

Supporting Information

Structure and Reactivity of Chromium(VI) Alkylidenes.

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General Considerations. All manipulations were carried out with standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, toluene and tetrahydrofuran were dried by passing through activated alumina and degassed prior to use. THF- d_8 and C_6D_6 were purchased from Cambridge Isotopes Laboratory, dried with sodium and stored under vacuum over Na/K alloy. Grignard reagents, PPh_3 , $SiMe_4$ and cyclopentene were purchased from Sigma Aldrich. $SiMe_4$ and cyclopentene were dried with molecular sieves and stored in an inert atmosphere glove box. $(ArN)_2CrCl_2$ ($Ar = 2,6$ -diisopropylphenyl) and $(ArN)_2Cr(CH_2^tBu)_2$ were prepared according to literature procedures.¹ 1H NMR spectra were taken on a Bruker AVIII-400 spectrometer and were referenced to the residual protons of the solvent ($C_6D_6 = 7.16$ ppm, THF- $d_8 = 3.58$ ppm and 1.72 ppm).² ^{13}C NMR spectra were taken on a Bruker AVIII-400 spectrometer or Bruker AVIII600 spectrometer and were referenced to the residual ^{13}C of the solvent ($C_6D_6 = 128.06$ ppm, THF- $d_8 = 67.21$ ppm and 25.31 ppm).² FT-IR spectra were obtained using a Nicolet Magna-IR 560 spectrometer with a resolution of 4 cm^{-1} . UV-vis spectra were obtained using a SILVER-Nova-TEC-X2 equipped with SL1-LED, which was purchased from StellarNet Inc. X-ray crystallographic studies were conducted in the X-ray Crystallographic Laboratory at the University of Delaware. Elemental analyses were obtained from Robertson Microlit, Ledgewood, NJ. LIFDI-MS were obtained using a Waters GCT Premier high-resolution time-of-flight mass spectrometer by liquid injection field desorption ionization (LIFDI-MS).

X-ray Crystallography.

Crystals of **5**, and **8** were mounted onto plastic mesh using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) for **5**; and with Cu- $K\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$) focused with Goebel mirrors for **8**. Unit cell parameters were obtained from 60 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with $P2_12_12_1$ for **5**. The data set for **5** was treated as an inversion twin with a refined distribution ratio of 73/27. No symmetry higher than triclinic was observed for **8** and solution in the centrosymmetric space group option, $P-1$, yielded chemically reasonable and computationally stable results of refinement. The data sets were treated

with absorption corrections based on redundant multiscan data (see *Apex3*; Bruker AXS Inc.: Madison, WI 2015). The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .³

The chromium, nitrogen atoms and metallacyclobutane ligand in **8** were found disordered in two positions with a refined site occupancy ratio of 81/19. The chemically analogous atoms between the disordered contributions were treated with equal atomic displacement parameters. The minor component was treated with similar 1,2 and 1,3 atom distance restraints based on the major component geometry.

One pentane molecule of solvation was found disordered in the asymmetric unit of **5**, which was treated as diffused contributions but was included in the sum formula.⁴

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.

The CIFs have been deposited with the Cambridge Crystallographic Database Centre under depositary numbers **5**: 1831804, and **8**: 1831803.

Crystals of **3**, **4**, and **6** were mounted onto plastic mesh using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω , from three different sections of the Ewald sphere. The systematic absences in the diffraction data are consistent with *Pbcm* or *Pca2*₁ for **6**; and, uniquely, with *P2*₁*2*₁*2*₁ for **3**; and with *P2*₁/*n* for **4**. Only the non-centrosymmetric space group option, *Pca2*₁, yielded chemically reasonable and computationally stable results of refinement for **6**. The absolute structure parameter refined to nil for **3** and **6** indicating that the true hand of each data set has been determined.⁵ The data sets were treated with absorption corrections based on redundant multiscan data. The structures were solved using intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 .³

An isopropyl group was found disordered in two positions in **3** with a refined site occupancy ratio of 77/23 that was treated with equal atomic displacement parameters for analogous atoms between disordered contributions and similar 1,2 and 1,3 atom distance restraints.

A severely disordered solvent molecule, found in the asymmetric unit of **6** that was treated as diffused contributions, could not be assigned a reasonable identity and was ignored.⁴

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.

The CIFs have been deposited with the Cambridge Crystallographic Database Centre under depositary numbers **3**: 1831800; **4**: 1831801; and **6**: 1831802.

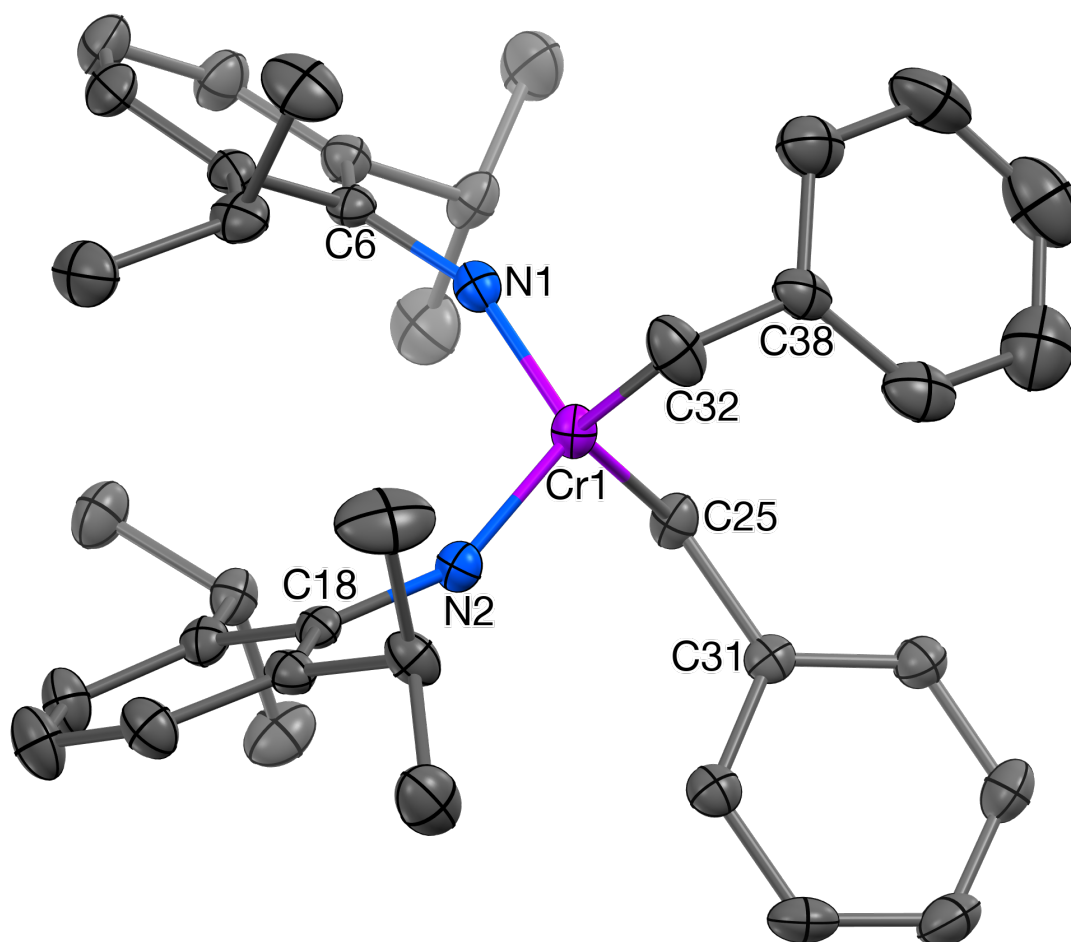


Figure S1. The molecular structure of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{Ph})_2$ (**3**); the synthesis of **3** has been reported,⁶ but its structure had not previously been determined. Selected interatomic distances (Å) and angles (°): Cr-N1 1.644(3), Cr-N2 1.653(3), Cr-C25 2.078(4), Cr-C32 2.044(4); N1-Cr-N2 110.51(14), N1-Cr-C25 103.47(15), N1-Cr-C32 104.32(18), N2-Cr-C25 103.99(16), N2-Cr-C32 105.54(16), C25-Cr-C32 128.51(17), Cr-C25-C31 117.0(2), Cr-C32-C38 90.4(3).

(ArN)₂Cr(CH₂SiMe₃)₂ (4):

(ArN)₂CrCl₂ (0.220 g, 0.465 mmol) was dissolved in 50 mL Et₂O giving a red solution. The solution was stored in freezer for 15 min before adding Grignard reagent. 2 equiv. of Me₃SiCH₂MgCl (0.93 mL, 0.930 mmol) were added into the pre-chilled (-30 °C) solution. The solution was stirred for 2 hrs., during which time the color changed to green. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract filtered through celite. The filtrate was concentrated to 4 mL then cooled to -30 °C overnight to yield green crystals of **4** (0.166 g, 62%)

Characterization:

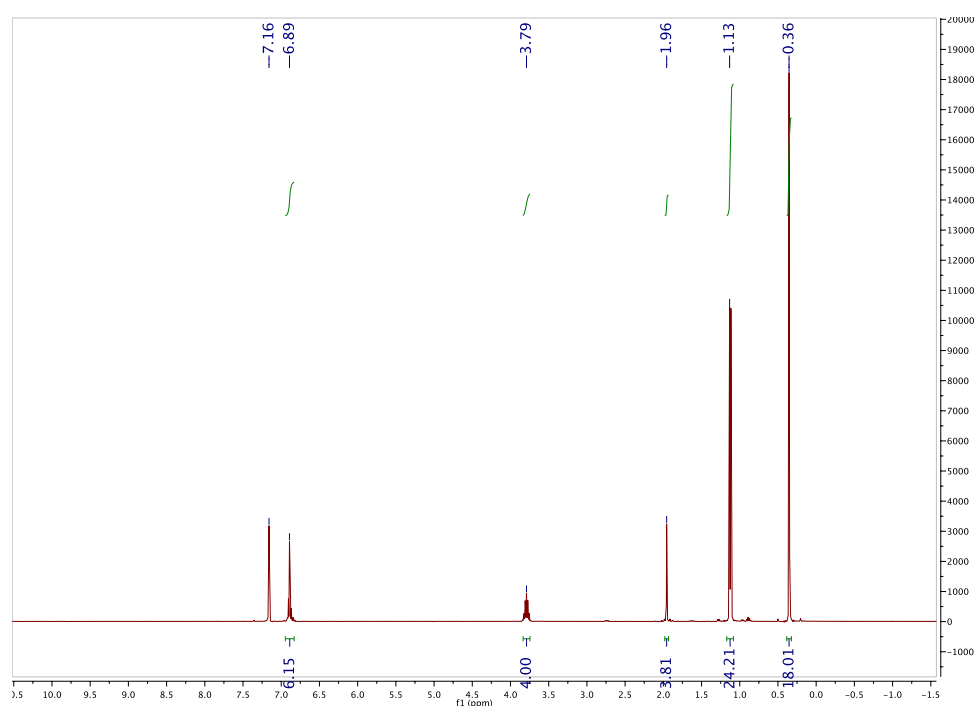


Figure S2. ¹H NMR spectrum (400 MHz, C₆D₆) of **4**: δ 6.89 (m, 6 H, ArN), 3.79 (sept, 4 H, CHMe₂), 1.96 (s, 4 H, CH₂SiMe₃), 1.12 (d, 24 H, CHMe₂), 0.35 (s, 18 H, CH₂SiMe₃) ppm.

