Supplemental Information

[CrL]$_2$ as an Electron Shuttle for Reductively Promoted Hydrazine Disproportionation

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Experimental

General Methods. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or in a glovebox under ultra-high purity nitrogen. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze-pump-thaw method thrice prior to use. Glassware was oven-dried at 150 °C overnight and flame dried prior to use. THF was stored over activated 4 Å molecular sieves and sodium metal pieces. Deuterated solvents, $THFd_8$, $DMSO-d_6$ were dried over CaH_2, subjected to three freeze-pump-thaw cycles, distilled and stored over 4 Å molecular sieves in the glovebox prior to use. All starting reagents were commercially available and used without further purification. All ^1H NMR spectra were collected at 25 °C on a Varian Inova-400 spectrometer operating at 400.11 MHz. ^1H NMR spectra of paramagnetic compounds were collected with 0.1 s relaxation delay and at least 1024 transients per spectra. Spectra were referenced to the residual respective protio impurities and solvent employed.

$[Cr_2L_2(PhNH_2)_2(PhHNN)]$. A portion of $[CrL]_2$ (25.0 mg, 0.033 mmol) was dissolved in $THFd_8$ and added to a Teflon-valve NMR tube via pipette. Phenylhydrazine (6.6 µL, 0.067 mmol) was added to the NMR tube via syringe. In time of mixing the reagents the color changed to a dark brown-yellow. The NMR tube was tumbled for 1 hour before collecting ^1H NMR spectra. **^1H NMR (400 MHz, 25 °C, THF_{d8}):** δ 31.7, 21.4, 18.5, 16.7, 8.2, 7.3, 7.0, 6.9, 6.7, 6.5, 5.9, 4.3, 3.0 (9H, tBu), 2.7 (9H, tBu), 2.5 (9H, tBu), 2.2 (9H, tBu), −7.6, −11.2, −18.2, −30.0, −35.9, −38.6, −43.2, −45.4, −71.5, −73.5, −103.9 ppm. **ESI-MS (+):** m/z, calc. for $C_{50}H_{61}Cr_2N_{14} = 961.4$, found = 961.4, $[Cr_2(HL)(L)(NHNHPh)_2]$; m/z calc. for $C_{44}H_{55}Cr_2N_{12} = 855.4$, found 855.3, $[Cr_2(HL)_2(NHNHPh)]$; m/z calc. for $C_{44}H_{53}Cr_2N_{12} = 853.3$, found = 853.3, $[Cr_2(L)_2(NHNHPh)]$; m/z calc. for $C_{38}H_{53}Cr_2N_{12} = 781.3$, found 781.3, $[Cr_2(HL)(L)(NH_3)_2]$.

The net conversion shown in eq 3 consumes two electrons, hence is not yet a closed cycle. We sought to close the synthetic cycle by the addition of H_2 or 9,10-dihydroanthracene to $[Cr_2L_2(PhNH_2)_2(PhHNN)]$. Both reagents failed to effect subsequent transformation in THF solvent at room temperature or up to 60 °C.

