

Carboalumination of a Cr-Cr Quintuple Bond

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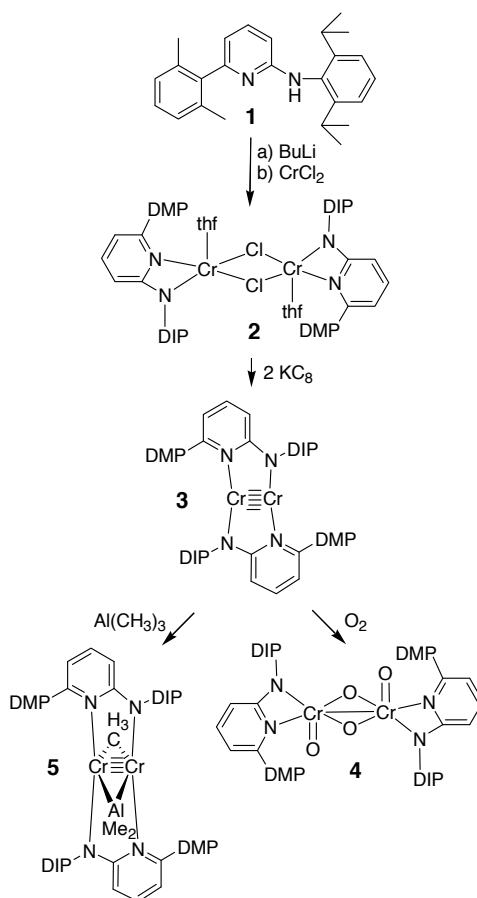
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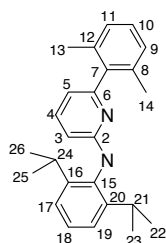
addressed to R.K. or M.K. and requests for materials to R.K.

Synthesis of the metal complexes

General: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N₂ filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O₂). Solvents were dried by distillation from sodium wire / benzophenone. Commercial CrCl₂ (Alfa Aesor) was used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Bruker 250 MHz and Varian 400 MHz at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. The effective magnetic moments were determined using Sherwood Scientific Magnetic Susceptibility Balance. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,^[1] SHELXL97^[2] and WinGX.^[3] CCDC-713544 (**2**), CCDC-713545 (**3**), CCDC-713546 (**4**) and CCDC-713547 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



Scheme S1. Synthesis of **2**, **3**, **4** and **5** (DIP = 2,6-diisopropylphenyl, DMP = 2,6-dimethylphenyl).



Scheme S2. Labeling of the NMR signals.

Synthesis of 2: BuLi (2.5 mL, 4.00 mmol) was added to **1** (1.434 g, 4.00 mmol) in THF (20 mL) at 0 °C and was stirred for two hours at room temperature. The lithiated solution was then added to CrCl₂ (0.492 g, 4.00 mmol) in THF (5 mL) at 0 °C. The resulting brownish green solution was allowed to warm to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with pentane (20 mL). The filtrate was allowed to stand overnight at -25 °C to afford green

crystalline material. Yield: 0.89 g (43 %). $C_{58}H_{74}Cl_2Cr_2N_4O_2$ (1035.4): Calcd. C 67.36 H 7.21 N 5.42; found C 66.69 H 6.86 N 5.38. $\mu_{\text{eff}}(298.6 \text{ K}) = 2.81 \mu_{\text{B}}$. ^1H NMR (250 MHz, C_6D_6): $\delta = 0.87$ (br s), 1.09 (br s), 1.23 (br s), 2.22 (s), 3.31 (br s), 3.98 (v br s), 5.87 (br s), 6.39 (br s) ppm.