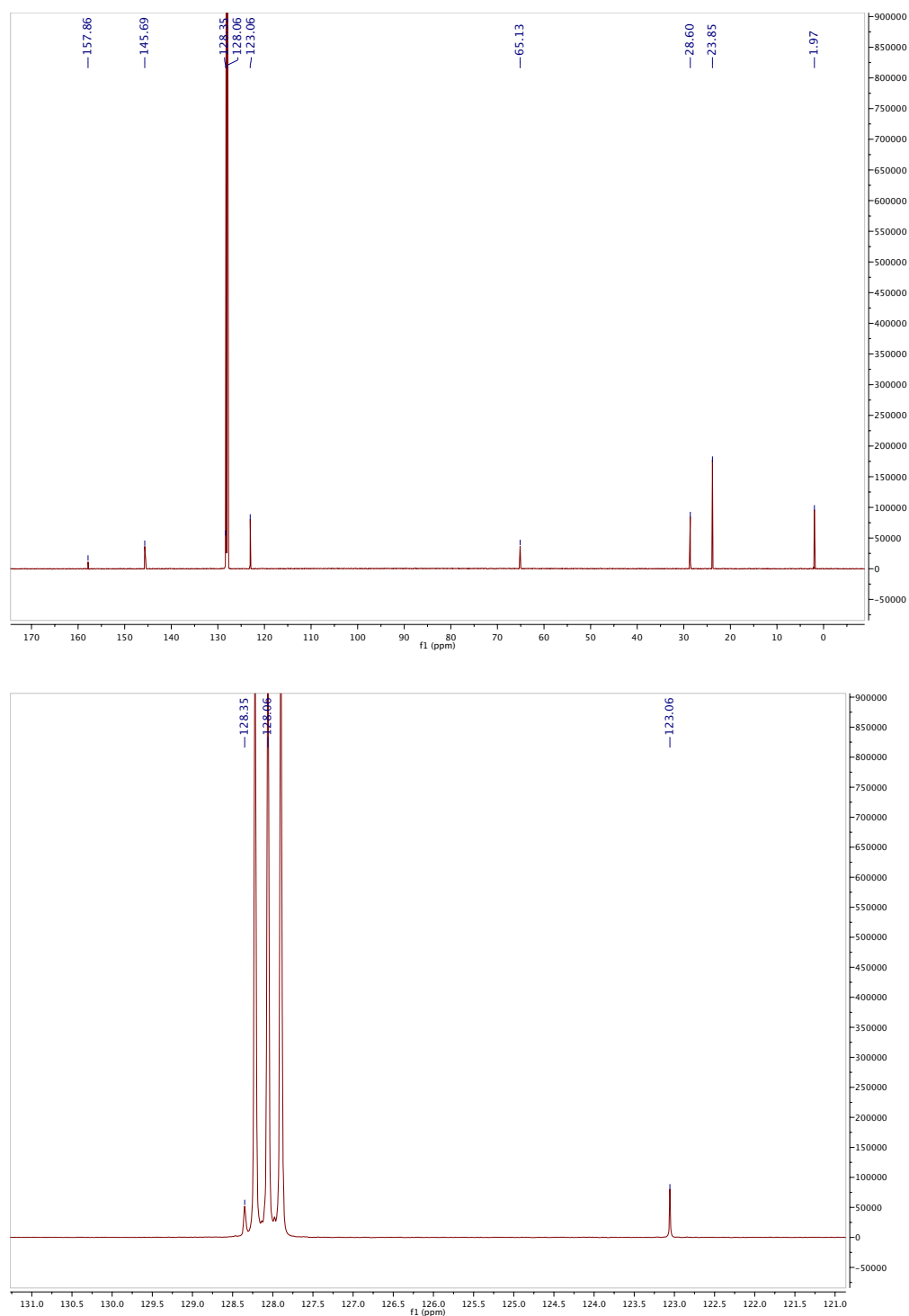


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (150 MHz, C_6D_6) of **4**: δ 157.86 (C_{ipso} of ArN), 145.69 (C_{ortho} of ArN), 128.35 (C_{para} of ArN), 123.06 (C_{meta} of ArN), 65.13 (CH_2SiMe_3), 28.60 (CHMe_2), 23.85 (CHMe_2), 1.97 (CH_2SiMe_3) ppm.

Elemental analysis of **4**: Calc'd for $\text{CrC}_{32}\text{H}_{56}\text{N}_2\text{Si}_2$: C 66.61, H 9.78, N 4.86. Found: C 66.57, H 9.70, N 4.80.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

34 formula(e) evaluated with 1 results within limits (up to 10 best isotopic matches for each mass)

Elements Used:

C: 32-32 H: 0-100 N: 0-100 Si: 2-2 Cr: 1-1

wpc 100317 ArN TMS 38 (0.634)

TOF MS FD+

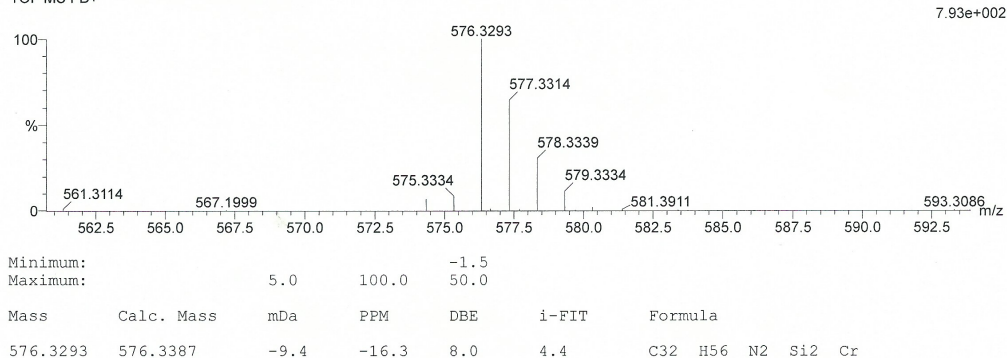


Figure S4. LIFDI – mass spectrum of **4**: m/z 576.3293 (Calcd. For M⁺: 576.3387)

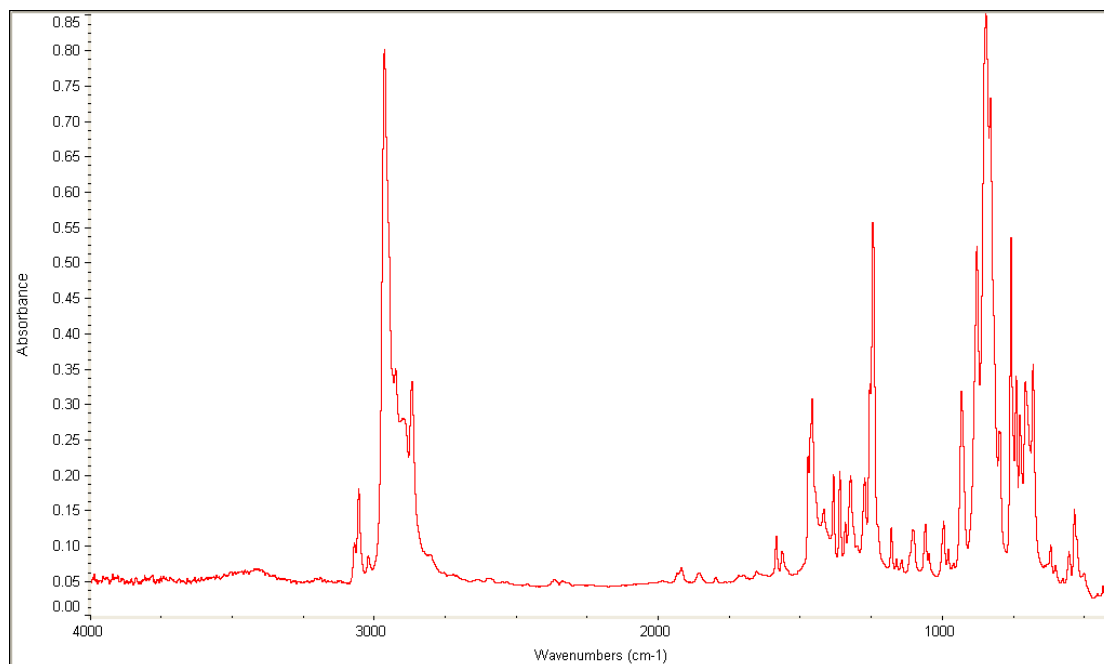


Figure S5. IR spectrum of **4** (KBr, cm⁻¹): 3054 (w), 2963 (s), 2867 (m), 1456 (w), 1382(w), 1359 (w), 1321 (w), 1273 (w), 1243 (m), 931 (w), 876 (m), 846 (s), 830 (s), 798 (w), 756 (m), 738 (w), 725 (w), 705 (w), 679 (w).

UV-vis spectrum of **4** (pentane): λ_{max} (ϵ) = 263 (4.876×10^4), 296 (4.270×10^4), 436 (8.049×10^3), 629 (6.809×10^3) nm (M⁻¹cm⁻¹).

M.P.: 154 °C

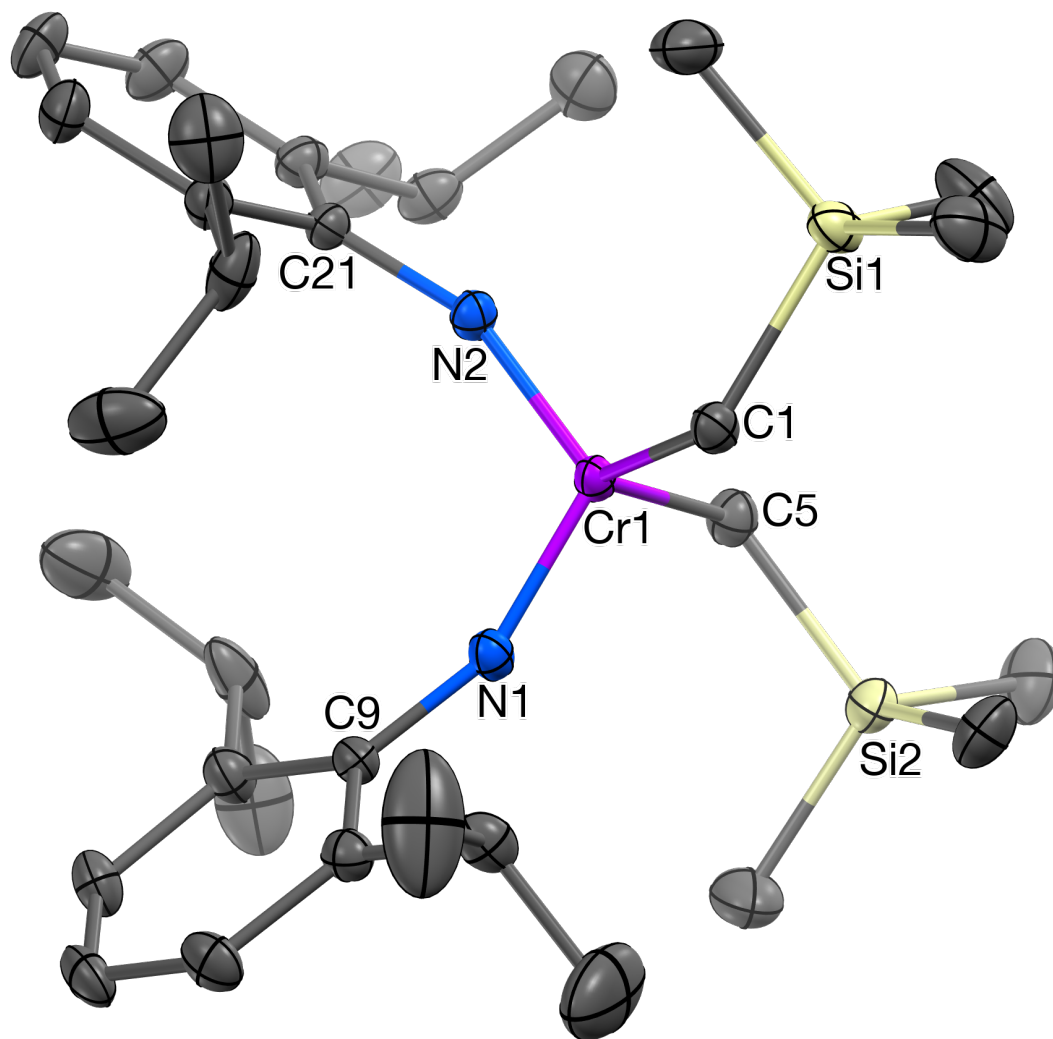


Figure S6. The molecular structure of $(\text{ArN})_2\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ (**4**); selected interatomic distances (Å) and angles ($^\circ$): Cr-N1 1.6496(15), Cr-N2 1.6522(15), Cr-C1 2.0182(18), Cr-C5 2.0113(19); N1-Cr-N2 113.85(7), N1-Cr-C1 106.74(7), N1-Cr-C5 104.84(8), N2-Cr-C1 106.03(8), N2-Cr-C5 106.89(8), C1-Cr-C5 118.82(8).

