Electron-Deficient Vanadium(III) Alkyl and Allyl Complexes with Amidinate Ancillary Ligands[†]

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Vanadium(III) amidinate complexes (amidinate)$_2$VCl and (amidinate)VCl$_2$(THF)$_2$ were prepared for two different amidinate ligands, [PhC(NSiMe$_3$)$_2$]$^-$ and [*t*-BuC(N*i*-Pr)$_2$]$^-$. These served as precursors for amidinate V(III) alkyl and allyl derivatives. The allyl ligand in (amidinate)$_2$V(allyl) is η^3-bound, indicating that the amidinates act as four-electron anionic ligands. The 12-electron alkyl complex [PhC(NSiMe$_3$)$_2$]$_2$VMe catalyzes the slow oligomerization of ethene to linear olefins at 80 °C. The bis-allyl complex [*t*-BuC(N*i*-Pr)$_2$]V(η^3-allyl)$_2$ was prepared and structurally characterized, but its analogue with the [PhC(NSiMe$_3$)$_2$] ligand already decomposes around −30 °C. This shows that the substituent pattern of the amidinate ancillary ligand can strongly affect the stability of organometallic derivatives.

Introduction

The reactivity of the 16-electron vanadium(III) vanadocene alkyls Cp$_2$VR[1] is strongly influenced by the presence of two unpaired valence electrons ($S = 1$ for these d^2 compounds). Interaction with Lewis-basic substrates requires the pairing of these electrons (or an η^5- to η^3-ring slippage of the Cp ligand) in order to free a suitable metal-centered orbital. The unfavorability of this is illustrated by the fact that the allyl ligand in Cp$_2$V(CH$_2$CH═CH$_2$) is η^1-bonded,[1b] whereas in the d^1 Ti(III) analogue this group is an η^3-allyl.[2] Thus reactivity of these V(III) species toward substrates of low polarity (such as olefins) is essentially absent (even (C$_5$Me$_5$)$_2$VH does not react with ethene up to a pressure of 17 bar[1d]). We sought to increase the reactivity of neutral vanadium(III) alkyls toward olefins by using amidinate ([RC(NR′)$_2$]$^-$) ancillary ligands instead of cyclopentadienyls. Amidinates can readily be prepared with a variety of substituents R and R′[3] and can impart substantial steric protection while formally contributing less valence electrons to the bonding than Cp ligands.[4] The one example known of a V(III) hydrocarbyl complex with amidinate ligands, [MesC(N*c*-C$_6$H$_{11}$)$_2$]$_2$VMes (Mes = 2,4,6-Me$_3$C$_6$H$_2$) formed by reaction of VMes$_3$(THF) with dicyclohexyl carbodiimide,[5] suggests that these ligands can be suitable to prepare electron-deficient V(III) hydrocarbyls. In this contribution we have used two different amidinate ligands, the ubiquitous *N*,*N*′-bis(trimethylsilyl)benzamidinate [PhC(NSiMe$_3$)$_2$]$^-$ ([A]$^-$)[3a,b] and the *N*,*N*′-bis(isopropyl)-*tert*-butylimidinate [*t*-BuC(N*i*-Pr)$_2$]$^-$ ([B]$^-$) recently employed by Jordan et al. in organoaluminum chemistry,[3f] to prepare new electron-deficient vanadium(III) alkyl and allyl species. Indeed, the reactivity of the V−C bond in the (amidinate)$_2$V(alkyl) species is enhanced relative to that in Cp$_2$V(alkyl), and [A]$_2$V(alkyl) was found to catalyze the oligomerization of ethene to linear olefins.

Results and Discussion

Synthesis of Amidinate Vanadium Chlorides. Amidinate vanadium(III) chlorides that are suitable precursors for amidinate vanadium(III) hydrocarbyl species were found to be readily accessible from VCl$_3$(THF)$_3$ and the lithium amidinates. The syntheses performed are summarized in Scheme 1.

The reaction of VCl$_3$(THF)$_3$ with 2 equiv of [A]Li(THF) in THF yields [A]$_2$VCl(THF) (**1**) as green crystals in 43% isolated yield after pentane extraction. Heating solid **1** in vacuo at 120 °C for 4 h liberates the coordinated THF to give the known compound [A]$_2$VCl (**2**), described previously by Gambarotta et al.[6] For the amidinate [B] the base-free [B]$_2$VCl (**3**) is directly obtained in 69% yield from the initial pentane extract, suggesting that the metal center in **3** has considerably less affinity toward THF than in **2**.

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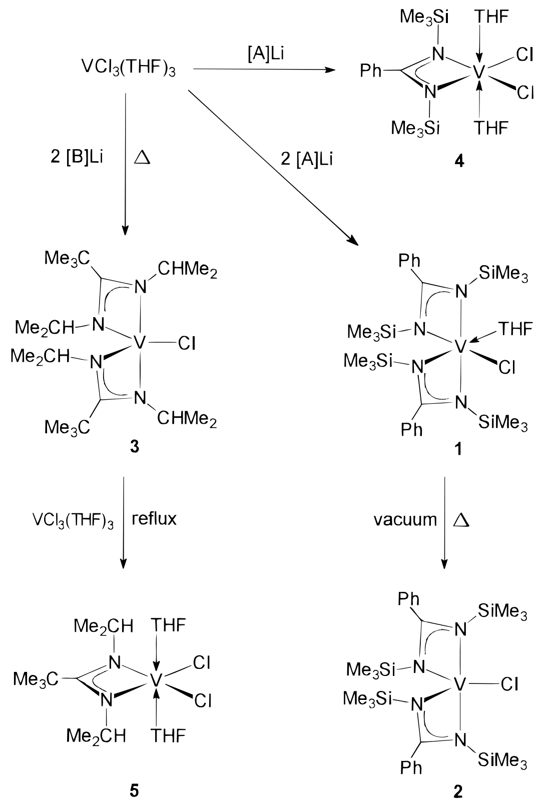
Scheme 1