Synthesis of 3: (1.39 g, 1.34 mmol) of **2** in THF (10 mL) was added to freshly prepared KC_8 (0.408 g, 3.00 mmol) in THF (20 mL) at -30°C and the resulting purple solution was stirred for 24 hours at room temperature. THF was removed and purple brown solution was then extracted with toluene (20 mL). The filtrate was reduced and allowed to stand overnight at low temperature to afford purple/red crystalline material. Crystals suitable for X-ray analysis were grown from C_6D_6 solution. Yield: 0.495 g (45 %). $C_{50}H_{58}Cr_2N_2$ (819): Calcd. C 73.32 H 7.14 N 6.84; found C 72.55, H 7.02, N 6.80. ^1H NMR (400 MHz, C_6D_6): $\delta = 0.83$ (d, 24H, $J = 6.8$ Hz, $H^{22,23,25,26}$), 1.52 (d, 24H, $J = 6.8$ Hz, $H^{22,23,25,26}$), 1.94 (s, 6H, $H^{13,14}$), 4.01 (sep, 4H, $J = 6.8$ Hz, $H^{21,24}$), 5.81 (m, 6H, $H^{9,10,11/17,18,19}$), 6.00 (d, 2H, $J = 6.8$ Hz, H^3), 6.78 (d, 2H, $J = 6.8$ Hz, H^5), 6.92 (m, 6H, $H^{9,10,11/17,18,19}$), 7.30 (t, 2H, $J = 7.8$ Hz, H^4) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 19.9$ ($C^{13,14}$), 24.0 ($C^{22,23,25,26}$), 25.2 ($C^{22,23,25,26}$), 29.0 ($C^{21,24}$), 107.1 (C^3), 109.5 (C^5), 123.3 ($C^{17,19}$), 124.7 (C^{18}), 126.7 ($C^{9,11}$), 127.0 (C^{10}), 132.6 ($C^{8,12}$), 135.8 (C^4), 137.8 (C^7), 143.8 ($C^{16,20}$), 143.9 (C^{15}), 155.6 (C^6), 172.2 (C^2) ppm.

Synthesis of 4: O_2 (1 bar) was introduced into **3** (0.1 g, 0.12 mmol) in hexane (10 mL) at room temperature with continuous stirring. A colour change from purple to brown was observed within five minutes. The reaction solution was further stirred for 4 hours and then filtered. The filtrate was kept at -30°C to afford brown crystals. Yield: 0.079 g (73 %). $C_{50}H_{58}Cr_2N_4O_4$ (883): Calcd. C 68.01 H 6.62 N 6.34; found C 67.71, H 6.88, N 6.10. ^1H NMR (400 MHz, C_6D_6): $\delta = 1.40$ (d, 12H, $J = 6.8$ Hz, $H^{22,23,25,26}$), 1.41 (d, 12H, $J = 6.8$ Hz, $H^{22,23,25,26}$), 1.80 (s, 6H, $H^{13,14}$), 2.24 (s, 6H, $H^{13,14}$), 2.46 (sep, 2H, $J = 6.8$ Hz, $H^{21,24}$), 4.76 (sep, 2H, $J = 6.8$ Hz, $H^{21,24}$), 5.40 (d, 2H, $J = 8.4$ Hz, H^3), 5.85 (d, 2H, $J = 6.8$ Hz, H^5), 6.74-7.38 (m, 14H, $H^{4,9,10,11,17,18,19}$) ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 19.8$ ($C^{13,14}$), 20.2 ($C^{13,14}$), 24.4 ($C^{22,23,25,26}$), 24.7 ($C^{22,23,25,26}$), 25.0 ($C^{22,23,25,26}$), 28.1 ($C^{21,24}$), 28.7 ($C^{21,24}$), 101.0 (C^3), 111.8 (C^5),

123.9 (C^{9,11}), 124.3 (C^{9,11}), 127.2 (C¹⁸), 127.5 (C^{17,19}), 136.2 (C¹⁰), 136.5 (C⁴), 136.7 (C^{8,12}), 140.2 (C⁷), 142.6 (C^{8,12}), 145.3 (C^{16,20}), 147.4 (C¹⁵), 157.9 (C⁶), 173.5 (C²) ppm.

