# **Supporting Information**

## A bis(amido) ligand set that supports two-coordinate chromium in the +1, +2, and +3 oxidation states

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## 1. Experimental Details, Synthetic Procedures, Spectroscopic Characterization

**General Considerations.** Unless otherwise noted, all experiments were conducted with dry, oxygen-free solvents using standard Schlenk techniques or in a  $N_2$  atmosphere glovebox. Benzene- $d_6$  was purchased from Cambridge Isotope Laboratories and dried by vacuum distillation from Na/K alloy. Dimethoxyethane (DME) was purchased from Sigma Aldrich, dried by vacuum distillation from K/benzophenone, and stored over 3 Å molecular sieves. Unless otherwise noted, reagents were obtained from commercial suppliers and used as received. Potassium hydride was purchased as a dispersion in mineral oil from Sigma Aldrich and washed with pentane before use. Tetrabutylammonium tetrakis(pentafluorophenyl)borate,<sup>1</sup> Benzyl potassium,<sup>2</sup> potassium graphite,<sup>3</sup> and ferrocenium tetrakis(pentafluorophenyl)borate<sup>4</sup> were prepared by standard literature procedures. The abbreviation "DIPP" refers to a 2,6-diisopropylphenyl moiety and "DME" refers to dimethoxyethane.

Analytical Methods. All <sup>1</sup>H NMR spectra were collected at ambient temperature (ca. 21 °C) on Bruker AVB-400, AVQ-400, AV-500, or AV-600 NMR spectrometers, each equipped with a 5 mm BB probe, and referenced to the residual proteo-solvent signals. Solution magnetic susceptibilities were determined by <sup>1</sup>H NMR spectroscopy using Evans' method.<sup>5,6</sup> For Evans' method measurements using only proteo-solvent, a sealed insert containing DMSO-*d*<sub>6</sub> was also included for a lock signal. IR spectra were collected on a Bruker Alpha-P FR-IR Spectrometer equipped with a "Platinum" Attenuated Total Reflection sample module. Solution UV-Vis spectra were collected using a Varian Cary 300 series spectrophotometer. Melting points were determined on a Mel-Temp II melting point apparatus. Elemental analyses were performed by the UC Berkeley College of Chemistry Microanalytical Facility.

**Cyclic Voltammetry Experiments.** Cyclic voltammetry experiments were conducted at ambient temperature in a Vacuum Atmospheres glovebox. Measurements employed a Bio-Logic SP-200 potentiostat with a standard three-electrode configuration. The working electrode was a 3mm diameter glassy carbon electrode purchased from ALS. Silver wire was used as a quasi-reference electrode and sublimed ferrocene was used as an internal potential reference. The counter electrode was a 1/8 inch diameter graphite rod purchased from Electron Microscopy Sciences. The glassy carbon electrode was polished with 1  $\mu$ m alumina prior to each use. The graphite rod was cleaned with acetone and dried prior to each use. Analyses of 1 were performed in a 0.1 M solution of tetrabutylammonium tetrakis(pentafluorophenyl)borate in 1,2-difluorobenzene with an analyte concentration of 1 mM at a scan rate of 100 mV/s. Solution resistance was corrected by applying *i*R compensation for each measurement. All potential values are reported as  $E_{1/2}$  for reversible events and  $E_p$  for irreversible events.

**X-ray Diffraction Experiments.** Single crystal X-ray diffraction experiments were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all compounds were performed on a Bruker APEX-II CCD area detector using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) monochromated using QUAZAR multilayer mirrors. Crystals were kept at 100(2) K throughout collection. Data collection, refinement, and reduction were performed with Bruker APEX2 software (v. 2013.4). All structures were solved using SIR97. Structures 1, 2a, 3, 4, and 5 were refined with SHELXL-97 with refinement of  $F^2$  against all reflections by full-matrix least

squares, while structures **2b** was refined with SHELXL-2013 with refinement of  $F^2$  against all reflections by full-matrix least squares. In all models, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically-calculated positions and refined using a riding model. Specific details can be found below, in section 4 of this document and in the included crystallographic information files.

