

# Synthesis and Structure of Amino-Functionalized Cyclopentadienyl Vanadium Complexes and Evaluation of Their Butadiene Polymerization Behavior

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Received February 27, 2002

We have synthesized a number of bis-1,1,-amino-functionalized vanadocenes and vanadocene monochlorides; the bis-1,1,-amino-functionalized vanadocenes represent the first examples of structurally characterized compounds of this type, and the bis-1,1,-amino-functionalized vanadocene monochlorides represent the first examples synthesized and characterized. We report the catalytic behavior of some of the complexes toward butadiene and observe that amino-functionalized cyclopentadienyl vanadium phosphine chloride complexes behave much differently from their nonfunctionalized cyclopentadienyl derivatives.

## Introduction

A cyclopentadienyl ligand with an amino-functionalized side chain may act as a bidentate ligand.<sup>1</sup> This could potentially stabilize electron-deficient metal centers by intramolecular coordination, thus providing a means of isolating and characterizing previously highly reactive intermediates and products.<sup>1</sup> The incorporation of an amino-functionalized group can often have a dramatic effect on the catalytic activity of organometallic complexes. For example, intramolecular coordination to a vacant coordination site is of particular interest for catalytic applications, e.g., polymerization of alkenes. This is illustrated by the following example. Despite the parent compound  $\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3$  being virtually inactive when used with MAO as a cocatalyst, the linked cyclopentadienyl-amino compound  $\text{Ti}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Cl}_3$  was found to exhibit good activity toward ethene and propene polymerization.<sup>2</sup> The study was later extended to include  $\text{Ti}(\eta\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Cl}_3$ <sup>3</sup> and the indenyl complex  $\text{Ti}(\eta\text{-C}_9\text{H}_7\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Cl}_3$ .<sup>4</sup> There are also a number of group IV linked cyclopentadienyl-amido complexes that exhibit catalytic behavior.<sup>5–8</sup>

Pendant arm group V complexes are less common. The vanadium complex  $\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NPr}^i\}\text{Cl}_2$  has been used to catalyze the polymerization of  $\alpha$ -olefins.<sup>9</sup>

Although under identical conditions, the titanium analogue has significantly higher productivity (532 kg PE (mol Ti)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup> cf. 209 kg PE (mol V)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup>). The polymer produced is also of much lower molecular weight for the vanadium system.  $\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NPr}^i\}\text{Cl}_2$  does not polymerize propene, whereas the titanium analogue is an active catalyst.<sup>9</sup> Monocyclopentadienyl complexes of vanadium have also been used to catalyze the hydrogenation and isomerization of alkenes.<sup>10,11</sup> Group VI monocyclopentadienyl chromium compounds with linked amino side chains have been investigated as a novel class of alkene polymerization catalysts.<sup>12,13</sup> These are very promising catalysts for the oligomerization and polymerization of ethene and copolymerization of ethene with 1-hexene.

Other types of catalysis using group V compounds include  $\text{V}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}$ , which has been reported as a catalyst for the polymerization of 1,3-dienes.<sup>14</sup> Unlike other known vanadium systems, which afford *trans* polymer, e.g.,  $\text{V}(\text{acac})_3$ , vanadocene monochloride gave material of a predominantly *cis* configuration.<sup>14</sup> Another type of catalyst is the monocyclopentadienyl complex  $\text{V}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{PET}_3)_2\text{Cl}_2$ , which has also been explored as a catalyst for the polymerization of butadiene.<sup>14</sup> It has considerably higher activity than vanadocene monochloride and also affords *cis* polybutadiene.

With this application in mind, it was decided that the synthesis and exploration of the potential catalytic behavior of a number of V(II), V(III), and V(IV) mono- and bis-cyclopentadienyl amino-functionalized cyclo-

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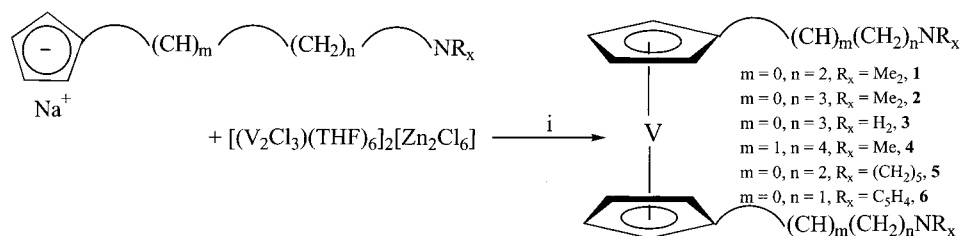
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Scheme 1<sup>a</sup><sup>a</sup> (i) THF.

pentadienyl complexes was of interest. To achieve this, it was necessary to find viable synthetic routes to the syntheses of these types of compounds, and this paper represents a summary of our methodology and results. Preliminary studies investigating the catalytic activity of these novel compounds toward butadiene and for the polymerization of olefins will be presented. We have previously communicated the preparation of the bis-1,1,-amino-functionalized vanadocenes.<sup>15</sup> We have also had success with these types of ligand systems in the isolation of rhodium,<sup>16,17</sup> sodium,<sup>16</sup> yttrium,<sup>18</sup> titanium,<sup>19,20</sup> and iron systems.<sup>15,21,22</sup>

## Results and Discussion

The characterization of vanadocenes is not facile due to the intrinsic properties of the complexes; vanadocenes are extremely air- and moisture-sensitive paramagnetic compounds. The problem is made even more difficult due to the inherent instability associated with amino-functionalized cyclopentadienyl metal complexes compared with the unsubstituted analogues. This has been observed by ourselves<sup>19,20</sup> and others with amino-functionalized Cp<sub>2</sub>TiCl<sub>2</sub> systems.<sup>23</sup> The problem of obtaining good characterizing data becomes even more exasperating since some of the vanadocenes are oils or low-melting solids, thus preventing single-crystal X-ray structure analysis. The reaction between 8 equiv of the amino-substituted cyclopentadienide sodium salts and [(V<sub>2</sub>Cl<sub>3</sub>)(thf)<sub>6</sub>]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>]<sup>24,25</sup> was found to yield the amino-functionalized vanadocenes V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}<sub>2</sub> (**1**), V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>}<sub>2</sub> (**2**), V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>}<sub>2</sub> (**3**), V{C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe<sub>2</sub>}<sub>2</sub> (**4**), V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub> (**5**), and V{η-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>N)}<sub>2</sub> (**6**) as shown in Scheme 1. Compounds **1–3** and **6** are extremely air- and water-

**Table 1. Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of 4 with Estimated Standard Deviations in Parentheses<sup>a</sup>**

V(1)–C(1)	2.3044(13)	C(1)–C(2)	1.434(2)
V(1)–C(2)	2.2734(13)	C(2)–C(3)	1.473(2)
V(1)–C(3)	2.3177(14)	C(3)–C(4)	1.407(2)
V(1)–C(4)	2.333(2)	C(4)–C(5)	1.457(2)
V(1)–C(5)	2.2845(13)	C(5)–C(1)	1.450(2)
V(1)–C(6)	2.2963(12)	C(6)–C(7)	1.449(2)
V(1)–C(7)	2.2726(13)	C(7)–C(8)	1.456(2)
V(1)–C(8)	2.324(2)	C(8)–C(9)	1.406(2)
V(1)–C(9)	2.324(2)	C(9)–C(10)	1.470(2)
V(1)–C(10)	2.2852(13)	C(10)–C(6)	1.429(2)
		average C–C	1.44
		V(1)–Cp(cent)(1)	1.95
		V(1)–Cp(cent)(2)	1.95
C(1)–C(2)–C(3)	109.92(13)	Cp(cent)(1)–V(1)–Cp(cent)(2)	179
C(2)–C(3)–C(4)	107.80(13)	C(11)–C(1)–Cp(cent)(1)	177
C(3)–C(4)–C(5)	106.95(13)	C(61)–C(6)–Cp(cent)(2)	175
C(4)–C(5)–C(1)	110.69(13)	average C–C–C	108
C(5)–C(1)–C(2)	104.63(12)		
C(6)–C(7)–C(8)	110.53(14)		
C(7)–C(8)–C(9)	106.75(13)		
C(8)–C(9)–C(10)	108.13(13)		
C(9)–C(10)–C(6)	109.59(13)		
C(10)–C(6)–C(7)	104.99(12)		

<sup>a</sup> Cp(cent)(1) and Cp(cent)(2) denote centroids of the rings C(1)–C(5) and C(6)–C(10), respectively.

sensitive bright purple oils and crystalline solids, and the oils proved particularly difficult to handle.

