

Bridging Azines in the Coordination Sphere of Low-Valent Vanadocene **Derivatives**[†]

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Complexes of vanadocene(II) and -(III) derivatives with aromatic N-heterocyclic ligands are scarcely known. Here we present the first syntheses of several mono-, di-, and trinuclear complexes of this type and their detailed characterization. Reactions of vanadocene(II) derivatives are limited to N-heterocycles with distinct π -acceptor ability such as 4,4'-azobis(pyridine), which reacts as a bridging ligand to form $[(Cp_2V)_2(\mu_2-Py_2N_2)]$ (13). In contrast Cp_2V^{II} reacts with, for example, 1,2-bis(4-pyridiyl)acetylene (C_2Py_2) solely to give the corresponding metallacyclopropene $[Cp_2V(\eta^2-C_2Py_2)]$ (12) without affecting the pyridyl moieties. On the other hand, the reactivity of vanadocene(III) cations with this class of ligands is unrestricted and dominated by the acid-base properties of the reactants. The application of permethylated cyclopentadienyl ligands (Cp*) significantly enhances the solubility of those complexes, which leads to a better crystallizability. Due to the cationic properties of vanadocenium(III) derivatives, reactions with the smallest aromatic bridging N-heterocycle, pyrazine, afforded the rarely known mononuclear pyrazine complexes $[Cp'_2V(Pz)][BPh_4]$ (Cp' = Cp (17), Cp^* (20); $Pz = C_4H_4N_2$), whereas other N-heterocycles with expanded π -systems such as 4,4'-bipyridine (4-Bipy), C₂Py₂, and 1,3,5-tris(4-pyridyl)-2,4,6-triazine (4-TPT) grant access to multinuclear vanadocenium(III) derivatives ($[(Cp*_2V)_2(\mu_2-4-Bipy)]$ -[BPh₄]₂ (21), [(Cp*₂V)₂(µ₂-Py₂C₂)][BPh₄]₂ (24), [(Cp*₂V)₃(µ₃-4-TPT)][BPh₄]₃ (26)). Compositions of all these complexes were confirmed by single-crystal X-ray diffraction.

Introduction

The design of highly ordered supramolecular architectures by metal-directed self-assembly has attracted more and more attention over the last few decades. Due to this concept, it is possible to create a wide variety of two- and three-dimensional structures by combining simple building blocks.^{1–9} Bridging ligands in those complexes are often based on aromatic N-heterocycles because of their great electronic and steric versatility.^{10,11} Among their ability to connect metal centers by forming metal-ligand bonds, the π -back-bonding properties of

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this class of ligands is of particular interest, which can effect electron transfer and delocalization between the metal centers.^{10,12–17} In contrast to the highly developed supramolecular chemistry of late transition metals, only a few examples are known of well-defined multinuclear architectures of early transition metals.^{15–21}

Within the scope of our investigations on the reactivity of low-valent titanocene precursors^{22,23} with aromatic N-heterocyclic ligands, we could establish new routes to form

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molecular squares and rectangles with formally tetrahedral coordinated metal corners, 15,16 as well as squares with endon and side-on coordinated metal centers.¹⁷ The latter is the first example of a trans to cis rearrangement of 4,4'-azobis-(pyridine) in metal complexes due to side-on coordination of the azo group, which is induced by the electronic properties of titanocene fragments. Furthermore, we described the synthesis and characterization of trinuclear titanocene chelate complexes with interesting redox and electronic properties.^{24,25}

Although a rich chemistry of titanocene derivatives is known, the metallocene chemistry of the adjacent group 5 element vanadium is much less developed. The lack of knowledge is primarily based on the odd electron numbers of vanadocene complexes, which induce paramagnetism and hence hinder further spectroscopic analysis. Therefore, the characterization of vanadocene derivatives is dominated by IR spectroscopy and especially by X-ray diffraction.

However, there are also some advantages of vanadocene chemistry in comparison to that of its titanium analogues. Vanadocene(II) (1) is the first stable metallocene of the 3d early transition metals, $^{26-28}$ whereas titanocene(II) derivatives need π -acceptor ligands to stabilize the highly reactive complexes in a *bent* metallocene structure.²⁹ The same applies to vanadocene(III) cations, in spite of being isoelectronic with titanocene(II); thus, there are no competitive ligands in the reactions of $1.^{30,31}$ Owing to their one additional electron in comparison to corresponding titanocene complexes, interesting electronic effects in multinuclear vanadocene complexes should be observed.

Thanks to the *high-spin* configurations of free low-valent vanadium sandwich compounds,^{30–33} coordination of more than one additional ligand is scarcely observed.^{29,34-38} Because of this, only a few binuclear vanadocene(II) and -(III) complexes are known in literature, using keto,³⁹ acetylene,^{40,41}

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Figure 1. Known low-valent vanadocene(II) and -(III) complexes with aromatic N-heterocyclic ligands.

and activated nitrile groups^{38,42} just as lithiated hydrocarbons⁴³ as binding sites. Multinuclear low-valent vanadocene complexes with, for example, aromatic N-heterocycles, one of the most common class of ligands in coordination chemistry, are still unknown.

Here we report on the synthesis and characterization of new bi- and trinuclear decamethylvanadocene(II) and -(III) complexes with some popular bridging aromatic N-heterocycles. Additionally, we present several mononuclear (decamethyl)vanadocenium(III) complexes with pyridine as well as pyrazine, which is quite inconvenient for the simplest six-membered aromatic N-heterocyclic bridging ligand. All structures have been confirmed by single-crystal X-ray diffraction.

Surprisingly, only two mononuclear low-valent vanadocene complexes with aromatic N-heterocyclic ligands (2 and 3) had been reported first by Floriani et al. until the beginning of our studies (Figure 1);^{37,44} therefore, new routes had to be established to enter this kind of vanadocene chemistry.

Results and Discussion

To gain access to vanadocene azine chemistry, we initially reproduced the 2,2'-bipyridine (2-Bipy) complex 2 of Floriani et al., in which the authors assumed a monodentate 2,2'-bipyridine coordination to avoid an unfavorable 19e complex, due to the lack of structural information. We were able to prove the bidentate coordination of the chelate ligand by X-ray diffraction; however, one cyclopentadienyl ring (Cp) performed a rarely observed ring slippage to η^3 coordination, even in the solid state to form the preferred 17e complex.⁴⁵ Formal one-electron oxidation of 2 by ferrocenium salt led to the stable 18e complex cation in which both Cp ligands were arranged in the usual η^5 coordination. Subsequently, we intensified our studies in vanadocene complexes with bridging N-heterocyclic ligands. In the following, we describe the synthesis and characterization of neutral complexes of vanadocene(II) derivatives and cationic complexes of vanadocenium(III) derivatives.

