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Supporting Information

For

Ligand-Controlled Synthesis of Vanadium(I) *β*-Diketiminates and Their Catalysis in Cyclotrimerization of Alkynes

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X-ray Crystal Structure of $[V\{\mu\text{-}(\eta^6\text{-}2,6\text{-}Me_2C_6H_3\text{-}N)C(Me)CHC(Me)C(N\text{-}2,6\text{-}Me_2C_6H_3)\}]_2$ (2), CCDC-788574

Dark brown crystals of **2** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.44 x 0.32 x 0.14 mm^3 was selected and mounted with wax on the end of a glass fiber. A total of 21437 reflections ($-11 \leqq h \leqq 11$, $-13 \leqq k \leqq 13$, $-20 \leqq l \leqq 20$) were collected at 200 (2) K in the θ range 2.21° to 25.01°, of which 3221 (Rint = 0.0680) 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 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands) and HFIX 137 (for the methyl groups attached to the sp^2 hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 0.677 and –0.645 $e \cdot Å^{-3}$, respectively. An empirical absorption correction

(multi-scan) was applied with maximum and minimum transmissions equal to 0.9251 and 0.7745, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0508$, $wR_2 = 0.1468$ based upon $I > 2\sigma(I)$ and GOF = 1.078 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{42}H_{50}N_4V_2$, space group P $2_1/n$, a = 9.9620(2) Å, b = 11.0806(2) Å, c = 16.8565(4) Å, β = 99.8910(10)°, V = 1833.05(7) $Å^3$, Z = 2, μ = 0.545 mm^{-1}, ρ(calc) = 1.291 g/cm^{-3}, F(000) = 752, R_1 (based on F) = 0.0680, wR_2 (based on F^2) = 0.1636.

X-ray Crystal Structure of [V{μ-(η^6-2,6-$Et_2C_6H_3$-N)C(Me)CHC(Me)C(N-2,6-$Et_2C_6H_3$)}]$_2$ (3), CCDC-788575

Dark brown crystals of **3** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.40 x 0.30 x 0.20 mm^3 was selected and mounted with wax on the end of a glass fiber. A total of 26211 reflections ($-13 \leqq h \leqq 13$, $-15 \leqq k \leqq 15$, $-16 \leqq l \leqq 16$) were collected at 200 (2) K in the θ range 2.07° to 25.09°, of which 7720 ($R_{int} = 0.0707$) 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 23 (for methylene groups), HFIX 33 (for methyl groups), HFIX 43 (for phenyl rings and Nacnac ligands), and HFIX 137 (for the methyl groups attached to the sp^2 hybridized carbons), and their orientation may not be totally reliable. The residual peak and hole electron density were 0.493 and –0.800 $e \cdot Å^{-3}$, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 0.9158 and 0.7981, respectively. The least squares refinement converged normally with residuals $R_1 = 0.0534$, $wR_2 = 0.1322$ based upon $I > 2\sigma(I)$ and GOF = 1.063 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{50}H_{66}N_4V_2$, space group P-1, a = 11.7457(3) Å, b = 13.2452(3) Å, c = 14.0750(4) Å, α = 92.5130(10)°, β = 91.6470(10)°, γ = 91.8330(10)°, V = 2185.48(10) $Å^3$, Z = 2, μ = 0.466 mm^{-1}, ρ(calc.) = 1.254 g/cm^{-3}, F(000) = 880, R_1 (based on F) = 0.0821, wR_2 (based on F^2) = 0.1501.

X-ray Crystal Structure of [V{μ-(η^6-9-anthracenyl-N)C(Me)CHC(Me)C(N-9-anthracenyl)}]$_2$ (4), CCDC-788576

Black crystals of **4** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.28 x 0.25 x 0.04 mm^3 was selected and

mounted with wax on the end of a glass fiber. A total of 37278 reflections (–29 ≦ h ≦ 27, –10 ≦ k ≦ 11, –29 ≦ l ≦ 30) were collected at 200 (2) K in the θ range 1.95° to 25.08°, of which 9846 (R_{int} = 0.1006) 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 33 (for methyl groups), and HFIX 43 (for phenyl rings and Nacnac ligands), and their orientation may not be totally reliable. The residual peak and hole electron density were 1.095 and –0.508 e·Å^{-3}, respectively. An empirical absorption correction (sphere) was applied with maximum and minimum transmissions equal to 0.9847 and 0.8997, respectively. The least squares refinement converged normally with residuals R_1 = 0.0714, wR_2 = 0.1662 based upon I > 2σ(I) and GOF = 1.012 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{72}H_{64}N_4V_2$, space group P 2/a, a = 24.8878(12) Å, b = 9.5634(5) Å, c = 25.2169(12) Å, α = 90°, β = 112.559(2)°, γ = 90°, V = 5542.7(5) Å^3, Z = 4, μ = 0.386 mm^{-1}, ρ(calc) = 1.303 g/cm^{-3}, F(000) = 2280, R_1 (based on F) = 0.1683, wR_2 (based on F^2) = 0.2118.