Synthesis of 5: Al(CH₃)₃ (0.1 mL) was added to **3** (42 mg) in hexane (5 mL) at room temperature. Reaction mixture was then heated overnight at 70 °C as colour changed from purple to brown and then filtered. The filtrate was kept at room temperature to afford brown red crystals. Yield: 0.042 g (92 %). C₅₃H₆₆AlCr₂N₄ (890.09): Calcd. C 71.52 H 7.47 N 6.29; found C 71.75, H 6.88, N 6.39. ¹H NMR (400 MHz, C₆D₆): δ = -0.13 (s, 6H, H^{AlCH₃}), 1.00 (s, 3H, H^{CH₃}), 1.12 (d, 6H, *J* = 6.8 Hz, H^{22,23,25,26}), 1.26 (d, 6H, *J* = 6.8 Hz, H^{22,23,25,26}), 1.28 (d, 6H, *J* = 6.8 Hz, H^{22,23,25,26}), 1.32 (d, 6H, *J* = 6.8 Hz, H^{22,23,25,26}), 1.96 (s, 6H, H^{13,14}), 2.09 (s, 6H, H^{13,14}), 3.73 (sep, 2H, *J* = 6.8 Hz, H^{21,24}), 3.82 (sep, 2H, *J* = 6.8 Hz, H^{21,24}), 5.76 (d, 2H, *J* = 6.8 Hz, H³), 6.07 (m, 4H, H^{17,19}), 6.25 (m, 2H, H¹⁸), 6.41 (d, 2H, *J* = 6.8 Hz, H⁵), 6.95 (m, 2H, H⁴), 7.00-7.11 (m, 6H, H^{9,10,11}) ppm. ¹³C NMR (100 MHz, C₆D₆): δ = -6.3 (C^{AlCH₃}), 14.3 (C^{CH₃}), 20.1 (C^{13,14}), 20.4 (C^{13,14}), 23.6 (C^{22,23,25,26}), 24.7 (C^{22,23,25,26}), 25.9 (C^{22,23,25,26}), 26.9 (C^{22,23,25,26}), 27.4 (C^{21,24}), 28.2 (C^{21,24}), 106.5 (C³), 110.7 (C⁵), 123.9 (C^{9,11}), 124.7 (C^{17,19}), 125.9 (C¹⁸), 127.3 (C¹⁰), 134.1 (C^{8,12}), 135.1 (C^{8,12}), 135.8 (C⁴), 141.0 (C⁷), 145.7 (C^{16,20}), 146.0 (C¹⁵), 156.5 (C⁶), 170.2 (C²) ppm.

Single Crystal X-Ray Diffraction Analyses: Compound **2**: C₂₉H₃₇ClCrN₂O, *M* = 517.06, green crystal (0.56 x 0.31 x 0.18 mm); Monoclinic, space group *P2(1)/n*; *a* = 14.5030(11), *b* = 8.4300(6), *c* = 22.0250(13) Å; β = 96.049(6) °; *V* = 2677.8(3) Å³; *Z* = 4; μ = 0.55 mm⁻¹; ρ_{ber.} = 1.283 g cm⁻³; 19000 measured reflections, 3641 no. of reflections obs. [*I* > 2σ (*I*)], 4609 unique; 309 parameters; largest max./min. in the final difference Fourier synthesis 0.58 eÅ⁻³/-0.48 eÅ⁻³; *R*₁ = 0.0524 (*I* > 2σ(*I*)), *wR*² (all data) = 0.1464. Compound **3**: C₆₅H₇₃Cr₂N₄, *M* = 1014.27, red brown (1.04 x 0.45 x 0.18 mm); Triclinic, space group *P-1*; *a* = 11.9930 (9), *b* = 12.5339 (10), *c* = 12.5675 (10) Å; α = 62.264 (6), β = 77.005 (6), γ = 63.040 (6) °; *V* = 1490.1(2) Å³; *Z* = 1; μ = 0.41 mm⁻¹; ρ_{ber.} = 1.130 g cm⁻³; 5634 measured reflections, 4178 no. of reflections obs. [*I* > 2σ (*I*)], 5634 unique; 324 parameters; largest max./min. in the final difference Fourier synthesis 0.81 eÅ⁻³/-0.47 eÅ⁻³; *R*₁ = 0.0640 (*I* > 2σ(*I*)), *wR*² (all data) = 0.1947.

