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Synthesis of vanadium(v) hydrazido complexes with tris(2-hydroxyphenyl)amine ligandst

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The reaction of the oxidovanadium(v) complexes with *N,N*-dimethylhydrazine was demonstrated to afford the corresponding vanadium(v) dimethylhydrazido complexes. The substituent at the 3-position of the tris(2-hydroxyphenyl)amine ligand was found to influence the electronic environment of the vanadium center. The crystal structure of the non-substituted vanadium(v) dimethylhydrazido complex exhibited a distorted trigonal bipyramidal geometry with phenolate oxygen atoms in equatorial positions and the near-linear V(1)-N(2)-N(3) angle. The vanadium(v) diphenylhydrazido complexes could be obtained by the reaction of the oxidovanadium(v) complexes with *N,N*-diphenylhydrazine. A distorted trigonal bipyramidal geometry with phenolate oxygen atoms in equatorial positions was also observed in the crystal structure of the non-substituted vanadium(v) diphenylhydrazido complex.

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Introduction

Much attention has been devoted to metal hydrazido compounds due to their intermediacy in dinitrogen activation.¹ In particular, most of the studies have focused on molybdenum hydrazido compounds because molybdenum is present in an active site of nitrogenases.² On the other hand, the biochemical roles of vanadium have gained growing interest which is related to the insulinomimetic ability of vanadium compounds³ and vanadium-dependent haloperoxidases.⁴ Although vanadium is known to be an essential constituent in certain nitrogenases,^{1a-d,5} vanadium hydrazido complexes have attracted less attention.⁶ We have already demonstrated that the substituents in the *para* position on the benzene rings of (arylimido)vanadium(v) complexes affect the nature of the imido bonds through π conjugation.⁷ The coordination from the apical nitrogen in the (arylimido)vanadium(v) triethanolamines was also performed to influence the electron donation from the imido nitrogen to vanadium metal.⁸ The substituent effect of the basal ligand in the vanadium(v) hydrazido complex has not been investigated so far. From these points of view, we herein report the synthesis of the vanadium(v) hydrazido complexes with tris(2-hydroxyphenyl)amine ligands to reveal the influence of the apical nitrogen and the substituent

of the tris(2-hydroxyphenyl)amine ligand on the vanadium center.

Results and discussion

The substituted tris(2-hydroxyphenyl)amines **2** were prepared by the deprotection of methoxy groups of the ligand precursors **1**, which were synthesized by Ullmann-type reaction of the substituted 2-methoxyaniline with 1-iodo-2-methoxybenzene. The reaction of $\text{VO}(\text{O}^{\prime}\text{Pr})_3$ with the substituted tris(2-hydroxyphenyl)amines **2** in dichloromethane at room temperature afforded the corresponding oxidovanadium(v) complexes **3** as shown in Scheme 1.⁹ The vanadium(v) dimethylhydrazido complexes **4** with the tris(2-hydroxyphenyl)amine ligand could be obtained by the treatment of the corresponding oxidovanadium(v) complexes **3** with *N,N*-dimethylhydrazine in dichloromethane at room temperature. ^{51}V NMR measurements were performed in order to clarify the substituent effect on the electronic environment of the vanadium species. The ^{51}V chemical shift of the non-substituted vanadium(v) dimethylhydrazido complex **4b** was detected at 335 ppm. In the ^{51}V NMR spectrum of **4a** with the electron-donating substituent, the ^{51}V chemical shift was observed at 328 ppm. In contrast, the electron-withdrawing substituent caused the ^{51}V chemical shift to higher frequency (**4c**: 381 ppm; **4d**: 378 ppm). The substituent at the 3-position of the tris(2-hydroxyphenyl)amine ligand was found to influence the electron density of the vanadium center directly. A similar substituent effect was observed in the vanadium(v) diphenylhydrazido complexes **5** (**5a**: 164 ppm; **5b**: 178 ppm; **5c**: 206 ppm; **5d**: 209 ppm), which were prepared by the reaction of the corresponding

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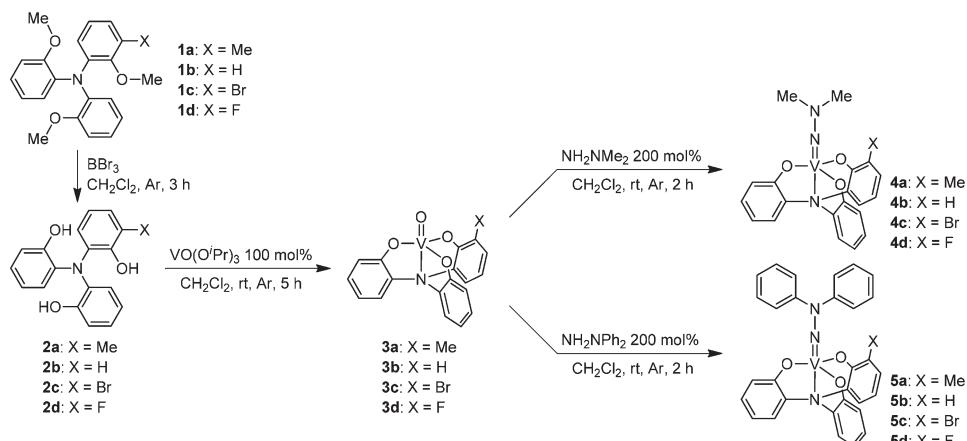
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Scheme 1 Synthesis of the vanadium(v) hydrazido complexes **4** and **5**.Table 1 Crystallographic data for **4b**, **4d-DMH-4d**, and **5b**

