Supplementary Information

Systematic reductive oligomerization of isocyanides with a vanadium(II) complex

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Contents

Experimental Section

General procedure

All manipulations were carried out using standard Schlenk techniques or in a glove-box under an atmosphere of argon. Anhydrous hexane, pentane and toluene were dried by passage through two columns of activated alumina and a Q-5 column, while anhydrous THF, Et_2O and DME were dried by passage through two columns of activated alumina. Anhydrous benzene and deuterated benzene (benzene-d_6) were dried and degassed over a potassium mirror prior to use. Complex [(ONO)V(THF)] (**1-THF**) was prepared by the literature procedure. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analyses (C, H and N) were carried out on an Elementar VarioMicroCube. Solid-state magnetic susceptibilities were measured on a Sherwood Scientific MSB-AUTO at ambient temperature. Corrections were applied for diamagnetism calculated for Pascal constants.

Synthesis of [{K(DME)}{(ONO)V(DME)}] (2-DME). A flask was charged with potassium (40.9 mg, 1.05 mmol), naphthalene (140.2 mg, 1.094 mmol) and DME (25 mL). The mixture was stirred until all of the potassium metal was dissolved. The resulting solution of potassium naphthalenide was added dropwise to [(ONO)V(THF)] (**1-THF**, 747 mg, 1.05 mmol) in DME (15 mL) at –35 ˚C. and the color of the solution immediately changed from green to deep yellow. After stirring at room temperature for 1 h, all volatiles were removed in vacuo. The residue was washed with hexane, and then dried under vacuum. The product **2-DME** was obtained as an orange powder (692.5 mg, 806.0 μmol) in 76.8% yield. μ_{eff} = 3.66 μ_B. Anal. Calcd (%) for $C_{49}H_{70}KNO_6V$: C 68.50, H 8.21, N 1.63; found: C 68.78, H 8.00, N 1.72.

Synthesis of [{K(DME)}{(ONO)V(DMAP)}$_2$] (2-DMAP). To a solution of **2-DME** (175.3 mg, 204.0 μmol) in DME (10 mL) was added 4-dimethylaminopyridine (DMAP, 49.8 mg, 0.408 μmol). The solution immediately turned deep purple. After stirring for 1 h, the solution was evaporated to dryness and washed with pentane. Complex **2-DMAP** was obtained as a light purple powder (191.6 mg, 189.1 μmol, 92.7%). μ_{eff} = 3.82 μ_B. Anal. Calcd (%) for $C_{59}H_{80}KN_5O_4V$: C 69.93, H 7.96, N 6.91; found: C 69.75, H 7.56, N 7.12.

Reaction of 2-DME with CuCl. Solid CuCl (11.2 mg, 113 μmol) was added to a solution of **2-DME** (100.7 mg, 117.2 μmol) in THF (10 mL) at room temperature. The mixture was stirred for 1 h, during which time the color of the solution changed from yellow to green with concomitant precipitation of copper metal particles. After removal of all volatiles in vacuo, the residue was extracted with toluene/hexane. The extract was evaporated to dryness, and then the residue was washed with pentane to give **1-THF** as a green powder (75.1 mg, 105 μmol, 92.9%).

Reaction of 2-DME with Me_3SiN_3. To a slurry of **2-DME** (31.3 mg, 36.3 μmol) in pentane (5 mL) was added Me_3SiN_3 (6.0 mg, 52.0 μmol) at room temperature. The color of the solution immediately turned green. The solution was stirred for 1 h, and then evaporated to dryness. Following crystallization from pentane (3 mL), the product [{K(DME)}{(ONO)VNSiMe$_3$}] was obtained as yellow crystals (23.6 mg, 27.6 μmol, 75.7%). μ_{eff} = 1.67 μ_B. Anal. Calcd (%) for $C_{48}H_{69}KN_2O_4SiV$: C 67.33, H 8.12, N 3.27; found: C 66.81, H 8.29, N 3.53.

Reaction of 2-DME with AdNC. To a solution of **2-DME** (218.8 mg, 254.7μmol) in toluene (10 mL) was added 1-adamantyl isocyanide (AdNC, 41.0 mg, 254.3 μmol) at room temperature. The color of the solution immediately turned green. After stirring for 1 h, all volatiles were removed in vacuo, the residue was dissolved in DME and then layered with hexane. The solvents were allowed to diffuse slowly, resulting in the formation of [K(DME)$_2$][(ONO)V(CN)] (**1-KCN**) as green crystals (92.4 mg, 86.7 μmol, 34.1%). IR (cm^{-1}; KBr): 2128 (ν_{C-N}). μ_{eff} = 2.73 μ_B. Anal. Calcd (%) for $C_{50}H_{70}KN_2O_6V$: C, 67.85; H, 7.97; N, 3.16. Found: C, 67.93; H, 7.41; N, 2.95%.

Isolation of 1-KCN-crypt

A solution of cryptand-222 (20.3 mg, 53.9 μmol) in THF (2 mL) was layered on a solution of **1-KCN** (53.2 mg, 86.7 μmol) in THF (2 mL) at room temperature. The resulting dark green crystals of [K(cryprtand-222)][(ONO)V(CN)] (**1-KCN-crypt**) were washed with hexane and

dried under vacuum (48.3 mg, 44.7 μmol, 89.3%). IR (cm^{-1}; KBr): 2101 (ν_{C-N}). μ_{eff} = 2.60 μ_B. Anal. Calcd for $C_{60}H_{86}KN_4O_8V$: C, 66.64; H, 8.02; N, 5.18. found: C, 66.26; H, 8.15; N, 4.86%.

Reaction of 2-DME with ^{t}BuNC. To a toluene solution of **2-DME** (61.4 mg, 71.5 μmol) was added ^{t}BuNC (0.2 mL, 147 μmol) at room temperature. Workup similar to the above produced **1-KCN** (42.2 mg, 39.6 μmol, 55.5%).

Synthesis of $[K(DME)]_2[\{[H(ONO)]V\}_2\{C_{16}H_6N_2(OMe)_2(N\text{-}PMP)_2\}]$ (3). A solution of PMPNC (26.6 mg, 200 μmol) in DME (4 mL) was added to a solution of **2-DME** (85.9 mg, 100 μmol) in toluene (4 mL) at room temperature. The color of the solution immediately turned from brown to dark brown. After stirring for 1 h, all volatiles were removed in vacuo, the residue was washed with Et_2O and dried under vacuum to give **3** as a dark brown powder (73.7 mg, 35.6 μmol, 71.2%). μ_{eff} = 3.00 μ_B (per V atom). Anal. Calcd for $C_{122}H_{148}K_2N_6O_{12}V_2$: C, 70.77; H, 7.20; N, 4.06. found: C, 70.79; H, 6.96; N, 4.59%.

Isolation of $[K\{K(DME)\{\{(ONO)V\}\{C_{16}H_8N_2(OMe)_2(N\text{-}PMP)_2\}\}]$ (4). A dark brown powder of **3** (50.0 μmol) was dissolved in toluene (4 mL) and then layered with hexane (8 mL). The solvents were allowed to diffuse slowly, resulting in the formation of **4** as orange crystals. The crystals were collected and washed with hexane, and then dried under vacuum, leaving an orange powder of **4** (54.4 mg, 40.6 μmol, 81.2%). μ_{eff} = 3.82 μ_B. Anal. Calcd for $C_{77}H_{88}K_2N_5O_8V$: C, 68.98; H, 6.62; N, 5.22. found: C, 69.44; H, 6.41; N, 5.30%.

Synthesis of $[\{K(DME)[(ONO)]V\}_2(XylNCCNXyl)]$ (5). To a solution of **2-DME** (62.0 mg, 72.2 μmol) in toluene (10 mL) was added XylNC (9.6 mg, 73 μmol, Xyl = 2,6-dimethylphenyl) at room temperature. The color of the solution immediately turned from yellow to green. After stirring for 1 h, the solution was evaporated to dryness. The residue was washed with hexane (3 mL), and then dried under vacuum, leaving a green powder of **5** (58.0 mg, 32.2 μmol, 89.3%). μ_{eff} = 2.84 μ_B (per V atom). Anal. Calcd (%) for $C_{108}H_{138}K_2N_4O_8V_2$: C 72.05, H 7.73, N 3.11; found: C 72.47, H 8.10, N 3.61.

