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Structural Characterization and Self-Association of (Arylimido)vanadium(V) Triisopropoxides

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(Arylimido)vanadium(V) triisopropoxides, [(p-RC$_6$H$_4$N)V(O^{i}Pr)$_3$] (R = NMe$_2$, OMe, H, CN, NO$_2$, Br), were prepared by the reaction of VO(O^{i}Pr)$_3$ with the aryl isocyanates without solvent. The structures of the (arylimido)vanadium(V) triisopropoxides were characterized by single-crystal X-ray structure determination to elucidate the substituent effect on the self-association properties. Controlled association of the (arylimido)vanadium(V) triisopropoxides to the μ-oxo-bridged dimer complexes or the μ-imido-bridged dinuclear complex was achieved by changing the p-substituent on the benzene rings, which regulates the nature of the imido bonds. Furthermore, the one-dimensional linear polymer complex or the one-dimensional zigzag one through μ-oxo-bridging was formed in a solid state with the bimetallic (arylimido)vanadium(V) complex, [(^{i}PrO)$_3$V(N-p-C$_6$H$_4$N)V(O^{i}Pr)$_3$] or [(^{i}PrO)$_3$V(N-m-C$_6$H$_4$N)V(O^{i}Pr)$_3$], respectively.

Introduction

Architectural control of transition metal-directed assembly is one of the current research areas to create organized nanostructures for advanced materials.[1] Imido ligands are recognized as a particularly suitable ligand for stabilization of transition metal complexes in high oxidation states through extensive ligand-to-metal π donation.[2] (Imido)vanadium(V) complexes have attracted much attention[3,4] because of their potential applications as catalysts for olefin polymerization,[5] C−H activation,[6] and other related reactions.[7] (Imido)vanadium(V) complexes with alkoxide ligands are known to dimerize through μ-oxo-bridging in the crystal structures.[3e,m] On the other hand, only few examples for the preparation of μ-imido-brigded vanadium(IV) complexes, cyclodivanadazenes, from (imido)vanadium(V) complexes have been reported[4a,d−f] although the imido nitrogen is considered to participate in the coordination to another metal center. A substituent of the imido ligand is expected to influence the properties of the imido bond sterically and electronically. We herein report the structural characterization and self-association of (arylimido)vanadium(V) triisopropoxides depending on the p-substituents of the benzene rings.

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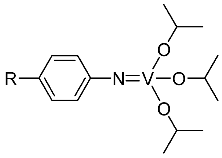
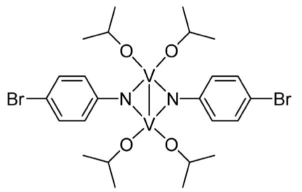
Results and Discussion

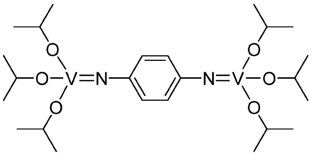
The (arylimido)vanadium(V) triisopropoxides bearing the electron-withdrawing *para*-substituents are not always obtained in good yields by general methods using a solvent. To overcome this problem, a synthetic approach to (arylimido)vanadium complexes was modified. The reaction of VO(O^{i}Pr)$_3$ with various *para*-substituted aryl isocyanates without solvent at 140 °C was performed to afford the corresponding (arylimido)vanadium(V) triisopropoxides, [(p-RC$_6$H$_4$N)V(O^{i}Pr)$_3$] (**1**: R = NMe$_2$, 88%; **2**: R = OMe, 87%; **3**: R = H, 72%; **4**: R = CN, 87%; **5**: R = NO$_2$, 61%). By using this synthetic approach, (arylimido)vanadium(V) triisopropoxides were found to be obtained with ease in good yields. In the ^{1}H NMR spectra of the (arylimido)vanadium(V) triisopropoxides, the aryl protons exhibited downfield shift as compared with the corresponding anulines, probably because of the electron-withdrawing nature of the imido bond (**1**: 7.12 and 6.47 ppm, *N*,*N*-dimethyl-*p*-phenylenediamine: 6.66−6.59 ppm; **2**: 7.15 and 6.72 ppm, *p*-anisidine: 6.71 and 6.62 ppm; **3**: 7.24, 7.17, and 7.05 ppm, aniline: 7.13, 6.73 and 6.67 ppm; **4**: 7.55 and 7.18 ppm, *p*-cyanoaniline: 7.42 and 6.66 ppm; **5**: 8.12 and 7.21 ppm, *p*-nitroaniline: 8.04 and 6.65 ppm;).



