Electronic Supplementary Information for

Reactivity of paramagnetic organometallic phenylenediamido chromium complexes

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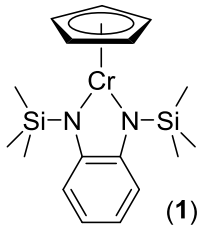
General Considerations: All reactions were carried out under nitrogen using standard Schlenk and glove box techniques. Hexanes, toluene, Et_2O and THF were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA, USA). Celite (Aldrich) was dried overnight at 120 °C before being evacuated and then stored under nitrogen. $CrCl_3$ (anhydrous), $LiN(SiMe_3)_2$, n-BuLi (1.6M in hexanes), NaCp (2.0M in THF), Me_3SiCH_2MgCl (1.0 M in Et_2O), $PbCl_2$, N_3Ad and 1,4-dioxane (anhydrous) were purchased from Aldrich and used as received. $(Me_3SiNH)_2C_6H_4$,[1] $(Me_3CCH_2NH)_2C_6H_4$,[2] $(PhNH)_2C_6H_4$[3], and $CpCrCl_2(THF)$,[4] and were prepared according to the literature procedures. $Li_2[R_2C_6H_4]$ were prepared by reaction of the corresponding neutral, doubly protonated ligand with BuLi. The azides: PhN_3, $TolN_3$, $MesN_3$,[5] N_3Ts[6] and $N_3Trisyl$[7] were prepared according to the literature procedures and freeze-pump-thaw degassed before use.

UV-vis spectroscopic data were collected on a Varian Cary 100 Bio UV-visible or a Shimadzu UV 2550 UV-vis spectrophotometer in hexane or THF solution in a specially constructed cell for air-sensitive samples: a Kontes Hi-Vac Valve with PTFE plug was attached by a professional glassblower to a Hellma 10 mm path length quartz absorption cell with a quartz-to-glass graded seal. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, ON, Canada or by the UBC Department of Chemistry microanalytical services.

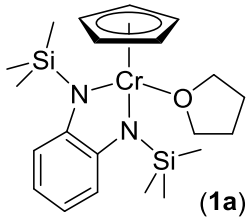


(**1**)

Synthesis of $CpCr[(Me_3SiN)_2C_6H_4]$ (1). Method A: To a solution of $CpCrCl_2(THF)$ (314 mg, 1.20 mmol) 30 ml Et_2O, $(Me_3SiNH)_2C_6H_4$ (351 mg, 1.39 mmol) was added, causing the solution to become dark green. Me_3SiCH_2MgCl (2.6 ml, 1.0 M in Et_2O, 2.6 mmol) was added and stirred for 4 h, during which time solution become dark red. 1,4-dioxane (1.3 ml, 15 mmol) was added, resulting in the immediate formation of a large quantity of white precipitate. After stirring for an additional 1 h, the solvent was removed *in vacuo*, the residue was extracted with 6 ml hexanes,

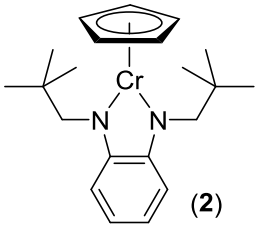
and then the dark red extracts were filtered through Celite and cooled to -35 °C. Black crystals of **1** were isolated in two different fractions (298 mg, 68%).

Method B: To a solution of $CpCrCl_2(THF)$ (421 mg, 1.62 mmol) 20 ml Et_2O, $Li_2[(Me_3SiN)_2C_6H_4]$ (468 mg, 1.77 mmol) was added, causing the solution to become dark red. After sitting for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 6 ml hexanes, and then the dark red extracts were filtered through Celite and cooled to -35 °C. Black crystals of **1** were isolated in two different fractions (316 mg, 53%). (Evans, C_6D_6): 3.49 μ_B. Anal. Calcd for $C_{17}H_{27}N_2Si_2Cr$: C, 55.55; H, 7.40; N, 7.62. Found: C, 54.84; H, 7.58; N, 6.07. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 359 (3100), 450 (1800), 501(1700), 869(1200).