NH_3 and benzene assays. The volatile material from the reaction of $[CrL]_2$ and $PhNHNH_2$ in a 1:4 mole ratio was vacuum transferred from a JY NMR tube (**A**) to another JY NMR tube (**B**) containing 1 mL of a 2mM $NaBArF_{24}$ solution in $DMSO_{d6}$ and 25 µL of 2 M HCl in Et_2O by vacuum transfer. JY NMR tube **B** was tumbled for 30 minutes prior to collecting ^1H NMR spectra. A T_1 experiment was conducted to ensure the relaxing delay (10 sec) was appropriate for quantifying the NMR yield of NH_4Cl. Assay for NH_3 and benzene from the reaction of $[CrL]_2$ and $PhNHNH_2$ in a 1:1.5 and 1:2 mole ratio was conducted in an analogous manner without the addition of $NaBArF_{24}$ as an internal standard.
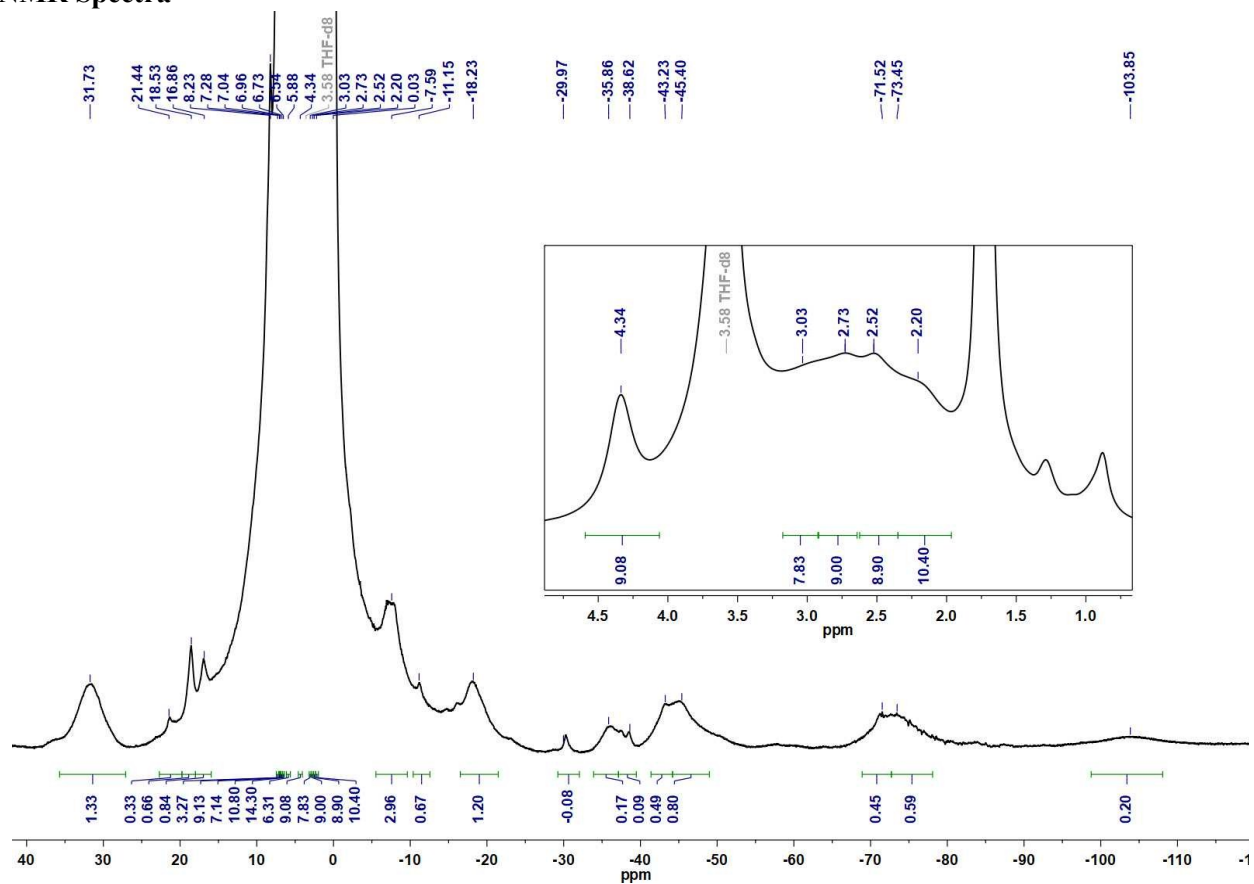
NMR Spectra