1: R = NMe$_2$ **2:** R = OMe
3: R = H **4:** R = CN
5: R = NO$_2$ **6a:** R = Br



6b



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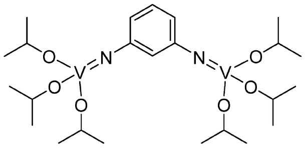

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The structural elucidation of the (arylimido)vanadium(V) triisopropoxides was performed by the single-crystal X-ray structure determination (Figure 1 and Table 1). The selected bond lengths and angles are listed in Tables 2 and 3, respectively. The solid state imido structure of **2** bearing the electron-donating methoxy group was characterized by the V(1)−N(1) distance of 1.677(2) Å and the nearly linear V(1)−N(1)−C(1) angle of 177.3(2)°, suggesting the greater participation of an sp-hybridized character in the nitrogen of the imido bond. Furthermore, a dimeric structure, in which each vanadium atom is coordinated in a trigonal-bipyramidal geometry ($\tau = 0.96$)[8] with the imido and bridging isopropoxide ligands in the apical positions, was observed in the crystal packing (Figure 1b and Table 4). The V(1)−V(1*) internuclear distance of 3.30 Å indicates the absence of any bonding interaction between the vanadiums. The axial V(1)−O(1*) bond is 0.40 Å longer than the equatorial V(1)−O(1) bond in the bridging isopropoxy group. The long axial V−O distance *trans* to the imido ligand suggests the weaker coordination.

The dimer complexes were also formed in the case of **1** bearing the electron-donating dimethylamino group and the nonsubstituted complex **3** in the crystals (Figure 1a and 1c, respectively). Linearity of the imido angles slightly decreased (**1**: V(1)−N(1)−C(1), 174.3(3)°; **3**: V(1)−N(1)−C(1), 175.1(1) and 175.6(1)°) although the V(1)−N(1) distance (1.678(3) Å for **1**, 1.673(1) and 1.674(1) Å for **3**) equals the one observed with **2**. In these (arylimido)vanadium(V) triisopropoxides, the greater participation of an sp-hybridized character in the nitrogen of the imido bond is suggested, resulting in the formation of the μ-oxo-bridged dimer complexes. The molecular structure of **4** bearing the electron-withdrawing cyano group was also characterized by the dimeric structure with the V(1)−N(1) distance of 1.674(2) Å and the nearly linear V(1)−N(1)−C(1) angle of 178.6(2)° (Figure 1d).

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(8) The structural parameter $\tau = (\beta - \alpha)/60$ for the coordination geometry of the five-coordinated complex proposed byAddison and Reedijik shows $\tau = 0.96$ for **2**, where α and β represent two basal angles ($\beta > \alpha$). The parameters for an ideal square pyramidal and trigonal bipyramidal geometries are $\tau = 0$ ($\alpha = \beta = 180°$) and $\tau = 1$ ($\alpha = 120°$ and $\beta = 180°$), respectively. The τ value of **2** indicates that the coordination geometry around the vanadium atom is a trigonal bipyramid. (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, *134*, 9–1356.

