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Dinitrogen Coordination and Cleavage Promoted by a Vanadium Complex of a σ,π,σ-Donor Ligand

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The deprotonation of the tripyrrole MeTPH$_2$ [MeTPH$_2$ = 2,5-[(2-pyrrolyl)(C$_6$H$_5$)$_2$C]$_2$(MeNC$_4$H$_2$)], containing one N-methylated pyrrolyl ring, was carried out with 2 equiv of KH. The corresponding dipotassium salt reacted with VCl$_3$(THF)$_3$ to afford the complex [(MeTP)VCl(THF)]•THF (**1**). While the two lateral pyrrolide rings are σ-bonded, the central one is perpendicularly oriented in a sort of π-fashion. However, the bond distances clearly indicated that only the quaternized N atom is forming a bonding contact. Subsequent reduction of **1** with Na yielded the corresponding divalent complex [(MeTP)V(THF)]•(C$_7$H$_8$)$_{0.5}$ (**2**) where the central N-methylated ring adopted a more regular π-orientation. When treated with a strong Lewis acid (AlMe$_3$), THF was extracted from the vanadium coordination sphere, forming the dinuclear dinitrogen complex [(MeTP)V(μ-N$_2$)]$_2$•(C$_7$H$_8$)$_{2.9}$ (**3**). Reduction of **3** with potassium graphite gave cleavage of dinitrogen, affording the mixed-valent nitride-bridged complex [(MeTP)V(μ-N)]$_2$•(THF) (**4**).

Introduction

Among the diversified transformations promoted by high-spin, octahedral d^3 complexes of vanadium, dinitrogen activation has traditionally provided the strongest motivation to justify synthetic efforts for developing the chemistry of the divalent state.[1] The discovery of the presence of vanadium as key element in some of the nitrogenase enzymes[2] still poses challenging questions about the role of this element in the reduction of dinitrogen to ammonia. As a result of the research activity sparked by these questions, a few cases of vanadium dinitrogen complexes[3] have been discovered, as well as formation of nitrides via the 6-electron reductive cleavage of the coordinated dinitrogen unit.[1b,3j,4]

Pyrrole-based ligand systems and especially di- and cyclic tetrapyrroles have shown a particular versatility in enhancing and supporting the reactivity of metals toward dinitrogen fixation and activation.[5] Their resilience to strongly reducing

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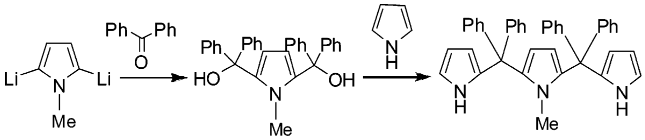
metals is most likely the basis of this useful behavior. However, ligand denticity also seems to be a rather critical factor. For example, simple monodentate pyrrolides, which adopt either the π- or σ-bonding modes depending on the nature of the metal,[6] to the best of our knowledge, have never produced a case of dinitrogen activation/fixation with any metal. On the contrary, the polypyrrolide ligand systems almost invariably adopt the dual σ- and π-bonding mode,[7] while favoring the assembly of cluster structures capable of cooperative dinitrogen reduction.[8]

While in combination with pyrrolide-based ligand systems, the behavior of divalent vanadium has been so far disappointing, having yielded standard σ-bonded complexes[9] with no sign of possible reactivity with dinitrogen. Recently, by using strong Lewis acids (such as AlR_3) capable of locking the pyrrolide nitrogen sp^2 orbital, a complex containing two π-bonded pyrrolide rings with an overall vanadocene-type of structure has been obtained.[10] However, no dinitrogen activation has been observed in this particular species in spite of the divalent state and the hemi-lability and dynamism of the monodentate pyrrolide ligand.[10] Hence, our design of the tripyrrolide 2,5-{2-[$(C_6H_5)_2C$]pyrrole}$_2$(N-Me-pyrrole) ($MeTPH_2$) ligand system used in this work for targeting low-valent vanadium. The empirical idea behind its design was to have a ligand in which the two terminally positioned pyrrolide rings provide two σ-bonded anionic N atoms. Indeed, the chemistry of the anionic amide complexes of both di- and trivalent vanadium has demonstrated the ability of anionic nitrogen donor atom to promote dinitrogen fixation.[3f−h,j] The central methylated pyrrolide ring was expected to provide the metal with a π-interaction[11] which, as suggested by the chemistry of low-valent lanthanides,[5,7,8] seems also beneficial to enhance and promote reactivity toward dinitrogen.

