

Structural tuning and self-association of (arylimido)vanadium(V) compounds*

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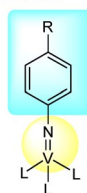
Abstract: Structural tuning and self-association of (arylimido)vanadium(V) compounds are demonstrated to be controlled through π -conjugation by the *para*-substituents of the aryl moieties.

Keywords: vanadium; imido bond; self-association; oxo-bridged dimer; imido-bridged dimer.

INTRODUCTION

The imido ligand coordinates through a metal-nitrogen multiple bond [1], in which the imido ligand can serve as an ancillary ligand. The imido ligand is known to be 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 the potential application as a catalyst for olefin polymerization [5], C–H activation [6], and others [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-bridged 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. Introduction of a substituent onto the imido ligands is expected to influence the steric structures and electronic properties of a vanadium center. In such a sense, design of the imido ligands is envisioned to be one of the key factors in the development of efficient catalysts and architectural control of metal-directed assembly. The substituent effect of the imido ligands has been reported only spectroscopically and theoretically [3e]. The systematic correlation between the imido structures and properties is to be investigated. In this paper, we summarize our ongoing research on structural tuning and self-association of (arylimido)vanadium(V) compounds [8].

Substituent Effect
Steric
Electronic



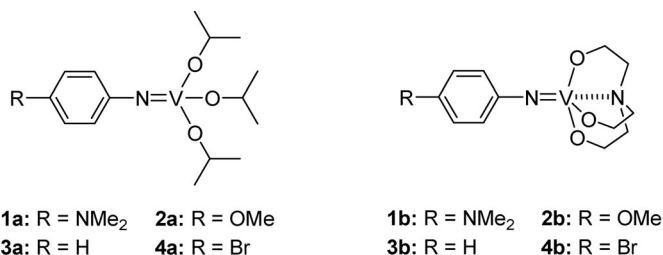
Imido complex

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SYNTHESIS AND STRUCTURAL TUNING OF (ARYLIMIDO)VANADIUM(V) COMPOUNDS

The reaction of $\text{VO}(\text{O}^i\text{Pr})_3$ with various *para*-substituted aryl isocyanates without solvent at 140 °C is performed to afford the corresponding (arylimido)vanadium(V) triisopropoxides, $[(p\text{-RC}_6\text{H}_4\text{N})\text{V}(\text{O}^i\text{Pr})_3]$ (**1a**: R = NMe₂, 88 %; **2a**: R = OMe, 87 %; **3a**: R = H, 72 %; **4a**: R = Br, 84 %). By using this synthetic approach, (arylimido)vanadium(V) triisopropoxides are found to be obtained with ease in good yields. The (arylimido)vanadium(V) triisopropoxides bearing the electron-withdrawing *para*-substituents are not always obtained in good yields by general methods using a solvent. In the ¹H NMR spectra of the (arylimido)vanadium(V) triisopropoxides, the aryl protons exhibit down-field shift as compared with the corresponding anilines, probably due to the electron-withdrawing nature of the imido bonds (**1a**: 7.12 and 6.47 ppm, *N,N*-dimethyl-*p*-phenylenediamine: 6.66–6.59 ppm; **2a**: 7.15 and 6.72 ppm, *p*-anisidine: 6.71 and 6.62 ppm; **3a**: 7.24, 7.17, and 7.05 ppm, aniline: 7.13, 6.73, and 6.67 ppm; **4a**: 7.36 and 7.04 ppm, *p*-bromoaniline: 7.21 and 6.57 ppm). To clarify the substituent effect on the electronic environment of the vanadium species, triethanolamine is used as a basal ligand to prevent the dimerization [9]. The ligand exchange reaction with triethanolamine in CH₂Cl₂ at room temperature affords the corresponding (arylimido)vanadium(V) triethanolaminates, $[(p\text{-RC}_6\text{H}_4\text{N})\text{V}(\text{TEA})]$ (**1b**: R = NMe₂, **2b**: R = OMe, **3b**: R = H, **4b**: R = Br, **1**).