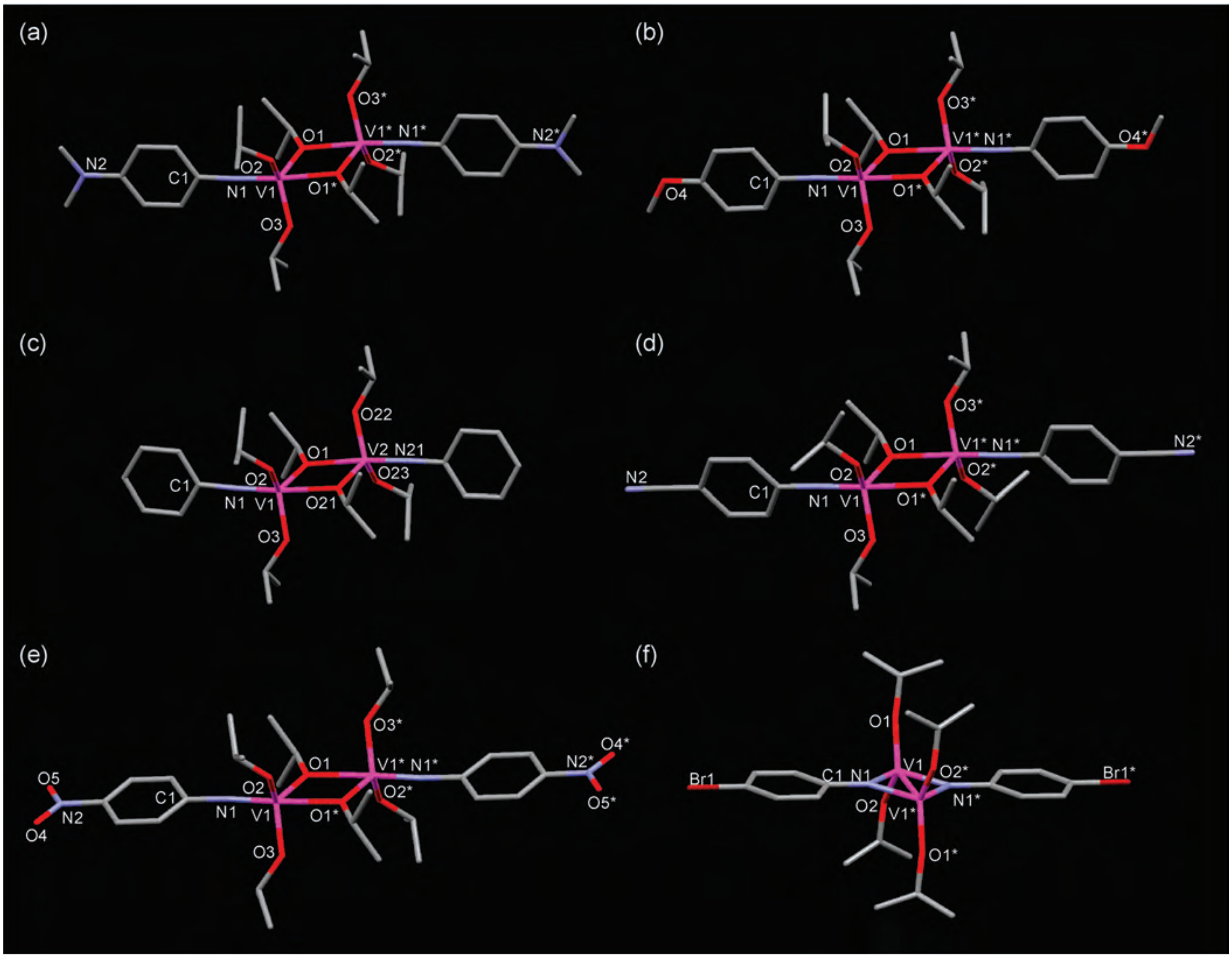

Figure 1. Molecular structures of (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** for the oxo-bridged dimer, and (f) **6b** for the imido-bridged dimer.