	4b	4d-DMH-4d	5b
Formula	C ₂₀ H ₁₈ N ₃ O ₃ V	C ₄₂ H ₄₂ N ₈ O ₆ F ₂ V ₂	C ₃₀ H ₂₂ N ₃ O ₃ V
Formula weight	399.31	894.72	523.45
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P ₂ ₁ /n (no. 14)	P ₂ ₁ (no. 4)	P ₂ ₁ /n (no. 14)
<i>a</i> (Å)	16.2235(5)	9.3304(11)	20.7200(15)
<i>b</i> (Å)	11.8240(3)	18.403(2)	9.1557(6)
<i>c</i> (Å)	18.6632(5)	12.1985(14)	25.6467(18)
β (°)	96.4640(10)	102.631(3)	99.487(2)
<i>V</i> (Å ³)	3557.32(18)	2043.9(4)	4798.8(6)
<i>Z</i>	8	2	8
<i>D</i> _{calcd} (g cm ⁻³)	1.491	1.454	1.449
<i>T</i> (°C)	-170	-150	-150
λ (Mo K α) (Å)	0.71075	0.71075	0.71075
<i>R</i> ₁ ^a	0.046	0.074	0.066
<i>wR</i> ₂ ^b	0.117	0.180	0.177

^a $R_1 = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|$. ^b $wR_2 = [\Sigma w(F_O^2) - |F_C^2|]^2 / \Sigma w(F_O^2)^2]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for **4b**^a and **5b**^a

	4b	5b
Bond lengths		
V1–N1	2.2751(18)	2.2782(18)
V1–N2	1.6891(19)	1.6837(19)
V1–O1	1.8685(16)	1.8572(16)
V1–O2	1.8536(16)	1.8548(16)
V1–O3	1.8538(15)	1.8574(16)
N2–N3	1.304(3)	1.312(3)
Bond angles		
V1–N2–N3	176.60(17)	173.11(16)
N1–V1–N2	178.88(8)	177.02(8)
N1–V1–O1	81.03(7)	81.18(7)
N1–V1–O2	80.92(7)	80.40(7)
N1–V1–O3	81.02(6)	81.35(6)
N2–V1–O1	99.00(8)	96.69(8)
N2–V1–O2	98.09(8)	99.04(8)
N2–V1–O3	99.95(8)	101.42(8)
O1–V1–O2	117.35(7)	121.21(7)
O1–V1–O3	116.25(7)	111.48(8)
O2–V1–O3	119.17(7)	120.00(7)

^a Two independent molecules exist in the asymmetric unit.

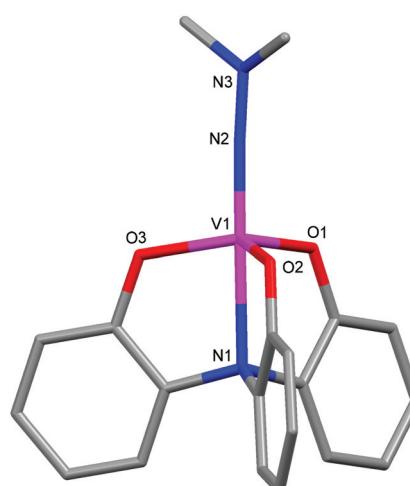
Fig. 1 Molecular structure of **4b**.

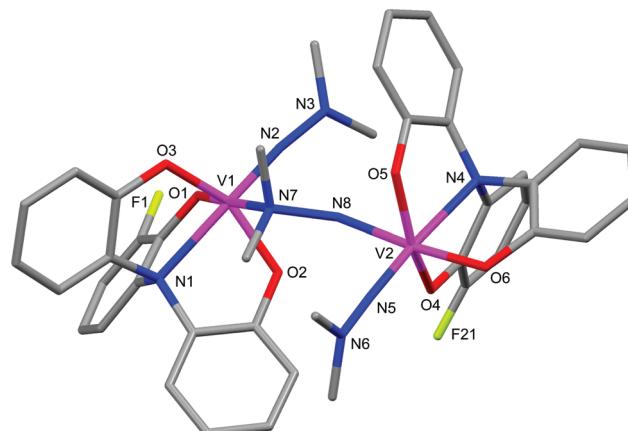
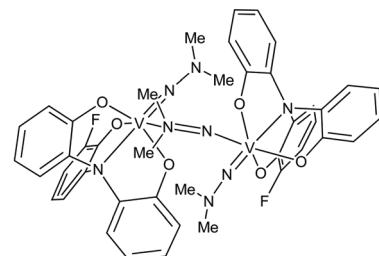
Table 3 Selected bond lengths (Å) and angles (°) for **4d-OMH-4d**