X-ray Crystal Structure of [η^4-2,6-^{i}Pr$_2$C$_6$H$_3$N(C$_6$H$_5$)CCHC(C$_6$H$_5$)]V(N-^{i}Pr$_2$C$_6$H$_3$)(OEt$_2$)] (5), CCDC-788577

Brown-green crystals of **5** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.55 x 0.40 x 0.30 mm^3 was selected and mounted with wax on the end of a glass fiber. A total of 27671 reflections (–12 ≦ h ≦ 14, –18 ≦ k ≦ 18, –17 ≦ l ≦ 23) were collected at 200 (2) K in the θ range 1.68° to 25.03°, of which 6603 (R_{int} = 0.0363) 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 attached to the sp^2 hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 0.830 and –0.458 e·Å^{-3}, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 0.9159 and 0.8532, respectively. The least squares refinement converged normally with residuals R_1 = 0.0590, wR_2 = 0.1472 based upon I > 2σ(I) and GOF = 1.016 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{43}H_{55}$

N_2OV, space group $P2_1/c$, a = 12.5137(3) Å, b = 15.6445(3) Å, c = 19.3631(4) Å, α = 90°, β = 97.6610(10)°, γ = 90°, V = 3756.89(14) $Å^3$, Z = 4, μ = 0.298 mm^{-1}, ρ(calc) = 1.179 g/cm^{-3}, F(000) = 1432, R_1 (based on F) = 0.0749, wR_2 (based on F^2) = 0.1568.

X-ray Crystal Structure of $(C_6H_5S)_2V[HC(C(Me)NC_6H_3\text{-}2,6\text{-}^iPr_2)_2]$ (7), CCDC-788578

Green crystals of **6** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.75 x 0.75 x 0.45 mm^3 was selected and mounted with wax on the end of a glass fiber. A total of 29685 reflections (−21 ≦ h ≦ 20, −14 ≦ k ≦ 14, −22 ≦ l ≦ 22) were collected at 200 (2) K in the θ range 2.04° to 25.33°, of which 6981 (Rint = 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. The 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 attached to the sp^2 hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 0.806 and –0.842 $e·Å^{-3}$, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 1.0594 and 0.6179, respectively. The least squares refinement converged normally with residuals R_1 = 0.0593, wR_2 = 0.1498 based upon I > 2σ(I) and GOF = 1.093 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{41}H_{51}N_2S_2V$, space group $P2_1/a$, a = 18.0540(3) Å, b = 12.1652(2) Å, c = 18.3858(3) Å, α = 90°, β = 108.0990(10)°, γ = 90°, V = 3838.28(11) $Å^3$, Z = 4, μ = 0.397 mm^{-1}, ρ(calc) = 1.189 g/cm^{-3}, F(000) = 1464, R_1 (based on F) = 0.0769, wR_2 (based on F^2) = 0.1712.

X-ray Crystal Structure of $(\eta^6\text{-}1,3,5\text{-}Ph_3C_6H_3)V[HC(C(Me)NC_6H_3\text{-}2,6\text{-}^iPr_2)_2]$ (8), CCDC-788579

Orange crystals of **7** were coated with Paratone N oil and placed on a microscope slide. A crystal of approximate dimensions 0.38 x 0.11 x 0.05 mm^3 was selected and mounted with wax on the end of a glass fiber. A total of 24184 reflections (−15 ≦ h ≦ 15, −16 ≦ k ≦ 15, −16 ≦ l ≦ 16) were collected at 200 (2) K in the θ range 2.04° to

25.29°, of which 7409 (R_{int} = 0.1441) 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 attached to the sp^2 hybridized carbons) and their orientation may not be totally reliable. The residual peak and hole electron density were 0.477 and –0.579 $e \cdot Å^{-3}$, respectively. An empirical absorption correction (multi-scan) was applied with maximum and minimum transmissions equal to 1.0901 and 0.8433, respectively. The least squares refinement converged normally with residuals R_1 = 0.1177, wR_2 = 0.2258 based upon $I > 2\sigma(I)$ and GOF = 1.016 based upon F^2. No extinction coefficient was applied to the refinement. Crystal and refinement data: formula $C_{53}H_{59}N_2V$, space group P-1, a = 13.2728(11) Å, b = 13.3879(11) Å, c = 14.0552(12) Å, α = 98.915(3)°, β = 117.457(4)°, γ = 92.696(3)°, V = 2169.3(3) $Å^3$, Z = 2, μ = 0.266 mm^{-1}, ρ(calc) = 1.186 g/cm^{-3}, F(000) = 828, R_1 (based on F) = 0.2764, wR_2 (based on F^2) = 0.3050.