Table 1. Crystallographic Data for **1**−**5**, **6b**, and **7**−**8**

	1	2	3	4	5	6b	7	8
empirical formula	$C_{17}H_{31}N_2O_3V_1$	$C_{16}H_{28}N_1O_4V_1$	$C_{15}H_{26}N_1O_3V_1$	$C_{16}H_{25}N_2O_3V_1$	$C_{15}H_{25}N_2O_5V_1$	$C_{24}H_{36}N_2O_4Br_2V_2$	$C_{24}H_{46}N_2O_6V_2$	$C_{24}H_{46}N_2O_6V_2$
formula weight	362.39	349.34	319.32	344.33	364.31	678.25	560.52	560.52
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.8688(8)	9.646(1)	13.9263(6)	9.3345(4)	9.4051(2)	9.1967(2)	11.6041(6)	9.9672(3)
b, Å	10.6487(8)	10.340(1)	13.2611(6)	12.8258(7)	10.7161(2)	9.2848(8)	10.1850(5)	33.138(1)
c, Å	11.823(1)	11.547(2)	19.1670(9)	16.0171(9)	19.2289(5)	18.4382(8)	13.9926(7)	19.6333(5)
α, deg	77.008(2)	83.156(3)				91.797(3)		
β, deg	68.593(2)	71.755(5)	90.803(1)	92.1714(9)	93.7582(9)	93.680(4)	107.412(2)	93.2869(8)
γ, deg	68.278(2)	63.172(5)				94.664(5)		
V, Å^3	1068.8(2)	975.8(2)	3539.4(3)	1916.2(2)	1933.84(8)	1564.9(2)	1578.0(1)	6474.0(3)
Z	2	2	8	4	4	2	2	8
D_{calcd}, g cm^{-3}	1.126	1.189	1.198	1.193	1.251	1.439	1.180	1.150
μ(Mo Kα), cm^{-1}	4.77	5.23	5.66	5.29	5.35	31.86	6.26	6.10
T, °C	4	4	4	23	23	2	4	4
λ(Mo Kα), Å	0.71075	0.71069	0.71075	0.71069	0.71069	0.71069	0.71069	0.71069
$R1^a$	0.057	0.065	0.039	0.064	0.049	0.071	0.039	0.078
$wR2^b$	0.224	0.188	0.145	0.166	0.146	0.200	0.144	0.199

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2=[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Linearity of the imido angle increased as compared with **2**, probably because of the contribution of π-conjugation. The slightly decreased imido angle (V(1)−N(1)−C(1), 172.8(1)°) with the V(1)−N(1) distance of 1.670(2) Å was observed in the case of **5** bearing the electron-withdrawing nitro group (Figure 1e). The *para*-substituent of the aryl moiety was found to affect the hybridized properties and structures of the (arylimido)vanadium(V) compounds through π-conjugation.

The imido structure is considered to be an important factor to control the assembly. The imido nitrogen with the larger contribution of an sp^2-hybridized character could coordinate to another metal center by using a lone pair although such

Table 2. Selected Bond Lengths (Å) for **1**−**5**, **6b**, and **7**−**8**

	1	**2**	**3**^{a}		**4**	**5**	**6b**^{a}		**7**^{b}	**8**^{a}			
V1−N1	1.678(3)	1.677(2)	1.673(1)	1.674(1)	1.674(2)	1.670(2)	1.853(6)	1.844(6)	1.678(2)	1.674(4)	1.664(4)	1.673(4)	1.668(4)
V1−N1*							1.856(6)	1.850(6)					
V1−V1*							2.524(3)	2.526(3)					
V1−O1	1.850(3)	1.843(2)	1.844(1)	1.846(1)	1.835(2)	1.842(1)	1.742(6)	1.763(5)	1.865(2)	1.845(4)	1.857(4)	1.844(3)	1.849(4)
V1−O2	1.798(3)	1.794(2)	1.794(1)	1.787(1)	1.785(2)	1.781(2)	1.741(7)	1.742(6)	1.788(2)	1.782(4)	1.792(4)	1.781(4)	1.783(4)
V1−O3	1.789(4)	1.792(3)	1.789(1)	1.797(1)	1.781(2)	1.786(2)			1.795(1)	1.789(4)	1.792(5)	1.790(4)	1.782(4)
V1−O1*	2.226(2)	2.245(1)	2.240(1)	2.233(1)	2.242(2)	2.239(1)			2.198(1)	2.245(4)	2.224(4)	2.216(4)	2.274(4)
C1−N1	1.375(4)	1.368(2)	1.378(2)	1.376(2)	1.375(4)	1.380(3)	1.41(1)	1.404(10)	1.372(2)	1.389(6)	1.399(7)	1.385(7)	1.383(7)

