

Supplementary Information

for

Synthesis and Reactions of β -Diketiminato Divanadium(I) Inverted-Sandwich Complexes

Yi-Chou Tsai^{*a}, Po-Yang Wang^a, Kuan-Ming Lin^a, Shin-An Chen^b,
Jin-Ming Chen^b

^a*Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan*

^b*National Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan, R.O.C.*

E-mail: yictsai@mx.nthu.edu.tw

Experimental

General Information. Unless stated otherwise, all operations were performed using standard Schlenk techniques or in a Vacuum Atmospheres dry box under an atmosphere of nitrogen. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled under nitrogen from purple sodium benzophenone ketyl. *n*-Hexane was distilled under nitrogen from CaH₂. Distilled solvents were transferred under vacuum into vacuum-tight glass vessels before being transferred into a dry box. C₆D₆ was purchased from Aldrich and was degassed and dried over 4 Å sieves. The 4 Å sieves and Celite were dried in vacuo overnight at a temperature just above 200 °C. VCl₂(Nacnac),¹ where Nacnac refers to the β-diketiminato ligand HC[CM₂NC₆H₃(*i*-Pr₂)]₂ was prepared following literature method.² All other compounds were used as received. ¹H and ¹³C NMR spectra were recorded on Varian Unity INOVA 500 MHz or Bruker DMX 600 MHz spectrometers at room temperature. ¹³C NMR spectra are proton decoupled. Chemical shifts for ¹H and ¹³C spectra are reported with respect to internal solvent: 7.16 ppm and 128.00(t) ppm (C₆D₆) and external solvent: 7.16 ppm (C₆D₆) for ²H spectra. The magnetization data were recorded on a SQUID magnetometer (MPMS7 Quantum Design company) with an external magnetic field of 1.0 T in the temperature range of 4 to 300 K.

Synthesis of (μ-η⁶:η⁶-C₇H₈)[V(Nacnac)]₂, **1.** A sample of 1.415 g (10.467 mmol) of KC₈ was slowly added to a deep brown-red solution of VCl₂(Nacnac) (2.259 g, 4.197 mmol) in 50 mL of toluene at -35 °C. The resultant solution quickly turned dark blue green, and was then allowed to warm to room temperature and stirred for another 15 h. After filtration through Celite, the dark blue green solution was stripped to dryness under vacuum to leave a dark solid, which was subsequently extracted into *n*-hexane and filtered through Celite. A dark solid was obtained after removing all volatile materials. Recrystallization from toluene at -35 °C furnished dark crystals of (μ-η⁶:η⁶-C₇H₈)[V(Nacnac)]₂ **1**, (1.427 g, 66.0% yield in one crop). Anal. Calcd for C₆₅H₉₀N₄V₂ (**1**): C, 75.85; H, 8.81; N, 5.44; Found: C, 75.79; H, 9.17; N, 5.00.

Synthesis of $(\mu\text{-O})[\text{V}(\text{O})(\text{Nacnac})]_2$, **2.** A sample of 0.502 g (0.488 mmol) of **1** was dissolved in 30 mL of ether in a 100 mL of Schlenk flask. To this stirred solution was introduced excess of gaseous N_2O at ambient temperature. The color of the solution quickly turned into orange accompanied with slight heat evolution. It was then stirred for further 2 h. All volatiles were removed to dryness under vacuum to leave an orange solid, which was extracted using *n*-hexane and filtered through Celite. The *n*-hexane solution was stripped down to dryness and the residue was re-dissolved in 10 mL of ether. Slow vaporization (2 days) of solvent at room temperature resulted in the formation dark orange X-ray quality crystals. The isolated yield of **2** was 34.6% (0.181 g) in one crop. Anal. Calcd for $\text{C}_{58}\text{H}_{82}\text{N}_4\text{O}_3\text{V}_2$ (**2**): C, 70.71; H, 8.39; N, 5.69; Found: C, 70.50; H, 8.06; N, 5.23. $\mu_{\text{eff}} = 2.71 \mu_{\text{B}}$ (Evans' method at 298 K, C_6D_6)