**Experimental Details:** 

Compound	Detector Distance (mm)	Image Width (°)	Exposure Time (s)
1	40	0.5	10
2a	50	0.5	20
2b	40	0.5	30
3	40	0.5	10
4	60	0.5	30
5	40	0.5	30

Synthesis of HN(Si'Pr<sub>3</sub>)DIPP. To a 250 mL Chemglass Air-Free Teflon-stoppered flask was added 2,6-diisopropylaniline (5.3 mL, 28 mmol) and 30 mL of THF. The solution was placed in an ice bath, and to the stirred solution was added *n*BuLi (1.6 M in hexanes, 18.4 mL, 29.4 mmol), dropwise *via* syringe. The yellow solution was removed from the ice bath and stirred for 20 minutes. To the stirred solution was then slowly added a solution of triisopropylsilyl chloride (6.0 mL, 28 mmol) in 10 mL of THF, *via* syringe. The solution was stirred for 23 h in a 75 °C oil bath. After allowing the reaction to cool to ambient temperature, the volatile materials were removed under reduced pressure. The resulting residue was distilled under 90 °C/ 0.05 mmHg to give a clear, light orange oil (7.3 g, 78%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C)  $\delta$  1.10 (d, *J*<sub>HH</sub> = 7.1 Hz, 18 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17-1.26 (m, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.43 (b s, 1 H, N-*H*), 3.56 (sep, 2 H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 7.05-7.16 (m, 3 H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR data in C<sub>6</sub>D<sub>6</sub> were consistent with values reported in the literature.<sup>7</sup>

**K**[**N**(**Si**<sup>*i*</sup>**Pr**<sub>3</sub>)**DIPP**]. To a 20 mL scintillation vial was added benzyl potassium (0.351, 2.7 mmol) and 6 mL of diethyl ether. To a 4 mL, 1 dram vial was added HN(Si<sup>*i*</sup>Pr<sub>3</sub>)DIPP (0.900 g, 2.7 mmol), and 2 mL of diethyl ether. Both vials were placed in a -30 °C freezer and allowed to cool for 30 min. Upon removal of both vials from the freezer, the suspension of benzyl potassium was stirred and the solution of HN(Si<sup>*i*</sup>Pr<sub>3</sub>)DIPP] was added dropwise. The contents of 4 mL vial were washed with an additional 2 mL of diethyl ether and the resulting solution in diethyl ether was then added to the 20 mL scintillation vial. The reaction mixture was stirred at ambient temperature for 70 min. The mixture was filtered and concentrated to a solid. The solid was washed with pentane (3 x 5 mL) and dried *in vacuo* to give an off-white powder (0.725, 72%), which was used without further purification.

 $Cr[N(Si'Pr_3)DIPP]_2$  (1). To a 20 mL scintillation vial was added chromium(II) chloride (0.100 g, 0.81 mmol) and 4 mL of THF. To a 4 mL, 1 dram vial was added K[N(Si'Pr\_3)DIPP] (0.610 g, 1.64 mmol) and 2 mL of THF, forming a clear, light yellow solution. Both vials were placed in a -30 °C freezer and allowed to cool for 10 min. Upon removal of both vials from the freezer, the suspension of chromium(II) chloride was stirred and the solution of K[N(Si'Pr\_3)DIPP] was added

