

## Supporting Information

For

### Reductive N-N Bond Cleavage and Coupling of Organic Azides Mediated by Chromium(I) and Vanadium(I) $\beta$ -Diketiminato

Kuan-Ming Lin,<sup>a</sup> Po-Yang Wang,<sup>a</sup> Yun-Jen Shieh,<sup>a</sup> Hong-Zhang Chen,<sup>a</sup>  
Ting-Shen Kuo,<sup>b</sup> and Yi-Chou Tsai<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, National Tsing Hua University, Hsinchu, 300, Taiwan

<sup>b</sup>Department of Chemistry, National Taiwan Normal University, Taipei, 116, Taiwan

#### X-ray crystal structure of Cr[ $\eta^2$ -(N-*p*-Tol-N)<sub>2</sub>](Nacnac)·THF (**5**), CCDC-764154

Orange crystals of **5** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.16 x 0.12 x 0.04 mm<sup>3</sup> was selected and mounted with wax on the end of a glass fiber. A total of 27281 reflections ( $-13 \leq h \leq 13$ ,  $-15 \leq k \leq 151$ ,  $-19 \leq l \leq 19$ ) were collected at 200 (2) K in the  $\theta$  range 2.26° to 25.43°, of which 7841 (Rint = 0.1139) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands) and HFIX 137 (for the methyl groups C(13), C(17), C(34), and C(41) attached to the sp<sup>2</sup> hybridized carbons) and their orientation may not be totally reliable. The disordered co-crystallized THF solvent molecule was squeezed by using PLATON SQUEEZE option. The residual peak and hole electron density were 0.474 and -0.444 e·Å<sup>-3</sup>, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 1.0043 and 0.8868, respectively. The least squares refinement converged normally with

residuals  $R_1 = 0.0850$ ,  $wR_2 = 0.2276$  based upon  $I > 2\sigma(I)$  and  $GOF = 0.988$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $C_{47}H_{63}CrN_6O$ , space group  $P -1$ ,  $a = 10.8881(5) \text{ \AA}$ ,  $b = 12.8734(5) \text{ \AA}$ ,  $c = 16.1682(2) \text{ \AA}$ ,  $\alpha = 105.496(2)^\circ$ ,  $\beta = 90.870(2)^\circ$ ,  $\gamma = 91.470(2)^\circ$ ,  $V = 2182.58(17) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 0.303 \text{ mm}^{-1}$ ,  $\rho(\text{calc}) = 1.187 \text{ g/cm}^{-3}$ ,  $F(000) = 838$ ,  $R_1$  (based on  $F$ ) = 0.1541,  $wR_2$  (based on  $F^2$ ) = 0.2268.

#### **X-ray Crystal structure of $V(N-p\text{-Tol})_2(\text{Nacnac})$ (6), CCDC-764812**

Reddish orange of **6** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions  $0.34 \times 0.31 \times 0.15 \text{ mm}^3$  was selected and mounted with wax on the end of a glass fiber. A total of 24352 reflections ( $-23 \leq h \leq 22$ ,  $-11 \leq k \leq 13$ ,  $-21 \leq l \leq 19$ ) were collected at 200 (2) K in the  $\theta$  range  $2.09^\circ$  to  $25.03^\circ$ , of which 3686 ( $R_{\text{int}} = 0.0568$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups C(13), C(20), and C(27) attached to the  $sp^2$  hybridized carbons), and their orientation may not be totally reliable. The residual peak and hole electron density were 0.497 and  $-0.748 \text{ e}\cdot\text{\AA}^{-3}$ , respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 0.9595 and 0.9114, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0564$ ,  $wR_2 = 0.1529$  based upon  $I > 2\sigma(I)$  and  $GOF = 1.032$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $C_{43}H_{55}N_4V$ , space group  $Pnma$ ,  $a = 19.4976(7) \text{ \AA}$ ,  $b = 11.2990(4) \text{ \AA}$ ,  $c = 18.3271(6) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4037.5(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 0.278 \text{ mm}^{-1}$ ,  $\rho(\text{calc.}) = 1.117 \text{ g/cm}^{-3}$ ,  $F(000) = 1456$ ,  $R_1$  (based on  $F$ ) = 0.1052,  $wR_2$  (based on  $F^2$ ) = 0.1918.