Synthesis of [{K(THF)$_2$}{(ONO)V}{XylNC(C$_{10}$H$_9$N)NXyl}] (6). To a solution of **2-DME** (58.1 mg, 67.6 μmol) in toluene (10 mL) was added XylNC (26.5 mg, 202 μmol) at room temperature. The color of the solution turned from yellow to brown. After stirring for 1 h, the solution was evaporated to dryness. The residue was recrystallized from THF/pentane, affording a brown crystals of **6** (68.7 mg, 59.1 μmol, 87.8%). μ_{eff} = 3.89 μ_B. Anal. Calcd (%) for $C_{76}H_{93}KN_4O_4V$: C 75.03, H 7.71, N 4.61; found : C 74.93, H 7.67, N 4.68.

Synthesis of [K(DME)$_4$][{K(DME)}{(ONO)V}$_2${(Xyl)$_3$N$_3$C$_3$}] (7). To a solution of **5** (61.6 mg, 34.2 μmol) in toluene (4 mL) was added XylNC (4.6 mg, 35.1 μmol) at –35 ˚C. The color of the solution turned dark brown. After stirring for 30 min, all volatiles were removed in vacuo, the residue was dissolved in DME and then layered with hexane. The solvents were allowed to diffuse slowly, resulting in the formation of **7** as reddish brown crystals (92.4 mg, 86.7 μmol, 34.1%). μ_{eff} = 2.86 μ_B (per V atom). Anal. Calcd (%) for $C_{129}H_{177}K_2N_5O_{14}V_2$: C 70.37, H 8.10, N 3.18; found : C 70.86, H 8.16, N 3.03.

Synthesis of [(ONO)V(CNPMP)$_2$] (1-PMPCN). To a solution of **1-THF** (39.7 mg, 55.8 μmol) in toluene (5 mL) was added PMPNC (14.8 mg, 111.2 μmol). The solution darkened to deep green. After stirring for 30 min, the solvent was removed in vacuo. The residue was crystallized from toluene/pentane. The product **1-PMPCN** was obtained as dark red crystals (45.8 mg, 50.5 μmol, 90.5%). IR (cm^{-1}; KBr): 2122, 2160 (ν_{C-N}). μ_{eff} = 2.41 μ_B. Anal. Calcd (%) for $C_{57}H_{64}N_3O_4V$: C 75.56, H 7.12, N 4.64; found : C 75.27, H 7.10, N 4.64.

Synthesis of [(ONO)V(CNXyl)] (1-XylNC). To a toluene (5 mL) solution of **1-THF** (142 mg, 0.199 mmol) was added XylNC (26.5 mg, 0.202 mmol) at room temperature. The color of the solution changed from green to dark brown. After stirring for 1 h, all volatiles were removed in vacuo to give dark brown powder, which was washed with pentane and dried to afford **1-XylNC** as a light brown powder (113 mg, 0.147 mmol, 73.5% yield). Anal. Calcd for

$C_{50}H_{59}N_2O_2V$: C, 77.89; H, 7.71; N, 3.63. Found: C, 77.73; H, 7.78; N, 3.62%. IR (KBr; ν/cm^{-1}): 2149 (NC). μ_{eff} (solid state, 297 K): 2.67 μ_B.

Reduction of 1-PMPNC. A solution of K($C_{10}H_8$) (75.0 μmol) in DME (10 mL) was added to a solution of **1-PMPNC** (68.0 mg, 75.0 μmol) in toluene (5 mL) at –37 °C. The resulting dark brown solution was stirred for 1 h, and then evaporated to dryness. The residue was washed with hexane (10 mL), and then dried under vacuum, leaving a dark brown powder of **3** (69.7 mg, 33.7 μmol, 89.7%).

Reduction of 1-XylNC. A solution of K($C_{10}H_8$) (99.4 μmol) in DME (10 mL) was added to **1-XylNC** (76.3 mg, 99.0 μmol). The resulting green solution was stirred for 1 h, and then evaporated to dryness. The residue was washed with hexane (2 mL), and then dried under vacuum, leaving a green powder of **5** (55.1 mg, 30.6 μmol, 61.8%).

X-ray Crystallography

Single crystals were immersed in immersion oil on micromount and transferred to a Rigaku Varimax with Saturn system, Rigaku XtaLab mini system, or a Rigaku XtaLAB Synergy-DW system equipped a Rigaku GNNP low temperature device. Data were collected under a cold nitrogen stream at 123 K using graphite-monochromated MoKα (λ = 0.71073 Å) or CuKα (λ = 1.54184 Å) radiation. Equivalent reflections were merged, and the images were processed with the CrysAlis^{Pro} software. Empirical absorption corrections were applied. All structures were solved by direct method using SHELXT[1] and refined by full-matrix least-squares method on F^2 for all data using SHELXL[2] with the Olex2 program[3]. All hydrogen atoms except NH were placed at their geometrically calculated positions. The positions of hydrogen atoms on nitrogen atoms were determined by difference Fourier synthesis and refined free of constrains. For **4**, **5** and **7**, some residual electron density was difficult to model, the program SQUEEZE[4] was used to remove the contribution of the electron density in the solvent region from the intensity data. For **1-KCN-crypt**, a hexane molecule was disordered. For **4**, a void space contains 135 electrons per unit cell, which could be attributed to distorted two toluene

molecules and a hexane molecule (one toluene and a half hexane molecules in the asymmetric unit). For **1-KNSiMe$_3$**, a *tert*-butyl group and a DME molecule was disordered. For **5**, four *tert*-butyl groups and a DME molecule were disordered. A void space contains 594 electrons per unit cell, which could be attributed to distorted twelve toluene molecules (one and a half molecules in the asymmetric unit). For **6**, four carbon atoms in the annulated ring, two methyl groups and three THF molecules were disordered. For **7**, a void space contains 116 electrons per unit cell, which could be attributed to distorted two hexane molecules (one molecule in the asymmetric unit). Molecular graphics were prepared using ORTEP-3 for Windows[5].