In the ⁵¹V NMR spectra of d⁰ diamagnetic vanadium complexes, the vanadium nuclei become increasingly shielded as the electronegativity of the ligand attached to the coordination center increases [3e]. ⁵¹V NMR measurements are performed in order to clarify the substituent effect on the electronic environment of the vanadium species. The ⁵¹V chemical shift of the nonsubstituted (phenylimido)vanadium(V) triethanolamine **3b** is detected at –327 ppm. In the ⁵¹V NMR spectra of the (arylimido)vanadium(V) triethanolaminates, ⁵¹V chemical shifts are observed at the lower field with increase of the electron-donating capability of the *para*-substituents (**1b**: –224 ppm, **2b**: –292 ppm). On the contrary, the electron-withdrawing substituent, in which the nitrogen atom of the imido bond becomes more electronegative to increase ⁵¹V nuclear shielding, causes the higher field shift (**4b**: –328 ppm). These results are consistent with those of the (arylimido)vanadium(V) trichlorides reported by Maatta and coworkers [3e].

Structural characterization of the (arylimido)vanadium(V) triethanolaminates is demonstrated by single-crystal X-ray structure determination to elucidate the substituent effect on the imido structures (Fig. 1). The important bond lengths and angles are listed in Table 1. The nonsubstituted (phenylimido)vanadium(V) triethanolamine **3b** reveals the imido structure with the V(1)–N(1) distance of 1.686(2) Å and the bent V(1)–N(1)–C(1) angle of 166.7(2)°, in which a monomeric structure with a pseudo-trigonal bipyramidal geometry at the metal center ($\tau = 0.99$) [10] is observed (Fig. 1c and Table 2). The vanadium atom is pulled out of the plane formed by triethanolamine oxygen atoms in the direction of the imido nitrogen. The three equatorial vanadium–oxygen bond distances are statistically identical.

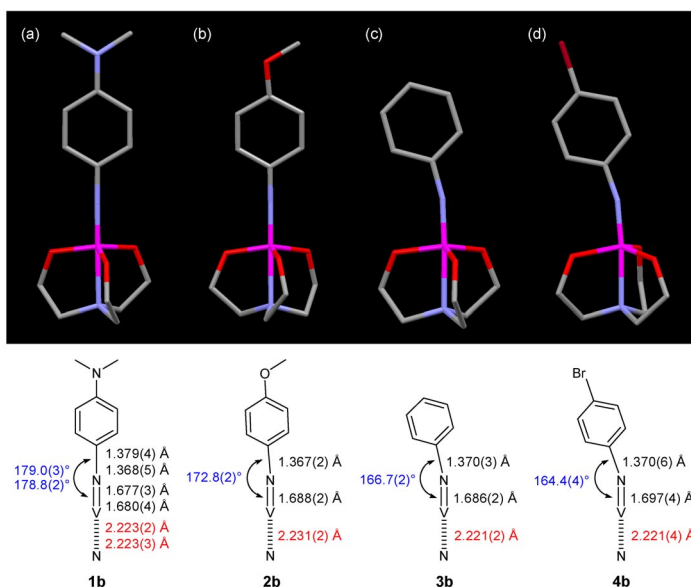


Fig. 1 Molecular structures and schematic representation of (a) **1b**, (b) **2b**, (c) **3b**, and (d) **4b**.

Table 1 Selected bond lengths (Å) and angles (deg.) for **1b–4b**.

