Structural Tuning of the Imido Bonds in (Arylimido)vanadium(V) Compounds

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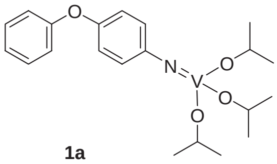
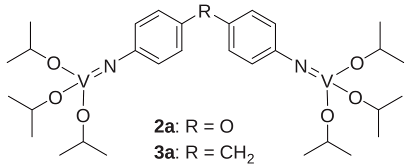
Structural characterization of (arylimido)vanadium(V) compounds was demonstrated to elucidate the ligand effect on the nature of the imido bonds. In the case of the triisopropoxide ligand, the nitrogen of the imido bond is suggested to possess an sp-hybridized character although the participation of an sp^2-hybridized character is indicated with the imido nitrogen derived from the triethanolaminate ligand.

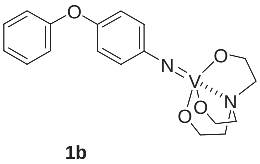
Since the initial work of (imido)vanadium(V) complexes by Preuss,[1] Maatta,[2] and Horton groups,[3] (imido)vanadium(V) complexes have been focused on, to design a catalyst for olefin polymerization,[4] C–H activation,[3b,3c,5] and others[1e,1f,6] because the imido ligands are known to be a particularly suitable ligand for stabilization of transition-metal complexes in high oxidation states through extensive ligand-to-metal π donation.[7] The steric and electronic properties of vanadium centers are expected to be influenced by coordination environment. We herein report the structural tuning of the imido bonds in (arylimido)vanadium(v) compounds.

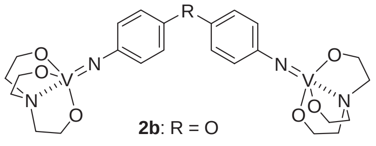
The reaction of $VO(O^iPr)_3$ with 4-phenoxyphenyl isocyanate without solvent at 140 °C afforded the (arylimido)vanadium(V) triisopropoxide **1a**, $[(C_6H_4–O–C_6H_4N)V(O^iPr)_3]$, in 76% yield. Structural characterization of **1a** was performed by the single-crystal X-ray structure determination as depicted in Figure 1a.[8] A dimeric structure, in which each vanadium atom is coordinated in a trigonal-bipyramidal geometry with the imido and bridging isopropoxide ligands in apical positions, is formed in the crystal packing. The V(1)–V(1*) internuclear distance of 3.29 Å indicates the absence of any bonding interaction between the metals. The axial V(1*)–O(1) bond is 0.36 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 a weaker coordination. On the other hand, only one kind of isopropyl resonance was detected in the ^1H NMR spectrum of **1a**, indicating that **1a** appears to be monomeric in CD_2Cl_2. The V(1)–N(1) distance of 1.673(2) Å and the nearly linear V(1)–N(1)–C(1) angle of 176.4(2)° suggest the nitrogen of the imido bond to possess an sp-hybridized character. The twist angle β defined as the angle between the least-squares plane of the benzene ring and the C(ipso)–imido bond is considered to be controlled by the imido bond. The almost perpendicular twist angle β was observed in the case of **1a** (94.97(8)°). These results suggest that the nitrogen of the imido bond is closely explained by an sp-hybridized character with a double V=N bond and the lone pair of electrons might be localized in a nitrogen p orbital, which is likely to interact with metal π-acceptor orbitals and aryl π orbitals.

The ligand effect was investigated more as follows. To prevent the dimerization, triethanolamine was used as a basal ligand which is expected to affect the nature of the imido moiety by trans influence based on the donor ability of triethanolamine nitrogen.[9] The ligand exchange reaction of **1a** with triethanolamine in CH_2Cl_2 at room temperature afforded the desired


1a


2a: R = O
3a: R = CH_2


1b


2b: R = O
3b: R = CH_2

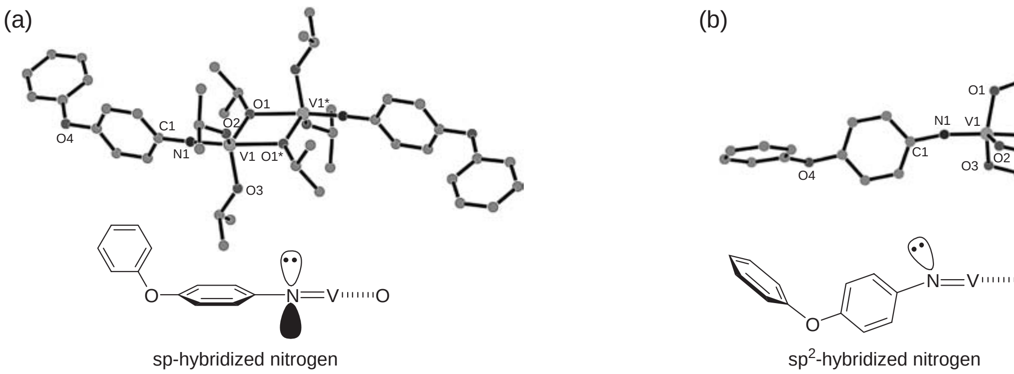


Figure 1. Molecular structure of (a) **1a** and (b) **1b** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): **1a**; V(1)–N(1) 1.673(2), V(1)–O(1) 1.852(2), V(1)–O(2) 1.786(2), V(1)–O(3) 1.780(2), V(1)–O(1*) 2.213(2), C(1)–N(1) 1.380(3), C(1)–N(1)–V(1) 176.4(2), N(1)–V(1)–O(1*) 173.17(8), **1b**; V(1)–N(1) 1.682(4), V(1)–N(2) 2.216(3), V(1)–O(1) 1.829(4), V(1)–O(2) 1.830(3), V(1)–O(3) 1.832(4), C(1)–N(1) 1.383(6), C(1)–N(1)–V(1) 167.0(3), N(1)–V(1)–N(2) 175.9(2).

