

Supporting Information for

Linear and Non-Linear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides

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1. X-Ray Crystallography

Second X-ray Crystallographic Structure for $V\{N(H)Ar^{iPr_6}\}_2$ (**1a**) (Crystallized in hexane).

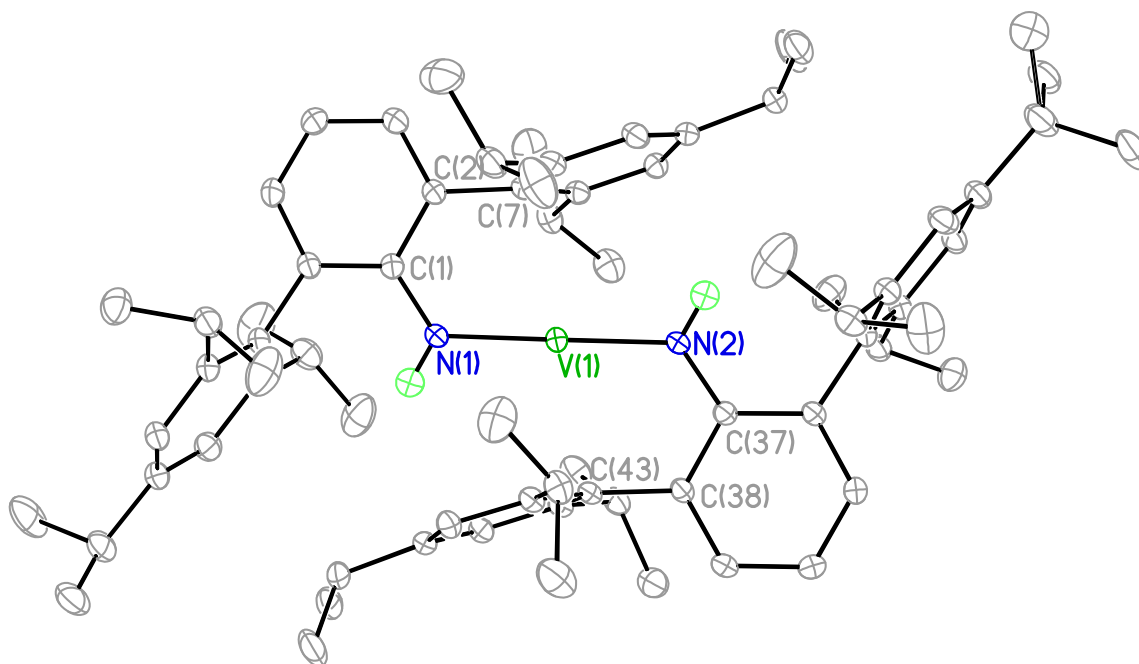


Figure SI(1a). X-ray crystal structure of $V\{N(H)Ar^{iPr_6}\}_2$ (**1a**) with a slightly bent coordination at vanadium shown. (Non-nitrogen H atoms are not shown for clarity, thermal ellipsoids are shown at 30% probability.) Select bond distances and angles are given in Table SI(1a).

Table SI(1a). Selected interatomic distances (Å) and angles (°) for the complex $V\{N(H)Ar^{iPr_6}\}_2$ (**1a**).

$V\{N(H)Ar^{iPr_6}\}_2$ (1a)	
M-N(1) Å	1.9948(12)
M-N(2) Å	1.9948(12)
M-C(7),C(43) Å	2.557/2.564
N(1)-M-N(2) (deg)	178.68(5)
M-N(1)-(H) (deg)	117.0
M-N(1)-C(1) (deg)	125.93(10)

Table SI(1b). Selected crystallographic and data collection parameters for the non-centrosymmetric structure of $V\{N(H)Ar^{iPr_6}\}_2$ (**1a**).

Compound	$V\{N(H)Ar^{iPr_6}\}_2$
Empirical formula	$C_{72}H_{100}N_2V$
Formula weight	1044.48 g/mol
Temperature	190(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
a (Å)	15.4038(3)
b (Å)	17.0341(3)

c (Å)	24.8449(5)
α (°)	90
β (°)	104.221(1)
γ (°)	90
Volume (Å ³)	6319.3(2)
Z	4
Density (calculated) (Mg/m ³)	1.098
Absorption coefficient (mm ⁻¹)	1.607
$F(000)$	2276
Crystal size (mm)	0.27 x 0.20 x 0.08
Crystal color and habit	Orange Plate
Theta range for data collection	2.96 to 68.24°.
Reflections collected	31143
Independent reflections	11146 [R(int) = 0.0240]
Observed reflections ($I > 2\sigma(I)$)	10328
Completeness to $\theta = 68.24^\circ$	96.2 %
Absorption correction	Numerical
Max. and min. transmission	0.8768 and 0.6745
Data / restraints / parameters	11146 / 8 / 704
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0409, wR2 = 0.1179
R indices (all data)	R1 = 0.0435, wR2 = 0.1202

