Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2014

# *Binding and Activation of Small Molecules by a Quintuply Bonded Chromium Dimer*

Jingmei Shen,[a,b] Glenn P. A. Yap,[a] and Klaus H. Theopold*[a]

[a] Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716; [b] Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60202.

# Supporting information

## Contents:

- **Synthesis and characterization of Cr Complexes**
- **Single crystal X-ray diffraction studies**

**General**. All manipulations of compounds were carried out using standard Schlenk, high vacuum line, and glove-box techniques under an atmosphere of $N_2$. Solvents were purchased from Fisher Scientific, degassed, and dried by passing through activated alumina. THF-$d_8$ and $C_6D_6$ were purchased from Cambridge Isotopes Laboratory and stored under vacuum over Na/K alloy. All other reagents were purchased from Aldrich or Acros and dried using standard procedures when necessary. Room temperature molar magnetic susceptibilities ($\chi_m$) in the solid state were determined using a Johnson Matthey magnetic susceptibility balance. They were corrected for diamagnetism using Pascal constants and converted into effective magnetic moments ($\mu_{eff}$).

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DRX-400 spectrometer and the former were referenced to the residual protons of the solvent. FTIR-spectra were taken on Magna-IR E. S. P. 560 spectrometer at a resolutionof 4 cm$^{-1}$. UV/vis spectra were taken using a Thermo UV-1 spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories.

## Synthesis and characterization of Cr Complexes

**Preparation of $[^{H}L^{iPr}Cr]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}H_2CCCMe_2)$ (2):** $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}{}^{H}L^{iPr})_2Cr_2$ (0.100g, 0.117mmol) was dissolved in 50ml diethyl ether or toluene in a Schlenk flask with a stir bar. The flask was then brought out of the dry box and attached to a Schlenk line. Approximately 18μl of 1,1-dimethylallene (0.183mmol) was injected in the solution. The color of the solution changed immediately from green to deep purple. The mixture was stirred one hour at room temperature. The solvent was removed and the ampoule was brought back in the dry box, where the residue was extracted with a mixture of pentane and diethyl ether. The extract was then filtered, concentrated and cooled to -30 °C, yielding dark purple crystals of **2** (0.076g, 70% yield). $^1$H NMR ($C_6D_6$): 7.017 (4H, m, aryl), 6.83 (4H, s, backbone), 6.72 (2H, d, aryl, *J*HH = 6 Hz), 6.44 (2H, d, aryl, *J*HH = 6 Hz), 6.25 (2H, d, aryl, *J*HH = 6 Hz), 5.71 (2H, d, aryl, *J*HH = 6 Hz), 4.053(2H, m, iPr), 3.451(2H, s, allene), 2.83(2H, m, iPr), 2.62 (2H, m, iPr), 2.53(3H, s, allene), 2.26(2H, m, iPr), 2.10(3H, s, allene), 1.92 (3H, s), 1.48(6H, d, *J*HH = 6 Hz, $CH_3$), 1.41(6H, d, *J*HH = 6 Hz, $CH_3$), 1.35(6H, d, *J*HH = 6 Hz, $CH_3$), 1.24(6H, d, *J*HH = 6 Hz, $CH_3$), 1.17(6H, d, *J*HH = 6 Hz, $CH_3$), 1.11(6H, d, *J*HH = 6 Hz, $CH_3$), 0.87(6H, d, *J*HH = 6 Hz, $CH_3$), 0.29(6H, d, *J*HH = 6 Hz, $CH_3$) ppm. IR (KBr): 3049 (w), 2959 (s), 2925 (m), 2866 (w), 1460 (m), 1441 (s), 1422 (m), 1383 (w), 1361 (w), 1323 (m), 1260 (s), 1222 (w), 1008 (w), 798 (w), 746 (m). Anal. Calcd. for $C_{57}H_{80}N_4Cr_2$: C, 73.99; H, 8.71; N, 6.06. Found: C, 73.21; H, 8.65; N, 6.19. UV/Vis (toluene): λmax (ε) = 490 (2538 $M^{-1}$ $cm^{-1}$), 702 (3762 $M^{-1}$ $cm^{-1}$). M. p.: 143 ºC (dec).