Bond lengths			
V1–N1	2.295(7)	V2–N4	2.270(7)
V1–N2	1.663(7)	V2–N5	1.690(7)
V1–N7	2.349(7)	V2–N8	2.245(7)
V1–O1	1.903(6)	V2–O4	1.913(6)
V1–O2	1.902(6)	V2–O5	1.895(6)
V1–O3	1.862(6)	V2–O6	1.910(6)
N2–N3	1.315(10)	N5–N6	1.300(10)
N7–N8	1.512(9)		
Bond angles			
V1–N2–N3	171.8(7)	V2–N5–N6	174.0(7)
V1–N7–N8	106.9(4)	V2–N8–N7	133.4(5)
N1–V1–N2	172.0(3)	N4–V2–N5	173.6(3)
N1–V1–N7	101.9(2)	N4–V2–N8	90.1(2)
N1–V1–O1	79.8(3)	N4–V2–O4	79.5(2)
N1–V1–O2	77.7(2)	N4–V2–O5	77.6(2)
N1–V1–O3	79.5(2)	N4–V2–O6	80.1(2)
N2–V1–N7	85.6(3)	N5–V2–N8	96.3(3)
N2–V1–O1	92.6(3)	N5–V2–O4	102.3(3)
N2–V1–O2	101.0(3)	N5–V2–O5	102.4(3)
N2–V1–O3	104.6(3)	N5–V2–O6	93.6(3)
N7–V1–O1	178.2(3)	N8–V2–O4	76.9(3)
N7–V1–O2	81.0(2)	N8–V2–Q5	85.3(3)
N7–V1–O3	82.3(3)	N8–V2–O6	168.6(3)
O1–V1–O2	98.9(3)	O4–V2–O5	150.9(2)
O1–V1–O3	98.6(3)	O4–V2–O6	95.4(3)
O2–V1–O3	148.2(2)	O5–V2–O6	98.2(2)

positions. The vanadium atom is pulled out of the plane formed by the phenolate oxygen atoms in the direction of the hydrazido nitrogen. Three equatorial vanadium–oxygen bond distances are statistically identical. The V(1)–N(2) distances of **4b** with the coordination from the apical nitrogen is longer than that of the vanadium(v) dimethylhydrazido complex, $[\text{V}(\text{NNMe}_2)(\text{OC}_6\text{H}_3^{\text{i}}\text{Pr}_2-2,6)_3]$, with tetrahedral geometry at the vanadium center (V(1)–N(2), 1.653(3) Å),^{6a} probably due to the coordination of the apical nitrogen. The electron donation from N(2) to vanadium metal might be weakened to some extent.

The *N,N*-dimethylhydrazine-bridged dinuclear vanadium(v) hydrazido complex **4d-DMH-4d** could be obtained by recrystallization of **4d** in the presence of *N,N*-dimethylhydrazine. The structure of **4d-DMH-4d** was confirmed by single-crystal X-ray structure determination. Table 3 shows the selected bond lengths and angles. The solid-state molecular structure reveals that two **4d** units are bridged by *N,N*-dimethylhydrazine to form the 2:1 complex in anti-configuration as depicted in Fig. 2. The 3-fluoro group on the benzene ring might decrease the electron density of the vanadium center, resulting in the coordination of *N,N*-dimethylhydrazine to the vanadium center to form a hexacoordinate geometry. This hydrazido complex **4d-DMH-4d** showed the near-linear V(1)–N(2)–N(3) angles of 171.8(7) and 174.0(7)° with the V(1)–N(2) distances of 1.663(7) and 1.690(7) Å, respectively. The V(1)–N(7) distance (2.349(7) Å) is longer than that of the V(2)–N(8) bond (2.245(7) Å) probably due to the steric hindrance of the dimethyl moieties.

The structure of the vanadium(v) diphenylhydrazido complex **5b** was also confirmed by single-crystal X-ray structure determination. The important bond lengths and angles are

**Fig. 2** Molecular structure of **4d-DMH-4d**.

shown in Table 2. As **5b** crystallized in the space group $P2_1/n$ with $Z = 8$, two independent molecules exist in the asymmetric unit. The metal centers are distorted trigonal bipyramidal geometries with phenolate oxygen atoms in equatorial positions as shown in Fig. 3. One molecule of **5b** shows the V(1)–N(2)–N(3) angle of 173.7(4)° with the V(1)–N(2) distance of 1.683(4) Å, indicating the high participation of an sp-hybridized character in the nitrogen of the imido bond. This hydrazido structure is almost similar to that of **4b**. The V(1)–N(2)–N(3) angle of 161.8(3)° with the V(1)–N(2) distance of 1.692(4) Å based on some contribution of an sp²-hybridized character in the nitrogen of the imido bond was observed in the crystal structure of another molecule as depicted in Fig. 3.