[A]Li = $[PhC(NSiMe_3)_2]Li·THF$

[B]Li = $[t\text{-}BuC(Ni\text{-}Pr)_2]Li$

Reaction of $VCl_3(THF)_3$ with 1 equiv of [A]Li(THF) in THF produces the green mono-benzamidinate derivative $[A]VCl_2(THF)_2$ (**4**), which was isolated in 58% yield after extraction with diethyl ether. The corresponding red-purple $[B]VCl_2(THF)_2$ (**5**) can be prepared in similar fashion, but is rather difficult to obtain in pure form from this reaction mixture. It is more conveniently prepared (in 83% isolated yield) by a comproportionation reaction between the bis-amidinate complex **3** and $VCl_3(THF)_3$ by refluxing in THF for 1 h. The compound was characterized by single-crystal X-ray diffraction (Figure 1) but loses THF rather easily in the solid state. The accuracy of the structure determination of **5** is diminished somewhat by the presence of disorder in the coordinated THF ligands, but it is clearly shown that the metal center is distorted octahedrally coordinated by two chlorides, two THF molecules, and the two nitrogens of the amidinate ligand. The THF molecules are oriented trans to each other, with the two chlorides in cis position. Pertinent bond lengths and angles are given in Table 1.

The amidinate vanadium(III) chlorides **1**−**5** are paramagnetic, which is expressed by their characteristically broad ^1H NMR spectra with line widths ($\Delta\nu_{1/2}$) up to 550 Hz. The spectra are still quite well resolved at ambient temperature, and for example, for the benzamidinate ligand [A] the individual aromatic protons can readily be identified in the region δ 11.5−7.0 ppm.

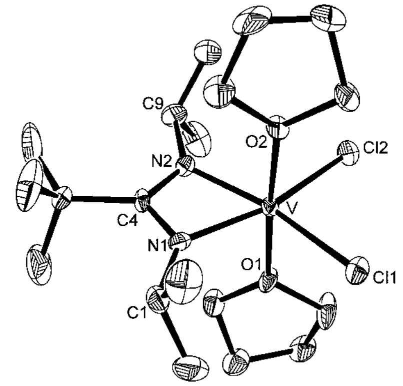


Figure 1. Structure of $[t\text{-}BuC(Ni\text{-}Pr)_2]VCl_2(THF)_2$ (**5**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for $[t\text{-}BuC(Ni\text{-}Pr)_2]VCl_2(THF)_2$ (5)

	Bond Distances (Å)		
V−Cl(1)	2.395(2)	V−N(1)	2.032(5)
V−Cl(2)	2.3796(18)	V−N(2)	2.034(5)
V−O(1)	2.058(4)	N(1)−C(4)	1.323(8)
V−O(2)	2.056(4)	N(2)−C(4)	1.341(8)
	Bond Angles (deg)		
N(1)−V−N(2)	63.46(19)	O(2)−V−N(1)	91.60(19)
Cl(1)−V−Cl(2)	94.00(7)	Cl(1)−V−O(1)	89.59(15)
O(1)−V−O(2)	176.7(2)	Cl(1)−V−O(2)	87.52(15)
Cl(1)−V−N(1)	102.15(15)	V−N(1)−C(1)	134.5(4)
Cl(2)−V−N(2)	100.46(14)	V−N(2)−C(9)	133.7(4)
O(1)−V−N(1)	90.49(19)	N(1)−C(4)−N(2)	106.7(5)

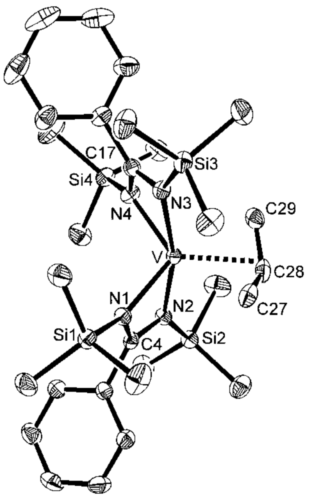


Figure 2. Structure of $[PhC(NSiMe_3)_2]_2V(\eta^3\text{-allyl})$ (**8**, major conformer). Hydrogen atoms are omitted for clarity.

Synthesis of Bis(amidinate) Vanadium Hydrocarbyls. Both base-free bis-amidinate compounds **2** and **3** react readily with alkyl and allyl Grignard reagents to give the corresponding hydrocarbyl compounds $[A]_2VR$ (R = Me, **6**; Et, **7**; allyl, **8**) and $[B]_2VR$ (R = Me, **9**; allyl, **10**), which were isolated as red or orange crystalline solids in typical yields of 60−70% by crystallization from pentane. The compounds again show broad resonances of the amidinate ligand protons in their ^1H NMR spectra, indicating their paramagnetic nature. Resonances due to the metal-bound hydrocarbyl groups could not be identified in the chemical shift range of $\delta \pm 250$ ppm.

