Vanadium (β-(Dimethylamino)ethyl)cyclopentadienyl Complexes with Diphenylacetylene Ligands

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Reduction of the V(III) (β-(dimethylamino)ethyl)cyclopentadienyl dichloride complex [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]VCl$_2$(PMe$_3$) (**1**) with 1 equiv of Na/Hg yielded the V(II) dimer {[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(μ-Cl)}$_2$ (**2**). This compound reacted with diphenylacetylene in THF to give the V(II) alkyne adduct [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]VCl(η^2-PhC≡CPh) (**3**). Further reduction of **2** with Mg in the presence of diphenylacetylene resulted in oxidative coupling of two diphenylacetylene groups to yield the diamagnetic, formally V(V), bent metallacyclopentatriene complex [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(C$_4$Ph$_4$) (**4**).

Amino-functionalized cyclopentadienyl transition-metal complexes have attracted much attention, owing to their dramatic effect on catalytic function compared to the case for the corresponding parent complexes.[1] Playing a major role in this area are titanium and chromium complexes, which exhibit good activity in ethene and propene polymerization.[2] However, there are relatively few reports concerning vanadium complexes of this type.[3] This is mainly due to the fact that such compounds are extremely air-sensitive and paramagnetic, due to the inherent instability of monocyclopentadienyl vanadium analogues. The limiting step in the development of this chemistry has been the absence of suitable organometallic vanadium starting materials. Amino-functionalized cyclopentadienyl ligands with additional pendant Lewis basic functionalities have been used to enhance the stability of metal complexes through the chelate effect, thus leading to interesting products. It has been recognized that such ligands can exhibit hemilabile behavior, in which the pendant functionality can reversibly dissociate from the metal center. This behavior can strongly affect the reactivity of such complexes: for instance, in catalytic conversions.[4] Recently, we described the chemistry of the vanadium(III) complex (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$NMe$_2$)VCl$_2$(PMe$_3$),[5] containing a (β-(dimethylamino)ethyl)cyclopentadienyl ligand, which seemed to us to be a suitable starting material for the development of new organovanadium chemistry.[6] Also, we observed that the tendency of the pendant amino group to bind to or dissociate from the vanadium center depends strongly on the nature of the other ligands bound to the vanadium atom.

In this contribution, we present the chemistry of the dimeric vanadium(II) (β-(dimethylamino)ethyl)cyclopentadienyl complex {[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(μ-Cl)}$_2$ (**2**). It has been found that the reaction of **2** with diphenylacetylene produces the V(II) alkyne adduct [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]VCl(η^2-PhC≡CPh) (**3**) and reduction of **2** with Mg in the presence of diphenylacetylene results in the formation of the bent V(V) metallacyclopentatriene complex [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(C$_4$Ph$_4$) (**4**), in which the Lewis basic amino group can bind to the vanadium center through the chelate effect.

Results and Discussion

Synthesis and Molecular Structure of {[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(μ-Cl)}$_2$ (2). The vanadium (β-(dimethylamino)ethyl)cyclopentadienyl complex [η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]VCl$_2$(PMe$_3$) (**1**)[5] was prepared in high yield by a straightforward reaction between VCl$_3$(PMe$_3$)$_2$ and Li[C$_5$H$_4$(CH$_2$)$_2$NMe$_2$] in THF. One-electron reduction of the V(III) complex **1** with 1 equiv of Na/Hg in THF afforded the red-violet dinuclear V(II) chloride-bridged complex {[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$]V(μ-Cl)}$_2$ (**2**; eq 1) in 56% isolated yield. Due to its paramagnetism, the ^{1}H NMR spectrum of **2** only shows a very broad resonance for