Scheme 1



In this first paper, we describe the synthesis and characterization of the V$^{(III)}$ and V$^{(II)}$ complexes of the tripyrrolide dianion of $MeTPH_2$, the formation of the corresponding dinitrogen vanadium complex and further cleavage to a dinuclear linearly bonded mononitride species.

Results and Discussion

In order to prepare the tripyrrole ligand $MeTPH_2$, the classical direct condensation between pyrrole and carbonyl derivatives cannot be used, as it tends to lead to either dipyrrole or porphyrinogen-type structures with only small amounts of tripyrrole being produced.[12] Thus, its synthesis (see Scheme 1) was obtained via double lithiation of the two 1-methyl pyrrole α-positions[13] followed by the subsequent addition of benzophenone and quenching. In a second step, the resulting diol 2,5-[$(C_6H_5)_2C(OH)$]$_2$(N-Me-pyrrole) was condensed with neat pyrrole, acting as both a solvent and reagent, affording $MeTPH_2$ in good yield (83%) of analytically pure solid. Deprotonation of the two terminal pyrroles and formation of the corresponding dipotassium salt $MeTPK_2$ was conveniently carried out in situ via standard treatment with KH in THF.

Reaction of $MeTPK_2$ with $VCl_3(THF)_3$ in THF formed dark red crystals of the corresponding [(MeTP)VCl(THF)]·THF (**1**) in moderate yield (Scheme 2).

The connectivity has been confirmed by an X-ray crystal structure. The only unexpected feature in the structure (Figure 1) is that the central N-methylated ring does not adopt the expected η^5-coordination mode, but formed instead a direct V−N σ-bond via quaternization of the nitrogen atom. The geometry around the metal center can be described in terms of a distorted trigonal bipyramidal geometry with the apical positions occupied by the N atom of the N-methylated central ring [V1−N2 = 2.232(3) Å] and the oxygen atom of one coordinated THF [V1−O1 = 2.107(2) Å]. The equatorial plane is comprised of two σ-bound pyrrolides N atoms [V1−N1 = 1.957(3) Å and V1−N3 = 1.958(3) Å] and the chloride [V1−Cl1 = 2.2526(11) Å]. The axial vector deviates a little from the linearity [N2−V1−O1 = 172.59(9)°], and a minor distortion is present in the equatorial plane [Cl1−V1−N3 = 119.98(8), Cl−V1−N1 = 117.44(8)°, N1−V1−N3 = 122.35(11)°].

The magnetic moment was as expected for the high-spin d^2 electronic configuration of mononuclear trivalent vanadium.

When complex **1** was reacted with metallic sodium in THF, a new species was isolated as dark purple crystals in moderate yield (Scheme 2). The formulation of this complex

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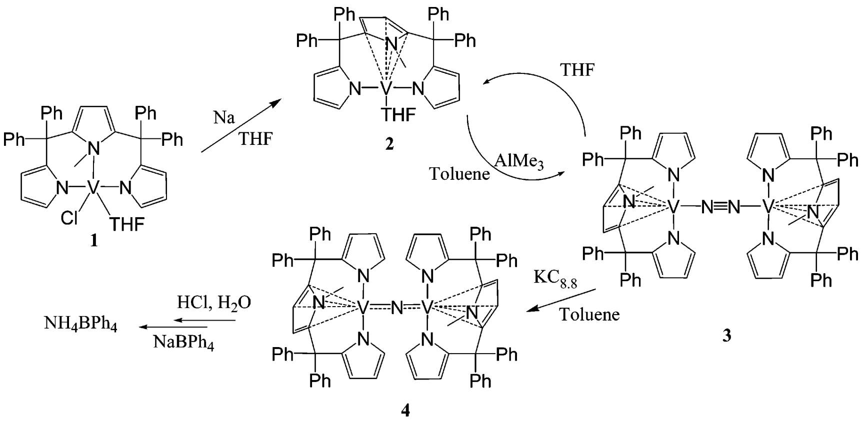
Scheme 2