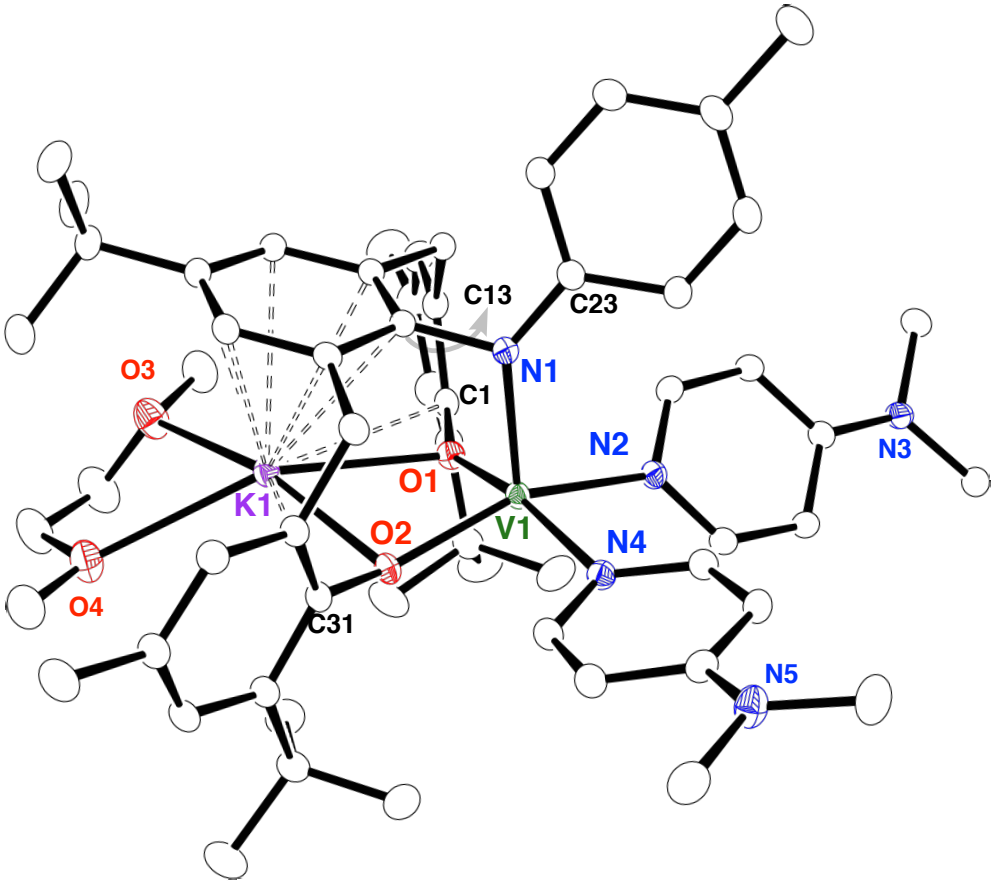

Fig. S1 Molecular structure of **2-DMAP** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 2.1142(9), V(1)–O(2) 2.0738(9), V(1)–N(1) 2.1022(11), V(1)–N(2) 2.1678(11), V(1)–N(4) 2.2671(11), K(1)–O(1) 2.6682(10), K(1)–O(2) 2.6828(10), K(1)–C(1) 3.2466(13), K(1)–C(31) 3.1370(13), O(1)–V(1)–N(2) 86.81(4), O(1)–V(1)–N(4) 167.57(4), O(2)–V(1)–O(1) 89.00(4), O(2)–V(1)–N(1) 105.03(4), O(2)–V(1)–N(2) 156.87(4), O(2)–V(1)–N(4) 89.05(4), N(1)–V(1)–O(1) 93.39(4), N(1)–V(1)–N(2) 97.93(4), N(1)–V(1)–N(4) 98.97(4), N(2)–V(1)–N(4) 90.18(4), C(1)–O(1)–V(1) 151.37(8), C(31)–O(2)–V(1) 149.40(8), C(13)–N(1)–V(1) 106.33(8), C(23)–N(1)–V(1) 136.25(9), C(23)–N(1)–C(13) 116.46(10).

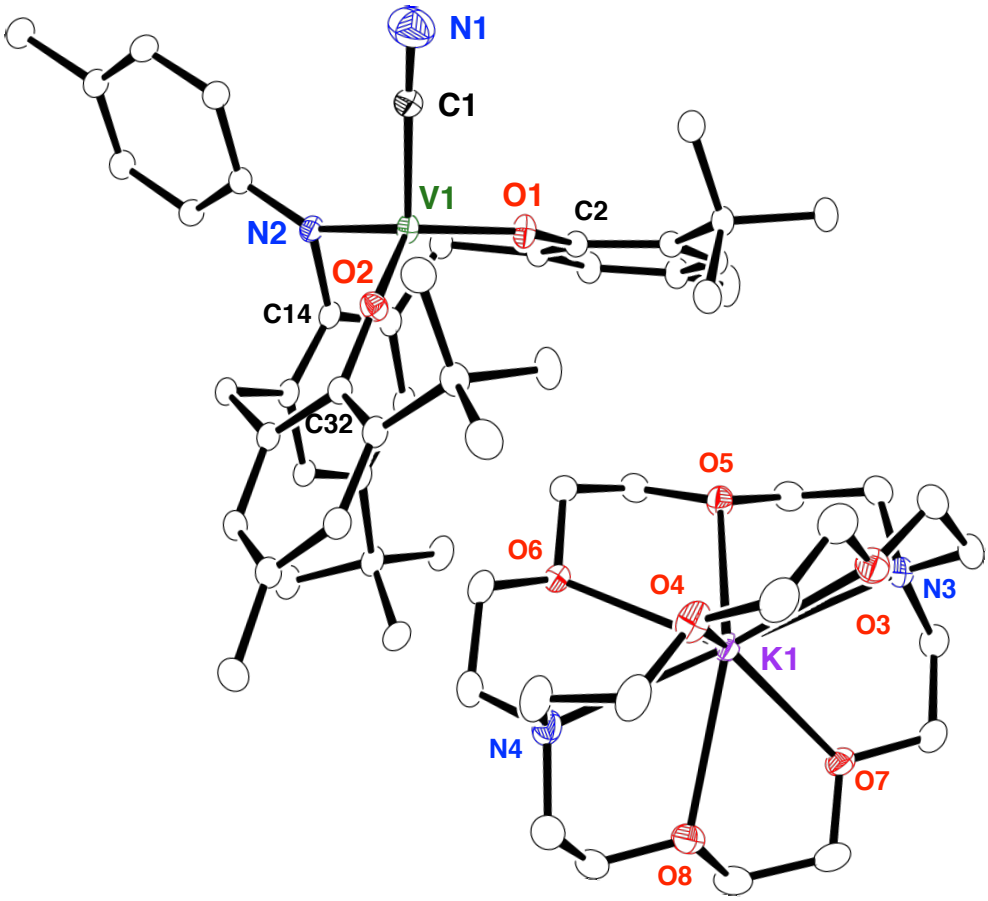

Fig. S2 Molecular structure of **1-KCN-crypt** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 1.8806(11), V(1)–O(2) 1.8625(11), V(1)–N(2) 1.8983(12), V(1)–C(1) 1.9873(17), V(1)–C(14) 2.5122(14), O(1)–C(2) 1.3386(18), O(2)–C(32) 1.3409(18), N(1)–C(1) 1.199(3), N(2)–C(14) 1.4305(19), O(1)–V(1)–N(2) 114.93(5), O(1)–V(1)–C(1) 100.88(6), O(1)–V(1)–C(14) 97.29(5), O(2)–V(1)–O(1) 122.26(5), O(2)–V(1)–N(2) 108.12(5), O(2)–V(1)–C(1) 101.29(6), O(2)–V(1)–C(14) 97.27(5), N(2)–V(1)–C(1) 107.04(6), N(2)–V(1)–C(14) 34.42(5), C(1)–V(1)–C(14) 141.30(6), N(1)–C(1)–V(1) 175.46(19).

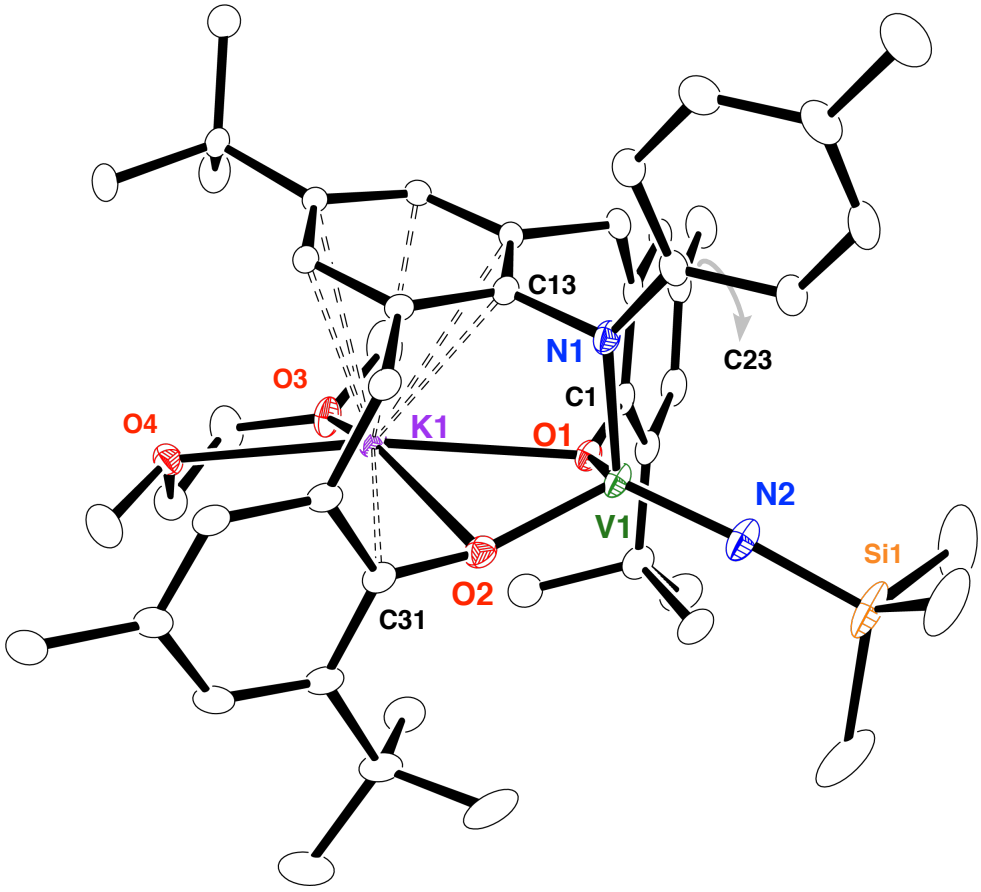

Fig. S3 Molecular structure of **1-KNSiMe$_3$**. with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 1.9241(12), V(1)–O(2) 1.8972(14), V(1)–N(1) 1.9266(16), V(1)–N(2) 1.6739(16), K(1)–O(1) 2.7114(12), K(1)–O(2) 2.8666(14), Si(1)–N(2) 1.7231(17), O(1)–C(1) 1.355(2), O(2)–C(31) 1.344(2), O(3)–C(45) 1.458(4), N(1)–C(13) 1.432(2), N(1)–C(23) 1.400(2), O(1)–V(1)–N(1) 108.39(6), O(2)–V(1)–O(1) 98.07(6), O(2)–V(1)–N(1) 102.83(6), N(2)–V(1)–O(1) 111.64(7), N(2)–V(1)–O(2) 123.21(8), N(2)–V(1)–N(1) 111.25(8), O(1)–V(1)–N(1) 108.39(6), O(2)–V(1)–O(1) 98.07(6), O(2)–V(1)–N(1) 102.83(6), N(2)–V(1)–O(1) 111.64(7), N(2)–V(1)–O(2) 123.21(8), N(2)–V(1)–N(1) 111.25(8), V(1)–N(2)–Si(1) 172.31(11).