Conclusions

In conclusion, the vanadium(v) hydrazido complexes with the tris(2-hydroxyphenyl)amine ligand were demonstrated to reveal the influence of the coordination from the apical nitrogen and the substituent of the tris(2-hydroxyphenyl)amine ligand on the vanadium center in solid and/or solution states. The coordination of the apical nitrogen to the vanadium center was performed to weaken the V–N multiple bond through the coordination from the apical nitrogen. The substituent at the 3-position of the tris(2-hydroxyphenyl)amine ligand was found to influence the electronic environment of the vanadium center directly. Further characterization of the hydrazido structures and the application of the vanadium(v) hydrazido complexes for catalysis are now in progress.



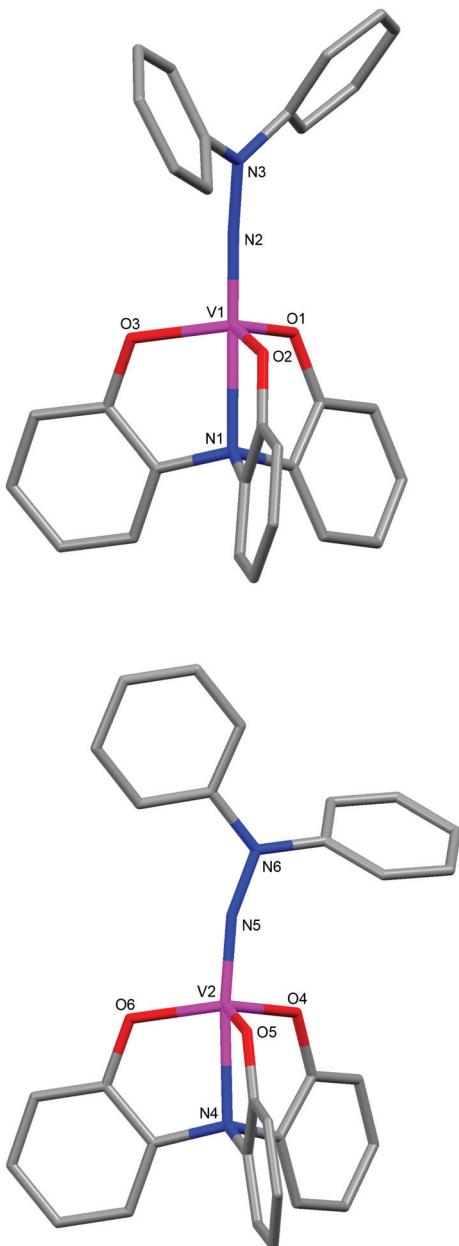


Fig. 3 Molecular structures of two independent molecules in the asymmetric unit of **5b**.

Experimental

General methods

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. All manipulations were carried out under nitrogen. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-ECP 400 (400 and 100 MHz, respectively) spectrometer with tetramethylsilane as an internal standard. ^{51}V NMR spectra were obtained with a JEOL JNM-ECP 400 (105 MHz) spectrometer with VOCl_3 as an

external standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer.

Synthesis of 2-methoxy-3-methyl-*N,N*-bis(2-methoxyphenyl)-aniline (**1a**)

A mixture of 2-methoxy-3-methylaniline (549 mg, 4.0 mmol), 1-iodo-2-methoxybenzene (1.56 mL, 12.0 mmol), Cu (890 mg, 14.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol) and 18-crown-6 (137 mg, 0.52 mmol) in 1,2-dichlorobenzene (50 mL) was refluxed under Ar for 24 h. After cooling, the insoluble inorganic material was filtered off. The solvent of the resulting filtrate was removed under reduced pressure and the residue was chromatographed on a silica-gel column (eluent, hexane-dichloromethane 1 : 1) to give the desired product **1a** (572 mg, 1.64 mmol) as a white solid.

1a: yield 41%; mp 80–82 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (td, 2H, J = 7.3, 1.8 Hz), 6.89–6.78 (m, 8H), 6.65 (dd, 1H, J = 7.3, 2.2 Hz), 3.63 (s, 3H), 3.56 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 153.9, 151.7, 141.7, 137.8, 132.1, 125.5, 125.2, 124.2, 123.4, 122.3, 121.0, 113.1, 58.8, 56.0, 16.4 ppm; HRMS (EI) m/z Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_1\text{O}_3$ (M^+), 349.1678; Found, 349.1677.

Synthesis of 3-bromo-2-methoxy-*N,N*-bis(2-methoxyphenyl)-aniline (**1c**)

A mixture of 3-bromo-2-methoxyaniline (1.62 g, 8.0 mmol), 1-iodo-2-methoxybenzene (3.12 mL, 24.0 mmol), Cu (1.78 g, 28.0 mmol), K_2CO_3 (5.53 g, 40.0 mmol) and 18-crown-6 (275 mg, 1.04 mmol) in 1,2-dichlorobenzene (80 mL) was refluxed under Ar for 24 h. After cooling, the insoluble inorganic material was filtered off. The solvent of the resulting filtrate was removed under reduced pressure and the residue was chromatographed on a silica-gel column (eluent, hexane-ethyl acetate 5 : 1) to give the desired product **1c** (1.39 g, 3.36 mmol) as a white solid.