as the divalent $[(\text{MeTP})\text{V(THF)}]\cdot(C_7H_8)_{0.5}$ (**2**) was again determined by an X-ray structure (Figure 2). In comparison to **1**, complex **2** has simply lost the chlorine atom as a result of the reduction to the divalent state. In the process, however, the N-methylated ring adopts a η^5-bonding mode although not perfectly centered over the V atom [V−centroid = 2.010(4) Å, V1−N2 = 2.193(3) Å, V1−C6 = 2.293(4) Å, V1−C7 = 2.430(5) Å]. Overall, the coordination geometry of the metal center can be described as distorted pseudo-tetrahedral [N1−V1−N3 = 106.68(14)°, N1−V1−O1 = 97.83(14)°, N1−V1−centroid = 107.59°] and is comprised by the centroid of the η^5-bound ring, the two N atoms of the two σ-bonded pyrrolides rings [V1−N1 = 2.067(4) Å and V1−N3 = 2.075(4) Å], and the O atom of one coordinated molecule of THF [V1−O1 = 2.115(3) Å]. Even in this case the magnetism did not show any unexpected feature.

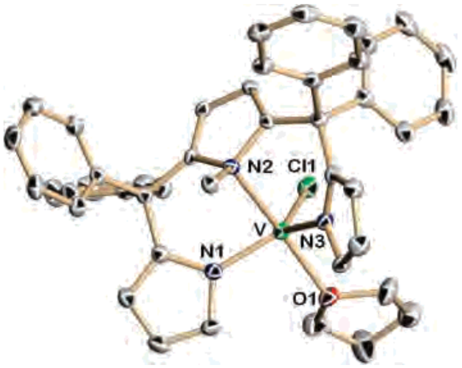


Figure 1. Crystal structure of **1** with thermal ellipsoids drawn at the 30% probability level.

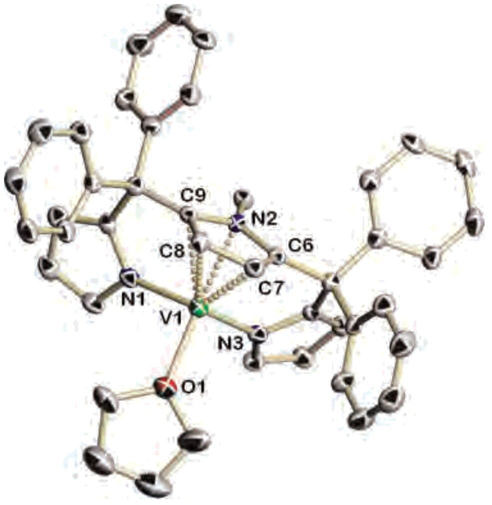


Figure 2. Crystal structure of **2** with thermal ellipsoids drawn at the 30% probability level.

The lack of dinitrogen fixation in this complex containing divalent vanadium can certainly be ascribed to the coordination of one THF molecule. The exchange of THF for a weakly ligated N_2 was previously observed in the chemistry of divalent vanadium amidinates.[3h] Thus, when the coordinated molecule of THF was extracted by a strong Lewis acid such as $AlMe_3$, coordination of dinitrogen was obtained with formation of the dinuclear dinitrogen-bridged complex $[(\text{MeTP})\text{V}(\mu\text{-}N_2)]_2\cdot(C_7H_8)_{2.9}$ (**3**), which crystallized from toluene in moderate yield.

The structure (Figure 3) shows the complex containing two metal centers, each surrounded by one tripyrrolide ligand system and bridged by one dinitrogen unit in an almost-linear V−N−N−V array [V1−N7−N8 = 177.7(2)°, N7−N8−V2 = 176.5(2)°]. Similar to complex **2**, each V center is in a pseudo-tetrahedral coordination geometry comprised of the η^5-bound ring [V1−centroid = 2.023(6) Å], the two σ-bonded pyrrolides [V1−N1 = 2.011(5) Å, V1−N3 = 2.024(6) Å, V1−N7 = 1.752(6) Å, N1−V1−N3 = 100.1(2)°, N1−V1−N7 = 106.3(2)°, N1−V1−centroid = 103.8(2)°] and one N atom of the bridging N_2 unit. The slightly elongated dinitrogen bond [N7−N8 = 1.248(5) Å vs 1.0968 Å for free

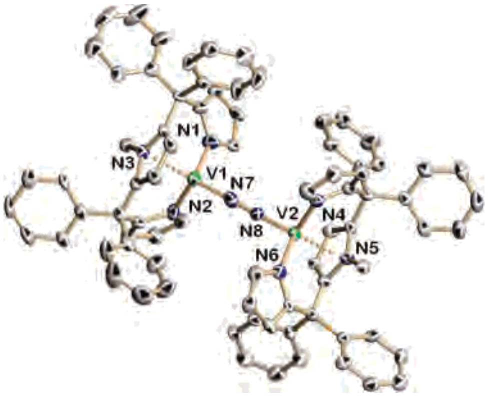


Figure 3. Crystal structure of **3** with thermal ellipsoids drawn at the 30% probability level.