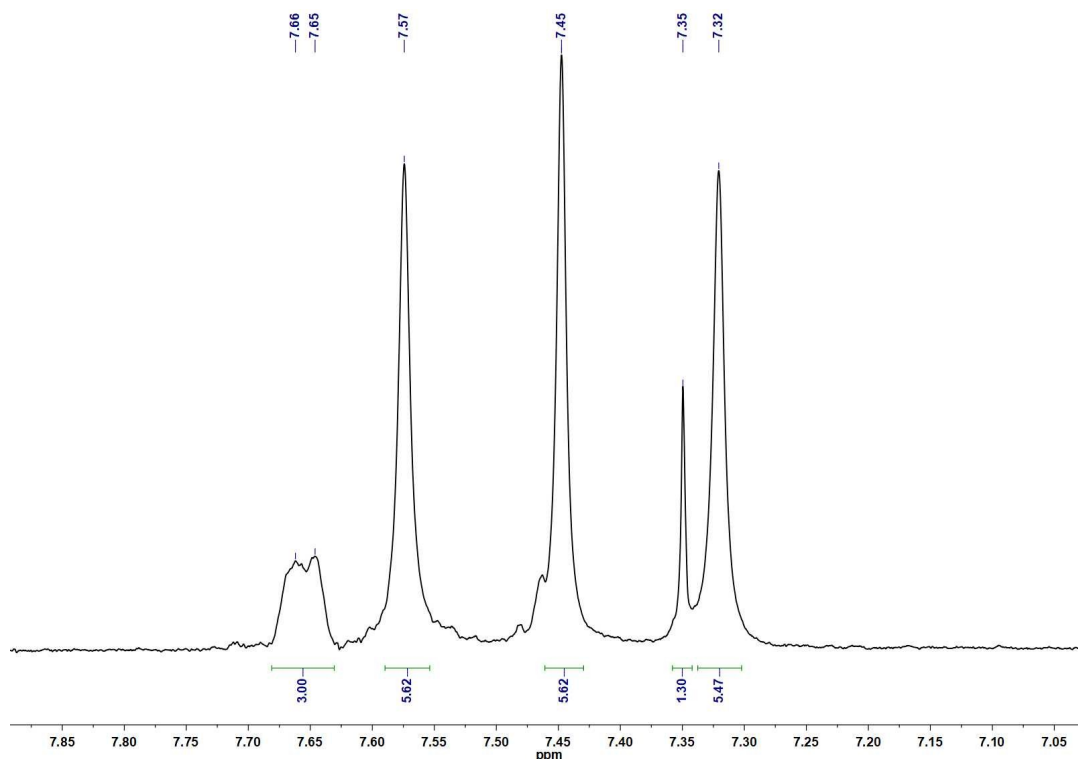**Figure S1.** ^{1}H NMR spectrum of reaction of [CrL]$_2$ and PhNHNH$_2$ in a 1:4 mole ratio in THF$_{d8}$.

Figure S2. ^{1}H NMR spectrum of volatile products from [Cr$_2$L$_2$(PhNH$_2$)$_2$(PhHNN)] synthesis, showing NH$_4^+$ triplet ($^1J_{N-H}$ = 50.7 Hz), and benzene singlet (7.35 ppm); BArF$_{24}$ signals at 7.62 ppm.
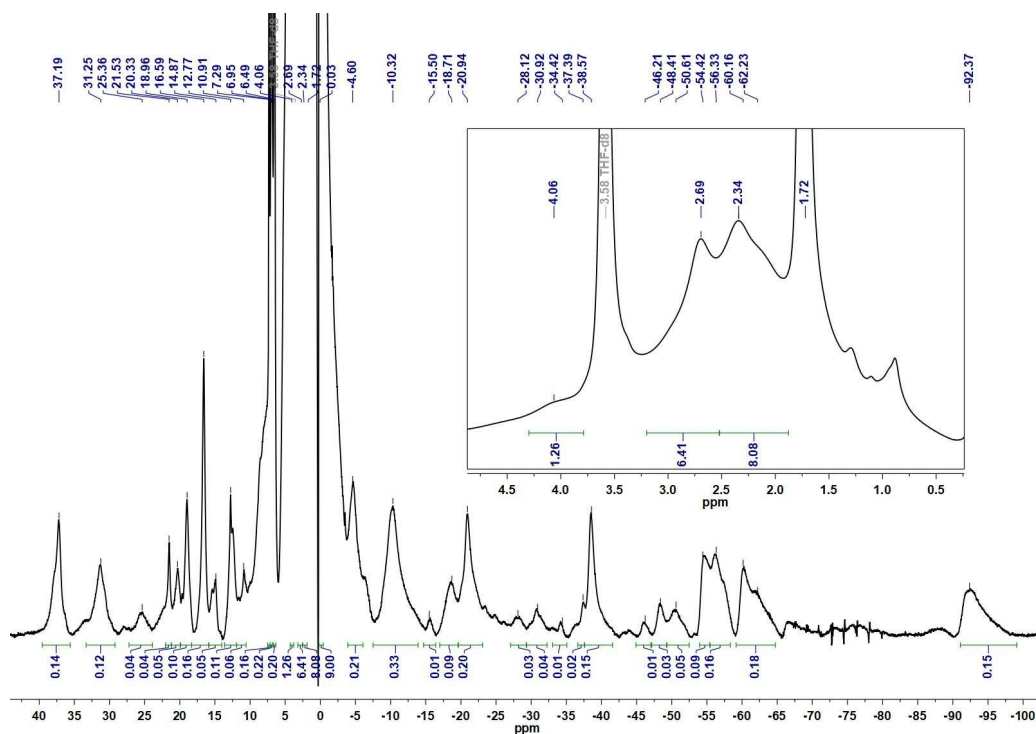