#### **X-ray Crystal structure of $V(N-1\text{-Ad})_2(\text{Nacnac})\cdot\text{Et}_2\text{O}$ (7), CCDC-764811**

Red crystals of **7** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions  $0.6 \times 0.2 \times 0.05 \text{ mm}^3$  was selected and mounted with wax on the end of a glass fiber. A total of 35759 reflections ( $-23 \leq h \leq 19$ ,  $-12 \leq k \leq 13$ ,  $-23 \leq l \leq 28$ ) were collected at 200 (2) K in the  $\theta$  range  $2.07^\circ$  to  $25.37^\circ$ , of which 8944 ( $R_{\text{int}} = 0.0972$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for

the methyl groups C(13) and C(17) attached to the  $sp^2$  hybridized carbons) and their orientation may not be totally reliable. The disordered co-crystallized solvent molecule,  $Et_2O$ , was squeezed by using PLATON SQUEEZE option. The residual peak and hole electron density were 0.491 and  $-0.514 e \cdot \text{\AA}^{-3}$ , respectively. An empirical absorption correction (sphere) was applied with maximum and minimum transmissions equal to 1.0881 and 0.8786, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0975$ ,  $wR_2 = 0.2259$  based upon  $I > 2\sigma(I)$  and  $GOF = 1.056$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $C_{102}H_{152}N_8OV_2$ , space group  $P 2_1/c$ ,  $a = 19.7038(4) \text{ \AA}$ ,  $b = 10.9155(3) \text{ \AA}$ ,  $c = 23.6118(6) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 104.1980(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4923.2(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 0.238 \text{ mm}^{-1}$ ,  $\rho(\text{calc}) = 1.085 \text{ g/cm}^3$ ,  $F(000) = 1748$ ,  $R_1$  (based on  $F$ ) = 0.1711,  $wR_2$  (based on  $F^2$ ) = 0.2565.

#### **X-ray Crystal structure of $Cr[N(\text{SiMe}_3)_2](\text{Nacnac})$ , (8), CCDC-764155**

Red crystals of **8** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions  $0.3 \times 0.2 \times 0.1 \text{ mm}^3$  was selected and mounted with wax on the end of a glass fiber. A total of 29834 reflections ( $-10 \leq h \leq 10$ ,  $-22 \leq k \leq 23$ ,  $-23 \leq l \leq 24$ ) were collected at 200 (2) K in the  $\theta$  range  $1.42^\circ$  to  $25.00^\circ$ , of which 6633 ( $R_{\text{int}} = 0.0450$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups C(13) and C(17) attached to the  $sp^2$  hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 1.009 and  $-0.492 e \cdot \text{\AA}^{-3}$ , respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 0.962 and 0.889, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0537$ ,  $wR_2 = 0.1476$  based upon  $I > 2\sigma(I)$  and  $GOF = 1.052$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $C_{35}H_{59}CrN_3Si_2$ , space group  $P2_1/n$ ,  $a = 9.1132(9) \text{ \AA}$ ,  $b = 20.144(2) \text{ \AA}$ ,  $c = 20.551(2) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90.350(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3772.7(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 0.392 \text{ mm}^{-1}$ ,  $\rho(\text{calc}) = 1.109 \text{ g/cm}^3$ ,  $F(000) = 1368$ ,  $R_1$  (based on  $F$ ) = 0.0767,  $wR_2$  (based on  $F^2$ ) = 0.1685.

#### **X-ray Crystal structure of $[Cr(\mu\text{-N}_3)(\text{THF})(\text{Nacnac})]_2$ (9), CCDC-764151**

Orange crystals of **9** were coated with Paratone N oil and placed on a microscope