	1b ^a		2b	3b	4b
Bond lengths					
V1–N1	1.677(3)	1.680(4)	1.688(2)	1.686(2)	1.697(4)
V1–N2	2.223(2)	2.223(3)	2.231(2)	2.221(2)	2.221(4)
V1–O1	1.838(2)	1.833(2)	1.830(1)	1.834(2)	1.826(3)
V1–O2	1.824(3)	1.828(2)	1.828(1)	1.815(2)	1.817(4)
V1–O3	1.835(3)	1.834(2)	1.829(1)	1.831(2)	1.833(3)
C1–N1	1.379(4)	1.368(5)	1.367(2)	1.370(3)	1.370(6)
Bond angles					
C1–N1–V1	179.0(3)	178.8(2)	172.8(2)	166.7(2)	164.4(4)
N1–V1–N2	179.1(1)	179.2(1)	178.20(8)	177.48(7)	175.2(2)
N1–V1–O1	98.7(1)	99.1(1)	97.79(8)	97.04(8)	100.0(2)
N1–V1–O2	99.6(1)	99.7(2)	100.14(7)	100.46(9)	102.7(2)
N1–V1–O3	99.5(1)	99.1(1)	100.18(7)	100.50(8)	95.5(2)
O1–V1–O2	116.1(1)	118.0(1)	118.04(6)	118.32(8)	115.6(2)
O1–V1–O3	118.1(1)	117.6(1)	117.09(6)	117.14(7)	118.4(1)
O1–V1–N2	80.6(1)	80.5(1)	80.42(6)	80.44(6)	80.7(2)
O2–V1–O3	118.2(1)	116.8(1)	117.08(6)	116.80(8)	118.2(2)
O2–V1–N2	81.16(10)	81.1(1)	80.61(6)	80.66(7)	81.1(2)
O3–V1–N2	80.5(1)	80.5(1)	80.86(5)	80.91(6)	80.1(2)

^a Two independent molecules exist in an asymmetric unit.

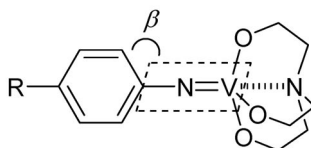
Table 2 The structural parameter τ of **1a–3a**, **5a**, and **1b–4b**.

	1a	2a	3a ^a	5a ^b	1b ^a	2b	3b	4b		
τ	0.95	0.96	0.92	0.93	0.89	1.02	1.02	1.00	0.99	0.95

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

In the case of the (arylimido)vanadium(V) triethanolaminate **2b** with the electron-donating methoxy group, linearity of the imido angle is increased [V(1)–N(1)–C(1), 172.8(2)°] although the V(1)–N(1) distance of 1.688(2) Å is equal to the one observed with **3b** (Fig. 1b). Furthermore, the imido angle is more straightened with the (arylimido)vanadium(V) triethanolaminate **1b** bearing the dimethylamino group. The V(1)–N(1)–C(1) angles of 179.0(3) and 178.8(2)° with the V(1)–N(1) distances of 1.677(3) and 1.680(4) Å are observed in the crystal structure (Fig. 1a). On the contrary, the introduction of the bromo group leads to the more bent imido bond (**4b**: V(1)–N(1)–C(1), 164.4(4)°; V(1)–N(1), 1.697(4) Å) than **3b** (Fig. 1d).

In the (arylimido)vanadium(V) triethanolaminates described in this paper, the structures of the triethanolamine moieties are almost the same and any notable difference is not observed in the V(1)–N(1) and C(1)–N(1) distances. It should be noted that the *para*-substituent of the aryl moiety is also found to affect the twist angle β defined as the angle between the least-squares planes of the benzene ring and the C(*ipso*)-imido bond (Fig. 2 and Table 3) which is considered to correlate to the properties of the imido bond. An almost perpendicular twist angle β is observed in the case of the complexes with the π -conjugative electron-donating substituents [43.11(9)° and 101.82(9)° for **1b**; 95.92(5)° for **2b**]. However, the benzene rings of other (arylimido)vanadium(V) triethanolaminates are nearly parallel to the least-squares planes of the corresponding C(*ipso*)-imido bonds [8.35(6)° for **3b**; 11.2(1)° for **4b**]. The linear imido angle and the almost perpendicular twist angle β of the (arylimido)vanadium(V) triethanolaminate with the π -conjugating electron-donating substituent might be due to greater participation of the sp hybrid character in the nitrogen of the imido bond (Fig. 3). The lone pair of electrons is likely to be localized in a nitrogen p-orbital, which is likely to interact with the metal π -acceptor orbitals and aryl π -orbitals. In contrast, the larger contribution of sp² hybrid character in the nitrogen of the imido bond is suggested because of the bent imido bond and the nearly parallel twist angle β in the case of the (arylimido)vanadium(V) triethanolaminate bearing no π -conjugating electron-donating substituent, wherein the filled imido π -orbital seems to interact with the aryl π -orbitals.