Figure S3. ^{1}H NMR spectrum of reaction of [CrL]$_2$ and PhNHNH$_2$ in a 1:1.5 mole ratio in THF$_{d8}$.
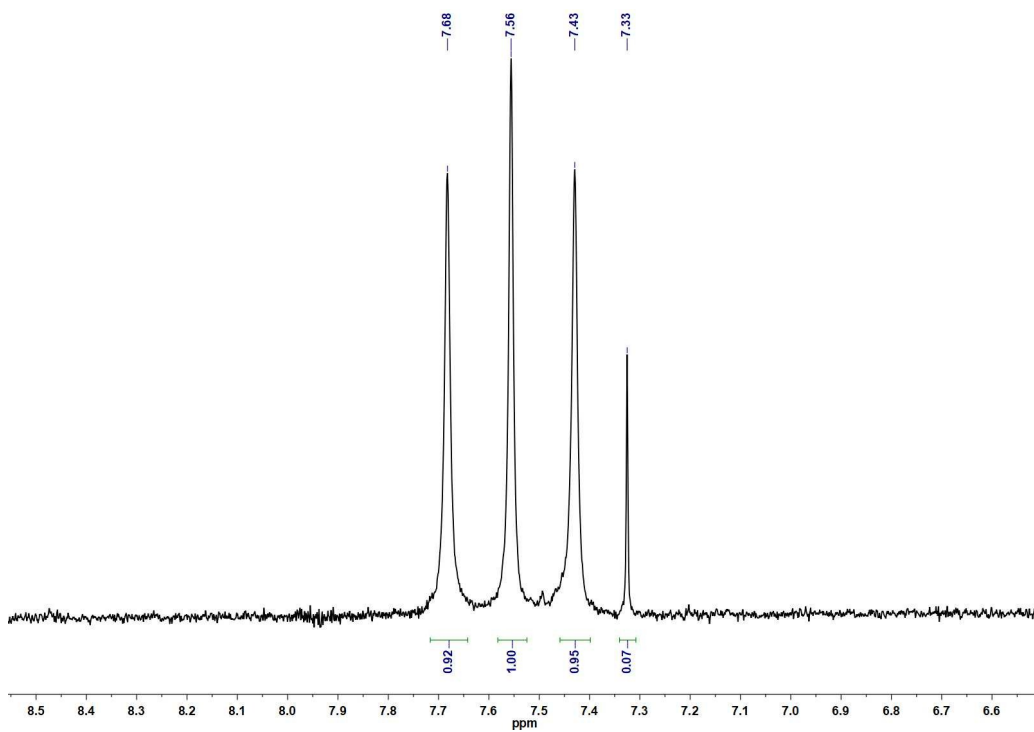
Figure S4. ^{1}H NMR spectrum of volatile products from [Cr$_2$L$_2$(PhNH$_2$)$_2$(PhHNN)] (1[CrL]$_2$:1.5PhNHNH$_2$ mole ratio) synthesis, showing NH$_4^+$ triplet, and benzene singlet (7.33 ppm).

Figure S5. ^{1}H NMR spectrum of [CrL]$_2$ and PhNHNH$_2$ in a 1:2 mole ratio in THF$_{d8}$.