**Preparation of $[^{H}L^{iPr}Cr]_2(S_2)$ (3):** To 10 mL of a (1:1) toluene/diethyl ether solution of 0.100 g (0.117 mmol) of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}{}^{H}L^{iPr})_2Cr_2$ was added 0.008 g (0.250 mmol) of elemental sulfur. The resulting mixture was allowed to stir for one hour at room temperature, during which time the color changed from green to deep blue. The solvent was then removed and the residue was washed with pentane and then dissolved in diethyl ether. The resulting solution was filtered, concentrated, and cooled to -30°C, to yield deep blue crystals of **3** in 20% yield (0.022 g). $^1$H NMR (toluene-$d_8$, 203K): 6.9 (s, 2H), 6.7 (s, 2H), 6.6 (s, 2H), 6.2 (s, 2H), 3.65 (s, 2H, iPr), 3.6 (s, 2H, iPr), 2.2 (s, 2H, iPr), 1.95 (s, 2H, iPr), 1.82 (s, 6H, iPr) 1.36 (s, 6H, iPr), 1.23 (s, 6H, iPr), 1.17 (s, 6H, iPr), 1.12 (s, 6H, iPr), 0.97 (s, 6H, iPr), 0.33 (6H, iPr), 0.27 (s, 6H, iPr) ppm. IR (KBr; $cm^{-1}$): 3059 (w), 2962 (s), 2865 (s), 1653 (w), 1525 (w), 1462 (s), 1442 (s), 1384 (w), 1361 (w), 1319 (w), 1258 (m), 1247 (m), 1179 (w), 1110 (w), 798 (m), 756 (m). Anal. Calcd. for $C_{52}H_{72}N_4Cr_2S_2$: C, 67.8; H, 7.88; N, 6.08. Found: C, 67.03; H, 7.82; N, 5.94. UV/Vis (Toluene; $\lambda_{max}$, nm (ε, $M^{-1}cm^{-1}$)): 500 (5972 $M^{-1}$ $cm^{-1}$), 704 (5286 $M^{-1}$ $cm^{-1}$). M.p.: 168°C (dec).

**Preparation of $[^{H}L^{iPr}Cr(\mu\text{-}NPh)]_2$ (4):** To solution of 0.100 g (0.117 mmol) of $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}{}^{H}L^{iPr})_2Cr_2$ in 10 mL of a diethyl ether was added 0.043 g (0.234 mmol) of azobenzene. The resulting mixture was allowed to stir overnight at room temperature, during which time the color changed from green to red-brown. The solvent was then removed and the residue dissolved in diethyl ether. The resulting solution was filtered, concentrated, and cooled to -30°C, to yield red-brown crystals of **4** in 35% yield (0.043 g). $^1$H NMR (THF-$d_8$): 12.3 (br, 4H), 11.2 (br, 2H), 8.0 (br, 2H), 7.9 (br, 2H), 7.5 (br, 4H), 7.4 (br, 2H), 7.3 (br, 2H), 7.1 (br, 2H), 6.9 (br, 8H), 6.6 (br, 2H), 5.9 (br, 4H, iPr), 1.5 (br, 24H, iPr), 0.83 (br, 24H, iPr) ppm. IR (KBr; cm$^{-1}$): 3061 (w), 2959 (s), 1915 (s), 2867 (m), 1660 (m), 1528 (m), 1510 (w), 1460 (s), 1447 (s), 1438 (s), 1334 (w), 1317 (s), 1277 (m), 1261 (m), 1222 (m), 1176 (w), 1146 (m), 1101 (w), 1074 (w), 1025 (w), 760 (m), 743 (w), 702 (s), 642 (m), 564 (m). UV/Vis (THF; $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)): 552 (7570), 638 (4307). $\mu_{eff}$ (294 K) = 3.0(1) $\mu_B$. M.p.: 193$^{o}$C (dec). Despite repeated attempts, this compound did not analyze satisfactorily.