Compound **4**: $C_{25}H_{29}CrN_2O_2$, $M = 441.5$, green ($0.37 \times 0.32 \times 0.23$ mm); Monoclinic, space group $P2(1)/c$; $a = 12.6130$ (10), $b = 14.6670$ (12), $c = 13.6720$ (12) Å; $\beta = 116.302$ (6) °; $V = 2267.4(3)$ Å³; $Z = 4$; $\mu = 0.53$ mm⁻¹; $\rho_{ber.} = 1.293$ g cm⁻³; 28836 measured reflections, 3181 no. of reflections obs. [$I > 2\sigma(I)$], 4289 unique; 273 parameters; largest max./min. in the final difference Fourier synthesis 0.79 eÅ⁻³/ -0.33 eÅ⁻³; $R_1 = 0.0528$ ($I > 2\sigma(I)$), wR^2 (all data) = 0.1333. Compound **5**: $C_{163}H_{204}Al_3Cr_6N_{12}O_2$, $M = 441.5$, orange brown ($0.40 \times 0.33 \times 26$ mm); Triclinic, space group $P-1$; $a = 12.3650$ (6), $b = 15.7570$ (8), $c = 20.6880$ (9) Å; $\alpha = 79.256$ (4), $\beta = 72.858$ (4), $\gamma = 85.939$ (4) °; $V = 3783.6(3)$ Å³; $Z = 1$; $\mu = 0.49$ mm⁻¹; $\rho_{ber.} = 1.203$ g cm⁻³; 51546 measured reflections, 11845 no. of reflections obs. [$I > 2\sigma(I)$], 14246 unique; 868 parameters; largest max./min. in the final difference Fourier synthesis 1.20 eÅ⁻³/ -0.57 eÅ⁻³; $R_1 = 0.0636$ ($I > 2\sigma(I)$), wR^2 (all data) = 0.1859.

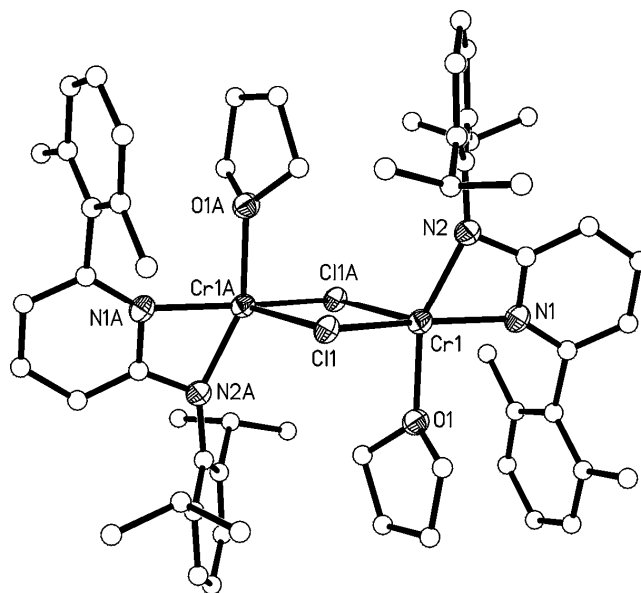


Figure S1. Molecular structure of **2** [ORTEP representation (on the 50 % probability level) for all non carbon atoms); Hydrogen atoms and two toluene molecules (per complex) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.085 (2), N2-Cr1 2.071 (2), C11-Cr1 2.4376 (8), C11A-Cr1 2.6409 (9), Cr1-O1 2.057 (2); N2-Cr1-N1 64.99 (9), O1-Cr1-N1 91.67 (3).

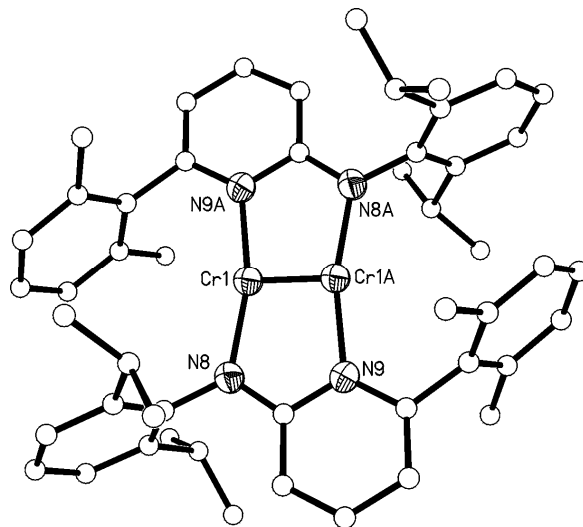


Figure S2. Molecular structure of **3** [ORTEP representation (on the 50 % probability level) for all non carbon atoms); Hydrogen atoms and two C_6D_6 molecules have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Cr1-Cr1A 1.7499 (10), Cr1-N8 2.000 (3), Cr1-N9 2.027 (3); Cr1-Cr1A-N8A 98.65 (8), Cr1-Cr1A-N9 96.34 (9), N2-Cr1-N1 165.01 (11).