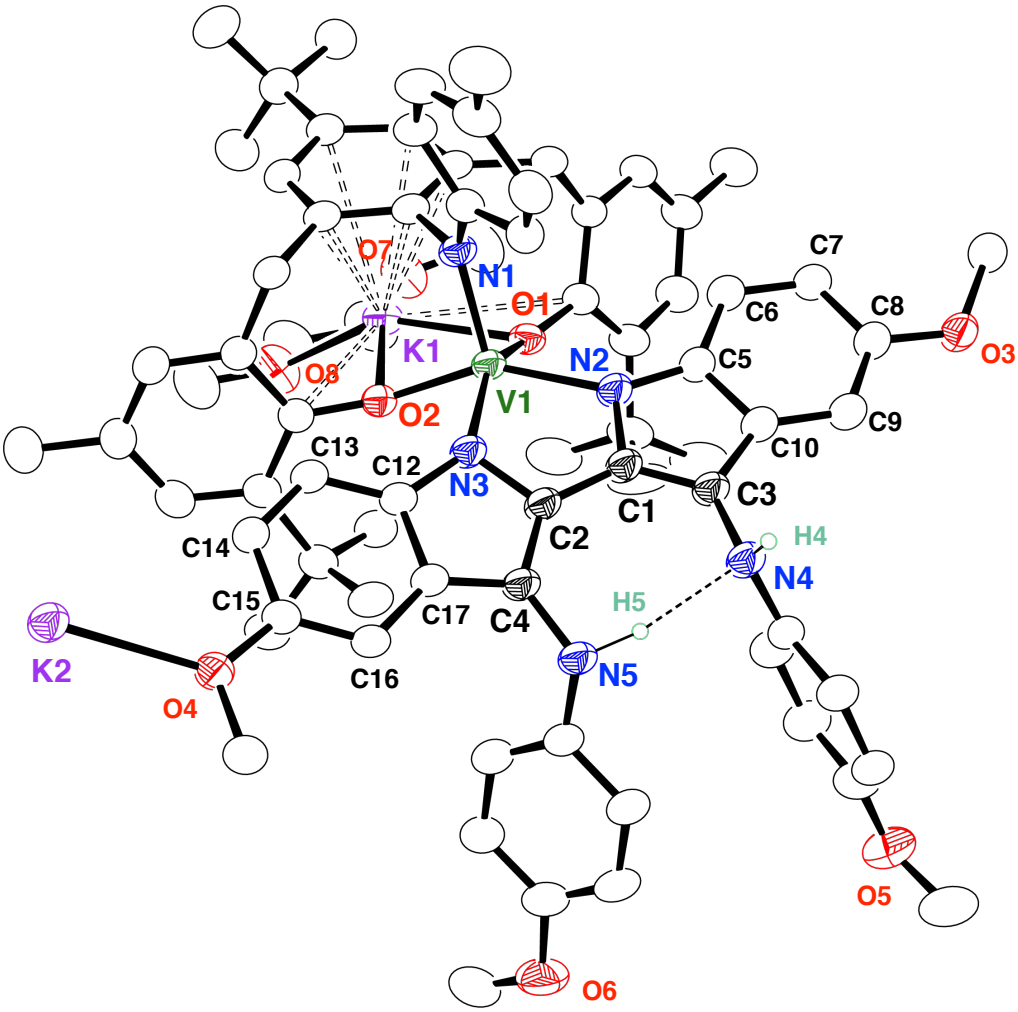

Fig. S4 Molecular structure of **4** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 2.009(2), V(1)–O(2) 1.988(2), V(1)–N(1) 1.923(3), V(1)–N(2) 2.080(3), V(1)–N(3) 2.109(3), N(2)–C(1) 1.391(4), N(2)–C(5) 1.379(4), N(3)–C(2) 1.402(4), N(3)–C(12) 1.390(4), N(4)–C(3) 1.429(4), N(4)–H(4) 0.94(3), N(4)–H(5) 1.95(4), N(5)–C(4) 1.422(4), N(5)–H(5) 1.02(4), C(1)–C(2) 1.444(4), C(1)–C(3) 1.381(5), C(2)–C(4) 1.397(4), C(3)–C(10) 1.421(4), C(5)–C(6) 1.394(5), C(5)–C(10) 1.432(5), C(6)–C(7) 1.387(5), C(7)–C(8) 1.399(5), C(8)–C(9) 1.380(5), C(9)–C(10) 1.392(5), O(1)–V(1)–N(2) 91.67(11), O(1)–V(1)–N(3) 152.36(10), O(2)–V(1)–O(1) 87.41(10), O(2)–V(1)–N(2) 151.79(11), O(2)–V(1)–N(3) 89.84(10), N(1)–V(1)–O(1) 99.76(10), N(1)–V(1)–O(2) 99.53(11), N(1)–V(1)–N(2) 108.40(12), N(1)–V(1)–N(3) 107.82(12), N(2)–V(1)–N(3) 78.09(10), N(3)–V(1)–K(1) 135.47(8), C(1)–N(2)–V(1) 113.6(2), C(5)–N(2)–V(1) 139.8(2), C(5)–N(2)–C(1) 105.5(3), C(2)–N(3)–V(1) 110.98(19), N(2)–C(1)–C(2) 115.3(3), C(3)–C(1)–N(2) 111.8(3), C(3)–C(1)–C(2) 132.9(3), N(3)–C(2)–C(1) 115.0(3), C(4)–C(2)–N(3) 111.4(3), C(4)–C(2)–C(1) 133.6(3), C(1)–C(3)–N(4) 126.4(3), C(1)–C(3)–C(10) 106.7(3), N(2)–C(5)–C(10) 110.3(3), C(3)–C(10)–C(5) 105.7(3).

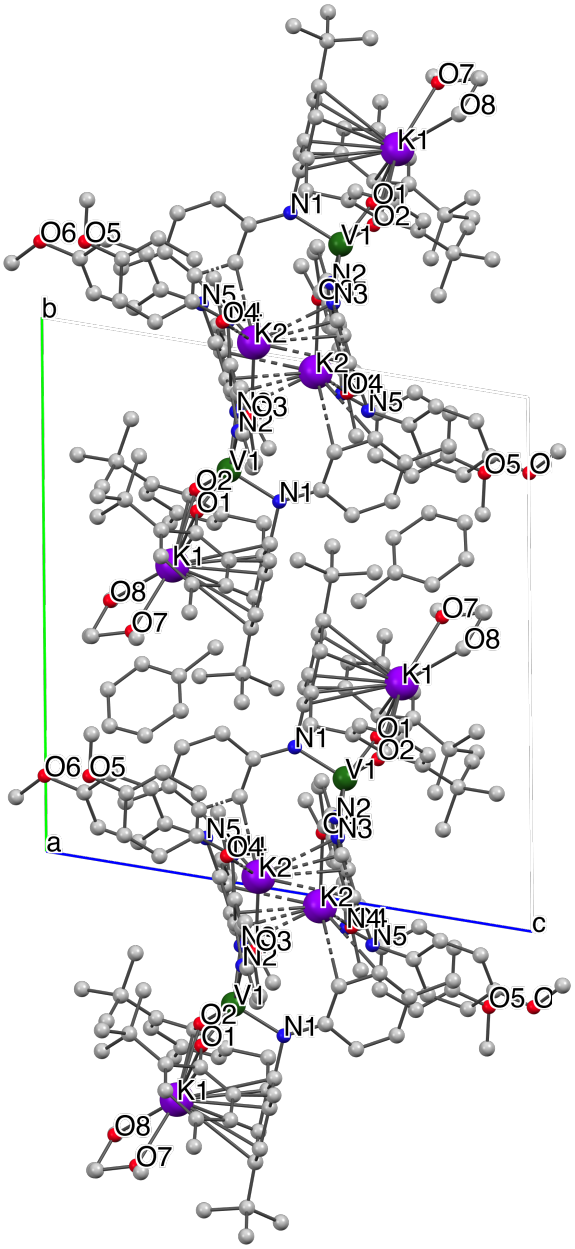

Fig. S5 Crystal packing view along *a* axis of **4**.