(**1a**)

Synthesis of $CpCr[(Me_3SiN)_2C_6H_4](THF)$ (1a). To a solution of $CpCrCl_2(THF)$ (105 mg, 0.405 mmol) 15 ml Et_2O, $(Me_3SiNH)_2C_6H_4$ (97 mg, 0.38 mmol) was added, causing the solution to become dark green. Me_3SiCH_2MgCl (0.85 ml, 1.0 M in Et_2O, 0.85 mmol) was added and 10 ml THF was also added to dissolve the precipitate in the solution. After stirring for 20 h, 1,4-dioxane (1.3 ml, 15 mmol) was added, resulting in the immediate formation of a large quantity of white precipitate. After stirring for an additional 1 h, the solvent was removed *in vacuo*, the residue was extracted with 4 ml hexanes, and then the dark red extracts were filtered through Celite and cooled to -35 °C. Black crystals of **1a** were isolated in two different fractions (131 mg, 77%). UV-vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 472 (1000). Due to the facile loss of THF from **1a**, a satisfactory elemental analysis for this complex was not obtained.

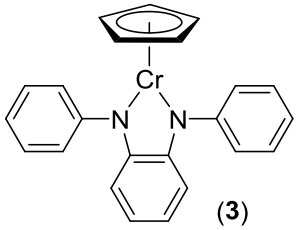


(**2**)

Synthesis of $CpCr[(Me_3CCH_2N)_2C_6H_4]$ (2). Method A: To a solution of $CpCrCl_2(THF)$ (100 mg, 0.384 mmol) 20 ml Et_2O, $(Me_3CCH_2NH)_2C_6H_4$ (111 mg, 0.447 mmol) was added, causing the solution to become dark green. Me_3SiCH_2MgCl (0.85 ml, 1.0 M in Et_2O, 0.85 mmol) was added and stirred for 4 h, during which time solution become dark blue. 1,4-dioxane (0.9 ml, 10.2 mmol) was added,

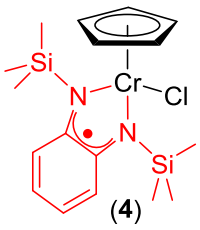
resulting in the immediate formation of a large quantity of white precipitate. After stirring for an additional 1 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexanes, and then the dark blue extracts were filtered through Celite and cooled to -35 °C. Black powders of **2** were isolated in one fraction (25.5 mg, 18%). (Evans, C_6D_6): 3.29 μ_B. Anal. Calcd for $C_{21}H_{31}N_2Cr$: C, 69.39; H, 8.60; N, 7.70. Found: C, 71.24; H, 9.81; N, 9.77. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 373 (3900), 519 (1600), 710 (1600). Despite repeated attempts, crystals of **2** suitable for X-ray diffraction were not obtained, and elemental analyses of the isolated powder consistently analyzed with higher than calculated values for C, H and N.

Method B: To a solution of $CpCrCl_2(THF)$ (45 mg, 0.17 mmol) 20 ml THF, $Li_2[(Me_3CCH_2N)_2C_6H_4]$ (50 mg, 1.9 mmol) was added, causing the solution to become dark blue. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 6 ml hexanes, and then the dark blue extracts were filtered through Celite. Crude solutions of **2** prepared by this route were used in further reactions to prepare $CpCr[(Me_3CCH_2N)_2C_6H_4](X)$ derviatives, as described below.



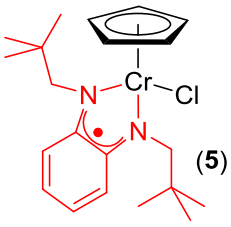
(**3**)

Synthesis of $CpCr[(PhN)_2C_6H_4]$ (3). To a solution of $CpCrCl_2(THF)$ (100 mg, 0.386 mmol) 10 ml Et_2O, $(PhNH)_2C_6H_4$ (123 mg, 0.472 mmol) was added, causing the solution to become dark green. $LiN(SiMe_3)_2$ (145 mg, 0.868 mmol) was added and was stirred for 20 h, during which time solution become dark blue. The solvent was removed *in vacuo*, the residue was extracted with 5 ml Et_2O, and then the dark blue extracts were filtered through Celite and cooled to -35 °C. Black crystals of **3** were isolated in two fractions (47 mg, 32%). (Evans, C_6D_6): 3.82 μ_B. Anal. Calcd for $C_{23}H_{19}N_2Cr$: C, 73.59; H, 5.10; N, 7.46. Found: C, 70.34; H, 5.25; N, 7.20. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 373 (6400), 657 (3100). Despite repeated attempts, crystals of **3** suitable for X-ray diffraction were not obtained, and elemental analyses of the isolated crystals gave lower than calculated values for carbon.



