Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information for the manuscript:

A Four-Coordinate Thionitrosyl Complex of Vanadium.

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Supporting Information

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Experimental Section

General Considerations. Unless otherwise state, all operations were performed in an M. Braun Lab Master Double-dry box under an atmosphere of purified nitrogen. Anhydrous hexanes, n-pentane, toluene, benzene and diethyl ether were purchased from Aldrich in sure-sealed kegs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. THF was distilled under argon from purple sodium benzophenone ketyl and stored over sodium metal and 4 Å molecular sieves. Distilled THF was transferred under vacuum into thick-walled reaction vessels and then brought into the dry box. Deuterated benzene (C_6D_6) and toluene (C_7D_8) were purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. Celite, alumina and 4 Å molecular sieves were activated under vacuum for 72 h at 200 ^{o}C. ^{15}N enriched sodium azide was purchased from CIL and used without further purification. ^{1}H, ^{13}C{^{1}H}, ^{15}N, ^{31}P{^{1}H} and ^{51}V NMR spectra were recorded on Varian 400 and 500 MHz NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported with reference to solvent resonances of C_6D_6 at 7.16 ppm and 128.0 ppm, respectively and assignment was conducted by performing ^{13}C{^{1}H} NMR spectra with reference to solvent resonances of C_6D_6 at 128.0 ppm. ^{51}V NMR chemical shifts are reported with respect to a neat external standard of $VOCl_3$ (0.0 ppm). ^{15}N NMR chemical shifts are reported with respect to a neat external standard of $MeNO_2$ (380.2 ppm). X-ray diffraction data were collected on a APEX II Kappa Duo (Bruker) system under a stream of N_2 (g) at a range 150 to 200K. Elemental analysis was performed at Indiana University, Bloomington. Infrared spectroscopy was performed on a Thermo Nicolet 6700 FT-IR equipped with software under PC control. NaN_3 was purified by stirring in anhydrous THF overnight and the resulting white solids were collected by filtration (washed with several portions of THF, then Et_2O) and the solids dried under vacuum for 24 h. (Nacnac)V(N)ODiiP was synthesized according to a previously published protocol[1].

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Purification of S_8

A 20 mL scintillation vial was charged with 3 grams of crude S_8 and 10 mL of toluene. The resulting heterogenous mixture was stirred under gentle heating until a homogenous solution was obtained. This solution was then filtered through a medium porosity frit containing Celite, storage overnight at -37^{o}C yielded canary yellow crystals of pure S_8.

Synthesis of (nacnac)V(NS)ODiiP (1)

A 20 mL scintillation vial was charged with (nacnac)V(N)(ODiiP) [150 mg, 0.21 mmol], a magnetic stir bar and 10 mL Et_2O. To this solution was added recrystallized S_8 (81 mg, 0.31 mmol) and after approximately an hour of stirring, the yellow-brown solution converted to dark-green. The solvent was removed under reduced pressure and the resulting dark-green solid was extracted into 10 mL pentane and filtered through a medium porosity frit containing Celite to remove unreacted S_8; storage of the filtrate at -37^{o}C overnight produced dark-green, crystalline product. The product was collected via vacuum filtration with a medium porosity frit and dried under reduced pressure. Extended reaction times in Et_2O or THF resulted in reduced yield and unidentified product decomposition. 53% Yield. ^{1}H NMR (25 ^{o}C, 400 MHz, C_6D_6): δ 7.34 (t, J_{H-H} = 8 Hz, 1H, Ar-H), 7.26-7.22 (m, 3H, Ar-H), 7.11-6.97 (m, 6H, Ar-H), 5.75 (m, 1 C*H*$(CH_3)_2$)), 4.96 (s, 1H, γ-H), 4.03 (m 2H, C*H*$(CH_3)_2$), 2.29 (m, 1H, C*H*$(CH_3)_2$), 2.22 (m, 2H, C*H*$(CH_3)_2$), 1.66 (d, J_{H-H} = 8 Hz, CH(C*H*$_3)_2$), 1.59 (s, 6H, CH(C*H*$_3)_2$), 1.01 (d, J_{H-H} = 7 Hz, 6H, CH(C*H*$_3)_2$), 0.97 (d, J_{H-H} = 7 Hz, 6H, CH(C*H*$_3)_2$), 0.93 (d, J_{H-H} = 7 Hz, 6 H, CH(C*H*$_3)_2$). ^{13}C (25 ^{o}C, 101 MHz, C_6D_6): δ 167.83 (ArN(CH$_3$)*C*CH*C*(CH$_3$)NAr), 162.02