IR spectroscopic data suggest an η^3-bonding mode for the allyl ligands (ν_{CCC} = 1518 cm^{-1} (**8**), 1499 cm^{-1} (**10**)), which was corroborated by a crystal structure determination of **8** (Figure 2, bond distances and angles in Table 2). The η^3-allyl ligand in **8** is disordered over two orientations that could be refined separately (0.7:0.3

Table 2. Selected Bond Distances and Angles for the Major Conformer of $[PhC(NSiMe_3)_2]_2V(\eta^3\text{-}C_3H_5)$ (8)

Bond Distances (Å)

V−N(1)	2.051(1)	C(27)−C(28)	1.387(15)
V−N(2)	2.144(1)	C(28)−C(29)	1.375(8)
V−N(3)	2.164(1)	N(1)−C(4)	1.340(2)
V−N(4)	2.051(1)	N(2)−C(4)	1.320(2)
V−C(27)	2.280(17)	N(3)−C(17)	1.315(2)
V−C(28)	2.293(3)	N(4)−C(17)	1.341(2)
V−C(29)	2.334(7)		

Bond Angles (deg)

N(1)−V−N(2)	64.82(5)	N(3)−V−C(28)	108.87(9)
N(3)−V−N(4)	64.57(5)	N(4)−V−C(28)	128.34(10)
C(27)−V−C(29)	64.0(4)	N(1)−V−N(3)	106.26(5)
C(27)−C(28)−C(29)	124.6(8)	N(1)−V−N(4)	109.10(5)
N(1)−V−C(28)	121.07(10)	N(2)−V−N(3)	164.97(5)
N(2)−V−C(28)	86.14(9)	N(2)−V−N(4)	105.76(5)

populations) and that correspond roughly with a rotation around the V-allyl “centroid” axis of nearly 180°. For both orientations the allyl C−C and V−C distances are consistent with a normal, undistorted trihapto-allyl group.[7] The contrast of the allyl binding mode in **8** and **10** with the (16-electron, $S = 1$) bis-cyclopentadienyl analogue Cp_2V(allyl), which has an η^1-allyl group,[1b] illustrates the four-valence electron nature of the amidinate monoanionic ligand. The vanadium center in **8** can be described as a highly distorted octahedron, coordinated by the four amidinate nitrogens and the two allyl methylene carbons.

The bis(amidinate) vanadium hydrocarbyls **6**−**10** are thermally quite robust, including the ethyl derivative **7**, and can be kept at 75−100 °C in C_6D_6 solution in sealed NMR tubes for days without noticeable decomposition. The systems are electron deficient (the alkyl derivatives are formally 12-electron compounds), though not extremely Lewis acidic (e.g., THF adducts of **6** and **9** could not be isolated). The formal electron count of (amidinate)$_2$V(alkyl) and the observation that the allyl ligand in (amidinate)$_2$V(allyl) is η^3-bound suggest that a suitable orbital is available for interaction with unsaturated substrates and that these species should be more reactive toward olefins than the Cp_2V(alkyl) compounds.

Oligomerization of Ethene by (Amidinate)$_2$V-(alkyl). The methyl complex **6** slowly catalyzes the oligomerization of ethene (in a closed NMR tube, C_6D_6 solvent) at 80 °C to give a Flory−Schultz distribution of linear 1- and 2-alkenes with $[C_n]/[C_{n-2}] = 0.60$. The observed product ratio 1-alkene/*Z*-2-alkene/*E*-2-alkene is 1:0.38:0.14. A quantitative analysis (using an internal cyclooctane standard) of the C_{odd} olefins, formed by initial insertion of ethene into the V−Me bond, suggests that the majority of metal centers present are active in the catalysis: on 10 μmol of **6** used in the experiment, 9.3(5) μmol of C_{odd} olefin was observed. The observed catalysis is slow (24 equiv of ethene are consumed over a period close to 24 h, the conversion can conveniently be followed by ^{1}H NMR spectroscopy) but persistent, as after full conversion of the ethene new portions of ethene added are consumed at a similar rate. This corresponds with the observed thermal robustness of the (amidinate)$_2$V(*n*-alkyl) species (vide supra).

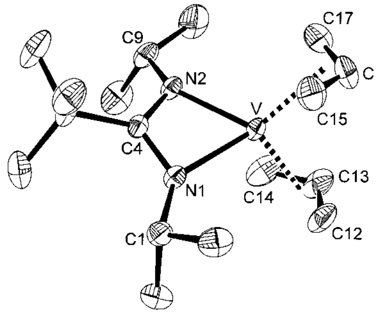


Figure 3. Structure of [*t*-BuC(N*i*-Pr)$_2$]V(η^3-allyl)$_2$ (**11**). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances and Angles for $[t\text{-}BuC(Ni\text{-}Pr)_2]V(\eta^3\text{-}C_3H_5)_2$ (11)

Bond Distances (Å)

V−N(1)	2.0981(19)	V−C(17)	2.340(3)
V−N(2)	2.0124(17)	N(1)−C(4)	1.320(3)
V−C(12)	2.335(3)	N(2)−C(4)	1.358(3)
V−C(13)	2.255(3)	C(12)−C(13)	1.377(4)
V−C(14)	2.233(3)	C(13)−C(14)	1.391(4)
V−C(15)	2.191(3)	C(15)−C(16)	1.378(5)
V−C(16)	2.278(3)	C(16)−C(17)	1.371(5)

Bond Angles (deg)

N(1)−V−N(2)	64.32(7)	V−N(1)−C(1)	137.75(14)
N(1)−V−C(13)	118.44(9)	V−N(2)−C(9)	136.64(16)
N(1)−V−C(16)	136.70(11)	N(1)−C(4)−N(2)	109.66(18)
N(2)−V−C(13)	132.78(9)	C(12)−C(13)−C(14)	122.6(3)
N(2)−V−C(16)	123.42(9)	C(15)−C(16)−C(17)	123.5(3)
C(13)−V−C(16)	87.93(12)		

Synthesis of (Amidinate)V(allyl)$_2$. Reaction of the mono-benzamidinate complex **4** with 2 equiv of allylMgCl in THF at −80 °C initially produces an orange solution that turns deep brown on warming above −40 °C. Workup at 0 °C did not allow isolation of vanadium allyl species from this reaction. In contrast, a similar reaction of [B]$VCl_2(THF)_2$ (**5**) afforded the paramagnetic amidinate bis-allyl complex [B]V(allyl)$_2$ (**11**) as red crystals in 43% yield after extraction with pentane at 0 °C followed by concentration and cooling of the solution to −80 °C. A crystal structure determination confirmed the identification of the compound as [B]V(η^3-allyl)$_2$ (Figure 3, pertinent bond distances and angles in Table 3). The η^3-bonding mode of the allyl ligands was also confirmed by IR spectroscopy ($\nu_{CCC} = 1514$ cm^{-1}).