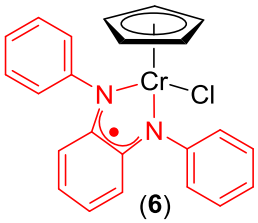
(**4**)

Synthesis of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$](Cl) (4). To a solution of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$] (67 mg, 0.18 mmol) in 10 ml Et$_2$O, PbCl$_2$ (30 mg, 0.12 mmol) was added, and was stirred for 20 h. During this time the solution colour changed to dark green. The solvent was then removed *in vacuo*, the residue was extracted with 5 ml hexane, and the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **4** were isolated in one fraction (44 mg, 59%). (Evans, C_6D_6): 2.73 μ_B. Anal. Calcd for $C_{17}H_{27}N_2Si_2CrCl$: C, 50.66; H, 6.75; N, 6.95. Found: C, 51.02; H, 6.70; N, 7.18. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 336 (5800), 380 (4600), 461 (1030), 530 (1700), 660 (2100) 731 (1500).



(**5**)

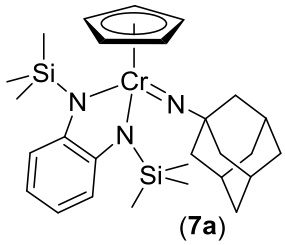
Synthesis of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](Cl) (5). To a solution of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] (0.769 mmol) in 10 ml Et$_2$O (prepared from CpCrCl$_2$(THF) and Li$_2$[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] as described in **2** method B, above), PbCl$_2$ (109 mg, 0.423 mmol) was added. The mixture was stirred for 20 h, during which time solution colour changed to dark green yellow. The solvent was then removed *in vacuo*, the residue was extracted with 9 ml hexane, and the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **5** were isolated in three fractions (70 mg, 23%). (Evans, C_6D_6): 2.62 μ_B. Anal. Calcd for $C_{21}H_{31}N_2CrCl$: C, 63.23; H, 7.83; N, 7.02. Found: C, 62.89; H, 7.81; N, 6.96. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 383 (7800), 450 (11200), 533 (1900), 632 (1500).



(**6**)

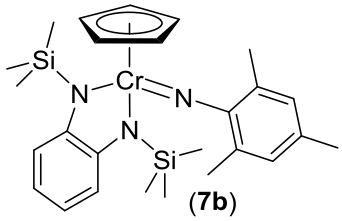
Synthesis of CpCr[(Ph)$_2$C$_6$H$_4$](Cl) (6). To a solution of CpCrCl$_2$(THF) (30 mg, 0.12 mmol) 10 ml Et$_2$O, (PhNH)$_2$C$_6$H$_4$ (33 mg, 0.13 mmol) was added, causing the solution to become dark green. LiN(SiMe$_3$)$_2$ (43 mg, 0.26 mmol) was added and the mixture was stirred for 20 h, during which time solution become dark blue. The solvent was removed *in vacuo*, the residue was extracted with 5 ml Et$_2$O, and then the dark blue extracts were filtered through Celite. PbCl$_2$ (67 mg, 0.24 mmol) was then added as a suspension in 20 ml THF. After stirring for 20 h, the solution colour

changed to dark green yellow. The solvent was then removed *in vacuo*, the residue was extracted with 4 ml hexane, and the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **6** were isolated in two fractions (23 mg, 48%). (Evans, C_6D_6): 2.53 μ_B. Anal. Calcd for $C_{23}H_{19}N_2CrCl$: C, 67.24; H, 4.66; N, 6.82. Found: C, 64.82; H, 4.80; N, 6.88. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 350 (8400), 452 (8900), 504 (2900), 538 (3000), 652 (2400). Elemental analysis of **6** repeatedly gave lower than calculated values for carbon.