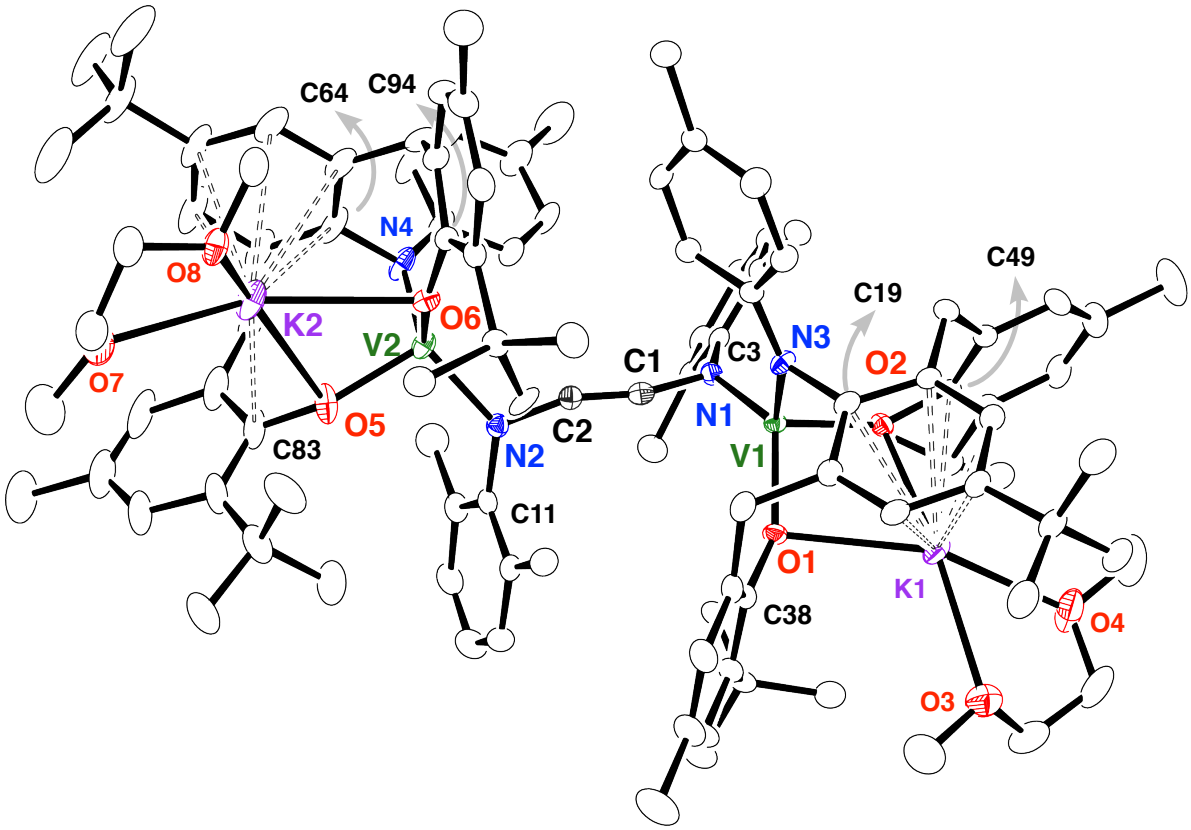

Fig. S6 Molecular structure of **5** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 1.912(2), V(1)–O(2) 1.950(2), V(1)–N(1) 1.945(3), V(1)–N(3) 1.926(3), V(1)–C(1) 2.519(4), V(2)–O(5) 1.931(3), V(2)–O(6) 1.893(2), V(2)–N(2) 1.966(3), V(2)–N(4) 1.925(3), N(1)–C(1) 1.345(4), N(2)–C(2) 1.341(4), N(1)–C(3) 1.431(4), N(2)–C(11) 1.448(4), N(3)–C(19) 1.433(4), N(4)–C(64) 1.444(5), C(1)–C(2) 1.225(5), O(1)–V(1)–O(2) 93.18(10), O(1)–V(1)–N(1) 124.60(11), O(1)–V(1)–N(3) 109.58(11), O(1)–V(1)–C(1) 105.32(11), O(2)–V(1)–C(1) 137.38(11), N(1)–V(1)–O(2) 106.77(11), N(3)–V(1)–O(2) 104.53(11), N(3)–V(1)–N(1) 114.06(12), N(3)–V(1)–C(1) 104.73(11), O(5)–V(2)–N(2) 102.12(12), O(6)–V(2)–O(5) 99.01(11), O(6)–V(2)–N(2) 122.37(11), O(6)–V(2)–N(4) 108.79(12), N(4)–V(2)–O(5) 104.92(13), N(4)–V(2)–N(2) 116.20(12), C(38)–O(1)–V(1) 147.7(2), C(49)–O(2)–V(1) 150.8(2), C(94)–O(6)–V(2) 151.0(2), C(1)–N(1)–V(1) 98.3(2), C(1)–N(1)–C(3) 120.3(3), C(3)–N(1)–V(1) 140.6(2), C(2)–N(2)–V(2) 110.0(2), C(2)–N(2)–C(11) 116.3(3), C(11)–N(2)–V(2) 133.4(2), C(19)–N(3)–V(1) 103.0(2), C(29)–N(3)–V(1) 140.9(2), C(29)–N(3)–C(19) 115.9(3), C(64)–N(4)–V(2) 104.1(2), N(1)–C(1)–V(1) 49.83(17), C(2)–C(1)–N(1) 163.2(4), C(1)–C(2)–N(2) 161.3(4).