Evidence for the difficulties in synthesis and characterization for vanadocenes is exemplified by the synthesis of V{η-C<sub>5</sub>H<sub>4</sub>R}<sub>2</sub> (R = Me, Pr<sup>i</sup>), which are oils for which there is no characterization data.<sup>26</sup> The oil V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}<sub>2</sub> was obtained by the in situ reduction of VCl<sub>3</sub>·3thf with LiAlH<sub>4</sub>.<sup>27</sup> We found this method difficult to repeat. Steric modifications of the pendant arm induce crystallinity to the sample. This paper represents the first examples of structurally characterized amino-substituted bis-cyclopentadienyl vanadium systems. Recrystallization of **4** from diethyl ether afforded crystals suitable for X-ray structure analysis (Table 1 shows selected bond lengths and selected bond angles). The molecular structure of V{η-C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe<sub>2</sub>}<sub>2</sub> (Figure 1) revealed it to be a metallocene, with a co-planar arrangement of cyclopentadienyl ligands. The structure of **4** is isomorphous with that of the ferrocene analogue Fe{η-C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe<sub>2</sub>}<sub>2</sub>.<sup>15</sup>

The molecular structure of **4** shows a C<sub>5</sub> semi-eclipsed ring configuration with an average C–M–M–C dihedral angle of 19°. The amino-functionalized pendant arms are well separated by ~165°, probably to minimize

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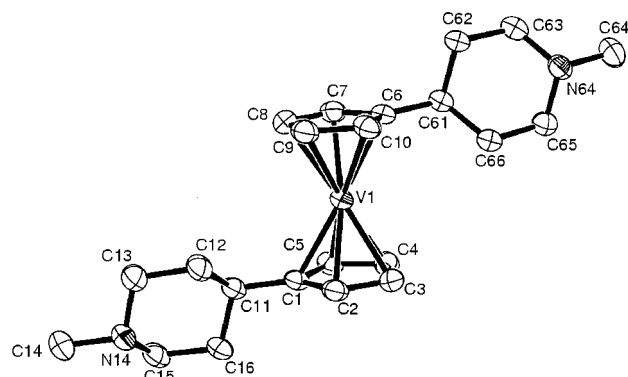
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**Figure 1.** Molecular structure of compound **4**, with 50% probability thermal ellipsoids.

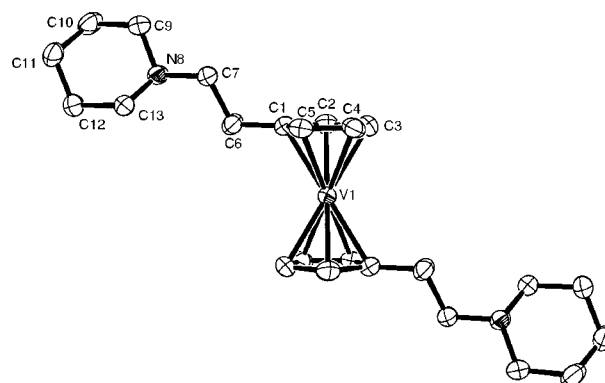
**Table 2. Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of **5** with Estimated Standard Deviations in Parentheses<sup>a</sup>**

V(1)–C(1)	2.281(3)	C(1)–C(2)	1.415(4)
V(1)–C(2)	2.265(3)	C(2)–C(3)	1.424(4)
V(1)–C(3)	2.255(3)	C(3)–C(4)	1.399(5)
V(1)–C(4)	2.273(3)	C(4)–C(5)	1.409(4)
V(1)–C(5)	2.271(3)	C(5)–C(1)	1.413(4)
		V(1)–Cp(cent)(1)	1.93
		average C–C	1.41
C(1)–C(2)–C(3)	108.3(3)	Cp(cent)–V(1)–Cp(cent)	180
C(2)–C(3)–C(4)	107.9(3)	C(6)–C(1)–Cp(cent)	178.5
C(3)–C(4)–C(5)	107.8(3)		
C(4)–C(5)–C(1)	109.2(3)		
C(5)–C(1)–C(2)	106.7(3)		

<sup>a</sup> Cp(cent)(1) and Cp(cent)(2) denote centroids of the rings C(1)–C(5) and C(12)–C(16), respectively.

steric crowding, and as expected, the presence of sterically demanding piperidinyl side chains results in lengthening of the V–Cp<sub>cent</sub> bond distance (1.95 Å compared to 1.91 Å for vanadocene<sup>28</sup> and 1.96 Å for decaphenyl vanadocene<sup>29</sup>).

A noteworthy feature of the structure is the relatively short bond length of C(3)–C(4) coupled with a relative lengthening of V(2)–C(3), with respect to the other V–C bonds of the C(1)–C(5) ring. This could indicate a contribution from olefinic bonding within the cyclopentadienyl ring C(3)–C(4) and  $\eta^3$  allylic bonding to the vanadium center from C(1), C(2), and C(5). The effect is mirrored in the other C<sub>5</sub> ring with olefinic bonding between C(8)–C(9) and  $\eta^3$  allylic bonding to the vanadium center from C(6), C(7), and C(10). Recrystallization of V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub> from diethyl ether afforded crystals of a quality suitable for X-ray structure analysis. The molecular structure of **5** is shown in Figure 2 and reveals a coplanar ligand arrangement similar to that seen for **4**. **5** possesses a crystallographic center of symmetry and thus a staggered conformation of C<sub>5</sub> rings (Table 2 shows selected bond lengths and selected bond angles). V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>, like compound **4**, is isomorphous with the corresponding ferrocene Fe{ $\eta$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>.<sup>22</sup> The molecular structure of **5** shows a Cp<sub>cent</sub>–V–Cp<sub>cent</sub> angle of 180° and maximum separation of the pendant arms (180°), consistent with



**Figure 2.** Molecular structure of compound **5**, with 50% probability thermal ellipsoids.

a crystallographic center of symmetry. The V–Cp<sub>cent</sub> bond lengths are slightly elongated with respect to the unsubstituted vanadocene (1.925 vs 1.915 Å), but to a lesser extent than **4**, which helps explain the fact that there is no evidence of apparent ring slippage.

The first reported bis-cyclopentadienyl vanadium(III) chloride was synthesized by the addition of 3 equiv of NaC<sub>5</sub>H<sub>5</sub> to VCl<sub>4</sub>.<sup>30</sup> The product was prepared in 23% yield and was characterized by elemental analysis. The addition of organic halides, e.g., benzyl chloride, to vanadocene also yields bis-cyclopentadienyl vanadium(III) chloride.<sup>31</sup> The yield of vanadocene monochloride was increased to >70% by conproportionation of V( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and V( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub><sup>31</sup> and then to >90% by reaction of VCl<sub>3</sub> with TiC<sub>5</sub>H<sub>5</sub>. More recently PbCl<sub>2</sub> has been used to generate V( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl and V( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl when reacted with V( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> or V( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, respectively. Other oxidizing agents used to prepare V( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl include HCl<sup>32</sup> and benzyl chloride.<sup>33</sup> Ring-alkylated vanadocene monochlorides have also been prepared by addition of PCl<sub>3</sub> to the appropriate vanadocene; this method has been used to prepare Me-, Pr<sup>*i*</sup>-, and Bu<sup>*t*</sup>-substituted cyclopentadienyl complexes.<sup>26</sup> PCl<sub>3</sub> may also be used to synthesize vanadocene dichloride<sup>34</sup> and ring-alkylated V derivatives as shown.<sup>26</sup> Oxidation of V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe}<sub>2</sub> (**4**) and V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub> (**5**) with PCl<sub>3</sub> afforded the corresponding vanadocene monochlorides (Scheme 2). Complexes **4** and **5** were used, since they are crystalline solids that can be handled more easily than **1–3** and **6**. V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe}<sub>2</sub>Cl (**7**) and V{ $\eta$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>Cl (**8**) were synthesized by the addition of 1 equiv of PCl<sub>3</sub> to **4** and **5** at room temperature, with stirring in a minimal volume of petroleum ether (bp 40–60 °C). On addition of PCl<sub>3</sub> to the violet vanadocene solution, a green precipitate was observed immediately with concomitant formation of a bright blue solution. Recrystallization from petroleum ether (bp 40–60 °C) afforded compounds **7** and **8** as blue crystalline platelets in 60% yield. The products were characterized by X-ray crystal structure analysis, elemental analysis, and <sup>1</sup>H NMR spectroscopy.

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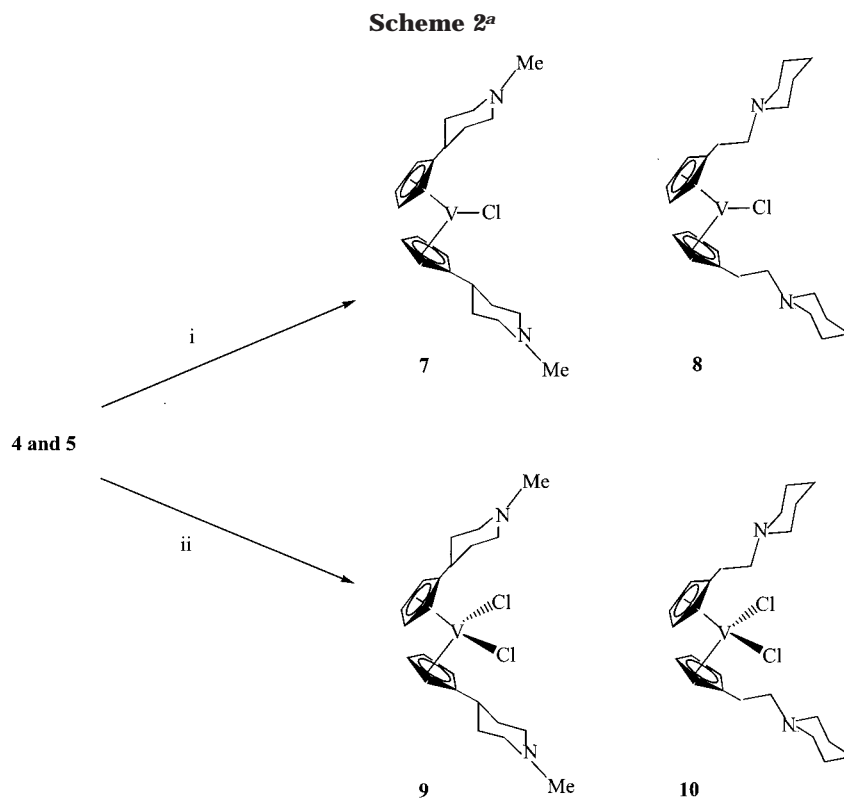
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<sup>a</sup> (i) 1 equiv  $\text{PCl}_3$ , (ii) excess  $\text{PCl}_3$ .