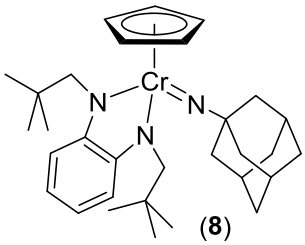
(**7a**)

Synthesis of CpCr[$(Me_3SiN)_2C_6H_4$](NAd) (7a). To a solution of CpCr[$(Me_3SiN)_2C_6H_4$] (67 mg, 0.18 mmol) in 12 ml Et_2O, N_3Ad (35 mg, 0.20 mmol) was added, causing the solution to become dark red yellow. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **7a** were isolated in three different fractions (56 mg, 59%). (Evans, C_6D_6): 2.09 μ_B. Anal. Calcd for $C_{27}H_{42}N_3Si_2Cr$: C, 62.75; H, 8.19; N, 8.13. Found: C, 62.67; H, 8.24; N, 8.22. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 459 (3800).



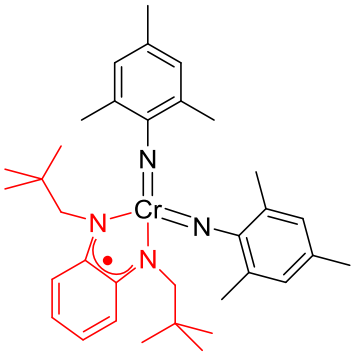
(**7b**)

Synthesis of CpCr[$(Me_3SiN)_2C_6H_4$](NMes) (7b). To a solution of CpCr[$(Me_3SiN)_2C_6H_4$] (29 mg, 0.079 mmol) in 8 ml Et_2O, N_3Mes (16 mg, 0.097 mmol) was added, causing the solution to become dark brown. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 2 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **7b** were isolated in one fraction (17 mg, 43%). (Evans, C_6D_6): 1.69 μ_B. Anal. Calcd for $C_{26}H_{38}N_3Si_2Cr$: C, 62.36; H, 7.65; N, 8.39. Found: C, 60.93; H, 7.75; N, 8.57. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 377 (5900). Elemental analysis of **7b** repeatedly gave lower than calculated values for carbon.



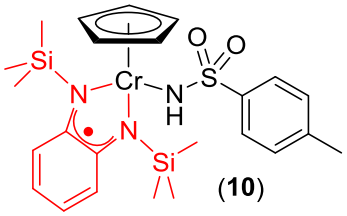
(**8**)

Synthesis of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NAd) (8). To a solution of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] (0.384 mmol) in 8 ml Et$_2$O (prepared from CpCrCl$_2$(THF) and Li$_2$[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] as described in **2** method B, above), N$_3$Ad (76 mg, 0.43 mmol) was added, causing the solution to become dark black. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 2 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **8** were isolated in one fraction (49 mg, 25%). (Evans, C$_6$D$_6$): 1.67 μ_B. Anal. Calcd for C$_{31}$H$_{46}$N$_3$Cr: C, 72.62; H, 9.04; N, 8.19. Found: C, 72.95; H, 9.41; N, 8.04. UV-vis (hexane; λ_{max}, nm (ε, M^{-1}cm^{-1})): 378 (6200).



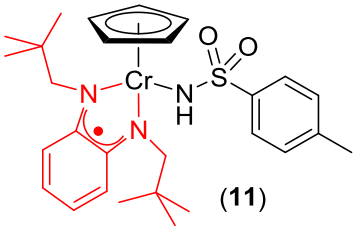
(**9**)

Synthesis of Cr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NMes)$_2$ (9). To a solution of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] (0.191 mmol) in 15 ml Et$_2$O (prepared from CpCrCl$_2$(THF) and Li$_2$[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] as described in **2** method B, above), N$_3$Mes (41 mg, 0.25 mmol) was added, causing the solution to become dark green. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of Cr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NMes)$_2$ **9** (16 mg, 25%) were obtained, as characterized by X-ray crystallography. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.03 (m, 2H, Ar-H), 6.92 (m, 2H, Ar-H), 6.64 (s, 4H, Mes-H), 4.3 (s, 4H, CH$_2$), 2.35 (s, 12H, *p*-Mes-CH$_3$), 2.08 (s, 6H, *o*-Mes-CH$_3$), 1.04 (s, 18H, ^{t}Bu-CH$_3$). Anal. Calcd for C$_{34}$H$_{48}$N$_4$Cr: C, 72.31; H, 8.57; N, 9.92. Found: C, 72.11; H, 8.61; N, 9.83. UV-vis (hexane; λ_{max}, nm (ε, M^{-1}cm^{-1})): 343 (17000), 582 (10000).