Complexes of Vanadocene(II) Derivatives. Vanadocene(II) derivatives are well-known 15e complexes with three unpaired electrons.^{32,33} This results in the occupation of all bonding orbitals of the metallocene with at least one electron. Thus, only donor ligands with certain π -back-donating properties have the ability to coordinate to the vanadium center by partial reduction. As mentioned above, this generally includes aromatic N-heterocycles. On the basis of redox potentials, which can be generally determined by cyclic voltammetry (CV), a

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Table 1. First Redox Potentials $(E_{1,2})$ of Applied Aromatic N-Heterocycles Converted to Fc/Fc⁺ Standard

| compd | $E_{1/2}\left(\mathbf{V}\right)^{a}$ | solvent | ref |
|----------------------|--------------------------------------|---------|-----|
| Py (5) | -3.215 | DMF | 50 |
| Pz (6) | -2.584 | DMF | 50 |
| 2-Bipy (7) | -2.617 | DMF | 50 |
| 4-Bipy (8) | -2.320 | DMF | 50 |
| $4 - C_2 P y_2 (9)$ | -2.232 | MeCN | 51 |
| $4 - N_2 P y_2$ (10) | -1.249 | DMF | 52 |
| 4-TPT (11) | -1.720 | PhCN | 53 |

^{*a*} Vs Fc/Fc⁺ standard.

qualitative valuation of the capability of vanadocene(II) derivatives to transfer electrons on these N-heterocycles should give an indication for suitable reactant combinations. However, it should be outlined that this method of comparison is by rule of thumb, due to great influences on the shape and orientation of cyclic voltammograms by experimental parameters such as the choice of solvent, scan rate, and the choice of electrodes. Though the much more positive redox potentials of the vanadocene(II) derivatives compared to those of most of the azine derivatives should limit the choice of potential ligands, because electron transfer can formally occur from the reactant with more negative potential to the reactant with more positive redox potential. Table 1 shows the redox potentials of applied aromatic N-heterocycles versus the Fc/Fc^+ couple⁴⁶ compared to vanadocene(II) (1, $E_{1/2} = -1.134$ V vs Fc/Fc⁺, thf)⁴⁷ and decamethyl-vanadocene(II) (4).⁴⁸ In contrast to that, more strongly reducing properties are found, as expected, in the case of titanocene complexes (Cp₂TiCl₂, $E_{1/2} = -1.38$, -2.68, -2.96 V vs Fc/ Fc⁺, thf).⁴⁹

The low affinity of vanadocene(II) derivatives to aromatic N-heterocycles was exemplified in the reaction of 1 with 1,2bis(4-pyridyl)acetylene (9, 4-C₂Py₂), exhibiting an acetylene spacer as a second sort of binding site between the pyridyl rings. Owing to the highly negative redox potential of N-heterocyclic ligand 9, vanadocene(II) (1) exclusively coordinated to the C–C-triple bond to form, even with an excess of the metal complex, the corresponding acetylene complex 12, best described as metallacyclopropene (Scheme 1), which could be proved by X-ray diffraction (Figure 2). Furthermore, the side-on coordination of the acetylene moiety was shown by IR spectroscopy ($\tilde{\nu}$ (C=C) 1782, 1771, 1745 cm⁻¹). For a complete characterization, the decomposition point (134–136 °C), mass spectra, and elemental analysis were determined.

The best yields were achieved by equimolar mixing of vanadocene(II) (1) and ligand 9 in toluene. During stirring of the resulting solution for 1 day at room temperature, its color changed from violet to yellow-brown. Brown crystals of 12, which were suitable for X-ray diffraction, could be obtained in

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Figure 2. ORTEP plot of the solid-state molecular structure of **12**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity; one of two independent molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): V1-C1 = 2.129(2), V1-C2 = 2.080(2), V1-Ct1 = 1.97, V1-Ct2 = 1.97, C1-C2 = 1.290(3), N1-C3 = 1.351(3), C3-C4 = 1.379(3), C4-C5 = 1.400(3), C5-C1 = 1.460(3), C5-C6 = 1.396(3), C6-C7 = 1.386(3), C7-N1 = 1.337(3), C2-C10 = 1.468(3), N2-C8 = 1.343(3), C8-C9 = 1.385(3), C9-C10 = 1.385(3), C1-C11 = 1.397(3), C11-C12 = 1.383(3), C12-N2 = 1.338(3); C1-V1-C2 = 35.67(8), Ct1-V1-Ct2 = 139.6 (Ct1 = ring centroid of C13-C17, Ct2 = ring centroid of C18-C22).

Scheme 1. Reaction of 1 and 9 To Give Metallacyclopropene 12



55% yield by cooling the reaction mixture to $-40 \,^{\circ}\text{C}$ for several days. Complex **12** crystallizes in the triclinic space group $P\overline{1}$ with four complex molecules per unit cell and two independent complex molecules in the asymmetric unit. The coordinated acetylene bridge is widened to 1.290 Å due to π -back-donation to the vanadium center, and the V–C bond lengths are in the range of comparable vanadocene(II) acetylene complexes (average 2.102 Å).^{54–56} In accordance with the changed hybridization of the coordinated C atoms C1 and C2, an C5–C1–C2 angle of 144.7(2)° (C1–C2–C10 = 139.5(2)°) was found. This value is comparable to those for typical acetylene complexes of early transition metals (e.g., Cp₂V(η^2 -C₂(C₆F₅)₂) 142.3(4)°,⁵⁵ Cp₂Ti(η^2 -C₂(SiMe₃)₂) average 146.7(4)°).²³

To the best of our knowledge, there is only one additional complex of **9** exhibiting an exclusively C–C coordination mode, found for the Co_2CO_6 fragment.^{57,58} Generally, derivatives of **9** are often used as building blocks employing late transition metals which have high affinity to the pyridyl

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Figure 3. ORTEP plot of the solid-state molecular structure of 13. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1-N1 = 2.126(2), V1-Ct1 = 2.01, V1-Ct2 = 2.01, N1-C1 = 1.383(4), C1-C2 = 1.370(4), C2-C3 = 1.436(5), C3-C4 = 1.461(5), C4-C5 = 1.396(4), C5-N1 = 1.368(4), C3-N2 = 1.365(4), N2-N2' = 1.372(6); Ct1-V1-Ct2 = 145.9 (Ct1 = ring centroid of C6-C10, Ct2 = ring centroid of C16-C20). Symmetry transformation for the generation of equivalent atoms: -x + 1, -y + 1, -z.

Scheme 2. Reaction of 4 with 10 Leading to the Formation of Binuclear Complex 13



moieties to form bi-⁵⁹ or multinuclear complexes, particularly in self-assembling processes.^{57,60,61}

In contrast to most of the N-heterocyclic ligands, the redox potential of 4,4'-azobis(pyridine) (10, $4-N_2Py_2$) seems to be located in an acceptable range with respect to the potentials of vanadocene(II) (1) and decamethylvanadocene(II) (4) to force a metal-to-ligand electron transfer which in turn afforded the complexation of the ligand to the metal center by the pyridyl moieties (vide supra). Reaction of 1 with 10 resulted in the precipitation of a brown amorphous solid that could not be identified. Due to the higher solubility of the permethylated vanadocene(II) derivative 4, we were able to grow crystals of the new binuclear complex 13 (mp 165-166 °C dec) by slow diffusion of a layered *n*-hexane solution of 10 into a toluene solution of decamethylvanadocene(II) (4). The color of the solution at the phase interphase changed immediately to dark brown, and black crystals of 13 grew over a period of a few days. The structural characterization proved the coordination of 4 to the pyridyl moieties of $4-N_2Py_2$ (10), which led to the formation of the first binuclear decamethylvanadocene(II) complex 13 with an N-heterocyclic bridging ligand in 56% vield (Scheme 2). In contrast to titanocene chemistry¹⁷ the usual trans modification of introduced 10 remained in the complex and complexation of the azo bridge by 4 was not observed, although side-on azo coordination of related azobenzene with vanadocene(II) (1) had been explored.^{62,63}

Binuclear complex 13 crystallizes in the monoclinic space group $P2_1/n$ with two complex molecules and four toluene molecules per unit cell. The crystal structure of 13 is shown in Figure 3.

Table 2. Comparison of Selected Bond Lengths (\AA) of the 4-N₂Py₂ Ligand (10) and Complex 13

| | 10 ^{<i>a</i>} | 13 |
|--------|-------------------------------|----------|
| C3-N2 | 1.444(2) | 1.365(4) |
| N2-N2′ | 1.251(2) | 1.372(6) |
| N1-C1 | 1.340(2) | 1.383(4) |
| N1-C5 | 1.336(2) | 1.368(4) |
| C1-C2 | 1.384(2) | 1.370(4) |
| C2-C3 | 1.393(2) | 1.436(5) |
| C3-C4 | 1.383(2) | 1.461(5) |
| C4-C5 | 1.388(2) | 1.396(4) |

^{*a*} Reference 17.