Synthesis of $\text{V}(\text{NPh})_2(\text{Nacnac})$, **3.** A sample of 0.735 g (0.714 mmol) of **1** was dissolved in 10 mL of ether in a 100 mL of Schlenk flask. To this stirred blue green solution was slowly added a 4 mL of orange solution of azobenzene (0.261g, 1.433 mmol) in ether at -35°C . The color of the solution quickly turned into green when the solution was warmed to room temperature and then yellow. The solution was then stirred for further 15 h. All volatiles were removed to dryness under vacuum to leave an orange solid, which was extracted using *n*-hexane and filtered through Celite. The *n*-hexane solution was stripped down to dryness and the residue was re-dissolved in 4 mL of ether. Orange brown crystals of **3** (0.635 g, 68.0% yield) were collected by layering *n*-hexane over the ethereal solution and storing in a -35°C refrigerator. ^1H NMR (C_6D_6 , 500 MHz): δ 7.14 (*t*, 2H), 7.09 (*d*, 4H), 6.94 (*t*, 4H), 6.88 (*d*, 4H), 6.64 (*t*, 2H), 5.54 (*s*, 1H), 3.52 (*sept*, 4H), 1.75 (*s*, 6H), 1.21 (*d*, 12 H), 1.15 (*d*, 12H). ^{13}C NMR (C_6D_6 , 125 MHz): δ 168.69, 163.88, 144.20, 142.45, 128.19, 127.18, 124.13, 122.91, 122.83, 101.08, 28.41, 25.27, 24.30, 23.98. ^{51}V NMR (C_6D_6 , 132 MHz): δ -192.82 . Anal. Calcd for $\text{C}_{41}\text{H}_{51}\text{N}_4\text{V}$ (**3**): C, 75.67; H, 7.90; N, 8.61; Found: C, 75.21; H, 7.64; N, 8.43.

Crystallographic Structure Determinations. The X-ray crystallographic data collections for **1**, **2**, and **3** were carried out on a Bruker-Nonius Kappa CCD four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) outfitted with a low-temperature, nitrogen-stream aperture. The structures were solved using direct methods, in conjunction with standard difference Fourier techniques and refined by full-matrix least-squares procedures. An empirical absorption correction (multi-scan) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. Unless otherwise specified, all hydrogen atoms were generated using HFIX 33 and their orientation may not be totally reliable.

The SQUEEZE option in PLATON was used to correct for heavily disordered solvent molecules in **1**, **2** and **3**.^{3,4} One half of *n*-hexane molecule for **1**, one half of ether molecule for **2** and one half of azobenzene molecule for **3** have been squeezed. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SIR92 or SHELXTL 97⁵ program suites, respectively. Crystal structures of complexes **1**, **2**, and **3** were deposited at The Cambridge Crystallographic Data Centre and the deposited numbers are CCDC-645658, CCDC-645659, and CCDC-645660, respectively.

X-ray Absorption Spectroscopy Experiments. Sample preparations were performed in a dry, nitrogen-filled, anaerobic-atmosphere glovebox. The sample were ground into a fine powder and dispersed as thinly as possible on Mylar tape. This procedure has been verified to minimize self-absorption effects. The samples were then mounted across the window of an aluminum plate. A 6.35 μm polypropylene film window protected the solid samples from exposure to air during transfer from the glovebox to the experimental sample chamber. XAS data were measured at the National Synchrotron Radiation Research Center (NSRRC) using the 17C Wiggler beamline with a double-crystal Si (111) monochromator at 1.5 GeV/300 mA ring conditions. During the measurements, the experimental sample chamber was filled with He atmosphere. The XAS measurements were collected in transmission mode (for reference compounds) or X-ray fluorescence yield mode (for air- and moisture-sensitive compound **1**) utilizing gas-ionization chambers as detectors and/or fluorescence detector.^{6,7} The gas-ionization chambers used

to measure the incident (I_0) and transmitted (I_t) photon intensities were filled with a mixture of N_2 and He gases and a mixture of N_2 and Ar gases, respectively.

The photon energy was calibrated by V K-edge XAS spectrum of V foil, run at intervals between the samples for fluorescence yield mode, or monitored simultaneously for transmission mode. The absorption edge energy of 5465 eV in the V K-edge XAS spectrum of vanadium foil corresponding to first inflection point of absorption feature is used for energy calibration. The consistency of this energy calibration between different experimental sessions on different beamlines was checked internally as well as against recorded XAS spectra of vanadium foil. The XAS spectrum of compound **1** was measured twice at least to ensure the reproducibility of the spectra. In the edge region, the step size was set to 0.25 eV and the monochromator resolution was ~ 0.7 eV at V K-edge region. The absorption edge energy is known to increase with increasing valency of the transition metal with the compounds. In comparison with the edge energy of the reference samples, the valency of compound **1** can be deduced as 1+.