(ArN)₂Cr(=CHCMe₃)(PPh₃) (5):

(ArN)₂CrNp₂ (**2**, 0.200 g, 0.367 mmol) was dissolved in 40 mL THF giving a green solution. 1 equiv. of PPh₃ (0.096 g, 0.367 mmol) was added. The solution was stirred for 3 days at room temperature during which time the color changed to red. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract filtered through celite. The filtrate was concentrated to 3 mL then cooled to -30 °C overnight to yield red crystals of **5** (0.226 g, 84%)

Characterization:

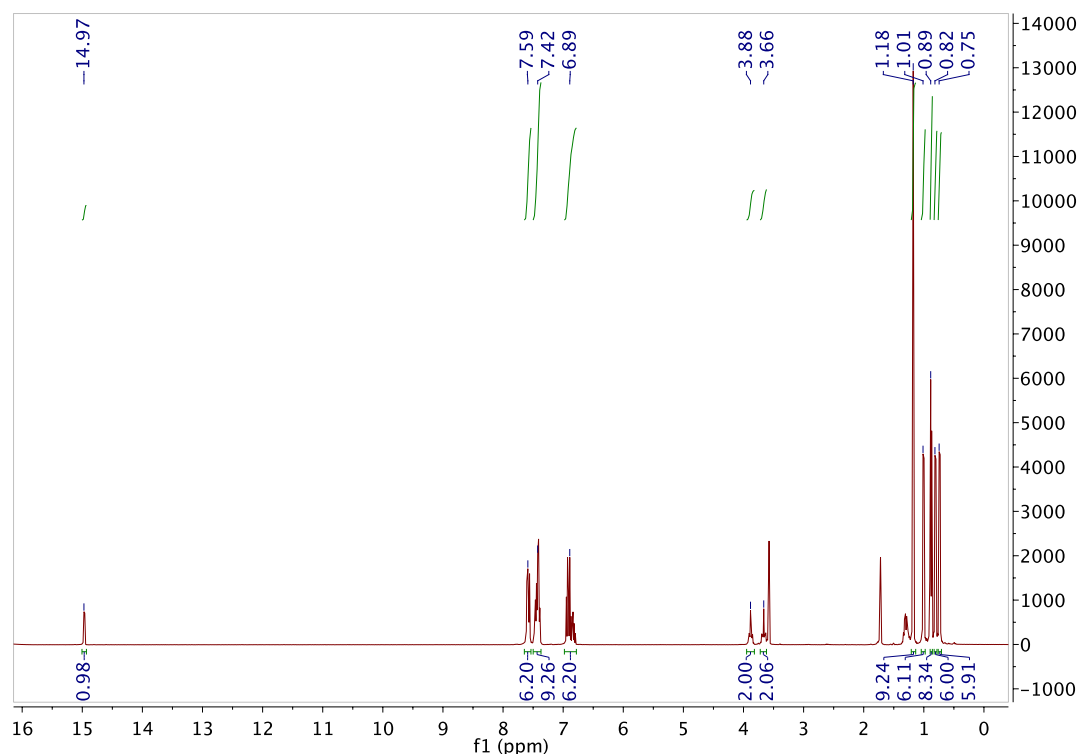


Figure S7. ¹H NMR spectrum (400 MHz, d₈-THF) of **5**: δ 14.97 (d, ³J_{PH} = 5.6 Hz, 1 H, CHCMe₃; ¹J_{CH} = 126.1 Hz), 7.59 (m, 6 H, PPh₃), 7.42 (m, 9 H, PPh₃), 6.89 (m, 6 H, ArN), 3.88 (sept, 2 H, CHMe₂), 3.66 (sept, 2 H, CHMe₂), 1.18 (s, 9 H, CHCMe₃), 1.00 (d, 6 H, CHMe₂), 0.88 (d, 6 H, CHMe₂), 0.81 (d, 6 H, CHMe₂), 0.74 (d, 6 H, CHMe₂) ppm.

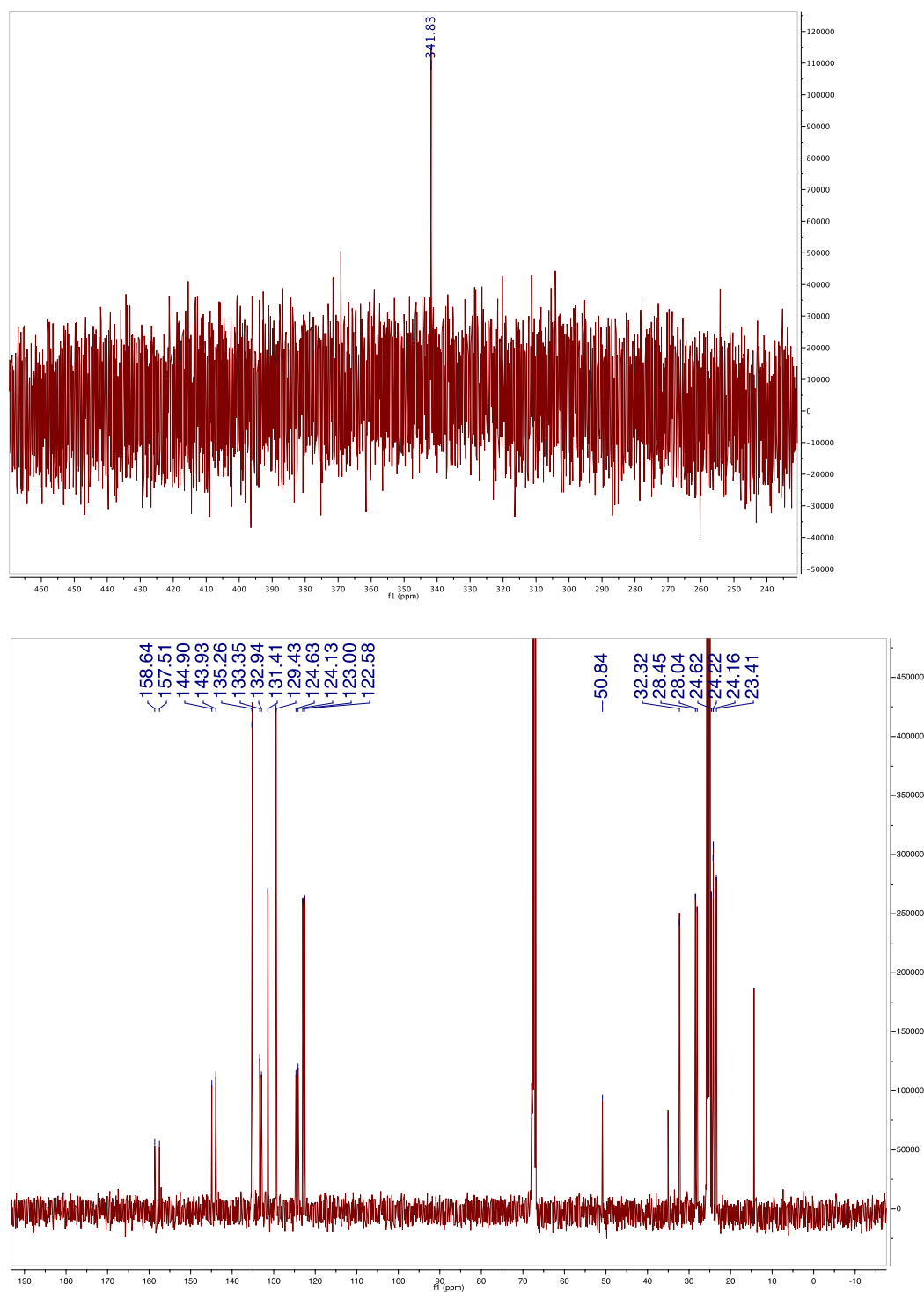


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, d8-THF) of **5**: δ 341.73 (d, $^2J_{\text{PC}} = 21.4$ Hz, CHCMe_3), 158.64 (C_{ipso} of ArN), 157.51 (C_{ipso} of ArN), 144.90 (C_{ortho} of ArN), 143.93 (C_{ortho} of ArN), 135.26 (C_{ortho} of PPh_3), 133.35 (C_{ipso} of PPh_3), 131.41 (C_{para} of PPh_3), 129.43 (C_{meta} of PPh_3), 124.63 (C_{para} of ArN), 124.13 (C_{para} of ArN), 123.00 (C_{meta} of ArN), 122.58 (C_{meta} of ArN), 50.84 (CHCMe_3), 32.32 (CHCMe_3), 28.45 (CHMe_2), 28.04 (CHMe_2), 24.62 (CHMe_2), 24.22 (CHMe_2), 24.16 (CHMe_2), 23.41 (CHMe_2) ppm.

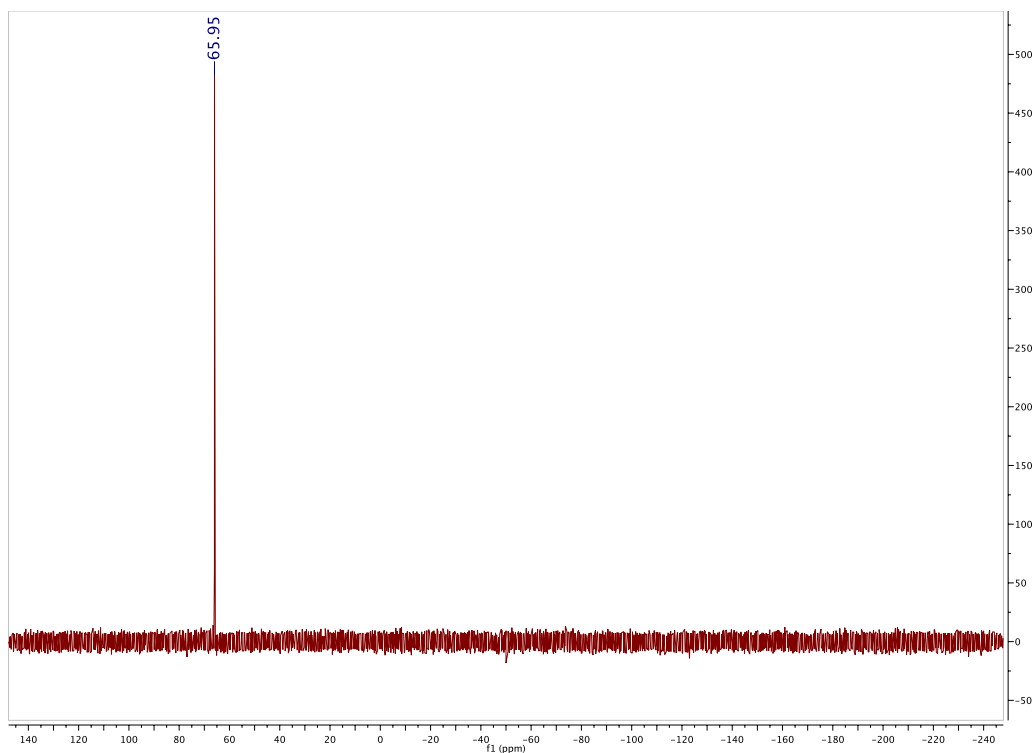


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, d8-THF) of **5**: δ 65.95 ppm.

