Self-Assembly

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# Arylimidovanadium(V) Complexes for a Tridendritic Centrosymmetric Structural Motif or Axial Chirality**

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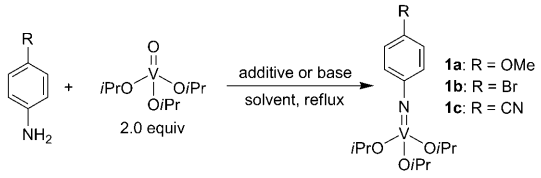
Imido ligands are recognized as particularly suitable for the stabilization of complexes containing metals in high oxidation states through extensive ligand-to-metal π-donation.[1] The imido ligand coordinates through a metal–nitrogen multiple bond,[2] and can serve as an ancillary or supporting ligand. Imidovanadium(V) complexes have attracted much attention[3] because of their potential applications as catalysts for olefin polymerization,[4] C–H activation,[5] and other related reactions.[6] One of the key factors in the development of efficient imidovanadium catalysts is considered to be the design of the imido ligands. Substituents in the *para* position on the benzene rings of arylimidovanadium(V) complexes affect the nature of the imido bonds through π conjugation.[7] Furthermore, the self-association of the arylimidovanadium(V) triisopropoxides is demonstrated to form either μ-isopropoxido-bridged dimer complexes or μ-arylimido-bridged dinuclear complexes.[8] Generally, imidovanadium(V) complexes are prepared by the reaction of oxovanadium(V) complexes with isocyanates. However, lack of an easy synthetic path to various isocyanates limits the scope for functional imidovanadium(V) complexes. Thus, a convenient route to imidovanadium(V) complexes would be highly desirable. The design of structurally defined molecular arrangements in the solid state is an area of intense current interest in the field of crystal engineering.[9] Furthermore, the architectural control of transition-metal-directed assembly to create organized nanostructures is of great importance for advanced materials research.[10] Herein, we report the one-pot synthesis of arylimidovanadium(V) triisopropoxides from aniline derivatives as a route to self-assembling multinuclear (arylimido)vanadium(V) complexes.

A solution of *p*-anisidine (1.0 equiv), $VO(OiPr)_3$ (2.0 equiv), and 1,1′-carbonyldiimidazole (CDI; 1.0 equiv) was heated to reflux in 1,3,5-trimethylbenzene for 2 h to afford the arylimidovanadium(V) triisopropoxide, [(*p*-$MeOC_6H_4N$)$V(OiPr)_3$], in 74% yield (**1a**; Table 1, entry 1). Quantitative formation of **1a** was achieved using 1.5 equivalents of CDI (Table 1, entry 2). The role of CDI in this reaction is likely to depend on the intermediary formation of the imidazolecarboxamide.

***Table 1:*** The one-pot synthesis of arylimidovanadium(V) triisopropoxides from aniline derivatives, using $VO(OiPr)_3$, in the presence of an additive or base.




| Entry | Substrate | Solvent | *t* [h] | Additive[a] (equiv) | Base[b] (equiv) | NMR Conversion [%] |
|---|---|---|---|---|---|---|
| 1 | *p*-anisidine | mesitylene | 2 | CDI (1.0) | – | **1a**: 74 |
| 2 | *p*-anisidine | mesitylene | 2 | CDI (1.5) | – | **1a**: 100 |
| 3 | *p*-bromoaniline | mesitylene | 2 | CDI (1.5) | – | **1b**: 83 |
| 4 | *p*-cyanoaniline | mesitylene | 2 | CDI (1.5) | – | **1c**: 46 |
| 5 | *p*-anisidine | mesitylene | 2 | – | NaH (1.2) | **1a**: 59 |
| 6 | *p*-anisidine | mesitylene | 2 | – | DBU (1.2) | **1a**: trace |
| 7 | *p*-anisidine | mesitylene | 2 | – | $Et_3N$ (1.2) | **1a**: trace |
| 8 | *p*-anisidine | octane | 16 | – | NaH (1.2) | **1a**: 84[c,d] |
| 9 | *p*-bromoaniline | octane | 16 | – | NaH (1.2) | **1b**: 89[c] |
| 10 | *p*-cyanoaniline | octane | 16 | – | NaH (1.2) | **1c**: 49[c] |

[a] CDI = 1,1′-carbonyldiimidazole. [b] DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene. [c] 1.2 Equivalents of $VO(OiPr)_3$ were used. [d] Yield of isolated product.