These are the first examples of bis-cyclopentadienyl vanadium(III) chlorides with an amino-functionalized side chain.

The  $^1\text{H}$  NMR spectra (300.1 MHz) of **7** ( $\text{C}_6\text{D}_6$ ) and **8** ( $\text{CD}_3\text{CN}$ ) were recorded at room temperature. As would be expected for the paramagnetic complexes **7** and **8**, the cyclopentadienyl ring protons are shifted downfield to give two very broad signals at  $\delta \sim 150$  and  $\sim 130$ . A second peak at  $\delta \sim 40$  was assigned to the protons closest to the  $\text{C}_5$  rings. Both the downfield shift and broadening of the resonances lessen on moving away from the vanadium center. The remaining resonances were assigned on this basis as well as with reference to their integral values and the  $^1\text{H}$  NMR spectrum of the parent sodium salts  $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}$  and  $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ . The molecular structures of **7** and **8** revealed a distorted trigonal planar geometry about the V atom and are shown in Figures 3a and 3b, respectively. Selected bond lengths and angles are shown in Tables 3 and 4. Contrastingly **7** exhibits an eclipsed conformation of the cyclopentadienyl rings, whereas **8** shows a staggered cyclopentadienyl ring configuration and possesses a crystallographic center of symmetry. The pendant arms are also dissimilarly placed with respect to one another. It can be seen that in **7**, where the cyclopentadienyl rings are almost eclipsed, the pendant arms are well separated, whereas in **8** the pendant arms are positioned almost above one another, directly above and below the chlorine atom, which is arguably a less effective conformer in minimizing steric crowding. One possible explanation for this is the presence of close  $\text{H}\cdots\text{Cl}$  contacts affording intramolecular  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonding in both complexes. Compound **7** features  $\text{H}\cdots\text{Cl}$  distances of 2.66 and 2.83 Å, whereas the closest  $\text{H}\cdots\text{Cl}$  distances in **8** are 2.61 Å (Figure 4a and 4b).

**Table 3. Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of **9** with Estimated Standard Deviations in Parentheses<sup>a</sup>**

V–C(1)	2.350(3)	C(1)–C(2)	1.425(4)
V–C(2)	2.289(3)	C(2)–C(3)	1.398(5)
V–C(3)	2.265(3)	C(3)–C(4)	1.415(5)
V–C(4)	2.276(3)	C(4)–C(5)	1.413(5)
V–C(5)	2.315(3)	C(1)–C(5)	1.408(4)
V–C(12)	2.336(3)	C(12)–C(13)	1.410(4)
V–C(13)	2.301(3)	C(13)–C(14)	1.420(5)
V–C(14)	2.276(3)	C(14)–C(15)	1.400(5)
V–C(15)	2.289(3)	C(15)–C(16)	1.405(5)
V–C(16)	2.302(3)	C(12)–C(16)	1.427(4)
V–Cp(cent)(1)	1.963		
V–Cp(cent)(2)	1.961		
V–Cl(1)	2.3840(10)		
C(1)–C(2)–C(3)	109.0(3)	Cp(cent)(1)–V(1)–Cl(1)	108.9
C(2)–C(3)–C(4)	107.6(3)	Cp(cent)(2)–V(1)–Cl(1)	108.2
C(3)–C(4)–C(5)	107.9(3)	Cp(cent)(1)–V(1)–Cp(cent)(2)	142.9
C(4)–C(5)–C(1)	108.6(3)		
C(5)–C(1)–C(2)	106.8(3)		
C(12)–C(13)–C(15)	108.2(3)		
C(13)–C(14)–C(15)	108.5(3)		
C(14)–C(15)–C(16)	107.7(3)		
C(15)–C(16)–C(12)	108.9(3)		
C(16)–C(12)–C(13)	106.7(3)		

<sup>a</sup> Cp(cent)(1) and Cp(cent)(2) denote centroids of the rings C(1)–C(5) and C(12)–C(16), respectively.

These interatomic distances are significantly shorter than the combined van der Waals radii of hydrogen and chlorine (1.20 and 1.75 Å, respectively).<sup>35</sup>

In **7**, the two pendant arms are positioned as far apart as possible without breaking the  $\text{H}\cdots\text{Cl}$  contacts (2.66 and 2.83 Å). Close  $\text{H}\cdots\text{Cl}$  contacts in **8** are facilitated by the conformation of the pendant arms, directly above and below the chlorine atom. **7** cannot, however, achieve

**Table 4. Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of 10 with Estimated Standard Deviations in Parentheses<sup>a</sup>**

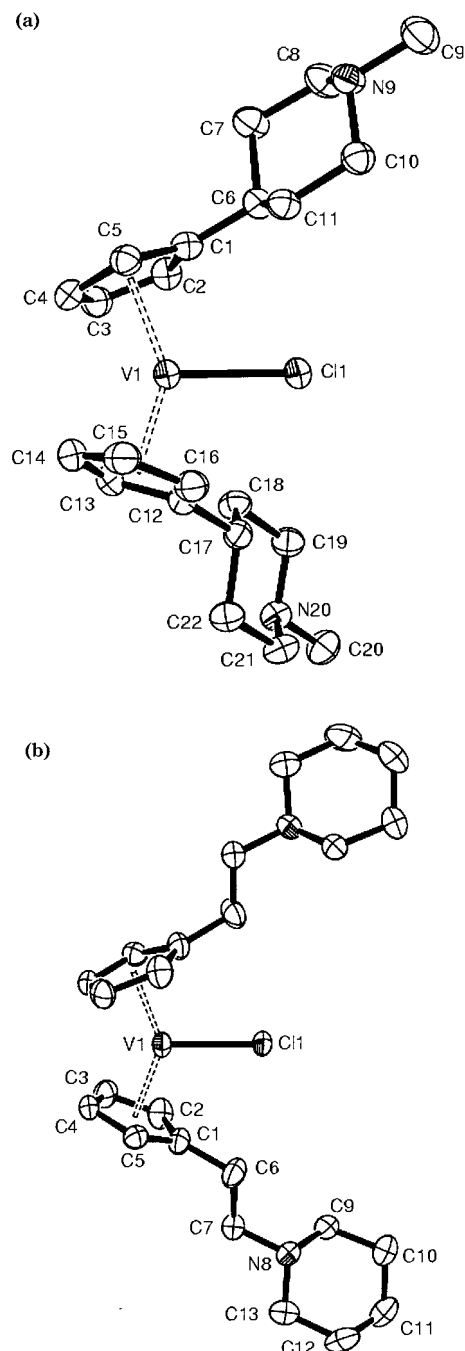
V–C(1)	2.390(3)	V–Cp(cent)(1)	1.978
V–C(2)	2.322(3)	V–Cl(1)	2.390(3)
V–C(3)	2.262(3)		
V–C(4)	2.260(3)		
V–C(5)	2.328(3)		
C(1)–C(2)	1.414(5)		
C(2)–C(3)	1.406(5)		
C(3)–C(4)	1.411(5)		
C(4)–C(5)	1.419(5)		
C(1)–C(5)	1.404(5)		
C(1)–C(2)–C(3)	108.5(3)	Cp(cent)(1)–V(1)–Cl(1)	109.6
C(2)–C(2)–C(4)	108.0(3)	Cp(cent)(1)–V(1)–Cp(cent)(1)'	140.9
C(3)–C(4)–C(5)	107.5(3)		
C(1)–C(5)–C(4)	108.4(3)		
C(5)–C(1)–C(2)	107.5(3)		

<sup>a</sup> Cp(cent)(1) denotes the centroid of the ring C(1)–C(5).

this “above and below” configuration, since in the absence of the ethyl bridge between the cyclopentadienyl and piperidinyl rings the two carbons of the arm would be forced into the chlorine atom.

The existence of both inter- and intramolecular hydrogen bonding of C–H donor units where chlorine acts as the acceptor atom has been reported previously.<sup>36,37</sup> It is difficult to compare this bonding situation with vanadocene monochlorides due to the few examples of such compounds. But, comparisons can be made with vanadocene dichlorides containing monoalkylated cyclopentadienyl ligands that have the substituents directly above and below the chlorine atoms when the alkyl group is Pr<sup>i</sup> (cf. **8**), whereas in the more rigid and sterically demanding Bu<sup>t</sup>-substituted complex the conformation of the cyclopentadienyl rings enables the alkyl groups to move farther apart.<sup>26</sup> The H···Cl contacts for these complexes are 2.84 and 2.70 Å, respectively.<sup>26</sup>

Bis-cyclopentadienyl vanadium(IV) chlorides with amino-functionalized side chains have not been previously reported. To prepare the amino-substituted vanadocene dichlorides **9** and **10** (Scheme 2), the corresponding vanadocenes **4** and **5** were dissolved in THF and 2 equiv of PCl<sub>3</sub> was added via syringe at room temperature. This afforded a green precipitate, with a blue solution, presumed to be the corresponding vanadocene(III) monochloride. The blue color dissipated very quickly, forming a green solid in high yield (80–90%). The vanadocene dichloride derivatives V{η-C<sub>5</sub>H<sub>4</sub>CH(CH<sub>2</sub>)<sub>4</sub>NMe<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub> (**9**) and V{η-C<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>}<sub>2</sub>Cl<sub>2</sub> (**10**) were characterized by EPR spectroscopy. For each complex the spectra collected at room temperature in CHCl<sub>3</sub> showed the expected eight-line nuclear hyperfine coupling, characteristic of the d<sup>1</sup> vanadium nucleus where *I* = 7/2. Furthermore, the signals for **9** and **10** were centered at *g* = 2.06. Each showed an average *a* value of 73.3 G. This is typical for bis-cyclopentadienyl vanadium(II) chlorides and is consistent with values of *g* = 2.00 and *a* = 75 G measured for V(η-C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>Cl<sub>2</sub> (R = Me, Pr<sup>i</sup>, Bu<sup>t</sup>).<sup>26</sup> There were solubility problems for these compounds to the extent that it was difficult to obtain consistent microanalyses or single crystals.