The V–N bond length in **13** (2.126(2) Å) is significantly longer than in 2-Bipy complex **2** (average 2.04 Å) due to the rigid chelate coordination of 2-bipy (7),⁴⁵ and the distances of η^5 -coordinated 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) ligands are within the expected range of decamethylvandocene complexes (2.01 Å).⁶⁴

An activation of the azo bridge is observable in regard to a significant widening of the azo double bond (N2=N2') from 1.251(2) Å in free 4,4'-azobis(pyridine) (10) to 1.372(2) Å, which is almost as long as the N-N single-bond length in 1,2-bis(4-pyridyl)hydrazine (1.3934(1) Å).¹⁷ In conjunction with the shortening of adjacent C3-N2 bonds (1.444(2) Å in 10 to 1.365(4) Å in 13) a reduction of the ligand by the metal centers can be assumed. A slight chinoid distortion of the pyridyl moieties in 13 confirms this assumption (Table 2).

Hence, in principle the proposed relation of redox potentials of vanadocene(II) derivatives and aromatic N-heterocycles to their coordination ability could give an indication of feasible reactant combinations in these reactions.

Owing to the activation of the azo bridge in 13, an N–N bond cleavage was found in the CI mass spectra. Even in high-resolution mode a decamethylvanadocene(II) complex

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Figure 4. ORTEP plot of the solid-state molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1-N1 = 2.1389(18), V1-Ct1 = 1.94, V1-Ct2 = 1.94, N1-C1 = 1.350(3), C1-C2 = 1.377(3), C2-C3 = 1.378(3), C3-C4 = 1.382(3), C4-C5 = 1.374(3), C5-N1 = 1.341(2), B1-C16 = 1.655(3), B1-C22 = 1.649(4), B1-C28 = 1.669(3), B1-C34 = 1.651(3); Ct1-V1-Ct2 = 143.1 (Ct1 = ring centroid of C6-C10, Ct2 = ring centroid of C11-C15).

Scheme 3. Preparation of 3 via Salt Metathesis of 14 and 15 Initiated by Pyridine Addition



with coordinated protonated 4-aminopyridine ligand was identified as the base peak (m/z 415.2). This was evidenced by the identification of the protonated 4-aminopyridine fragment (m/z 95.1) as well as the ionic decamethylvanadocene fragment (m/z 321.2).

Complexes of Cationic Vanadocenium(III) Derivatives. Up to now, there have only been two examples of vanadocenium(III) complexes with aromatic N-heterocyclic ligands. In addition to our recently reported 2-Bipy complex of vanadocenium(III) cation,⁴⁵ Floriani et al. produced the cationic vanadocenium(III) pyridine complex **3** by salt metathesis of vanadocene(III) chloride (**14**)⁶⁵ with sodium tetraphenylborate (**15**) initiated by an excess of basic pyridine (**5**, Py) (Scheme 3).³⁷

In order to confirm their results by X-ray diffraction, we succeeded in growing crystals of the complex by slight modification of the literature procedure. Complex **3** crystallizes in the orthorhombic space group $Pna2_1$ with four ion pairs per unit cell. The crystal structure confirms the coordination of one pyridine ligand to form a cationic 16e complex (Figure 4). This behavior is quite usual for vanadocenium(III) derivatives. Coordination of one additional ligand to build up a stable 18e complex is not preferred, because of the low energy gap between the two singly occupied orbitals, making spin pairing unfavorable.⁶⁶ Furthermore, in contrast to

Scheme 4. Formation of Mononuclear Complex 17 by Reaction of [Cp₂V][BPh₄] (16) with Pyrazine (6)



vanadocene(II) derivatives, the coordination of N-heterocyclic ligands to vanadocenium(III) derivatives is not hindered, thanks to the lack of one electron in this oxidation state. Hence, free electron pairs of N-heterocycles are allowed to donate into the unoccupied bonding orbital.

The crystal structure of **3** shows that the V1–N1 bond length is not significantly longer than in decamethylvanadocene(II) complex **13** (2.1389(18) Å) and V–Ct distances are within the expected range (average 1.94 Å). The decomposition point was determined to be 210–212 °C.

Application of the salt metathesis concept to other Nheterocyclic ligands such as pyrazine (6, Pz) or 4, 4'-bipyridine (8, 4-Bipy) failed because of the poor solubility of the formed cationic vanadocenium(III) complexes. However, a procedure we recently established for reactions of vanadocenium-(III) cations with chelating aromatic N-heterocycles led to a crystalline product for the reaction with Pz(6).⁴⁵ Therefore, a thf solution of vanadocenium(III) tetraphenylborate (16, $[Cp_2V][BPh_4]$ ³⁰ was layered with a small amount of diethyl ether that was layered with an *n*-hexane solution of **6** as well. In spite of the solubility properties of the uncoordinated metallocenium salt as well as the product, dark blue crystals, which were suitable for X-ray diffraction, were grown after several days on the wall of the flask. The crystal structure confirmed the formation of mononuclear complex 17 in 43% yield (Scheme 4), even with an excess of vanadium(III) compound 16. This behavior is in contrast to that of the isoelectronic titanium(II) fragments, which form tetranuclear complexes with pyrazine.^{15,16}

Compound 17 crystallizes in the orthorhombic space group $Pna2_1$ with cell parameters almost identical with those of the very similar pyridine complex 3 (Figure 5). The mononuclear coordination of pyrazine seems to be a result of the deactivation of its second nitrogen moiety, thanks to the positive charge introduced by the vanadocenium(III) cation. To the best of our knowledge, this coordination mode of pyrazine is completely unknown for early transition metals, but there are several examples of singly coordinated pyrazine complexes with late transition metals in the literature.^{67–74}

The second nitrogen does not have any effect on the V1–N1 bond length (2.135(3) Å) in 17 compared to pyridine complex 3 (2.1389(18) Å), but the cell parameters of both crystal structures

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Figure 5. ORTEP plot of the solid-state molecular structure of **17**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1-N1 = 2.135(3), N1-C1 = 1.372(4), C1-C2 = 1.398(6), C2-N2 = 1.300(6), N2-C3 = 1.295(6), C3-C4 = 1.373(6), C4-N1 = 1.372(4), B1-C15 = 1.702(4), B1-C21 = 1.709(4), B1-C27 = 1.717(3), B1-C33 = 1.707(4), V1-Ct1 = 1.94, V1-Ct2 = 1.95; Ct1-V1-Ct2 = 142.6 (Ct1 = ring centroid of C5-C9, Ct2 = ring centroid of C10-C14).

give detailed information about the steric demands of both heterocyclic ligands (Table 4). The volume of the unit cell of pyridine complex **3** is 14.2 Å³ larger than of the pyrazine complex **17**. Because the C–H group is spatially larger than the nitrogen with its free electron pair, the Py ligand needs approximately $3.5 Å^3$ more space in the crystal lattice than the Pz ligand calculated for four ion pairs per unit cell. In addition, a significant distortion of the coordinated Pz ligand in **17** is visible. The N–C bonds of the coordinated N1 atom (1.372(4) Å) are 0.072–0.077 Å longer than those of the uncoordinated N2 atom (1.295(6), 1.300(6) Å).