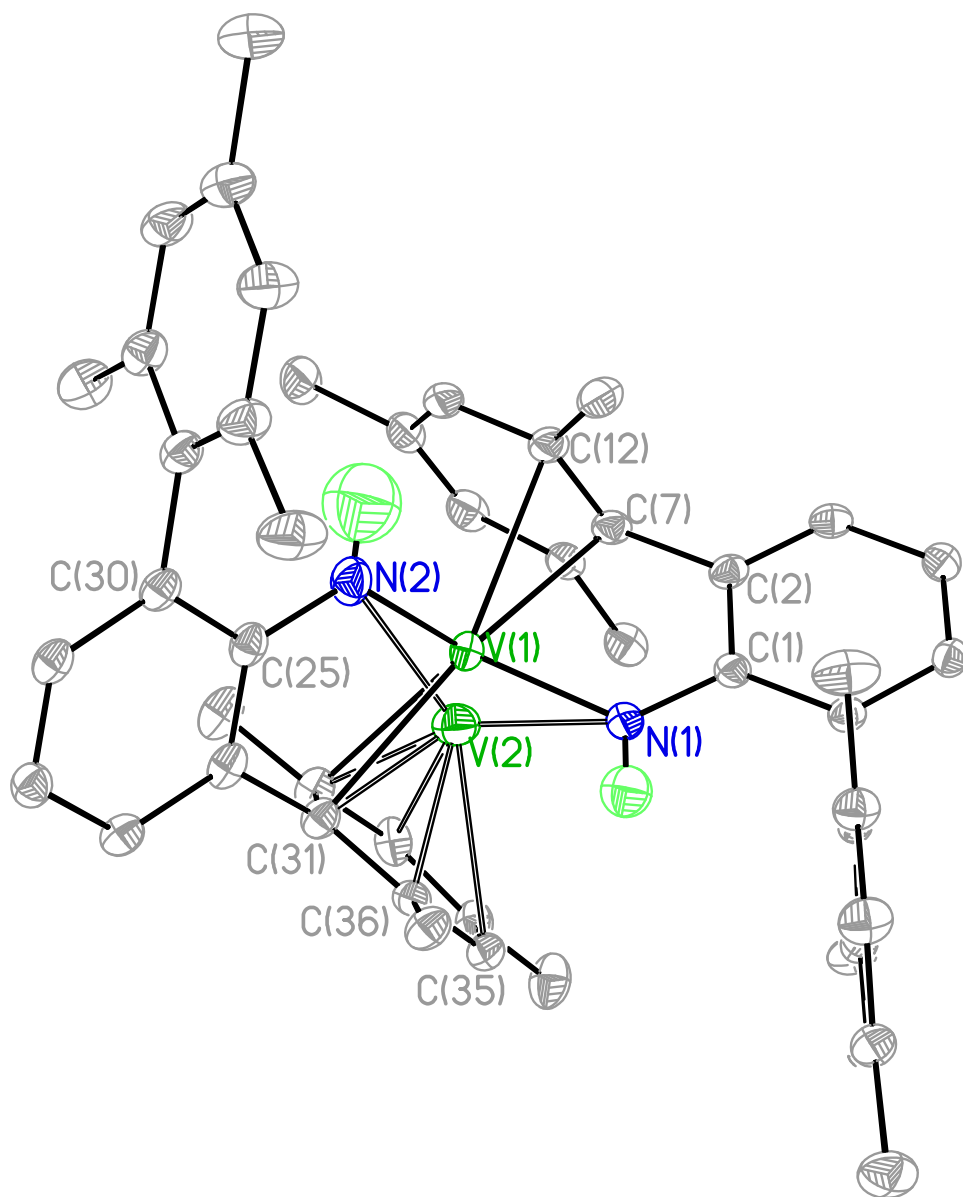


Figure SI(1b). X-ray crystal structure of the two-coordinate $[\text{V}\{\text{N}(\text{H})\text{Ar}^{\text{Me}_6}\}_2]_2$ illustrating both vanadium sites. V(1) represents has 80% occupancy and V(2) 20%. (Non-nitrogen H atoms are not shown for clarity, thermal ellipsoids are shown at 30% probability.) Select bond distances and angles are given in Table SI(1c) .