1c: yield 42%; mp 94–95 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (dd, 1H, J = 7.6, 1.8 Hz), 7.04 (td, 2H, J = 7.8, 2.0 Hz), 6.89–6.81 (m, 6H), 6.74 (t, 1H, J = 7.6 Hz), 6.71 (dd, 1H, J = 8.0, 2.0 Hz), 3.65 (s, 3H), 3.57 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 154.0, 150.1, 143.4, 137.1, 126.6, 126.0, 124.8, 124.6, 123.3, 121.1, 118.2, 113.0, 59.3, 55.9 ppm; HRMS (FAB) m/z Calcd for $\text{C}_{21}\text{H}_{20}\text{Br}_1\text{N}_1\text{O}_3$ (M^+), 413.0627; Found, 413.0631.

Synthesis of 3-fluoro-2-methoxy-*N,N*-bis(2-methoxyphenyl)-aniline (**1d**)

A mixture of 3-fluoro-2-methoxyaniline (602 μL , 5.0 mmol), 1-iodo-2-methoxybenzene (1.95 mL, 15.0 mmol), Cu (1.05 g, 16.5 mmol), K_2CO_3 (3.46 g, 25.0 mmol) and 18-crown-6 (172 mg, 0.65 mmol) in 1,2-dichlorobenzene (60 mL) was refluxed under Ar for 24 h. After cooling, the insoluble inorganic material was filtered off. The solvent of the resulting filtrate was removed under reduced pressure and the residue was chromatographed on a silica-gel column (eluent, hexane-dichloromethane 1 : 1) to give the desired product **1d** (1.3 g, 3.7 mmol) as a white solid.

1d: yield 74%; mp 107–108 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (td, 2H, J = 7.8, 1.8 Hz), 6.9–6.7 (m, 8H), 6.56 (dt, 1H, J = 8.2, 1.8 Hz), 3.59 (s, 6H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 156.8 (d, $^1\text{J}_{\text{F}-\text{C}}$ = 244.4 Hz), 154.0, 143.5 (d, $^3\text{J}_{\text{F}-\text{C}}$ = 3.8 Hz), 141.1 (d, $^2\text{J}_{\text{F}-\text{C}}$ = 12.5 Hz) 137.4, 125.8, 124.7, 122.7 (d, $^3\text{J}_{\text{F}-\text{C}}$ = 9.6 Hz), 121.1, 119.3, 113.1, 110.5 ($^2\text{J}_{\text{F}-\text{C}}$ = 19.2 Hz), 60.1 (d, $^4\text{J}_{\text{F}-\text{C}}$ = 3.8 Hz), 56.0 ppm; HRMS (EI) m/z Calcd for $\text{C}_{21}\text{H}_{20}\text{F}_1\text{N}_1\text{O}_3$ (M^+), 353.1427; Found, 353.1429.

Synthesis of 2-hydroxy-3-methyl-*N,N*-bis(2-hydroxyphenyl)-aniline (2a)

To a dichloromethane (15 mL) solution of 2-methoxy-3-methyl-*N,N*-bis(2-methoxyphenyl)aniline (**1a**) (349 mg, 1.0 mmol) was added a 1 M BBr_3 in dichloromethane (3.0 mL, 3.0 mmol) solution under Ar at –78 °C. The resulting mixture was stirred at –78 °C for a few minutes. The mixture was allowed to warm to room temperature and was stirred for 3 h. The resulting mixture was diluted with ethyl acetate and washed with water. After evaporation of the solution, the desired product **2a** was isolated as a white solid (239 mg, 0.78 mmol) by reprecipitation from ethyl acetate and hexane.

2a: yield 78%; mp 120–121 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.11 (td, 2H, J = 8.0, 1.4 Hz), 7.01–6.77 (m, 9H), 5.33 (s, 1H), 5.15 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 150.1, 148.6, 133.5, 132.8, 128.6, 126.4, 125.5, 123.3, 121.7, 120.8, 117.4, 16.1 ppm; HRMS (EI) m/z Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_1\text{O}_3$ (M^+), 307.1208; Found, 307.1210.

Synthesis of 3-bromo-2-hydroxy-*N,N*-bis(2-hydroxyphenyl)-aniline (2c)

To a dichloromethane (15 mL) solution of 3-bromo-2-methoxy-*N,N*-bis(2-methoxyphenyl)aniline (**1c**) (207 mg, 0.5 mmol) was added a 1 M BBr_3 in dichloromethane (2.0 mL, 2.0 mmol) solution under Ar at room temperature. The resulting mixture was stirred at room temperature for 3 h. The resulting mixture was diluted with ethyl acetate and washed with water. After evaporation of the solution, the desired product **2c** was isolated as a white solid (80 mg, 0.21 mmol) by reprecipitation from ethyl acetate and hexane.

2c: yield 43%; mp 138–139 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, 1H, J = 8.2, 1.4 Hz), 7.12 (td, 2H, J = 8.0, 1.4 Hz), 6.98–6.85 (m, 7H), 6.72 (t, 1H, J = 7.8 Hz) 5.52 (s, 1H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) 150.7, 147.0, 135.0, 133.5, 128.8, 127.1, 126.2, 124.7, 121.9, 121.3, 117.0 ppm; HRMS (FAB) m/z Calcd for $\text{C}_{18}\text{H}_{14}\text{Br}_1\text{N}_1\text{O}_3$ (M^+), 371.0157; Found, 371.0168.