The structure of **11** can be described as a strongly distorted octahedron, with vanadium coordinated by the N atoms and the allyl CH_2 groups and with the three large angles around V being N(1)−V−C(17) = 150.67(11)°, N(2)−V−C(12) = 150.04(9)°, and C(14)−V−C(15) = 145.36(11)°. The V−C(14/15) distances are about 0.1 Å longer than the V−C(12/17) distances, which is possibly due to a larger trans-influence of the carbon ligands. Thus the η^3-bonding of the allyl ligands in **11** appears to be much more asymmetrical than, for example, in CpM(η^3-allyl)$_2$ (M = Cr, Mo),[8] although this is not reflected in an asymmetry of the C−C distances within the allyl groups.

The 14-electron bis-allyl complex **11** is still thermally quite labile and decomposes in C_6D_6 solution at 20 °C with a half-life of about 6 h (1.5 h at 50 °C), releasing a mixture of propene and 1,5-hexadiene. No well-defined

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(7) The highly distorted allyl moiety observed in [A]$_2$Ti(allyl) could possibly be due to a similar type of disorder. Dick, D. G.; Duchateau, R.; Edema, J. J. H.; Gambarotta, S. *Inorg. Chem.* **1993**, *32*, 1959.

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organovanadium compounds could be isolated from the decomposition. Thus **11** is less stable than the 16-electron complex CpV(allyl)$_2$,[9] but significantly more stable than the [A]V(allyl)$_2$ analogue that appears to decompose below −30 °C in solution (vide supra). Like CpV(allyl)$_2$, **11** is able to catalyze the isomerization of 1-hexene to 2-hexenes, but conversion is limited due to the thermolability of the system.

Conclusions

In conclusion, we have shown that amidinates are suitable ancillary ligands for electron-deficient vanadium(III) hydrocarbyl species. The four-electron nature of the amidinate ligand is evident from the η^3-bonding of the allyl in (amidinate)$_2$V(allyl) and the ability of (amidinate)$_2$V(alkyl) compounds to catalyze the oligomerization of ethene (albeit slowly). The bis(amidinate) vanadium hydrocarbyls are all thermally robust, but for the 14-electron (amidinate)V(η^3-allyl)$_2$ species the stability crucially depends on the nature of the amidinate ligand. Apart from the differences in steric shielding of the metal center, it is likely that the electronic differences between the two amidinate ligands used in this study (as shown, for example, in the significantly different colors of isostructural derivatives of the two ligands) are of importance. This aspect, and its effects on complex reactivity, will be a subject of further study.

Experimental Section

General Considerations. All vanadium compounds described here are highly air and moisture sensitive, and all experiments were performed under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use. Other solvents were distilled from Na/K alloy (diethyl ether, pentane, THF) or Na (toluene) before use. [PhC(NSiMe$_3$)$_2$]Li(THF)[3a,b] and [*t*-Bu(N*i*-Pr)$_2$]Li[3f] were prepared according to literature procedures. Ethene (Union Carbide, 99.99%) was used as received. NMR spectra were run on Varian Gemini 200 and VXR-300 spectrometers. IR spectra were recorded from Nujol mulls between KBr disks on a Mattson-4020 Galaxy FT-IR spectrometer. GC/MS analyses were run on a Hewlett-Packard 6890 GC system with HP-5NS cross-linked 5% PHME siloxane column and HP 5973 mass selective detector. The results were quantified using a GC system equipped with FID detector and cyclooctane as internal standard. Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. Found values are the average of at least two independent determinations.

Synthesis of [PhC(NSiMe$_3$)$_2$]$_2$VCl(THF) (1). [PhC(NSiMe$_3$)$_2$]Li(THF) (4.90 g, 14.3 mmol) was added to a solution of VCl$_3$(THF)$_3$ (2.67 g, 7.2 mmol) in THF (50 mL) at −78 °C. Upon warming to room temperature a green color formed. The volatiles were removed in vacuo after 3 h stirring at room temperature. To remove residual THF, the residue was stirred with 20 mL of ether, which was subsequently pumped off. After extraction of the residue with 40 mL of ether, the resulting solution was concentrated and cooled to −20 °C, affording 2.1 g (3.1 mmol, 43%) of **1** as green bar-shaped plates. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ 10.43 ($\Delta\nu_{1/2} = 20$ Hz, 4H, Ph), 8.84 ($\Delta\nu_{1/2} = 110$ Hz, 4H, Ph), 7.34 ($\Delta\nu_{1/2} = 16$ Hz, 2H, Ph), 2.20 ($\Delta\nu_{1/2} = 19$ Hz, 8H, THF α-H), 0.60 ($\Delta\nu_{1/2} = 150$ Hz, 36H, SiMe$_3$ + 8H, THF β-H). IR (Nujol mull, KBr, cm^{-1}): 1667(w), 1601(w), 1507(m), 1404(m), 1348(s), 1246(s), 1167(w), 1074(w), 1030(w), 1009(w), 999(w), 974(s), 922(w), 841(s), 785(m), 766(s), 727(m), 704(m), 637(w), 615(w), 606(w), 536(m), 513(w), 444(w). Anal. Calcd for C$_{30}$H$_{54}$N$_4$Si$_4$ClOV: C, 52.56; H, 7.94; N, 8.17; V, 7.43; Cl, 5.17. Found: C, 52.24; H, 8.14; N, 7.73; V, 7.18; Cl, 5.32.