Table SI(1c). Selected interatomic distances (Å) and angles (°) for the 20% site of vanadium in complex **2**.

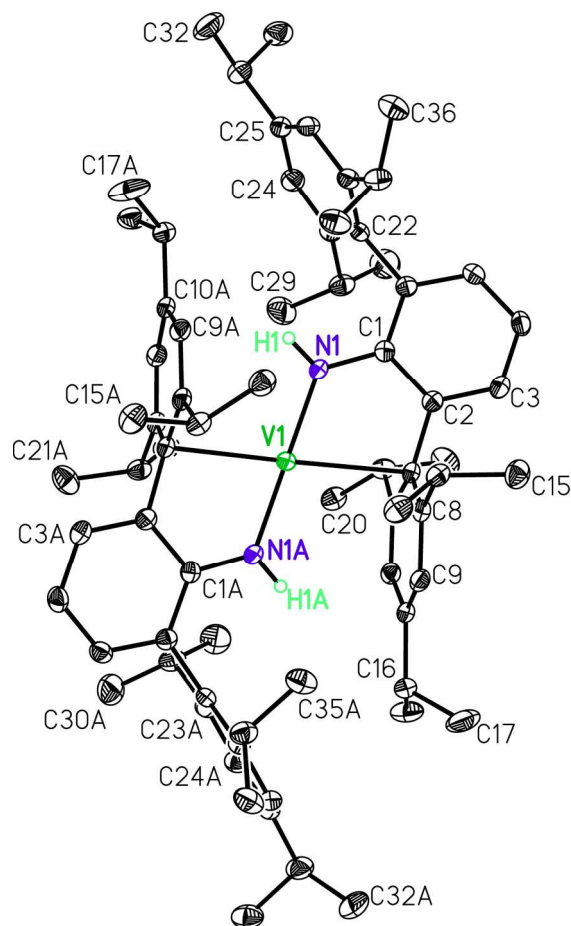
	V{N(H)Ar ^{Me6} } ₂ (2)
V(2)-N(1) Å	1.939(3)
V(2)-N(2) Å	2.328(3)
V(2)---(<i>i</i> -MesC) Å	1.839
N(1)-V(2)-N(2) (deg)	107.33(14)
V(2)-N(1)/N(2)-(H) (deg)	97
V(2)-N(1)/N(2)-	143.29(18)
C(1)/C(25) (deg)	/105.00(15)

V{N(H)Ar^{*i*Pr6}}₂ (**1**)

A red block with approximate dimensions 0.264 x 0.13 x 0.09mm was placed and optically centered on the Bruker Duo¹ APEXII CCD diffractometer at –183°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Sixteen ω and phi-scan data frame series were collected [CuK α] with 0.5° wide scans and variable frame times based upon diffraction angle. The crystal to detector distance was 4.96cm, thus providing a nearly complete sphere of data with processing to $2\theta_{\text{max}}=138.42^\circ$.

Structure determination and refinement:

All crystallographic calculations were performed on an iMac with an Intel Core i7 2.80GHz processor and 8GB of extended memory at 1067MHz DDR3. Data collected were corrected for Lorentz and polarization effects with Saint¹ and absorption using Blessing's method and merged as incorporated with the program Sadabs^{2,3}. The SHELXTL⁴ program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic space group C2/c (no. 15). The structure was determined by direct methods with a majority of the non-hydrogen atoms from the molecule of interest being located directly using the program XT⁵. Refinement of the structure was achieved using the program SHELXL-2012⁶. Difference-Fourier refinement cycles were required to locate the remaining non-hydrogen atoms. The toluene molecule was disordered upon itself in two orientations that were optimized to be C41-C47:C41b-C47b, 0.70:0.30. Refinement converged to approximately $R_F=4.3\%$ for all observed data. It was evident from the outset that the structure possessed more than a single domain when examining the individual frames so reflections were thresholded in APEX¹ and these reflections were input into Cellnow⁷ that determined the twin relationship between the two components and generated the orientation matrices for the components and output a useable