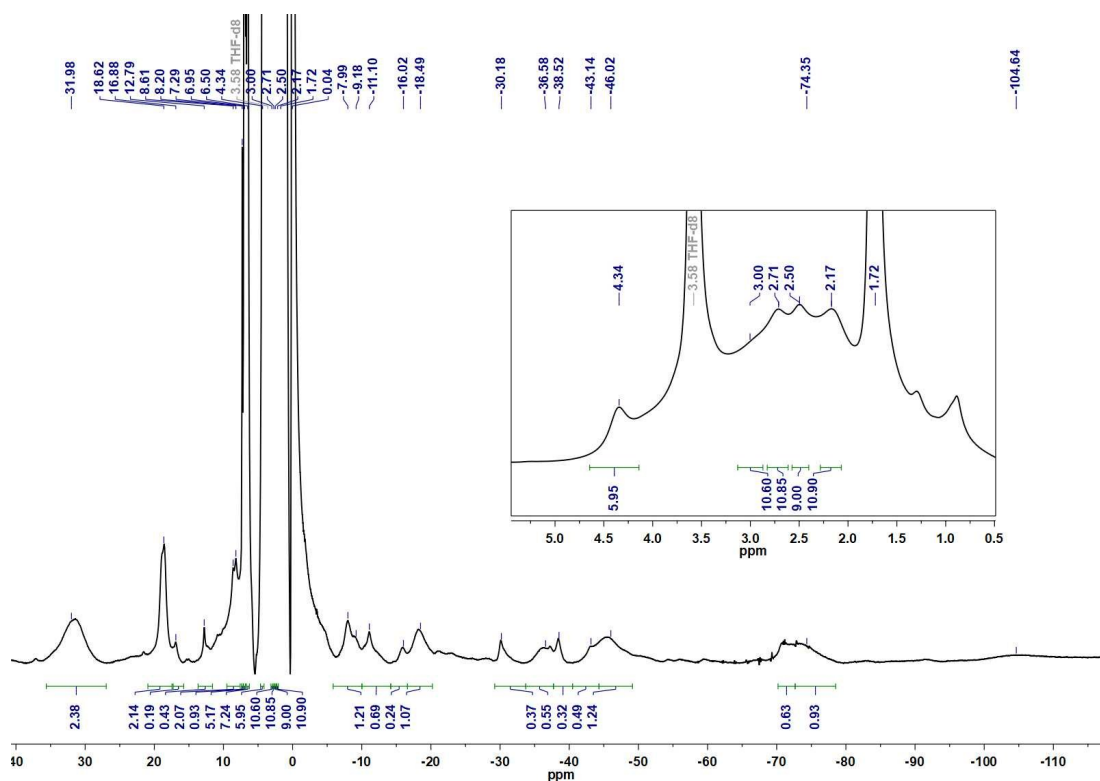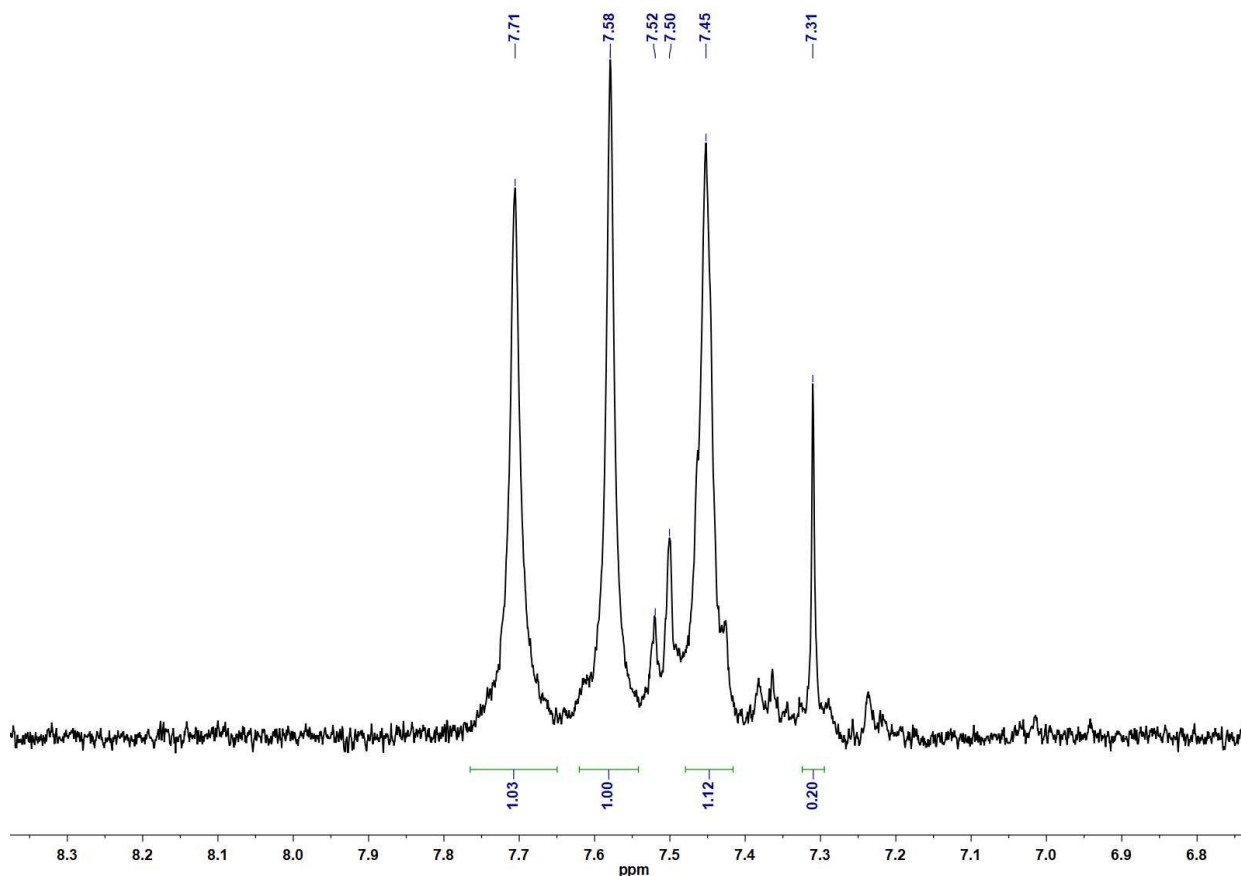**Figure S6.** ^{1}H NMR spectrum of volatile products from [Cr$_2$L$_2$(PhNH$_2$)$_2$(PhHNN)]
(1[CrL]$_2$:2PhNHNH$_2$ mole ratio) synthesis, showing NH$_4^+$ triplet, and benzene singlet (7.31 ppm).