To explore the coordination behavior of the other bridging N-heterocycles with extended π systems, it was mainly necessary to increase the solubility of the applied vanadocenium(III) salts. The substitution of the Cp ligand with Cp* led to success. Decamethylvanadocenium(III) tetraphenylborate (18, [Cp*₂V]-[BPh₄])³¹ is quite soluble in thf and other polar solvents. Hence, for comparison reasons we tested the reactivity of 18 to already described simple N-heterocycles Py (5) and Pz (6). Reactions occurred in thf solution by heating at 60 °C for several days without stirring. In contrast to the reactions with unsubstituted [Cp₂V][BPh₄] (16), reaction products remained in solution, whose color changed from brown to green. The resulting complexes are more soluble than free 18. After they were cooled to room temperature, the reaction mixtures were filtered from the remaining solids and the solutions were layered with the same amount of n-hexane, which forced crystallization of the products. Both pyridine complex 19 (48%) and pyrazine complex 20 (32%) had compositions identical with those of their unsubstituted derivatives (Scheme 5).

Especially, the renewed formation of mononuclear pyrazine complex **20** confirms the great influence of oxidized vanadium-(III) centers on the donating properties of the second nitrogen moiety of the bis(azine) ligand **6**. However, a comparison of cell parameters is not possible. Due to certain solvent insertions, the permethylated complexes crystallize in different space groups. All molecular parameters are within the expected ranges. For

detailed structural information, the crystal structures of **19** and **20** are given in the Supporting Information. Furthermore, the characterization of these complexes was completed by mass spectrometry, infrared spectroscopy, and determination of decomposition points as well as elemental analysis.

Owing to the interesting inhibition of a second (decamethyl)vanadocenium(III) coordination at the pyrazine ligand, the influence of the bridge length of N-heterocycles on the coordination behavior of decamethylvanadocenium(III) cations was explored.

4,4'-Bipyridine (8, 4-Bipy) is a very common bridging ligand in coordination chemistry.^{4,16,75,76} The reaction with $[Cp*_2V][BPh_4]$ (18) in thf at 60 °C afforded the first binuclear decamethylvanadocenium(III) complex, 21 (mp 258–260 °C dec) with an N-heterocyclic bridging ligand within several days (Scheme 6). By layering of the green reaction mixture with *n*-hexane at room temperature, 21 crystallized as green-brown blocks in 51% yield. The expanded π system of 4-Bipy (8) compared to Pz (6) allows complexation of both binding sites; thus, the inhibition effect of the first cationic decamethylvanadocenium(III) complexation no longer influences the coordination of the nitrogen moiety in the second pyridyl ring. Dicationic complex 21 crystallizes in the monoclinic space group C2/c with 4 dications and 8 tetraphenylborate anions as well as 16 disordered thf molecules in the unit cell (Figure 6).

The V–N bond lengths in complex **21** (2.142(2) Å) are almost as long as in vanadocenium(III) complexes **3** and **17**. A closer look at the bond lengths of the bridging ligand confirms that an electron transfer from the metal on the ligand is prohibited in **21**. In contrast, for the isoelectronic neutral decamethyltitanocene 4-Bipy complex, a metal–ligand charge transfer (MLCT) band is observed.⁷⁷ The reduction was verified by a shortening of the C–C bond between both pyridyl rings (1.392(7) Å) and coplanarity of the bridging ligand, due to the formation of a chinoid ligand π system (Scheme 7).¹⁶

However, in the decamethylvanadocenium(III) complex **21** the C3–C3' bond length is comparable to that of free 4-Bipy (**8**) as well as the twist angle of the pyridyl rings against each other. Table 3 compares the structural parameters of **21** with corresponding datas of free 4-Bipy (**8**) and reduced trimethylsilyl-substituted derivative **23**, which have already been reported by our group.¹⁶

Additionally, mass spectrometric and infrared spectroscopic investigations as well as elemental analysis confirmed the composition of complex **21**.

1,2-Bis(4-pyridyl)acetylene (9) is another suitable bridging ligand. Although the reactivity of the pyridyl moieties to vanadocene(II) derivatives is low (vide supra), the complexation of vandocenium(III) derivatives to the pyridyl nitrogens was successful. Reaction of $[Cp*_2V][BPh_4]$ (18) with 9 in thf afforded small brown needles of binuclear complex 24 (mp 265–267 °C dec), which precipitated directly from the solution in 6% yield (Scheme 8).

We were able to prove the composition of **24** by X-ray diffraction, but due to the small size of the crystals, a discussion of bond lengths and angles was not reasonable. Therefore, the synthesis of **24** had to be modified to obtain larger crystals. In the end we were able to get larger crystals as well as a higher yield

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Scheme 5. Reaction of [Cp*₂V][BPh₄] (18) with Pyridine (5) and Pyrazine (6) to Give Mononuclear Decamethylvanadocenium(III) Complexes 19 and 20



Figure 6. ORTEP plot of the solid-state molecular structure of **21**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1–N1 = 2.142(2), N1–C1 = 1.360(3), C1–C2 = 1.389(3), C2–C3 = 1.394(4), C3–C4 = 1.403(3), C4–C5 = 1.382(4), C5–N1 = 1.351(3), C3–C3' = 1.495(5), V1–Ct1 = 1.99, V1–Ct2 = 1.99; Ct1–V1–Ct2 = 147.5; B1–C26 = 1.656(4), B1–C32 = 1.655(4), B1–C38 = 1.662(4), B1–C44 = 1.664(4) (Ct1 = ring centroid of C6–C10, Ct2 = ring centroid of C16–C20). Symmetry transformation for the generation of equivalent atoms: -x + 1, y, $-z + \frac{1}{2}$.

Scheme 6. Formation of Binuclear Complex 21 by Reaction of 18 with N-heterocyclic Ligand 8





Scheme 7. General Reduction of 4,4'-Bipyridine



Table 3. Bond Lengths and Twist Angles for Free (8), Reduced (23), and Coordinated 4,4'-Bipyridine (21)

| | C'–C' [Å] | Twist angle [deg.] | Ref. |
|----|------------|--------------------|-----------|
| | 1.4842(19) | 34.1 | 16 |
| 8 | 1.4895(18) | 18.1 | |
| | 1.381(3) | 0 | 16 |
| 21 | 1.495(5) | 32.1 | this work |

Scheme 8. Reaction of [Cp*₂V][BPh₄] (18) and 4-C₂Py₂ (9) to Give Binuclear Complex 24



of 24 by a totally unexpected route. The main purpose of the reaction of acetylene complex 12 with $[Cp*_2V][BPh_4]$ (18) was the formation of the trinuclear mixed-valent complex 25, in which two V(III) centers were connected via pyridyl coordination with the side-on-coordinated V(II) center (Scheme 9). However, 24 crystallized solely as large brown needles directly from the reaction mixture. After that observation the reaction procedure was optimized by starting with an in situ reaction of vanadocene(II) (1) with ligand 9 in thf to form the acetylene complex 12. Subsequent addition of a thf solution of $[Cp*_2V]$ [BPh₄] (18) and heating to 60 °C for several days without stirring caused a slow precipitation of 24 in 42% yield, which was suitable for X-ray diffraction (Scheme 9). We presume that the