**Preparation of $[^{H}L^{iPr}Cr]_2(NAd)$ (5):** To a 10 mL diethyl ether solution of 0.100 g (0.117 mmol) ($\mu$-$\eta^1$:$\eta^1$-$^{H}L^{iPr}$)$_2$Cr$_2$ was added 0.041 g (0.234 mmol) of adamantyl azide. The resulting solution was allowed to stir for four hours at room temperature, during which time the color changed from green to brown. The solvent was then removed and the residue dissolved in diethyl ether. The resulting solution was then filtered, concentrated, and cooled to -30$^{o}$C, to yield brown crystals of **5** in 38% yield (0.045 g). $^1$H NMR ($C_6D_6$): 8.4 (s, 4H), 8.15 (s, 4H), 3.23 (s, 4H, iPr), 3.09 (s, 4H, iPr), 2.8-0.86 (m, 63H) ppm. IR (KBr; cm$^{-1}$): 2964 (w), 2904 (m), 2846 (s), 2361 (m), 1734 (m), 1699 (m), 1653 (m), 1576 (w), 1535 (m), 1506 (m), 1468 (m), 1438 (m), 1384 (m), 1359 (m), 1342 (2), 1315 (m), 1260 (w), 1194 (w), 1173 (w), 1109 (w), 1098 (w), 1017 (s), 796 (s), 760 (m), 752 (w). Anal. Calcd. for $C_{62}H_{87}N_5Cr_2$: C, 73.99; H, 8.71; N, 6.96. Found: C, 73.26; H, 8.28; N, 6.99. UV/Vis (Toluene; $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)): 512 (6750 M$^{-1}$ cm$^{-1}$), 706 (5003 M$^{-1}$ cm$^{-1}$). M.p.: 181$^{o}$C (dec).

**Preparation of $[^{H}L^{iPr}Cr(\mu\text{-}OCPh_2)]_2$ (6):** To a 10 mL diethyl ether solution of 0.100 g (0.117 mmol) of ($\mu$-$\eta^1$:$\eta^1$-$^{H}L^{iPr}$)$_2$Cr$_2$ was added 0.043 g (0.234 mmol) of benzophenone. The resulting solution was allowed to stir overnight at room temperature, during which time the color remained green. The solvent was then removed and the residue dissolved in a pentane/diethyl ether mixture (1:1). The resulting solution was then filtered, concentrated, and cooled to -30$^{o}$C, to yield green crystals of **6** in 52% yield (0.142 g). $^1$H NMR ($C_6D_6$): 96 (br, 8H), 14.6 (br, 4H), 7.16 ($C_6H_6$), 7.1 (br, 20H), 3.2 (br, 8H), 1.56 (br, 48H), -13.0 (br, 4H) ppm. IR (KBr; cm$^{-1}$): 3058 (w), 2959 (s), 2925 (m), 2866 (m), 1660 (m), 1527 (m), 1512 (w), 1460 (m), 1445 (s), 1432 (m), 1383 (w), 1335 (m), 1309 (m), 1260 (s), 1222 (w), 1100 (w), 1025 (w), 966 (w), 940 (w), 875 (w), 746 (w), 702 (m), 635 (m). Anal. Calcd. for $C_{78}H_{92}N_4Cr_2O_2$: C, 76.69; H, 7.59; N, 4.59. Found: C, 76.11; H, 7.75; N, 5.00. UV/Vis (pentane; $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)): 523 (3257), 612 (937). $\mu_{eff}$ (294 K) = 5.1(2) $\mu_B$. M.p.: 163$^{o}$C (dec).

**Preparation of $^{H}L^{iPr}Cr(\kappa^2\text{-}N_2C_{28}H_{22})$ (7):** To a 10 mL diethyl ether solution of 0.100 g (0.117 mmol) of ($\mu$-$\eta^1$:$\eta^1$-$^{H}L^{iPr}$)$_2$Cr$_2$ was added 0.085 g (0.468 mmol) of trans-benzylideneaniline. The resulting solution was allowed to stir overnight at room temperature, during which time the color changed from green to brown. The solvent was then removed and the residue dissolved in diethyl ether. The resulting solution was then filtered, concentrated, and cooled to -30ºC, to yield brown crystals of **7** in 47% yield (0.086 g). $^1$H NMR ($C_6D_6$): 20.9 (br, 2H), 12.8 (br, 2H), 7.16 ($C_6H_6$), 6.9 (br, 7H), 3.5 (br, 4H), 1.5 (br, 24H), 0.4 (br, 12H), -0.7 (br, 12H) ppm. IR (KBr; cm$^{-1}$): 3062 (w), 2959 (s), 2927 (m), 2869 (w), 1448 (m), 1440 (s), 1425 (m), 1396 (w), 1364 (w), 1329 (m), 1257 (s), 1220 (w), 1013 (w), 798 (w), 746 (m). Anal. Calcd. for $C_{52}H_{58}N_4Cr$: C, 78.95; H, 7.39; N, 7.08. Found: C, 78.31; H, 7.08; N, 6.64. UV/Vis (pentane; $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$cm$^{-1}$)): 500 (4127), 724 (1057). $\mu_{eff}$ (294 K) = 2.9(1) $\mu_B$. M.p.: 115$^{o}$C (dec).