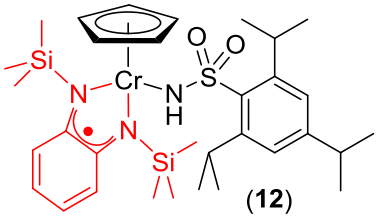
(**10**)

Synthesis of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$](NHTs) (10). To a solution of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$] (27 mg, 0.073 mmol) in 15 ml Et$_2$O, N$_3$Ts (27 mg, 0.14 mmol) was added, causing the solution to become dark green. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **10** were isolated in one fraction (17 mg, 44%). (Evans, C$_6$D$_6$): 2.32 μ_B. Anal. Calcd for $C_{24}H_{35}N_3Si_2CrSO_2$: C, 53.61; H, 6.56; N, 7.81. Found: C, 53.41; H, 6.25; N, 8.57. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 450 (6400), 643 (1500).



(**11**)

Synthesis of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NHTs) (11). To a solution of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] (0.393 mmol) in 15 ml Et$_2$O (prepared from CpCrCl$_2$(THF) and Li$_2$[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$] as described in **2** method B, above), N$_3$Ts (91 mg, 0.46 mmol) was added and causing the solution to become dark green. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **11** were isolated in one fraction (24 mg, 11%). (Evans, C$_6$D$_6$): 2.49 μ_B. Anal. Calcd for $C_{32}H_{51}N_3CrSSi_2O_2$: C, 59.14; H, 7.91; N, 6.46. Found: C, 59.33; H, 7.69; N, 6.81. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 378 (8300), 440 (8500), 637 (1700).



(**12**)

Synthesis of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$](NHTrisyl) (12). To a solution of CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$] (28 mg, 0.075 mmol) in 8 ml C$_6$H$_6$, N$_3$Trisyl (27 mg, 0.14 mmol) was added, causing the solution to become dark green yellow. After stirring for 20 h, the solvent was removed *in vacuo*, the residue was extracted with 3 ml hexane, and then the extracts were filtered through Celite and cooled to -35 °C. Black crystals of **12** were isolated in one fraction (8 mg, 16%). (Evans, C$_6$D$_6$): 2.37 μ_B. Anal. Calcd for $C_{32}H_{51}N_3CrSi_2SO_2$: C, 59.14; H, 7.91; N,

6.46. Found: C, 59.33; H, 7.69; N, 6.81. UV-vis (hexane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 451 (8000), 641 (1900).

Cyclization of N_3Trisyl with 3.

To a solution of CpCr[$(PhN)_2C_6H_4$] (10 mg, 0.026 mmol, 20 mol%) in 1 ml of C_6H_6, was added N_3Trisyl (41 mg, 0.13 mmol) and was stirred for 65 hr at 70 ºC. The solvent was then removed *in vacuo*, the residue was extracted with 0.5 ml $CDCl_3$ then filtered through Celite into an air-tight J. Young NMR tube. The crude cyclized product was identified by ^{1}H NMR ($CDCl_3$, 400 MHz). The solvent was then removed *in vacuo* again, the residue was purified by flash chromatography with a gradient solvent system of 100:0 (hexanes: ethyl acetate) to 50:50 (hexanes: ethyl acetate), the product is eluted. Removal of solvent *in vacuo* gave a white powder (34 mg, 84%) that was identified as the previously reported[7] benzosultam complex by ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.2, 6.9 (s, 2H, Ar-H), 4.4 (s, 1H, NH), 3.5 (sept, 1H, ^{i}Pr-CH), 2.9 (sept, 1H, ^{i}Pr-CH), 1.5 (s, 6 H, ^{i}Pr-Me), 1.2 (d, 6 H, ^{i}Pr-Me), 1.1 (d, 6 H, ^{i}Pr-Me).