multiple matrix input file for the integration program SAINT¹. Saint was run five times using the output optimized merged matrix file from the previous run. Data collected were now corrected for absorption using TWINABS^{2,8} and Blessing's method and merged generating both HKLF4 and HKLF5 files. Convergence of the structure proceeded quickly using both the HKLF5 and HKLF4 files. All of the non-hydrogen atoms were refined anisotropically and using the HKLF5 determined the percentage of the two domains being present as follows: major:minor component 0.80:0.20 as indicated from the batch scale factor. Since this process did not yield superior results to the single component approach, the single component approach HKLF4 format file was chosen for structure completion. All of the hydrogen atoms were idealized throughout the final convergence cycles. The final structure was refined to convergence with $R(F)=4.25\%$, $wR(F^2)=10.51\%$, $GOF=1.036$ for all 6422 reflections [$R(F)=4.12\%$, $wR(F^2)=10.45\%$ for those 6309 data with $F_o > 4\sigma(F_o)$]. A final difference-Fourier map was featureless indicating that the structure is therefore both correct and complete.

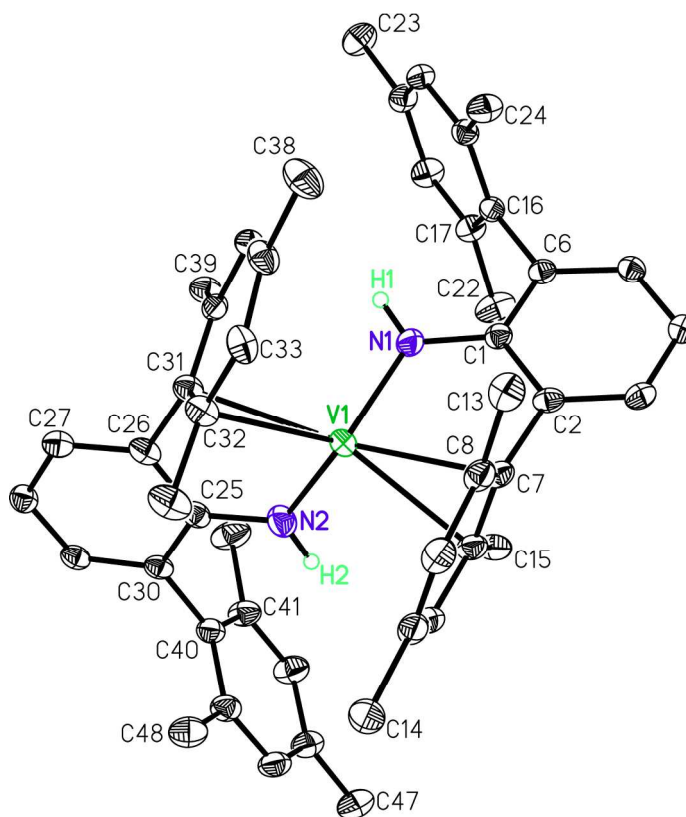
$V\{N(H)Ar^{Me_6}\}_2$ (2)

A red block with approximate dimensions 0.71 x 0.58 x 0.33mm was placed and optically centered on the Bruker Duo¹ APEXII CCD diffractometer at -183°C . The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Sixteen ω and phi-scan data frame series were collected [CuK_α] with 0.5° wide scans and variable frame times based upon diffraction angle. The

crystal to detector distance was 4.96cm, thus providing a nearly complete sphere of data with processing to $2\theta_{\text{max}}=136.98^\circ$.

Structure determination and refinement:

All crystallographic calculations were performed on an iMac with an Intel Core i7 2.80GHz processor and 8GB of extended memory at 1067MHz DDR3. A total of 21163 reflections were collected and corrected for Lorentz and polarization effects in SAINT¹ and absorption using crystal faces and Blessing's method as incorporated into the program SADABS^{2,3,9} with 6917 unique. The SHELXTL⁴ program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences and intensity statistics indicated the centrosymmetric triclinic space group P-1 (no. 2). The



structure was determined by direct methods with the successful location of a majority of the molecule of interest using the program XS⁵. The structure was refined with XL⁶. The 21163 data collected were merged, based upon identical indices, resulting in 13028 data [R(int)=0.0278] that were further merged and truncated to a resolution limit of 0.83Å during least-squares refinement to 6723 unique data [R(int)=0.0188]. The central Vanadium atom is disordered, optimized to be major:minor, 0.80:0.20, with the remaining atoms present

