, 10.43; N, 3.70.

Synthesis of $\{[\eta^5,\eta^2\text{-}C_5H_4(CH_2)_2N(Me)CH_2]V(PMe_3)_2\}[BPh_4]$ (3). A mixture of **2** (0.32 g, 0.87 mmol) and $[PhNMe_2H][BPh_4]$ (0.36 g, 0.85 mmol) was dissolved in 20 mL of THF at 0 °C. After stirring overnight, the solution was concentrated and cooled to −30 °C to yield the title compound (0.36 g, 0.54 mmol, 65%) as dark red crystals. IR (Nujol/KBr): 3048 (w), 3022 (vw), 1579 (mw), 1420 (m), 1326 (vw), 1307 (w), 1287 (m), 1266 (mw), 1247 (vw), 1225 (mw), 1181 (w), 1152 (m), 1120 (m), 1107 (m), 1065 (mw), 1029 (mw) 1016 (w), 945 (s), 862 (vw), 842 (w), 814 (m), 741 (sh), 731 (s), 705 (s), 667 (vw) cm^{-1}. ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 13 ($\Delta\nu_{1/2} = 700$ Hz, PMe_3), 7.3 and 6.8 (BPh_4), −7.5 ($\Delta\nu_{1/2} = 660$ Hz). Anal. Calcd for $C_{39}H_{51}BNP_2V$: C, 71.24; H, 7.82; N, 2.13. Found: C, 71.09; H, 7.71; N, 2.06.

Toepler Pump Experiment of the Reaction of 2 with $[PhNMe_2H][BPh_4]$. On a vacuum line, 3 mL of THF was condensed onto a mixture of **2** (81 mg, 0.22 mmol) and

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[16] Stirring **3** or **6** in toluene in the presence of isobutyl alumoxane impurity scavenger (Al:V = 10:1) at ambient temperature under 5 bar ethene pressure for 30 min did not yield any polyethene.

[17] Prepared according to *Inorg. Synth.* **1989**, *26*, 7, but using MeMgI instead of MeMgBr.

[18] $[PhNMe_2H][BPh_4]$ was prepared using *N*,*N*-dimethylaniline following the procedure reported for $[Et_3NH][BPh_4]$: Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H. *Organometallics* **1992**, *11*, 362.

Table 4. Crystal Data for Compounds 1, 2, 3, and 6

	1	**2**	**3**	**6**
empirical formula	$C_{12}H_{23}Cl_2NPV$	$C_{17}H_{38}NP_2V$	$C_{39}H_{51}BNP_2V$	$C_{39}H_{48}BNPV$
fw	334.12	369.38	657.54	623.54
temperature (K)	180(2)	100(1)	100(1)	100(1)
cryst size (mm)	0.15 × 0.25 × 0.25	0.53 × 0.41 × 0.17	0.14 × 0.12 × 0.09	0.48 × 0.38 × 0.09
space group	$P2_1/n$	$P2_1/c$	$Pna2_1$	$Pna2_1$
a (Å)	10.119(1)	14.1732(8)	23.287(1)	23.038(2)
b (Å)	11.660(1)	9.6636(5)	15.1524(7)	15.084(1)
c (Å)	13.184(1)	16.6389(9)	10.2341(4)	9.8631(8)
β (deg)	98.75(1)	111.624(1)		
V (Å^3)	1537.4(2)	2118.5(2)	3611.1(3)	3427.5(5)
Z	4	4	4	4
d_c (g cm^{-3})	1.444	1.158	1.209	1.208
μ (cm^{-1})	10.8	6.15	3.91	3.63
F(000)	696	800	1400	1328
θ range (deg)	2.34 to 27.47	2.48 to 27.45	2.21 to 24.56	2.22 to 25.02
index range	$-13 \leq h \leq 12$	$-18 \leq h \leq 18$	$-31 \leq h \leq 31$	$-24 \leq h \leq 27$
	$0 \leq k \leq 15$	$-12 \leq k \leq 12$	$-19 \leq k \leq 19$	$-16 \leq k \leq 17$
	$0 \leq l \leq 17$	$-21 \leq l \leq 21$	$-13 \leq l \leq 12$	$-11 \leq l \leq 11$
no. of reflns collected	3833	17844	32392	19082
no. of unique reflns	3502	4793	8792	5951
no. of reflns with $F_o \geq 4\sigma(F_o)$	2814	4335	7193	4043
$wR(F^2)$	0.0942	0.0692	0.1449	0.2127
a, b	0.0581, 0.2038	0.0421, 0.4119	0.0759, 1.66	0.1, 0.0
$R(F)$	0.0355	0.0254	0.0582	0.0855
no. of data/params/restraints	3502/246/0	4793/342/0	8792/574/1	5951/463/1
Flack's x			0.02(3)	0.08(6)
GOF on F^2	1.073	1.027	1.037	1.217
largest diff peak/hole (e Å^{-3})	0.87(8), −0.44(8)	0.40(5), −0.15(5)	1.06(8), −0.58(8)	0.7(1), −0.5(1)