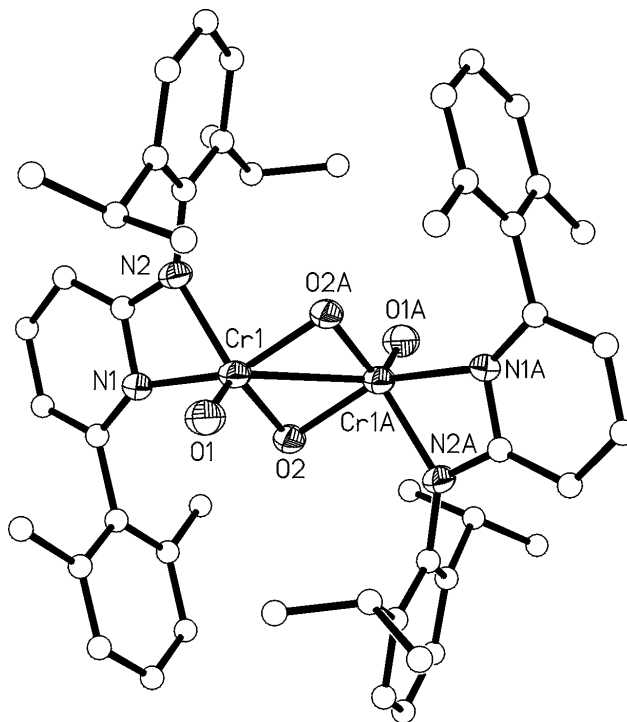


Figure S3. Molecular structure of **4** [ORTEP representation (on the 50 % probability level) for all non carbon atoms); Hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Cr1-N1 2.053 (2), Cr1-N2 1.946 (2), O1-Cr1 1.563 (2), O2-Cr1 1.791 (2), Cr1-Cr1A 2.5314 (10); Cr1-Cr1A-O1A 121.69 (9), Cr1-Cr1A-O2 45.02 (7), N2-Cr1-N1 65.20 (10).

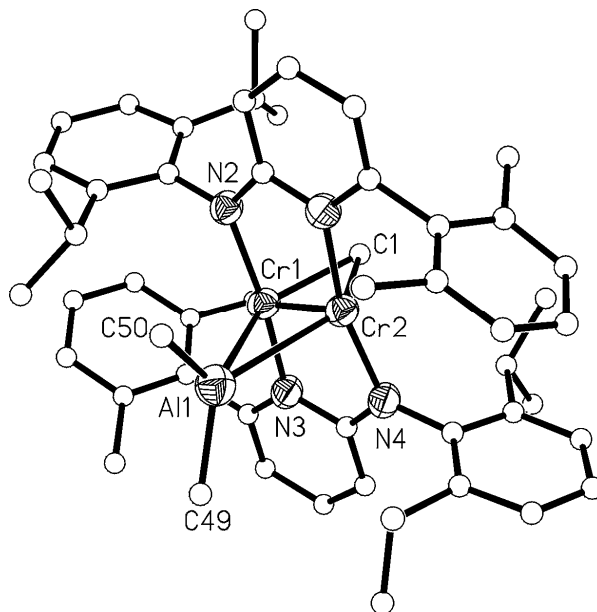


Figure S4. Molecular structure of **5** [ORTEP representation (on the 50 % probability level) for all non carbon atoms); Hydrogen atoms and 0.5 ether molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1-Cr2 1.8365 (8), Cr1-N2 2.014 (3), Cr2-N1 2.040 (3), C1-Cr1 2.227 (4), C1-Cr2 2.252 (4), Al1-Cr1 2.8945 (14), Al1-Cr2 2.9076 (14); Cr2-Cr1-N2 98.13 (8), Cr2-Cr1-N3 94.81 (8), Cr1-Cr2-N1 94.60 (8), Cr1-Cr2-C1 65.08 (12), Cr1-Cr2-Al1 71.16 (4), N2-Cr1-N1 166.16 (12).