**X-ray structure determinations:** Crystallographic structural analysis for compounds **2** – **7**. Crystals were mounted using viscous oil on plastic mesh and cooled to the data collection temperatures. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3º ω, from three different sections of the Ewald sphere. The systematic absences and equivalent reflections in the diffraction data are consistent with *Cc* and *C*2/*c* for **2**, and, uniquely, with $P2_1/n$ for **3** and **7**. No symmetry higher than triclinic was observed for the other data sets. Solution in the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data (Sheldrick, G., Bruker-AXS Inc, Madison, WI, 2001).

One molecule of pentane is located near a two-fold axis in **2**. A toluene and a tetrahydrofuran molecule are located in the asymmetric unit of **5**. The disordered solvent molecules in **2** and **5** were treated with geometry and equivalent isotropic parameters restrained as idealized rigid bodies. In each of the following unit cells were located severely disordered solvent molecules that were treated as diffused contributions (Squeeze, Platon: Spek, A. L., J. Appl. Cryst., 2003, 36, 7-13): two pentane molecules in **4**; and two diethylether molecules in **6**.

These compounds deposit as multiple, weakly diffracting crystals that are dark and virtually opaque that exclude screening by polarized light. These characteristics conspire to result in weak diffraction data with poor coverage as seen in the level A check CIF (http://checkcif.iucr.org) alert in **6** and level A and B alerts in **7**. Slight, unresolvable disorder cause by rotation of the isopropyl moieties increases the *Ueq* range in **3**, **4**, and **7** causing level B alerts. Level B alerts in **4** and **6** regarding molecular formulae are consequences of the use of Squeeze. The data herein represent the best of several trials for each compound.

The structures were solved using direct methods and refined with full-matrix, least-squares procedures on $F^2$. The compound molecule is located at a two-fold axis in **2** and at an inversion center in **4**. Two symmetry-unique compound molecules are in the asymmetric unit of **5**. All non-hydrogen atoms were refined with anisotropic coefficients. Hydrogen atoms were assigned calculated positions with isotropic parameters equal to 1.2 (or 1.5 for methyl) of the equivalent isotropic parameter of the attached atom. Atomic scattering factors are contained in the SHELXL 2013 program library (Sheldrick, G. M., Göttingen, Germany, 2013). These structures have been deposited at the Cambridge Crystallographic Data Centre under CCDC 971178-971183.