To explore the scope of this procedure, other aniline derivatives were also examined. The reaction of *para*-bromoaniline under similar conditions yielded [(*p*-$BrC_6H_4N$)$V(OiPr)_3$] (**1b**) in 83% yield (Table 1, entry 3); however, in the case of *p*-cyanoaniline, [(*p*-$NCC_6H_4N$)$V(OiPr)_3$] (**1c**) was obtained in a lower yield (46%), probably owing to the low nucleophilicity of the *para*-cyanoanilino group (Table 1, entry 4).

Arylimidovanadium(V) triisopropoxide **1a** could be obtained in 59% yield in the presence of NaH (1.2 equiv)

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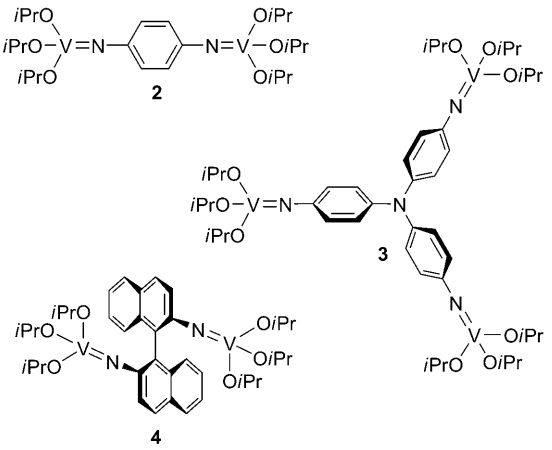
as the base instead of CDI (Table 1, entry 5), whereas 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or $Et_3N$ gave trace amounts of product (Table 1, entries 6 and 7, respectively). Furthermore, when the reaction of *p*-anisidine was conducted in octane with NaH as the base, the amount of $VO(OiPr)_3$ could be reduced to 1.2 equivalents whilst still affording **1a** in 84% yield (Table 1, entry 8). From these results, we established our optimized conditions for the reaction. Arylimidovanadium(V) triisopropoxides **1b** and **1c** were also synthesized under these conditions in 89% and 49% yields, respectively (Table 1, entries 9 and 10).

Having achieved the one-pot preparation of arylimidovanadium(V) triisopropoxides from aniline derivatives, we expect that the commercial availability of a wide range of aromatic amines will allow the straightforward synthesis of a variety of arylimidovanadium(V) triisopropoxides. For example, a solution of 1,4-phenylenediamine, $VO(OiPr)_3$ (2.4 equiv), and NaH (2.4 equiv) was heated to reflux in octane for 16 h to afford the binuclear arylimidovanadium(V) triisopropoxide, $[(OiPr)_3V(N\text{-}p\text{-}Ph\text{-}N)V(OiPr)_3]$, (**2**) in 74% yield. The structure of **2** had previously been reported to form linear one-dimensional μ-isopropoxido-bridging polymer complexes in a crystalline state.[8b]




Transition-metal-directed assembly is a convenient approach to organized nanostructures for advanced materials. We embarked upon the design of multinuclear arylimidovanadium(V) complexes to create a highly organized self-assembly using our one-pot route to arylimidovanadium(V) triisopropoxides. Therefore, reaction of tris(4-aminophenyl)-amine with $VO(OiPr)_3$ (6.0 equiv) in the presence of NaH (4.5 equiv) in octane afforded trinuclear arylimidovanadium(V) triisopropoxide, $[N[(\text{-}p\text{-}Ph\text{-}N)V(OiPr)_3]_3]$, (**3**) in 80% yield. The single-crystal X-ray diffraction pattern of **3** revealed a tridendritic centrosymmetric structural motif that has a distorted pyramidal geometry at the central nitrogen atom (Figure 1a).[10] The imido structure, with a V1–N1 distance of 1.657(3) Å and an almost linear V1-N1-C1 angle of 173.3(2)°, indicates that there is large amount of sp-character in the imido nitrogen atom. The steric interaction between the hydrogen substituents at the *ortho* positions of the benzene rings causes a propeller twist of 63.38(10)°