dropwise. The contents of 4 mL vial were washed with an additional 2 mL of THF and the resulting solution in THF was then added to the 20 mL scintillation vial. The reaction mixture was stirred at ambient temperature for 1 h. The red solution was concentrated under reduced pressure to a green and orange solid, which was extracted into 10 mL of pentane. The pentane extract was filtered, then concentrated under reduced pressure to a volume of 4 mL, and placed in a -30 °C freezer for several hours, to yield 0.263 g (45%) of Cr[N(Si<sup>i</sup>Pr<sub>3</sub>)DIPP]<sub>2</sub> (1) as green, block-like crystals which were isolated by decantation and dried in vacuo. The supernatant was collected and the volatile components were removed under reduced pressure. A second crystallization was set up in an identical fashion using the resulting residue with a minimal amount of hexamethyldisiloxane, yielding an additional 0.096 g of 1. Total yield: 0.349 g (60%). The <sup>1</sup>H NMR spectrum of 1 in  $C_6D_6$  contains non-distinctive, broad and unintegrable signals, attributed to the paramagnetism of 1;  $\mu_{eff} = 4.92 \ \mu_B$  (C<sub>6</sub>D<sub>6</sub>, 19.2 °C, Evans' method). IR (neat solid, cm<sup>-1</sup>) 2863 m, 929 m, 879 s, 766 s, 766 s, 722 m, 669 m. UV-vis (DME) λ<sub>max</sub> (ε): 437 nm  $(5.4 \times 10^3 \text{ mol}^{-1} \text{ L cm}^{-1})$ . Mp: 77-80 °C (color change from green to red), 137-140 °C (decomposition). Anal. Calcd. for C<sub>42</sub>H<sub>76</sub>N<sub>2</sub>CrSi<sub>2</sub>: C, 70.33%, H, 10.68%, N, 3.91%. Found: C, 70.55%, H, 10.42%, N, 3.81%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

[K(DME)<sub>n</sub>]{Cr[N(Si<sup>P</sup>r<sub>3</sub>)DIPP]<sub>2</sub>} (2a). To a 20 mL scintillation vial was added 1 (0.200 g, 0.279 mmol) and 10 mL of diethyl ether. The solution was placed in a -30 °C freezer and allowed to cool for 20 minutes. Upon removal of the vial from the freezer, the solution was stirred and potassium graphite (0.042 g, 0.307 mmol) was added as a solid. The reaction mixture was stirred at ambient temperature for 30 min. The mixture was filtered and concentrated to a red solid under reduced pressure. The solid was dissolved in 1 mL of DME, upon which was layered 9 mL of pentane. The layered solution was placed in a -30 °C freezer overnight, yielding orange crystals which were isolated by decantation and dried in vacuo, resulting in a 0.242 g (0.270 mmol, 97%) of [K(DME)<sub>1.5</sub>]{Cr[N(Si<sup>i</sup>Pr<sub>3</sub>)DIPP]<sub>2</sub>} (MW 891.53) as an orange solid. The relative amount of residual DME was determined after each workup by <sup>1</sup>H NMR spectroscopy, using hexamethylbenzene as an internal standard. Apart from residual DME, the <sup>1</sup>H NMR spectrum of 2a in C<sub>6</sub>D<sub>6</sub> contains non-distinctive, broad and unintegrable signals, attributed to the paramagnetism of 2a;  $\mu_{eff} = 5.2 \ \mu_B \ (C_6 D_6, \ 20 \ ^\circ C, \ Evans' \ method)$ . UV-vis (DME)  $\lambda_{max} \ (\epsilon)$ : 244  $(1.8 \times 10^4)$ , 282  $(7.2 \times 10^3)$ , 330  $(5.7 \times 10^3)$ , 429  $(5.2 \times 10^3)$  nm (mol<sup>-1</sup> L cm<sup>-1</sup>). Anal. Calcd. for C<sub>42</sub>H<sub>76</sub>N<sub>2</sub>CrKSi<sub>2</sub>·1.4C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>: C, 64.78%, H, 10.30%, N, 3.17%. Found: C, 64.46%, H, 10.41%, N, 2.96%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

 $[N^nBu_4]{Cr[N(Si^iPr_3)DIPP]_2}$  (2b). To a 20 mL scintillation vial was added 1 (0.200 g, 0.279 mmol) and 8 mL of diethyl ether. The solution was placed in a -30 °C freezer and allowed to cool for 30 minutes. Upon removal of the vial from the freezer, the solution was stirred and potassium graphite (0.042 g, 0.307 mmol) was added as a solid. The reaction mixture was stirred at ambient temperature for 30 min. Tetrabutylammonium bromide (0.090 g, 0.279 mmol) was then added directly to the stirring reaction. The mixture was stirred for an additional 1 h at ambient temperature. The mixture was filtered, and the filtrate was concentrated to a volume of 4 mL. The solution was placed in a -30 °C freezer for two days, affording 0.196 g (73%) of  $[N^nBu_4]{Cr[N(Si'Pr_3)DIPP]_2}$  (2b) as orange crystals, which were isolated by decantation and dried *in vacuo*. The <sup>1</sup>H NMR spectrum of 2b in C<sub>6</sub>D<sub>6</sub> contains non-distinctive, broad and