Elemental analysis: Calc'd for $\text{CrC}_{47}\text{H}_{59}\text{N}_2\text{P}$: C 76.81, H 8.09, N 3.81. Found: C 77.30, H 8.63, N 4.21.

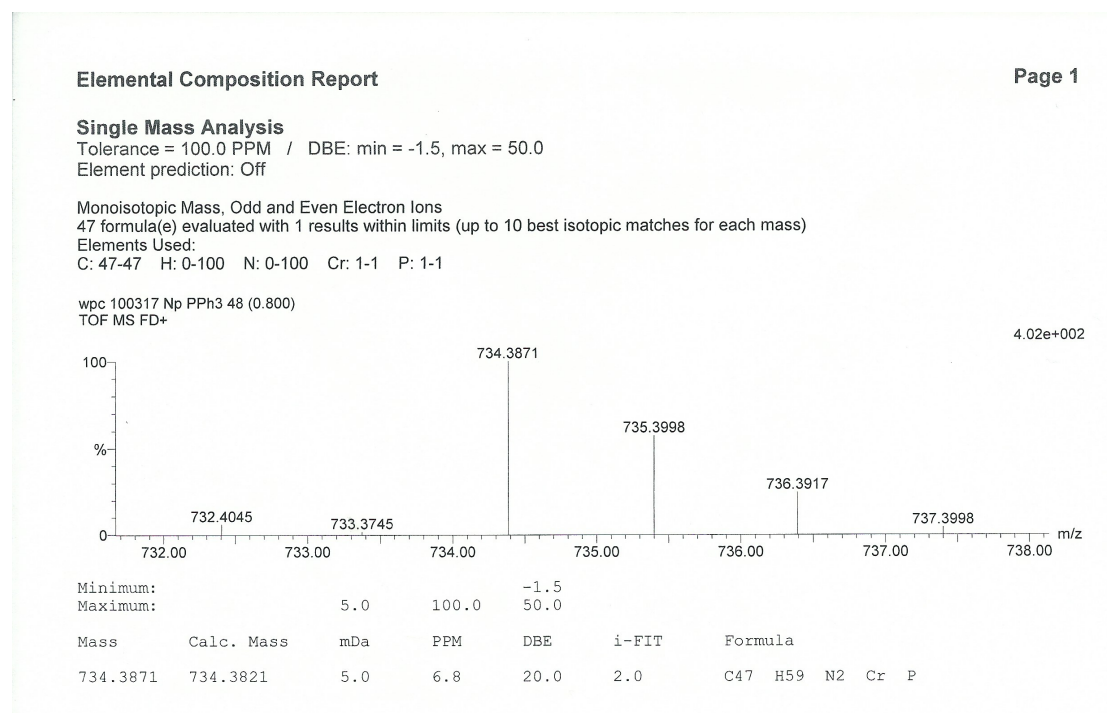


Figure S10. LIFDI mass spectrum of **5**: m/z 734.3871 (Calcd. For M^+ : 734.3822)

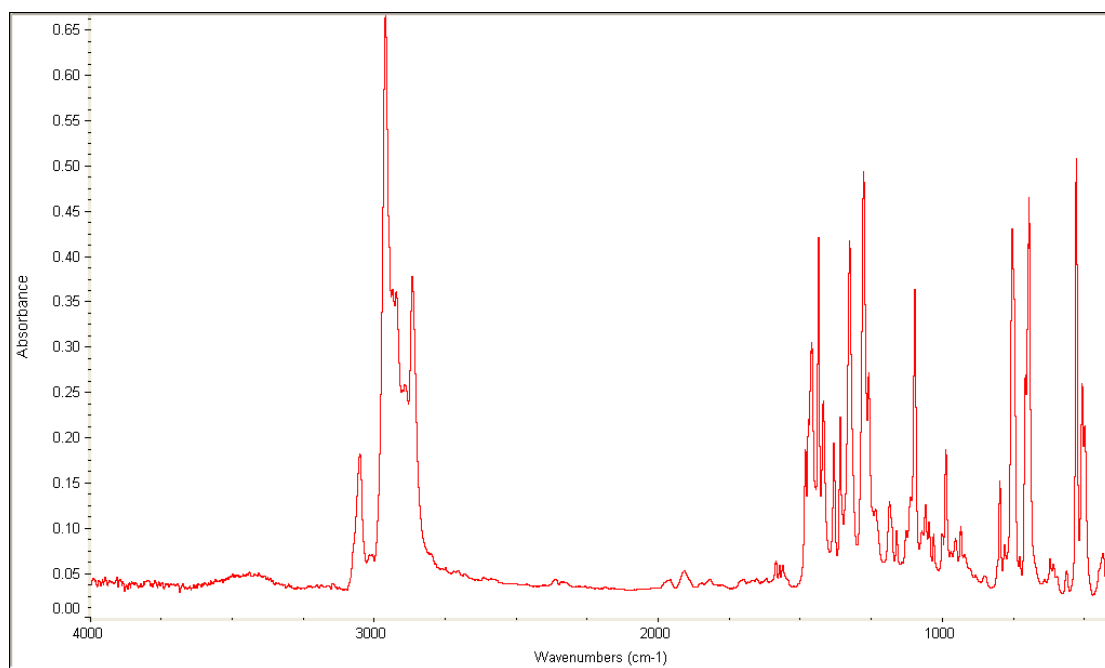


Figure S11. IR spectrum (KBr, cm^{-1}) of **5**: 3050 (w), 2959 (s), 2865 (m), 1480 (w), 1458 (w), 1435 (m), 1418 (w), 1380 (w), 1358 (w), 1324 (m), 1277 (m), 1258 (w), 1096 (m), 990 (w), 796 (w), 752 (m), 694 (m), 527 (m), 506 (w).

UV-vis (pentane): λ_{max} (ϵ) = 260 (4.312×10^4), 324 (2.139×10^4), 430 (7.643×10^3) nm ($\text{M}^{-1}\text{cm}^{-1}$).

M.P.: 222 °C

(ArN)₂Cr(=CHSiMe₃)(PPh₃) (6)

4 (0.174 g, 0.302 mmol) was dissolved in 20 mL THF giving a green solution. 1 equiv. of PPh₃ (0.079 g, 0.302 mmol) was added. The solution was transfer into an ampule, which then was degassed. The solution was stirred for 10 days at 80 °C during which time the color changed to red. The solvent was then removed in vacuum and the residue was extracted with pentane and the extract filtered through celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield red crystals of **6** (0.194 g, 86%)

Characterization:

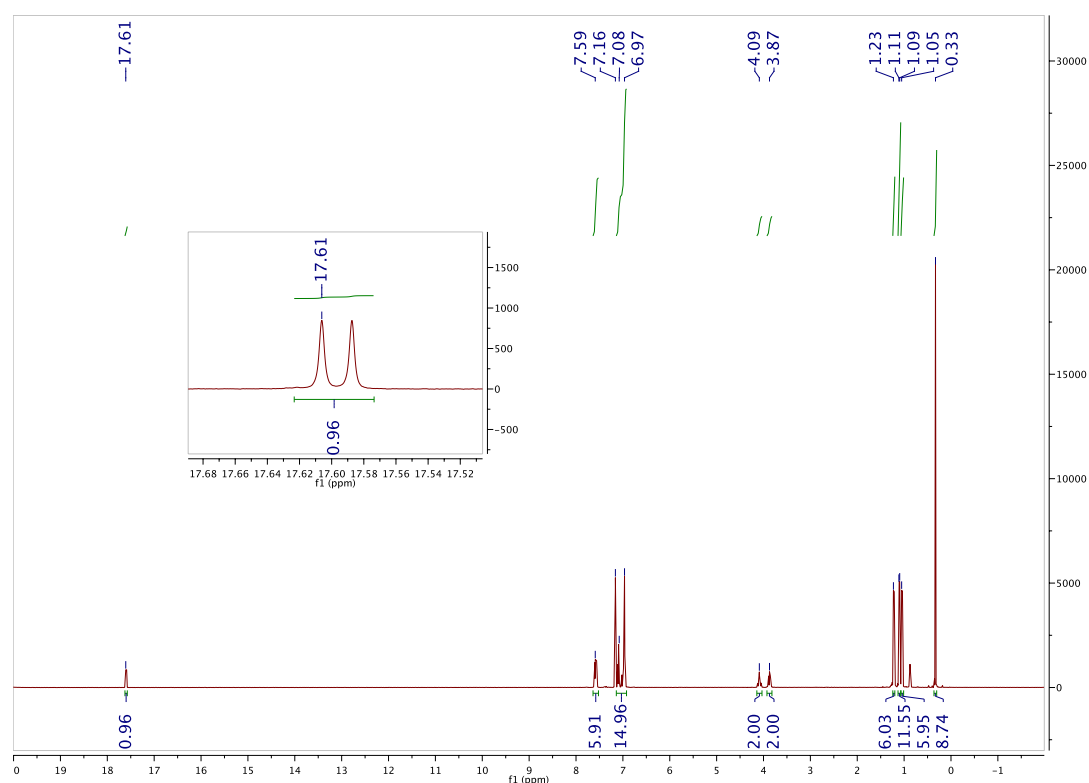


Figure S12. ¹H NMR spectrum (400 MHz, C₆D₆) of **6**: δ 17.60 (d, ³J_{PH} = 7.6 Hz, 1 H, CHSiMe₃; ¹J_{CH} = 119.9 Hz), 7.59 (m, 6 H, PPh₃), 7.08 (m, 9 H, PPh₃), 6.97 (m, 6 H, ArN), 4.09 (sept, 2 H, CHMe₂), 3.87 (sept, 2 H, CHMe₂), 1.22 (d, 6 H, CHMe₂), 1.11 (d, 6 H, CHMe₂), 1.10 (d, 6 H, CHMe₂), 1.04 (d, 6 H, CHMe₂), 0.33 (s, 9 H, CHSiMe₃) ppm.

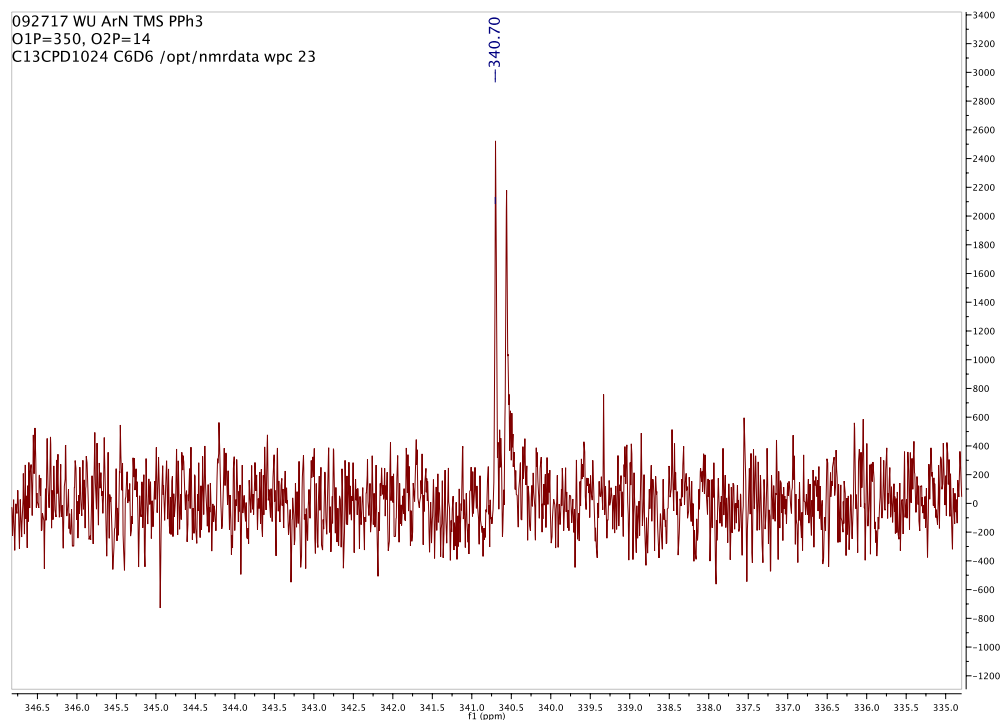


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (150 MHz, C_6D_6) of **6**: δ 340.63 (d, $^2J_{\text{PC}} = 21.0$ Hz, CHSiMe_3) ppm.