Crystallographic Information

MSC#S18013 [Cr$_2$L$_2$(PhNH$_2$)$_2$(PhHNN)] Labrum
CCDC 1906015

A brown crystal (approximate dimensions 0.070 x 0.040 x 0.020 mm^3) was placed on the tip of a glass capillary and mounted on a Huber three-circle diffractometer and measured at 100 K. investigated with synchrotron radiation at the ChemMatCARS beamline, Advanced Photon Source, Argonne National Laboratory, Chicago, utilizing the SCrAPS program (http://www.iumsc.indiana.edu/projects/SCrAPS/index.html).

Data collection
The data collection was carried out using synchrotron radiation (λ = 0.41328, silicon 111 and 311 monochromators, two mirrors to exclude higher harmonics) with a frame time of 3.0 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of hemispheres. Two major sections of frames were collected with 0.50° steps in ϕ and a detector position of 0° in 2θ. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 6128 strong reflections

from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2] Refer to Table S1 for additional crystal and refinement information.

Structure solution and refinement

The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using Superflip[3] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[4] The result of the soluton provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding. The final full matrix least squares refinement converged to R1 = 0.0854 and wR2 = 0.2568 (F^2, all data).

Structure description

The structure was found as an $[CrL]_2$ dimer with a bridging phenyldiazene moiety. The coordination sphere about Cr2 also contains two aniline ligands, in addition to the pincer ligand. The pincer ligands are deprotonated and hydrogen bond to the aniline moieties.

Table S1. Crystal data and structure refinement for S18013.

Empirical formula	C65 H86 Cr2 N14 O1
Formula weight	1183.48
Crystal color, shape, size	brown block fragment, 0.070 x 0.040 x 0.020 mm³
Temperature	100 K
Wavelength	0.41328 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 15.7688(17) Å $\quad$ α= 90°.
	b = 15.4878(16) Å $\quad$ β= 99.1594(17)°.
	c = 26.500(3) Å $\quad$ γ = 90°.
Volume	6389.3(12) Å³
Z	4
Density (calculated)	1.230 Mg/m³
Absorption coefficient	0.100 mm⁻¹
F(000)	2520
Data collection	
Diffractometer	Huber three-circle
Theta range for data collection	0.905 to 14.274°.
Index ranges	-18<=h<=18, -18<=k<=18, -31<=l<=31
Reflections collected	129860
Independent reflections	11249 [R(int) = 0.168]
Observed Reflections	7007

Completeness to theta = 12.990°	99.2 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.98
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with $P = (Fo^2 + 2 Fc^2)/3$, A = 0.124 , B = 15.090
Data / restraints / parameters	11206 / 78 / 734
Goodness-of-fit on F^2	1.0097
Final R indices [I>2sigma(I)]	R1 = 0.0854, wR2 = 0.2161
R indices (all data)	R1 = 0.1326, wR2 = 0.2568
Largest diff. peak and hole	1.41 and -0.86 e.Å^{-3}

References
1.   Bruker Analytical X-Ray Systems, Madison, WI, **current version**.
2.   R. Blessing, *Acta Crystallographica Section A*, 1995, **51**, 33-38.
3.   L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786-790.
4.   P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.