unintegrable signals, attributed to the paramagnetism of **2b**;  $\mu_{eff} = 5.74 \ \mu_B$  (THF, 20 °C, Evans' method). UV-vis (DME)  $\lambda_{max}$  ( $\epsilon$ ): 243 (1.8 × 10<sup>4</sup>), 282 (8.8 × 10<sup>3</sup>), 330 (7.4 × 10<sup>3</sup>), 427(6.3 × 10<sup>3</sup>) nm (mol<sup>-1</sup> L cm<sup>-1</sup>). UV-vis (toluene)  $\lambda_{max}$  ( $\epsilon$ ): 327 (1.0 × 10<sup>4</sup>), 424 (7.2 × 10<sup>3</sup>) nm (mol<sup>-1</sup> L cm<sup>-1</sup>). Anal. Calcd. for C<sub>58</sub>H<sub>112</sub>N<sub>3</sub>CrSi<sub>2</sub>: C, 72.59%, H, 11.76%, N, 4.38%. Found: C, 72.32%, H, 11.90%, N, 4.25%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

 ${Cr[N(Si'Pr_3)DIPP]_2}[B(C_6F_5)_4]$  (3). To a 20 mL scintillation vial was added 1 (0.100 g, 0.140 mmol) and 4 mL of 1,2-difluorobenzene, to produce an orange solution. The solution was placed in a -30 °C freezer and allowed to cool for 50 min. Upon removal of the vial from the freezer, the solution was stirred and ferrocenium tetrakis(pentafluorphenyl)borate) (0.121 g, 0.140 mmol) in 4 mL of 1,2-difluorobenzene was added dropwise. The reaction was stirred at ambient temperature for 1 h. The volatile components of the reaction mixture were removed under reduced pressure and the resulting residue was washed with 5 portions of 2 mL of pentane, until the pentane from washing was no longer visibly yellow. The residue was dissolved in 1,2difluorobenzene, and the resulting solution was filtered and then concentrated to a volume of 2 mL, upon which was layered 8 mL of hexamethyldisiloxane. The layered solution was placed in a -30 °C freezer for two days, yielding 0.161 g (82%) of  $\{Cr[N(Si^{i}Pr_{3})DIPP]_{2}\}[B(C_{6}F_{5})_{4}]$  (3) as very dark red crystals, which were isolated by decantation and dried in vacuo. The <sup>1</sup>H NMR spectrum of **3** in  $C_6D_6$  contains non-distinctive, broad and unintegrable signals, attributed to the paramagnetism of 3;  $\mu_{eff}$  = 3.83  $\mu_B$  (THF, 20 °C, Evans' method). UV-vis (DME)  $\lambda_{max}$  ( $\epsilon$ ): 355  $(5.1 \times 10^3)$ , 391  $(5.1 \times 10^3)$  nm (mol<sup>-1</sup> L cm<sup>-1</sup>). Anal. Calcd. for C<sub>66</sub>H<sub>76</sub>N<sub>2</sub>BCrF<sub>20</sub>Si<sub>2</sub>: C, 56.77%, H, 5.49%, N, 2.01%. Found: C, 56.49%, H, 5.38%, N, 1.75%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