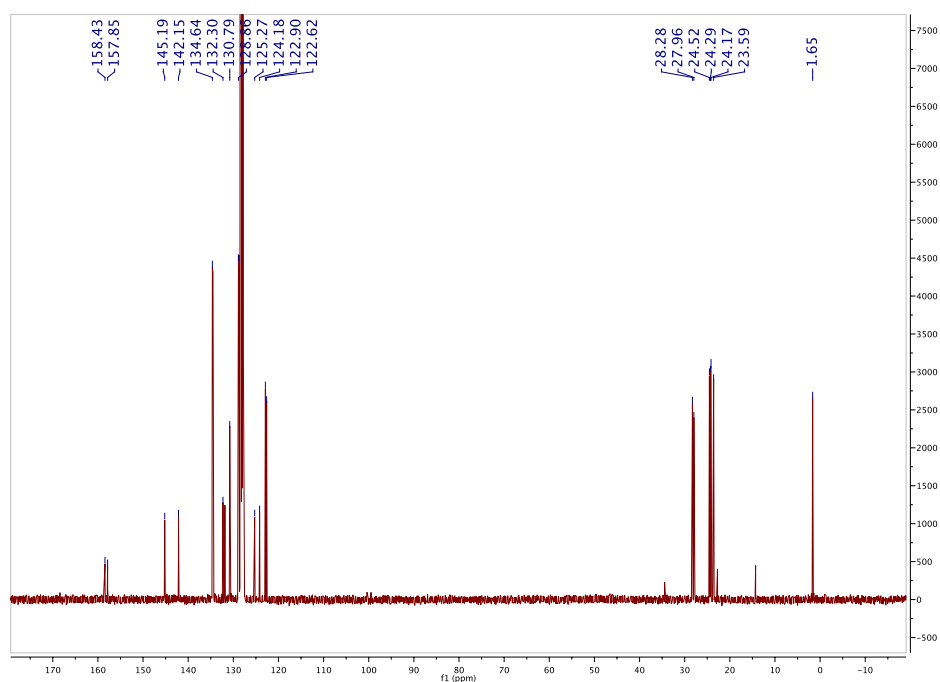


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, C_6D_6) of **6**: δ 158.43 (C_{ipso} of ArN), 157.85 (C_{ipso} of ArN), 145.19 (C_{ortho} of ArN), 142.15 (C_{ortho} of ArN), 134.64 (C_{ortho} of PPh₃), 132.30 (C_{ipso} of PPh₃), 130.79 (C_{para} of PPh₃), 128.86 (C_{meta} of PPh₃), 125.27 (C_{para} of ArN), 124.18 (C_{para} of ArN), 122.90 (C_{meta} of ArN), 122.62 (C_{meta} of ArN), 28.28 (CHMe_2), 27.96 (CHMe_2), 24.52 (CHMe_2), 24.29 (CHMe_2), 24.17 (CHMe_2), 23.59 (CHMe_2), 1.65 (CHSiMe_3) ppm.

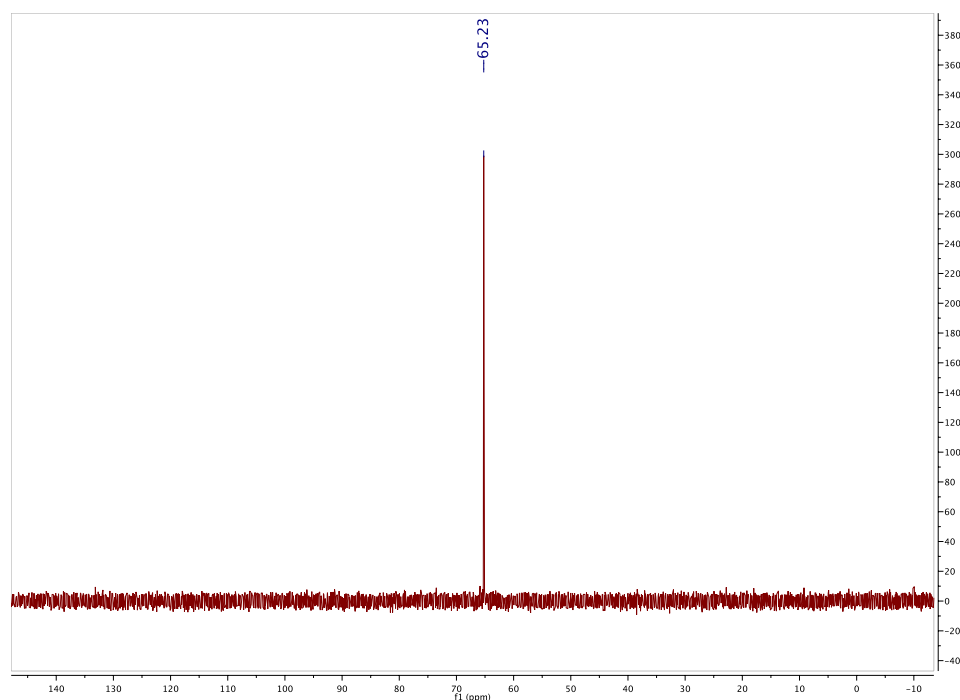


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, C_6D_6) of **6**: δ 65.23 ppm.

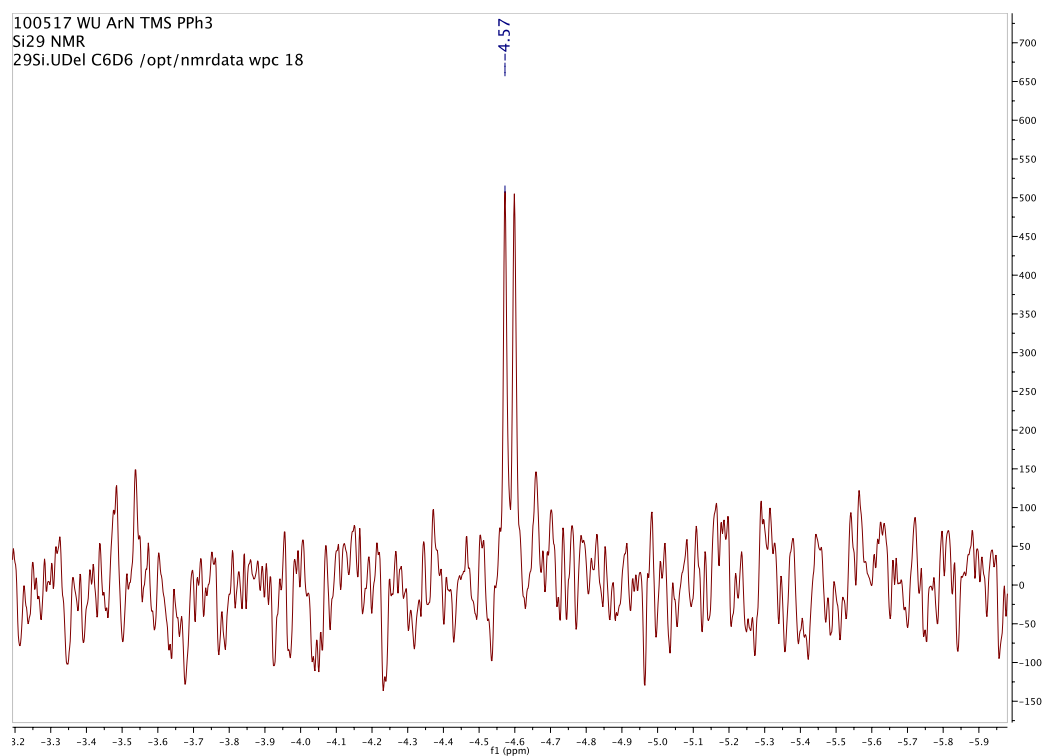


Figure S16. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (120 MHz, C_6D_6) of **6**: δ -4.59 ($^3J_{\text{SiP}} = 3.24$ Hz) ppm.

Elemental analysis: Calc'd for $\text{CrC}_{46}\text{H}_{59}\text{N}_2\text{PSi}$: C 73.56, H 7.92, N 3.73. Found: C 73.94, H 7.94, N 3.71.

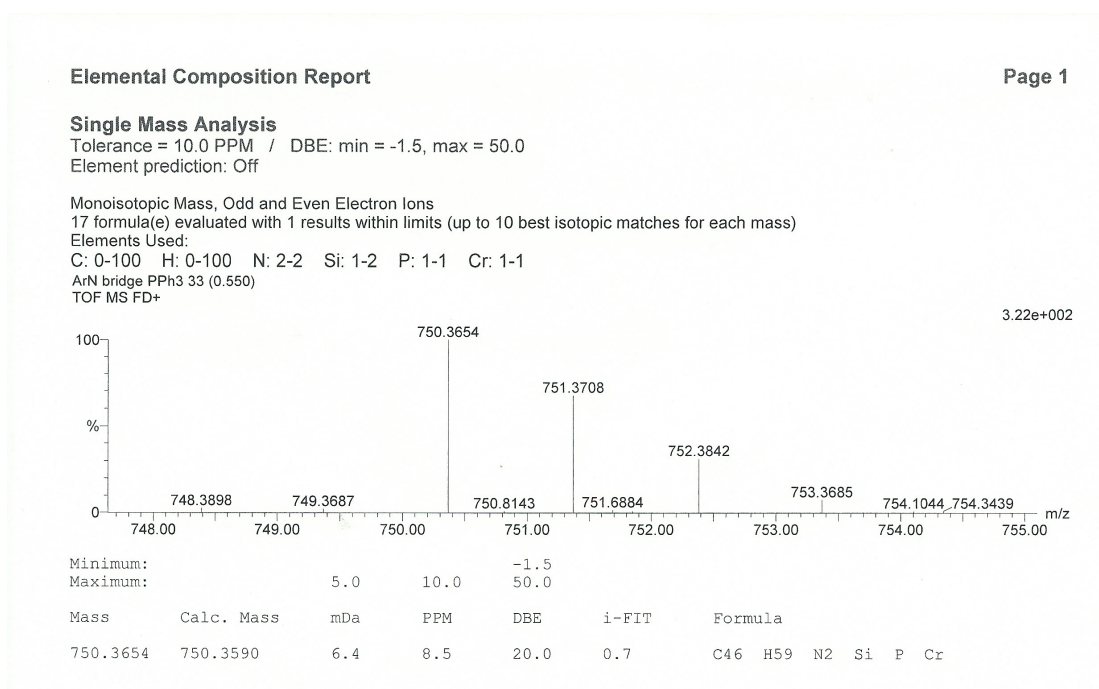


Figure S17. LIFDI mass spectrum of **6**: m/z 750.3654 (Calc'd. For M⁺: 750.3591)