Susceptibility measurements:

Susceptibility measurements were carried out with a Quantum-Design MPMS-5S SQUID magnetometer equipped with a 5 Tesla magnet in the range from 2 to 300 K at a magnetic field of 0.5 T. The powdered samples were contained in a teflon bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the sample holder and the teflon bucket. The molar susceptibility data were corrected using the Pascal constant and the increment method according to Haberditzel. Simulation of the experimental magnetic data was performed with the julX program developed by E. Bill (Max-Planck Institute for Bioinorganic Chemistry, Mülheim/Ruhr, Germany).

Fitting of the experimental data is indicative of a $S = 0$ ground state and temperature independent paramagnetism TIP due to Zeeman perturbation. Best fit for compound **3** (see Figure S5) was found with a paramagnetic impurity $PI = 4.5\%$ per Cr ($S = 3/2$) and $TIP = 280 \cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$. For compound **5** best fit could be obtained with a PI of 0.3% per Cr ($S = 3/2$) and a TIP of $97 \cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$.

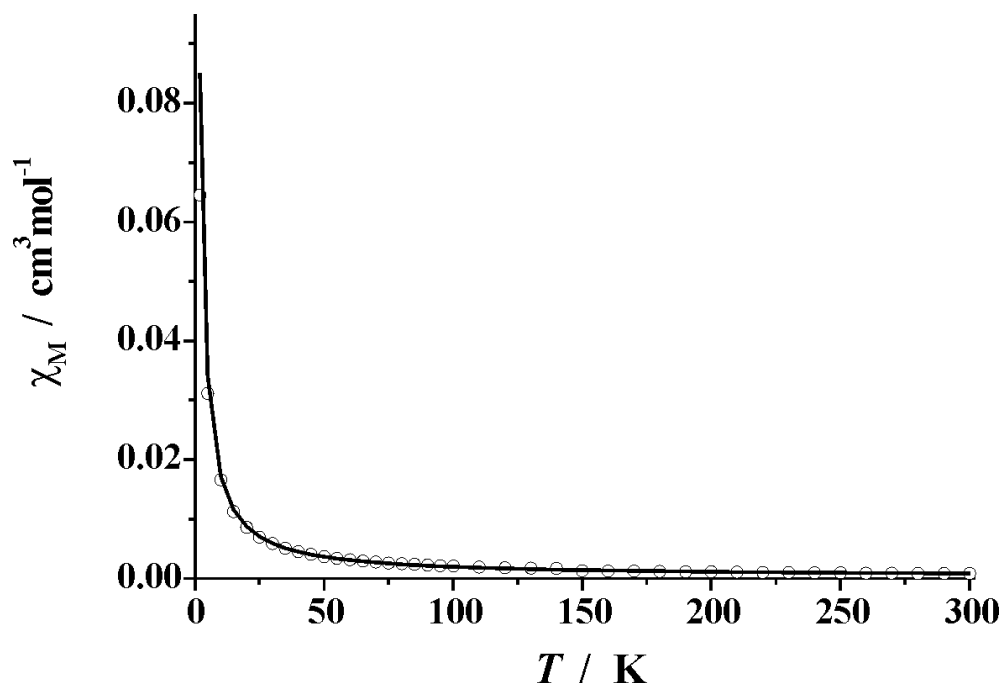


Figure S5. The temperature dependence of the molar magnetic susceptibility of **3**. The open points are the observed susceptibility, the black line reproduces the best fit with the parameters $PI = 4.5\%$ (per Cr, $S = 3/2$) and $TIP = 280 \cdot 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$.

Further Computational Details

Optimization of the positions of the hydrogen atoms, based on the X-ray structure data, was performed with the TURBOMOLE V5.10 program package.^[4,5] NBO/NPA analysis used the Gaussian 03 program package, Revision B.04.^[6] Analyses of the electron localization function was done with a locally modified version of the TopMod program.^[7,8] Figure S6 shows the simplified model structures used in the bonding analyses. Table S1 provides NPA charges for fragments of the two models, Table S2 the Wiberg bond indices. Figure S7 gives color-scale plots of the ELF of the model for **5** in two different planes.