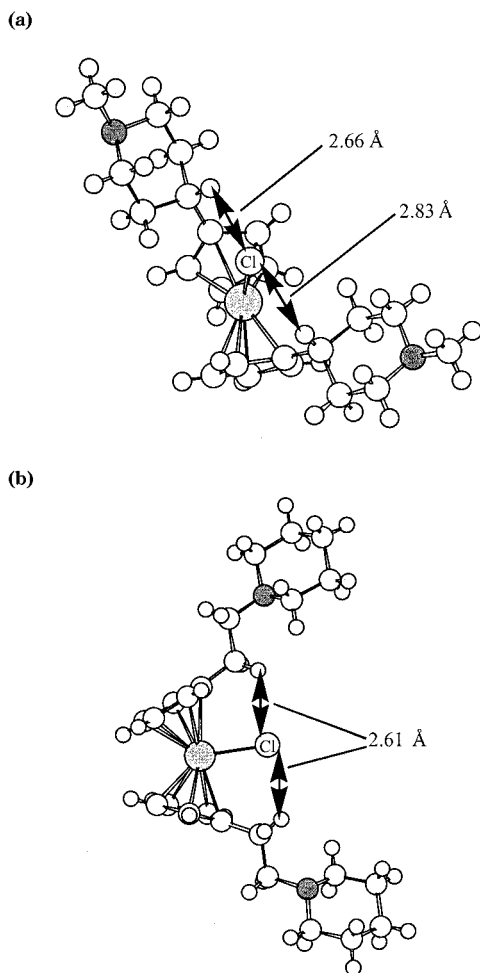
**Figure 3.** (a) Molecular structure of compound **7**, with 50% probability thermal ellipsoids. (b) Molecular structure of compound **8**, with 50% probability thermal ellipsoids.

We were interested in comparing the structures and reactivity of “piano-stool” amino-functionalized monocyclopentadienyl complexes with the amino-functionalized vanadocene chlorides. A convenient starting material is V(PR<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (R = Me, Et),<sup>11</sup> which is readily prepared by addition of phosphine to VCl<sub>3</sub>·3thf. V(PR<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> can be used in situ to give V(η-C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> by addition of MCp (M = Na, Tl, SnBu<sup>3</sup>, 0.5 Mg).<sup>11</sup> This strategy has been used to synthesize ring-alkylated half-sandwich vanadium complexes<sup>38</sup> and amido-functionalized monocyclopentadienyl vanadium derivatives.<sup>9</sup> Using the salt metathesis route described above, a series

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**Figure 4.** (a) Representation of the C–H···Cl hydrogen bonding in **7**. (b) Representation of the C–H···Cl hydrogen bonding in **8**.

of novel pendant arm half-sandwich complexes have been synthesized. For example,  $V\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}\}\text{Cl}_2(\text{PMe}_3)_2$  (**13**) is prepared by reaction of  $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}$  with  $V(\text{PMe}_3)_2\text{Cl}_3$  (Scheme 3). This reaction worked better when the  $V(\text{PMe}_3)_2\text{Cl}_3$  was used in situ. After stirring overnight the solvent was removed under reduced pressure and the product washed with petroleum ether, affording **13** as a purple crystalline solid. Analogous reactions were performed with the corresponding sodium salts afforded  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2\}(\text{PMe}_3)_2\text{Cl}_2$  (**11**) and  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2\}(\text{PMe}_3)_2\text{Cl}_2$  (**12**) as oils and  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}(\text{PMe}_3)_2\text{Cl}_2$  (**14**) as a solid. Compounds **11** and **12** were characterized by  $^1\text{H}$  NMR spectroscopy, and **13** and **14** were characterized by  $^1\text{H}$  NMR spectroscopy, X-ray crystal structure analysis, and microanalysis. The molecular structure of **13** (Figure 5) revealed a square-pyramidal piano-stool geometry about the V center. Selected bond lengths and angles are shown in Table 5. The molecular structure and geometry of **13** are comparable to  $V(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}_2$ ,<sup>11</sup> but the presence of the piperidinyll side chain eliminates the mirror plane bisecting the chlorine atoms through the vanadium and one carbon of the cyclopentadienyl ring. The molecular structure of **14** was found to be monomeric with a square-pyramidal piano-stool geometry about V and is shown in Figure 6 (selected bond lengths and angles are shown

in Table 6). The most noteworthy feature exhibited by the molecular structure of **14** is a close H···Cl contact of 2.66 Å. This could help account for the piperidinyll ring orientating itself toward one phosphine ligand and not centrally between them, which would potentially be favored for steric reasons. **13** and **14** represent the first X-ray crystal structures of monocyclopentadienyl vanadium complexes with an amino-functionalized side chain that does not coordinate intramolecularly to the metal center.

$^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 300.1 MHz, 300 K) were collected for compounds **12** and **13**. It was expected that the cyclopentadienyl protons would be observed at  $\delta \sim 150$ , i.e., similar to those of the bis-cyclopentadienyl vanadium(III) complexes. No cyclopentadienyl resonances were observed in the range  $\delta$  400 downfield to 200 upfield. This is probably due to unfavorable electron spin relaxation rates, as was reportedly found for  $V(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}_2$  and  $V(\eta\text{-C}_5\text{H}_4\text{Me})(\text{PMe}_3)_2\text{Cl}_2$ .<sup>11</sup> The phosphine resonances are readily observed in the region  $\delta -15$  to  $-25$  and are similar to those found for  $V(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_2\text{Cl}_2$  and  $V(\eta\text{-C}_5\text{H}_4\text{Me})(\text{PMe}_3)_2\text{Cl}_2$ .<sup>11</sup>

**Polymerization Studies.** Industrial production of polybutadiene is based upon homogeneous catalysis using metal complex catalysts of Ti, Co, Ni, or Nd. However the use of both heterogeneous and homogeneous vanadium compounds to catalyze the stereoselective polymerization of butadiene is also known.<sup>39</sup> Heterogeneous systems based on vanadium(III) and -(IV) chlorides and homogeneous systems such as  $V(\text{-cac})_3$  give polymers with a 1,4-*trans* microstructure.<sup>40,41</sup> More recently  $V(\eta\text{-C}_5\text{H}_5)_2\text{Cl}$  and  $V(\eta\text{-C}_5\text{H}_4\text{Me})(\text{PEt}_3)_2\text{Cl}_2$  were found to effectively catalyze the polymerization of butadiene to give 1,4-*cis*-polybutadiene.<sup>14</sup>

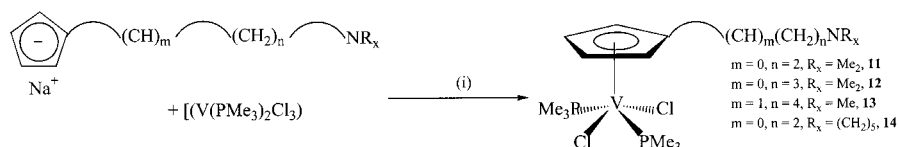
The analogous amino-functionalized vanadium(III) cyclopentadienyl complexes were investigated for potential catalytic activity toward the polymerization of butadiene. It was hoped to establish the activity and stereoselectivity of the catalysts. Furthermore any effect of the pendant amino functionality upon the performance of the catalyst could be observed. It should be emphasized that the catalytic trials to be presented were carried out under nonoptimized conditions.

Therefore, trial polymerizations of butadiene were carried out using  $V\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}\}_2\text{Cl}$ , **7**,  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}_2\text{Cl}$ , **8**,  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2\}(\text{PMe}_3)_2\text{Cl}_2$ , **11**,  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2\}(\text{PMe}_3)_2\text{Cl}_2$ , **12**,  $V\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}\}(\text{PMe}_3)_2\text{Cl}_2$ , **13**, and  $V\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}(\text{PMe}_3)_2\text{Cl}_2$ , **14**, in single polymerization runs. These trials were all conducted in analogous fashion under nitrogen using normal Schlenk line techniques. In each run MAO was used as a cocatalyst in a ratio of 100:1 with respect to the catalyst. Butadiene was used as a 1.8 M solution in toluene. In the instance where **7** or **8** was used as catalyst, MAO was added to the butadiene solution. The catalyst was added as a bright blue toluene solution, and an immediate color change to orange-brown was observed. After stirring for