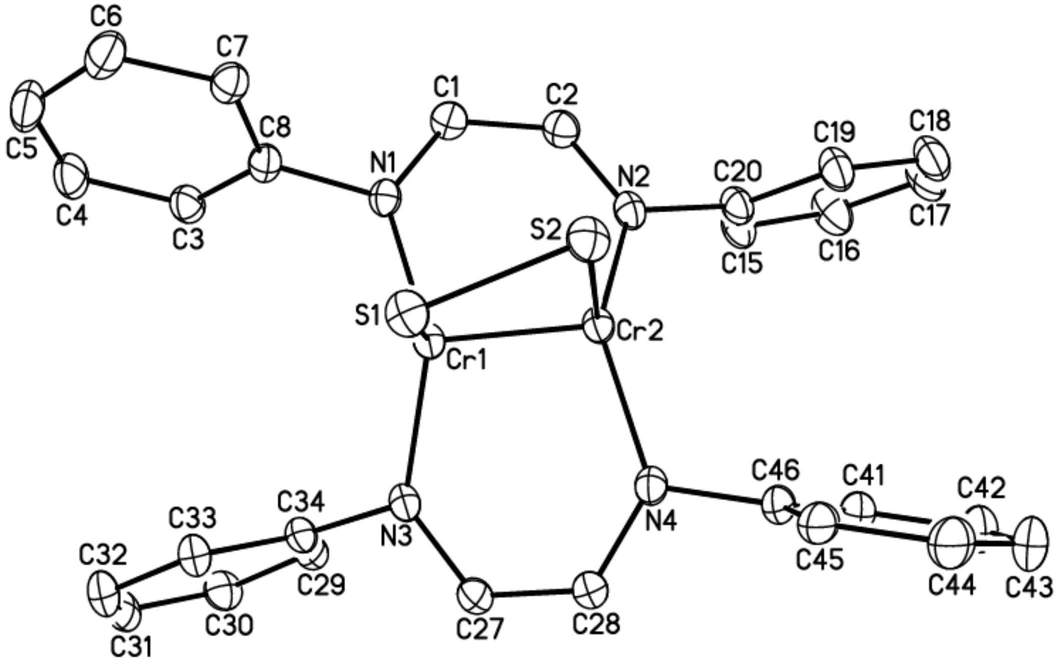

**Figure S1** Molecular structure of $[^{H}L^{iPr}Cr]_2(S_2)$ (3) at 30% probability level. Isopropyl groups and hydrogen atoms have been omitted for clarity.

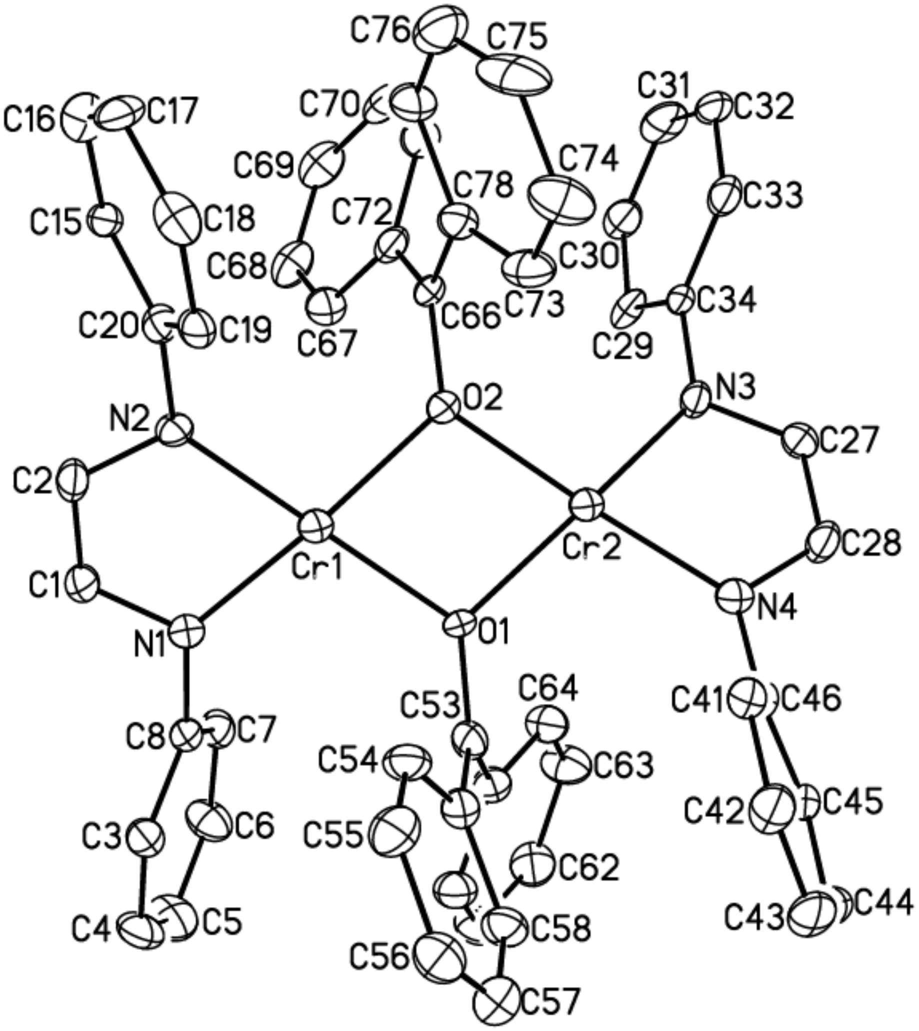

**Figure S2.** **Molecular structure of [$^{H}L^{iPr}$Cr($\mu$-OCPh$_2$)]$_2$ (6) at 30% probability level. One diethyl ether molecule, isopropyl groups and hydrogen atoms have been eliminated for clarity.**