**Fig. 2** The twist angle β defined as the angle between the least-squares planes of the benzene ring and the C(*ipso*)-imido bond.**Table 3** The twist angle β defined as the angle between the least-squares planes of the benzene ring and the C(*ipso*)-imido bond of **1b–4b**.

	1b ^a	2b	3b	4b	
β	43.11(9)	101.82(9)	95.92(5)	8.35(6)	11.2(1)

^a Two independent molecules exist in an asymmetric unit.

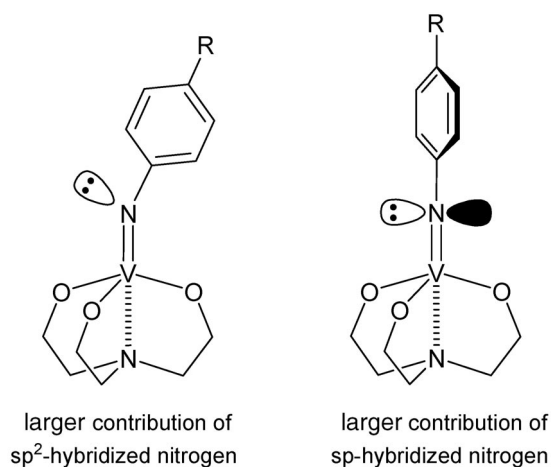


Fig. 3 Proposal valence bond structures for a vanadium bound imido ligand.

SELF-ASSOCIATION OF (ARYLIMIDO)VANADIUM(V) COMPOUNDS

Architectural control of transition-metal-directed assembly is one of the current research areas for creating organized nanostructures for advanced materials [11]. (Arylimido)vanadium(V) triisopropoxides are considered to dimerize through μ -oxo-bridging in the crystal states [3e,m]. The substituent effect on the self-association properties of (arylimido)vanadium(V) triisopropoxides is examined by single-crystal X-ray structure determination (Fig. 4). The important bond lengths and angles are listed in Table 4. The solid-state imido structure of **2a** bearing the electron-donating methoxy group is

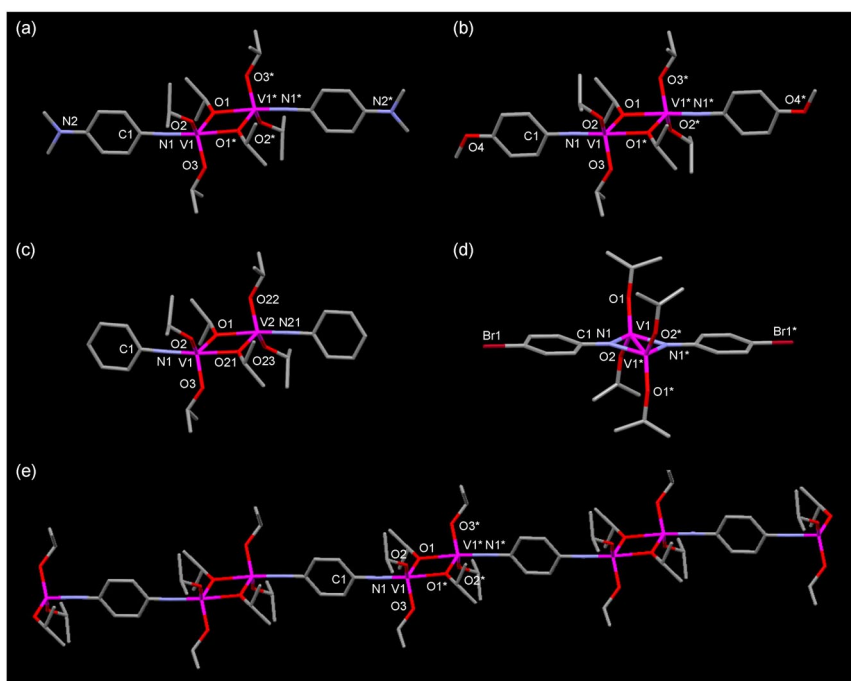


Fig. 4 Molecular structures of (a) **1a**, (b) **2a**, and (c) **3a** for the oxo-bridged dimer complex, (d) **4c** for the imido-bridged dimer complex, and (e) **5a** for the oxo-bridged one-dimensional linear polymer complex.