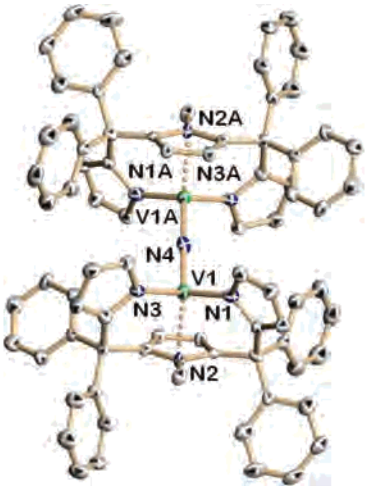


Figure 4. Crystal structure of **4** with thermal ellipsoids drawing at the 30% probability level.

N_2] and short V−N_2 distance [1.752(6) Å] along with the nearly linear arrangement of the V1−N_2−V2 atoms [V1−N7−N8 = 177.7(2)° and N7−N8−V2 = 176.5(2)°] would tend to indicate significant double-bond character and thus a two-electron reduction. However, similar to the case of other dinitrogen-bridged vanadium complexes[13] the magnetic moment ($\mu_{\text{eff}} = 3.52\ \mu_B$ per vanadium atom) indicates that the extent of reduction is rather minimal and that the metal center is predominantly in the divalent state. Accordingly, treatment of **3** with THF instantly reformed the purple **2**.

Further reduction of **3** in toluene in the presence of $KC_{8.8}$ afforded the nitride-bridged, mixed-valence complex $[(\text{MeTP})V]_2(\mu\text{-N})\cdot(\text{THF})$ (**4**) which was crystallized from THF in moderate yield. As in the previous cases, the central pyrrole ring is interacting with the metal center in the η^5-mode [V1−centroid = 2.040(7) Å] (Figure 4). Each V center assumes a slightly distorted tetrahedral coordination geometry comprised of the η^5-bonded ring, the two pyrrolides, and the bridging nitride [V1−N1 = 2.020(7) Å, V1−N2 = 2.001(7) Å, V1−N4 = 1.7680(15) Å, N1−V1−N3 = 103.2(2)°, N1−V1−N4 = 108.4(2)°, N1−V1−centroid = 103.8(2)°]. The short V−N bond length and perfectly linear arrangement of the V−N−V bond [180.0(2)°] are strong indicators of multiple bond character between the nitride and the metal centers.

In order to unequivocally identify the bridging atom as a nitride, a degradation experiment was carried out by simply treating complex **4** with a diluted HCl solution. The resulting solution was reacted with $NaBPh_4$, affording a white precipitate of NH_4BPh_4 in good yield. The solid was analyzed via electrospray mass spectrometry and by comparison of the spectroscopic properties with those of an analytically pure sample. Finally, when the preparation of **3** and its further reduction were carried out under $^{15}N_2$ atmosphere and the corresponding complex **4** degraded in the same manner, a sample of $^{15}NH_4BPh_4$ was obtained which showed the expected pattern in the mass spectrum. This not only conclusively identified the bridging atom as nitrogen but also demonstrated that its origin is from atmospheric dinitrogen. The room-temperature magnetic moment of **4** [$\mu_{\text{eff}} = 1.74\ \mu_B$] is in agreement for the nitride-bridged mixed-valent $V^{(III)}$−$V^{(IV)}$ dimer with an overall one unpaired electron configuration.

The formation of the mono-nitrido-bridged species **4** from dinitrogen cleavage is of some interest and displays a few aspects of novelty. The apparent stability of the dinitrogen-bridged **3** in the absence of coordinating solvents implies that the N−N cleavage is not performed by the two $V^{(II)}$ d^3 centers, but instead by some other reduced species generated by the attack of KC_8. This behavior is in contrast with that of a divalent tris-amide vanadium complexes where the possibility of $V^{(II)}$ cleaving coordinated dinitrogen into nitride-bridged di-vanadium complexes has been clearly demonstrated by the pioneering work of Cloke.[3j] In that case, DFT calculations have pointed out that the sideways coordination of a transient $V^{(II)}$ species to dinitrogen is followed by further attack by a second unit, ultimately leading to the six-electron reduction and consequent N−N triple bond cleavage.[4c] In the case of the formation of **4**, reduction instead occurs by funneling electrons into the end-on bridged dinitrogen complex **3**. It is tempting to speculate that this reductive pathway might in fact follow a pathway not dissimilar from that proposed by Schrock for his vanadium system.[3a] The formation of **4** from **3** as reported in Scheme 1 is a nonbalanced equation. Therefore, intriguing questions arise about the formation and the nature of possible byproducts. At this stage, we did not succeed in isolating or obtaining any evidence for the presence of other vanadium-containing complexes. We speculate that perhaps some K_3N, undetected in the graphitic residue, may accompany the formation of **4**.