(I)Cr[N(Si<sup>?</sup>Pr<sub>3</sub>)DIPP]<sub>2</sub> (4). To a stirred solution of 1 (0.389 g, 0.542 mmol) in 10 mL of diethyl ether was added dropwise a solution of iodine (0.069 g, 0.271 mmol) in 4 mL of diethyl ether. The reaction was stirred for 2 h at ambient temperature and then concentrated to a solid under reduced pressure. The solid was dissolved in pentane, and the resulting solution was filtered and the pentane was removed under reduced pressure to afford a red solid. Crystallization from pentane at -30 °C afforded 0.264 g (58%) of (I)Cr[N(Si<sup>?</sup>Pr<sub>3</sub>)DIPP]<sub>2</sub> (4) as dark red crystals, which were isolated by decantation and dried *in vacuo*. The supernatant was collected and the volatile components were removed under reduced pressure. Subsequent recrystallizations were set up in an identical fashion, yielding an additional 0.084 g of 4. Total yield: 0.348 g (76%). The <sup>1</sup>H NMR spectrum of 4 in C<sub>6</sub>D<sub>6</sub> contains non-distinctive, broad and unintegrable signals, attributed to the paramagnetism of 4;  $\mu_{eff} = 3.35 \ \mu_B (C_6D_6, 26 \ ^{\circ}C, Evans' method)$ . UV-vis (DME)  $\lambda_{max}$  ( $\epsilon$ ): 286 (1.5 × 10<sup>4</sup>), 355 (6.5 × 10<sup>3</sup>), 480 (1.4 × 10<sup>4</sup>) nm (mol<sup>-1</sup> L cm<sup>-1</sup>). Anal. Calcd. for C<sub>42</sub>H<sub>76</sub>N<sub>2</sub>CrISi<sub>2</sub>: C, 59.76%, H, 9.08%, N, 3.32%. Found: C, 59.92%, H, 9.34%, N, 3.41%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

 $(Me)Cr[N(Si'Pr_3)DIPP]_2$  (5). To a 20 mL scintillation vial was added 4 (0.084 g, 0.100 mmol) and 4 mL of diethyl ether. The solution was placed in a -30 °C freezer allowed to cool for 10 min. Upon removal of the vial from the freezer, the solution was stirred and methylmagnesium chloride (0.1 M in THF, 1.00 mL, 0.100 mmol) was added dropwise *via* syringe. The reaction was stirred for 2 h at ambient temperature and then concentrated to a red-orange solid under

reduced pressure. The solid was triturated with 6 mL of pentane and dried *in vacuo*. The solid was dissolved in pentane, and the resulting solution was filtered and re-concentrated to a solid. Recrystallization from pentane at -30 °C afforded 0.052 g (71%) of (Me)Cr[N(Si'Pr<sub>3</sub>)DIPP]<sub>2</sub> (**5**) as red crystals, which were isolated by decantation and dried *in vacuo*. The <sup>1</sup>H NMR spectrum of **5** in C<sub>6</sub>D<sub>6</sub> contains non-distinctive, broad and unintegrable signals, attributed to the paramagnetism of **5**;  $\mu_{eff} = 3.57 \ \mu_B (C_6D_6, 26 \ ^{\circ}C, Evans' method)$ . UV-vis (DME)  $\lambda_{max}$  ( $\epsilon$ ): 244 (1.7 × 10<sup>4</sup>), 340 (7.6 × 10<sup>3</sup>), 450 (4.7 × 10<sup>3</sup>) nm (mol<sup>-1</sup> L cm<sup>-1</sup>). Anal. Calcd. for C<sub>43</sub>H<sub>79</sub>N<sub>2</sub>CrSi<sub>2</sub>: C, 70.53%, H, 10.87%, N, 3.83%. Found: C, 70.27%, H, 11.21%, N, 3.69%. Crystals suitable for single crystal X-ray diffraction studies were obtained from the workup described above.

## 2. Cyclic Voltammogram



Cr[N(SiiPr3)(DIPP)]2 in 0.1 M [NnBu4][B(C6F5)4] with Fc Standard

### **3. ORTEP Diagrams**

Carbon atoms are shown in light gray, chromium in light blue, silicon in yellow and nitrogen in dark blue in all of the following diagrams.



ORTEP diagram of  $Cr[N(Si'Pr_3)DIPP]_2$  (1). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)-N(1): 2.0036(12), C(1)-N(1): 1.402(2), N(1)-Si(1): 1.7146(13), Cr(1)-C(1): 2.2709(14), N(1)-Cr(1)-N(1)': 180.00(8), C(1)-N(1)-Cr(1): 81.59(8), Si(1)-N(1)-Cr(1): 137.87(8), C(1)-N(1)-C(1)': 180.0(1).