(ipso), 143.77 (Ar), 143.11 (Ar), 142.29 (Ar), 138.87 (Ar), 136.17 (Ar), 125.12 (Ar), 124.88 (Ar), 124.56 (Ar), 122.51 (Ar), 122.42 (Ar), 99.15 (ArN(CH_3)C*C*HC(CH_3)NAr), 29.74 (*C*H(CH_3)$_2$), 28.61 (*C*H(CH_3)$_2$), 27.38 (*C*H(CH_3)$_2$), 27.14 (*C*H(CH_3)$_2$), 26.29 (CH(*C*H_3)$_2$), 25.65 (CH(*C*H_3)$_2$), 24.69 (ArN(*C*H_3)CCHC(*C*H_3)NAr), 24.07 (CH(*C*H_3)$_2$), 23.88 (CH(*C*H_3)$_2$). ^{15}N (25 ^{o}C, 50.6 MHz, C_6D_6) δ 410.47 ($\Delta\nu_{1/2}$ = 200.0 Hz).^{51}V NMR (25 ^{o}C, 131.5 MHz, C_6D_6): δ 1567 ($\Delta\nu_{1/2}$ = 1416 Hz). FT-IR (KBr, Nujul, cm^{-1}) 1070 (VNS), 1042 (VN^{15}S). Anal. Calcd for $C_{41}H_{58}N_3OSV$: C, 71.17; H, 8.45; N, 6.07. Found: C, 71.37; H 8.76; N, 5.94. The synthesis of the ^{15}N isotopomer, [(nacnac)V(^{15}NS)(ODiiP) was prepared following the same procedure using ^{15}N enriched nitride.

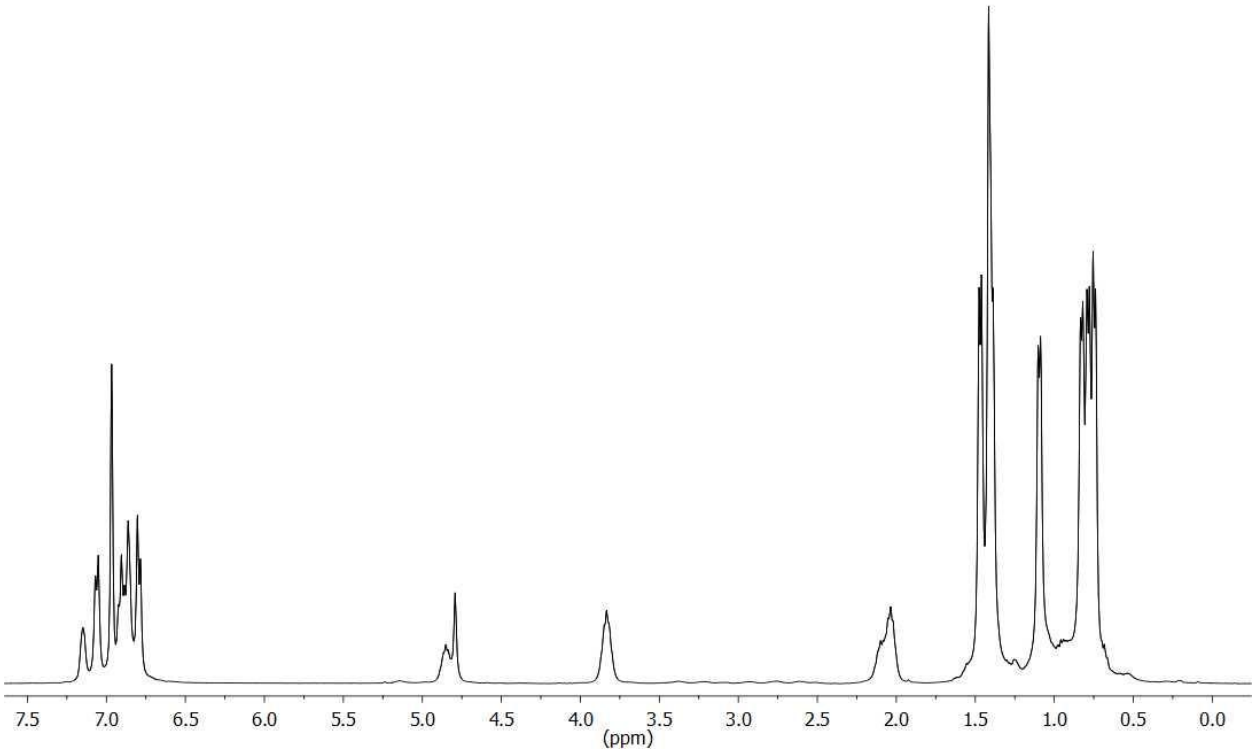

Figure S1. ^{1}H NMR Spectrum of **1** at 25^{o}C in C_6D_6.