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 the sp hybrid character in the nitrogen of the imido bond. Furthermore, a dimeric structure, in which each vanadium atom is coordinated in a trigonal-bipyramidal geometry ($\tau = 0.96$) with the imido and bridging isopropoxide ligands in the apical positions, is observed in the crystal packing (Fig. 4b). 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.

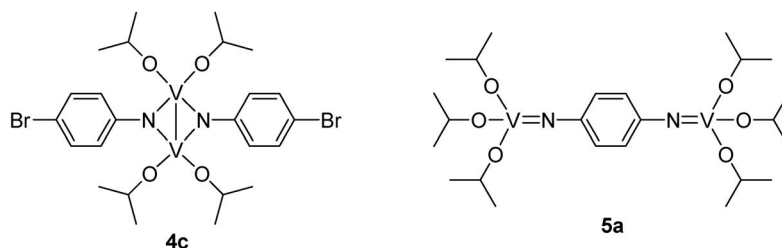
Table 4 Selected bond lengths (Å) and angles (deg.) for **1a–3a**, **4c**, and **5a**.

	1a	2a	3a ^a		4c ^a		5a ^b
Bond lengths							
V1–N1	1.678(3)	1.677(2)	1.673(1)	1.674(1)	1.853(6)	1.844(6)	1.678(2)
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)	1.742(6)	1.763(5)	1.865(2)
V1–O2	1.798(3)	1.794(2)	1.794(1)	1.787(1)	1.741(7)	1.742(6)	1.788(2)
V1–O3	1.789(4)	1.792(3)	1.789(1)	1.797(1)			1.795(1)
V1–O1*	2.226(2)	2.245(1)	2.240(1)	2.233(1)			2.198(1)
C1–N1	1.375(4)	1.368(2)	1.378(2)	1.376(2)	1.41(1)	1.404(10)	1.372(2)
Bond angles							
C1–N1–V1	174.3(3)	177.3(2)	175.1(1)	175.6(1)	138.0(5)	135.7(5)	177.8(1)
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)			107.74(6)
N1–V1–O1	101.9(1)	101.92(9)	101.82(6)	101.74(6)	113.5(3)	111.9(3)	100.90(7)
N1–V1–O2	100.0(1)	101.85(9)	100.01(6)	102.56(6)	112.4(3)	111.4(3)	100.64(7)
N1–V1–O3	101.9(2)	101.0(1)	102.61(6)	99.88(6)			100.40(8)
N1–V1–O1*	175.0(2)	174.88(9)	173.87(5)	174.22(5)			173.15(7)
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)	111.6(3)	112.8(3)	118.75(7)
O1–V1–O3	116.9(1)	117.45(9)	116.54(5)	118.23(5)			119.65(7)
O1–V1–O1*	73.4(1)	72.97(7)	72.57(4)	72.69(4)			72.26(6)
O2–V1–O3	113.9(1)	113.78(10)	113.22(5)	113.68(6)			111.55(7)
O2–V1–O1*	80.98(10)	81.13(6)	80.99(5)	81.66(5)			82.68(6)
O3–V1–O1*	82.0(1)	81.35(8)	82.40(5)	81.79(5)			83.76(6)