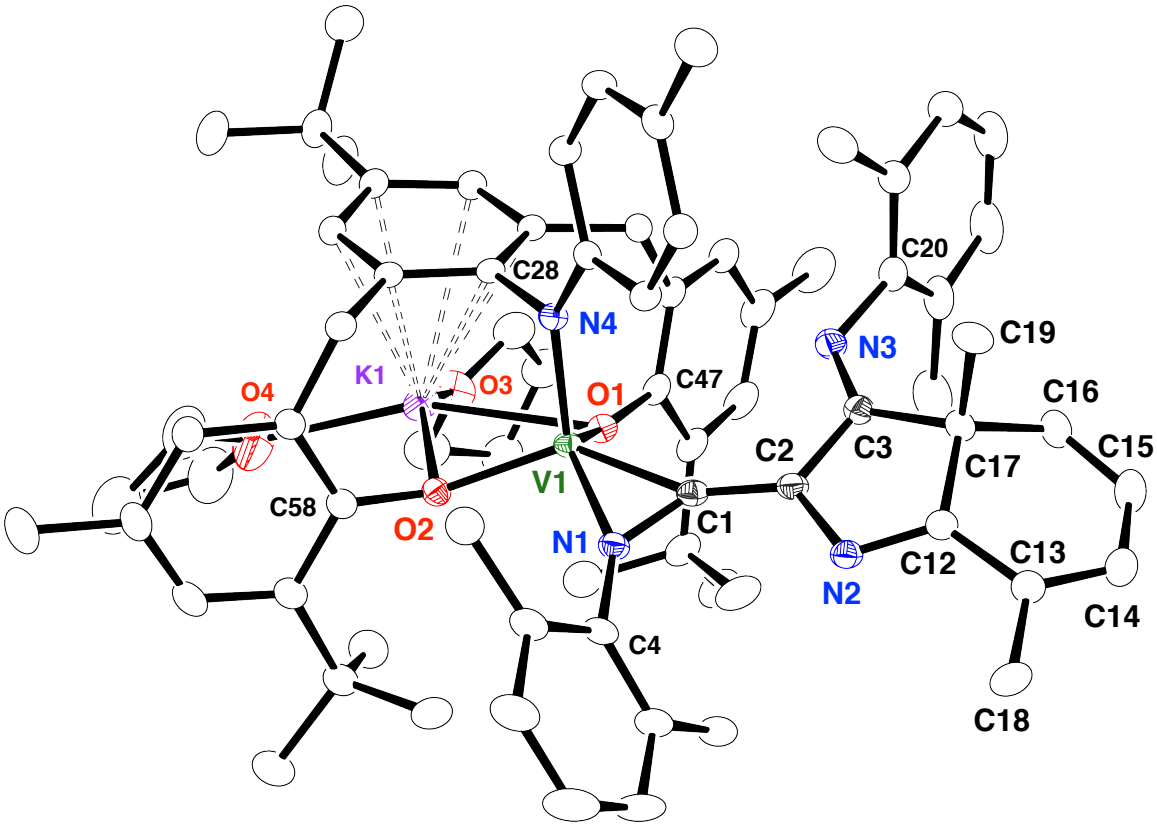

Fig. S7 Molecular structure of **6** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 1.8519(14), V(1)–O(2) 1.9356(14), V(1)–N(1) 1.9477(17), V(1)–N(4) 1.8722(17), V(1)–C(1) 2.002(2), N(1)–C(1) 1.321(3), N(2)–C(2) 1.412(3), N(2)–C(12) 1.295(5), N(3)–C(3) 1.281(3), C(1)–C(2) 1.362(3), C(2)–C(3) 1.465(3), C(3)–C(17) 1.542(4), C(12)–C(13) 1.445(6), C(12)–C(17) 1.495(10), C(13)–C(14) 1.346(6), C(14)–C(15) 1.446(5), C(15)–C(16) 1.330(5), C(16)–C(17) 1.499(5), C(13)–C(18) 1.483(5), C(17)–C(19) 1.563(5), O(1)–V(1)–O(2) 98.61(6), O(1)–V(1)–N(1) 128.87(7), O(1)–V(1)–N(4) 106.19(7), O(1)–V(1)–C(1) 104.61(8), O(2)–V(1)–N(1) 98.86(7), O(2)–V(1)–C(1) 137.10(7), N(1)–V(1)–C(1) 39.04(8), N(4)–V(1)–O(2) 105.16(7), N(4)–V(1)–N(1) 114.76(7), N(4)–V(1)–C(1) 102.30(8), C(1)–N(1)–V(1) 72.70(12), C(1)–N(1)–C(4) 133.21(19), C(4)–N(1)–V(1) 154.07(15), C(12)–N(2)–C(2) 108.5(4), C(3)–N(3)–C(20) 124.49(19), C(28)–N(4)–V(1) 103.83(12), N(1)–C(1)–V(1) 68.26(12), N(1)–C(1)–C(2) 137.9(2), C(2)–C(1)–V(1) 153.35(17), N(2)–C(2)–C(3) 110.91(18), C(1)–C(2)–N(2) 123.89(19), C(1)–C(2)–C(3) 125.18(19), N(3)–C(3)–C(2) 124.3(2), N(3)–C(3)–C(17) 131.7(3), C(2)–C(3)–C(17) 103.6(2), N(2)–C(12)–C(13) 124.7(7), N(2)–C(12)–C(17) 114.3(5), C(13)–C(12)–C(17) 120.7(4), C(14)–C(13)–C(12) 116.7(4), C(13)–C(14)–C(15) 121.4(3), C(16)–C(15)–C(14) 123.2(3), C(15)–C(16)–C(17) 118.6(3), C(3)–C(17)–C(19) 107.7(3), C(12)–C(17)–C(3) 101.4(3), C(12)–C(17)–C(16) 111.2(5), C(12)–C(17)–C(19) 108.4(6), C(16)–C(17)–C(3) 120.6(3), C(16)–C(17)–C(19) 107.0(3).