Synthesis of [PhC(NSiMe$_3$)$_2$]$_2$VCl (2). Compound **1** (0.50 g, 0.73 mmol) was heated for 4 h in a vacuum (0.01 mbar) at 120 °C. The loss of the THF ligand was accompanied by a color change from green to red. Recrystallization of the red residue from toluene gave **2** as red crystals (0.34 g, 0.55 mmol, 75%). ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ 10.20 ($\Delta\nu_{1/2} = 250$ Hz, 4H, Ph), 9.44 ($\Delta\nu_{1/2} = 49$ Hz, 4H, Ph), 7.43 ($\Delta\nu_{1/2} = 20$ Hz, 2H, Ph), 1.29 ($\Delta\nu_{1/2} = 285$ Hz, 36H, SiMe$_3$). IR (Nujol mull, KBr, cm^{-1}): 1628(w), 1601(w), 1576(w), 1507(s), 1447(s), 1404(m), 1348(s), 1246(s), 1167(m), 1093(w), 1074(w), 1030(w), 1009(m), 999(m), 974(s), 922(m), 841(s), 783(m), 766(s), 727(m), 704(s), 694(m), 637(w), 615(w), 606(w), 536(m), 515(w), 446(w). The IR spectrum corresponds to the one described by Gambarotta *et al.*[6b]

Synthesis of [*t*-BuC(N*i*-Pr)$_2$]$_2$VCl (3). [*t*-BuC(N*i*-Pr)$_2$]Li (4.10 g, 21.6 mmol) and VCl$_3$(THF)$_3$ (4.03 g, 10.8 mmol) in 50 mL of toluene were heated at 50 °C for 0.5 h. A color change from purple to brown-orange was observed. After removal of the solvent, the residue was extracted with pentane (30 mL). Concentration of the solution and cooling to −20 °C yielded 2.92 g of **3**. Concentration of the mother liquor afforded a second crop of 0.43 g (3.35 g, 7.4 mmol, 69% in total). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 25 °C): δ 5.08 ($\Delta\nu_{1/2} = 135$ Hz, 24H, CH(CH_3)$_2$), 3.53 ($\Delta\nu_{1/2} = 540$ Hz, 18H, C(CH$_3$)$_3$). IR (Nujol mull, KBr, cm^{-1}): 1491(m), 1400(m), 1323(s), 1304(s), 1227(w), 1179(s), 1159(m), 1121(m), 1018(m), 966(w), 921(w), 812(w), 721(m), 681(m), 671(m), 503(m). Anal. Calcd for C$_{22}$H$_{46}$N$_4$ClV: C, 58.33; H, 10.24; N, 12.37. Found: C, 58.18; H, 10.23; N, 12.18.

Synthesis of [PhC(NSiMe$_3$)$_2$]VCl$_2$(THF)$_2$ (4). Addition of [PhC(NSiMe$_3$)$_2$]Li(THF) (2.13 g, 6.2 mmol) to a solution of VCl$_3$(THF)$_3$ (2.32 g, 6.2 mmol) in THF (50 mL) afforded a green solution. The solution was stirred for 3 h, after which the solvent was removed in vacuo. The remaining solid was stripped by 20 mL of pentane and subsequently extracted with 40 mL of ether. Concentration and cooling to −20 °C yielded 1.90 g (3.6 mmol, 58%) of **4** as green crystals. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 25 °C): δ 11.30 ($\Delta\nu_{1/2} = 27$ Hz, 2H, Ph), 9.30 ($\Delta\nu_{1/2} = 410$ Hz, 2H, Ph), 6.97 ($\Delta\nu_{1/2} = 21$ Hz, 1H, Ph), 3.55 ($\Delta\nu_{1/2} = 55$ Hz, 8H, THF α-H), 1.47 ($\Delta\nu_{1/2} = 41$ Hz, 8H, THF β-H), −0.60 ($\Delta\nu_{1/2} = 48$ Hz, 18H, SiMe$_3$). IR (Nujol mull, KBr, cm^{-1}): 1674(w), 1643(w), 1589(w), 1568(w), 1499(w), 1443(s), 1393(s), 1343(w), 1246(m), 1181(w), 1076(w), 1037(w), 1020(m), 1003(w), 986(m), 918(w), 862(s), 843(s), 785(m), 762(m), 700(m), 685(w), 521(w), 451(w). Anal. Calcd for C$_{21}$H$_{39}$N$_2$Si$_2$Cl$_2$O$_2$V: C, 47.63; H, 7.42; N, 5.29; V, 9.62. Found: C, 47.07; H, 7.49; N, 5.01; V, 9.36.