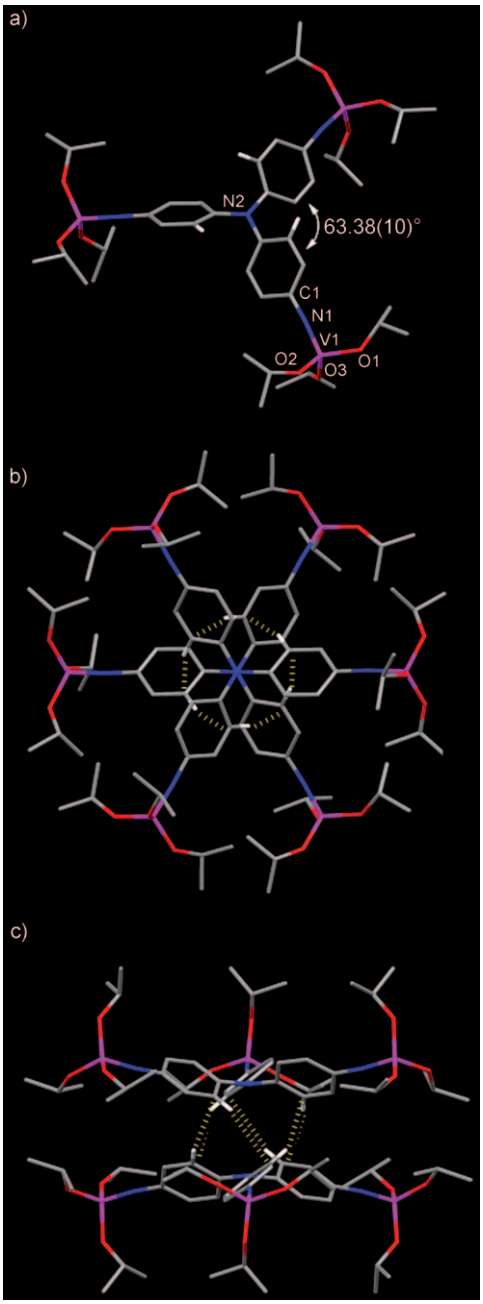



***Figure 1.*** a) Molecular structure of **3**. b), c) Two orthogonal views of a "gear-pair-like" dimeric structure of **3** connected through six intermolecular CH–π interactions. The dotted yellow lines represent intermolecular CH–π interactions.

between the rings around the central nitrogen atom. Trinuclear complex **3** crystallized in the space group $R\bar{3}$ ($Z = 6$), with two mirror-imaged molecules in the asymmetric unit; the triphenylamine moieties of these molecules adopt a mirror-imaged propeller-twist conformation. Unlike the formation of μ-isopropoxido-bridged polymer complexes, as observed in **2**,[8b] these molecules pack in a face-to-face manner to form a "gear-pair-like" dimeric structure which is held together by six intermolecular CH–π interactions between the aryl moieties (the distance between the hydrogen atom and the phenyl carbon(α) atom is 2.87 Å). The triphenylamine centers

are surrounded by imidovanadium(V) triisopropoxide moieties (Figure 1b,c), and the vanadium atoms all adopt a square pyramidal geometry ($\tau = 0.002$).[11] Furthermore, each molecule of **3** is arranged in a hexagonal pattern in the crystalline state, in which the triphenylamine and imidovanadium(V) triisopropoxide moieties individually pack into columns (Figure 2).