| | | Table 4. Crystal Str | ucture Data for Comp | ounds 3, 12, 13, 17, 21 | , 24, and 26 | | |
|--|---|--|--|---|---|---|---|
| | 3 | 12 | 13 | 17 | 21 | 24 | 26 |
| empirical formula formula wt | C ₃₉ H ₃₅ BNV 579.43 | C ₂₂ H ₁₈ N ₂ V 361.32 | C ₆₄ H ₈₄ N ₄ V ₂ 1011.23 | C ₃₈ H ₃₄ BN ₂ V 580.42 | $\begin{array}{c} C_{114}H_{140}B_2N_2O_4V_2\\ 1725.78 \end{array}$ | C ₁₀₀ H ₁₀₈ B ₂ N ₂ V ₂ 1461.38 | $\begin{array}{c} C_{186}H_{206}B_{3}F_{8}N_{6}V_{3}\\ 2862.82 \end{array}$ |
| color | blue | yellow-brown | brown | blue | green-brown | black | black |
| cryst dimens (mm) | 0.50	imes 0.40	imes 0.03 | 0.35 	imes 0.15 	imes 0.06 | 0.40	imes 0.26	imes 0.14 | 0.30 	imes 0.18 	imes 0.16 | 0.35 	imes 0.22 	imes 0.19 | 1.30 	imes 0.22 	imes 0.12 | 1.30 	imes 0.26 	imes 0.26 |
| cryst syst | orthorhombic | triclinic | monoclinic | orthorhombic | monoclinic | monoclinic | trigonal |
| space group | $Pna2_1$ | PI | $P2_1/n$ | $Pna2_1$ | C2/c | $P2_{1/C}$ | P3c1 |
| a (Å) | 19.5674(14) | 7.9771(7) | 11.3996(6) | 20.7795(10) | 19.5977(8) | 11.6718(6) | 22.8523(11) |
| $p\left(\overset{\circ}{A}\right)$ | 9.8425(5) | 14.1609(17) | 13.5491(11) | 9.4920(6) | 15.6230(9) | 24.0590(16) | 22.8523(11) |
| $c(\mathbf{A})$ | 15.7720(9) | 15.860(2) | 18.5308(10) | 15.3284(14) | 32.2035(14) | 15.1460(7) | 18.2102(7) |
| a (deg) | 90 | 89.351(15) | 90 | 90 | 90 | 90 | 06 |
| β (deg) | 90 | 87.114(13) | 103.220(6) | 90 | 91.522(5) | 104.370(6) | 90 |
| γ (deg) | 90 | 75.525(12) | 90 | 90 | 90 | 90 | 120 |
| $V(\dot{A}^3)$ | 3037.6(3) | 1732.5(4) | 2786.3(3) | 3023.4(4) | 9856.4(8) | 4120.1(4) | 8235.8(6) |
| Ζ | 4 | 4 | 2 | 4 | 4 | 2 | 2 |
| $D_{\rm calcd} ({\rm g} {\rm cm}^{-3})$ | 1.267 | 1.385 | 1.205 | 1.275 | 1.163 | 1.178 | 1.154 |
| $\mu (\mathrm{mm}^{-1})$ | 0.355 | 0.578 | 0.378 | 0.358 | 0.243 | 0.275 | 0.229 |
| $T(\mathbf{K})$ | 153(2) | 153(2) | 153(2) | 153(2) | 153(2) | 153(2) | 153(2) |
| θ range (deg) | 2.32 - 26.09 | 2.69 - 26.20 | 2.26 - 26.12 | 2.36 - 26.06 | 2.08 - 26.15 | 2.16 - 26.11 | 2.06 - 26.13 |
| no. of rflns collected | 24 512 | 21 785 | 25917 | 25675 | 43 251 | 44 272 | 70 703 |
| no. of indep rflns $(R(int))$ | 5983 (0.0562) | 6455(0.0671) | 5335 (0.0997) | 5903 (0.0711) | 9772 (0.0744) | 7736 (0.0554) | $10\ 314\ (0.0736)$ |
| no. of rflns with $I > 2\sigma(I)$ | 4244 | 3597 | 2848 | 3756 | 5498 | 5274 | 6385 |
| abs cor | numerical | numerical | numerical | numerical | numerical | numerical | numerical |
| max, min transmissn | 0.9894/0.8424 | 0.9661/0.8233 | 0.9490/0.8635 | 0.9450/0.9003 | 0.9553/0.9199 | 0.9677/0.7161 | 0.9429/0.7553 |
| no. of data/restraints/params final R indices $(I > 2\sigma(I))$ | 5983/1/379 | 6455/0/451 | 5335/0/326 | 5903/1/331 | 9772/20/543 | 7736/0/488 | 10 314/19/523 |
| R1 | 0.0281 | 0.0302 | 0.0449 | 0.0406 | 0.0521 | 0.0319 | 0.0608 |
| wR2 | 0.0509 | 0.0490 | 0.0932 | 0.0791 | 0.1254 | 0.0664 | 0.1606 |
| R indices (all data) | | | | | | | |
| R1 | 0.0481 | 0.0708 | 0.0932 | 0.0676 | 0.0930 | 0.0540 | 0.0864 |
| wR2 | 0.0536 | 0.0536 | 0.1024 | 0.0840 | 0.1363 | 0.0702 | 0.1687 |
| $\operatorname{GOF} \operatorname{on} F^2$ | 0.767 | 0.695 | 0.794 | 0.770 | 0.843 | 0.842 | 0.880 |
| largest diff peak/hole (e A^{-3}) | 0.312/-0.149 | 0.237 / -0.274 | 0.947 / -0.325 | 0.503 / -0.429 | 0.553/-0.543 | 0.249/-0.275 | 0.672/-0.448 |



Figure 7. ORTEP plot of the solid-state molecular structure of **24**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1-N1 = 2.1311(13), N1-C1 = 1.3468(19), C1-C2 = 1.378(2), C2-C3 = 1.399(2), C3-C4 = 1.403(2), C3-C6 = 1.432(2), C4-C5 = 1.378(2), C5-N1 = 1.350(2), C6-C6' = 1.197(3), V1-Ct1 = 1.99, V1-Ct2 = 1.99; Ct1-V1-Ct2 = 148.1; B1-C27 = 1.648(2), B1-C33 = 1.6564(19), B1-C39 = 1.651(2), B1-C45 = 1.638(2) (Ct1 = ring centroid of C7-C11, Ct2 = ring centroid of C17-C21). Symmetry transformation for the generation of equivalent atoms: -x, -y + 2, -z.

Scheme 9. Synthesis of 24 by Reaction of Acetylene Complex 12 with [Cp*₂V][BPh₄] (18)



reaction starts with the coordination of decamethylvanadocenium(III) cations to the nitrogen binding sites of the pyridyl rings. As in pyrazine complexes **17** and **20**, the complexation provokes a deactivation of the acetylene bridge, by which the dissociation of already complexed vanadocene(II) (1) occurs, accompanied by a back-formation of the C–C triple bond. This was also confirmed by the infrared spectrum of **24**, in which the characteristic band for the complexed acetylene moiety of **12** disappeared.

Complex **24** crystallizes in the monoclinic space group $P2_1/c$, exhibiting two complex dications and four tetraphenylborate anions per unit cell (Figure 7). The V–N bond lengths are within the range of already presented decamethylvanadocenium(III) complexes (2.1311(13) Å) as well as the V–Ct distances (1.99 Å). The bond lengths of the bridging ligand **9** hardly differ from the values for the free ligand **9**.⁷⁸ Hence, as expected, a reduction of the C–C triple bond by metal-to-ligand charge transfer which would lead to bond alternations is not observed.⁵¹ Also, the pyridyl rings in **24** prefer, as in free **9**, a coplanar orientation, because there is no steric hindrance of ortho hydrogens next to the pyridyl connecting bond as in 4,4'-bipyridine, thanks to the acetylene spacer.

The presented complexes show that a connection of a vanadocene center with two additional vanadocene complexes is not possible. Because of that, the only chance to create multinuclear vanadocene complexes with more than two vanadium centers is to enhance the number of pyridyl binding sites of the ligand. In that case, a very well-known example is 1,3,5-tris(4-pyridyl)-2,4,6-triazine (11, 4-TPT), which exhibits three pyridyl moieties connected in para

positions by a central triazine ring.^{53,79–81} A mixture of 4-TPT (11) with 18 in thf was heated to 60 °C for several days without stirring, which led to a green solution. After filtration of the reaction mixture from the remaining poorly soluble ligand 11 at room temperature, the solution was layered with *n*-hexane. Yellow-green crystalline needles of trinuclear complex 26 grew slowly at the phase interphase. The results of our X-ray structural analysis of 26, despite the inclusion of considerable thf in the lattice, were sufficient to establish unequivocally its atom connectivity but not to discuss bond lengths and angles of the complex. By substitution of the reaction solvent thf with the more polar, but also more rigid, noncoordinating 1,2-difluorobenzene,^{31,82} we obtained dark green needles of **26** (mp 248–250 °C dec) in 26% yield, which were suitable for X-ray diffraction (Scheme 10).