ORTEP diagram of  $[K(DME)_4]{Cr[N(Si^Pr_3)DIPP]_2}$  (2a). Hydrogen atoms and potassium cation coordinated by DME have been omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)–N(1): 2.054(3), Cr(1)–N(2): 2.061(3), C(1)–N(1): 1.416(5), C(22)–N(2): 1.425(5), N(1)–Si(1): 1.703(3), N(2)–Si(2): 1.697(3), Cr(1)–C(1): 2.840(5), Cr(1)–C(22): 2.854(3), N(1)–Cr(1)–N(2): 175.02(13), C(1)–N(1)–Cr(1): 108.4(2), C(22)–N(2)–Cr(1): 108.5(2), Si(1)–N(1)–Cr(1): 123.67(18), Si(2)–N(2)–Cr(1): 125.79(17), C(1)–N(1)–N(2)–C(22): ±44.1(3).



ORTEP diagram of  $[N^nBu_4]$ {Cr[N(Si<sup>*i*</sup>Pr<sub>3</sub>)DIPP]<sub>2</sub>} (**2b**). Hydrogen atoms and tetrabutylammonium cation have been omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)–N(1): 2.051(2), Cr(1)–N(2): 2.047(2), C(1)–N(1): 1.405(3), C(22)–N(2): 1.407(3), N(1)–Si(1): 1.699(2), N(2)–Si(2): 1.703(2), Cr(1)–C(1): 2.836(3), Cr(1)–C(22): 2.789(3), N(1)–Cr(1)–N(2): 175.63(9), C(1)–N(1)–Cr(1): 108.86(16), C(22)–N(2)–Cr(1): 106.19(16), Si(1)–N(1)–C(22):  $\pm$ 39.8(2).



ORTEP diagram of  $\{Cr[N(Si^{7}Pr_{3})DIPP]_{2}\}[B(C_{6}F_{5})_{4}]$  (4). Hydrogen atoms have been omitted for clarity. Solvent and  $B(C_{6}F_{5})_{4}$  anions have been excluded. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)-N(1): 1.872(2), Cr(2)-N(2): 1.869(2), C(1)-N(1): 1.433(3), C(22)-N(2): 1.433(3), N(1)-Si(1): 1.796(2), N(2)-Si(2): 1.785(2), Cr(1)-C(1): 2.225(2), Cr(2)-C(22): 2.217(2), N(1)-Cr(1)-N(1)': 180.000(1), N(2)-Cr(2)-N(2)': 180.0, C(1)-N(1)-Cr(1): 83.48(14), C(22)-N(2)-Cr(2): 83.24(13), Si(1)-N(1)-Cr(1): 142.58(12), Si(2)-N(2)-Cr(2): 141.09(12), C(1)-N(1)'-C(1)': 180.0(2), C(22)-N(2)-N(2)'-C(22)': 180.0(2).



ORTEP diagram of  $(I)Cr[N(Si^{i}Pr_{3})DIPP]_{2}$  (4). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)–N(1): 1.906(4), Cr(1)–N(2): 1.889(4), Cr(1)–I(1): 2.5929(8), C(1)–N(1): 1.457(6), C(22)–N(2): 1.465(6), N(1)–Si(1): 1.808(4), N(2)–Si(2): 1.815(4), Cr(1)–C(1): 2.924(5), Cr(1)–C(22): 2.965(5), N(1)–Cr(1)–N(2): 139.49(17), N(1)–Cr(1)–I(1): 110.31(12), N(2)–Cr(1)–I(1): 110.19(12), C(1)–N(1)–Cr(1): 120.2(3), C(22)–N(2)–Cr(1): 123.8(3), Si(1)–N(1)–Cr(1): 121.2(2), Si(2)–N(2)–Cr(1): 120.1(2), C(1)–N(1)–N(2)–C(22): ±136.5(4).