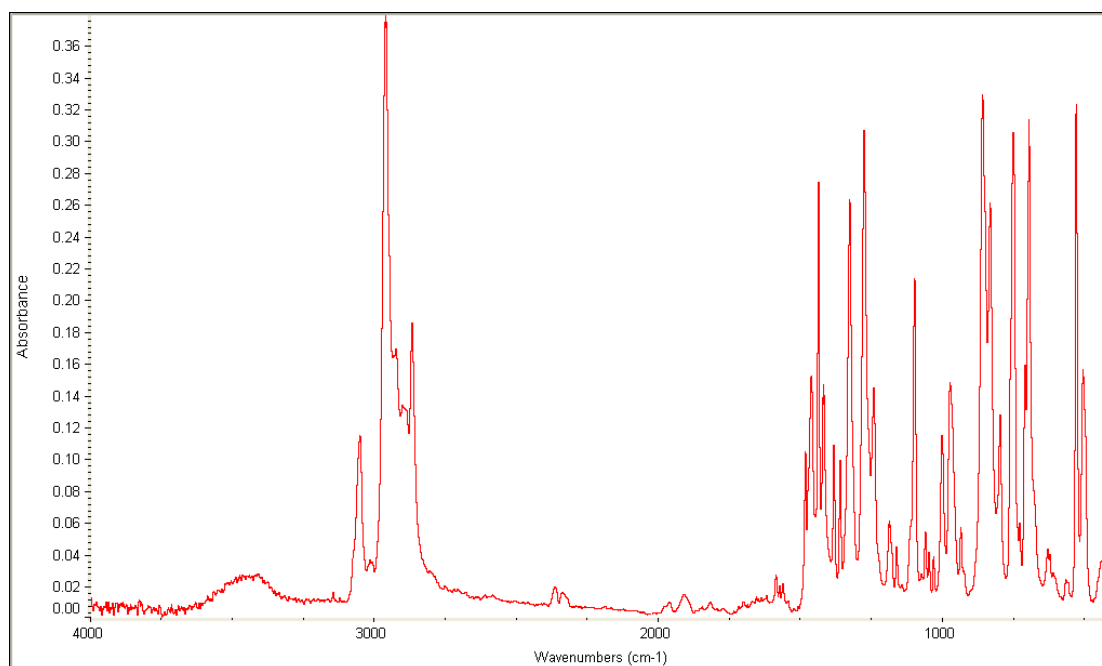


Figure S18. IR spectrum (KBr, cm⁻¹) of **6**: 3050 (w), 2959 (s), 2866 (w), 1480 (w), 1459 (w), 1435 (m), 1418 (w), 1380 (w), 1358 (w), 1324 (m), 1274 (m), 1240 (w), 1096 (m), 999 (w), 972 (w), 856 (s), 831 (m), 795 (w), 748 (m), 706 (w), 694 (m), 527 (m), 503 (w)

UV-vis spectrum of **6** (pentane): λ_{max} (ϵ) = 253 (7.379×10^4), 336.5 (2.626×10^4), 421 (8.254×10^3) nm(M⁻¹cm⁻¹).

M.P.: 204 °C

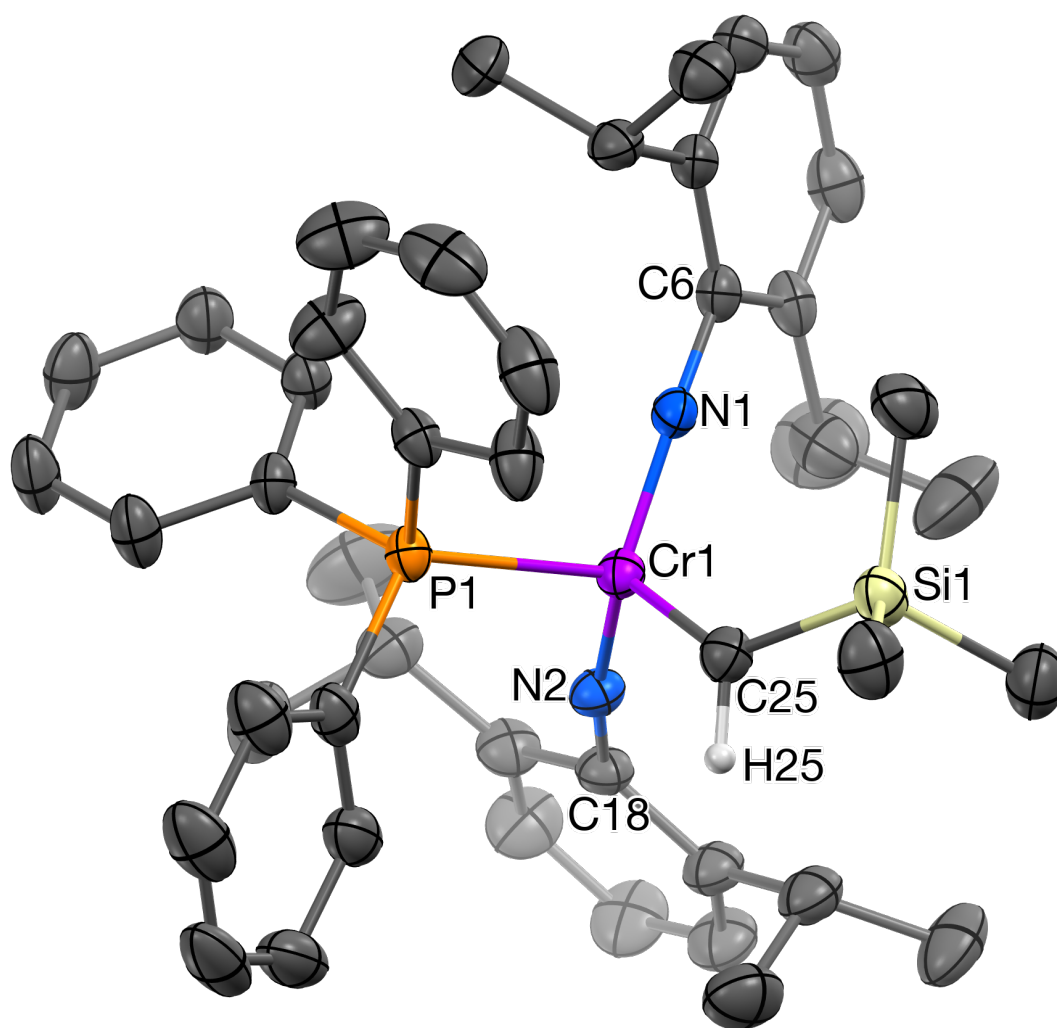


Figure S19. The molecular structure of $(\text{ArN})_2\text{Cr}(=\text{CHSiMe}_3)(\text{PPh}_3)$ (**6**); selected interatomic distances (Å) and angles (°): Cr-N1 1.668(3), Cr-N2 1.668(3), Cr-C25 1.843(4), Cr-P1 2.3503(10); N1-Cr-N2 122.60(14), N1-Cr-C25 111.40(16), N1-Cr-P1 106.92(9), N2-Cr-C25 107.29(16), N2-Cr-P1 106.46(11), P1-Cr-C25 99.64(12), Cr-C25-Si1 133.1(2)

(ArN)₂Cr(CH₂CMe₃)(CH₂SiMe₃) (7)

2 (0.123 g, 0.226 mmol) was dissolved in 20 mL SiMe₄, giving a green solution. The solution was stirred for 3 days at room temperature during which time no color change was observed. SiMe₄ was then removed in vacuum and the residue was extracted with pentane and the extract filtered through celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield green crystals of **7** (0.051 g, 40%)

Characterization:

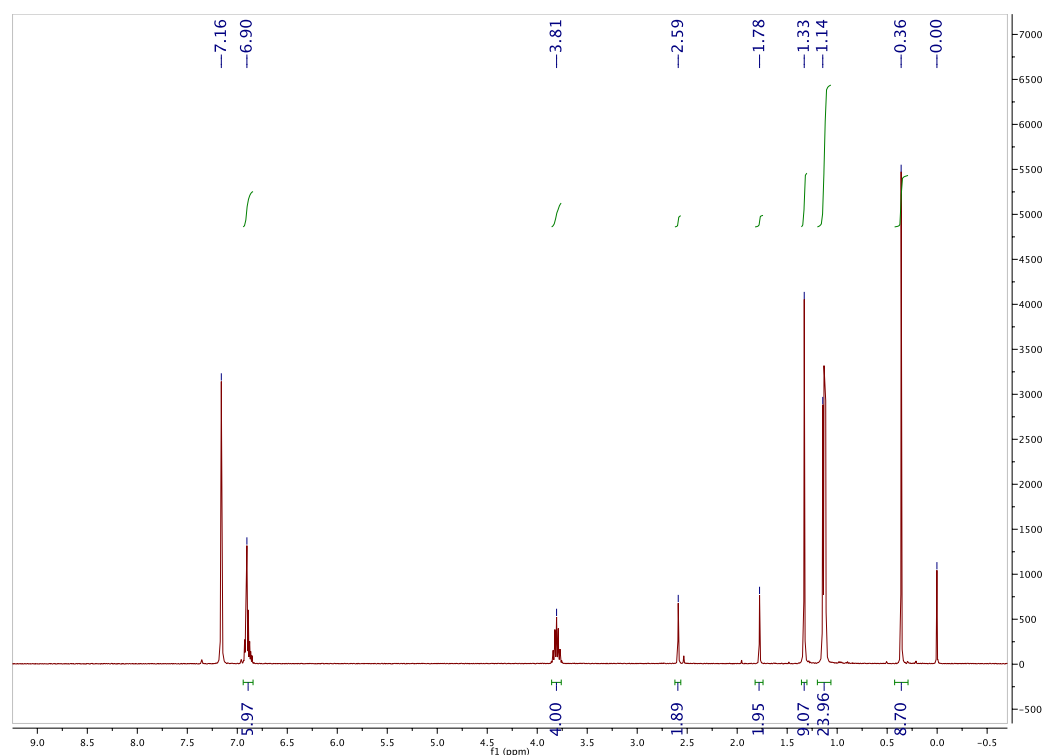


Figure S20. ¹H NMR spectrum (400 MHz, C₆D₆) of **7**: δ 6.90 (m, 6 H, ArN), 3.81 (sept, 4 H, CHMe₂), 2.59 (s, 2 H, CH₂CMe₃), 1.78 (s, 2 H, CH₂SiMe₃), 1.33 (s, 9 H, CH₂CMe₃), 1.14 (d, 12 H, CHMe₂), 1.12 (d, 12H, CHMe₂), 0.36 (s, 9H, CH₂SiMe₃) ppm.