Complex **26** crystallizes from 1,2-difluorobenzene/*n*-hexane in the trigonal space group P3c1, exhibiting two tricationic complexes and six tetraphenylborate anions in the unit cell (Figure 8). Owing to symmetry generation of the complex cation a disorder of the central triazine ring is observable, which effects a bending of pyridyl rings toward the triazine plane (13.4°) and a relatively large elongation of the C4–C1a bond length in comparison to that of the free ligand **11** (average 1.490(2) Å;⁸³ **26**, average 1.535(9) Å). In addition, the distortion of the pyridyl rings to the triazine plane is

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Figure 8. ORTEP plot of the solid-state molecular structure of **26**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and tetraphenylborate anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): V1-N2 = 2.135(3), N2-C2 = 1.360(5), C2-C3 = 1.379(6), C3-C4 = 1.374(6), C4-C5 = 1.386(7), C5-C6 = 1.386(6), C6-N2 = 1.348(5), C4-C1a = 1.526(8), C4-C1b = 1.543(9), C1a-N1a = 1.351(9), C1b-N1b = 1.331(10), V1-Ct1 = 1.98, V1-Ct2 = 2.00; Ct1-V1-Ct2 = 148.1 (Ct1 = ring centroid of C7-C11, Ct2 = ring centroid of C17-C21). Symmetry transformation for the generation of equivalent atoms: (a) -y, x - y, z; (b) -x + y, -x, z.

Scheme 10. Reaction of [Cp*₂V][BPh₄] (18) and 4-TPT (11) To Give Trinuclear Complex 26



11.9°, which is also larger than in the crystal structure of free 4-TPT (11: 6.8, 7.9°). However, the V–N bond lengths are again within the range of already presented complexes (2.135(3) Å). An inclusion of 4 equiv of 1,2-difluorobenzene is observed. Three of them undergo $\pi - \pi$ interactions with one Cp* ligand of the decamethylvanadocenium(III) centers



Figure 9. Diamond plot of the solid-state structure of **26**, showing the orientations of 1,2-difluorobenzene molecules (green) and tetraphenylborate anions (purple) with respect to the complex cation.

(3.35–4.14 Å), respectively, and additionally C–H···F interactions with corresponding methyl Cp*-groups are found (2.33 Å). Particularly, one 1,2-difluorobenzene molecule is oriented parallel to the central triazine ring of the 4-TPT ligand (π stacking: 3.35 Å). Furthermore, C–H···F interactions of one phenyl substituent of the tetraphenylborate anions and 1,2-difluorobenzene occur (C–H···F = 2.28 Å). The tetraphenylborate anions are located next to the Cp* ligands, which do not interact with 1,2-difluorobenzene molecules (Figure 9). In turn, the space between them is filled with the adjacent complex cation, which can also be regarded as a structure-defining motive.

The triply charged cation of **26** was also identified by CI and HR-CI mass spectrometry (m/z 425.2162).

Conclusions and Outlook

Aromatic N-heterocycles are useful building blocks in coordination chemistry. Especially, bis(azines) are applicable to build up molecular architectures, which can be partially accompanied by C-C coupling reactions. The latter dominates the chemistry of strongly reducing titanocene derivatives, which is caused by the distinct donor-acceptor properties of the applied complexes and ligands. In contrast, the presented vanadium(II) and -(III) complexes showed a decreased reactivity. Generally, due to the lower reducing properties, no metal-induced C-C couplings were observable. However, N-heterocycles with a certain electron affinity, such as $4-N_2Py_2$ (10), are able to form binuclear complexes with vanadocene(II) derivatives, which, for example, led to the formation of 13. Furthermore, acetylene coordination of vanadocene(II) is preferred in comparison to N-coordination, as can be seen in complex 12. On the other hand, the chemistry of vanadocenium(III) cations is dominated by their Lewis acidity, accompanied by comparably low back-bonding properties. In contrast to the isoelectronic titanocene(II) fragments with their tetrahedral coordination sphere, the vanadocene units formed solely complexes with trigonally coordinated V(III) centers. In addition, the formation of multinuclear vanadocene-(III) complexes required N-heterocyclic ligands with extended π systems, which means with more than one aromatic ring, such as 4-Bipy (8), 4-C₂Py₂ (9), and 4-TPT (11). However, smaller bis(azines) such as Pz (6) were not suitable; hence, only the mononuclear complexes 17 and 20 were formed. Further analytical explorations about electronic and magnetic properties of these complexes are in progress.

Experimental Section

Reagents and General Techniques. All operations were performed under a nitrogen atmosphere with rigorous exclusion of oxygen and moisture using glovebox and Schlenk techniques. All chemicals used were reagent grade or higher and were purified according to standard protocols. Solvents were distilled over Na/K alloy and benzophenone under a nitrogen atmosphere. Chemical ionization (CI) mass spectra were taken on a Finnigan-MAT 95 spectrometer. Isobutane was used as ionization gas. Electrospray ionization (ESI) mass spectra were measured on a Finnigan-LCQ spectrometer. IR spectra were recorded on a Bruker VECTOR 22 spectrometer using KBr pellets. Elemental analyses were carried out by using an EA Euro 3000 from EuroVector, Milan, Italy. Melting points were determined using a Mel-Temp by Laboratory Devices, Cambridge, U.K. Pyridine (5), pyrazine (6), 4,4'-bipyridine (8), and sodium tetraphenyl borate (15) were purchased from Aldrich. Vanadocene(II) (1),²⁶ decamethylvanadocene(II) (4),³² vanadocene(III) chloride (14),⁶⁵ [Cp₂V^{III}][BPh₄] (16),³⁰ [Cp*₂V^{III}][BPh₄] (18),³¹ 1,2-bis(4-pyridyl)-acetylene (9),⁸⁴ 4,4' azobis(pyridine) (10),⁸⁵ and 1,3,5-tris(4-pyridyl)-2,4,6-triazine $(11)^{81}$ were prepared according to literature procedures.

X-ray Diffraction. Single-crystal experiments were carried out on a STOE IPDS diffractometer and a Bruker AXS X8 Apex II diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct phase determination with SHELXS-97 and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.⁸⁶ Crystallographic details of presented crystal structures are given in Table 4. Crystallographic data of the solid-state structures of complexes 19 ([Cp*₂V(Py)][BPh₄]) and 20 ([Cp*₂V(Pz)][BPh₄]) are given in the Supporting Information.

Synthesis of [Cp₂V(Py)][BPh₄] (3).³⁷ Vanadocene(III) chloride (14, 50 mg, 0.23 mmol) and 79 mg (0.23 mmol) of sodium tetraphenylborate (15) were suspended in 7 mL of thf, and 75 μ L (0.92 mmol) of pyridine (5) was added via syringe. The supension was stirred for 30 s and left overnight at room temperature. The solution turned slowly from blue to blue-violet, and amorphous NaCl precipitated. After 18 h blue-violet plates of 3, which were suitable for X-ray diffraction, were separated from the suspension on a large-pored frit by hot filtration. Washing with *n*-hexane and drying under vacuum afforded 54 mg (0.09 mmol, 41%) of 3. Mp: 210–212 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3450 (br), 3090 (w), 3054 (m), 2989 (w), 1604 (m), 1578 (m), 1477 (m), 1444 (m), 1422 (m), 1359 (w), 1250 (w), 1175 (w), 1152 (w), 1129 (w), 1068 (m), 1032 (w), 1017 (m), 1005 (m), 828 (s), 751 (m), 734 (s), 704 (s), 610 (m), 458 (w). MS (CI, isobutane): m/z(relative intensity, %) 262.0 (2), 261.0 (19), 260.0 (100) [M]⁺; 181.0 (14) [Cp₂V]⁺; 80.0 (100) [(pyH)]⁺. HR-MS (CI, isobutane): m/z calcd for C₁₅H₁₅NV⁺ 260.0644, found 260.0648 (100). Anal. Calcd for C₃₉H₃₅BNV: C, 80.84; H, 6.09; N, 2.42. Found: C, 80.12; H, 6.51; N, 2.44.