^{a} Two independent molecules exist in an asymmetric unit. ^{b} The molecule sits on an inversion center.

Table 3. Selected Bond Angles (deg) for **1**−**5**, **6b**, and **7**−**8**

	1	2	3^a		4	5	6b^a		7^b	8^a			
C1−N1−V1	174.3(3)	177.3(2)	175.1(1)	175.6(1)	178.6(2)	172.8(1)	138.0(5)	135.7(5)	177.8(1)	171.9(4)	179.8(4)	177.0(4)	177.9(4)
C1−N1−V1*							136.2(5)	138.0(5)					
V1−N1−V1*							85.8(3)	86.3(3)					
V1−O1−V1*	106.6(1)	107.03(7)	107.49(5)	107.17(5)	107.61(10)	108.12(6)			107.74(6)	107.7(2)	108.0(2)	105.9(2)	108.1(2)
N1−V1−O1	101.9(1)	101.92(9)	101.82(6)	101.74(6)	101.3(1)	103.75(7)	113.5(3)	111.9(3)	100.90(7)	103.1(2)	101.4(2)	101.0(2)	101.0(2)
N1−V1−O2	100.0(1)	101.85(9)	100.01(6)	102.56(6)	102.5(1)	100.06(8)	112.4(3)	111.4(3)	100.64(7)	102.2(2)	101.0(2)	101.9(2)	101.1(2)
N1−V1−O3	101.9(2)	101.0(1)	102.61(6)	99.88(6)	100.8(1)	100.31(8)			100.40(8)	99.6(2)	101.8(2)	100.5(2)	101.8(2)
N1−V1−O1*	175.0(2)	174.88(9)	173.87(5)	174.22(5)	173.6(1)	175.59(7)			173.15(7)	174.9(2)	173.4(2)	174.6(2)	173.1(2)
N1*−V1-O1							112.4(3)	112.8(3)					
N1*−V1-O2							111.5(3)	112.9(3)					
N1−V1−N1*							94.2(3)	93.7(3)					
N1−V1−V1*							47.2(2)	46.9(2)					
O1−V1−O2	118.0(2)	116.93(10)	118.65(5)	116.67(5)	115.75(10)	118.42(7)	111.6(3)	112.8(3)	118.75(7)	115.3(2)	117.2(2)	118.2(2)	118.0(2)
O1−V1−O3	116.9(1)	117.45(9)	116.54(5)	118.23(5)	118.5(1)	117.04(7)			119.65(7)	118.9(2)	118.8(2)	117.0(2)	117.6(2)
O1−V1−O1*	73.4(1)	72.97(7)	72.57(4)	72.69(4)	72.39(10)	71.88(6)			72.26(6)	72.3(2)	72.0(2)	73.6(1)	72.1(1)
O2−V1−O3	113.9(1)	113.78(10)	113.22(5)	113.68(6)	114.1(1)	113.08(7)			111.55(7)	114.0(2)	112.5(2)	113.9(2)	113.2(2)
O2−V1−O1*	80.98(10)	81.13(6)	80.99(5)	81.66(5)	81.73(9)	81.89(6)			82.68(6)	82.0(2)	82.2(1)	81.1(2)	82.0(2)
O3−V1−O1*	82.0(1)	81.35(8)	82.40(5)	81.79(5)	81.61(8)	82.44(6)			83.76(6)	81.1(2)	82.1(2)	82.3(2)	82.5(2)

^{a} Two independent molecules exist in an asymmetric unit. ^{b} The molecule sits on an inversion center.