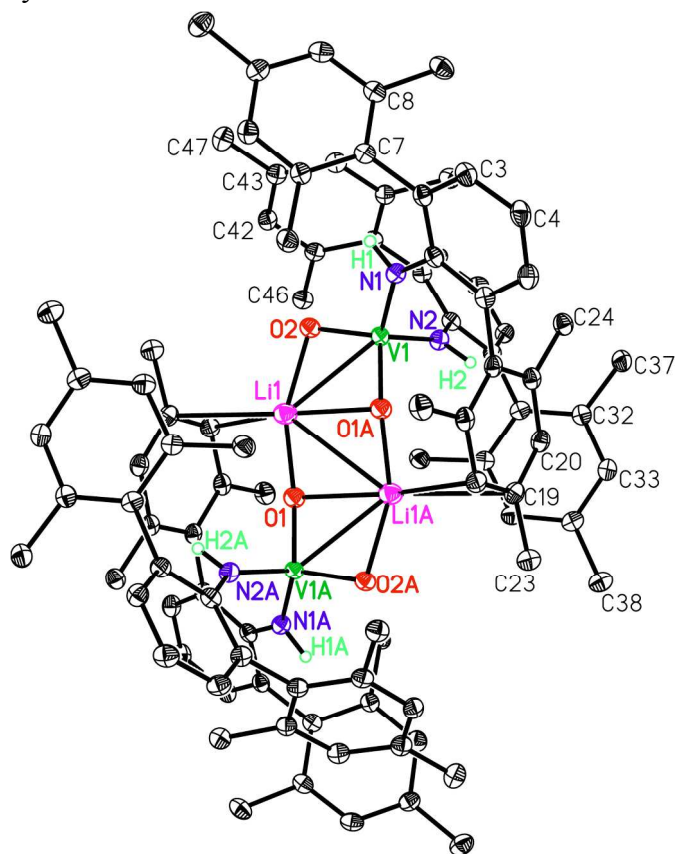
representing the majority occupancy Vanadium position while the minor 20% orientation is not apparent. Hydrogen atoms attached to the two nitrogen atoms had their thermal parameters refined but were otherwise idealized. All remaining hydrogen atoms were placed in idealized positions throughout the refinement process. The final structure was refined to convergence with $R(F)=5.33\%$, $wR(F^2)=15.57\%$, $GOF=1.049$ for all 6723 unique reflections [$R(F)=5.25\%$, $wR(F^2)=15.48\%$ for those 6547 data with $F_o > 4\sigma(F_o)$]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

[V{N(H)Ar^{Me6}}₂]₂ (μ -O-Li-O)₂ (3)

An orange trapezoid with approximate dimensions 0.42 x 0.39 x 0.21mm was placed and optically centered on the Bruker Duo APEXII¹ CCD system at -183°C (90K). The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Six ω and phi-scan data frame series were collected [$\text{CuK}\alpha$] with 0.5° wide scans and variable frame times based upon diffraction angle. The crystal to detector distance was 4.96cm, thus providing a nearly complete sphere of data with processing to $2\theta_{\text{max}}=136.50^\circ$.

Structure determination and refinement:

All crystallographic calculations were performed on an iMac with an Intel Core i7 2.80GHz processor and 8GB of extended memory at 1067MHz DDR3. For the initial structure determination the data were processed and corrected for Lorentz and polarization effects in SAINT¹ and absorption using Blessing's method as incorporated into the program SADABS^{2,3}. The SHELXTL⁴ program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the non-standard



centrosymmetric monoclinic space group $P2_1/n$ (no. 14). The structure was determined by direct methods with the successful location of a majority of the molecule using the program XT⁵. The structure was refined with XL12⁶. Refinement converged to approximately $R_F=14\%$ for all observed data. There were a few odd peaks in the difference map and the weighting scheme was quite large along with data frames displaying peak splitting throughout so it was believed that the crystal might be slightly twinned so reflections were thresholded in APEX¹ and these reflections were input into Cellnow⁷ that determined the twin relationship between the two components and generated the orientation matrices for the components and output a useable multiple matrice input file for the integration program SAINT¹. The twin relationship was found to be a 3.2 degree rotation about the reciprocal axis 1,0,-0.2. Saint was run four