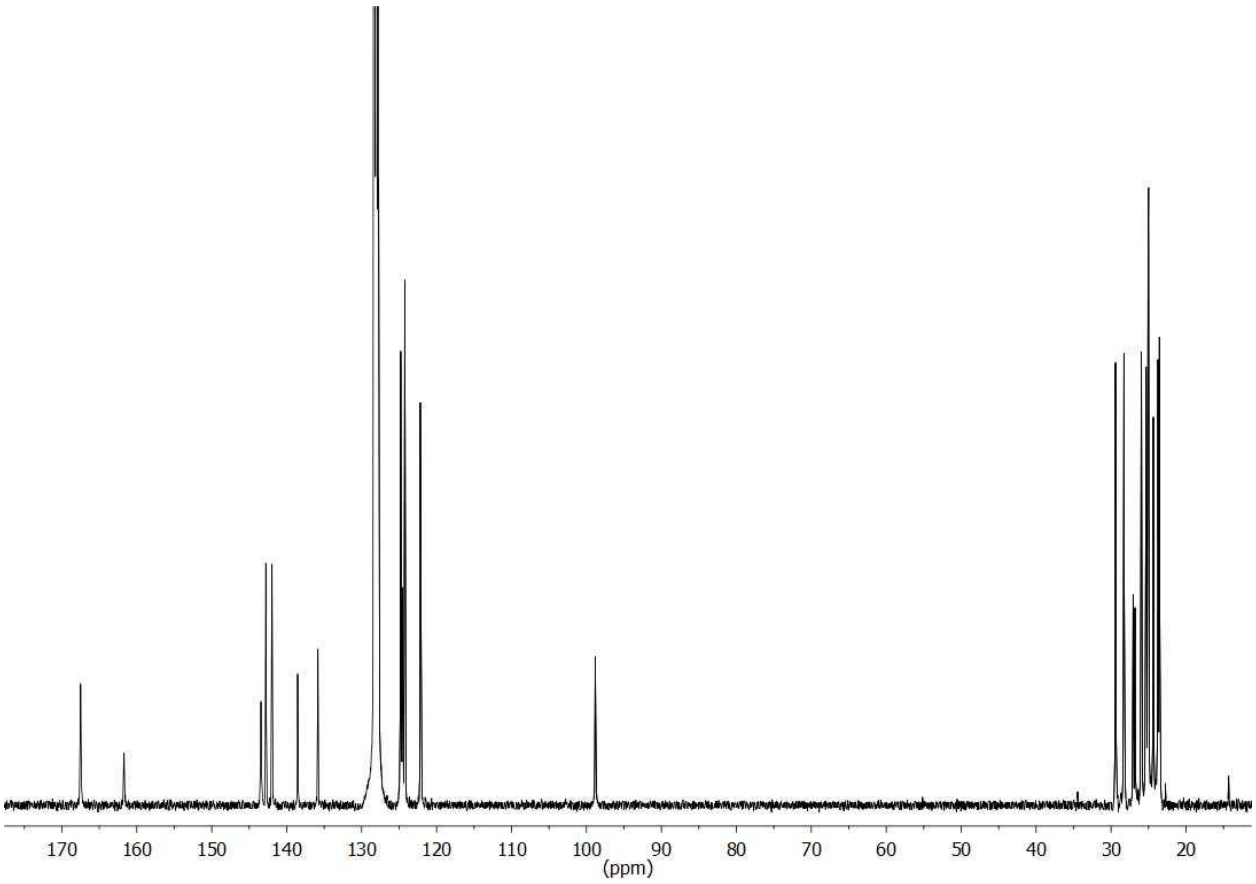

Figure S2. $^{13}C\{^{1}H\}$ NMR Spectrum of **1** 25°C in C_6D_6.

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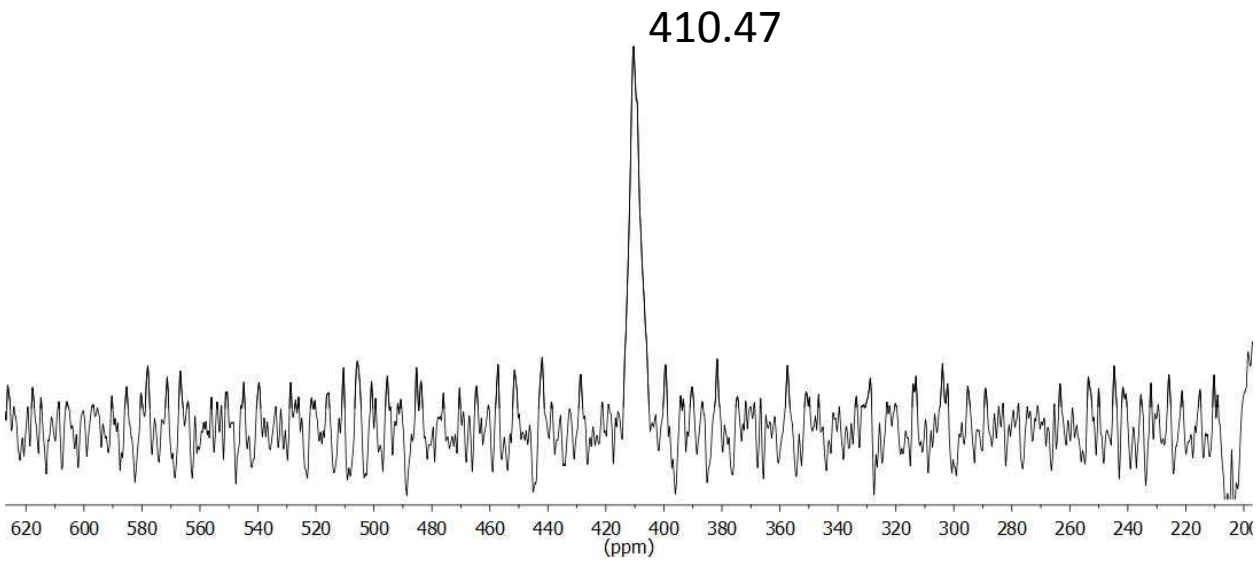

Figure S3. ^{15}N NMR Spectrum of **1** at 25^{o}C.