$[PhNMe_2H][BPh_4]$ (97 mg, 0.22 mmol) frozen in liquid nitrogen. The mixture was thawed out and stirred at ambient temperature overnight. Repeated freeze−thaw cycles on the Toepler pump yielded 0.423 mmol of gas, determined by CG to be methane (1.92 equiv per V).

Synthesis of $[\eta^5$-$C_5H_4(CH_2)_2NMe_2]V(\eta^3$-$C_3H_5)Cl(PMe_3)$ (4). Allylmagnesium chloride (1.41 mmol as a 0.80 M solution in diethyl ether) was added dropwise to a solution of **1** (0.47 g, 1.41 mmol) in 10 mL of THF cooled to 0 °C. After stirring at this temperature for 3 h, the volatiles were removed in vacuo and any residual solvent was removed by stirring the residue twice with 10 mL of pentane (0 °C), which was subsequently pumped off. The mixture was repeatedly extracted with 30 mL of pentane. Concentration and cooling of the extract to −80 °C yielded the title compound as a red oil (0.22 g, 0.65 mmol, 47%). IR (neat/KBr): 3080 (m), 2966 (s), 2928 (s), 2907 (s), 2814 (m), 2778 (m), 2766 (m), 1517 (mw), 1416 (s), 1426 (m), 1280 (m), 1262 (m), 1200 (mw), 1096 (w), 1042 (m), 1020 (m), 1003 (w), 955 (s), 921 (w), 861 (mw), 803 (s), 779 (sh), 730 (w) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 27 ($\Delta\nu_{1/2} = 900$ Hz), 2.3 ($\Delta\nu_{1/2} = 30$ Hz, NMe_2), −8.5 ($\Delta\nu_{1/2} = 410$ Hz, PMe_3), −21 ($\Delta\nu_{1/2} = 480$ Hz). Two other broad, relatively small and partially obscured resonances are found around δ 12 and −11 ppm.