To the best of our knowledge no conclusive information is available in the literature about the possibility of actually protonating the nitride atoms bonded to vanadium when formed from dinitrogen in the way it has been documented in detail for molybdenum.[14,15] In fact, the vanadium analogues of the versatile Mo−nitride species have proven to be rather elusive. A mononuclear, terminally bonded vanadium dinitrogen complex, isolelectronic with the catalytically active Mo complex, has been obtained.[3a] The nitride, the imido, and the ammonia complexes have also been prepared.[3a] It was also conclusively established that these species are interlinked in an overall cycle for ammonia formation.[3a,16] However, these important intermediates so far have not been prepared from dinitrogen itself, and the simple protonation of the V−nitride as obtained from dinitrogen cleavage has so far escaped characterization. Protonation of **4** to NH_4^+ was found to be very facile, although obviously the vanadium

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moiety is completely hydrolyzed in this case, therefore preventing the possibility of obtaining a step by step catalytic cycle similar to that designed for Mo.[15b]

In conclusion, in this work we have shown that the tripyrrolide ligand system is capable of supporting dinitrogen fixation and activation in vanadium chemistry. The ligand displayed some rather interesting flexibility in terms of interchanging from σ- to π-bonding mode of the central alkylated ring depending on the metal oxidation state. While the trivalent complex prefers to adopt a σ-type of bonding with the simple quaternization of the N$-$Me atom, the softer divalent centers (both as THF or as N_2 complexes) display the expected symmetrical π-bonding mode. It is tempting to speculate that, similar to the case of lanthanides, the simultaneous presence of both σ- and π-bonded pyrrolides is indeed central to the occurrence of dinitrogen activation. As stated above, V(II) complexes of pyrrolide ligands solely having either of the two types of bonding[9,10] do not display reactivity with N_2. Finally, in the cleavage of the coordinated N_2 unit, rather than a dinuclear complex with two bridging nitrides as previously reported in a few instances in the chemistry of vanadium dinitrogen, [3j,4b−d] for the first time a simple linearly bonded hydrolyzable nitride has been obtained from dinitrogen.

Experimental Section

General Experimental Details. All reactions were carried out under a dry nitrogen atmosphere unless otherwise stated. Solvents were dried using an aluminum oxide solvent purification system. $VCl_3(THF)_3$ was prepared via standard procedure.[17] A solution of *n*-BuLi and benzophenone was purchased from Aldrich and used with no further purification. Reagent grade pyrrole was also purchased from Alrich and used after distillation under reduced pressure (~50 Torr). Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a drybox, except in the case of air-stable products. Samples for magnetic susceptibility were preweighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey magnetic susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. NMR data was collected on a Varian INOVA 500 spectrometer and referenced to $SiMe_4$. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1 K Smart CCD area detector. Electrospray mass spectrometry was performed by a Micromass Quattro-LC electrospray-triple quadrupole mass spectrometer in a dilute THF solution.