Synthesis of [*t*-BuC(N*i*-Pr)$_2$]VCl$_2$(THF)$_2$ (5). A mixture of VCl$_3$(THF)$_3$ (0.78 g, 2.08 mmol) and [*t*-BuC(N*i*-Pr)$_2$]$_2$VCl (0.94 g, 2.08 mmol) in THF (30 mL) was refluxed for 1 h. The red-purple solution was evaporated to dryness, resulting in an intense purple solid, which was stripped three times with pentane (15 mL) and subsequently washed with pentane (3 × 5 mL). Crystallization by diffusion of pentane (25 mL) into a THF (10 mL) solution yielded red-purple bar-shaped crystals of **5** (0.78 g, 1.74 mmol, 83%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 25 °C): δ 6.89 ($\Delta\nu_{1/2} = 110$ Hz, 12H, CH(CH_3)$_2$), 3.34 ($\Delta\nu_{1/2} = 28$ Hz, 8H, THF α-H), 1.52 ($\Delta\nu_{1/2} = 24$ Hz, 8H, THF β-H),1.10 ($\Delta\nu_{1/2} = 345$ Hz, 9H, C(CH$_3$)$_3$). IR (Nujol mull, KBr, cm^{-1}): 1323(s), 1246(w), 1186(s), 1128(m), 1094(w), 1017(s), 957(w), 924(m), 856(w), 719(m), 681(m), 480(m), 459(m), 426(m).

Synthesis of [PhC(NSiMe$_3$)$_2$]$_2$VMe (6). [PhC(NSiMe$_3$)$_2$]$_2$VCl(THF) (0.85 g, 1.24 mmol) was dissolved in THF (25 mL) and cooled to −78 °C. To this intense green solution was added MeMgCl (0.41 mL of a 3 M solution in THF, 1.24 mmol). On

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[9] Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *262*, 157.

warming to room temperature, the color changed to orange-brown. The reaction mixture was stirred for 1 h at room temperature before removing the solvent under reduced pressure. The resulting orange solid was stripped twice with pentane (10 mL) and subsequently extracted with 30 mL of pentane. Concentration and cooling to −80 °C yielded 0.45 g (0.76 mmol, 61%) of **6** as orange crystals. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 10.62 ($\Delta\nu_{1/2} = 145$ Hz, 4H, Ph), 9.44 ($\Delta\nu_{1/2} = 31$ Hz, 4H, Ph), 7.20 ($\Delta\nu_{1/2} = 19$ Hz, 2H, Ph), 1.86 ($\Delta\nu_{1/2} = 205$ Hz, 36H, $SiMe_3$). IR (Nujol mull, KBr, cm^{-1}): 1630(w), 1600(w), 1578(w), 1505(m), 1258(m), 1244(s), 1177(w), 1169(w), 1157(w), 1102(w), 1074(w), 1032(w), 1000(m), 978(s), 916(m), 843(s), 785(m), 758(s), 721(m), 700(m), 683(m), 635(w), 613(w), 604(w), 575(w), 532(m), 442(w). Anal. Calcd for $C_{27}H_{49}N_4Si_4V$: C, 54.69; H, 8.33; N, 9.45. Found: C, 54.55; H, 8.33; N, 9.23.

Synthesis of $[PhC(NSiMe_3)_2]_2VEt$ (7). A suspension of 1.30 g (2.12 mmol) of $[PhC(NSiMe_3)_2]_2VCl$ in 25 mL of ether was cooled to −80 °C. Subsequently, EtMgBr (1.60 mL of a 1.34 M solution in ether, 2.14 mmol) was added. Upon warming to room temperature, the orange reaction mixture was stirred for 30 min, after which the solvent was evaporated. The remaining solid was extracted with 25 mL of pentane. Concentration and cooling of the solution at −80 °C yielded **7** as an orange microcrystalline powder (0.85 g, 1.40 mmol, 66%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C): δ 10.50 ($\Delta\nu_{1/2} = 170$ Hz, 4H, Ph), 9.38 ($\Delta\nu_{1/2} = 34$ Hz, 4H, Ph), 7.50 ($\Delta\nu_{1/2} = 17$ Hz, 2H, Ph), 0.79 ($\Delta\nu_{1/2} = 340$ Hz, 36H, $SiMe_3$). IR (Nujol mull, KBr, cm^{-1}): 1499(m), 1258(m), 1246(s), 1167(w), 1121(w), 1072(w), 1030(w), 1001(m), 980(s), 922(w), 845(s), 785(m), 762(s), 745(m), 725(m), 702(m), 683(m), 615(w), 604(w), 527(m), 442(w).

Synthesis of $[PhC(NSiMe_3)_2]_2V(\eta^3\text{-}C_3H_5)$ (8). To a solution of $[PhC(NSiMe_3)_2]_2VCl$ (0.73 g, 1.19 mmol) in THF (25 mL) was added C_3H_5MgCl (1.7 mL of a 0.72 M solution in THF, 1.22 mmol) at −78 °C. The red solution was stirred for 1 h at room temperature, after which the solvent was removed in vacuo and the solid residue was stripped two times with 10 mL of pentane and subsequently extracted with 30 mL of pentane. The filtrate was concentrated and cooled overnight at −80 °C, yielding 0.50 g (0.81 mmol, 68%) of **8** as red-colored block-shaped crystals. ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 10.26 ($\Delta\nu_{1/2} = 230$ Hz, 4H, Ph), 9.17 ($\Delta\nu_{1/2} = 34$ Hz, 4H, Ph), 8.28 ($\Delta\nu_{1/2} = 19$ Hz, 2H, Ph), 1.14 ($\Delta\nu_{1/2} = 191$ Hz, 36H, $SiMe_3$). IR (Nujol mull, KBr, cm^{-1}): 1664(w), 1630(w), 1518(w), 1499(m), 1310(w), 1260(m), 1242(s), 1169(w), 1163(w), 1099(w), 1072(w), 1028(w), 1003(m), 978(s), 918(w), 841(s), 783(m), 764(s), 725(m), 700(m), 690(m), 635(w), 613(w), 606(w), 515(m), 465(w), 442(w). Anal. Calcd for $C_{29}H_{51}N_4Si_4V$: C, 56.27; H, 8.30; N, 9.05. Found: C, 56.25; H, 8.32; N, 8.93.