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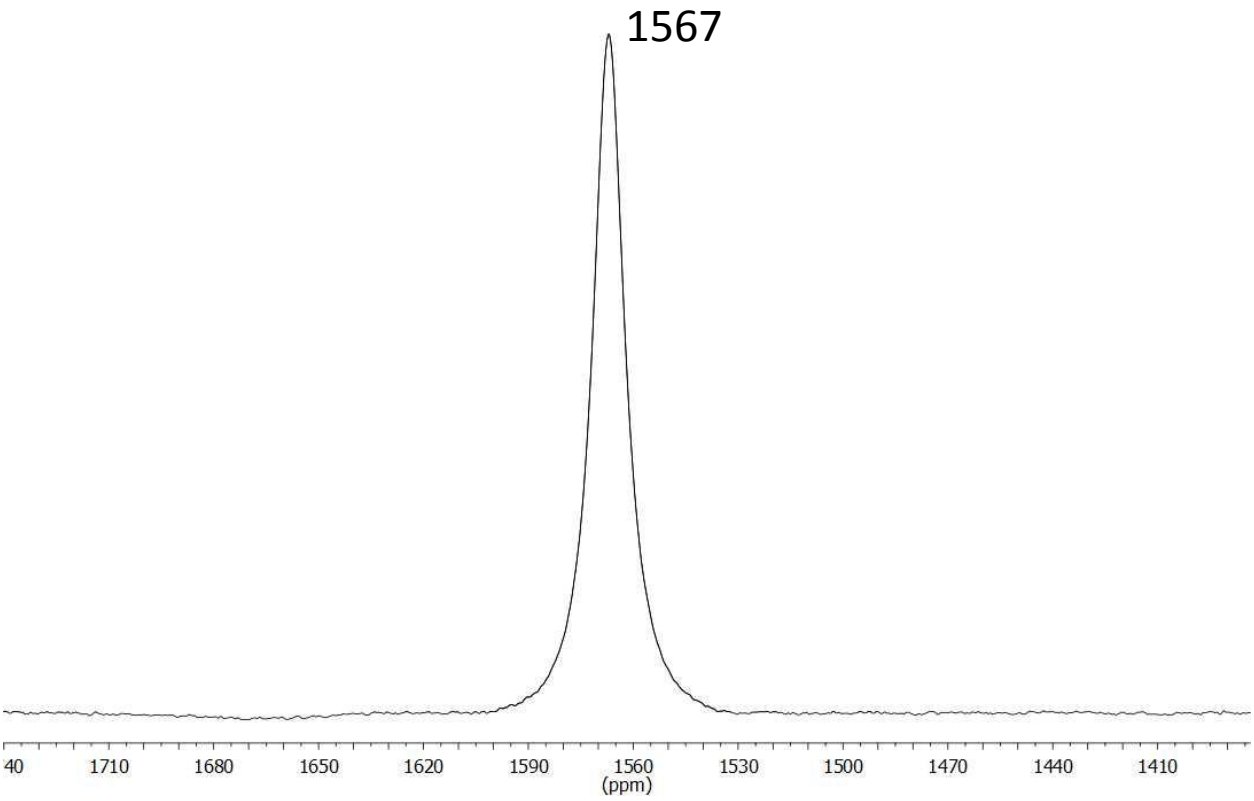