Synthesis of $[Cp_2V(\eta^2-C_2Py_2)]$ (12). Vanadocene(II) (1; 37 mg, 0.2 mmol) and 36 mg (0.2 mmol) of 1,2-bis(4-pyridyl)acetylene (9) were dissolved in 20 mL of toluene and stirred overnight. The solution changed immediately from violet to yellow-brown. The product was obtained by crystallization at -40 °C as brown crystals, which were suitable for X-ray diffraction. After the mother liquor was decanted, the product was washed with 5 mL of *n*-hexane and dried under vacuum to afford 12 in 55% yield (40 mg, 0.11 mmol). Mp: 134–136 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3067 (w), 1782 (m), 1771 (m), 1745 (m), 1579 (s), 1526 (m), 1479 (m), 1432 (w), 1408 (m), 1385 (w), 1308 (w), 1267 (w), 1212 (w), 1019 (w), 1010 (w), 989 (m), 814 (s), 684 (w), 558 (m), 550 (m). MS (CI, isobutane): m/z (relative intensity, %) 363.2 (9), 362.2 (39), 361.2 (100) $[M]^+$. HR-MS (CI, isobutane): m/z calcd for C₂₂H₁₈N₂V⁺ 361.0910, found 361.0912 (100). Anal. Calcd for C₂₂H₁₈N₂V: C, 73.13; H, 5.02; N, 7.75. Found: C, 72.66; H, 5.40; N, 7.69.

Synthesis of $[(Cp*_2V)_2(\mu_2-Py_2N_2)]$ (13). Decamethylvanadocene(II) (4; 80 mg, 0.25 mmol) was dissolved in 10 mL of toluene and layered with 5 mL of a 1:1 mixture of toluene/ n-hexane. Then a solution of 47 mg (0.25 mmol) of 4,4'-azobis-(pyridine) (10) in 18 mL of *n*-hexane was layered. After several days black crystals of 12 were formed, which were suitable for X-ray diffraction. The mother liquor was decanted, and the crystals were washed with 5 mL of *n*-hexane. Drying under vacuum afforded 70 mg (0.07 mmol, 56% relating to 4) of 13. Mp: 165–166 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3020 (w), 2962 (m), 2904 (m), 2852 (m), 1604 (s), 1512 (m), 1493 (m), 1429 (m), 1379 (m), 1300 (m), 1261 (w), 1201 (w), 1178 (m), 1065 (w), 1005 (s), 943 (w), 802 (m), 731 (w), 694 (w), 613 (w), 534 (w), 505 (w), 465 (w), 422 (w). MS (CI, isobutane): m/z (relative intensity, %) 417.2 (4), 416.2 (24), 415.2 (100) [(Cp*₂V(4-PyNH₂))]⁺; 323.2 (1), 322.2 (13), 321.2 (58) $[(Cp*_2V)]^+$; 95.1 (24) $[(4-PyNH_2+H)]^+$. HR-MS (CI, isobutane): m/z calcd for C₂₅H₃₆N₂V⁺ 415.2313, found 415.2320 (100). Anal. Calcd for C₅₀H₆₈N₄V₂: C, 72.62; H, 8.29; N, 6.77. Found: C, 72.40; H, 8.74; N, 7.15.

Synthesis of $[Cp_2V(Pz)][BPh_4]$ (17). $[Cp_2V][BPh_4]$ (16; 20 mg, 0.04 mmol) was dissolved in 20 mL of thf. The solution was filtered from the remaining solid and layered with 3 mL of diethyl ether. Then a solution of 6 mg (0.08 mmol) of pyrazine (6) in 10 mL of *n*-hexane was layered. Dark blue crystals of 17 formed after several days, which were suitable for X-ray diffraction. The mother liquor was decanted, and the product was washed with 5 mL of *n*-hexane. Drying under vacuum afforded 9 mg (0.015 mmol, 43%) of 17. Mp: 197–199 °C. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3105 (w), 3049 (m), 2995 (m), 2981 (m), 2895 (w), 1579 (w), 1477 (m), 1425 (m), 1265 (w), 1182 (w), 1149 (w), 1122 (w), 1066 (w), 1020 (m), 874 (m), 824 (s), 743 (s), 735 (s), 708 (s), 625 (w), 604 (m), 478 (w), 461 (w).

Synthesis of [Cp*2V(Py)][BPh4] (19). [Cp*2V][BPh4] (18; 100 mg, 0.16 mmol) was suspended in 20 mL of thf, and 30 μ L (30 mg, 0.37 mmol) of pyridine (5) was added via syringe. When the resulting suspension was heated to 60 °C for 2 weeks without stirring, its color changed from brown to green and most of the solid 18 was dissolved. The solution was filtered from the remaining solids at room temperature and layered with 20 mL of *n*-hexane to get green plates of **19**, which were suitable for X-ray diffraction. After decanting of the mother liquor the crystals were washed with 5 mL of n-hexane and dried under vacuum to obtain 30 mg (0.08 mmol, 48% relating to **18**) of pure **19**. Mp: 217–219 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3051 (m), 3034 (m), 2978 (m), 2910 (m), 2852 (m), 1943 (w), 1867 (w), 1803 (w), 1759 (w), 1643 (w), 1603 (m), 1578 (m), 1478 (m), 1443 (m), 1421 (m), 1381 (m), 1309 (m), 1259 (m), 1211 (m), 1182 (m), 1155 (m), 1120 (m), 1065 (m), 1032 (m), 1018 (m), 985 (m), 860 (w), 841 (m), 804 (w), 762 (m), 744 (m), 731 (s), 710 (s), 698 (s), 623 (w), 611 (s), 500 (w), 467 (w), 432 (w). MS (CI, isobutane): m/z (relative intensity, %) 402.3 (3), 401.3 (23), 400.3 (68) [M]⁺; 323.3 (9), 322.3 (38), 321.3 (100) [(Cp*₂V)]⁺; 80.1 (12) [(PyH)]⁺. HR-MS (CI, isobutane): *m/z* calcd for C₂₅H₃₅NV⁺ 400.2209, found 400.2207 (100). Anal. Calcd for

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 $C_{49}H_{55}BNV:$ C, 81.77; H, 7.70; N, 1.95. Found: C, 80.86; H, 8.49; N, 1.64.