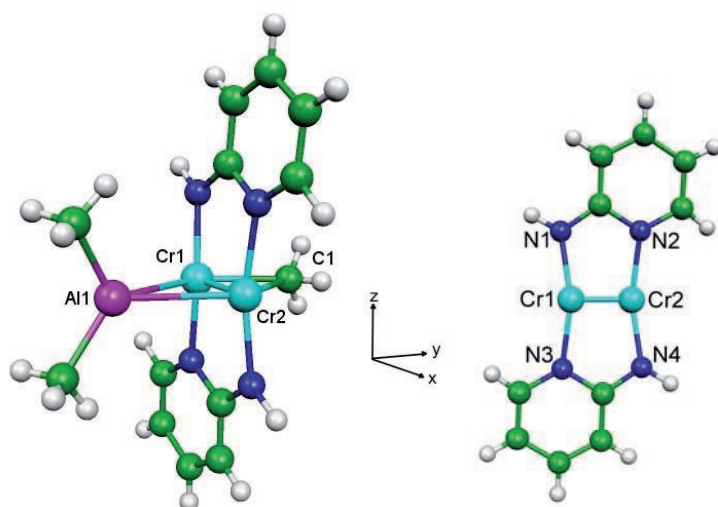


Figure S6. Model structures for **3** (left) and **5** (right).

Table S1. NPA atomic and fragment charges

Compound	Atom/Fragment	Charge
3	Cr 1	0.48943
	Cr 2	0.48948
	Pyridylamido-ligand 1	-0.48945
	Pyridylamido-ligand 2	-0.48948
5	Cr 1	0.67193
	Cr 2	0.66258
	Pyridylamido-ligand 1	-0.37228
	Pyridylamido-ligand 2	-0.36944
	Al(CH ₃) ₂	-0.12253
	CH ₃	-0.46898

Table S2. Wiberg bond indices

Compound	Bond	Bond index
3	Cr1 - Cr2	4.3569
	Cr1 - Amido-N1	0.4193
	Cr2 - Amido-N4	0.4194
	Cr1 - Pyridyl-N3	0.4764
	Cr2 - Pyridyl-N2	0.4763
	5	Cr1 - Cr2
Cr1 - Amido-N1		0.4537
Cr2 - Amido-N4		0.4558
Cr1 - Pyridyl-N3		0.5222
Cr2 - Pyridyl-N2		0.5325
Cr1 - Al1		0.3383
Cr2 - Al2		0.2549
Cr1 - C1		0.1986
Cr2 - C1		0.3401

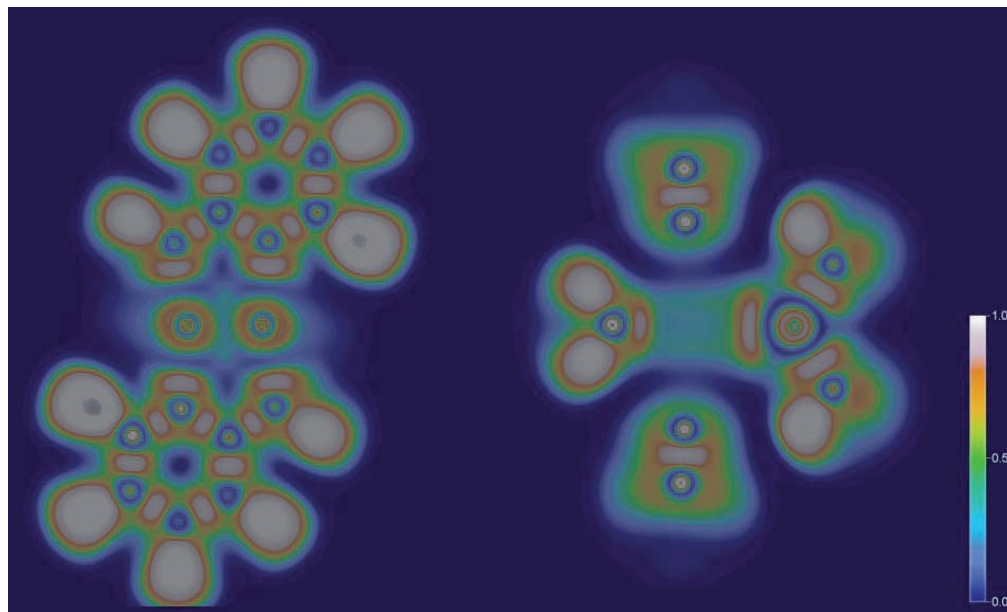


Figure S7. ELF color-scale plot for the model of **5**. Left side: xz-plane. Right side: yz-plane.

References

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