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(1) (a) Baretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, *86*, 1–864. (b) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663–674. (c) Britovesk, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447. (d) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953–1976. (e) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145–179.
(2) (a) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140–4142. (b) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1996**, *29*, 8030–8035. (c) Blais, M. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 3775–3783. (d) van Beek, J. A. M.; van Doremaele, G. H. J.; Gruter, G. J. M.; Arts, H. J.; Eggels, G. H. M. R. *WO 96/13529*, 1995, issued to DSM NV. (e) Ypey, E. G.; van Beek, J. A. M.; Gruter, G. J. M. *WO 97/42157*, 1997, issued to DSM NV. (f) van Beek, J. A. M.; Gruter, G. J. M. *EP 0805142 A1*, 1997, issued to DSM NV. (g) Herberich, G. E.; Schmidt, B.; Schmitz, A.; van Beek, J. A. M. *WO 97/23493*, 1997, issued to DSM NV. (h) van Beek, J. A. M.; van Doremaele, G. H. J.; Gruter, G. J. M.; Arts, H. J.; Eggels, G. H. M. R. *U.S. Patent 5,986,029*, 1999, issued to DSM NV. IJolly, P. W.; Joans, K.; Verhovnik, G. P. J.; Döhring, A.; Göhre, J.; Weber, J. C. *WO 98/04570*, 1998, issued to Studiengesellschaft Kohle MBH. (k) Jolly, P. W.; Jonas, K.; Verhovnik, G. P. J. *DE 19630580*, 1998, assigned to Studiengeselschaft Kohle mbH.
(3) Bradley, S.; Camm, K. D.; Furtado, S. J.; Gott, A. L.; McGowan, P. C.; Podesta, T. J.; Thornton-Pett, M. *Organometallics* **2002**, *21*, 3443–3453.
(4) (a) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516–2519. (b) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122–5135. (c) de Bruin, T. J. M.; Magna, L.; Raybaud, P.; Toulhoat, H. *Organometallics* **2003**, *22*, 3404–3413.
(5) Liu, G. H.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914–3920.
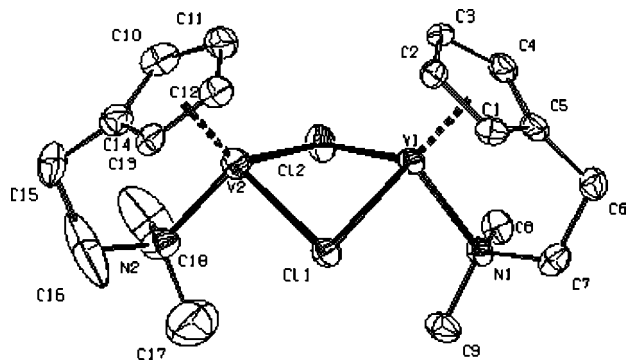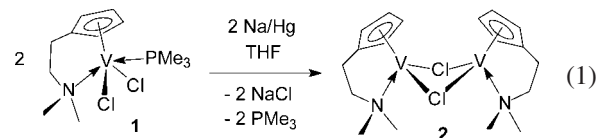
Figure 1. Molecular structure of $\{[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(\mu\text{-}Cl)\}_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

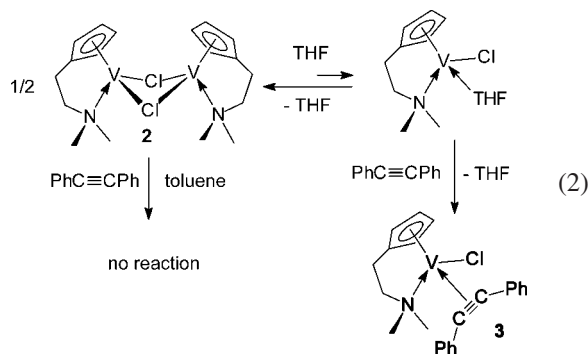**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2**

V(1)−Cl(1)	2.443(2)	V(1)−C(1)	2.277(7)
V(1)−Cl(2)	2.434(2)	V(1)−C(2)	2.308(7)
V(2)−Cl(1)	2.430(2)	V(1)−C(3)	2.326(7)
V(2)−Cl(2)	2.454(2)	V(1)−C(4)	2.290(7)
V(1)−N(1)	2.251(5)	V(1)−C(5)	2.253(7)
V(2)−N(2)	2.258(7)		
Cl(1)−V(1)−Cl(2)	92.78(7)	Cl(1)−V(2)−N(2)	100.22(18)
Cl(1)−V(1)−N(1)	93.43(15)	Cl(2)−V(2)−N(2)	91.21(17)
Cl(2)−V(1)−N(1)	93.81(14)	V(1)−Cl(1)−V(2)	76.43(6)
Cl(1)−V(2)−Cl(2)	92.60(7)	V(1)−Cl(2)−V(2)	76.16(6)