References

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Table S1. Crystallographic Data for **1**, **2** and **3**.

Compound	1	2	3
Empirical formula	C ₆₅ H ₉₀ N ₄ V ₂ ·0.5C ₆ H ₁₄	C ₁₂₈ H ₁₉₂ N ₈ O ₆ V ₄ ·C ₄ H ₁₀ O	C ₄₁ H ₅₁ N ₄ V·0.5C ₁₂ H ₁₀ N ₂
fw	1072.38	2216.78	741.91
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
a (Å)	17.6990(5)	13.7676(2)	12.7056(4)
b (Å)	15.3858(5)	21.2023(4)	17.7171(6)
c (Å)	24.9682(7)	23.5956(5)	18.9744(9)
α (deg)			
β (deg)	107.898(2)	106.4620(10)	98.778(2)
γ (deg)			
vol (Å ³)	6470.1(3)	6605.3(2)	4221.2(3)
Z	4	2	4
d (calc. g/cm ³)	1.101	1.115	1.167
μ (mm ⁻¹)	0.329	0.328	0.272
temperature (K)	200	200	200
final R indices	R1 = 0.0974	R1 = 0.0721	R1 = 0.0848
[I > 2σ(I)] ^{a,b}	wR2 = 0.2198	wR2 = 0.1911	wR2 = 0.1952
R indices	R1 = 0.1746	R1 = 0.0940	R1 = 0.1687
(all data)	wR2 = 0.2533	wR2 = 0.2076	wR2 = 0.2292

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}}{w}, \quad w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \quad \text{where } P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)] / 3$$

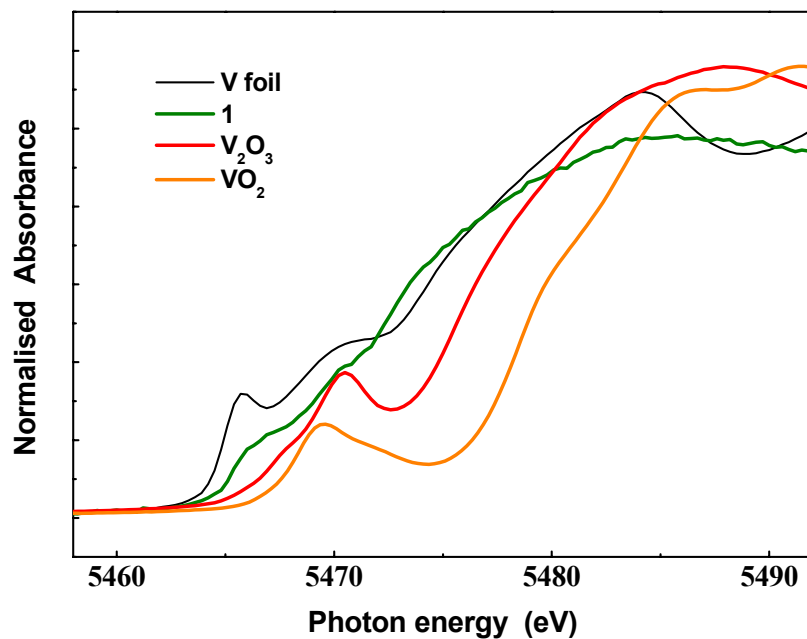


Figure S1. X-ray absorption near edge spectroscopy (XANES) of V: K-edge spectra of V foil, **1**, V₂O₃, and VO₂. The curve for **1** is less smooth than the other three curves for reference compounds, this is due to low signal/noise ratio resulted by small amount of **1** being measured.