ORTEP diagram of  $(Me)Cr[N(Si'Pr_3)DIPP]_2$  (5). Hydrogen atoms have been omitted for clarity. Disordered chromium and silicon atoms have been excluded. Thermal ellipsoids shown at 50% probability. Selected bond distances [Å], angles [°], and torsions [°]: Cr(1)–N(1): 1.893(2), Cr(1)–N(2): 1.906(2), Cr(1)–C(43): 2.058(3), C(1)–N(1): 1.458(4), C(22)–N(2): 1.460(4), N(1)–Si(1): 1.793(3), N(2)–Si(2): 1.783(3), Cr(1)–C(1): 2.949(3), Cr(1)–C(22): 2.905(3), N(1)–Cr(1)–N(2): 142.89(11), N(1)–Cr(1)–C(43): 107.92(12), N(2)–Cr(1)–C(43): 109.14(12), C(1)–N(1)–Cr(1): 122.71(19), C(22)–N(2)–Cr(1): 118.75(19), Si(1)–N(1)–Cr(1): 120.45(14), Si(2)–N(2)–Cr(1): 121.61(13), C(1)–N(1)–N(2)–C(22):  $\pm$ 138.2(2).

## 4. X-ray Data Tables

#### Compound 1:

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta =  $25.00^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

#### Compound 2a:

Empirical formula	C58 H116 Cr K N2 O8	8 Si2
Formula weight	1116.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 15.8187(7)  Å	a= 90°.
	b = 17.0756(8) Å	b= 90°.
	c = 25.0015(13)  Å	g = 90°.
Volume	6753.2(6) Å <sup>3</sup>	

C42 H76 Cr N2 Si2 717 23 100(2) K 0.71073 Å Triclinic P-1 a = 10.6605(3) Å $\alpha = 98.9810(10)^{\circ}$ . b = 10.8266(3) Å  $\beta = 104.6850(10)^{\circ}$ . c = 11.4767(3) Å  $\gamma = 118.9100(10)^{\circ}$ . 1059.18(5) Å<sup>3</sup> 1  $1.124 \text{ Mg/m}^3$ 0.356 mm<sup>-1</sup> 394 0.09 x 0.09 x 0.06 mm<sup>3</sup> 1.94 to 31.24°. -13<=h<=15, -15<=k<=13, -14<=l<=16 24671 5882 [R(int) = 0.0420]99.4 % Semi-empirical from equivalents 0.9790 and 0.9687 Full-matrix least-squares on F<sup>2</sup> 5882 / 0 / 224 1.021 R1 = 0.0405, wR2 = 0.0852R1 = 0.0675, wR2 = 0.09500.365 and -0.302 e.Å<sup>-3</sup>

Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta =  $25.00^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Absolute structure parameter Largest diff. peak and hole

#### Compound **2b**:

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Z Density (calculated) Absorption coefficient F(000)Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta = 25.000° Absorption correction Max. and min. transmission Refinement method 4  $1.098 \text{ Mg/m}^3$ 0.313 mm<sup>-1</sup> 2452 0.11 x 0.10 x 0.01 mm<sup>3</sup> 1.44 to 30.70°. -10<=h<=22, -19<=k<=22, -31<=l<=32 54941 16443 [R(int) = 0.0409] 100.0 % Semi-empirical from equivalents 0.9969 and 0.9664 Full-matrix least-squares on F<sup>2</sup> 16443 / 158 / 677 1.037 R1 = 0.0729, wR2 = 0.1814R1 = 0.0961, wR2 = 0.19950.00 1.261 and -0.615 e.Å<sup>-3</sup>

C58 H112 Cr N3 Si2 959.68 100(2) K 0.71073 Å Monoclinic P 21/n a = 14.7215(4) Å  $\alpha = 90^{\circ}$ .  $\beta = 90.949(2)^{\circ}$ . b = 28.4194(8) Å c = 14.8687(4) Å $\gamma = 90^{\circ}$ . 6219.9(3) Å<sup>3</sup> 4  $1.025 \text{ Mg/m}^3$ 0.257 mm<sup>-1</sup> 2132 0.100 x 0.100 x 0.040 mm<sup>3</sup> 1.558 to 25.376°. -17<=h<=17, -30<=k<=34, -17<=l<=17 36473 11368 [R(int) = 0.0567]99.8 % Semi-empirical from equivalents 0.942 and 0.828 Full-matrix least-squares on F<sup>2</sup>