all protons. However, it is clear that **2** is a phosphine-free complex, as confirmed by the disappearance of the PMe$_3$ proton resonances in the ^{1}H NMR spectrum. A crystal structure determination of **2** (Figure 1, with selected bond lengths and angles given in Table 1) shows a puckered V$_2$Cl$_2$ core with the cyclopentadienyl ligands in a cis arrangement. It strongly resembles the dimeric V(II) monochloride triethylphosphine complex [Cp(Et$_3$P)V(μ-Cl)]$_2$ reported previously,[6g,h] with very similar V−Cl distances in the puckered V$_2$Cl$_2$ unit, which is essentially equilateral. The V−Cl distances (2.443(2), 2.434(2), 2.430(2), and 2.454(2) Å) are comparable to those observed in other chloride-bridged dimeric vanadium complexes (2.4128(15) and 2.5365(15) Å in [V(=NAr)Cl$_2$(dppm)]$_2$[7] and 2.459(2) and 2.373(2) Å in {[(Me$_3$Si)NCH$_2$CH$_2$]$_2$N(Me$_3$Si)}$_2$V$_2$(μ-Cl$_2$)),[8] although there are slight differences. Furthermore, the Cl−V−Cl angles of 92.78(7) and 93.43(15)° in the dimeric complex **2** are obviously larger than those observed in a closely related dimeric titanium complex (77.11(5), 78.21(7), and 78.63(7)° in (C$_5$H$_4$)$_2$TiCl$_2$)$_2$),[9] indicating the steric nature of the β-aminoethyl-functionalized cyclopentadienyl ligand. Apparently the (Cp-ethylamino)VCl fragment prefers to form dimeric **2** rather than

(6) (a) Nieman, J.; Scholtens, H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *186*, C12–C14. (b) Hessen, B.; Meetsma, A.; Van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925–1936. (c) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946–948. (d) Hessen, B.; Lemmen, T. H.; Luttikhedde, H. J. G.; Teuben, J. H.; Petersen, J. L.; Jagner, S.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1987**, *6*, 2354–2362. (e) Hessen, B.; Buijink, J. K. F.; Meetsma, A.; Teuben, J. H.; Helgesson, G.; Hakansson, M.; Jagner, S.; Spek, A. L. *Organometallics* **1993**, *12*, 2268–2276. (f) Hessen, B.; Van Bolhuis, F.; Teuben, J. H.; Petersen, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 295–296. (g) Nieman, J.; Teuben, J. H. *Organometallics* **1986**, *5*, 1149–1153. (h) Nieman, J.; Teuben, J. H.; Hulsbergen, F. B.; de Graaff, R. A. G.; Reedijk, J. *Inorg. Chem.* **1987**, *26*, 2376. (i) Hessen, B.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4860–4861.

(7) Feghali, K.; Harding, D. J. H.; Reardon, D.; Gambarotta, S.; Yap, G.; Wang, Q. *Organometallics* **2002**, *21*, 968–976.

(8) Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2003**, *42*, 673–675.

(9) Jungst, R.; Dekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *7*, 1645–1655.

to bind the PMe$_3$ ligand. This behavior was also observed for the CpVCl(PR$_3$) system (R = Et, Me), although for R = Me it was seen that the equilibrium may be shifted to the side of CpVCl(PMe$_3$)$_2$ when an excess of PMe$_3$ is added.[6g]

(1)

