Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

The Dual Roles of a V(III) Centre for Substrate Binding and Oxygen Atom Abstraction; Nitrite Reduction Mediated by a V(III) Complex

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General materials and physical method:

All procedures were carried out under argon or dinitrogen with standard Schlenk techniques or glove box. $H_3[PS3'']$ ($[P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3]^{3-}$) , and $VCl_3(THF)_3$ were synthesized according to the literature procedures.[1] Solvents were dried by distillation from drying reagents. Other reagents were commercially available.

The crystal was mounted on a glass fiber and quickly coated in epoxy resin. Di□raction measurements were performed with a Nonius Kappa di□ractometer equipped with a CCD detector. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all nonhydrogen atoms and fixed hydrogen atoms was based on F^2. ASADABS absorption correction was made.[2] The SHELXTL structural refinement program was employed.[3] All non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were calculated using the riding model. CCDC 2017300 contains the supplementary crystallographic data of ($[PPh_4]$[**2**], for this paper. UV-vis-NIR spectra were measured with Hewlett Packard 8453 spectrophotometer. The spectra were recorded in the range of 190-1100 nm. All air-sensitive samples were prepared in glovebox and a specially designed UV cell was used to avoid air exposure. The LTQ Orbitrap XL, Thermo-Fisher spectrometer, was used to measure the ESI-MS spectroscopy at Instrument Development Center of National Cheng Kung University. ^1H, ^{31}P and ^{51}V NMR samples were characterized by BRUKER AMX500 spectrometer. The spectra were referenced to residual proton-solvent peak, PPh_3 and $VOCl_3$ for ^1H, ^{31}P and ^{51}V NMR, respectively. Perkin-Elmer Spectrum RX I spectrophotometer was as the tool to record fourier transform infrared spectroscopy. The sample was prepared in the glove box. The compound was grinded with KBr and the mixture powder was pressed to pellet by the pellet press brochure. Elemental analysis data were measured with Elemetar vario EL III by Miss Chia-Chen Tsai at Instrument Center of National Cheng Kung University.

Synthesis of $[PPh_4][V(PS3'')(NO]$ ($[PPh_4]$[2]) :

Method A. Adding NBu_4NO_2 (0.027 mg, 0.095 mmol) into $[PPh_4][V(PS3'')(Cl)]$ ($[PPh_4]$[**1**]) (0.100 mg, 0.095 mmol) in CH_3CN generated a green solution. After placing the solution at -30 ^oC for 3-5 days, a green crystalline solid of $[PPh_4][V(PS3'')(NO)]$ ($[PPh_4]$[**2**]) was precipitated. (yield: 35.3 %).

Method B. A mixture of $H_3[PS3'']$ (0.2000 g, 0.348 mmol) and Li (0.0074 g, 1.043) was dissolved in methanol. The addition of $VCl_3(THF)_3$ (0.1302 g, 0.3485 mmol) and NBu_4NO_2 (0.2010 g, 0.6968 mmol) to the reaction mixture generated a green solution. A methanol solution of PPh_4Br (0.1460 g, 0.3484 mmol) was added into the reaction and a dark green crystalline solid of [PPh$_4$][V(PS3”)(NO] ([PPh$_4$][**2**]) was obtained at -15 °C after 3~5 days.(yield: 38%).

UV-vis-NIR in THF (λ, nm; ε, $M^{-1}cm^{-1}$): 453 nm (6.27 × 10^3), 655 nm (7. 12 × 10^2). IR (KBr,ν_{NO}, cm^{-1}): 1565; IR (KBr,$\nu_{^{15}NO}$, cm^{-1}):1532. ^{1}H NMR in d_2-DCM (ppm): δ 7.98 (t, 3H), δ 7.89 (m, 4H), δ 7.74 (m, 8H), δ 7.62 (m, 8H), δ 7.44 (d, 3H), δ 6.96 (t, 3H), δ 0.33 (s, 27H). ^{31}P NMR in d_2-DCM (ppm): δ 79.3, δ 21.7. ^{51}V NMR in d_2-DCM (ppm): δ 579.3. Anal. Calcd for $C_{51}H_{56}VNOP_2S_3Si_3$: C, 61.73; H, 5.69; N, 1.41; S, 9.69. Found: C, 60.85; H, 5.72; N, 1.45; S, 9.78.