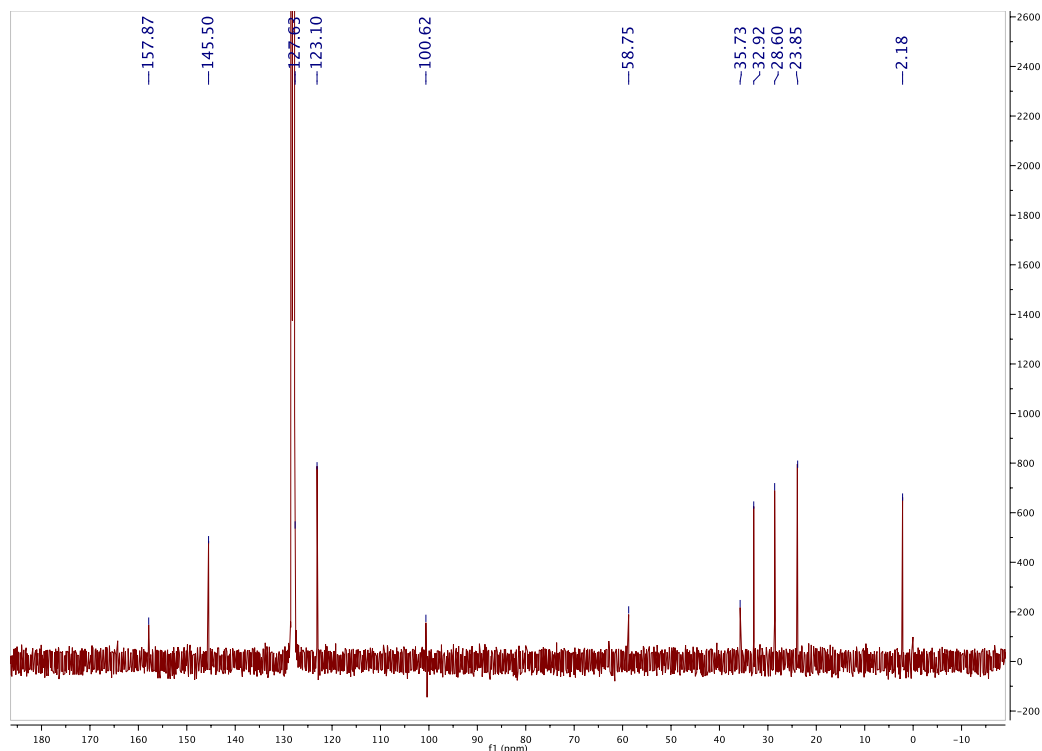


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, C_6D_6) of **7**: δ 157.87 (C_{ipso}), 145.50 (C_{ortho}), 127.63 (C_{para}), 123.10 (C_{meta}), 100.62 (CH_2CMe_3), 58.75 (CH_2SiMe_3), 35.73 (CH_2CMe_3), 32.92 (CH_2CMe_3), 28.60 (CHMe_2), 23.91 (CHMe_2), 23.85 (CHMe_2), 2.18 (CH_2SiMe_3) ppm.

Elemental analysis: Calc'd for $\text{CrC}_{33}\text{H}_{56}\text{N}_2\text{Si}$: C 70.66, H 10.06, N 4.99. Found: C 71.34, H 10.45, 4.96.

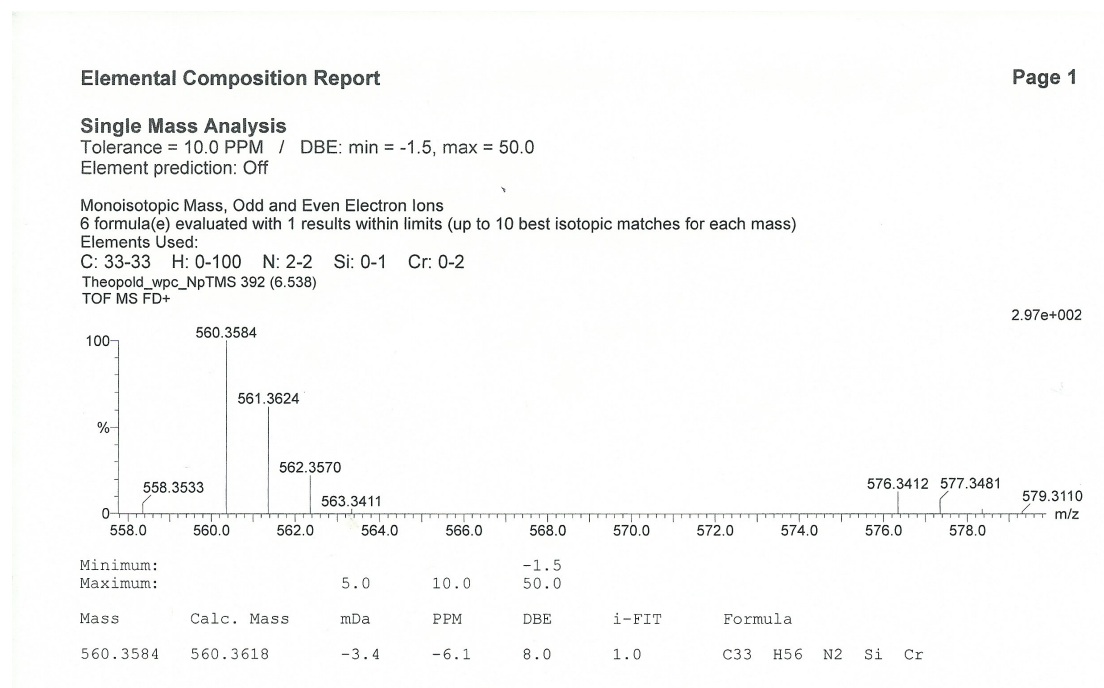


Figure S22. LIFDI mass spectrum of **7**: m/z 560.3584 (Calcd. for M^+ : 560.3618).

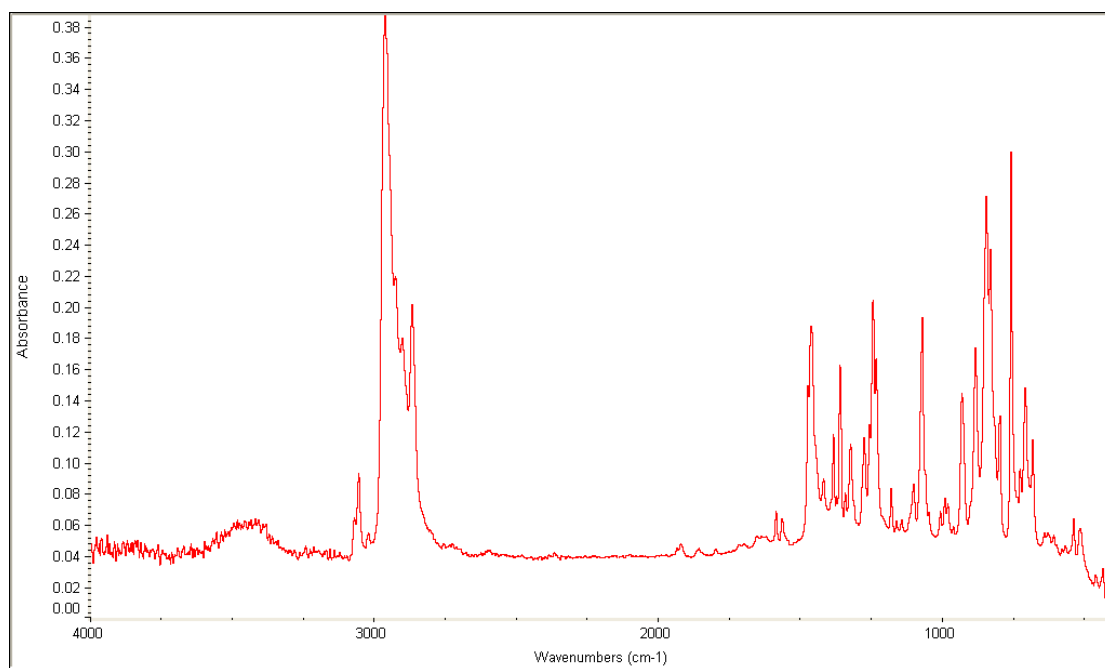


Figure S23. IR spectrum (KBr, cm^{-1}) of **7**: 3055 (w), 2957 (s), 2866 (m), 1460 (m), 1382 (w), 1359 (w), 1321 (w), 1274 (w), 1243 (m), 1231 (w), 1069 (m), 929 (w), 881 (w), 844 (m), 829 (m), 795 (w), 756 (m), 705 (w), 681 (w).

UV-vis spectrum (pentane) of **7**: λ_{max} (ϵ) = 252.5 (3.676×10^4), 284 (2.549×10^4), 434 (4.907×10^3), 616 (3.898×10^3) $\text{nm}(\text{M}^{-1}\text{cm}^{-1})$.

M.P.: 133 °C

Metallacycle (ArN)₂Cr(C₁₀H₁₈) (**8**)

2 (0.132 g, 0.242 mmol) was dissolved in 20 mL cyclopentene, giving a green solution. The solution was stirred for 3 days at room temperature during which time the color changed to red. Cyclopentene was then removed in vacuum and the residue was extracted with pentane and the extract filtered through celite. The filtrate was concentrated to 2 mL then cooled to -30 °C overnight to yield red crystals of **6** (0.084 g, 64%)

Characterization:

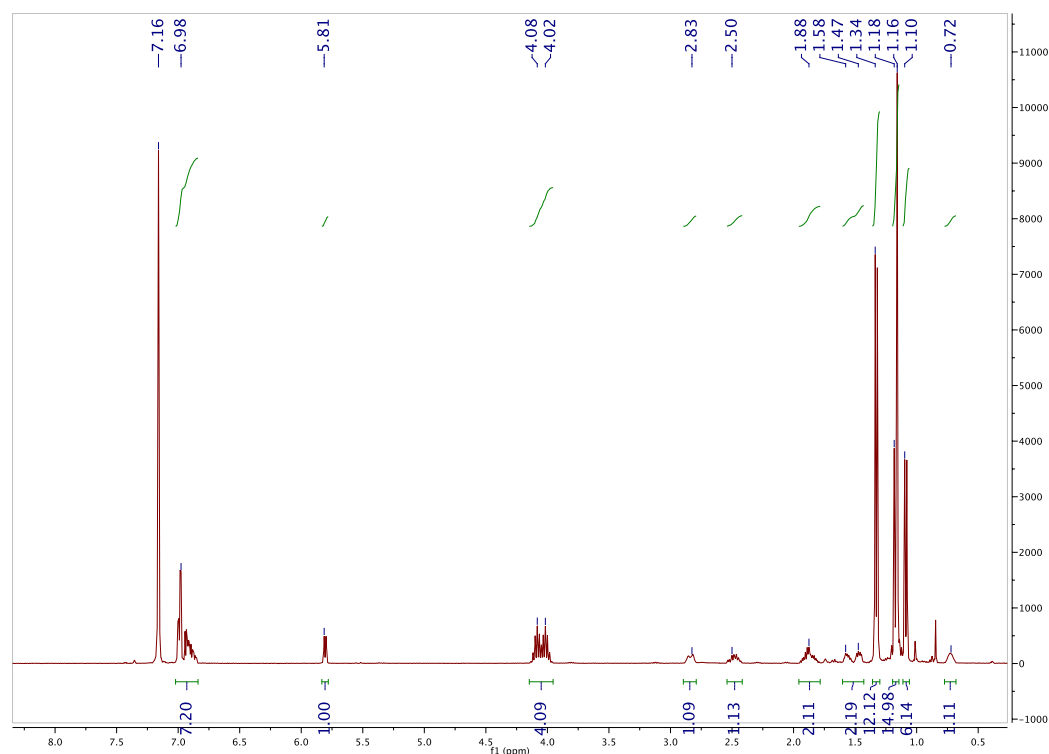


Figure S24. ¹H NMR spectrum (400 MHz, C₆D₆) of **8**: δ 6.98 (m, 6 H, Ar), 6.98 (m, 1 H, α-CH of chromacyclobutane), 5.81 (d, 1 H, CHCMe₃), 4.08 (sept, 2 H, CHMe₂), 4.02 (sept, 2 H, CHMe₂), 2.83 (m, 1 H, β-CH₂), 2.50 (m, 1 H, β-CH₂), 1.88 (m, 2 H, CH₂), 1.58 (m, 1 H, CH₂), 1.47 (m, 1 H, CH₂), 1.33 (d, 12 H, CHMe₂), 1.17 (d, 6 H, CHMe₂), 1.16 (s, 9H, CMe₃), 1.09 (d, 6 H, CHMe₂), 0.72 (m, 1 H, β-CH)