Generation of $[\eta^5$-$C_5H_4(CH_2)_2NMe_2]V(\eta^3$-$C_3H_5)Me(PMe_3)$ (5) and Synthesis of $\{[\eta^5,\eta^1$-$C_5H_4(CH_2)_2NMe_2]V(\eta^3$-$C_3H_5)$-$(PMe_3)\}[BPh_4]$ (6). MeLi (0.66 mmol as a 1.6 M solution in diethyl ether) was added dropwise to a solution of **4** (0.22 g, 0.66 mmol) in 5 mL of THF, cooled at −70 °C. After addition, the mixture was allowed to warm to −20 °C and was stirred for 2 h at this temperature. The solvent was removed in vacuo, and residual THF was removed by stirring the mixture twice with 5 mL of cold (0 °C) pentane, which was subsequently pumped off. The solid was repeatedly extracted with 30 mL of pentane. Concentrating the extract to a small volume and cooling to −30 °C precipitated **5** as a brown-red oil, of which 0.10 g (0.32 mmol) was recovered. This was dissolved in 10 mL of THF together with $[PhNMe_2H][BPh_4]$ (131 mg, 0.30 mmol). After stirring overnight, the solution was concentrated and cooled to −30 °C to yield **6** (76 mg, 0.12 mmol, 41% on **5**) as red crystals. IR (Nujol/KBr): 3048 (w), 1579 (w), 1523 (w), 1291 (w), 1261 (m), 1150 (w), 1096 (mw), 1028 (m), 1017 (m), 951 (mw), 874 (w), 812 (m), 743 (sh), 732 (s), 707 (s) cm^{-1}. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.3 and 6.8 (BPh_4), −2.0 ($\Delta\nu_{1/2} = 430$ Hz, PMe_3). No other well-defined resonances could be discerned. Anal. Calcd for $C_{39}H_{49}BNPV$: C, 75.00; H, 7.91; N, 2.24. Found: C, 75.15; H, 7.86; N, 2.29.

Toepler Pump Experiment of the Reaction of 5 with $[PhNMe_2H][BPh_4]$. On a vacuum line, THF (5 mL) was condensed onto a mixture of crude **5** (obtained as described above, 130 mg, 0.41 mmol) and $[PhNMe_2H][BPh_4]$ (163 mg, 0.37 mmol) frozen in liquid nitrogen. The mixture was thawed out and stirred overnight at ambient temperature. Repeated freeze−thaw cycles on the Toepler pump yielded 0.31 mmol of gas, determined by CG to be methane (0.83 equiv per anilinium). No formation of propene was observed.

Structure Determinations. Suitable crystals for single-crystal X-ray diffraction were obtained by cooling solutions of the compounds in THF (**1**, **3**, and **6**) or pentane (**2**). Crystals were mounted on a glass fiber inside a drybox and transferred under inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer (**2**, **3**, and **6**) or an Enraf-Nonius CAD-4F diffractometer (**1**). Intensity data were collected with Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS[19]). The structures were solved by Patterson methods, and extension of the models was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[20] Hydrogen atom coordinates and isotropic thermal parameters were refined freely unless mentioned otherwise. For **3**, the hydrogen atoms on C(17), C(18), and C(19) were included riding on their carrier atoms. The crystals of **6** that could be obtained showed weak scattering power. In the difference Fourier map a peak of 3.7 e Å^{-3} was observed at a distance of about 1 Å of the V atom. This suggests that in the lattice the complex is also present

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[19] Sheldrick, G. M. *SADABS* Version 2, Empirical Absorption Correction Program; University of Göttingen: Germany, 2000.

[20] Beurskens, P. T.; Beurskens, G.; De Gelder, R.; García-Granda, S.; Gould, R. O.Israël, R.; Smits, J. M. M. The *DIRDIF*-99 program system; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.

in a different orientation. The metal center was refined as occupying two positions, with the smallest fraction, V(1b), refining to a sof of 0.22. It was impossible to locate the ligand set belonging to this orientation, resulting in some atoms showing unrealistic displacement parameters. Nevertheless, the connectivity of the non-hydrogen atoms of the major component could be unequivocally established. All refinements and geometry calculations were performed with the program packages SHELXL[21] and PLATON.[22] Crystallographic data and details of the data collections and structure refinements are listed in Table 4.

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Supporting Information Available: Crystallographic data for **1**, **2**, **3**, and **6** including atomic coordinates, full bond distances and bond angles, as well as anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049660T

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[21] Sheldrick, G. M. *SHELXL*-97, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.

[22] Spek, A. L. *PLATON*, Program for the Automated Analysis of Molecular Geometry, Version April 2000; University of Utrecht: The Netherlands, 2000.