Figure S4. ^{51}V NMR Spectrum of **1** at 25^{o}C**.**

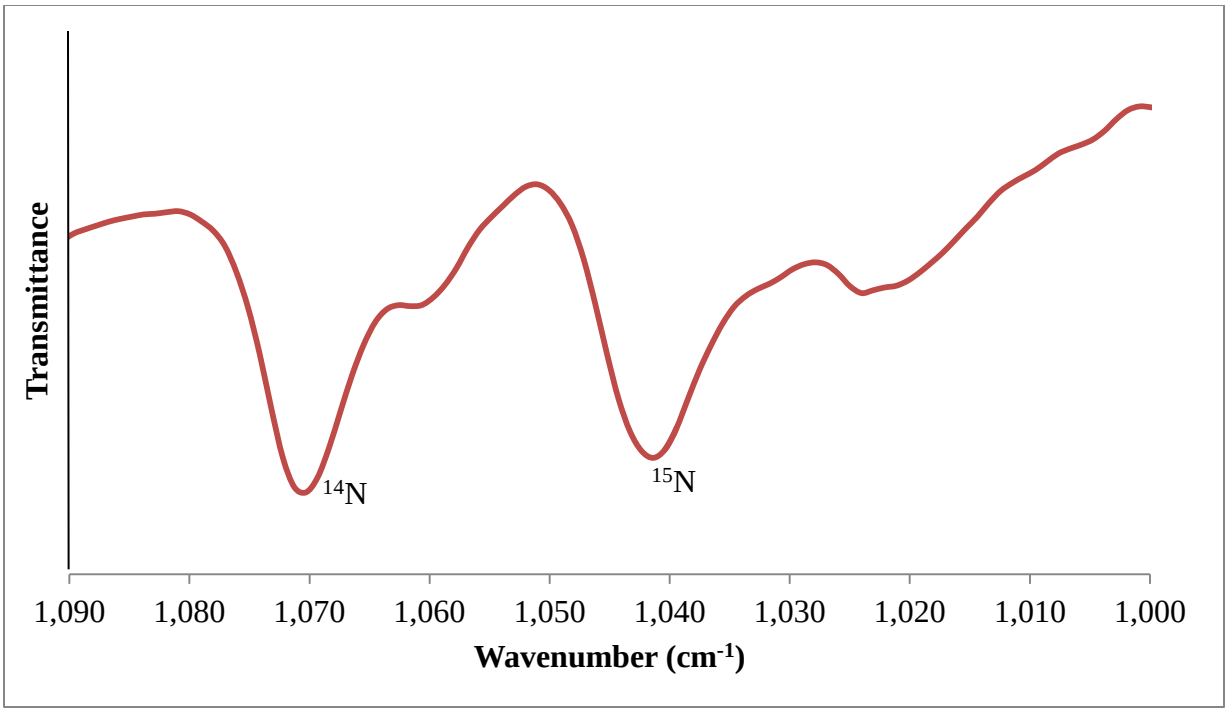

Figure S5. FT-IR (Nujol) Spectrum of nacnacV(^{15}NS)ODiiP **1** with the VNS region expanded.

Crystal Structure Collection Data for Complex 1:

The space group $P12_1/c1$ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004 and refined with SHELXL-97. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0483 and wR2 = 0.1450(F2, all data).

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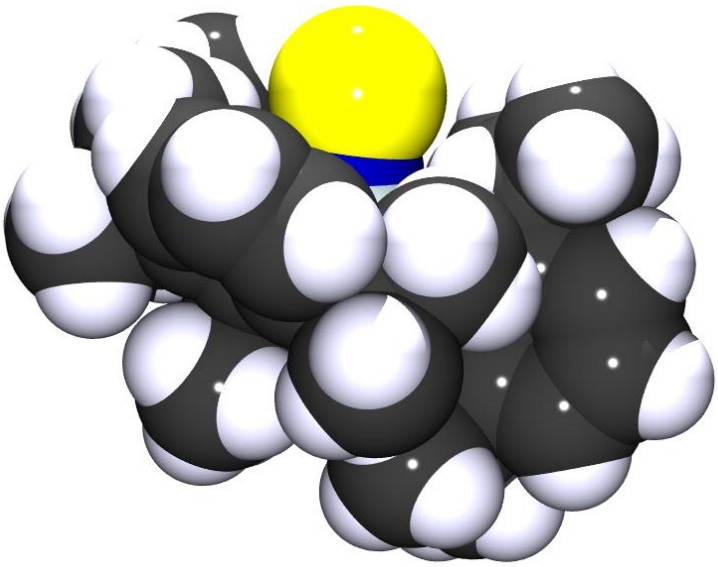

Figure S6. Space-filling model of **1**

Table S1. Summary of crystallographic data and parameters for **1**

	1
Molecular Formula	$C_{45}H_{68}N_3O_2SV$
Fw	766.061
Temp(K)	150(2)
Crystal System	Monoclinic
Space Group	$P12_1/c1$
Cell Constants	
a(Å)	11.914
b(Å)	21.113
c(Å)	18.224
α(deg)	90.00
β(deg)	107.72
γ(deg)	90.00
Z	4
V(Å^3)	4366.58
Abs Coeff, μ_{calc} (mm^{-1})	0.313
δ_{calc} (g/cm^3)	1.165
F(000)	1656.0
Crystal Dimensions (mm)	0.581 x 0.275 x 0.201
Radiation	Mo Kα (λ = 0.71073 Å)
h,k,l Ranges Collected	-14 < h <16, -29 < k < 29, -25 < l < 25
θ Range (deg)	1.519–30.145
No. of Reflections Collected	51184
No. of Unique Reflections	12804
No. of Parameters	469

Data/Parameter Ratio	27.30
Refinement Method	Full-matrix least-squares of F^2
$R(F)^a$	0.0483
$R_w(F^2)^b$	0.1450
$GOF_w{}^c$	1.0148
Largest Diff Peak and Hole (c/Å^3)	1.09 and -0.55

[a] $R = [\Sigma |\Delta F| / \Sigma |F_a|]$ [b] $R_w = [\Sigma w(\Delta F)^2 / \Sigma w F_a^2]$ [c] Goodness of fit on F^2

Computational Details

All calculations were carried out using density functional theory as implemented in the Jaguar 7.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis.[6-8]

The models used in this study consist of up to ~100 atoms,[9] which represent the non-truncated molecules that were also used in the related experimental work. These calculations challenge the current state of computational capabilities, and the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable timeframe.