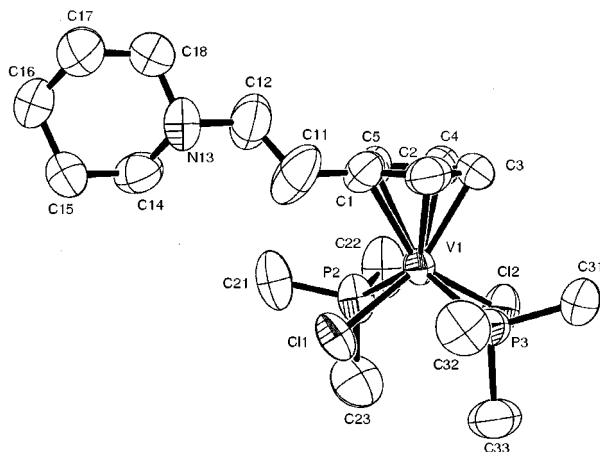
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Scheme 3<sup>a</sup><sup>a</sup> (i) toluene.**Table 5.** Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of 13 with Estimated Standard Deviations in Parentheses<sup>a</sup>

V(1)–C(1)	2.334(2)	V(1)–P(1)	2.5263(6)
V(1)–C(2)	2.274(2)	V(1)–P(2)	2.5141(6)
V(1)–C(3)	2.281(2)	V(1)–Cl(1)	2.4103(6)
V(1)–C(4)	2.322(2)	V(1)–Cl(2)	2.3990(6)
V(1)–C(5)	2.381(2)	V(1)–Cp(cent)(1)	1.98
C(1)–C(2)	1.428(3)	average V–C	2.32
C(2)–C(3)	1.403(3)	average C–C	1.415
C(3)–C(4)	1.412(3)	average P–C	1.82
C(4)–C(5)	1.420(3)		
C(5)–C(1)	1.414(3)		
C(1)–C(2)–C(3)	108.0(2)	P(1)–V(1)–P(2)	133.39(2)
C(2)–C(3)–C(4)	107.68(19)	Cl(1)–V(1)–Cl(2)	124.63(2)
C(3)–C(4)–C(5)	109.3(2)	Cl(1)–V(1)–Cp(cent)(1)	118.1
C(4)–C(5)–C(1)	106.63(19)	Cl(2)–V(1)–Cp(cent)(1)	117.2
C(5)–C(1)–C(2)	108.43(19)	P(1)–V(1)–Cp(cent)(1)	112.5
average C–C–C	108	P(2)–V(1)–Cp(cent)(1)	114.1
C(6)–C(5)–Cp(cent)(1)	176.1		

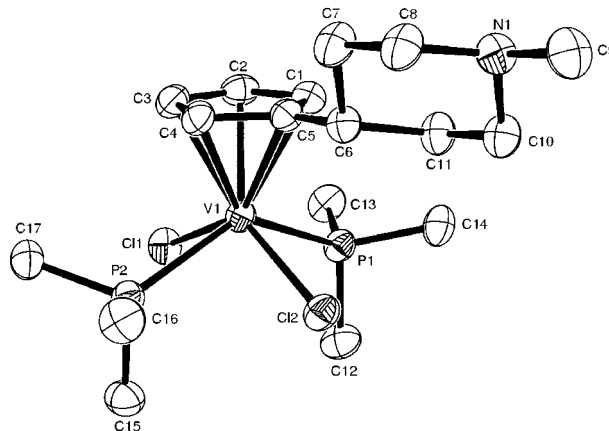
<sup>a</sup> Cp(cent)(1) denotes the centroid of the ring C(1)–C(5).**Figure 5.** Molecular structure of compound 13, with 50% probability thermal ellipsoids.

20 min at room temperature the solution had become orange-green with a small amount of white precipitate. After 1 h the reaction was quenched with methanol. HCl was added to dissolve inorganic aluminum salts, and any solid polymer was collected by filtration. The polymerization mixture was extracted with toluene, and the solvent was removed under reduced pressure, affording the polymer. Where the vanadium(III) monocyclopentadienyl complexes 11, 12, 13, and 14 were used as catalysts, the polymerization was carried out in a fashion similar to that described above. In each case the catalyst was added as a purple solution in toluene and an immediate color change to red was observed when each solution was injected into the butadiene/MAO mixture. The polymer was collected as before.

The three types of polymer produced are *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadiene. The expected chemi-

**Table 6.** Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of 14 with Estimated Standard Deviations in Parentheses<sup>a</sup>

V(1)–C(1)	2.362(3)	V(1)–P(2)	2.5102(10)
V(1)–C(2)	2.297(4)	V(1)–P(3)	2.5096(10)
V(1)–C(3)	2.274(4)	V(1)–Cl(1)	2.3992(9)
V(1)–C(4)	2.281(4)	V(1)–Cl(2)	2.4037(10)
V(1)–C(5)	2.323(3)	V(1)–Cp(cent)(1)	1.98
C(1)–C(2)	1.399(5)	average V–C	2.31
C(2)–C(3)	1.391(6)	average C–C	1.4
C(3)–C(4)	1.395(6)	average P–C	1.8
C(4)–C(5)	1.418(5)		
C(5)–C(1)	1.400(5)		
C(1)–C(2)–C(3)	110.0(4)	P(2)–V(1)–P(3)	135.57(4)
C(2)–C(3)–C(4)	107.6(3)	Cl(1)–V(1)–Cl(2)	121.84(5)
C(3)–C(4)–C(5)	107.3(4)	Cl(1)–V(1)–Cp(cent)(1)	119.6
C(4)–C(5)–C(1)	108.9(4)	Cl(2)–V(1)–Cp(cent)(1)	118.6
C(5)–C(1)–C(2)	106.2(4)	P(2)–V(1)–Cp(cent)(1)	112.2
average C–C–C	108	P(3)–V(1)–Cp(cent)(1)	112.2
C(11)–C(1)–Cp(cent)(1)	179.6		

<sup>a</sup> Cp(cent)(1) denotes the centroid of the rings C(1)–C(5).**Figure 6.** Molecular structure of compound 14, with 50% probability thermal ellipsoids.

cal shifts in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the three stereoregular polymers have been determined.<sup>40,42,43</sup> The stereochemistry of the resultant polymers was investigated by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. The bis-cyclopentadienyl vanadium(III) chloride derivatives 7 and 8 gave percentages of conversion of butadiene of 10% and 2%, respectively, which compare favorably with similar complexes found in the literature; V(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl is reported to polymerize butadiene with 8% conversion.<sup>14</sup> The reported *cis*-1,4-:*trans*-1,4-:1,2- stereoselectivity of the vanadocene chloride (87.2:1.1:11.7)<sup>14</sup> is comparable to that found for compounds 7 and 8 (91:0:9 and 89:0:11, respectively). Percentages of the different polybutadiene microstructures are shown in Table 7.

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**Table 7. Ratios of Polybutadiene Obtained via Vanadium(III) Complex Catalysts**

catalyst	<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
V( $\eta$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	87	1	12
<b>7</b>	91	0	9
<b>8</b>	89	0	11
V( $\eta$ -C <sub>5</sub> H <sub>4</sub> Me)(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	82	2	16
<b>11</b>	27	59	4
<b>12</b>	37	45	18
<b>13</b>	41	59	0
<b>14</b>	21	62	17

The monofunctionalized monocyclopentadienyl complexes **11–14** show relatively low conversions as well (conversion 3–11%). Interestingly however, **11–14** gave results quite unlike those reported for a similar complex without the pendant arm; V( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> gives a high *cis:trans* ratio (82.4:2.1),<sup>14</sup> whereas compounds **11–14**, favor a *trans*-1,4-stereochemistry.

It has been suggested that the stereospecificity of these types of catalysts is based on the *cis* vs *trans* mode of monomer coordination and the rate of isomerization of the *anti* vs *syn* butenyl, relative to the rate of insertion. In the V(acac)<sub>3</sub> system the fast rate of isomerization of the butenyl group is the determining factor; hence a *trans* polymer conformation is favored. The high *cis* stereoselectivity of V( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl and V( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> is reportedly due to the isomerization rate of the butenyl group being slower than monomer coordination, for which a *cis* configuration is favored.<sup>14</sup> For each of the catalysts used it would be expected that the action of the MAO would be to generate a cationic active species. It has been proposed in the half-sandwich complex a cationic methyl intermediate is likely, which would result in a 14-electron compound.<sup>14</sup>

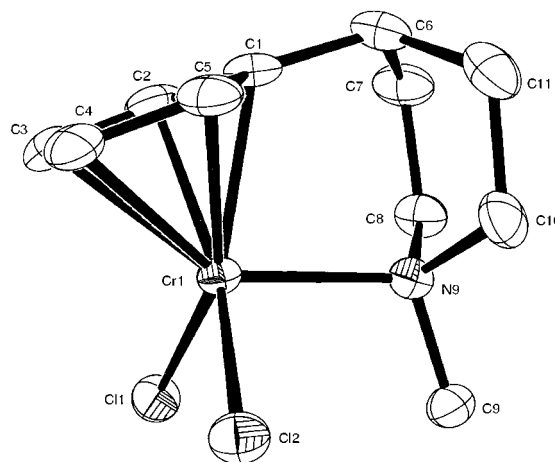
Subsequently, the most probable explanation for the observed stereoselectivity in the catalysts presented here is the differing electronic configuration of the active species and the influence of the pendant arm thereupon. It is suggested that the pendant arm might promote *trans*  $\eta^2$  coordination of butadiene in the half-sandwich complexes in one or both of two ways; the pendant arm could sterically hinder *cis*  $\eta^4$  coordination of butadiene, promoting *trans*  $\eta^2$  coordination. Alternatively the *trans* selectivity of the monocyclopentadienyl complexes could be due to  $\eta^2$  coordination of the butadiene monomer being promoted by intramolecular coordination of the pendant arm amino group.