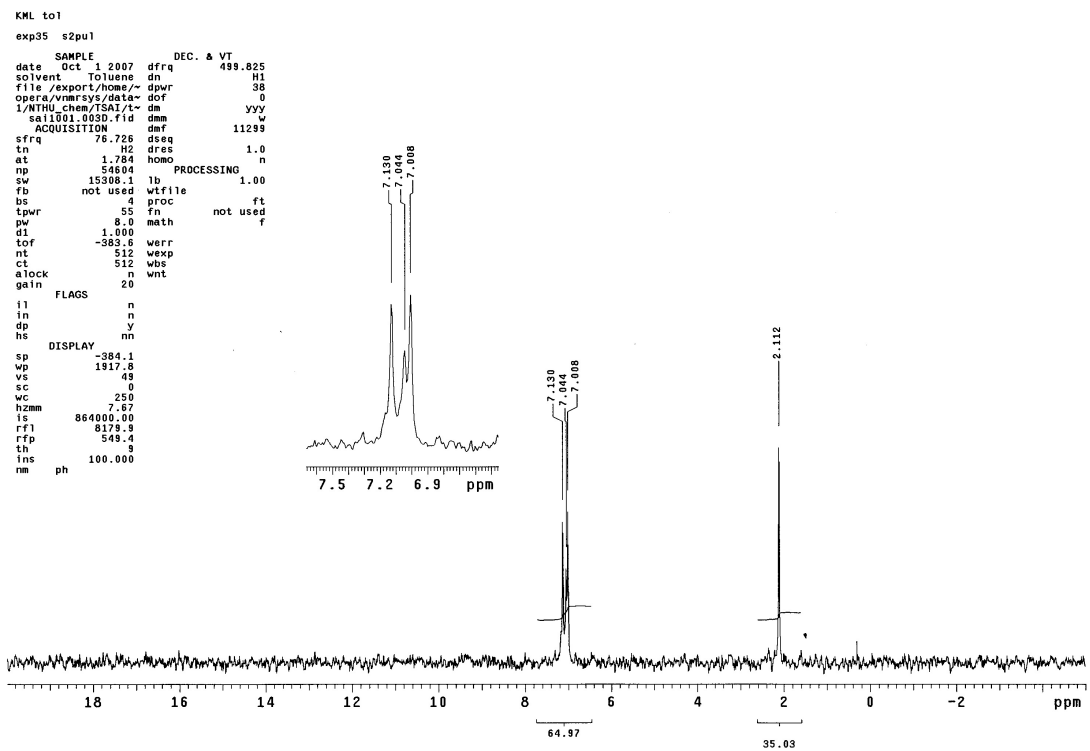


Figure S2. The ^2H NMR spectrum of toluene, in which the chemical shifts are referenced to external C_6D_6 .