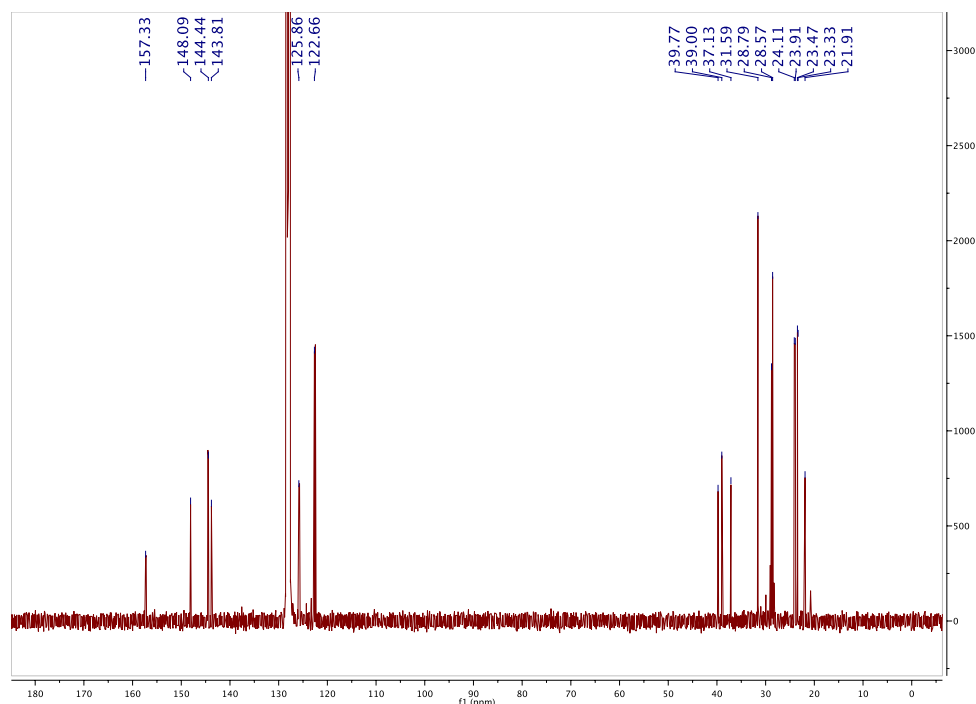


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, C_6D_6) of **8**: δ 157.33 (C_{ipso}), 157.21 (C_{ipso}), 148.09 (CHCMe_3), 144.55 (C_{ortho}), 144.44 (C_{ortho}), 143.81 ($\alpha\text{-C}$ of cyclobutane, not CHCMe_3), 125.86 (C_{para}), 125.71 (C_{para}), 122.66 (C_{meta}), 122.46 (C_{meta}), 39.77 (CH_2), 39.00 (CMe_3), 37.13 (CH_2), 31.59 ($\text{C}(\text{CH}_3)_3$), 28.79 (CHMe_2), 28.57 (CHMe_2 , CH_2), 24.11 (CHMe_2), 23.91 (CHMe_2), 23.47 (CHMe_2), 23.33 (CHMe_2), 21.91 ($\beta\text{-CH}$)

Elemental analysis: Calc'd for $\text{CrC}_{34}\text{H}_{52}\text{N}_2$: C 75.51, H 9.69, N 5.18. Found: C 75.33, H 9.59, N 5.13.

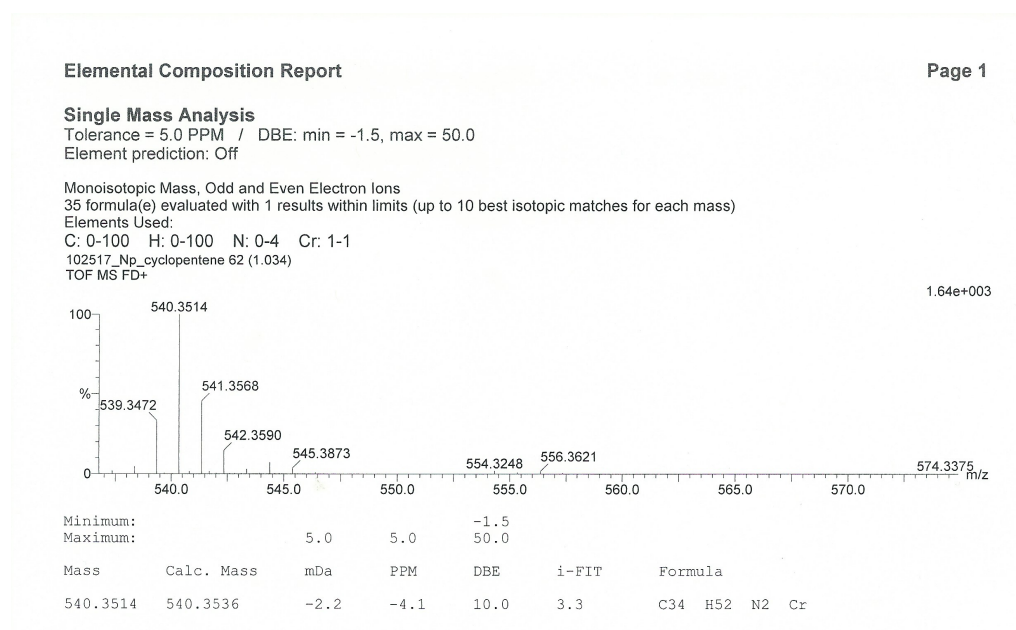


Figure S26. LIFDI mass spectrum of **8**: m/z 540.3514 (Calc'd for M^+ : 540.3536)

IR

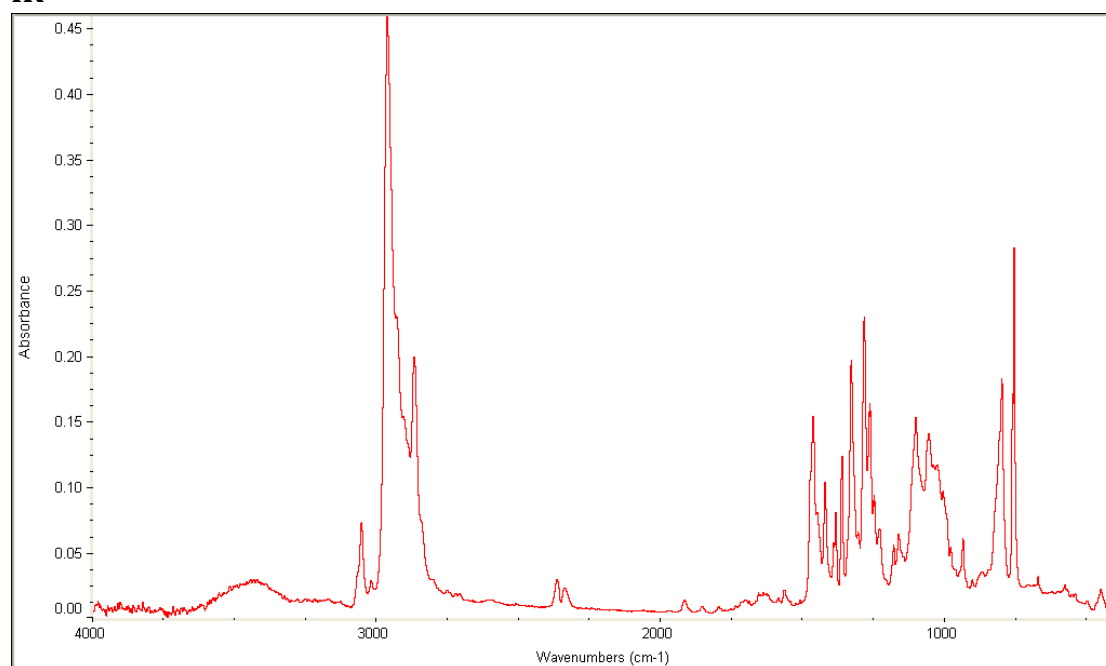


Figure S27. UV-vis spectrum (pentane) of **8**: λ_{max} (ϵ) = 253(8.391*10⁴), 306.5(4.779*10⁴), 486(1.058*10⁴) (M⁻¹cm⁻¹).

M.P.: 173 °C

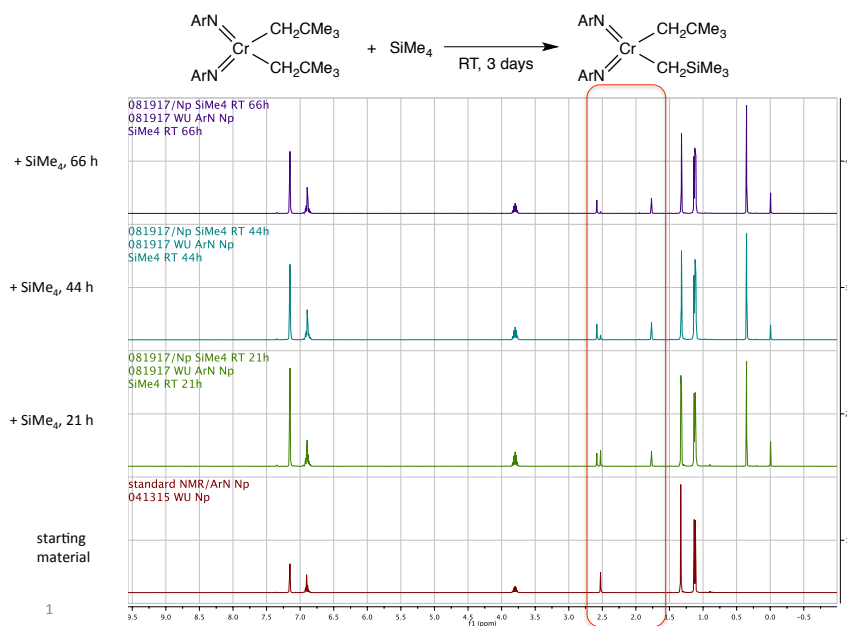


Figure S28. Reaction of **2** with SiMe₄ at room temperature, monitored by ¹H NMR.

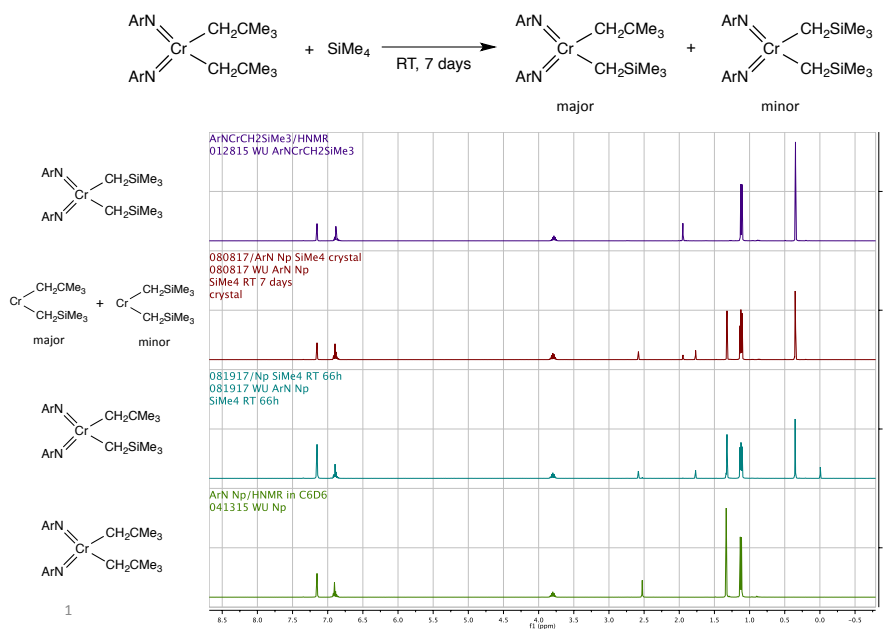


Figure S29. Comparison of the ¹H NMR spectra of pure **2**, **7**, and **4** with a mixture generated by reaction of **2** with neat SiMe₄ for 7 days at room temperature (second from top).

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