times using the output optimized merged matrix file from the previous run. Data collected were now corrected for absorption using TWINABS^{2,8} and Blessing's method with 14977 (11.2), 14880 (5.7) and 1461(12.0) reflections representing components one, two and both, respectively with the mean I/sigma in brackets for each. A total of 10187 reflections were output as a non-merged HKLF4 format file and 8502 for the merged HKLF5 format reflection file. The HKLF4 formatted file was input into Xprep. Convergence of the structure proceeded quickly using both the HKLF5 and HKLF4 files. All of the non-hydrogen atoms were refined anisotropically and using the HKLF5 determined the percentage of the two domains being present as follows: major:minor component 0.82:0.18 as indicated from the batch scale factor. A disordered solvent pair of THF:Dioxane was optimized for disorder lying on the same site with the ratio determined to be 0.82:0.18, respectively. In this case, the HKLF4 format file yielded superior results so it was chosen for structure completion. All of the hydrogen atoms were idealized throughout the final convergence cycles. The final structure was refined to convergence with R(F)=7.71%, wR(F²)=18.32%, GOF=1.065 for all 9991 reflections [R(F)=6.53%, wR(F²)=17.52% for those 5846 data with Fo > 4σ(Fo)]. A final difference-Fourier map was featureless indicating that the structure is therefore both correct and complete.

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2. Magnetic Measurements

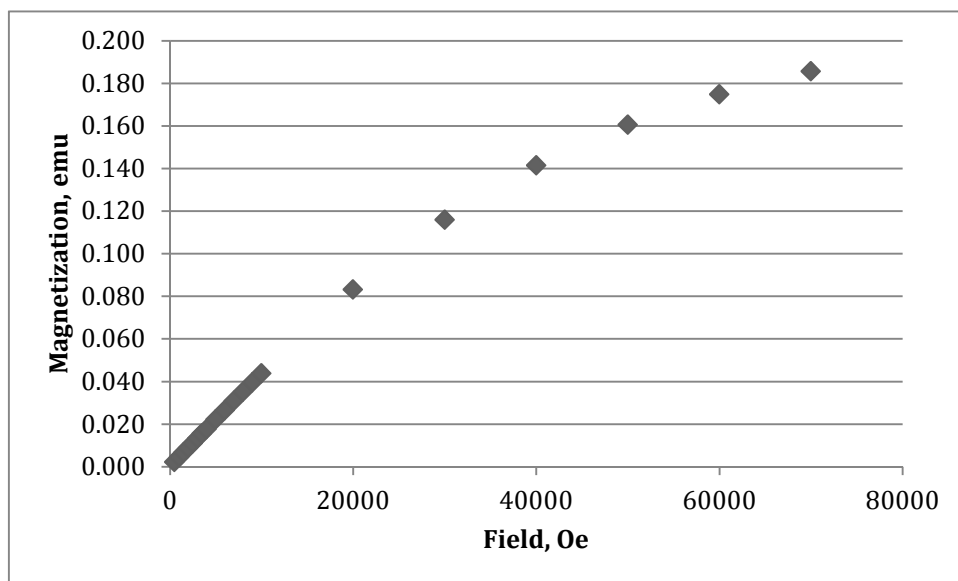


Figure SI(2a). Linear $V\{N(H)Ar^{iPr_6}\}_2$ (**1**) magnetization versus field plot from 0 to 7 tesla.

3. UV-Visible Spectra

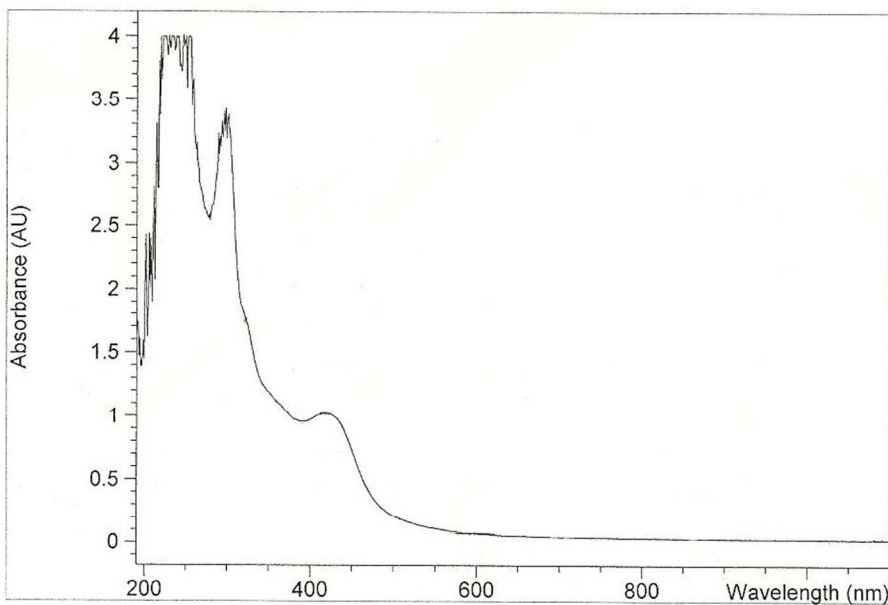


Figure SI(3a). Linear $V\{N(H)Ar^{iPr_6}\}_2$ (**1**) absorbance vs wavelength (nm) UV-visible spectra.