References

1. (a) L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 138; (b) E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 2327-2329.
2. G. M. Sheldrick, University of Go(?)ttingen, Germany, 1996, 1996.
3. G. M. Sheldrick, Siemens Analytical X-ray Instruments Inc.: MAdison, WI, 1994, 1994.

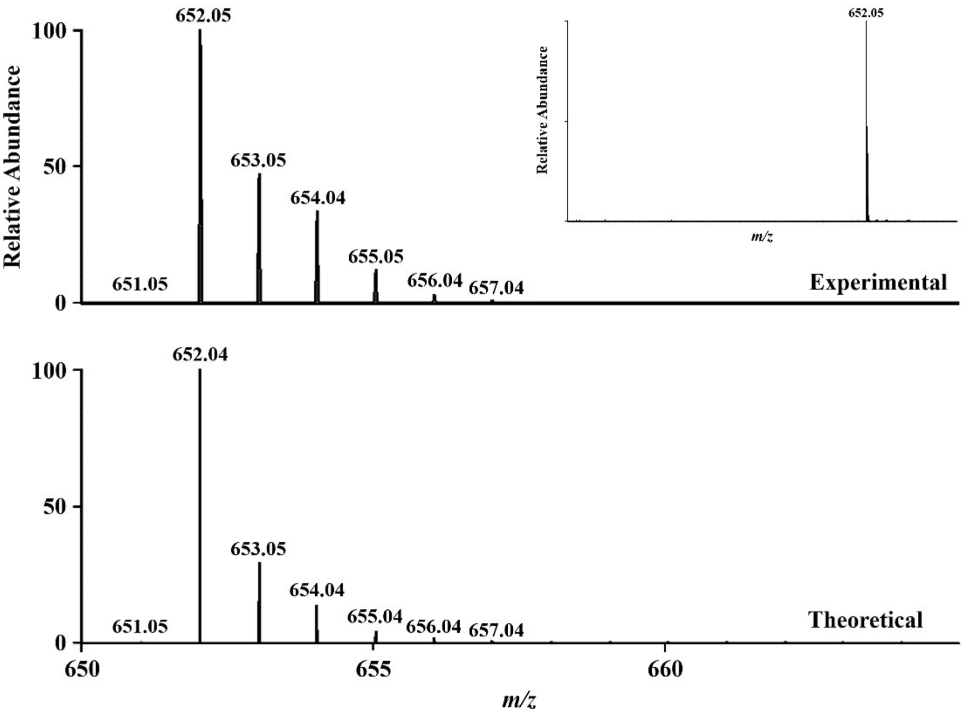

Figure S1. The negative mode ESI-MS spectrum of [V(PS3”)(NO)]$^-$ (**2**). The molecular ion peaks display isotopic distribution at 652.05 *m/z* (top), consistent with the calculated pattern of $C_{27}H_{36}NOPS_3Si_3V$ formulation (bottom).