Synthesis of 3-fluoro-2-hydroxy-*N,N*-bis(2-hydroxyphenyl)-aniline (2d)

To a dichloromethane (15 mL) solution of 3-fluoro-2-methoxy-*N,N*-bis(2-methoxyphenyl)aniline (**1d**) (353 mg, 1.0 mmol) was added a 1 M BBr_3 in dichloromethane (3.0 mL, 3.0 mmol) solution under Ar at –78 °C. The resulting mixture was stirred at –78 °C for a few minutes. The mixture was allowed to warm to room temperature and was stirred for 3 h. The resulting mixture was diluted with ethyl acetate and washed with water.

After evaporation of the solution, the desired product **2d** was isolated as a white solid (168 mg, 0.54 mmol) by reprecipitation from ethyl acetate and hexane.

2d: yield 54%; mp 138–139 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.11 (td, 2H, J = 7.6, 1.6 Hz), 6.99–6.85 (m, 7H), 6.78 (td, 1H, J = 8.2, 6.0 Hz), 6.72 (dt, 1H, J = 8.2, 1.4 Hz), 5.56 (s, 2H), 5.33 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) 152.2 (d, $^1\text{J}_{\text{F}-\text{C}}$ = 239.6 Hz), 150.6, 138.3 (d, $^2\text{J}_{\text{F}-\text{C}}$ = 15.3 Hz), 135.8 (d, $^3\text{J}_{\text{F}-\text{C}}$ = 2.9 Hz), 133.4, 127.1, 126.2, 121.4, 120.4 (d, $^3\text{J}_{\text{F}-\text{C}}$ = 8.6 Hz), 120.2, 117.1, 112.4 ($^2\text{J}_{\text{F}-\text{C}}$ = 18.2 Hz) ppm; HRMS (EI) m/z Calcd for $\text{C}_{18}\text{H}_{14}\text{F}_1\text{N}_1\text{O}_3$ (M^+), 311.0958; Found, 311.0954.

Synthesis of oxidovanadium(v) complex **3a**

A mixture of the tris(2-hydroxyphenyl)amine ligand **2a** (154 mg, 0.50 mmol) and $\text{VO}(\text{O}'\text{Pr})_3$ (118 μL , 0.50 mmol) was stirred in dichloromethane (15 mL) under Ar at room temperature for 3 h. After evaporation of the solution, the oxidovanadium(v) complex **3a** was isolated as a blue-purple solid (122 mg, 0.33 mmol) by reprecipitation from dichloromethane and hexane.

3a: yield 66%; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, 2H, J = 8.0, 1.4 Hz), 7.56 (d, 1H, J = 8.2 Hz), 7.22 (t, 2H, J = 7.8 Hz), 7.08 (d, 1H, J = 7.3 Hz), 6.93 (t, 2H, J = 7.8 Hz), 6.85 (t, 1H, J = 7.8 Hz), 6.59 (d, 2H, J = 7.8 Hz), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 164.2, 162.7, 140.8, 140.7, 131.8, 130.4, 127.5, 126.1, 124.8, 123.9, 123.7, 115.7, 16.7 ppm; ^{51}V NMR (105 MHz, CDCl_3) –292 ppm; HRMS (FAB) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_1\text{O}_4\text{V}_1$ (M^+), 371.0362; Found, 371.0362.

Synthesis of oxidovanadium(v) complex **3c**

A mixture of the tris(2-hydroxyphenyl)amine ligand **2c** (186 mg, 0.50 mmol) and $\text{VO}(\text{O}'\text{Pr})_3$ (118 μL , 0.50 mmol) was stirred in dichloromethane (15 mL) under Ar at room temperature for 3 h. After evaporation of the solution, the oxidovanadium(v) complex **3c** was isolated as a blue-green solid (218 mg, 0.50 mmol) by reprecipitation from dichloromethane and hexane.

3c: yield 100%; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 3H), 7.44 (dd, 1H, J = 8.2, 1.4 Hz), 7.23 (td, 2H, J = 1.8, 8.2 Hz), 6.93 (td, 2H, J = 7.8, 1.4 Hz), 6.80 (t, 1H, J = 8.2 Hz), 6.58 (dd, 2H, J = 8.0, 1.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) 164.2, 140.9, 140.4, 137.5, 133.9, 130.6, 127.3, 127.1, 124.4, 124.2, 115.7 ppm; ^{51}V NMR (105 MHz, CDCl_3) –299 ppm; HRMS (FAB) m/z Calcd for $\text{C}_{18}\text{H}_{11}\text{Br}_1\text{N}_1\text{O}_4\text{V}_1$ (M^+), 434.9311; Found, 434.9314.

Synthesis of oxidovanadium(v) complex **3d**

A mixture of the tris(2-hydroxyphenyl)amine ligand **2d** (156 mg, 0.50 mmol) and $\text{VO}(\text{O}'\text{Pr})_3$ (118 μL , 0.50 mmol) was stirred in dichloromethane (15 mL) under Ar at room temperature for 3 h. After evaporation of the solution, the oxidovanadium(v) complex **3d** was isolated as a blue-purple solid (184 mg, 0.49 mmol) by reprecipitation from dichloromethane and hexane.