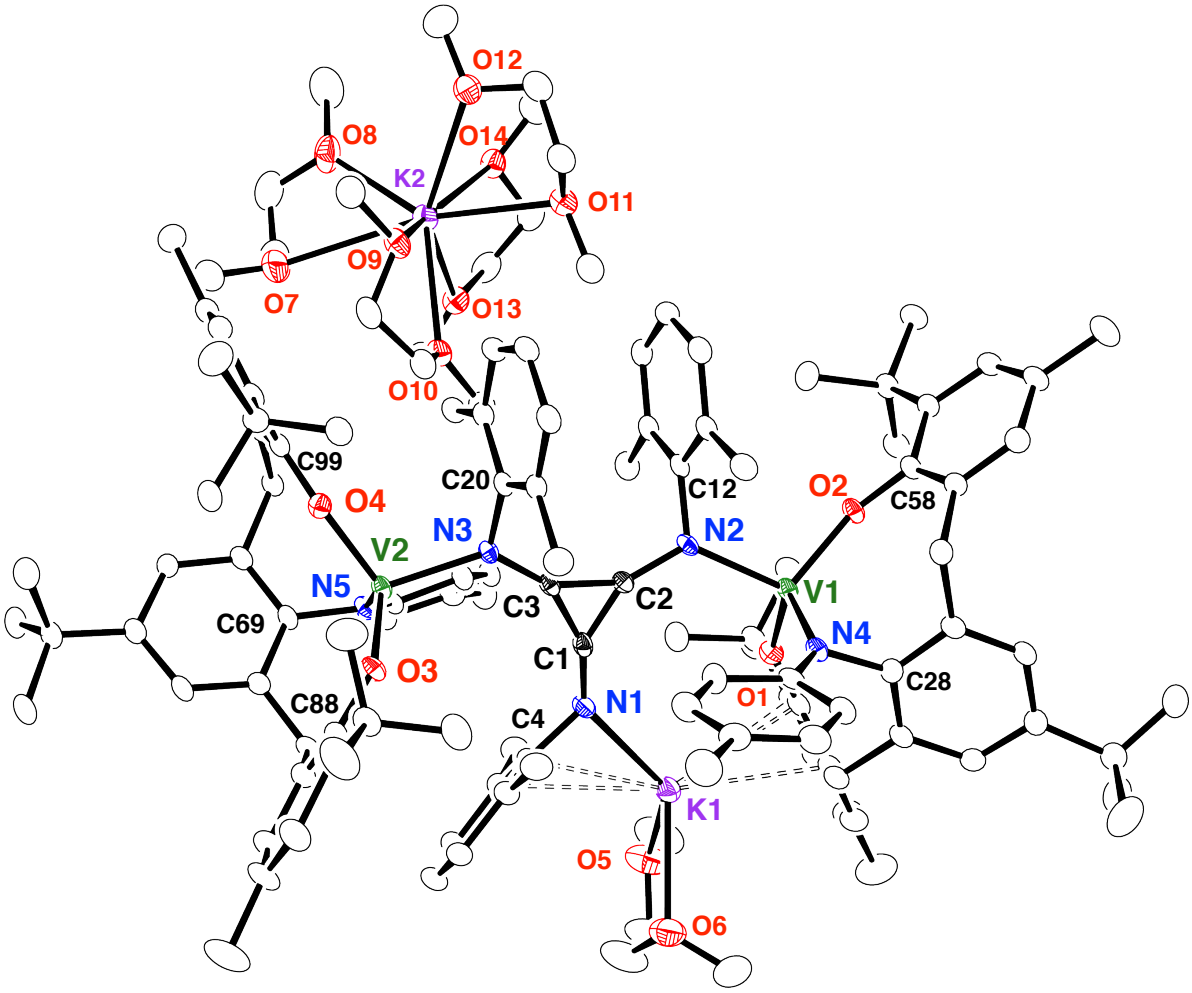

Fig. S8 Molecular structure of **7** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–N(2) 2.030(3), V(2)–N(3) 2.040(3), V(1)–N(4) 1.911(3), V(1)–O(1) 1.916(3), V(1)–O(2) 1.904(2), V(2)–N(5) 1.930(3), V(2)–O(3) 1.892(2), V(2)–O(4) 1.895(2), C(1)–C(2) 1.402(5), C(1)–C(3) 1.427(5), C(2)–C(3) 1.388(5), C(1)–N(1) 1.324(5), C(2)–N(2) 1.369(4), C(3)–N(3) 1.355(4), N(1)–K(1) 2.688(3), N(4)–V(1)–N(2) 109.88(12), N(4)–V(1)–O(1) 107.30(12), O(1)–V(1)–N(2) 104.08(11), O(2)–V(1)–N(2) 106.57(11), O(2)–V(1)–N(4) 110.03(11), O(2)–V(1)–O(1) 118.66(10), N(3)–V(2)–C(69) 139.66(11), N(5)–V(2)–N(3) 106.08(12), O(3)–V(2)–N(3) 105.87(11), O(3)–V(2)–N(5) 117.18(12), O(3)–V(2)–O(4) 113.35(11), O(3)–V(2)–C(69) 102.99(11), O(4)–V(2)–N(3) 107.21(11), O(4)–V(2)–N(5) 106.52(12), O(4)–V(2)–C(69) 86.00(11), C(2)–C(1)–C(3) 58.8(2), C(3)–C(2)–C(1) 61.5(2), C(2)–C(3)–C(1) 59.7(2), N(1)–C(1)–C(2) 145.1(3), N(1)–C(1)–C(3) 155.8(3), C(1)–N(1)–C(4) 123.5(3), N(2)–C(2)–C(1) 149.5(3), N(2)–C(2)–C(3) 149.0(3), N(3)–C(3)–C(1) 150.0(3), N(3)–C(3)–C(2) 150.1(3), C(2)–N(2)–V(1) 125.6(2), C(2)–N(2)–C(12) 113.9(3), C(12)–N(2)–V(1) 120.4(2), C(3)–N(3)–V(2) 128.7(2), C(3)–N(3)–C(20) 114.1(3), C(20)–N(3)–V(2) 117.1(2).

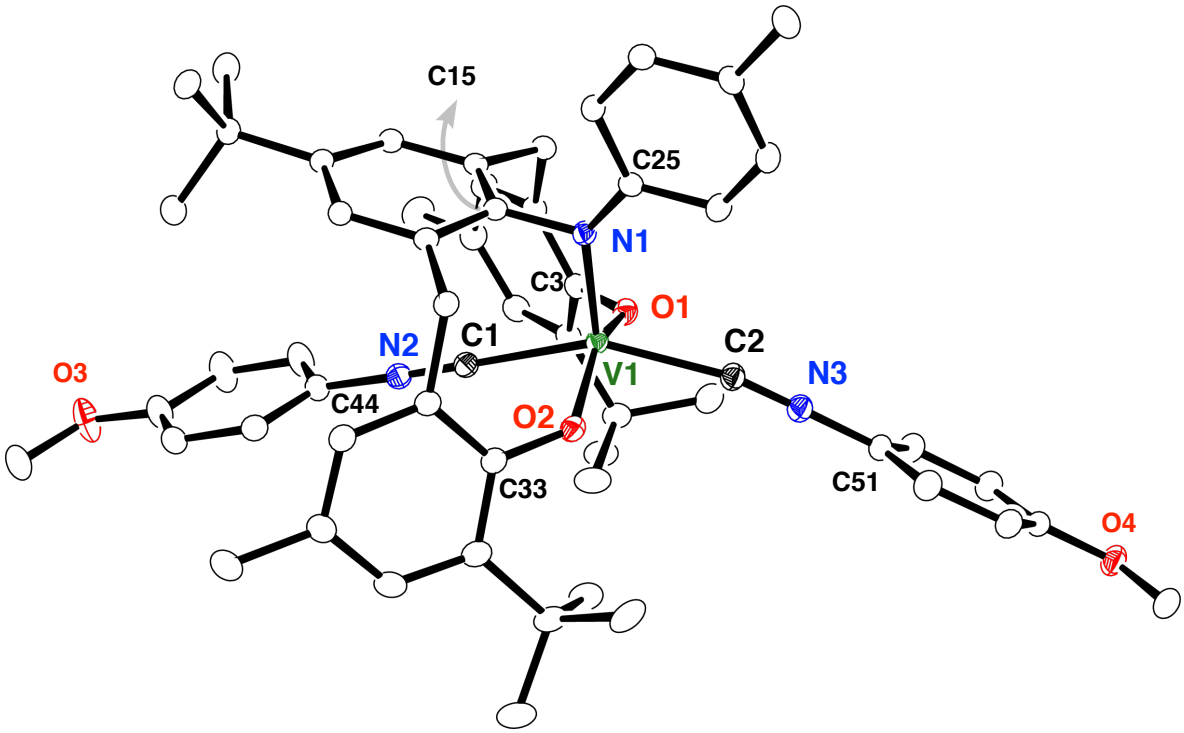

Fig. S9 Molecular structure of **(ONO)V(CNPMP)$_2$** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)-O(1) 1.9154(10), V(1)-O(2) 1.9067(10), V(1)-N(1) 1.9018(11), V(1)-C(1) 2.2002(14), V(1)-C(2) 2.1539(14), O(1)-C(3) 1.3502(17), O(2)-C(33) 1.3461(17), N(1)-C(15) 1.4296(16), N(1)-C(25) 1.3951(16), N(2)-C(1) 1.1522(18), N(3)-C(2) 1.1526(19), N(2)-C(44) 1.3933(18), N(3)-C(51) 1.3955(18), O(1)-V(1)-C(1) 86.48(5), O(1)-V(1)-C(2) 84.34(5), O(2)-V(1)-O(1) 150.89(4), O(2)-V(1)-C(1) 86.93(5), O(2)-V(1)-C(2) 88.06(5), N(1)-V(1)-O(1) 105.75(5), N(1)-V(1)-O(2) 103.35(5), N(1)-V(1)-C(1) 102.33(5), N(1)-V(1)-C(2) 106.21(5), C(2)-V(1)-C(1) 151.41(5), C(3)-O(1)-V(1) 130.54(8), C(33)-O(2)-V(1) 129.91(8), C(15)-N(1)-V(1) 103.70(8), C(25)-N(1)-V(1) 137.05(9), C(25)-N(1)-C(15) 117.68(10), C(1)-N(2)-C(44) 178.21(14), C(2)-N(3)-C(51) 178.85(15), N(2)-C(1)-V(1) 179.49(13), N(3)-C(2)-V(1) 165.26(12).

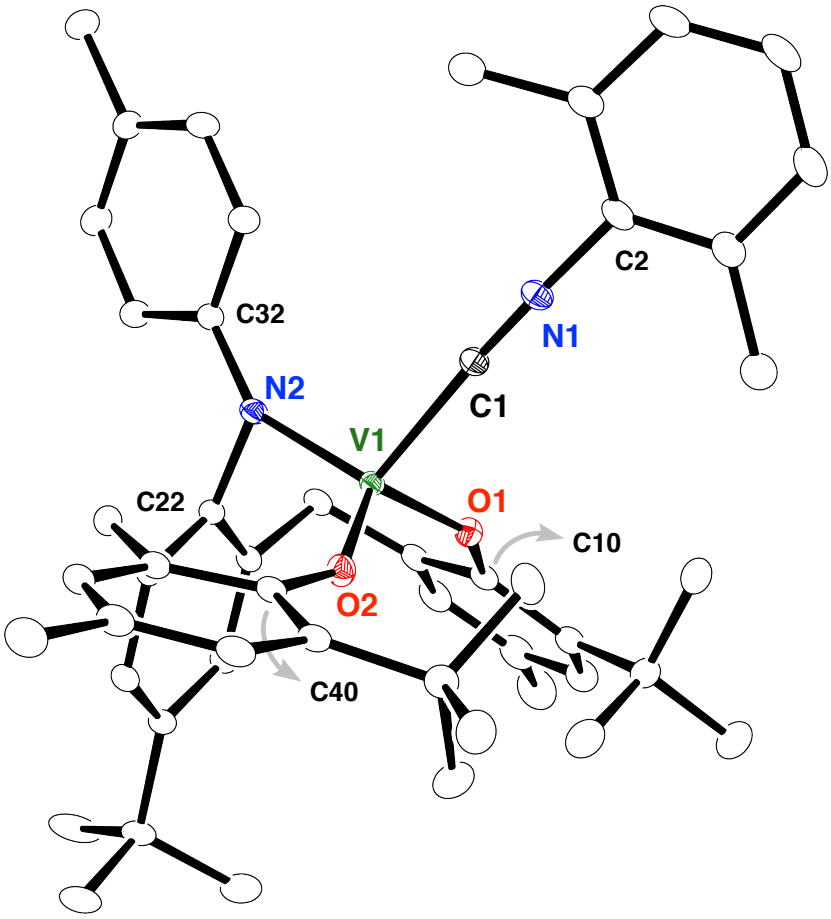

Fig. S10 Molecular structure of **1-XylNC** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)–O(1) 1.8543(9), V(1)–O(2) 1.8570(8), V(1)–N(2) 1.8786(10), V(1)–C(1) 2.0890(12), N(1)–C(1) 1.1569(16), N(1)–C(2) 1.4033(15), N(2)–C(22) 1.4374(15), N(2)–C(32) 1.3934(15), O(1)–V(1)–O(2) 118.70(4), O(1)–V(1)–N(2) 116.09(4), O(1)–V(1)–C(1) 95.15(4), O(2)–V(1)–N(2) 114.23(4), O(2)–V(1)–C(1) 102.99(4), N(2)–V(1)–C(1) 105.48(4), C(10)–O(1)–V(1) 148.26(8), C(40)–O(2)–V(1) 146.45(8), C(1)–N(1)–C(2) 176.43(12), C(22)–N(2)–V(1) 88.58(7), C(32)–N(2)–V(1) 148.01(8), C(32)–N(2)–C(22) 122.12(10), N(1)–C(1)–V(1) 175.73(10).