Reaction of 2 with Diphenylacetylene: Synthesis and Molecular Structure of $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl(\eta^2\text{-}PhC\equiv CPh)$ (3). Reaction of metal chloride complexes with alkynes can result in highly interesting derivatives.[10] However, for vanadium compounds, only several examples have been reported.[11] In this case, when a toluene solution of **2** was treated with 1 equiv of phenylacetylene at ambient temperature, no reaction was observed and **2** could be recovered unchanged. However, when the same reaction was performed in THF solution, the V(II) diphenylacetylene adduct $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl(\eta^2\text{-}PhC\equiv CPh)$ (**3**) was isolated as red crystals in 57% yield after recrystallization from pentane. Apparently, the coordination of the alkyne to the V(II) center is thermodynamically favorable, but diphenylacetylene is kinetically unable to cleave the (μ-Cl)$_2$ bridge in dinuclear **2**. Although the low-valent metal center is expected to have a relatively low affinity for THF, the ether apparently is kinetically competent to cleave **2** to give a transient mononclear THF adduct, from which the THF subsequently is displaced by the alkyne (eq 2). The alkyne adduct **3** was characterized by single-crystal X-ray diffraction, and its structure is shown in Figure 2 (selected bond lengths and angles are given in Table 2). Its structure is geometrically similar to that of the V(I) complex CpV(PMe$_3$)$_2$(η^2-PhC≡CPh).[6b] In the latter, the alkyne C≡C bond lies approximately in the same plane as one of the V−P bonds. In **3** the alkyne is similarly oriented relative to the V−N bond. As was observed in CpV(PMe$_3$)$_2$(η^2-PhC≡CPh), the bonding of the cyclopentadienyl moiety to vanadium in **3** is noticeably distorted from the regular η^5 mode, with the longest V−C distances to C(3) and C(4) (2.35–2.36 Å) and the shortest to C(1) (2.24 Å). A closer look at the coordinated alkyne reveals that both the C≡C distance of 1.312(3) Å and the C−C−C(Ph) angles of 139° are indications of a somewhat lesser extent of π-back-donation in the V(II) complex **3** than in the V(I) complex CpV(PMe$_3$)$_2$(η^2-PhC≡CPh), where the related parameters are 1.328(3) Å and 136°.

(2)

Reduction of 2 in the Presence of Diphenylacetylene: Synthesis and Molecular Structure of $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(C_4Ph_4)$ (4). Further reduction of the V(II) complex **2** by Mg in THF in the presence of diphenylacetylene (performed

Figure 2. Molecular structure of $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl(\eta^2\text{-}PhC\equiv CPh)$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

V(1)−Cl(1)	2.3366(6)	V(1)−C(1)	2.239(3)
V(1)−N(1)	2.276(3)	V(1)−C(2)	2.284(3)
V(1)−C(16)	1.969(3)	V(1)−C(3)	2.351(2)
V(1)−C(17)	2.003(2)	V(1)−C(4)	2.360(3)
C(16)−C(17)	1.312(3)	V(1)−C(5)	2.305(3)
C(16)−V(1)−C(17)	38.56(9)	N(1)−V(1)−C(17)	88.66(9)
Cl(1)−V(1)−C(16)	103.43(7)	N(1)−V(1)−Cl(1)	90.69(5)
Cl(1)−V(1)−C(17)	109.09(7)	C(15)−C(16)−C(17)	139.1(2)
N(1)−V(1)−C(16)	127.19(9)	C(16)−C(17)−C(18)	138.2(3)

at low temperature, −30 to –5 °C) resulted in the isolation of a diamagnetic red crystalline compound that was characterized by single-crystal X-ray diffraction as the bent metallacyclopentatriene complex $[\eta^5\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(C_4Ph_4)$ (**4**; eq 3). It is likely to be formed by reduction of the vanadium to V(I) and coordination of two alkyne molecules to the metal center followed by an oxidative coupling of the diphenylacetylene ligands to yield a metallacycle. It was observed previously that the metallacycle of the formula $CpV(C_4R_4)(PMe_3)$ takes on a bent metallacyclopentatriene structure rather than the more common planar metallacyclopentadiene structure.[6b] The crystal structure of **4** (Figure 3, with selected bond lengths and angles given in Table 3) shows two short V−C bond distances of 1.888(5) and 1.895(4) Å, which are shorter than that of 1.922 Å in a benzylidene complex.[13] Such short V−C bond distances

(10) (a) Marschner, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6770–6771. (b) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884–900. (c) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456–471. (d) Beweries, T.; Burlakov, V. V.; Bach, M. A.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 247–249.

(11) (a) Köhler, F. H.; Hofmann, P.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 6359–6367. (b) Köhler, F. H.; Prössdorf, W.; Schubert, U. *Inorg. Chem.* **1981**, *20*, 4096–4101. (c) Buijink, J. K. F.; Kloetstra, K. R.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 2523–2533. (d) Evans, W. J.; Bloom, I.; Doedens, R. J. *J. Organomet. Chem.* **1984**, *265*, 249–255. (e) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282–2287.