3d: yield 98%; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (dd, 2H, J = 8.0, 1.4 Hz), 7.50 (d, 1H, J = 7.8 Hz), 7.21 (t, 2H, J = 8.7 Hz), 6.99 (t, 1H, J = 8.7 Hz), 6.92 (td, 2H, J = 8.7 Hz), 6.85 (td, 1H,



J = 8.2, 5.5 Hz), 6.59 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) 164.3, 152.5 (d, $^2J_{\text{F-C}}$ = 11.5 Hz), 146.5 (d, $^1J_{\text{F-C}}$ = 251.1 Hz), 141.2, 139.7, 130.2, 127.1, 124.2, 123.0 (d, $^3J_{\text{F-C}}$ = 7.7 Hz), 122.4 (d, $^3J_{\text{F-C}}$ = 3.8 Hz), 117.1 (d, $^2J_{\text{F-C}}$ = 17.3 Hz), 115.4 ppm; ^{51}V NMR (105 MHz, CDCl_3) –304 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{18}\text{H}_{11}\text{F}_1\text{N}_1\text{O}_4\text{V}_1$ (M^+), 375.0112; Found, 375.0112.

Synthesis of vanadium(v) dimethylhydrazido complexes 4a–d

A mixture of the corresponding oxidovanadium(v) complex 3 (0.10 mmol), *N,N*-dimethylhydrazine (15 μL , 0.20 mmol) and a small amount of MS4A (4 \AA molecular sieves) was stirred in dichloromethane (10 mL) under an atmosphere of nitrogen in a drybox at room temperature for 2 h. The resulting solution was filtered off, and the filtrate was evaporated under reduced pressure. The resulting red-brown solid was washed with hexane to give the desired vanadium(v) dimethylhydrazido complex 4.

4a: yield 56%; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, 2H, *J* = 8.0, 1.4 Hz), 7.46 (d, 1H, *J* = 6.9 Hz), 7.09 (td, 2H, *J* = 7.8, 1.4 Hz), 6.75–6.69 (m, 4H), 6.67 (t, 1H, *J* = 7.8 Hz), 3.57 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 164.1, 162.8, 137.5, 136.8, 130.7, 129.6, 126.0, 125.9, 123.4, 120.2, 119.9, 117.1, 43.7, 16.1 ppm; ^{51}V NMR (105 MHz, CDCl_3) 328 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_3\text{V}_1$ (M^+), 413.0944; Found, 413.0955.

4b: yield 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, 3H, *J* = 8.1, 1.4 Hz), 7.14 (td, 3H, *J* = 8.1, 1.4 Hz), 6.76 (m, 6H), 3.58 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 164.3, 137.3, 129.6, 125.8, 120.3, 117.1, 43.7 ppm; ^{51}V NMR (105 MHz, CDCl_3) 335 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_3\text{V}_1$ (M^+), 399.0788; Found, 399.0805.

4c: yield 62%; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, 1H, *J* = 7.8 Hz), 7.48 (d, 2H, *J* = 7.8 Hz), 7.33 (d, 1H, 7.8 Hz), 7.08 (t, 2H, *J* = 7.6 Hz), 6.75–6.68 (m, 4H), 6.59 (t, 1H, *J* = 7.8), 3.56 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 164.3, 161.9, 137.5, 137.0, 132.3, 129.2, 125.3, 124.6, 119.9, 119.8, 117.0, 110.6, 43.8 ppm; ^{51}V NMR (105 MHz, CDCl_3) 382 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{20}\text{H}_{17}\text{Br}_1\text{N}_3\text{O}_3\text{V}_1$ (M^+), 476.9893; Found, 476.9911.

4d: yield 53%; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, 2H, *J* = 7.8 Hz), 7.35 (d, 1H, *J* = 8.2 Hz), 7.12 (td, 2H, *J* = 7.8, 1.4 Hz), 6.92 (td, 1H, *J* = 9.0, 1.4 Hz), 6.76–6.71 (m, 4H), 6.64 (td, 1H, *J* = 8.2, 5.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) 164.3, 153.1 (d, $^2J_{\text{F-C}}$ = 13.4 Hz), 149.5 (d, $^1J_{\text{F-C}}$ = 247.2 Hz), 139.1 (d, $^3J_{\text{F-C}}$ = 3.8 Hz), 136.9, 129.6, 125.8, 121.0, 120.3, 118.8 (d, $^3J_{\text{F-C}}$ = 7.7 Hz), 117.1, 116.0 (d, $^2J_{\text{F-C}}$ = 18.2 Hz), 43.7 ppm; ^{51}V NMR (105 MHz, CDCl_3) 378 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_1\text{N}_3\text{O}_3\text{V}_1$ (M^+), 417.0694; Found, 417.0700.