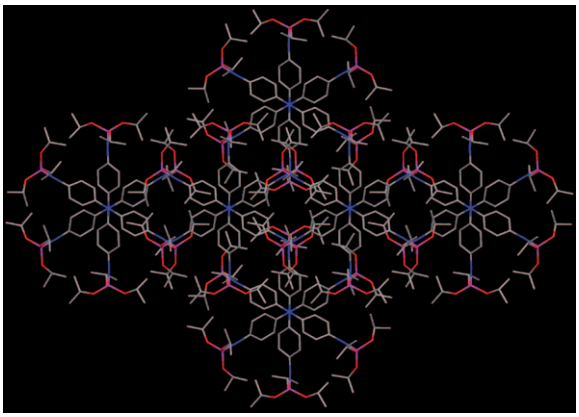


***Figure 2.*** A portion of a layer containing a hexagonal arrangement in the crystal packing of **3**.

The utilization of an axially chiral binaphthyl unit is expected to produce a helically ordered molecular assembly. Axially chiral binuclear arylimidovanadium(V) triisopropoxide, $[(O\mathit{i}Pr)_3V(\mathit{N}\text{-}(\mathit{R})\text{-}1,1'\text{-BN-N})V(O\mathit{i}Pr)_3]$, (**4**) was obtained from the reaction between (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (1,1′-BN-N) and $VO(O\mathit{i}Pr)_3$ (2.5 equiv) in the presence of NaH (2.4 equiv; 69 % yield). The bimetallic imido structure of **4** was confirmed by X-ray crystallographic analysis (Figure 3a,b).[10] The hydrogen atom on the methine carbon atom almost faces the π system of the naphthalene ring with the distance 2.75 Å, thus suggesting a CH–π edge-to-face interaction. As a result of this CH–π interaction, the binaphthyl moiety adopts a conformation with a dihedral angle of 78.99(9)° between the naphthalene planes (Figure 3b). The bent imido structures, with V1-N1-C1 angles of 161.7(3), 167.8(3), 167.0(4), and 168.0(4)°, are presumably a result of CH–π interactions and steric hindrance. It should be noted that axially chiral binuclear complex **4** has an intermolecular CH–π interaction; two independent molecules are connected alternately through intermolecular CH–π interactions in the asymmetric unit cell, thereby creating a left-handed helically ordered arrangement in the crystal packing (Figure 3c,d). The imidovanadium(V) triisopropoxide moieties self-assembled around a helical naphthalene core. The circular dichroism spectrum of **4** has signals pertaining to the positive Cotton effect at 326 nm and the negative Cotton effect at 421 nm, in the approximate absorbance region of the imidovanadium(V) triisopropoxide moieties (Figure 4), thus supporting the axially chiral structure.

In conclusion, the versatile synthesis of arylimidovanadium(V) triisopropoxides from the reaction between their corresponding aniline derivatives and $VO(O\mathit{i}Pr)_3$, using NaH as a base, has been achieved. This one-pot procedure has been