Preparation of 2,5-[$(C_6H_5)_2C(OH)]_2$(N-Me-pyrrole). A solution of *N*-Methylpyrrole (10.0 mL, 0.113 mol) in hexane (150 mL) was treated with neat TMEDA (51.0 mL, 0.338 mol) and then cooled to 0 °C in an ice bath. A solution of *n*-BuLi in hexane (0.338 mol) was added dropwise while stirring. The reaction mixture was warmed up to room temperature and refluxed for 4 h. The resulting off-white suspension was filtered and the solid portion was washed with hexane (3 × 50 mL), yielding a white product. The solid was dried under vacuum (1 h) and redissolved in THF (100 mL), and the resulting solution cooled to −20 °C. In a separate flask, 2.0 equiv of benzophenone (41.18 g, 0.226 mol) were dissolved in THF (100 mL) and cooled to −20 °C. The two solutions were then combined, resulting in the formation of a deep blue solution. This solution was then stirred for 12 h, after which time the solvent was removed under vacuum. Hexane (200 mL) was then added along with 4 equiv of water (8 mL, 0.452 mol), affording an off-white suspension. This suspension was then filtered, and the solid washed with hexanes (4 × 50 mL). The product was extracted using several portions of CH_2Cl_2 (5 × 40 mL) and dried under vacuum, yielding the final product as an off-white solid. Yield 26.68 g (53.1%). Anal. Calcd (Found) for $C_{31}H_{27}O_2N$: C 83.57 (83.52); H 6.11 (6.05); N 3.14 (3.11). [M^+] 445, found 445. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.86 (br, 2H, OH), 3.13 (s, 3H, N$-CH_3$), 5.29 (s, 2H, central pyrrole) 7.27 (m, 20H, phenyl). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 35.00 (N$-CH_3$), 78.72 (C$-$OH), 110.06 (pyrrole), 126.90 (phenyl), δ 127.13 (phenyl), δ 127.74 (phenyl), δ 145.55 (ipso-phenyl). IR (KBr pellet, cm^{-1}) ν 3484 s, br (OH); 3084, 3058, 3025, 2946 s; 1597, m; 1490, 1447, s; 1411, w; 1329, 1293, s; 1234, w; 1204, m; 1153, s; 1092, s; 1061, w; 1018, 1001, s; 924, 899, m; 867, m; 792, w; 755, 721, 701, s; 670 s; 628, 612, m; 559 w.

Preparation of 2,5-[(2-pyrrolyl) $(C_6H_5)_2C]_2(MeNC_4H_2)$ ($MeTPH_2$). Neat 2,5-[$(C_6H_5)_2C(OH)]_2$(N-Me-pyrrole) (15.00 g, 0.034 mol) was dissolved in hot (~80 °C) pyrrole (60 mL). The addition of 6 drops of methanesulfonic acid resulted in the formation of a dark red suspension. After 72 h of stirring and heating, the suspension was cooled to room temperature. The solid was filtered and washed with cold methanol (3 × 30 mL), yielding the title compound as a white solid. The product was dried under vacuum and used without need for further purification (15.27 g, 0.021 mol, 63.4%). Anal. Calcd (Found) for $C_{39}H_{33}N_3$: C 86.15 (86.27), H 6.12 (6.17), N 7.73 (7.79). [M^+] 543, found 543. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.14 (s, 3H, N$-CH_3$), 5.46 (s, 2H, central pyrrole), 5.98 (m, 2H, pyrrole), 6.05 (m, 2H, pyrrole), 6.68 (m, 2H, pyrrole), 7.07 (m, 8H, phenyl), 7.13 (m, 4H, phenyl), 7.18 (m, 8H, phenyl), 7.69 (br s, 2H, N$-$H). ^{13}C NMR ($CDCl_3$, 500 MHz) δ 34.80 (N-**C**H3), 56.19 (quatenary), 108.10 (pyrrole), 109.37 (pyrrole), 110.35 (pyrrole), 117.26 (phenyl), 126.73 (phenyl), 127.93 (phenyl), 129.66 (ipso-pyrrole), 139.06 (ipso-central pyrrole), 145.52 (ipso-phenyl). IR_{neat} (cm^{-1}): 3426, m; 3085, 3065, 3026, 2954, m; 1955, 1899, 1816, w; 1595, 1550, m; 1490, 1443, s; 1410, 1394, m; 1233, 1299, 1267, 1231, 1183 m; 1115, 1093, 1042, 1031, m; 1002, w; 962, 930, w; 903, 885, 847, m; 799, 761, 747, 722, 704, s; 622, w; 568, 548 s.

Preparation of [(MeTP)VCl(THF)]·THF (1). Solid $MeTPH_2$ (0.200 g, 0.368 mmol) was dissolved in 10 mL of THF and treated with KH (0.030 g, 0.754 mmol). After stirring for 4 h, $VCl_3(THF)_3$ (0.137 g, 0.368 mmol) was added to the solution, which turned brick-red. After stirring overnight, the solution was centrifuged to remove the small amount of insoluble material and layered with hexanes. After several days, dark red X-ray quality crystals of **1** were formed (0.123 g, 0.159 mmol, 43.3%). Anal. Calcd (Found) for $C_{47}H_{47}ClN_3O_2V$: C 73.09 (73.21); H 6.13 (6.17); N 5.44 (5.50). $\mu_{eff} = 2.85\ \mu_B$.