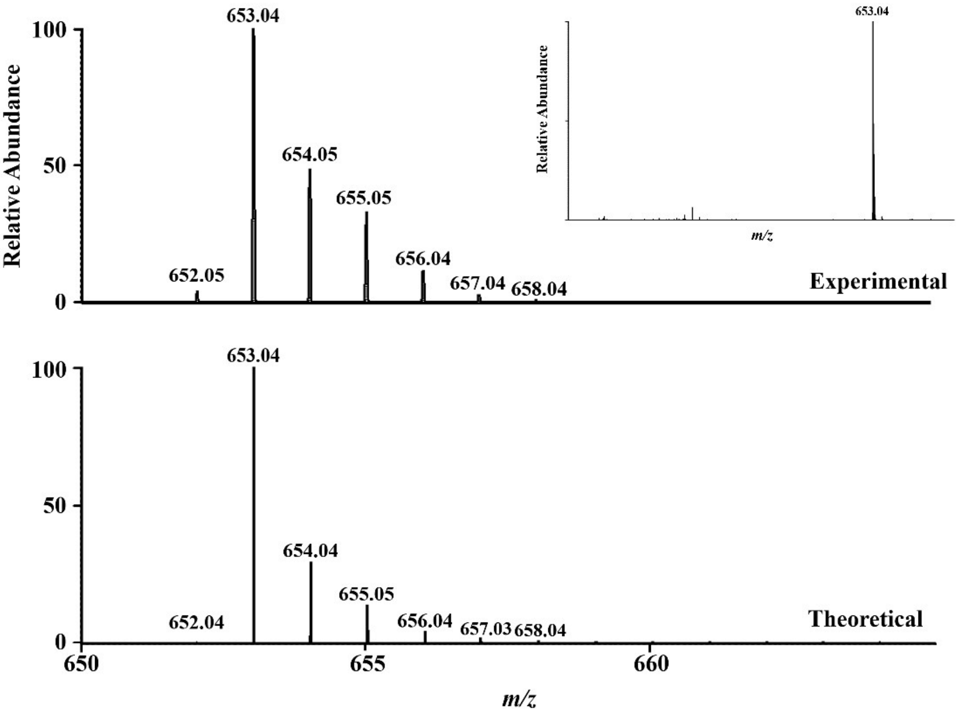

Figure S2. The negative mode ESI-MS spectrum of [V(PS3”)(^{15}NO)]$^{-}$(^{15}N-**2**). The molecular ion peaks display isotopic distribution at 653.04 *m/z* (top), consistent with the calculated pattern of $C_{27}H_{36}{}^{15}NOPS_3Si_3V$ formulation (bottom).

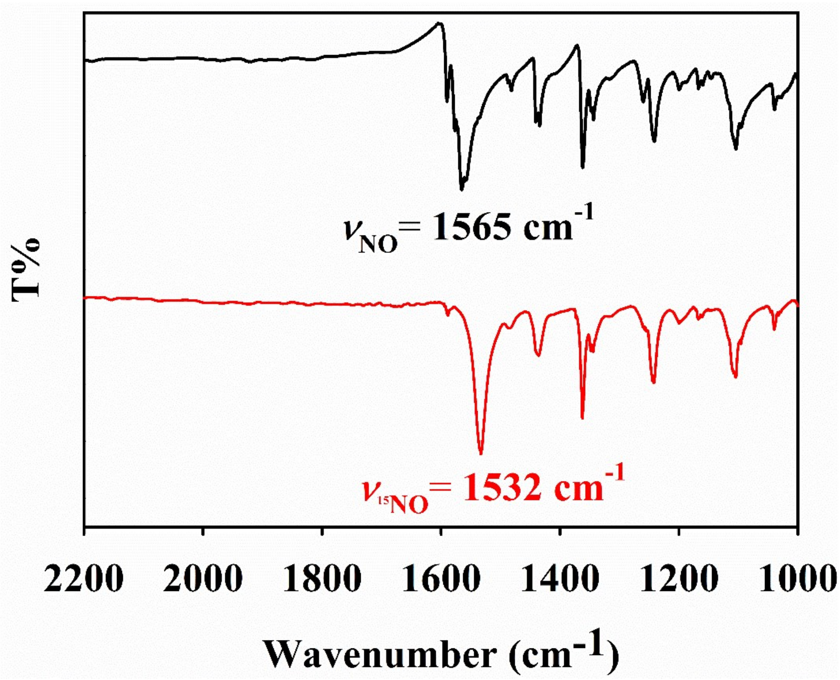

Figure S3. The infrared spectra of PPh$_4$][V(PS3”)(NO)] ([PPh$_4$][**2**]) (top) and [PPh$_4$][V(PS3”)(^{15}NO)] (bottom) in KBr.

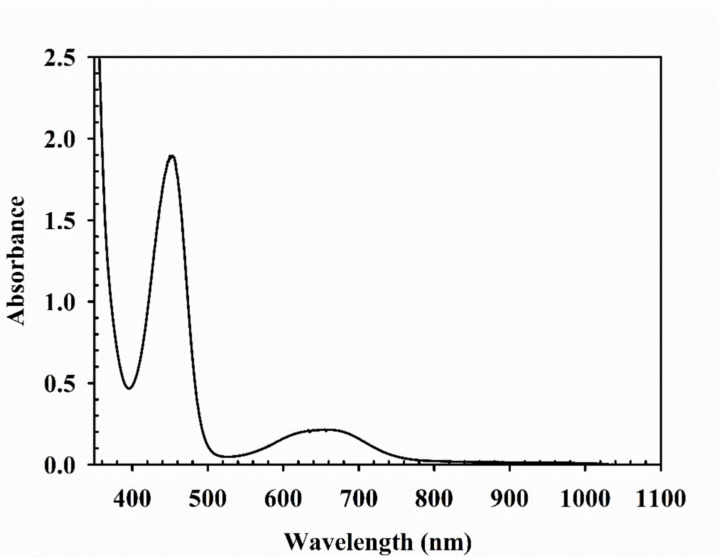

Figure S4. The UV-vis-NIR spectrum of [PPh$_4$][V(PS3”)(NO)] ([PPh$_4$][**2**]) in THF solution.