slide. A crystal of approximate dimensions 0.8 x 0.7 x 0.45 mm<sup>3</sup> was selected and mounted with wax on the end of a glass fiber. A total of 36768 reflections ( $-15 \leq h \leq 15$ ,  $-18 \leq k \leq 18$ ,  $-24 \leq l \leq 24$ ) were collected at 200 (2) K in the  $\theta$  range 2.13° to 25.43°, of which 12143 ( $R_{\text{int}} = 0.0837$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. One of the isopropyl groups is disordered in two methyl substituents C44 and C45; the ratio of the occupancy of the major (C44 and C45) to the minor (C44A and C45A) components refined to 3:1. The bond distances of C(43)-C(44) and C(43)-C(44A) and C(43)-C(45) and C(43)-C(45A) were restrained to be equal by *SADI* 0.005 instructions in *SHELXL97* (Sheldrick, 1997). The Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups C(13), C(17), C(46), and C(50) attached to the sp<sup>2</sup> hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 1.587 and -0.747 e·Å<sup>-3</sup>, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 1.0021 and 0.6874, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0907$ ,  $wR_2 = 0.2529$  based upon  $I > 2\sigma(I)$  and  $\text{GOF} = 1.053$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula C<sub>66</sub>H<sub>98</sub>Cr<sub>2</sub>N<sub>10</sub>O<sub>2</sub>, space group P -1,  $a = 12.5550(2)$  Å,  $b = 15.3520(2)$  Å,  $c = 20.1740(4)$  Å,  $\alpha = 75.3030(10)^\circ$ ,  $\beta = 74.1560(10)^\circ$ ,  $\gamma = 67.1920(10)^\circ$ ,  $V = 3399.93(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.367$  mm<sup>-1</sup>,  $\rho(\text{calc}) = 1.140$  g/cm<sup>3</sup>,  $F(000) = 1256$ ,  $R_1$  (based on  $F$ ) = 0.1157,  $wR_2$  (based on  $F^2$ ) = 0.2796.

#### **X-ray Crystal structure of V(NSiMe<sub>3</sub>)<sub>2</sub>(Nacnac) (10), CCDC-764152**

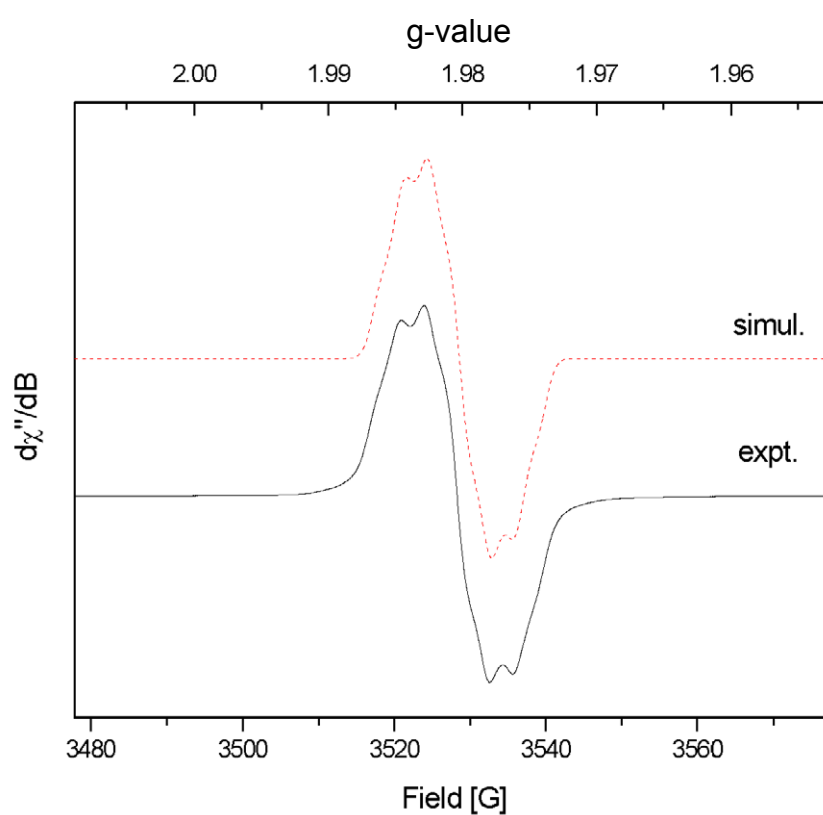
Reddish orange of **10** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.20 x 0.13 x 0.08 mm<sup>3</sup> was selected and mounted with wax on the end of a glass fiber. A total of 22517 reflections ( $-21 \leq h \leq 21$ ,  $-12 \leq k \leq 12$ ,  $-25 \leq l \leq 24$ ) were collected at 200 (2) K in the  $\theta$  range 2.24° to 25.33°, of which 6905 ( $R_{\text{int}} = 0.0860$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups C(13) and C(17) attached to the sp<sup>2</sup> hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density