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

The dimer complexes are also formed in the case of **1a** bearing the electron-donating dimethylamino group and the nonsubstituted complex **3a** in the crystals (Figs. 4a and 4c, respectively). Linearity of the imido angles slightly decreases [**1a**: V(1)–N(1)–C(1), 174.3(3)°; **3a**: V(1)–N(1)–C(1), 175.1(1) and 175.6(1)°] although the V(1)–N(1) distances [1.678(3) Å for **1a**, 1.673(1) and 1.674(1) Å for **3a**] are equal to the one observed with **2a**. 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 imido structure is considered to be an important factor to control the assembly. The imido nitrogen with the larger contribution of the sp^2 hybrid character could coordinate to another metal center by using a lone pair although such coordination is not possible with the greater participation of the sp hybrid character. The self-association is found to be controlled by the characteristics of the V–N imido bond, which depends on the difference in π -conjugation of the *para*-substituent on the benzene ring. It should be noted that the μ -imido-bridged dinuclear vanadium(IV) complex **4c**, $[\text{V}(\mu\text{-N-}p\text{-C}_6\text{H}_4\text{Br})(\text{O}^i\text{Pr})_2]_2$, is obtained in 83 % yield by recrystallization of the (arylimido)vanadium(V) triisopropoxide **4a**, $[(p\text{-BrC}_6\text{H}_4\text{N})\text{V}(\text{O}^i\text{Pr})_3]$, which is 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 **4c**. The single-crystal X-ray structure determination of the complex **4c**, wherein two independent molecules exist in an asymmetric unit, reveals a dinuclear structure with two imido ligands bridging two $\text{V}(\text{O}^i\text{Pr})_2$ moieties. Each vanadium atom is coordinated in a distorted tetrahedral geometry as shown in Fig. 4d. The torsion angles $\text{V}(1)\text{-N}(1)\text{-V}(1^*)\text{-N}(1^*)$ [0.0 and $0.0000(1)^\circ$] indicate that the V_2N_2 core is almost planar. The $\text{V}(1)\text{-V}(1^*)$ 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 [$\text{V}(1)\text{-N}(1) = 1.853(6)$ and $1.844(6)$ Å, $\text{V}(1)\text{-N}(1^*) = 1.856(6)$ and $1.850(6)$ Å] are ca. 0.17 Å longer than those of **2**. The $\text{V}(1)\text{-N}(1)\text{-V}(1^*)$ angles of the V_2N_2 core are $85.8(3)$ and $86.3(3)^\circ$, 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 **5a**, $[(\text{O}^i\text{Pr})_3\text{V}(\text{N-}p\text{-C}_6\text{H}_4\text{N})\text{V}(\text{O}^i\text{Pr})_3]$, is produced by the treatment of $\text{VO}(\text{O}^i\text{Pr})_3$ with 1,4-phenylenediisocyanate in 80 % yield. The structure of **5a** is confirmed by X-ray crystallographic analysis. Due to the conjugation, the V–N–Ph–N–V core is almost linear with the $\text{V}(1)\text{-N}(1)$ distance of 1.678(2) Å and the $\text{V}(1)\text{-N}(1)\text{-C}(1)$ angle of $177.8(1)^\circ$. As expected, the one-dimensional linear polymer complex is formed through μ -oxo-bridging in the crystal packing as shown in Fig. 4e.

CONCLUSION

A variety of (arylimido)vanadium(V) triethanolamines, $[(p\text{-RC}_6\text{H}_4\text{N})\text{V}(\text{TEA})]$, are synthesized by the ligand-exchange reaction of the corresponding (arylimido)vanadium(V) triisopropoxides, $[(p\text{-RC}_6\text{H}_4\text{N})\text{V}(\text{O}^i\text{Pr})_3]$, which are prepared by the reaction of $\text{VO}(\text{O}^i\text{Pr})_3$ with various *para*-substituted aryl isocyanates without solvent. Structural characterization of the (arylimido)vanadium(V) triethanolamines is demonstrated by single-crystal X-ray structure determination to elucidate the substituent effect on the imido structures, in which the imido structures are found to be controlled through π -conjugation by the *para*-substituents of the aryl moieties. Also, the *para*-substituents of the aryl moieties are found to affect the electronic environment of the vanadium centers through π -conjugation, which is considered to control the electronic properties of the vanadium centers. Regulation of the redox properties of the vanadium centers is one of the key factors in the development of an efficient vanadium catalytic system [12]. Furthermore, the *para*-substituents of the aryl moieties is demonstrated to control

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.

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