(12) Johnson, S. A.; Liu, F. Q.; Suh, M. C.; Surcher, S.; Haufe, M.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 4199–4211.

(13) Buijink, J.-K. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922–2924.

(14) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *Chem. Commun.* **1997**, 643–644.

are close to that of 1.876(7) Å in the vanadium(V) bicyclic carbene−amide complex $(Me_3Si)_2NVN(SiMe_3)SiMe_2CH_2C(Ph)\text{-}C(Ph)C(Ph)C(Ph)$[14] and are similar to those of 1.891(3) and 1.883 (3) Å in the vanadium(V) bis(carbene) complex $CpV(C_4Me_2Ph_2)(PMe_3)$.[6b] These results clearly indicate that **4** is a vanadium(V) bis(carbene) complex, similar to the dinuclear molybdenum bis(carbene) complex $Mo_2Br_2(\equiv CHSiMe_3)_2\text{-}(PMe_3)_4$ (Mo=C = 1.949(5) Å).[15] These V−C bond distances are consistent with V≡C bond orders as reviewed by Mindiola recently.[16] In addition, the C−C distances within the metallacycle are all similar in length, with the central C(17)−C(24) distance being fractionally shorter. A contrast with the structure of $CpV(C_4Me_2Ph_2)(PMe_3)$ is that the metallacycle in **4** is bent away from the cyclopentadienyl group (*supine* orientation of the C₄R₄ fragment), whereas in the former it is bent toward the Cp group (*prone* orientation). In this sense **4** is similar to the first bent metallacyclopentatriene to be structurally characterized, $CpMo(C_4Ph_4)Cl$.[17] In the ^{13}C NMR spectrum of **4**, the V=C resonance is located at 263.6 ppm, essentially identical with that in $CpV(C_4Ph_4)(PMe_3)$, and the resonance of both central carbon atoms at 94.9 ppm is downfield from that in the reference compound. The absence of potentially coordinating PMe_3 ligands appears to facilitate the alkyne coupling reaction, allowing it to occur even at relatively low temperature (−5 °C). In contrast, the diphenylacetylene complex $CpV(PhC\equiv CPh)\text{-}(PMe_3)_2$ only reacts with additional diphenylacetylene at elevated temperatures (60 °C) to form the metallacyclopentatriene complex $CpV(C_4Ph_4)PMe_3$.[6b]

In conclusion, the vanadium(III) (β-(dimethylamino)ethyl)-cyclopentadienyl dichloride complex $(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2NMe_2)\text{-}VCl_2(PMe_3)$ is a convenient precursor for synthesis of a range of organometallic vanadium derivatives. It has also been recognized that amino-functionalized cyclopentadienyl ligands with additional pendant Lewis basic functionalities can enhance the stability of the vanadium complexes through the chelate effect, thus resulting in novel complexes.

Experimental Section

(15) Ahmed, K. J.; Chisholm, M. H.; Huffman, J. C. *Organometallics* **1985**, *4*, 1168–1174.

(16) (a) Basuli, F.; Kilgore, U. J.; Hu, X. L.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3156–3159. (b) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813–821.

(17) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218–5221.

Figure 3. Molecular structure of the cation of $[\eta^5:\eta^1\text{-}C_5H_4\text{-}(CH_2)_2NMe_2]V(C_4Ph_4)$ (**4**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

V(1)−C(10)	1.888(5)	C(10)−C(17)	1.433(6)
V(1)−C(31)	1.895(4)	C(24)−C(31)	1.438(6)
V(1)−C(17)	2.360(5)	C(17)−C(24)	1.417(5)
V(1)−C(24)	2.339(5)	V(1)−N(1)	2.254(4)
C(10)−V(1)−C(31)	92.7(2)	N(1)−V(1)−C(31)	116.32(15)
C(10)−V(1)−C(17)	37.40(15)	C(24)−C(31)−V(1)	88.0(3)
C(17)−V(1)−C(24)	35.11(14)	V(1)−C(10)−C(17)	89.5(3)
C(24)−V(1)−C(31)	37.91(16)	C(17)−C(24)−C(31)	118.0(4)
N(1)−V(1)−C(10)	112.60(15)	C(10)−C(17)−C(24)	116.8(4)