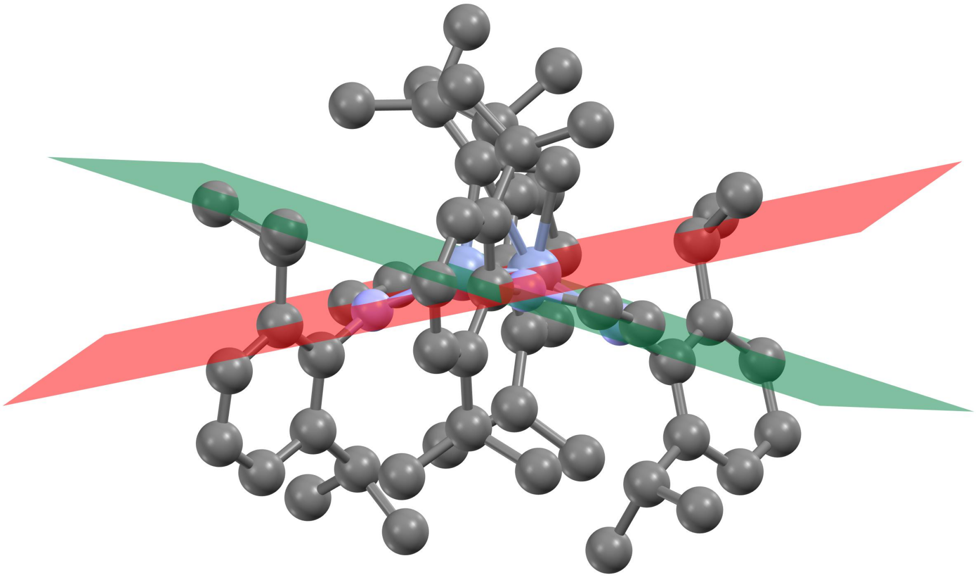

**Figure S3.** Red and green planes indicate the mean planes calculated for the 6-membered rings formed by the chromium atoms and the nitrogen and carbon atoms of the two α-diimine ligands for **2**. The angle between these planes (δ) is 151°. The graphical visualization program Mercury (version 3.1.1) was used for mean plane analysis.

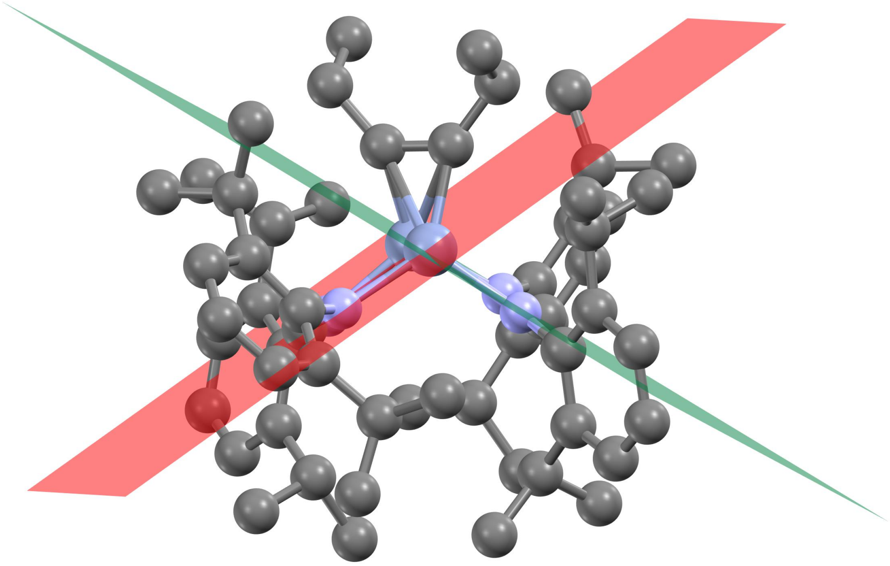

**Figure S4.** Red and green planes indicate the mean planes calculated for the 5-membered rings formed by the chromium atoms and the nitrogen and carbon atoms of the two amidopyridinato ligands for Kempe's compound 'nermaa' (obtained from CSD). The angle between these planes (δ) is 107$^{o}$. The graphical visualization program Mercury (version 3.1.1) was used for mean plane analysis.