Synthesis of $[t\text{-}BuC(Ni\text{-}Pr)_2]_2VMe$ (9). To a THF (15 mL) solution of $[t\text{-}BuC(Ni\text{-}Pr)_2]_2VCl$ (**3**) (0.40 g, 0.88 mmol) was added MeMgCl (0.3 mL of a 3.0 M THF solution, 0.90 mmol) at −80 °C. Upon warming up to room temperature, the color of the solution changed to brown-yellow. The mixture was stirred for 0.5 h. After evaporation of the volatiles the brown-orange residue was stripped with pentane (2 × 10 mL) and subsequently extracted with 25 mL of pentane. Concentration and cooling of the solution at −80 °C afforded **9** as plate-shaped orange crystals (0.13 g, 0.30 mmol, 34%). ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 4.65 ($\Delta\nu_{1/2} = 144$ Hz, 24H, $CH(CH_3)_2$), 3.56 ($\Delta\nu_{1/2} = 475$ Hz, 18H, $C(CH_3)_3$). IR (Nujol mull, KBr, cm^{-1}): 1491(s), 1402(s), 1358(s), 1327(s), 1306(s), 1225(w), 1181(s), 1159(m), 1128(m), 1119(m), 1017(m), 945(w), 926(w), 891(w), 874(w), 837(w), 814(w), 758(w), 719(m), 681(m), 669(m), 573(w), 552(w), 507(m), 425(w). Anal. Calcd for $C_{23}H_{49}N_4V$: C, 63.86; H, 11.42; N, 12.72. Found: C, 63.34; H, 11.35; N, 12.72.

Synthesis of $[t\text{-}BuC(Ni\text{-}Pr)_2]_2V(\eta^3\text{-}C_3H_5)$ (10). AllylMgCl (0.9 mL of a 0.89 M THF solution) was added to a solution of $[t\text{-}BuC(Ni\text{-}Pr)_2]_2VCl$ (**3**) (0.37 g, 0.82 mmol) in THF (20 mL) After removal of the solvent the red residue was extracted with pentane (30 mL). Concentration and cooling to −20 °C gave 0.17 g of **10** as red crystals. Concentration of the mother liquor yielded an additional 0.1 g (0.27 g, 0.59 mmol, 72% in total). ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 4.31 ($\Delta\nu_{1/2} = 110$ Hz 24H, $CH(CH_3)_2$), 2.48 ($\Delta\nu_{1/2} = 450$ Hz, 18H, $C(CH_3)_3$). IR (Nujol mull, KBr, cm^{-1}): 3077(w), 1508(m), 1402(s), 1331(s), 1308(s), 1262(m), 1223(w), 1179(s), 1128(m), 1088(w), 1017(m), 974(w), 928(w), 891(w), 874(w), 801(m), 772(w), 746(m), 721(m), 665(w), 627(w), 550(w), 480(m), 442(w), 424(w). Anal. Calcd for $C_{25}H_{51}N_4V$: C, 65.47; H, 11.21; N, 12.22. Found: C, 65.07; H, 11.23; N, 12.08.

Synthesis of $[t\text{-}BuC(Ni\text{-}Pr)_2]V(\eta^3\text{-}C_3H_5)_2$ (11). To a cold solution of $[t\text{-}BuC(Ni\text{-}Pr)_2]VCl_2(THF)_2$ (**5**) (1.26 g, 3,34 mmol) in 20 mL of THF was added 7.5 mL of a 0.89 M allylMgCl solution in THF. The reaction mixture was slowly warmed to −20 °C, and the red-orange solution was stirred for half an hour. After removing the volatiles in vacuo the residue was stripped with pentane (15 mL) and subsequently extracted with 30 mL of pentane. Concentration of the solution and cooling to −80 °C yielded **11** as red bar-shaped crystals (0.45 g, 1.42 mmol, 43%). ^{1}H NMR (C_6D_6, 200 MHz, 25 °C): δ 5.93 ($\Delta\nu_{1/2} = 57$ Hz, 12H, $CH(CH_3)_2$), 2.00 ($\Delta\nu_{1/2} = 250$ Hz, 9H, $C(CH_3)_3$). IR (Nujol mull, KBr, cm^{-1}): 3077(w), 3063(w), 1630(w), 1514(s), 1489(m), 1398(m), 1360(m), 1325(s), 1310(s), 1262(w), 1246(w), 1181(s), 1130(m), 1117(m), 1082(w), 1018(m), 920(w), 874(w), 828(s), 812(s), 775(m), 756(w), 723(m), 675(w), 662(w), 615(m), 552(w), 500(w), 465(m), 424(w). Anal. Calcd for $C_{17}H_{33}N_2V$: C, 64.53; H, 10.51; N, 8.85. Found: C, 64.00; H, 10.60; N, 8.56.

Ethene Oligomerization by $[PhC(NSiMe_3)_2]_2VMe$ (6). An NMR tube equipped with a Teflon stopcock (which can be attached to a vacuum line) was charged with a solution of 6 mg (0.010 mmol) of $[PhC(NSiMe_3)_2]_2VMe$ in 0.4 mL of benzene-d_6. On a vacuum line, a portion of ethene (0.24 mmol, 24 equiv) was condensed into the NMR tube, after which the stopcock was closed and the tube warmed to 80 °C (**CAUTION**: the initial pressure in the tube is calculated to be about 3 bar). This procedure was repeated four more times with intervals of 24 h (monitoring the reaction by NMR spectroscopy showed full consumption of one portion of the ethene in that period). After full conversion of the last portion of ethene the reaction mixture was quenched with a drop of methanol and filtered over silica. The filtrate was analyzed by GC/MS and quantified using an internal cyclooctane standard (4.1 mg, 0.036 mmol).