were 0.841 and  $-0.687 \text{ e}\cdot\text{\AA}^{-3}$ , respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 1.0066 and 0.9142, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0747$ ,  $wR_2 = 0.1789$  based upon  $I > 2\sigma(I)$  and  $\text{GOF} = 1.045$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $\text{C}_{35}\text{H}_{59}\text{N}_4\text{Si}_2\text{V}$ , space group  $P 2_1/c$ ,  $a = 18.3009(6) \text{ \AA}$ ,  $b = 10.2668(3) \text{ \AA}$ ,  $c = 20.8551(7) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 96.0850(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3896.4(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 0.343 \text{ mm}^{-1}$ ,  $\rho(\text{calc}) = 1.045 \text{ g/cm}^{-3}$ ,  $F(000) = 1392$ ,  $R_1$  (based on  $F$ ) = 0.1308,  $wR_2$  (based on  $F^2$ ) = 0.2253.

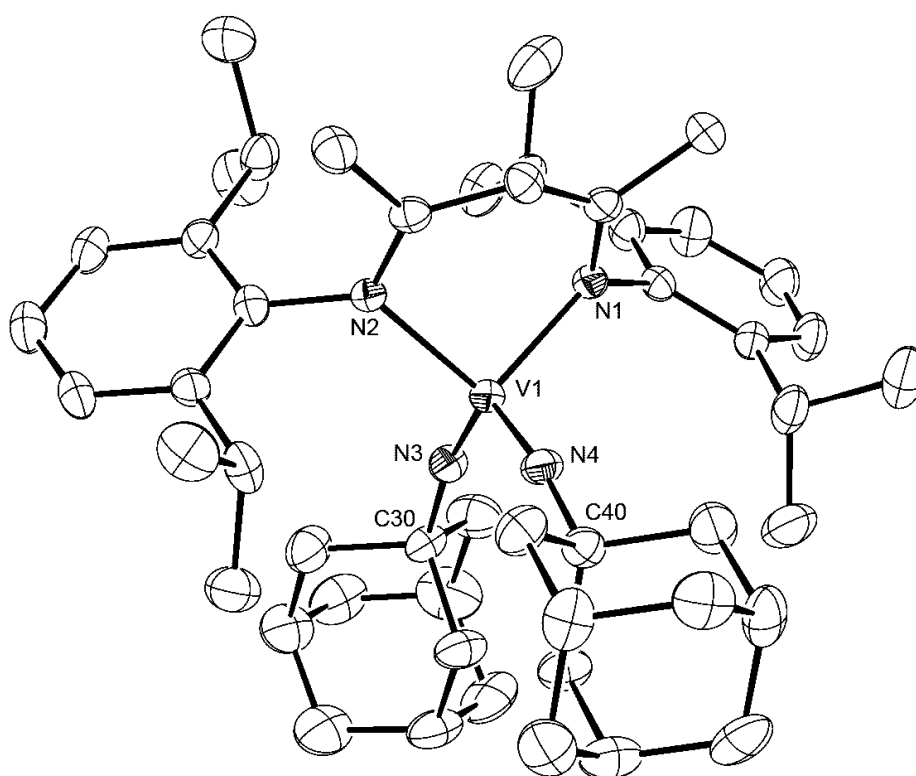
### X-ray Crystal structure of

### **V(N(TMS)(N-Dipp)[N(TMS)C(CH<sub>3</sub>)CHC(CH<sub>3</sub>)N(Dipp)] (Dipp = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (11), CCDC-764153**