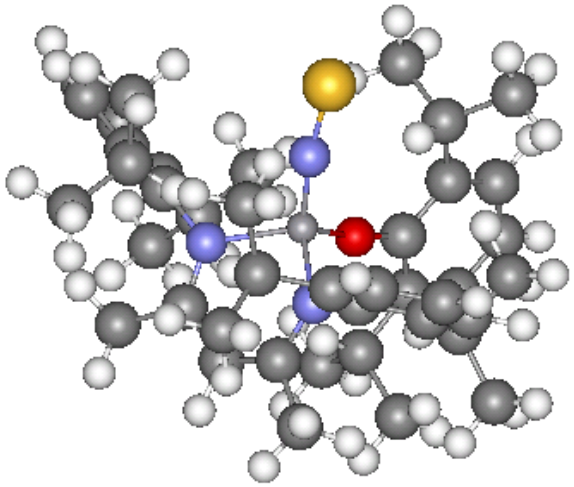

Table S2. Cartesian coordinates of the optimized geometry of **1**

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VNS_structure

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V -0.074188716 -0.016840893 0.066292682

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S	0.283083288	0.057717764	3.296756041
O	1.517166072	-0.099925059	-0.777412149
N	-1.260053565	-1.488931787	-0.448688598
N	-1.195961745	1.461269809	-0.617949161
N	-0.049726343	0.053130343	1.732210134
C	-1.376951828	-2.734358219	0.279824222
C	-0.420637962	-3.760884406	0.111890196
C	-0.585043444	-4.941982692	0.848051004
H	0.141484993	-5.741625481	0.733980571
C	-1.657357354	-5.115848554	1.713574705
H	-1.767262934	-6.043898781	2.268202251
C	-2.588355488	-4.093899498	1.868151193
H	-3.425312039	-4.232607821	2.546743987
C	-2.468211749	-2.888899433	1.169521889
C	0.778141566	-3.649654134	-0.827579763
H	0.724243204	-2.685064110	-1.340142058
C	0.781303986	-4.757470719	-1.901390697
H	1.629106966	-4.625231358	-2.582636952
H	0.877094776	-5.751451531	-1.450644542
H	-0.135664041	-4.757792112	-2.500144610
C	2.100150744	-3.674675836	-0.035373058
H	2.951669009	-3.498989812	-0.700707421
H	2.248646996	-4.642951533	0.456280086
H	2.109805210	-2.903935232	0.739535791
C	-3.519437616	-1.801452176	1.383100713
H	-3.202274092	-0.912945178	0.832252605
C	-4.896646336	-2.224368273	0.831291657
H	-5.629798225	-1.422429050	0.975457767
H	-5.275113571	-3.115434577	1.344677035
H	-4.857048818	-2.450883960	-0.239440970
C	-3.624707836	-1.403157023	2.867822589
H	-4.351961268	-0.592639287	2.990179850
H	-3.962746661	-2.240243404	3.488780842
H	-2.660159002	-1.060724786	3.253438271
C	-1.924577054	-1.340295598	-1.613856870
C	-2.156503145	-0.091166637	-2.212868355
H	-2.689365847	-0.127805026	-3.155379771
C	-1.916028281	1.213234928	-1.720944518
C	-2.494071345	-2.556301731	-2.314558972
H	-3.093629316	-2.265146558	-3.178658375

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H	-3.112976424	-3.151102548	-1.638397352
H	-1.684846972	-3.208218065	-2.658553861
C	-2.535243850	2.351285144	-2.505964433
H	-3.364314470	1.989984970	-3.117342462
H	-2.894285300	3.143265099	-1.846062441
H	-1.794077829	2.799619925	-3.175877055
C	-1.072697645	2.810352539	-0.107133527
C	-1.893917237	3.204558466	0.978378063
C	-1.759305581	4.506466675	1.470403833
H	-2.385846928	4.829330057	2.295324277
C	-0.833497851	5.393388535	0.931517760
H	-0.741292079	6.398497477	1.334271830
C	-0.025389261	4.986781416	-0.121553853
H	0.699590354	5.682083634	-0.535018791
C	-0.125209398	3.700546878	-0.669023750
C	-2.929476943	2.267704886	1.595232301
H	-2.627225497	1.245286076	1.355503210
C	-2.987450287	2.375567129	3.129307884
H	-3.652120547	1.604767400	3.530892128
H	-3.379503392	3.343520850	3.461640450
H	-1.998384273	2.228373791	3.571367745
C	-4.326671737	2.504344871	0.982152291
H	-5.062628205	1.824094302	1.426262612
H	-4.666301218	3.530389588	1.166322601
H	-4.333263043	2.340813474	-0.100542550
C	0.795302651	3.342198119	-1.836183806
H	0.537321808	2.339593471	-2.188171547
C	2.268507978	3.303447903	-1.383951375
H	2.924122104	3.027494615	-2.216481839
H	2.593525346	4.281739263	-1.012972891
H	2.417898888	2.572120650	-0.587816751
C	0.635524113	4.319806956	-3.020561423
H	1.223905118	3.977538659	-3.878863510
H	-0.405845495	4.419590982	-3.342867617
H	0.992260896	5.322492088	-2.761006317
C	2.794673373	-0.290758574	-1.190929137
C	3.848099801	-0.403556399	-0.247032760
C	5.145864938	-0.582910589	-0.735501152
H	5.968041951	-0.666102876	-0.030875577
C	5.409348898	-0.666686509	-2.100890129