Table 4. Structural Parameter τ of **1**−**5** and **7**−**8**

	1	2	3^a		4	5	7^b	8^a			
τ	0.95	0.96	0.92	0.93	0.92	0.95	0.89	0.93	0.91	0.94	0.92

^{a} Two independent molecules exist in an asymmetric unit. ^{b} The molecule sits on an inversion center.

coordination is not possible with the greater participation of an sp-hybridized character. The self-association was found to be controlled by the characteristics of the V−N imido bond, which depends on the difference in π-conjugation of the *p*-substituent on the benzene ring. It should be noted that the μ-imido-brigded dinuclear vanadium(IV) complex **6b**, $[V(\mu\text{-N-}p\text{-}C_6H_4Br)(O^iPr)_2]_2$, was obtained in 83% yield by recrystallization of the (arylimido)vanadium(V) complex **6a**, $[(p\text{-}BrC_6H_4N)V(O^iPr)_3]$, which was initially formed by the reaction with 4-bromophenylisocyanate in 84% yield. The lone pair on the nitrogen atom coordinates to the vanadium center to afford the cyclodivanadazene **6b**. The single-crystal X-ray structure determination of the complex **6b**, wherein two independent molecules exist in an asymmetric unit, revealed a dinuclear structure with two imido ligands bridging two $V(O^iPr)_2$ moieties. Each vanadium atom is coordinated in a distorted tetrahedral geometry as shown in Figure 1f. The torsion angles V(1)−N(1)−V(1*)−N(1*) (0.0 and 0.0000(1)°) indicate that the V_2N_2 core is almost planar. The V(1)−V(1*) distances of 2.524(3) and 2.526(3) Å are close to those found in the cyclodivanadazenes so far reported.[4a,b,d−f,h−j,7f] The V−N distances (V(1)−N(1) = 1.853(6) and 1.844(6)Å, V(1)−N(1*) = 1.856(6) and 1.850(6)Å) are about 0.17 Å longer than that of **2**. The V(1)−N(1)−V(1*) angles of the V_2N_2 core are 85.8(3) and 86.3(3)°, indicating no hybridization on the nitrogen atom.

A bimetallic complex containing the bridging isopropoxide ligands is envisioned to expand self-association through μ-oxo-bridging in a crystal state. The complex **7**, $[(O^iPr)_3V(N\text{-}p\text{-}C_6H_4N)V(O^iPr)_3]$, was produced by the treatment of $VO(O^iPr)_3$ with 1,4-phenylenediisocyanate in 80% yield. The structure of **7** was confirmed by X-ray crystallographic analysis. Because of the conjugation, the V−N−Ph−N−V core is almost linear with the V(1)−N(1) distance of 1.678(2) Å and the V(1)−N(1)−C(1) angle of 177.8(1)°. As expected, the one-dimensional linear polymer complex was formed through μ-oxo-bridging in the crystal packing as shown in Figure 2a. The bimetallic complex **8**, $[(O^iPr)_3V(N\text{-}m\text{-}C_6H_4N)V(O^iPr)_3]$, which was prepared from 1,3-phenylenediisocyanate in 60% yield, afforded the one-dimensional zigzag polymer complex through μ-oxo-bridging as depicted in Figure 2b.