Table 4. Crystallographic Data for 2−4

	2	3	4
mol formula	$C_{18}H_{28}Cl_2N_2V_2$	$C_{23}H_{24}ClNV$	$C_{37}H_{34}NV$
fw	445.20	400.82	543.59
diffractometer	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD
temp (K)	100(1)	100(1)	100(1)
cryst syst	monoclinic	trigonal	monoclinic
space group	$P2_1/c$	$R\overline{3}$	$P2_1/n$
a (Å)	7.736(2)	31.948(2)	9.5142(9)
b (Å)	16.663(3)	31.948(2)	30.774(3)
c (Å)	16.225(3)	11.0765(7)	10.501(1)
β (deg)	99.529(3)		116.330(2)
V (Å³)	2062.6(8)	9790.9(11)	2755.6(5)
Z	4	18	4
d_{calcd} (g cm^{-3})	1.434	1.224	1.310
F(000)	920	3672	1144
ν(Mo Kα), cm^{-1}	11.67	5.84	3.87
θ range (deg)	2.44, 26.02	2.21, 28.28	2.41, 24.73
$R_w(F^2)$	0.2044	0.1257	0.1612
no. of indep rflns	4062	5403	4842
no. of params	221	331	354
$R(F)$ for $F_o >$ 4.0σ(F_o)	0.0736	0.0391	0.0678
GOF	1.012	1.158	0.986
largest diff peak/hole (e Å^{-3})	1.2(1), −0.7(1)	0.43(10), −0.28	1.12(10), −0.43

(Young) stopcock. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrometer from Nujol mulls between KBr disks unless stated otherwise. Elemental analyses were performed by Kolbe Analytical Laboratories, Mülheim a.d. Ruhr, Germany.

Preparation of $\{[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(\mu\text{-}Cl)\}_2$ (2). Na sand (0.090 g, 3.90 mmol) was added to 45 g of frozen Hg and carefully dissolved by thawing out the Hg. When the Na/Hg was at room temperature, it was added to a solution of complex **1** (1.30

g, 3.90 mmol) in 30 mL of dry THF. The deep purple solution turned violet over 2 h. After it had been stirred overnight, the violet THF solution was transferred into a new Schlenk flask and the residual Hg was washed twice with 5 mL of THF. All the THF solutions were combined, the volatiles were removed in vacuo, and the resulting violet solid was stripped twice with 15 mL of pentane. The violet-red solid was repeatedly extracted with 30 mL portions of pentane. The violet-red extracts were filtered and concentrated to 10 mL. Cooling to −30 °C produced violet-red crystals of **2** (0.98 g; 2.2 mmol; 56%). IR (Nujol mull): 635, 678, 754, 772, 786, 817, 920, 953, 996, 1022, 1046, 1098, 1117, 1167, 1210, 1236, 1267, 1323, 1377, 1402, 1461, 2831, 2887, 2910, 2942, 2963 cm^{-1}. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 50.69 (s), 47.68 (s), 35.89 ($\Delta\nu_{1/2}$ = 1240 Hz), 31.19 ($\Delta\nu_{1/2}$ = 749 Hz), 21.58 ($\Delta\nu_{1/2}$ = 480 Hz), 12.19 ($\Delta\nu_{1/2}$ = 429 Hz), 11.18 ($\Delta\nu_{1/2}$ = 342 Hz), −2.39 ($\Delta\nu_{1/2}$ = 146 Hz), −4.59 ($\Delta\nu_{1/2}$ = 240 Hz). Anal. Calcd for $C_{18}H_{28}Cl_2N_2V_2$: C, 48.56; H, 6.34; N, 6.29. Found: C, 48.53; H, 6.33; N, 6.09.