The vanadocene monochloride catalysts **7** and **8** produced no *trans*-1,4-polymer, regardless of the steric bulk of the pendant arm and the potential for intramolecular amino coordination. It is suggested that the very electron-deficient 12-electron active species favors  $\eta^4$  butadiene coordination, resulting in a *cis* coordination and, accordingly, a *cis* polymer. As described, the amino-functionalized cyclopentadienyl ligand has an effect on the catalytic behavior of a vanadium system. One of the aspects that interested us regarding these ligand systems was to examine the effects of flexibility of the pendant arm and the electron-donating ability of the nitrogen atom on another catalytic system. A suitable system to compare the ability to form an intramolecular dative covalent bond was the half-sandwich monofunctionalized cyclopentadienyl chromium systems of Jolly.<sup>12,13</sup> These (in conjunction with MAO) have been shown to be remarkably active ethene polymerization

**Table 8. Selected Interatomic Distances (Å) and Angles between Interatomic Vectors (deg) of **15** with Estimated Standard Deviations in Parentheses<sup>a</sup>**

C(1)–Cr(1)	2.2024(16)	C(4)–C(5)	1.422(3)
C(2)–Cr(1)	2.2095(17)	C(1)–C(5)	1.423(2)
C(3)–Cr(1)	2.2494(18)	N(9)–Cr(1)	2.1493(14)
C(4)–Cr(1)	2.2531(18)	Cl(1)–Cr(1)	2.3084(5)
C(5)–Cr(1)	2.2124(17)	Cl(2)–Cr(1)	2.2988(4)
C(1)–C(2)	1.419(3)	C(9)–N(9)	1.486(2)
C(2)–C(3)	1.415(3)	Cr(1)–Cp(cent)(1)	1.98
C(3)–C(4)	1.397(3)		
C(3)–C(2)–C(1)	108.22(17)	C(6)–C(11)–C(10)	111.75(15)
C(4)–C(3)–C(2)	108.44(17)	N(9)–C(8)–C(7)	113.64(14)
C(3)–C(4)–C(5)	108.14(17)	N(9)–C(10)–C(11)	113.80(15)
C(4)–C(5)–C(1)	107.97(17)	C(8)–N(9)–C(10)	109.35(14)
C(2)–C(1)–C(5)	107.22(16)	C(9)–N(9)–C(10)	107.47(14)
C(5)–C(1)–C(6)	126.17(17)	C(9)–N(9)–C(8)	107.69(13)
C(2)–C(1)–C(6)	126.21(17)	Cl(2)–Cr(1)–Cl(1)	98.968(17)
C(1)–C(6)–C(11)	111.74(15)	N(9)–Cr(1)–Cl(2)	95.73(4)
C(1)–C(6)–C(7)	111.46(15)	N(9)–Cr(1)–Cl(1)	95.64(4)
C(11)–C(6)–C(7)	108.01(17)	C(8)–N(9)–Cr(1)	112.37(11)
C(6)–C(7)–C(8)	112.00(15)	C(9)–N(9)–Cr(1)	109.86(10)
		C(10)–N(9)–Cr(1)	109.95(11)
Cl(1)–Cr(1)–Cp(cent)(1)	123.25		
Cl(2)–Cr(1)–Cp(cent)(1)	121.43		
N(9)–Cr(1)–Cp(cent)(1)	115.80		

<sup>a</sup> Cp(cent)(1) denotes the centroid of the ring C(1)–C(5).

**Figure 7.** Molecular structure of compound **15**, with 50% probability thermal ellipsoids.

catalysts. Therefore  $\eta$ -C<sub>5</sub>H<sub>4</sub>{CH(CH<sub>2</sub>)<sub>4</sub>NCH<sub>3</sub>}CrCl<sub>2</sub> (**15**) and  $\eta$ -C<sub>5</sub>H<sub>4</sub>{CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N}CrCl<sub>2</sub> (**16**) were synthesized. Polymerization experiments were carried out as described in the Experimental Section. The (nonoptimized) polymerization data are shown in the Experimental Section. The two compounds have very similar activity, and a crystal structure of **15** (Figure 7, and selected bond lengths and angles are shown in Table 8) may help to explain why this is the case, since the pendant amino arm is bound to the chromium center. Therefore we found that the differences in the flexibility of the arm have no effect on the catalytic rate.

## Conclusion

Having synthesized a number of new vanadium(II), vanadium(III), and vanadium(IV) compounds, we isolated and crystallized the first examples of amino-functionalized vanadocenes and vanadocene monochlorides. A series of amino-functionalized cyclopentadienyl vanadium phosphine chloride complexes were also synthesized, and their catalytic behavior toward the



polymerization of butadiene was examined. It was found that the amino-functionalized cyclopentadienyl vanadium phosphine chloride complexes behaved much differently from their nonfunctionalized cyclopentadienyl counterparts.

### Experimental Details

Unless otherwise stated all manipulations were conducted using standard Schlenk-line techniques, under an inert atmosphere of dinitrogen or argon, using a modified dual vacuum/dinitrogen (or argon) line or in a Braun Labmaster 100 glovebox under an atmosphere of dinitrogen. Diethyl ether, petroleum ether (bp 40–60 °C), THF, and toluene were predried with Na metal and distilled over Na or Na/benzophenone under dinitrogen.  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$  were predried and distilled over CaH under  $\text{N}_2$ . All solvents were subsequently stored in ampules under  $\text{N}_2$ .  $\text{PCl}_3$  was degassed using freeze–pump–thaw cycles and dried over 4 Å molecular sieves prior to use.

**Crystallographic Data Collection and Structure Solution. X-ray Crystallography.** Data for compounds **4**, **5**, **9**, **10**, and **13–15** were collected on a Nonius KappaCCD area-detector diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $1.0^\circ \phi$ -rotation frames. Pertinent crystallographic details are given in Table 9.

The structures of all compounds were solved by direct methods using SHELXS 86. Refinement, by full-matrix least squares on  $F^2$  using SHELXL 97, was similar for all seven compounds. Hydrogen atoms were constrained to idealized positions using a riding model (with free rotation for methyl groups).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2\}_2$ , **1**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2$  (0.75 g, 0.005 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (0.8 g, 0.0005 mol) with stirring. The cold bath was removed, and the solution became purple on warming to room temperature. The reaction mixture was stirred overnight, the solvent was removed under reduced pressure, and the product was extracted into diethyl ether (100 mL). Solvent was removed in vacuo to give **1** as a distillable bright purple oil ( $\sim 200^\circ\text{C}$ ,  $10^{-2}$  mmHg) (0.6 g, 0.002 mol, 94%, based on vanadium).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300.1 MHz, 300 K):  $\delta$  345 (br s, 8H,  $\Delta\omega_{1/2} = 9700$  Hz), 79 (br s, 4H,  $\Delta\omega_{1/2} = 1200$  Hz), 2 (br m, 16H,  $\Delta\omega_{1/2} = 65$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2\}_2$ , **2**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2$  (4.0 g, 0.023 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (4.7 g, 0.003 mol) with stirring. The reaction mixture was worked up in the same way as **1** to give **2** as a distillable bright purple oil ( $\sim 200^\circ\text{C}$ ,  $10^{-2}$  mmHg) (3.2 g, 0.009 mol, 79% based on vanadium).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300.1 MHz, 300 K):  $\delta$  349 (br s, 8H,  $\Delta\omega_{1/2} = 11\,000$  Hz), 80 (br s, 4H,  $\Delta\omega_{1/2} = 1600$  Hz), 9 (br s, 4H,  $\Delta\omega_{1/2} = 170$  Hz), 2 (br m, 16H,  $\Delta\omega_{1/2} = 90$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NH}_2\}_2$ , **3**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NH}_2$  (2.0 g, 0.013 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (2.8 g, 0.002 mol) with stirring. The reaction mixture was worked up in the same way as **1** to give **3** as a distillable purple oil ( $\sim 200^\circ\text{C}$ ,  $10^{-2}$  mmHg) (1.2 g, 0.004 mol, 59% based on vanadium).  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 300.1 MHz, 300 K):  $\delta$  8 (br s, 4H,  $\Delta\omega_{1/2} = 170$  Hz), 4 (br m, 4H,  $\Delta\omega_{1/2} = 250$  Hz), 3.3 (br m, 8H,  $\Delta\omega_{1/2} = 130$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2\}_2$ , **4**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2$  (2.4 g, 0.015 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (2.6 g, 0.002 mol) with stirring. The cold bath was removed, and the solution became purple on warming to room temperature. The reaction mixture was stirred overnight, the solvent was removed under reduced pressure, and the product was extracted into THF (100 mL). **4** was recrystallized from THF