In the ^{51}V NMR spectra of d^0 diamagnetic vanadium complexes, the vanadium nuclei become increasingly shielded as the electronegativity of the ligand attached to the coordination center increases.[3e] ^{51}V NMR was measured to clarify the electronic environment of the vanadium atom. The ^{51}V chemical shift of the nonsubstituted (phenylimido)vanadium(V) complex **3** was detected at −628 ppm. In the ^{51}V NMR spectra of the (arylimido)vanadium(V) triisopropoxides, ^{51}V chemical shifts were observed at a lower field with increase of the electron-donating capability of the *para*-substituent (**1**: −549 ppm, **2**: −602 ppm). On the contrary, the electron-withdrawing substituent, in which the imido nitrogen atom becomes more electronegative to increase ^{51}V nuclear shielding, caused the higher field shift (**4**: −640 ppm, **5**: −642 ppm). These results are consistent with those of

Figure 2. A portion of a layer containing the one-dimensional linear molecular assembly through oxo-bridging in the crystal packing of (a) **7** and (b) **8**.

the (arylimido)vanadium(V) trichlorides reported by Maatta and co-workers.[3e] It should be noted that the imido-brigded dinuclear vanadium(IV) complex **6b** exhibited the ^{51}V chemical shift at 226 ppm despite of the d^1 vanadium(IV) species. The formation of the V−V single bond, in which each vanadium serves as a σ donor, is considered to cause the deshielding of the ^{51}V nuclei in the imido-bridged dimer.[4f,j] The conjugated bimetallic complex **7** showed the ^{51}V chemical shift at −602 ppm, indicating that the electronic environment of the vanadium atom of **7** is likely to be almost the same as that of **2** bearing the electron-donating methoxy group. On the other hand, the ^{51}V chemical shift of the *meta*-substituted bimetallic complex **8** was observed at −637 ppm, which is close to that of **4** bearing the electron-withdrawing cyano group. These results indicate that the electronic environment of the vanadium atom appears to be controlled by the π conjugated substituent.

Conclusions

The (arylimido)vanadium(V) and the corresponding bimetallic triisopropoxides were prepared by the reaction of VO(O^{i}Pr)$_3$ with the aryl isocyanates and diisocyanates, respectively, without solvent. Structural characterization by the single-crystal X-ray structure determination indicates the substituent effect on the self-association properties. The *para*-substituent of the aryl moiety controls the assembly of the (arylimido)vanadium(V) triisopropoxides to give the μ-oxo-bridged dimer complexes or the μ-imido-bridged dinuclear complex. The present architectural control of the dimensional structures is considered to be a useful approach to artificial organized metallic systems. Furthermore, the *para*-substituent was demonstrated to affect the electronic properties of the vanadium center by the π conjugation. Regulation of the redox properties of the vanadium center is considered to be one of the key factors to develop of an efficient vanadium catalytic system.[9] The application of (arylimido)vanadium(V) complexes for catalysis is now in progress.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Solvents were dried by refluxing in the presence of appropriate drying reagents, distilled under an atmosphere of nitrogen, and were stored in the drybox. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 (400 MHz) or Varian MERCURY 300 (300 MHz) spectrometer. The chemical shifts were referenced to the residual resonances of deuterated solvents. ^{51}V NMR spectra were obtained with a JEOL JNM-ECP 400 (105 MHz) spectrometer with VOCl$_3$ as an external standard.

General Procedure for the Preparation of (Arylimido)vanadium(V) Triisopropoxide by Using *para*-Substituted Aryl Isocyanate. A mixture of vanadium(V) oxytriisoproxide (495 μL, 2.1 mmol) and the corresponding *para*-substituted aryl isocyanate (2.0 mmol) was stirred in no solvent under an atmosphere of nitrogen at 140 °C for 3 h. The resulting mixture was then allowed to be cooled to room temperature, and then 20 mL of dichloromethane was added. The resulting solution was filtered off, and the filtrate was evaporated under reduced pressure. The resultant residue was recrystallized from hexane or dichloromethane at −30 °C, giving the desired (arylimido)vanadium(V) triisoproxide.

1: Isolated yield 88%; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.12 (d, $J = 9.1$ Hz, 2H), 6.47 (d, $J = 9.1$ Hz, 2H), 5.13 (sept, $J = 6.0$ Hz, 3H), 2.97 (s, 6H), 1.34 (d, $J = 6.0$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −549 ppm (t, $^1J_{51V/14N} = 114$ Hz).