Preparation of [($MeTPH_2$)V(THF)]·$(C_7H_8)_{0.5}$ (2). A dark red solution of **1** (0.410 g, 0.586 mmol) in THF (20 mL) was stirred with Na (0.015 g, 0.655 mmol) for about 4 h until all of the Na was consumed. The solvent was then removed under vacuum. The dry residue was redissolved in fresh THF (10 mL) and the suspension centrifuged to remove a small amount of insoluble material. Toluene (2 mL) was added to reduce the solubility, and the resulting dark brown mixture was cooled to −35 °C. Dark purple crystals of **2** suitable for X-ray diffraction were obtained (0.164 g, 0.231 mmol, 39.4%). Anal. Calcd (Found) for $C_{46.50}H_{43}N_3OV$: C 78.57 (78.21), H 6.10 (6.07), N 5.91 (5.60). $\mu_{eff} = 3.88\ \mu_B$.

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Table 1. Crystal Data and Structure Analysis Results for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{47}H_{47}ClN_3O_2V$	$C_{46.50}H_{43}N_3OV$	$C_{98.13}H_{85}N_8V_2$	$C_{86}H_{78}N_7V_2O$
fw	772.27	710.78	1478.12	1343.44
space group	monoclinic, ***P***2(1)/*c*	triclinic, $P\bar{1}$	monoclinic, ***C****c*	triclinic, $P\bar{1}$
a (Å)	13.551(4)	11.7083(18)	30.376(3)	11.872(5)
b (Å)	10.846(3)	13.427(2)	14.4526(16)	13.197(5)
c (Å)	26.981(8)	13.625(2)	24.201(3)	14.158(5)
α (deg)	90	93.545(3)	90	68.906(6)
β (deg)	100.833(5)	92.316(3)	126.7260(10)	86.868(6)
γ (deg)	90	113.775(3)	90	67.678(6)
V ($Å^3$)	3895(2)	1951.4(5)	8515.7(16)	1905.9(13)
Z	4	2	4	2
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
T (K)	209(2)	213(2)	201(2)	208(2)
D_{calcd} (g cm^{-3})	1.317	1.210	1.153	1.170
μ_{calcd} (mm^{-1})	0.367	0.292	0.270	0.296
F_{000}	1624	748	3103	705
$R, R_w{}^a$	0.0571, 0.1245	0.0605, 0.1535	0.0712, 0.1232	0.0885, 0.2109
GOF	1.002	1.054	1.040	1.016

[a] $R = \sum|F_o| - |F_c|/\sum|F|$. $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Selected Bond Distances and Angles

1	**2**	**3**	**4**
V1−N1 = 1.957(3)	V1−N1 = 2.067(4)	V1−N1 = 2.011(5)	V1−N1 = 2.018(7)
V1−N3 = 1.958(3)	V1−N3 = 2.075(4)	V1−N3 = 2.024(6)	V1−N3 = 2.002(7)
V1−O1 = 2.107(2)	V1−O1 = 2.115(3)	V1−centroid = 2.023(6)	V1−centroid = 2.040(7)
V1−N2 = 2.232(3)	V1−N2 = 2.193(3)	V1−N7 = 1.752(6)	V1−N4 = 1.7680(15)
V1−Cl1 = 2.2526(11)	V1−C6 = 2.293(4)	N7−N8 = 1.248(5)	
N3−V1−N1 = 122.35(11)	V1−C9 = 2.309(4)		N1 −V1−N3 = 103.2(2)
N3 −V1−O1 = 94.87(10)	V1−C7 = 2.430(4)	N1 −V1−N3 = 100.1(2)	N1 −V1−N4 = 108.4(2)
N1 −V1−O1 = 92.40(10)	V1−C8 = 2.454(4)	N1 −V1−N7 = 106.3(2)	N3 −V1−N4 = 104.9(2)
N3 −V1−N2 = 83.50(10)	N1−V1−N3 = 106.68(14)	N3 −V1−N7 = 105.7(2)	centroid−V1−N1 = 75.6(3)
N1 −V1−N2 = 82.46(10)	N1−V1−O1 = 97.83(14)	centroid−V1−N1 = 103.8(2)	centroid−V1−N3 = 120.5(3)
O1 −V1−N2 = 172.59(9)	N3−V1−O1 = 97.72(14)	centroid−V1−N3 = 105.02	centroid−V1−N4 = 132.5(2)
N3 −V1−Cl1 = 119.98(8)	N1−V1−N2 = 87.71(13)	centroid−V1−N7 = 131.7(2)	V1−N4−V1a = 180.0(2)
N1 −V1−Cl1 = 117.44(8)	N3−V1−N2 = 89.13(13)	V1−N7−N8 = 177.7(2)	
O1 −V1−Cl1 = 87.24(7)	O1−V1−N2 = 169.51(13)	N7−N8−V2 = 176.5(2)	
N2 −V1−Cl1 = 99.85(7)			