Table S1. Crystallographic Data.

	2-DMAP	**1-KCN-crypt**
Formula	$C_{59}H_{80}KN_5O_3V$, C_6H_{14}	$C_{42}H_{50}N_2O_2V$, $C_{18}H_{36}KN_2O_6$, C_4H_8O
Formula Mass (g mol^{-1})	1099.49	1153.47
Temperature (*K*)	123	123
Crystal system	*Monoclinic*	*Triclinic*
Space group	*C*2/*c* (#15)	*P*–1
Crystal color	Dark brown	Dark green
Crystal size (mm)	0.21 × 0.11 × 0.06	0.20 × 0.13 × 0.05
a (Å)	39.7195(2)	13.0496(2)
b (Å)	17.1396(1)	13.9185(2)
c (Å)	18.6902(1)	20.5273(3)
α (°)	90	94.291(1)
β (°)	93.079(1)	106.075(1)
γ (°)	90	116.436(1)
V (Å^3)	12705.48(12)	3121.80(8)
Z	8	2
ϱ_{calc} (g cm^{-3})	1.150	1.227
Radiation (Å)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
μ (cm^{-1})	2.260	2.380
Reflections collected	43475	47417
Independent reflections	12888	12949
R_{int}	0.0196	0.0293
R_1 [$I > 2\sigma(I)$] [a]	0.0363	0.0396
wR_2 (all data) [b]	0.1026	0.1081
Goodness of fit on F^2	1.066	1.041
Largest diff. peak/hole (e Å^{-3})	0.452/–0.393	0.51/-0.57

(a) $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, (b) $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$

Table S1. Crystallographic Data (cont.).

	1-KNSiMe$_3$	**4**
Formula	$C_{48}H_{69}KN_2O_4SiV$	$C_{77}H_{88}K_2N_5O_8V$, 0.5 (C_6H_{14}), 2 (C_7H_8)
Formula Mass (g mol^{-1})	856.18	1568.01
Temperature (*K*)	123	123
Crystal system	*Monoclinic*	*Triclinic*
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
Crystal color	Light green	Dark brown
Crystal size (mm)	0.18 × 0.10 × 0.05	0.09 × 0.07 × 0.03
a (Å)	14.2203(4)	16.1228(3)
b (Å)	22.6239(7)	17.1683(4)
c (Å)	15.3959(4)	17.5730(6)
α (°)	90	96.746(2)
β (°)	96.580(2)	116.027(2)
γ (°)	90	94.642(2)
V (Å^3)	4920.5(2)	4292.6(2)
Z	4	2
ϱ_{calc} (g cm^{-3})	1.156	1.213
Radiation (Å)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
μ (cm^{-1})	0.352	2.289
Reflections collected	61038	64966
Independent reflections	11356	17767
R_{int}	0.0701	0.0738
R_1 [$I > 2\sigma(I)$] [a]	0.0465	0.0776
wR_2 (all data) [b]	0.1107	0.2423
Goodness of fit on F^2	1.027	0.99
Largest diff. peak/hole (e Å^{-3})	0.28/–0.46	1.09/–0.46

(a) $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, (b) $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$

Table S1. Crystallographic Data (cont.).

	5	**6**
Formula	$C_{108}H_{138}K_2N_4O_8V_2$, 3.5 ($C_7H_8$)	$C_{76}H_{93}KN_4O_4V$,C_6H_{14}, C_4H_8O
Formula Mass (g mol^{-1})	2122.76	1374.85
Temperature (*K*)	123	123
Crystal system	*Orthorhombic*	*Triclinic*
Space group	*Pbca* (#61)	*P*–1 (#2)
Crystal color	Yellowish green	Black
Crystal size (mm)	0.20 × 0.16 × 0.14	0.32 × 0.24 × 0.18
a (Å)	28.8046(5)	13.4233(3)
b (Å)	28.1999(6)	16.9491(4)
c (Å)	29.2972(5)	19.8449(4)
α (°)	90	67.448(2)
β (°)	90	81.026(2)
γ (°)	90	69.914(2)
V (Å^3)	23797.8(8)	3914.58(17)
Z	8	2
ϱ_{calc} (g cm^{-3})	1.185	1.166
Radiation (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
μ (cm^{-1})	0.285	0.233
Reflections collected	197084	41424
Independent reflections	27447	18014
R_{int}	0.1584	0.0332
R_1 [$I > 2\sigma(I)$] [a]	0.0882	0.0591
wR_2 (all data) [b]	0.1966	0.1717
Goodness of fit on F^2	1.026	1.030
Largest diff. peak/hole (e Å^{-3})	0.517/–0.513	0.595/–0.542

(a) $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, (b) $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$

Table S1. Crystallographic Data (cont.).

	7	**(ONO)V(CNPMP)$_2$**
Formula	$C_{113}H_{137}KN_5O_6V_2$, $C_{16}H_{40}KO_8$, C_6H_{14}	$C_{57}H_{64}N_3O_4V$
Formula Mass (g mol^{-1})	2288.00	906.05
Temperature (*K*)	123	123
Crystal system	*Triclinic*	*Triclinic*
Space group	*P*–1 (#2)	*P*–1 (#2)
Crystal color	Reddish brown	Dark red
Crystal size (mm)	0.12 × 0.10 × 0.08	0.19 × 0.08 × 0.04
a (Å)	16.6092(6)	12.3804(2)
b (Å)	17.7479(6)	14.2439(3)
c (Å)	22.6639(7)	16.3950(3)
α (°)	78.203(3)	73.837(2)
β (°)	88.731(3)	70.960(2)
γ (°)	83.903(3)	68.344(2)
V (Å^3)	6502.7(4)	2498.70(9)
Z	2	2
ϱ_{calc} (g cm^{-3})	1.169	1.204
Radiation (Å)	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)
μ (cm^{-1})	0.268	2.033
Reflections collected	67077	34634
Independent reflections	29676	10344
R_{int}	0.0926	0.0291
R_1 [$I > 2\sigma(I)$] [a]	0.0797	0.0361
wR_2 (all data) [b]	0.2236	0.0992
Goodness of fit on F^2	0.976	1.083
Largest diff. peak/hole (e Å^{-3})	0.519/–0.658	0.38/–0.41

(a) $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, (b) $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$

Table S1. Crystallographic Data.

	1-XylNC
Formula	$C_{50}H_{59}N_2O_2V$
Formula Mass (g mol^{-1})	770.93
Temperature (*K*)	123
Crystal system	*Triclinic*
Space group	*P*–1 (#2)
Crystal color	Dark green
Crystal size (mm)	0.119 × 0.042 × 0.012
a (Å)	11.5027(1)
b (Å)	13.6419(1)
c (Å)	14.8864(2)
α (°)	78.8902(8)
β (°)	80.2544(9)
γ (°)	70.2618(8)
V (Å^3)	2143.72(4)
Z	2
ϱ_{calc} (g cm^{-3})	1.194
Radiation (Å)	Cu Kα (λ = 1.54184)
μ (cm^{-1})	2.238
Reflections collected	30565
Independent reflections	8890
R_{int}	0.0248
R_1 [$I > 2\sigma(I)$] [a]	0.0317
wR_2 (all data) [b]	0.0862
Goodness of fit on F^2	1.092
Largest diff. peak/hole (e Å^{-3})	0.28/–0.33

(a) $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, (b) $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{0.5}$

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