as a bright purple crystalline solid (1.3 g, 0.003 mol, 54% based on vanadium). Anal. Found: C 67.9; H 8.3; N 7.1.  $\text{VC}_{22}\text{H}_{32}\text{N}_2$  requires: C 70.4; H 8.6; N 7.5.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  337 (br s, 8H,  $\Delta\omega_{1/2} = 11\,000$  Hz), 55 (br s, 2H,  $\Delta\omega_{1/2} = 1300$  Hz), 11 (br m, 4H,  $\Delta\omega_{1/2} = 110$  Hz), 8.5 (br m, 4H,  $\Delta\omega_{1/2} = 100$  Hz), 3 (br m, 8H,  $\Delta\omega_{1/2} = 580$  Hz), 3 (br s, 6H,  $\Delta\omega_{1/2} = 50$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}_2$ , **5**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$  (5.1 g, 0.023 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (5.2 g, 0.003 mol) with stirring. The reaction mixture was worked up in the same way as **4** to give a bright purple crystalline solid (3.4 g, 0.008 mol, 66% based on vanadium). Anal. Found: C 69.5; H 9.1; N 6.75.  $\text{VC}_{24}\text{H}_{36}\text{N}_2$  requires: C 71.4; H 9.0; N 6.9.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  337 (br s, 8H,  $\Delta\omega_{1/2} = 10\,500$  Hz), 77 (br s, 4H,  $\Delta\omega_{1/2} = 1800$  Hz), 3 (br s, 4H,  $\Delta\omega_{1/2} = 120$  Hz), 1.7 (br m, 8H,  $\Delta\omega_{1/2} = 70$  Hz), 1.5 (br m, 12H,  $\Delta\omega_{1/2} = 80$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{N}\}_2$ , **6**.** To a Schlenk tube charged with  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{N}$  (2.65 g, 0.015 mol) and THF (150 mL) and cooled to  $-78^\circ\text{C}$  was added  $[(\text{V}_2\text{Cl}_3)(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$  (3.0 g, 0.002 mol) with stirring. The cold bath was removed, and the solution became purple on warming to room temperature. The reaction mixture was stirred overnight, the solvent was removed under reduced pressure, and the product was extracted into THF (100 mL). The solvent was removed under reduced pressure, affording **6** as a bright purple oil (1.5 g, 0.004 mol, 56%).  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 300.1 MHz, 300 K):  $\delta$  331 (br s, 8H,  $\Delta\omega_{1/2} = 10\,500$  Hz), 78 (br s, 4H,  $\Delta\omega_{1/2} = 1420$  Hz), 8 (br m, 2H,  $\Delta\omega_{1/2} = 140$  Hz), 7 (br m, 4H,  $\Delta\omega_{1/2} = 50$  Hz), 6.5 (br m, 2H,  $\Delta\omega_{1/2} = 50$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2\}_2\text{Cl}$ , **7**.** To a Schlenk tube charged with a solution of **4** (0.4 g, 0.001 mol) in petroleum ether (bp 40–60 °C) (20 mL) was added  $\text{PCl}_3$  (0.1 mL, 0.001 mol) via syringe with stirring. The solution changed color from purple to blue with concomitant formation of a green precipitate. The solvent was immediately removed in vacuo, and the product was extracted into petroleum ether (bp 40–60 °C). Recrystallization from petroleum ether (bp 40–60 °C) yielded 7 as bright blue crystalline platelets (0.24 g, 0.0006 mol, 54%). Anal. Found: C 64.2; H 7.75; N 7.1; Cl 8.25. Required for  $\text{VC}_{22}\text{H}_{32}\text{N}_2\text{-Cl}$ : C 64.3; H 7.8; N 6.8; Cl 8.6.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\text{CD}_3\text{CN}$ , 300.1 MHz, 300 K):  $\delta$  148.86 (br s, 4H,  $\Delta\omega_{1/2} = 2700$  Hz), 128.93 (br s, 4H,  $\Delta\omega_{1/2} = 2700$  Hz), 40.72 (br s, 2H,  $\Delta\omega_{1/2} = 900$  Hz), 5.77 (br s, 4H), 3.56 (br s, 4H), 2.62 (br s, 3H), 1.89 (br s, 4H), 1.43 (br s, 4H).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}_2\text{Cl}$ , **8**.** To a Schlenk tube charged with a solution of **5** (1.6 g, 0.004 mol) in petroleum ether (bp 40–60 °C) (20 mL) was added  $\text{PCl}_3$  (0.4 mL, 0.004 mol) via syringe with stirring. The reaction mixture was worked up in the same way as **7** to give **8** as bright blue crystalline platelets (0.93 g, 0.002 mol, 53%). Anal. Found: C 62.2; H 8.4; N 3.9. Required for  $\text{VC}_{24}\text{H}_{36}\text{N}_2\text{Cl}$ : C 65.7; H 8.3; N 6.4.  $^1\text{H}$  NMR ( $\text{CD}_3\text{-CN}$ , 300.1 MHz, 300 K):  $\delta$  147.17 (br s, 4H,  $\Delta\omega_{1/2} = 2500$  Hz), 127.41 (br s, 4H,  $\Delta\omega_{1/2} = 2500$  Hz), 38.33 (br s, 4H,  $\Delta\omega_{1/2} = 600$  Hz), 5.87 (br s, 4H), 4.13 (br s, 8H), 1.49 (br s, 12H).

**$\text{V}\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2\}_2\text{Cl}_2$ , **9**.** To a Schlenk tube charged with a solution of **4** (0.5 g, 0.0013 mol) in THF (80 mL) was added  $\text{PCl}_3$  (1.0 mL, 0.010 mol). The solution rapidly became colorless from purple through blue, with concomitant formation of a fluffy green precipitate. The solvent was filtered from the solid via cannula. Residual THF was removed in vacuo to afford **9** as a bright green powdery solid. The product was washed with THF ( $2 \times 30$  mL) (0.51 g, 0.0011 mol, 88%). EPR ( $\text{CHCl}_3$ , 298 K) 8-line hyperfine coupling,  $g = 2.06$ ,  $a = 73.3$  G.

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}_2\text{Cl}_2$ , **10**.** To a Schlenk tube charged with a solution of **5** (1.6 g, 0.004 mol) in THF (80 mL) was added  $\text{PCl}_3$  (1.0 mL, 0.010 mol). The reaction mixture was worked up in the same way as **9** to give a bright green powder. The product was washed with THF ( $2 \times 30$  mL) (1.6

Table 9. Crystallographic Data for 4, 5, 9, 10, and 13–15

	4	5	9	10	13	14	15
formula	C <sub>22</sub> H <sub>32</sub> N <sub>2</sub> V	C <sub>22</sub> H <sub>36</sub> N <sub>2</sub> V	C <sub>22</sub> H <sub>32</sub> ClN <sub>2</sub> V	C <sub>24</sub> H <sub>36</sub> ClN <sub>2</sub> V	C <sub>18</sub> H <sub>36</sub> Cl <sub>2</sub> NP <sub>2</sub> V	C <sub>17</sub> H <sub>34</sub> Cl <sub>2</sub> NP <sub>2</sub> V	C <sub>11</sub> H <sub>16</sub> Cl <sub>2</sub> CrN
mol wt	375.44	403.49	410.89	438.94	450.26	436.23	285.15
temperature (K)	190(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71069	0.71073
[Mo K $\alpha$ ] (Å)							
cryst syst	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	P $\bar{1}$	P2 <sub>1</sub> /c	P $\bar{1}$	C2/c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> /a	P2 <sub>1</sub> /c
a (Å)	7.6238(2)	6.01030(10)	7.4989(13)	9.3569(6)	7.7777(2)	12.7420(4)	7.89940(10)
b (Å)	10.4591(3)	11.5924(2)	10.0473(14)	7.3280(4)	12.3567(3)	10.1132(5)	12.6044(2)
c (Å)	13.8715(2)	15.6388(3)	15.745(3)	33.766(2)	25.3634(7)	17.4682(8)	12.0900(3)
$\alpha$ (deg)	102.695(2)	90	106.673(11)	90	90	90	90
$\beta$ (deg)	98.438(2)	97.8780(11)	93.165(7)	97.528(2)	90	99.374(3)	98.0140(8)
$\gamma$ (deg)	101.3270(12)	90	102.437(11)	90	90	90	90
volume (Å <sup>3</sup> )	1036.97(4)	1079.33(3)	1101.0(3)	2295.3(2)	2437.59(11)	2220.93(17)	1192.01(4)
Z	2	2	2	4	4	4	4
density(calcd)	1.202	1.242	1.239	1.27	1.227	1.305	1.589
$\mu$ (mm <sup>-1</sup> )	0.485	0.470	0.579	0.56	0.759	0.831	1.373
cryst size (mm)	0.24 $\times$ 0.24 $\times$ 0.22	0.65 $\times$ 0.52 $\times$ 0.39	0.35 $\times$ 0.25 $\times$ 0.06	0.48 $\times$ 0.17 $\times$ 0.06	0.45 $\times$ 0.22 $\times$ 0.1	0.78 $\times$ 0.78 $\times$ 0.65	0.26 $\times$ 0.15 $\times$ 0.03
no. of reflns coll'd	12 278	7907	9199	4200	14 717	16 759	22 221
no. of ind reflns	4434	2082	4095	2143	4766	4983 [R(int) = 0.0875]	2348 [R(int) = 0.0547]
no. of data/restraints/params	[R(int) = 0.0322] 4434/0/229	[R(int) = 0.0534] 2082/0/125	[R(int) = 0.0586] 4095/0/237	[R(int) = 0.0707] 2143/0/129	[R(int) = 0.0431] 4766/0/224	4983/0/209	2348/0/137
Goodness-of-fit on F <sup>2</sup>	1.095	1.148	1.066	1.114	1.011	1.032	1.044
final R indices [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0339, wR <sub>2</sub> = 0.0974	R <sub>1</sub> = 0.0614, wR <sub>2</sub> = 0.1578	R <sub>1</sub> = 0.0568, wR <sub>2</sub> = 0.1436	R <sub>1</sub> = 0.0616, wR <sub>2</sub> = 0.1529	R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.0926	R <sub>1</sub> = 0.0472, wR <sub>2</sub> = 0.1215	R <sub>1</sub> = 0.0248, wR <sub>2</sub> = 0.0645
R indices (all data)	R <sub>1</sub> = 0.0405, wR <sub>2</sub> = 0.0996	R <sub>1</sub> = 0.0635, wR <sub>2</sub> = 0.1591	R <sub>1</sub> = 0.0664, wR <sub>2</sub> = 0.1517	R <sub>1</sub> = 0.0666, wR <sub>2</sub> = 0.1567	R <sub>1</sub> = 0.0542, wR <sub>2</sub> = 0.1012	R <sub>1</sub> = 0.0534, wR <sub>2</sub> = 0.1268	R <sub>1</sub> = 0.0308, wR <sub>2</sub> = 0.0668
largest diff peak and hole (e Å <sup>-3</sup> )	0.222 and -0.324	1.073 and 0.238	0.581 and 0.643	0.641 and 0.576	0.351 and -0.252	0.558 and -0.509	0.336 and -0.539

g, 0.0034 mol, 84%). EPR ( $\text{CHCl}_3$ , 298K) 8-line hyperfine coupling,  $g = 2.06$ ,  $a = 73.3$  G.