Preparation of $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]VCl(\eta^2\text{-}PhC\equiv CPh)$ (3). A solution of **2** (148 mg, 0.33 mmol) together with PhC≡CPh (118 mg, 0.66 mmol) in 5 mL of THF was stirred overnight at room temperature. The solvents were removed in vacuo, and the resulting solid was stripped with two portions of 5 mL of ether. The red solid was repeatedly extracted with 30 mL portions of ether. The red extracts were filtered and concentrated to 5 mL. Cooling to −30 °C produced red crystals of **3** (152 mg, 0.38 mmol, 57%). IR (Nujol mull): 689, 722, 754, 773, 802, 912, 921, 1001, 1024, 1044, 168, 1098, 1260, 1377, 1461, 1498, 1587, 1603, 1636, 2854, 2924, 2954 cm^{-1}. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 5.12 ($\Delta\nu_{1/2}$ = 11 Hz), 5.07 ($\Delta\nu_{1/2}$ = 18 Hz), 4.89 (s, 2H, Ph), 4.87 (s, Ph), 4.86 (s, Ph), 4.66 ($\Delta\nu_{1/2}$ = 12 Hz), 4.61 (s), 4.46 (s). Anal. Calcd for $C_{23}H_{24}ClNV$: C, 68.92; H, 6.04; N, 3.49. Found: C, 69.11; H, 5.89; N, 3.36.

Preparation of $[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2NMe_2]V(C_4Ph_4)$ (4). To 0.3 g of activated Mg (12.3 mmol) was added a solution of **2** (124 mg, 0.28 mmol) together with PhC≡CPh (200 mg, 1.12 mmol) in 5 mL of THF at −30 °C. After 20 min, the solution changed from violet to deep red. The solution was warmed to −5 °C over another 40 min. The solvent was removed in vacuo and the residue stripped with two 5 mL portions of pentane. The brown-red solid was repeatedly extracted with 30 mL of pentane. The extracts were filtered and concentrated to 5 mL. Cooling to −30 °C produced brown-red crystals of **4** (193 mg; 0.36 mmol; 59.6%). IR (Nujol mull): 695, 721, 753, 773, 784, 828, 842, 925, 957, 995, 1023, 1071, 1097, 1113, 1152, 1262, 1326, 1377, 1461, 1484, 1584, 2853, 2923, 2951 cm^{-1}. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 7.61, 7.59 (d, 4 H, Ph), 7.00–6.88 (m, 12 H, Ph), 6.37 (t, 2 H, J = 2.1 Hz, Cp), 4.45 (t, 2 H, J = 2.1 Hz, Cp), 1.79 (t, 2H, J = 6.3 Hz, CpCH_2), 1.44 (t, 2H, J = 6.3 Hz, CH_2N), 1.28 (s, 6 H, NMe$_2$). ^{13}C NMR (benzene-d_6, 20 °C, 75.4 MHz): δ 25.45 (t, CpCH_2), 48.52 (q, NMe$_2$), 69.70 (t, NCH_2), 94.93 (b, C═C), 104.42 (b, Cp C), 123.70, 124.02, 125.14, 127.14, 127.39, 127.61, 133.91, 141.55, 150.92 (all, b, Ph C), 263.64 (b, V═C). Anal. Calcd for $C_{37}H_{34}NV$: C, 81.75; H, 6.30; N, 2.58. Found: C, 81.75; H, 6.38; N, 2.50.

Structure Determinations. Suitable crystals for single-crystal X-ray diffraction were obtained by cooling solutions of the compounds in pentane (**2** and **4**) and diethyl ether (**3**). Crystals were mounted on a glass fiber inside a drybox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were collected with Mo Kα radiation (λ = 0.710 73 Å). Intensity data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS[18]). The structures were solved by Patterson methods, and extention of the

(18) Sheldrick, G. M. SHELXL-97 Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

models was accomplished by direct methods applied to difference structure factors using the grogram DIRDIF.[19] Hydrogen atom coordinates and isotropic thermal parameters were refined freely unless mentioned otherwise. All refinements and geometry calculations were performed with the program packages SHELXL and PLATON. Crystallographic data and details of the data collections and structure refinements are given in Table 4.

(19) Spek, A. L. PLATON Program for the Automated Analysis of Molecular Geometry, Version April 2000; University of Utrecht, Utrecht, The Netherlands, 2000.

Supporting Information Available: CIF files giving details of the structure determinations of **2**–**4**, including crystal data, positional and thermal parameters, and interatomic distances and angles. This material is available free of charge via the Internet at http:/pubs.acs.org.

OM8000718