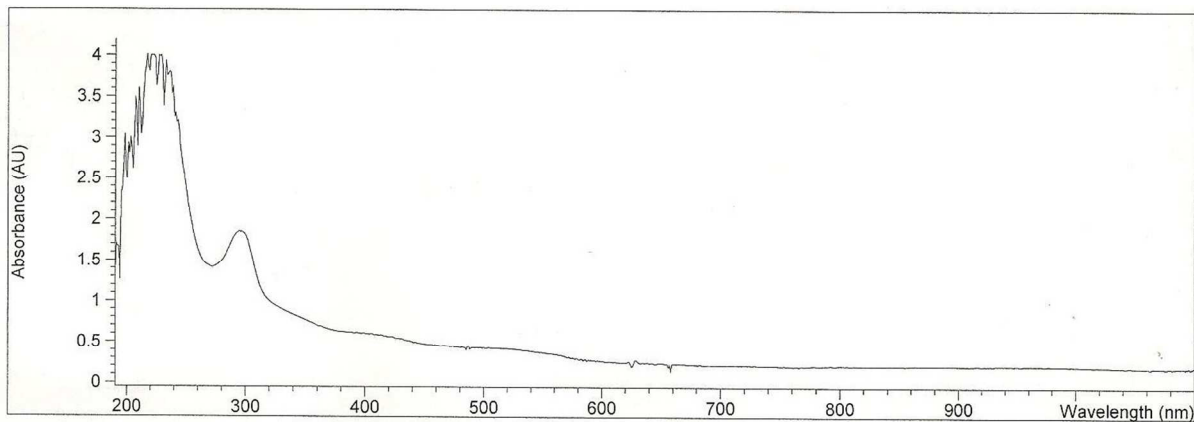


Figure SI(3b). Bent $V\{N(H)Ar^{Me_6}\}_2$ (**2**) absorbance vs wavelength (nm) UV-visible spectra.