2: Isolated yield 87%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.15 (d, $J = 9.0$ Hz, 2H), 6.72 (d, $J = 9.0$ Hz, 2H), 5.12 (sept, $J = 6.1$ Hz, 3H), 3.78 (s, 3H), 1.34 (d, $J = 6.1$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −602 ppm (t, $^1J_{51V/14N} = 114$ Hz).

3: Isolated yield 72%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.24 (dd, $J = 8.4$, 7.3 Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 5.14 (sept, $J = 6.2$ Hz, 3H), 3.78 (s, 3H), 1.35 (d, $J = 6.2$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −628 ppm (t, $^1J_{51V/14N} = 114$ Hz).

4: Isolated yield 87%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 (d, $J = 8.1$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 5.11 (sept, $J = 6.0$ Hz, 3H), 1.34 (d, $J = 6.0$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −640 ppm (t, $^1J_{51V/14N} = 116$ Hz).

5: Isolated yield 61%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.21 (d, $J = 9.0$ Hz, 2H), 5.13 (sept, $J = 6.0$ Hz, 3H), 3.78 (s, 3H), 1.35 (d, $J = 6.0$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −642 ppm (t, $^1J_{51V/14N} = 114$ Hz).

6a: Isolated yield 84%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.36 (d, $J = 8.7$ Hz, 2H), 7.04 (d, $J = 8.7$ Hz, 2H), 5.11 (sept, $J = 6.3$ Hz, 3H), 1.34 (d, $J = 6.3$ Hz, 18H); ^{51}V NMR (105 MHz, CD_2Cl_2) −629 ppm (t, $^1J_{51V/14N} = 116$ Hz).

7: Isolated yield 80%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.02 (s, 4H), 5.11 (sept, $J = 6.1$ Hz, 6H), 1.33 (d, $J = 6.1$ Hz, 36H); ^{51}V NMR (105 MHz, CD_2Cl_2) −602 ppm (t, $^1J_{51V/14N} = 114$ Hz).

8: Isolated yield 60%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.10 (t, $J = 8.0$ Hz, 1H), 6.96 (s, 1H), 6.86 (d, $J = 8.0$ Hz, 2H), 5.11 (sept, $J = 6.2$ Hz, 6H), 1.34 (d, $J = 6.2$ Hz, 36H); ^{51}V NMR (105 MHz, CD_2Cl_2) −637 ppm (t, $^1J_{51V/14N} = 115$ Hz).

Preparation of the μ-Imido-Brigded Dinuclear Vanadium(IV) Complex 6b. The recrystallization of the (arylimido)vanadium(V) complex **6a** (2.0 mg, 0.005 mmol) from 1.5 mL of hexane and 0.5 mL of dichloromethane at room temperature afforded the μ-imido-brigded dinuclear vanadium(IV) complex **6b** in 83% yield.

6b: Isolated yield 83%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54 (d, $J = 8.7$ Hz, 4H), 7.36 (d, $J = 8.7$ Hz, 4H), 4.13 (sept, $J = 6.0$ Hz, 4H), 0.91 (d, $J = 6.0$ Hz, 24H); ^{51}V NMR (105 MHz, CD_2Cl_2) 226 ppm (br s, the line width at half-height is 390 Hz).

X-ray Structure Analysis. All measurements for **1**−**5**, **6b**, and **7**−**8** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structures of **2**−**5**, and **7**−**8** were solved by direct methods and expanded using Fourier techniques. The structures of **1** and **6b** were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. The rather high $R1$ and $wR2$ for **6b** and **8** are probably due to the data quality. Crystallographic details are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2 and Table 3, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC-668956 for **1**, CCDC-656899 for **2**, CCDC-668957 for **3**, CCDC-656902 for **4**, CCDC-668958 for **5**, CCDC-656901 for **6b**, CCDC-656900 for **7**, and CCDC-668959 for **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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