Data / restraints / parameters	11368 / 0 / 601		
Goodness-of-fit on F <sup>2</sup>	1.013		
Final R indices [I>2sigma(I)]	R1 = 0.0574, $wR2 = 0.1120$		
R indices (all data)	R1 = 0.1036, $wR2 = 0.1308n/a$		
Extinction coefficient			
Largest diff. peak and hole	1.353 and -0.480 e.Å-	3	
Compound 3:			
Empirical formula	C69 H77 B Cr F21 N2	2 Si2	
Formula weight	1452.32		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system, space group	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 13.4838(8)  Å	$\alpha = 67.150(3) \text{ deg.}$	
	b = 15.8748(9)  Å	$\beta = 89.637(3) \text{ deg.}$	
	c = 18.4544(10)  Å	$\gamma = 69.398(3) \text{ deg.}$	
Volume	3368.3(3) Å <sup>3</sup>		
Ζ	2		
Calculated density	$1.432 \text{ Mg/m}^3$		
Absorption coefficient	0.307 mm <sup>-1</sup>		
F(000)	1502		
Crystal size	0.13 x 0.06 x 0.02 mn	0.13 x 0.06 x 0.02 mm	
Theta range for data collection	1.49 to 25.45 deg.		
Limiting indices	-16<=h<=15, -19<=k<=19, -22<=l<=22		
Reflections collected / unique	55268 / 12395 [R(int) = 0.0321]		
Completeness to theta $= 25.00$	100.0 %		
Absorption correction	None		
Max. and min. transmission	0.9939 and 0.9612		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	12395 / 0 / 897		
Goodness-of-fit on F <sup>2</sup>	1.032		
Final R indices [I>2sigma(I)]	R1 = 0.0494, $wR2 = 0.1204$		
R indices (all data)	R1 = 0.0600, wR2 = 0.1282		
Largest diff. peak and hole	2.339 and -0.829 e.Å <sup>-3</sup>		

## Compound 4

Empirical formula Formula weight Temperature Wavelength Crystal system

C42 H76 Cr I N2 Si2 844.13 100(2) K 0.71073 Å Monoclinic Space group Unit cell dimensions Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta =  $25.00^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

#### Compound 5

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Z Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections

P2(1)/ca = 11.0285(5) Å $\alpha = 90^{\circ}$ .  $\beta = 90.515(3)^{\circ}$ . b = 23.0870(10) Åc = 17.0353(7) Å $\gamma = 90^{\circ}$ . 4337.3(3) Å<sup>3</sup> 4 1.293 Mg/m<sup>3</sup> 1.061 mm<sup>-1</sup> 1788 0.04 x 0.03 x 0.01 mm<sup>3</sup> 1.76 to 25.43°. -13<=h<=13, 0<=k<=27, 0<=l<=20 7912 7912 [R(int) = 0.0808]99.1 % Semi-empirical from equivalents 0.9895 and 0.9588 Full-matrix least-squares on F<sup>2</sup> 7912 / 0 / 453 1.050 R1 = 0.0523, wR2 = 0.0978R1 = 0.0854, wR2 = 0.10470.977 and -0.583 e.Å<sup>-3</sup>

C43 H79 Cr N2 Si2	
732.26	
100(2) K	
0.71073 Å	
Monoclinic	
P2(1)/c	
a = 11.0453(7)  Å	a= 90°.
b = 23.1010(16)  Å	b=90.156(3)°
c = 16.8139(10)  Å	g = 90°.
4290.2(5) Å <sup>3</sup>	-
4	
1.134 Mg/m <sup>3</sup>	
0.353 mm <sup>-1</sup>	
1612	
0.09 x 0.09 x 0.02 mm <sup>3</sup>	
1.50 to 25.41°.	
-13<=h<=13, -27<=k<=2	7, <b>-</b> 20<=l<=20
47476	
7802 [R(int) = 0.0811]	

- Completeness to theta =  $25.00^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole
- 99.4 % Semi-empirical from equivalents 0.9930 and 0.9689 Full-matrix least-squares on F<sup>2</sup> 7802 / 0 / 468 1.067 R1 = 0.0515, wR2 = 0.1176 R1 = 0.0607, wR2 = 0.1222 0.517 and -0.375 e.Å<sup>-3</sup>

## **5. References**

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