X-ray Crystallography: Single crystals were mounted on glass fibers and measurements were made on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of -100 ± 1 ˚C in a series of φ and ω scans in 0.50˚ oscillations. Data were collected and integrated using the Bruker SAINT software package[1] and were corrected for absorption effects using the multi-scan technique (SADABS).[2] The data were corrected for Lorentz and polarization effects and the structure was solved by direct methods.[3] Compounds **1a, 8** and **9** crystallize on a mirror plane, with one half-molecule in the asymmetric unit. Additionally, the Cp ring and THF of compound **1a** were disordered and subsequently modeled in two orientations. Compound **6** crystallizes with two independent molecules in the asymmetric unit. One of CH_2CMe_3 group of compound **9** was disordered and subsequently modeled in two orientations. For complex **6**, data were corrected for absorption effects using the multiscan technique (TWINABS). All non-hydrogen atoms in complex **6** were refined anisotropically except for C1, C21, C22, C42 and C44. All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS.[4] The molecular drawings were generated by the use of ORTEP-3[5] and POV-Ray.

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1 *SAINT*, *version 7.46A*; Bruker Analytical X-ray System: Madison, WI, 1997-2007.

2 *SADABS*. *Bruker Nonius area detector scaling and absorption correction, V2.10*; Bruker AXS Inc.: Madison, WI, 2003.

3 *SIR92*. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

4 *SHELXTL, Version 5.1*; Bruker AXS Inc.: Madison, WI, 1997.

5 Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *32*, 565.

Table S1. X-ray crystallographic data for complexes **1a**, **5** and **6**.

Compound Number	**1a**	**5**	**6**
Formula	$C_{21}H_{35}N_2OSi_2Cr$	$C_{21}H_{31}N_2CrCl$	$C_{23}H_{19}N_2CrCl$
Formula Weight	439.69	398.93	410.85
Crystal Color, Habit	black, prism	black, plate	black, irregular
Crystal Dimensions, mm	0.10 × 0.15 × 0.25	0.05 × 0.25 × 0.30	0.10 × 0.20 × 0.26
Crystal System	monoclinic	orthorhombic	triclinic
Space Group	*C* 2/*m*	*P bna*	*P* -1
a, Å	13.073(2)	13.5642(10)	10.747(4)
b, Å	15.574(3)	16.8668(13)	12.676(4)
c, Å	12.961(2)	18.2940(14)	16.141(5)
α, °	90.00	90.00	90.420(6)
β, °	118.861(9)	90.00	107.496(6)
γ, °	90.00	90.00	110.920(5)
V, $Å^3$	2310.9(7)	4185.4(5)	1942.6(11)
Z	4	8	4
D calc, g/cm^3	1.264	1.266	1.405
F_{000}	940	1696	848
μ(MoKα), cm^{-1}	6.12	6.80	7.36
Data Images (no., *t*/s)	1239	587.00	2427
$2\theta_{max}$	57.46	57.42	45.28
Reflections measrd	11469	23860	28907
Unique reflcn, R_{int}	3025, 0.0433	5426, 0.0462	4962, 0.1822
Absorption, T_{min}, T_{max}	0.712, 0.869	0.871, 0.967	0.543, 0.929
Observed data (I>2.00σ(I))	2104	3888	4070
No. parameters	165	226	462
R1, wR2 (F^2, all data)	0.0767, 0.1127	0.0656, 0.0952	0.1531, 0.3480
R1, wR2 (F, I>2.00σ(I))	0.0424, 0.0977	0.0364, 0.0814	0.1357, 0.3382
Goodness of Fit	1.044	1.010	1.099
Max, Min peak, $e^-/Å^3$	0.495, -0.514	0.363, -0.416	2.343, -1.140

Table S2. X-ray crystallographic data for complexes **7a**, **7b** and **8**.