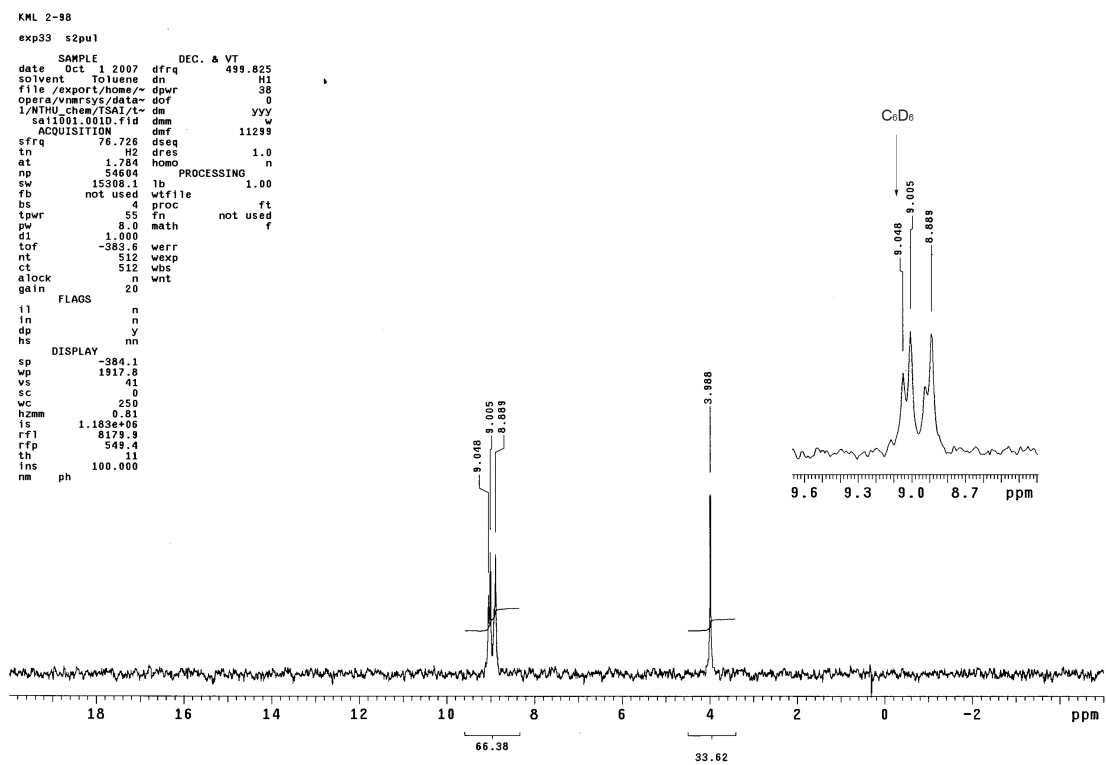


Figure S3. The ^2H NMR spectrum of complex $(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{D}_6)[\text{V}(\text{Nacnac})]_2$ in toluene. The chemical shifts are referenced to external C_6D_6 .

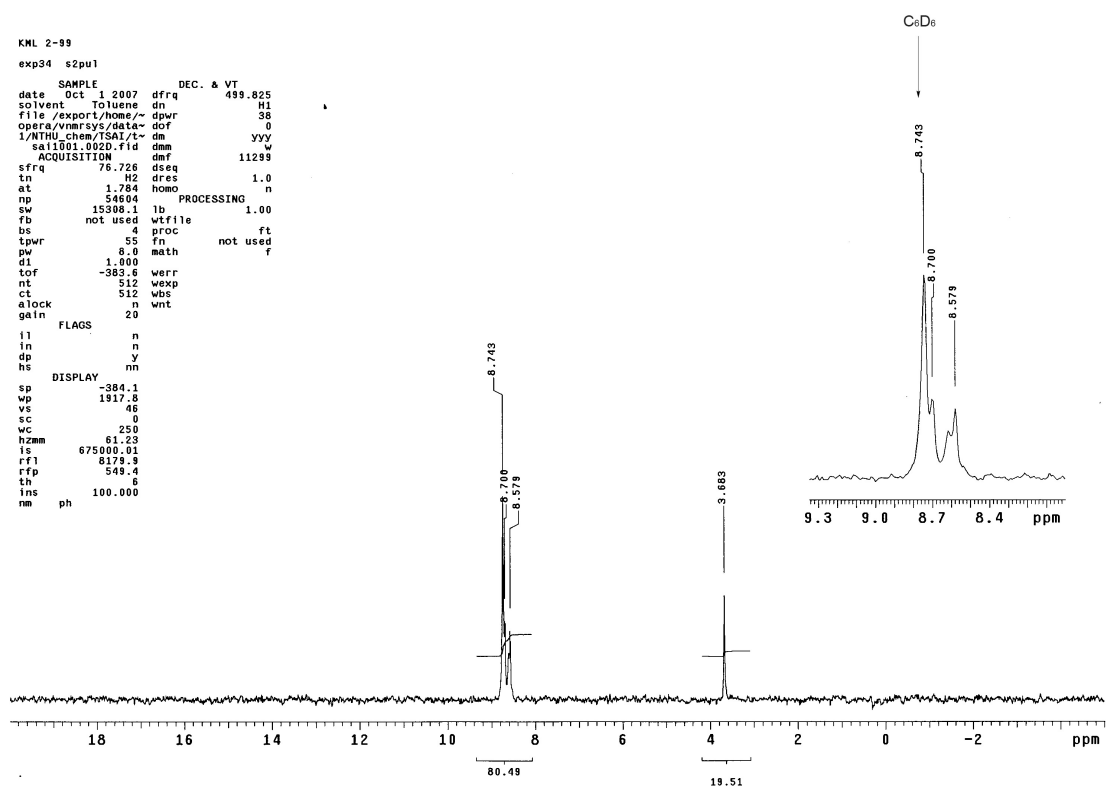


Figure S4. The ²H NMR spectrum of complex (μ-η⁶:η⁶-C₆D₆)[V(Nacnac)]₂ with extra 2 equiv. of C₆D₆ in toluene solution. The chemical shifts are referenced to external C₆D₆.