H	6.427084847	-0.810613122	-2.453419051
C	4.360200440	-0.573285262	-3.009863252
H	4.567890344	-0.649657642	-4.074487159
C	3.041358418	-0.382181752	-2.584825137
C	3.584562542	-0.315368439	1.252004606
H	2.534170321	-0.565149345	1.422250814
C	3.799684138	1.118045777	1.778493103
H	3.571011094	1.169071853	2.848096653
H	3.152371109	1.836576387	1.268440314
H	4.839291912	1.433910758	1.630063632
C	4.421514200	-1.312855898	2.073000103
H	4.078741903	-1.312284943	3.113063000
H	4.329533305	-2.332719299	1.686313472
H	5.485827908	-1.051388654	2.081499126
C	1.916400240	-0.294178343	-3.612460096
H	0.992838240	-0.062879629	-3.074482639
C	1.707048021	-1.637962141	-4.337846181
H	0.869511460	-1.571962199	-5.042807501
H	1.493624925	-2.444724072	-3.631143311
H	2.598619092	-1.923462620	-4.907739001
C	2.153512144	0.830028608	-4.639210864
H	1.295934168	0.919960330	-5.316530878
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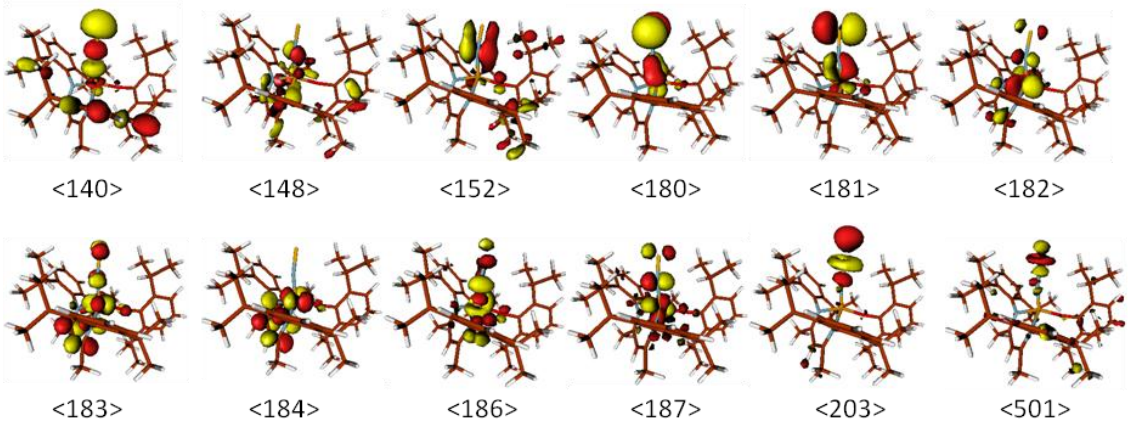

Figure S7. Electronic structure of relevant orbitals in **1.**

Table S3. Calculated vibrational modes of **1.** The VNS stretch is bolded.