Synthesis of vanadium(v) diphenylhydrazido complexes 5a–d

A mixture of the corresponding oxidovanadium(v) complex 3 (0.10 mmol), *N,N*-diphenylhydrazine (33 μL , 0.20 mmol) and a small amount of MS4A (4 \AA molecular sieves) was stirred in dichloromethane (10 mL) under an atmosphere of nitrogen in a drybox at room temperature for 2 h. The resulting solution was filtered off, and the filtrate was evaporated under reduced

pressure. The resulting red-purple solid was washed with hexane to give the desired vanadium(v) diphenylhydrazido complex 5.

5a: yield 68%; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (dd, 4H, *J* = 8.0, 0.8 Hz), 7.66 (dd, 2H, *J* = 7.6, 1.2 Hz), 7.52 (d, 1H, *J* = 6.8 Hz), 7.50 (t, 4H, *J* = 7.6 Hz), 7.18 (td, 2H, *J* = 8.4, 2.0 Hz), 7.08 (d, 1H, *J* = 7.2 Hz), 6.82 (td, 2H, *J* = 8.0, 1.2 Hz), 6.76 (t, 1H, *J* = 7.6 Hz), 6.72 (dd, 2H, *J* = 8.4, 1.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) 164.1, 149.4, 141.3, 137.8, 131.1, 130.1, 129.5, 129.4, 129.2, 126.8, 126.2, 123.6, 122.1, 120.9, 120.7, 120.1, 119.6, 118.0, 117.1, 16.2 ppm; ^{51}V NMR (105 MHz, CDCl_3) 164 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_3\text{O}_3\text{V}_1$ (M^+), 537.1257; Found, 537.1256.

5b: yield 68%; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, 4H, *J* = 8.7, 0.9 Hz), 7.66 (dd, 3H, *J* = 8.0, 1.4 Hz), 7.50 (t, 4H, *J* = 8.7 Hz), 7.31–7.15 (m, 5H), 7.17 (td, 3H, *J* = 8.2, 1.4 Hz), 6.83 (td, 3H, *J* = 7.8, 1.4 Hz), 6.73 (dd, 3H, *J* = 8.2, 1.4 Hz); ^{13}C NMR (100 MHz, CDCl_3) 117.2, 119.6, 120.1, 121.1, 126.2, 126.9, 129.2, 129.4, 130.2, 137.8, 141.2, 164.2 ppm; ^{51}V NMR (105 MHz, CDCl_3) 178 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_3\text{O}_3\text{V}_1$ (M^+), 523.1101; Found, 523.1099.

5c: yield 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.75 (m, 3H), 7.62 (dd, 1H, *J* = 6.0, 1.6 Hz), 7.60 (dd, 1H, *J* = 6.4, 1.2 Hz), 7.52–7.47 (m, 3H), 7.31–7.16 (m, 8H), 6.98 (td, 1H, *J* = 8.0, 1.2 Hz), 6.81 (td, 2H, *J* = 8.0, 1.2 Hz), 6.73–6.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) 164.0, 149.3, 141.1, 138.5, 137.3, 133.3, 130.4, 129.6, 129.2, 127.1, 126.0, 125.4, 122.1, 121.4, 121.2, 120.2, 119.6, 117.2 ppm; ^{51}V NMR (105 MHz, CDCl_3) 206 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{30}\text{H}_{21}\text{Br}_1\text{N}_3\text{O}_3\text{V}_1$ (M^+), 601.0206; Found, 601.0223.

5d: yield 61%; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, 4H, *J* = 8.7, 0.9 Hz), 7.64 (dd, 2H, *J* = 8.2, 1.4 Hz), 7.50 (t, 4H, *J* = 7.8 Hz), 7.45 (d, 1H, *J* = 8.4 Hz), 7.39–7.17 (m, 7H), 6.84 (td, 2H, *J* = 7.8, 1.4 Hz), 6.78–6.71 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) 164.1, 152.7 (d, $^2J_{\text{F-C}}$ = 12.5 Hz), 149.3, 148.9 (d, $^1J_{\text{F-C}}$ = 249.2 Hz), 141.0, 139.4 (d, $^3J_{\text{F-C}}$ = 3.8 Hz), 137.2, 130.3, 129.2, 127.0, 126.0, 122.1, 121.6 (d, $^3J_{\text{F-C}}$ = 2.9 Hz), 119.6, 117.2, 116.6 (d, $^2J_{\text{F-C}}$ = 18.2 Hz) ppm; ^{51}V NMR (105 MHz, CDCl_3) 209 ppm; HRMS (FAB) *m/z* Calcd for $\text{C}_{30}\text{H}_{21}\text{F}_1\text{N}_3\text{O}_3\text{V}_1$ (M^+), 541.1007; Found, 541.1004.

X-ray structure analysis

All measurements for **4d-DMH-4d** and **5b** were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation. All measurements for **4b** were made on a Rigaku R-AXIS RAPID diffractometer using filtered Mo $\text{K}\alpha$ radiation. The structures of **4b**, **4d-DMH-4d** and **5b** were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the Crystal Structure crystallographic software package except for the refinement, which was performed using SHELXL-97. 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. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the



Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-925607 for **4b**, CCDC-925608 for **4d-DMH-4d** and CCDC-925609 for **5b**.

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