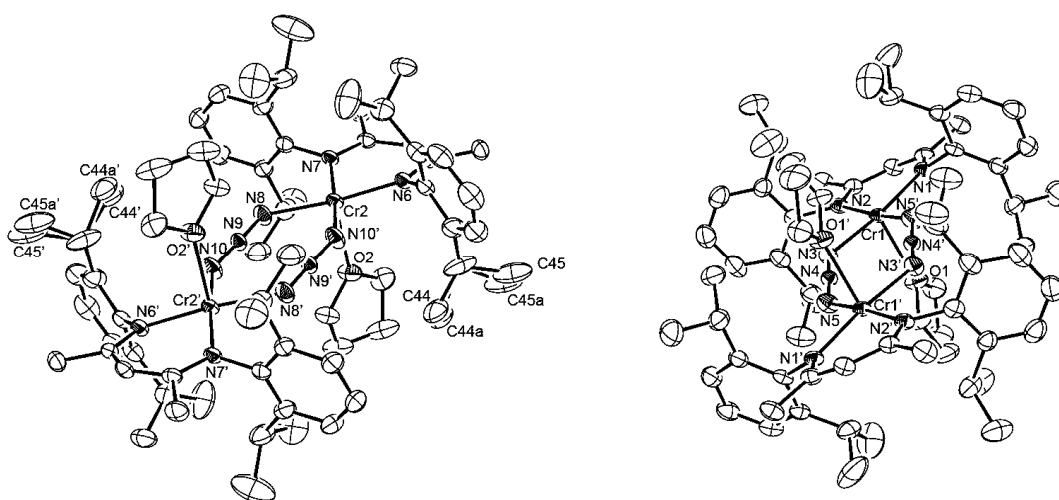
Red crystals of **11** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions  $0.28 \times 0.25 \times 0.2 \text{ mm}^3$  was selected and mounted with wax on the end of a glass fiber. A total of 34322 reflections ( $-14 \leq h \leq 14$ ,  $-23 \leq k \leq 23$ ,  $-19 \leq l \leq 19$ ) were collected at 200 (2) K in the  $\theta$  range  $2.10^\circ$  to  $25.35^\circ$ , of which 7027 ( $R_{\text{int}} = 0.1146$ ) were unique. The structure was solved using direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using HFIX 13 (for methine groups), HFIX 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups C(4) and C(8) attached to the  $\text{sp}^2$  hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 0.474 and  $-0.633 \text{ e}\cdot\text{\AA}^{-3}$ , respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 0.9822 and 0.8545, respectively. The least squares refinement converged normally with residuals  $R_1 = 0.0819$ ,  $wR_2 = 0.1764$  based upon  $I > 2\sigma(I)$  and  $\text{GOF} = 1.098$  based upon  $F^2$ . No extinction coefficient was applied to the refinement. Crystal and refinement data: formula  $\text{C}_{35}\text{H}_{59}\text{N}_4\text{Si}_2\text{V}$ , space group  $P 2_1/n$ ,  $a = 12.2715(3) \text{ \AA}$ ,  $b = 19.3946(3) \text{ \AA}$ ,  $c = 16.4428(5) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 100.0740(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3853.07(18) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu = 0.346 \text{ mm}^{-1}$ ,  $\rho(\text{calc}) = 1.108 \text{ g/cm}^{-3}$ ,  $F(000) = 1392$ ,  $R_1$  (based on  $F$ ) = 0.1358,  $wR_2$  (based on  $F^2$ ) = 0.2081.



**Figure S1.** X-band EPR spectrum of **4** in THF at 300 K. Experimental conditions: microwave frequency,  $\nu = 9.779$  GHz; power, 19.971 mW; modulation amplitude, 1.60 G. Simulated parameters;  $g_{\text{iso}} = 1.98036$ ;  $A_{\text{iso}}[^{53}\text{Cr} (9.54\%)] = 5.0$  G;  $A_{\text{iso}}[^{14}\text{N} (99.63\%)] = 3.3$  G;  $A_{\text{iso}}[^{14}\text{N} (99.63\%)] = 3.3$  G;  $A_{\text{iso}}[^{14}\text{N} (99.63\%)] = 1.9$  G;  $A_{\text{iso}}[^{14}\text{N} (99.63\%)] = 1.3$  G; line width 2.4 G.



**Figure S2.** The solid state molecular structure of **7**, with thermal ellipsoids set at 35% probability and all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): V(1)-N(1), 2.001(4); V(1)-N(2), 2.010(4); V(1)-N(3), 1.666(4); V(1)-N(4), 1.697(4); N(1)-V(1)-N(2), 96.51(16); N(2)-V(1)-N(3), 108.99(17); N(3)-V(1)-N(2), 111.92(18); N(4)-V(1)-N(1), 108.77(18); N(3)-V(1)-N(1), 110.09(18); N(3)-V(1)-N(4), 118.3(2); C(40)-N(4)-V(1), 170.6(4); C(30)-N(3)-V(1), 164.6(4).



**Figure S3.** Two independent molecules of **9** crystallize in an asymmetric unit, and each lies about an inversion centre in the crystal. Displacement ellipsoids of the molecular structures with an intrinsic inversion centre are shown at 35% probability. One of the  $i$ Pr substituents of the 2,6- $i$ Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> group on N6' displays two disorder methyl carbons C(44') and C(45'), and they are modeled with a restraint SADI 0.005.