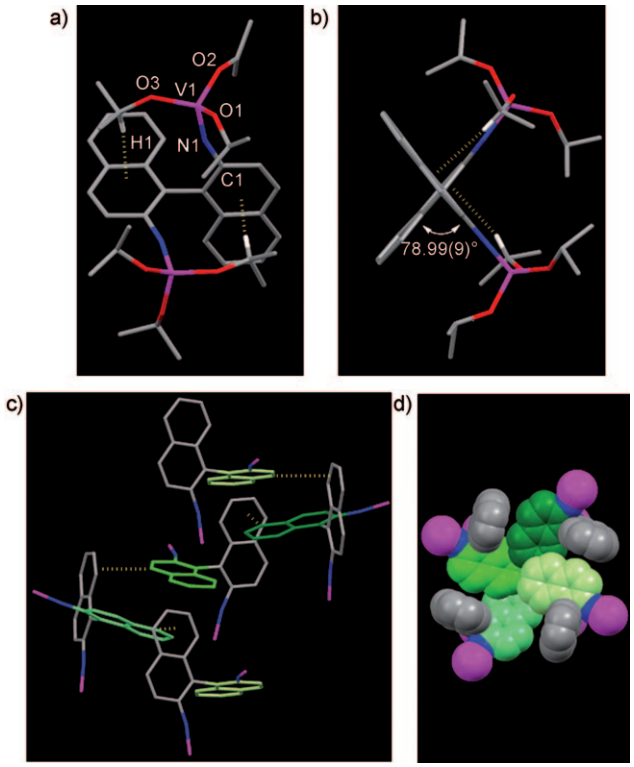



***Figure 3.*** a), b) Two orthogonal views of the molecular structure of **4**. c) Portion of a layer containing the helically ordered molecular assembly, held together through CH–π interactions in the crystal packing of **4** (isopropoxy groups are omitted for clarity). d) Space-filling representation of the crystal packing of **4** (isopropoxy groups are omitted for clarity). The dotted yellow lines represent intermolecular CH–π interactions.

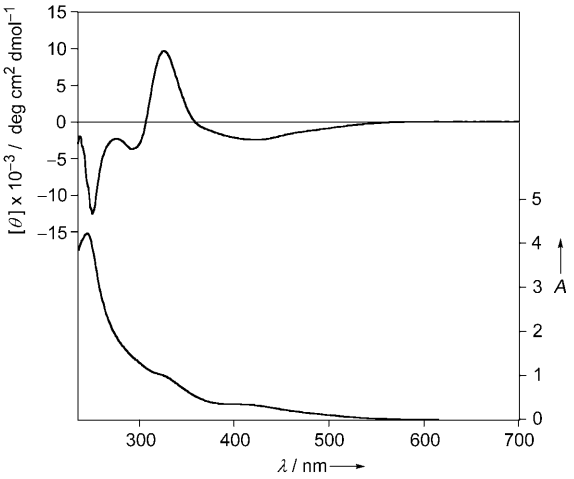



***Figure 4.*** UV/Vis (blue line) and CD (red line) spectra of **4** in dichloromethane ($1.0 \times 10^{-4}$ M).

used to furnish a trinuclear arylimidovanadium(V) triisopropoxide with a tridendritic centrosymmetric structural motif and a binuclear arylimidovanadium(V) triisopropoxide with axial chirality. A noteworthy structural feature of the multinuclear arylimidovanadium(V) triisopropoxides is their strong tendency to self-assemble through CH–π interactions

to create a unique highly ordered molecular arrangement in the crystalline state. These structures, which utilize the self-assembling properties of arylimidovanadium(V) complexes, are expected to be a useful approach to artificial organized nanostructures. Future work will concentrate on the application of the arylimidovanadium(V) complexes for catalysis.

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[10] Crystal data for **3**: $C_{45}H_{75}N_4O_9V_3$, $M_r = 968.93$, trigonal, space group $R\bar{3}$ (No. 148), $a = 19.369(1)$, $c = 23.893(2)$ Å, $V = 7762.7(10)$ Å$^3$, $Z = 6$, $T = -150.0$ °C, $\rho_{calc} = 1.244$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 5.82$ cm$^{-1}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å), $R1 = 0.057$, $wR2 = 0.181$. Crystal data for **4**: $C_{38}H_{54}N_2O_6V_2$, $M = 736.74$, monoclinic, space group $P2_1$ (No. 4), $a = 18.8471(9)$, $b = 11.7368(6)$, $c = 19.2279(9)$ Å, $\beta = 98.867(1)$°, $V = 4202.5(4)$ Å$^3$, $Z = 4$, $T = 4.0$ °C, $\rho_{calc} = 1.164$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 4.86$ cm$^{-1}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å), $R1 = 0.065$, $wR2 = 0.186$. CCDC 747482 (**3**) and CCDC 747483 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] The structural parameter proposed by Addison and Reedijik, $\tau = (\beta - \alpha)/60$, for the coordination geometry of the five-coordinate complex **3** is $\tau = 0.002$, where $\alpha$ and $\beta$ represent two basal angles ($\beta > \alpha$). The parameters for 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 **3** indicates that the coordination geometry is square pyramidal about the vanadium atom. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356.

  