| | **2** (0026a) | **3** (0119) | **4** (0762d-sr) |
|---|---|---|---|
| Formula | $C_{59.5}H_{86}Cr_2N_4$ | $C_{52}H_{72}Cr_2N_4S_2$ | $C_{69}H_{94}Cr_2N_6$ |
| Formula Wt. | 961.32 | 921.25 | 1111.50 |
| Space group | *C2/c* | $P2_1/_n$ | *P-1* |
| Color | purple | brown | red |
| a, Å | 25.960(7) | 13.703(5) | 10.073(2) |
| b, Å | 12.029(3) | 19.311(7) | 13.461(3) |
| c, Å | 37.245(8) | 19.558(7) | 13.590(3) |
| α, deg | 90 | 90 | 79.66(3) |
| β, deg | 110.265(9) | 99.039(6) | 81.58(3) |
| γ, deg | 90 | 90 | 80.96(3) |
| V, Å3 | 10911(5) | 5111(3) | 1777.0(7) |
| Z | 8 | 4 | 1 |
| D(calcd), g•cm-3 | 1.170 | 1.197 | 1.039 |
| μ(Mo Kα), mm-1 | 0.438 | 0.544 | 0.345 |
| Temp, K | 195 | 200 | 200 |
| Tmax/Tmin | 1.0000/0.7773 | 0.9548/0.8534 | 0.961/0.852 |
| no. data/params | 13590/590 | 12708/557 | 6958/333 |
| GOF on F2 | 1.020 | 1.038 | 1.007 |
| R(F), %[a] | 7.03 | 4.75 | 8.66 |
| Rw(F2), %[a] | 17.27 | 12.02 | 23.46 |

[a] Quantity minimized: $R_w(F^2) = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)|$.

| | **5** (946) | **6** (854s-sr) | **7** (880) |
|---|---|---|---|
| Formula | $C_{67.5}H_{95}Cr_2N_5O_{0.5}$ | $C_{82}H_{102}Cr_2N_4O_3$ | $C_{52}H_{58}CrN_4$ |
| Formula Wt. | 1088.48 | 1295.67 | 791.02 |
| Space group | *P-1* | *P-1* | $P2_1/n$ |
| Color | brown | Blue-green | brown |
| a, Å | 13.946(3) | 12.257(4) | 10.213(3) |
| b, Å | 21.212(4) | 13.447(4) | 23.838(8) |
| c, Å | 22.202(4) | 22.146(7) | 18.280(6) |
| α, deg | 70.368(4) | 90.757(6) | 90 |
| β, deg | 87.412(4) | 100.752(5) | 97.142(6) |
| γ, deg | 80.550(4) | 97.594(6) | 90 |
| V, $Å^3$ | 6102(2) | 3551.9(18) | 4416(3) |
| Z | 4 | 2 | 4 |
| D(calcd), $g\bullet cm^{-3}$ | 1.185 | 1.211 | 1.190 |
| μ(Mo Kα), $mm^{-1}$ | 0.401 | 0.357 | 0.298 |
| Temp, K | 200 | 200 | 200 |
| Tmax/Tmin | 0.9860/0.8994 | 0.959/0.671 | 1.0000/0.7944 |
| no. data/params | 30190/1362 | 17665/791 | 11097/522 |
| GOF on $F^2$ | 1.017 | 0.933 | 0.995 |
| R(F), %[a] | 9.18 | 8.31 | 9.62 |
| Rw($F^2$), %[a] | 16.51 | 10.67 | 8.59 |

[a] Quantity minimized: $R_w(F^2) = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o-F_c)|$.