Crystal Structure Determinations. Suitable crystals of **5**, **8**, and **11** were mounted on a glass needle in a drybox and transferred under inert atmosphere into the cold nitrogen stream on an Enraf-Nonius CAD4-F diffractometer (monochromated Mo Kα radiation, $\Delta\omega = 0.90 + 0.34 \tan \theta$). Accurate cell parameters and an orientation matrix were determined from the setting angles (SET4[10]) of 22 reflections in the ranges $11.90° < \theta < 18.42°$ (**5**), $17.69° < \theta < 20.78°$ (**8**), and $12.22° < \theta < 18.21°$ (**11**). Reduced cell calculations did not indicate any higher lattice symmetry.[11] Crystal data and details on data collection and refinement are presented in Table 4. Intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by Patterson methods and subsequent difference Fourier techniques (DIRDIF[12]). All calculations were performed on a HP9000/735 computer with the program packages *SHELXL*[13] (least-squares refinements) and *PLATON*[14] (cal-

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Table 4. Crystallographic Data for 5, 8, and 11

	5	**8**	**11**
formula	$C_{19}H_{39}Cl_3N_2O_2V$	$C_{29}H_{51}N_4Si_4V$	$C_{17}H_{33}N_2V$
mol wt	449.38	619.03	316.40
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	12.593(1)	10.900(1)	12.800(1)
b, Å	12.216(1)	11.849(1)	16.380(1)
c, Å	14.945(1)	15.208(1)	18.531(1)
α, deg		112.598(4)	
β, deg	92.85(1)	99.134(5)	109.331(7)
γ, deg		93.208(4)	
V, Å^3	2296.2(3)	1775.3(3)	3666.2(4)
Z	4	2	8
D_{calc}, g cm^{-3}	1.300	1.158	1.146
$F(000)$	960	664	1376
μ(Mo K$\bar{\alpha}$), cm^{-1}	6.8	4.4	5.4
cryst size, mm	0.25 × 0.34 × 0.50	0.25 × 0.30 × 0.45	0.12 × 0.20 × 0.44
	Data Collection		
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ(Mo $K\alpha$), Å	0.710 73	0.710 73	0.710 73
T, K	130	130	130
θ range, deg	1.36, 27.0	1.40, 27.0	1.17, 26.0
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
data set	0:14, 0:14, −19:17	−13:13, −15:13, 0:19	−15:0, 0:20, −21:22
horz, vert aperture, mm	3.2 + tan θ; 4.0	3.2 + tan θ; 4.0	3.2 + tan θ; 4.0
ref reflns, rms dev in %	222, 2.85	−1−14, 0.8	−2−20, 3.3
	2−20, 1.43	021, 1.0	−3−1−2, 2.5
	2−22, 1.44	400, 0.7	−2−21, 1.8
drift correction	1.000−1.040	1.000−1.009	1.000−1.007
X-ray exposure time, h	107.8	107.36	76.9
no. of total data	4516	7990	3894
no. of unique data	4091	7694	3587
no. of data with criterion: ($F_o \geq 4.0\sigma(F_o)$)	2293	6601	2649
$R_{int} = \sum[\lvert F_o^2 - F_o^2(\mathrm{mean})\rvert]/\sum[F_o^2]$	0.046	0.010	0.0302
$R_{sig} = \sum\sigma(F_o^2)/\sum[F_o^2]$	0.105	0.018	0.0354
	Refinement		
no. of rflns ($F_o^2 \geq 0$)	4091	7347	3587
no. of refined params	243	570	313
$wR(F^2)^a$	0.2108	0.0797	0.0930
weighting scheme:^{b} a, b	0.0977, 2.00	0.0486, 0.519	0.0530, 0.0
$R(F)$	0.0803	0.0308	0.0401
goodness of fit	1.047	1.032	0.995
min, max resid density, e/Å^3	−0.54, 1.13(12)	−0.37, 0.40(5)	−0.25, 0.56(5)
$(\Delta/\sigma)_{max}$ final cycle	<0.001	<0.001	<0.001

[a] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 0$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R(F) = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$ for $F_o > 4.0\sigma(F_o)$.

culation of geometric data and the ORTEP illustrations). For **5**, the hydrogen atoms were included in the final refinement riding on their carrier atoms with $U = cU_{equiv}$ of their parent atom, where $c = 1.2$ for the aromatic/non-methyl hydrogen atoms and $c = 1.5$ for the methyl hydrogen atoms and where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl groups were refined as rigid groups, which were allowed to rotate free. Some atoms showed large thermal displacement parameters, suggesting some degree of disorder, which is in line with the weak scattering power of the crystals investigated. For **8**, refinement was complicated by a specific disorder problem: from the solution it was clear that the C(28) atom position (of the allyl ligand) was disordered over two positions, indicating two disordered geometries for the ligand. In the final refinement the minor component of the disordered allyl ligand was restrained to the major component. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, except those belonging to the minor component of the allyl ligand. These hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using hybridization at the C atom as appropriate with $U_{iso} = 1.2U_{equiv}$ of their parent atom and at a multiplicity due to the disorder of the minor fraction. The sof of the major component of the disordered allyl ligand model refined to a value of 0.700(7). For **11**, the positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, of which the coordinates and isotropic thermal displacement parameters were refined.

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Supporting Information Available: Full details of the structure determinations of **5**, **8**, and **11** including lists of atomic coordinates, bond distances and angles, and thermal parameters (18 pages). Ordering information is given on any current masthead page.

OM980431E

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