==========

VNS Vibrations

==========

23.71 28.79 30.76 35.79 36.68 41.99

48.35 51.74 53.26 54.27 57.30 66.57

70.40 72.68 78.23 78.66 81.60 85.36

91.02 98.64 114.03 119.19 123.94 125.69

131.90 135.37 136.54 138.90 143.96 146.78

157.80 165.40 194.94 201.58 216.22 220.26

224.21 227.17 234.28 235.42 237.44 240.09

242.20 246.81 248.07 255.71 256.05 259.29

263.11 263.54 265.65 271.20 273.35 283.33

285.95 289.40 295.86 301.21 318.46 319.87

320.20 322.83 329.49 331.85 342.60 364.40

401.11 401.87 426.42 436.52 439.63 441.58

442.29 443.57 447.51 450.39 462.20 508.28

523.96 541.19 547.16 548.91 555.14 557.48

558.15 573.21 575.57 601.72 602.64 617.86

618.89 635.76 636.99 640.10 646.46 651.39

668.23 728.20 730.12 738.61 774.44 778.01

783.82 811.81 813.49 813.71 816.76 820.01

824.55 825.86 878.07 879.68 889.99 892.96

893.30 926.31 929.89 930.86 932.13 934.76

937.08 937.65 938.72 939.12 940.28 947.81

948.53 949.09 958.14 963.21 963.72 964.98

965.83 967.52 968.16 969.97 985.03 998.73

999.37 1039.02 1052.35 1053.60 1059.82 1069.35

1070.43 1072.01 1080.50 1081.82 1085.15 1120.32

1121.96 1122.70 1124.47 1125.53 1126.20 1131.95

1134.79 1137.40 **1162.63** 1174.14 1179.51 1180.91

1191.61 1193.67 1194.57 1196.50 1207.25 1208.95

1210.72 1213.48 1235.38 1256.78 1267.28 1283.10

1283.50 1284.09 1284.42 1288.34 1298.37 1299.95

1301.95 1304.65 1345.18 1347.06 1349.23 1350.40

1353.58 1357.16 1359.39 1360.11 1365.61 1384.63

1386.42 1388.98 1408.30 1409.16 1410.01 1411.54

1412.18 1414.35 1414.58 1419.06 1420.95 1429.67

1430.36 1433.27 1435.49 1435.97 1436.33 1468.47

1475.19 1478.12 1483.00 1488.03 1494.98 1495.43

1496.21 1497.78 1497.86 1498.94 1499.89 1500.20

1500.91 1501.63 1503.19 1503.89 1504.18 1505.06

1506.10 1506.91 1508.97 1513.85 1515.63 1516.42

1516.92 1519.31 1519.64 1520.95 1521.54 1522.38

1522.61 1525.39 1526.70 1545.39 1571.00 1628.64

1635.21 1636.27 1641.03 1644.63 1644.99 3034.92

3036.26 3036.82 3038.59 3040.37 3041.05 3041.22

3042.68 3043.48 3045.87 3046.51 3050.98 3066.93

3067.07 3081.40 3085.10 3087.58 3090.79 3091.82

3092.56 3098.50 3102.29 3104.27 3106.04 3108.28

3109.05 3109.37 3109.99 3112.33 3112.50 3116.49

3117.61 3117.92 3118.46 3118.82 3120.69 3121.19

3127.64 3130.55 3130.59 3131.06 3132.25 3133.34

3136.93 3137.41 3155.78 3156.16 3159.79 3171.52

3177.97 3179.88 3186.49 3189.56 3196.27 3201.47

3202.71 3210.50 3213.04

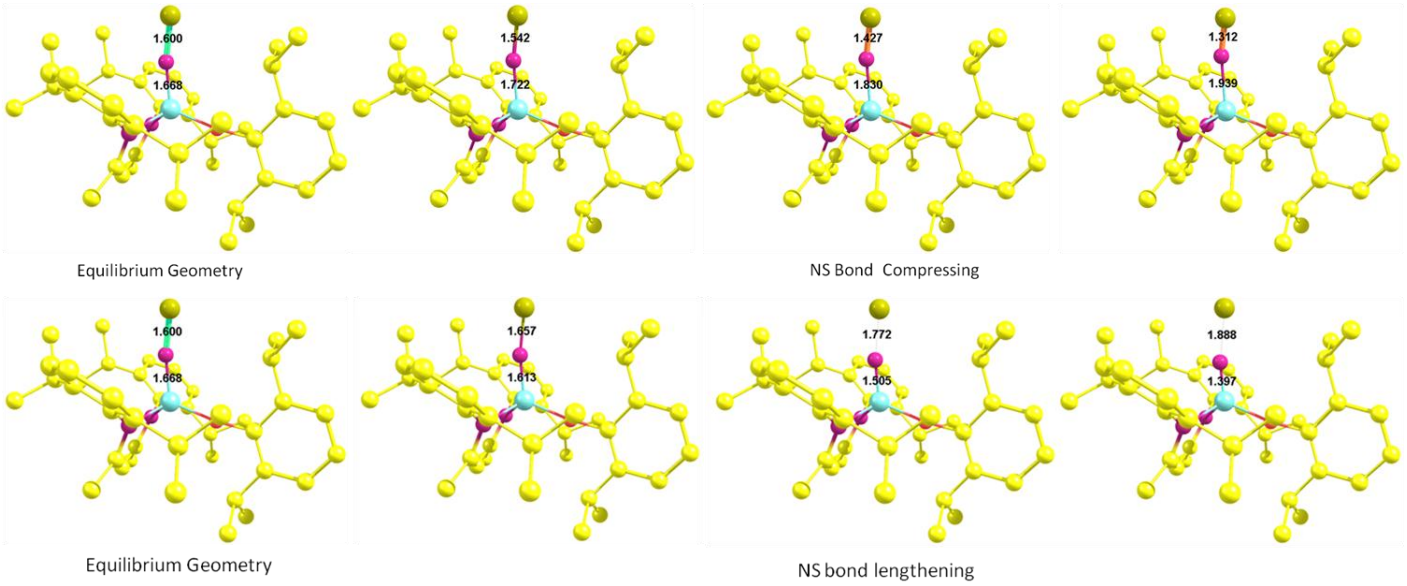

Figure S8. Progression of VNS vibration in computational model of complex **1**

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