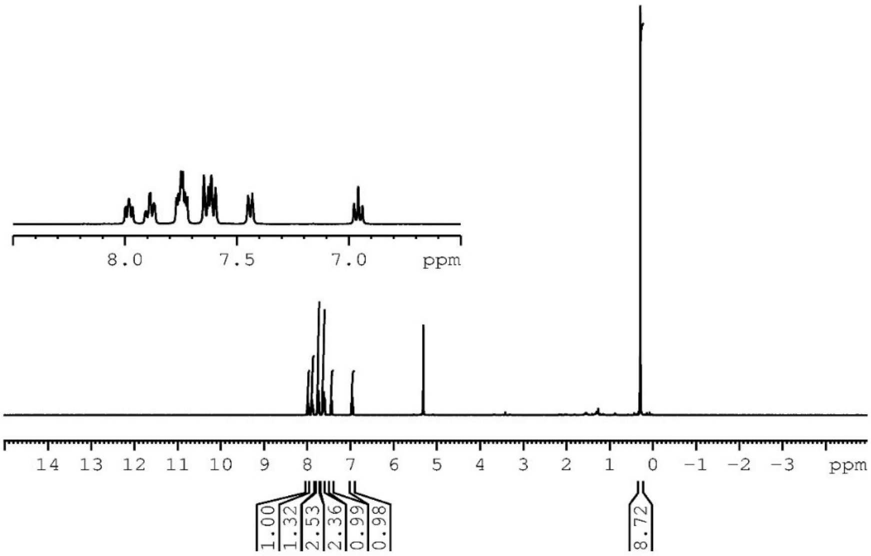

Figure S5. 400MHz ^{1}H NMR spectrum of[PPh$_4$][V(PS3”)(NO)] ([PPh$_4$][**2**]) in CD$_2$Cl$_2$.

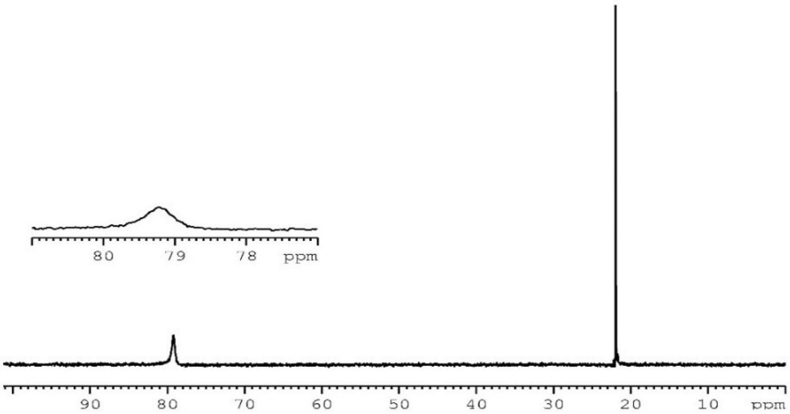

Figure S6. ^{31}P NMR spectrum of [PPh$_4$][V(PS3”)(NO)] ([PPh$_4$][**2**]) in CD$_2$Cl$_2$. Complex **2** displays a peak at δ = 79.3 ppm attributed to the PS3” ligand and a peak at δ =21.7 ppm associated with the PPh$_4^+$ cation.

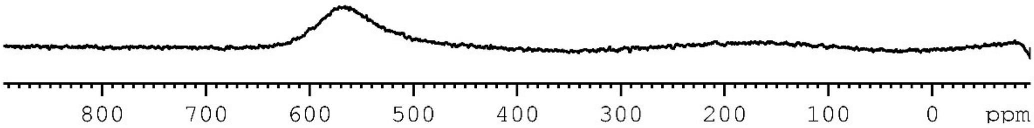

Figure S7. ^{51}V NMR spectrum of [PPh$_4$][V(PS3”)(NO)] ([PPh$_4$][**2**]) in CD$_2$Cl$_2$.