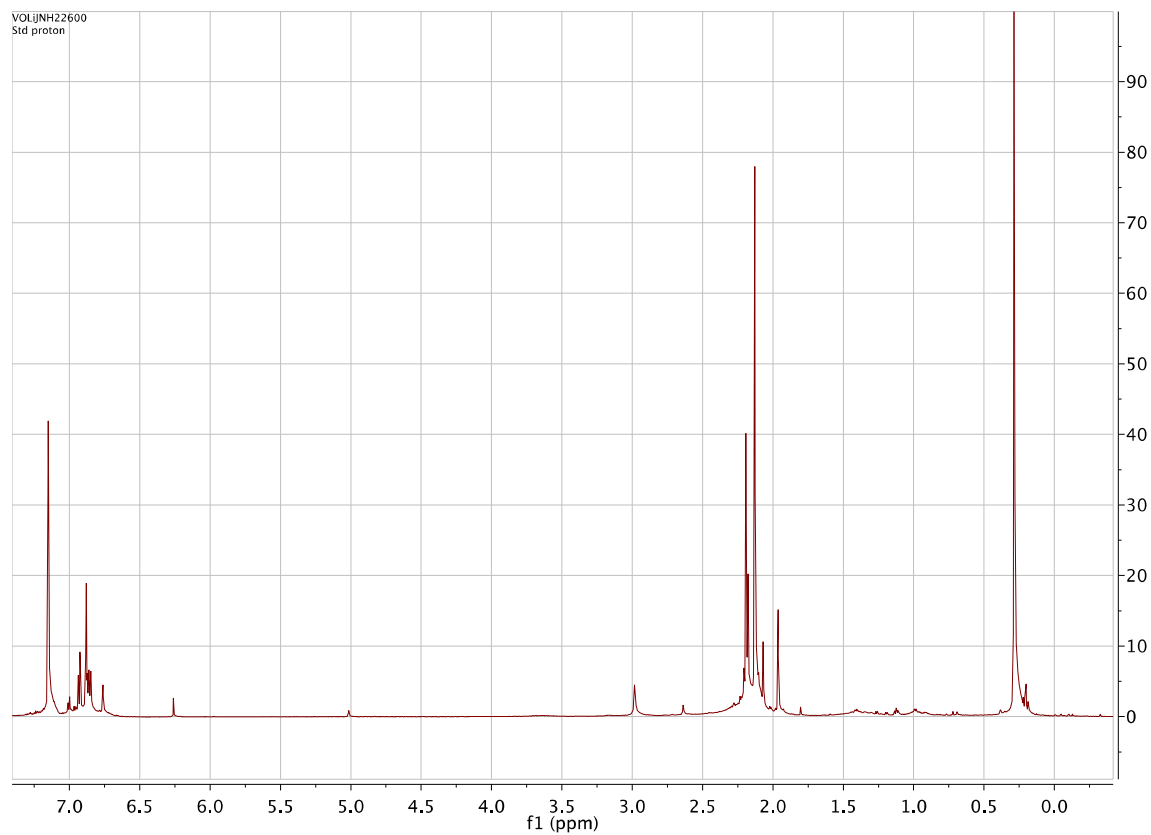


Figure SI(5a): Plot of the ^1H NMR spectrum of **3** recorded in C_6D_6 .

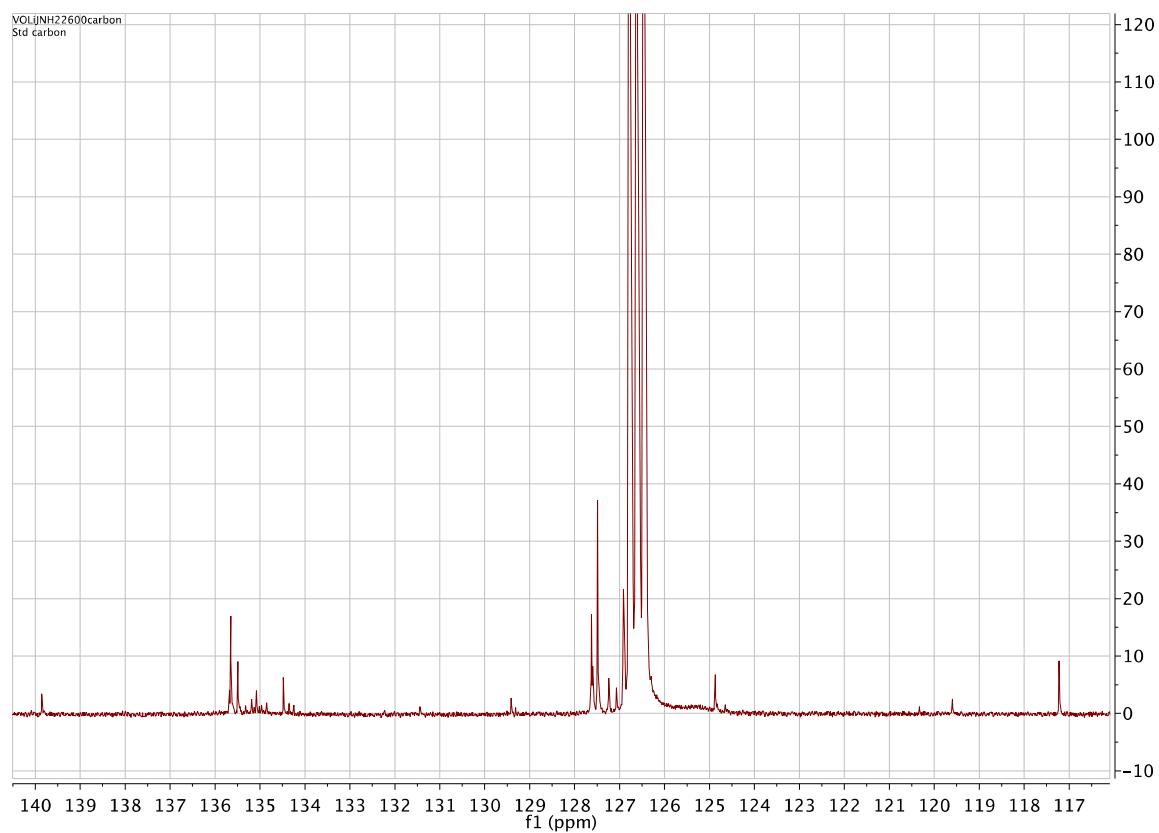


Figure SI(5b): Plot of the ^{13}C NMR spectrum of **3** recorded in C_6D_6 .

4. Full Reference 22.¹

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