(arylimido)vanadium(V) triethanolaminate **1b**, [(C_6H_4–O–C_6H_4N)V(TEA)], in 86% yield. The crystal structure of **1b** revealed the imido structure with the V(1)–N(1) distance of 1.682(4) Å and the bent V(1)–N(1)–C(1) angle of 167.0(3)°, in which a monomeric structure with a pseudo-trigonal-bipyramidal geometry around the metal center was observed (Figure 1b).[8] 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. The benzene ring of **1b** is close to parallel to the least-squares plane of the C(ipso)–imido bond ($\beta = 27.8(1)^\circ$). Furthermore, the longer imido bond and more bent angle of **1b** probably due to the donor ability of the triethanolamine nitrogen were observed as compared with **1a**. From these results, the contribution of an sp^2-hybridized character is suggested in the case of the imido nitrogen of **1b**, wherein the filled imido π orbital seems to interact with aryl π orbitals. The basal ligand was demonstrated to control the nature of the imido bonds. Furthermore, the CH–π interaction between the phenyl moiety of one molecule and the aryl moiety of another molecule was observed to form the dimer in the crystal packing.

^{51}V NMR measurements were performed in order to clarify the electronic environment of the vanadium atoms. ^{51}V chemical shift of the triisopropoxide **1a** in CD_2Cl_2 was observed at −614 ppm. On the contrary, the triethanolaminate **1b** showed ^{51}V chemical shift at −310 ppm probably due to the donor ability of the triethanolamine nitrogen.

The bimetallic (arylimido)vanadium(V) triisopropoxide **2a**, [(O^{i}Pr)$_3$V(NC_6H_4–O–C_6H_4N)V(O^{i}Pr)$_3$], connected by the oxy spacer and **3a**, [(^{i}PrO)$_3$V(NC_6H_4–CH_2–C_6H_4N)V(O^{i}Pr)$_3$], connected by the methylene spacer could be obtained in 62% and 51% yields by the reaction with 4,4′-oxybis(phenyl isocyanate) or 4,4′-methylenebis(phenyl isocyanate), respectively. The bimetallic (arylimido)vanadium(V) triisopropoxide **2a** and **3a** are suggested to be present as a monomeric structure in CD_2Cl_2 by the ^{1}H NMR studies. The ligand-exchange reaction of **2a** and **3a** with triethanolamine in CH_2Cl_2 at room temperature led to the formation of the (arylimido)vanadium(V) triethanolaminates, [(TEA)V(NC_6H_4–O–C_6H_4N)V(TEA)] (**2b**) and [(TEA)V(NC_6H_4–CH_2–C_6H_4N)V(TEA)] (**3b**), in 90% and 94% yields, respectively. ^{51}V chemical shifts of **2** and **3** (**2a**: −617 ppm, **3a**: −621 ppm, **2b**: −312 ppm, **3b**: −315 ppm) are almost identical with the corresponding monomeric compound **1**. These results indicate that the electronic environment around the vanadium atoms of **2** and **3** are likely to be almost the same as that of **1**, suggesting no interaction between the vanadium centers in solution.

In conclusion, the (arylimido)vanadium(V) compounds were synthesized and characterized structurally. The basal ligand was found to control the nature of the imido bonds. The imido nitrogen of the triisopropoxide **1a** depends on an sp-hybridized character although the contribution of an sp^2-hybridized character was suggested in the case of the triethanolaminate **1b**. Studies on the application of the (arylimido)vanadium(V) complexes as a catalyst are now in progress.

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8 Crystal data for **1a**: $C_{21}H_{30}N_1O_4V_1$, $M_r = 411.41$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.1115(7)$, $b = 9.7377(6)$, $c = 14.1306(9)$ Å, $\alpha = 95.699(2)^\circ$, $\beta = 91.858(3)^\circ$, $\gamma = 113.789(5)^\circ$, $V = 1137.9(1)$ Å^3, $Z = 2$, $T = 2.0\,^\circ$C, $D_{\mathrm{calcd}} = 1.201$ g cm^{-3}, μ(Mo Kα) = 4.59 cm^{-1}, Mo Kα radiation ($\lambda = 0.71069$ Å), $R1 = 0.052$, $wR2 = 0.150$. CCDC-656969 for **1a**. Crystal data for **1b**: $C_{18}H_{21}N_2O_4V_1$, $M_r = 380.32$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.9590(9)$, $b = 10.8442(9)$, $c = 15.2471(9)$ Å, $\beta = 100.609(2)^\circ$, $V = 1781.0(2)$ Å^3, $Z = 4$, $T = 4.0\,^\circ$C, $D_{\mathrm{calcd}} = 1.418$ g cm^{-3}, μ(Mo Kα) = 5.81 cm^{-1}, Mo Kα radiation ($\lambda = 0.71069$ Å), $R1 = 0.062$, $wR2 = 0.172$. CCDC-656970 for **1b**.

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