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2\}\{\text{PMe}_3\}_2\text{Cl}_2$ , **11**.** To a Schlenk tube charged with  $\text{V}(\text{PMe}_3)_2\text{Cl}_3$  (1.1 g, 0.004 mol) and toluene (80 mL) and cooled to 0 °C was added  $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2$  (0.6 g, 0.004 mol) as a suspension in toluene (40 mL) via cannula with stirring. The color changed immediately to purple, and the reaction mixture was stirred overnight before removal of the solvent in vacuo. The bright purple oily solid was washed with petroleum ether (bp 40–60°) (50 mL) and extracted once with THF (150 mL). Volatiles were removed in vacuo to give **11** as a crystalline purple solid (0.73 g, 0.0023 mol, 64%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  –23 (br m,  $\Delta\omega_{1/2} = 1200$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2\}\{\text{PMe}_3\}_2\text{Cl}_2$ , **12**.** To a Schlenk tube charged with  $\text{V}(\text{PMe}_3)_2\text{Cl}_3$  (1.1 g, 0.004 mol) and toluene (80 mL) and cooled to 0 °C was added  $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2$  (0.6 g, 0.004 mol) as a suspension in toluene (40 mL) via cannula with stirring. The color changed immediately to purple, and the reaction mixture was stirred overnight before removal of the solvent in vacuo. The bright purple oily solid was washed with petroleum ether (bp 40–60°) (50 mL) and extracted once with THF (150 mL). Volatiles were removed in vacuo to give **12** as a crystalline purple solid (0.80 g, 0.0024 mol, 68%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  –23 (br m,  $\Delta\omega_{1/2} = 1200$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2\}\{\text{PMe}_3\}_2\text{Cl}_2$ , **13**.** To a Schlenk tube charged with  $\text{V}(\text{PMe}_3)_2\text{Cl}_3$  (1.1 g, 0.004 mol) and toluene (80 mL) and cooled to 0 °C was added  $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2$  (0.7 g, 0.004 mol) as a suspension in toluene (40 mL) via cannula with stirring. The color changed immediately to purple, and the reaction mixture was stirred overnight before removal of the solvent in vacuo. The bright purple oily solid was washed with petroleum ether (bp 40–60°) (50 mL) and extracted into THF (150 mL). Volatiles were removed in vacuo to give **13** as a crystalline purple solid (0.76 g, 0.0022 mol, 65%). Anal. Found: C 46.9; H 7.9; N 3.1; P 14.1.  $\text{VC}_{14}\text{H}_{43}\text{N}_2\text{P}_2\text{Cl}_2$  requires: C 46.8; H 7.9; N 3.2; P 14.1.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  –23 (br s,  $\Delta\omega_{1/2} = 1100$  Hz).

**$\text{V}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}\{\text{PMe}_3\}_2\text{Cl}_2$ , **14**.** To a Schlenk tube charged with  $\text{V}(\text{PMe}_3)_2\text{Cl}_3$  (1.1 g, 0.004 mol) and toluene (80 mL) and cooled to 0 °C was added  $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$  (0.7 g, 0.004 mol) as a suspension in toluene (40 mL) via cannula with stirring. The color changed immediately to purple, and the reaction mixture was stirred overnight before removal of the solvent in vacuo. The bright purple oily solid was washed with petroleum ether (bp 40–60°) (50 mL) and extracted once with THF (150 mL). Volatiles were removed in vacuo to give **14** as a crystalline purple solid (0.83 g, 0.0023 mol, 65%). Anal. Found: C 47.8; H 7.8; N 3.1; Cl 15.7.  $\text{VC}_{14}\text{H}_{43}\text{N}_2\text{P}_2\text{Cl}_2$  requires: C 48.0; H 8.1; N 3.1; Cl 15.8.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz, 300 K):  $\delta$  –23 (br s,  $\Delta\omega_{1/2} = 1100$  Hz).

**$\text{Cr}\{\eta\text{-C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NCH}_3\}\text{Cl}_2$ , **15**.** To a Schlenk tube charged with  $\text{CrCl}_3$  (0.85 g, 0.0054 mol) and THF (100 mL) was added a suspension of  $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}$  (1 g, 0.0054 mol) in THF (100 mL). The mixture was allowed to reflux overnight to give a deep blue-green solution and precipitate of NaCl. The solvent was removed in vacuo and the product extracted in DCM to give a deep blue solution. Removal of the solvent in vacuo afforded a deep blue powder (0.74 g, 0.0024 mol, 43.7%). Anal. Found: C 46.3; H 5.7; N 3.2%. Calcd for

$\text{CrC}_{11}\text{H}_{10}\text{NCl}_2$ : C 46.3; H 5.7; N 4.9. FAB mass spectrum:  $m/z$  285 –  $\text{C}_5\text{H}_4\{\text{CH}(\text{CH}_2)_2\text{NCH}_3\}\text{CrCl}_2$ .

**$\text{Cr}\{\eta\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{N}\}\text{Cl}_2$ , **16**.** To a Schlenk tube charged with  $\text{CrCl}_3$  (0.88 g, 0.0056 mol) and THF (100 mL) was added a suspension of  $\text{NaC}_5\text{H}_4\{\text{CH}_2\text{C}_5\text{H}_4\text{N}\}$  (1 g, 0.0054 mol) in THF (100 mL). The mixture was allowed to reflux overnight to give a deep blue-green solution and precipitate of NaCl. The solvent was removed in vacuo and the product extracted in DCM to give a deep blue solution. Removal of the solvent in vacuo afforded a deep blue powder (0.7 g, 0.0025 mol, 46.4%). Anal. Found: C 52.3; H 4.2; N 5.2. Calcd for  $\text{CrC}_{11}\text{H}_{10}\text{NCl}_2$ : C 47.3; H 3.6; N 5.0. FAB mass spectrum:  $m/z$  279 –  $\text{C}_5\text{H}_4\{\text{CH}_2\text{C}_5\text{H}_4\text{N}\}_2\text{CrCl}_2$ .

**Polymerization of Butadiene.** Butadiene polymerization trials were carried out using compounds **7**, **8**, **12**, and **13** as catalysts. Butadiene was used as a 1.8 M solution in toluene. For polymerization runs of **7** and **8** 50  $\mu\text{mol}$  of catalyst was used. For polymerization runs of **12** and **13** 100  $\mu\text{mol}$  of catalyst was used. One hundred equivalents of MAO was used as a cocatalyst for each run as a 10% solution in toluene. Polymerization trials for all catalysts were carried out under identical conditions. A typical run is given as an example.

To a Schlenk tube containing a toluene solution of butadiene (35 mL, 0.063 mol) was added MAO (7 mL, 0.01 mol) via syringe.  $\text{V}\{\text{C}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}_2\}(\text{PMe}_3)_2\text{Cl}_2$  (0.044 g, 100  $\mu\text{mol}$ ) was added as a toluene solution (10 mL). The mixture was stirred vigorously, and after 60 min MeOH was added dropwise, then in excess. HCl (80 mL) was added and any polymer was collected by filtration and dried.

**Polymerization of Ethene.** To a solution of MAO (1.7 mL, 100:1 MAO/Cr ratio) in toluene (20 mL) under an ethylene flow of 1 atm was added **15** (0.007 g, 25  $\mu\text{mol}$ ) in toluene (10 mL). The temperature was maintained at 20 °C and the reaction allowed to run (20 min). The polymerization was terminated by addition of MeOH (5 mL) and the reaction mixture added to MeOH (150 mL). Concentrated HCl was added and the polymer precipitated out of solution. The resulting polymers were washed ( $\text{CHCl}_3/\text{MeOH}$  (3  $\times$  5 mL)) and dried to give white polyethylene (1.57 g). The same procedure was carried out for **16** to give white polyethylene (1.69 g).

#### Polymerization Activity and Characterization

catalyst precursor	amt. of cat. ( $\mu\text{mol}$ )	amt. PE (g)	activity (kg PE/mol Cr/h)
15	25	1.69	202.8
16	25	1.57	189.2

The physical properties of the polymers were tested by RAPRA Technology.

$\eta\text{-C}_5\text{H}_4\{\text{CH}_2\text{C}_5\text{H}_4\text{N}\}_2\text{CrCl}_2$ : MW = 403 000; PD = 5.9.

$\eta\text{-C}_5\text{H}_4\{\text{CH}(\text{CH}_2)_2\text{NCH}_3\}\text{CrCl}_2$ : MW = 642 000; PD = 9.4.

**Acknowledgment.** We would like to thank Rapra Technology Limited, Shropshire, U.K., for characterization data for the polyethylene and the EPSRC for funding.

**Supporting Information Available:** This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020170F