Synthesis of [Cp*₂V(Pz)][BPh₄] (20). [Cp*₂V][BPh₄] (18; 96 mg, 0.15 mmol) and 12 mg (0.15 mmol) of pyrazine (6) were suspended in 20 mL of thf and heated to 60 °C without stirring. The solution changed slowly from brown to green, and most of the solid 18 was dissolved during the reaction. After 2 weeks the solution was filtered from the remaining solids at room temperature and layered with 20 mL of n-hexane to obtain yellow-brown plates of 20, which were suitable for X-ray diffraction. After decanting of the mother liquor the crystals were washed with 5 mL of *n*-hexane and dried under vacuum to obtain 38 mg (0.05 mmol, 33%) of pure **20**. Mp: 211–213 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3051 (m), 3037 (m), 2980 (m), 2906 (m), 2856 (m), 1944 (w), 1879 (w), 1817 (w), 1764 (w), 1579 (m), 1478 (m), 1451 (w), 1426 (m), 1412 (m), 1381 (w), 1309 (m), 1241 (m), 1182 (w), 1146 (m), 1064 (w), 1050 (w), 1031 (w), 1018 (m), 985 (m), 914 (w), 841 (w), 809 (m), 731 (s), 705 (s), 612 (m), 604 (m), 480 (w), 440 (w). MS (CI, isobutane): m/z (relative intensity, %) 401.1 (4), 400.1 (23), 399.1 (63) [(M-2H)]⁺; 323.1 (3), 322.1 (27), 321.1 (100) $[(Cp^*_2V)]^+$. MS (ESI, thf; pos): m/z(relative intensity, %) 388.2 (5), 387.2 (22), 386.2 (29), 385.2 (100) $[(M - CH_2 - H)]^+, [(M - CH_2 - 2H)]^+$. HR-MS (CI, isobutane): m/z calcd for C₂₄H₃₄N₂V⁺ 401.2162, found 401.2165 (100). Anal. Calcd for C48H54BN2V.0.5C6H14: C, 80.20; H, 8.05; N, 3.67. Found: C, 78.40; H, 8.17; N, 3.69.

Synthesis of [(Cp*₂V)₂(µ₂-4-Bipy)][BPh₄]₂ (21). [Cp*₂V][BPh₄] (18; 96 mg, 0.15 mmol) and 24 mg (0.15 mmol) of 4,4'-bipyridine (8) were suspended in 20 mL of thf and heated to 60 °C without stirring. The color of the solution changed slowly from brown to green, and most of the solid 18 was dissolved during the reaction. After 3 days the solution was filtered from the remaining solids at room temperature and layered with 20 mL of n-hexane to give green-brown blocks of 21, which were suitable for X-ray diffraction. After decanting of the mother liquor the crystals were washed with 5 mL of *n*-hexane and dried under vacuum to obtain 60 mg (0.04 mmol, 51% relating to 18) of pure 21. Mp: 258-260 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3052 (m), 3035 (m), 2996 (m), 2982 (m), 2904 (m), 1939 (w), 1878 (w), 1816 (w), 1606 (m), 1579 (m), 1479 (m), 1450 (m), 1426 (m), 1410 (m), 1380 (m), 1308 (w), 1261 (m), 1211 (w), 1182 (m), 1148 (m), 1064 (m), 1031 (m), 1018 (m), 845 (w), 821 (m), 731 (s), 704 (s), 612 (m), 604 (m), 439 (w). MS (CI, isobutane): m/z (relative intensity, %) 842.8 (2), 841.8 (11), 840.8 (50), 839.7 (100) [(M + C₃H₆)]⁺. HR-MS (CI, isobutane): m/z calcd for $C_{50}H_{68}N_2V_2^{2+}$ 399.2131, found 399.2127 (100). Anal. Calcd for C₉₈H₁₀₈B₂N₂V₂·2C₄H₈O: C, 80.49; H, 7.90; N, 1.77. Found: C, 81.18; H, 8.07; N, 2.03.

Synthesis of $[(Cp^*_2V)_2(\mu_2-Py_2C_2)]$ [BPh₄]₂ (24). Vanadocene(II) (1; 18 mg, 0.1 mmol) and 18 mg (0.1 mmol) of 1,2-bis(4-pyridyl)acetylene (9) were dissolved in 20 mL of thf and stirred overnight to form complex 12 in situ. A suspension of 128 mg (0.2 mmol) of [Cp*_2V][BPh_4] (18) in 20 mL of thf was added, and the resulting reaction mixture was heated to 60 °C for 2 weeks without stirring. During that time 24 precipitated as brown

needles which were suitable for X-ray diffraction. After cooling to room temperature the mother liquor was decanted and the crystals were washed with 5 mL of *n*-hexane. Drying under vacuum afforded 61 mg (0.04 mmol, 42% relating to **18**) of pure **24**. Mp: 265–267 °C dec. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3053 (m), 2998 (m), 2982 (m), 2904 (m), 1607 (m), 1581 (w), 1501 (w), 1478 (m), 1427 (m), 1411 (m), 1379 (m), 1318 (w), 1262 (m), 1207 (w), 1181 (w), 1147 (w), 1059 (w), 1018 (m), 844 (m), 804 (w), 741 (m), 729 (s), 704 (s), 604 (m), 552 (w), 481 (w), 461 (w), 439 (w). MS (CI, isobutane): *m/z* (relative intensity, %) 841.7 (7), 840.7 (31), 839.7 (52) [(M + CH₃ + 2H)]⁺; 323.1 (5), 322.1 (48), 321.1 (100), 320.1 (31) [(Cp*₂V)]⁺, [(BPh₄ + 2H)]⁺; 181.1 (38) [(C₂Py₂ + H)]⁺; 165.1 (65) [(BPh₂)]⁺; 135.2 (27) [Cp*]⁺. Anal. Calcd for C₁₀₀H₁₀₈B₂N₂V₂: C, 82.18; H, 7.45; N, 1.92. Found: C, 81.43; H, 8.18; N, 2.14.

Synthesis of [(Cp*₂V)₃(μ_3 -4-TPT)][BPh₄]₃ (26). [Cp*₂V][BPh₄] (18; 100 mg, 0.16 mmol) and 16 mg (0.05 mmol) of 4-TPT (11) were suspended in 30 mL of 1,2-difluorobenzene and heated to 60 °C without stirring. The color of the solution changed slowly from brown to green, and most of the solid **18** was dissolved during the reaction. After 2 weeks the solution was filtered from the remaining solids at room temperature and layered with 30 mL of *n*-hexane to give green-black needles of 25, which were suitable for X-ray diffraction. After decanting of the mother liquor the crystals were washed with 5 mL of n-hexane and dried under vacuum to obtain 30 mg (0.01 mmol, 26% relating to 18) of pure 26. Mp: 248-250 °C. IR (KBr; cm⁻¹): $\tilde{\nu}$ 3053 (m), 3032 (m), 2997 (m), 2981 (m), 2908 (m), 2854 (w), 1940 (w), 1876 (w), 1817 (w), 1759 (w), 1616 (w), 1570 (m), 1516 (s), 1508 (s), 1479 (m), 1450 (m), 1425 (m), 1371 (s), 1315 (w), 1263 (m), 1182 (w), 1138 (w), 1099 (w), 1057 (m), 1032 (m), 1018 (m), 964 (w), 845 (w), 812 (m), 733 (s), 704 (s), 656 (w), 611 (m), 532 (w), 469 (w), 440 (w). MS (CI, isobutane): m/z (relative intensity, %) 417.1 (4), 416.1 (20), 415.1 (100) [M - (2CH₂) · (2H)]³⁺. HR-MS (CI, isobutane): m/z calcd for $C_{78}H_{102}N_6V_3^{3+}$ 425.2162, found 425.2164 (100). Anal. Calcd for C150H162B3N6V3. C₆H₁₄: C, 80.75; H, 7.65; N, 3.62. Found: C, 79.38; H, 7.67; N, 3.70.

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Supporting Information Available: Tables of crystal data and ORTEP drawings of 19 and 20 and CIF files giving crystallographic data for structures 3, 12, 13, 17, 19, 20, 21, 24, and 26. This material is available free of charge via the Internet at http:// pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 736231 (26), CCDC 736232 (12), CCDC 736233 (24), CCDC 736234 (3), CCDC 736235 (13), CCDC 736236 (17), CCDC 736237 (21), CCDC 736238 (19), and CCDC 736239 (20). Copies of data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, +44 1223 336 033; e-mail, deposit@ ccdc.cam.ac.uk).