Preparation of [(MeTP)V(*μ*-N_2)]·(C_7H_8)$_{2.9}$ (3). A solution of Me_3Al in toluene (0.300 mL, 2 M, 0.597 mmol) was added to a solution of complex **2** (0.425 g, 0.597 mmol) in the same solvent (15 mL) at −35 °C. The color of the mixture immediately changed from dark purple to dark black-brown. The resulting suspension was centrifuged, and the dark brown solution afforded dark brown crystals of **3** upon standing 2 days at −35 °C (0.688 g, 0.466 mmol, 78%yield). Anal. Calcd (Found) for $C_{98.13}H_{85}N_8V_2$: C 79.73 (79.66), H 5.80 (5.72), N 7.58 (7.44). $\mu_{eff} = 3.52\ \mu_B$ (per vanadium atom). Addition of an equivalent amount of THF to a dark brown solution of **3** in toluene instantly turns the color to purple. Microcrystalline **2** can then be separated upon freezing (78%).

Preparation of [(MeTP)V]$_2$(*μ*-N)]·(THF) (4). A suspension of **3** (0.510 g, 0.345 mmol) in toluene (20 mL) was stirred at room temperature for ∼7 days in the presence of $KC_{8.8}$ (0.010 g, 0.690 mmol). During this reaction, the color of the mixture gradually changed from purple to dark green. After 7 days of stirring, the dark green solution was centrifuged to remove a small amount of precipitate and concentrated to ∼12 mL. Dark green crystals of **4** were formed after standing at −35 °C for 3 days (0.120 g, 0.179 mmol, 52%). Anal. Calcd (Found) for $C_{86}H_{78}N_7O_2V_2$: C 76.88 (76.84), H 5.85 (5.81), N 7.30(7.27). $\mu_{eff} = 1.74\ \mu_B$

Degradation of 4 and Isolation of NH_4BPh_4. An analytically pure sample of **4** (0.200 g) was treated with a 10% HCl/H_2O solution. After centrifugation of the solution and addition of $NaBPh_4$, a white solid was collected, washed, and identified by IR, NMR, and MS spectra as NH_4BPh_4 (43% isolated product) by comparison to the spectra of an analytically pure sample (Aldrich). The degradation test was also performed on the ^{15}N adduct of complex **4.** The IR displays the characteristic isotopic shift of NH stretching band from 3218 to 3248 cm^{-1}. The MS spectrum also exhibits the ammonium ion peak at 19 *m*/*z* compared to the 18 *m*/*z* peak for the non-isotopically enriched sample. The ^{15}N NMR resonance was located at 340.1 ppm (referenced to $CH_3{}^{15}NO_2$).[18]

X-ray Crystallography. A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data was collected on a Bruker AXS SMART 1K CCD diffractometer using 0.3° *ω* scans at 0°, 90°, 180°, and 270° in *ϕ* for the triclinic cells and 0°, 120°, and 240° in *ϕ* for the monoclinic cells. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[19] The diffraction data and unit-cell parameters were consistent with the reported space group $P\bar{1}$ for complexes **2** and **4**. No symmetry higher than triclinic was observed, and the solution in the centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The data for complex **1** were consistent with the space group *P*2(1)/*c*, and those for **3** were consistent with *Cc*. All structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were

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treated as idealized contributions. Structure **2** was treated with the Squeeze routine of PLATON[20] due to two lattice toluene molecules which were disordered over four positions. The anisotropic refinement parameters for a CH_2Cl_2 lattice molecule were only satisfactory when the occupancy was reduced to 3/4. Structure **3** was also treated with the Squeeze routine due to four lattice toluene molecules which were disordered over four positions. The anisotropic refinement parameters for a toluene lattice molecule were only satisfactory when the occupancy was reduced to 0.72. All scattering factors are contained in the SHELXTL 6.12 program library.[21] Relevant crystal data and selected bond distances and angles are reported in Tables 1and 2, respectively.

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Supporting Information Available: Complete crystallographic data for complexes **1**−**4** the $MeTPH_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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