Compound Number	**7a**	**7b**	**8**
Formula	$C_{27}H_{42}N_3Si_2Cr$	$C_{26}H_{38}N_3Si_2Cr$	$C_{31}H_{46}N_3Cr$
Formula Weight	516.82	500.77	512.71
Crystal Color, Habit	black, plate	black, prism	black, plate
Crystal Dimensions, mm	0.10 × 0.40 × 0.40	0.15 × 0.20 × 0.25	0.10 × 0.15 × 0.25
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	*P* $2_1/n$	*P* $2_1/c$	*C* 2/*m*
a, Å	10.5631(12)	9.4360(14)	15.964(3)
b, Å	19.238(2)	26.568(4)	13.0182(19)
c, Å	14.5072(16)	11.3270(17)	14.345(3)
α, °	90.00	90.0	90.0
β, °	111.307(6)	108.782(3)	113.436(5)
γ, °	90.00	90.0	90.0
V, $Å^3$	2746.5(5)	2688.3(7)	2735.2(8)
Z	4	4	4
D calc, g/cm^3	1.25	1.237	1.245
F_{000}	1108	1068	1108
μ(MoKα), cm^{-1}	5.24	5.33	4.42
Data Images (no., *t*/s)	993.00	1008	1081
$2\theta_{max}$	51.50	60.14	56.00
Reflections measrd	17253	31476	12656
Unique reflcn, R_{int}	5084, 0.0767	7880, 0.0376	3404, 0.0359
Absorption, T_{min}, T_{max}	0.811, 0.949	0.877, 0.923	0.860, 0.957
Observed data (I>2.00σ(I))	3241	6367	2645
No. parameters	298	291	169
R1, wR2 (F^2, all data)	0.1148, 0.1868	0.0556, 0.0992	0.0598, 0.1073
R1, wR2 (F, I>2.00σ(I))	0.0653, 0.1667	0.0406, 0.0927	0.0393, 0.0976
Goodness of Fit	1.080	1.067	1.053
Max, Min peak, $e^-/Å^3$	0.844, -0.593	0.456, -0.424	0.418, -0.371

Table S3. X-ray crystallographic data for complexes **9**, **11** and **12**.

Compound Number	**9**	**11**	**12**
Formula	$C_{34}H_{48}N_4Cr$	$C_{28}H_{38}N_3SO_2Cr$	$C_{32}H_{51}N_3O_2Si_2SCr$
Formula Weight	564.76	533.68	650.00
Crystal Color, Habit	black, prism	black, prism	black, prism
Crystal Dimensions, mm	0.06 × 0.11 × 0.27	0.025 × 0.075 × 0.100	0.06 × 0.095 × 0.175
Crystal System	triclinic	orthorhombic	monoclinic
Space Group	*P* -1	*P bca*	*P* $2_1/n$
a, Å	12.1837(4)	19.539(2)	15.9850(18)
b, Å	12.1849(3)	9.9443(11)	11.6860(13)
c, Å	12.4184(4)	27.280(3)	19.444(2)
α, °	106.3990(10)	90.0	90.00
β, °	91.635(2)	90.0	110.836(3)
γ, °	113.395(2)	90.0	90.00
V, $Å^3$	1602.36(8)	5300.6(10)	3394.6(7)
Z	2	8	4
D calc, g/cm^3	1.171	1.338	1.272
F_{000}	608.00	2272	1392
μ(MoKα), cm^{-1}	3.84	5.41	5.01
Data Images (no., *t*/s)	1736	930	1144
$2\theta_{max}$	55.86	46.04	60.14
Reflections measrd	29214	27184	39849
Unique reflcn, R_{int}	7442, 0.0280	3682, 0.1263	9932, 0.0576
Absorption, T_{min}, T_{max}	0.862, 0.977	0.780, 0.987	0.917, 0.970
Observed data (I>2.00σ(I))	6059	2370	7024
No. parameters	358	311	371
R1, wR2 (F^2, all data)	0.0558, 0.1152	0.1084, 0.1338	0.0743, 0.0969
R1, wR2 (F, I>2.00σ(I))	0.0417, 0.1072	0.0579, 0.1153	0.0409, 0.0855
Goodness of Fit	1.049	1.078	1.004
Max, Min peak, $e^-/Å^3$	0.508, -0.426	0.659, -0.375	0.444, -0.400

Figure S1. Thermal ellipsoid diagram (50%) of **1a** (CCDC 1001249). All hydrogen atoms have been removed for clarity.

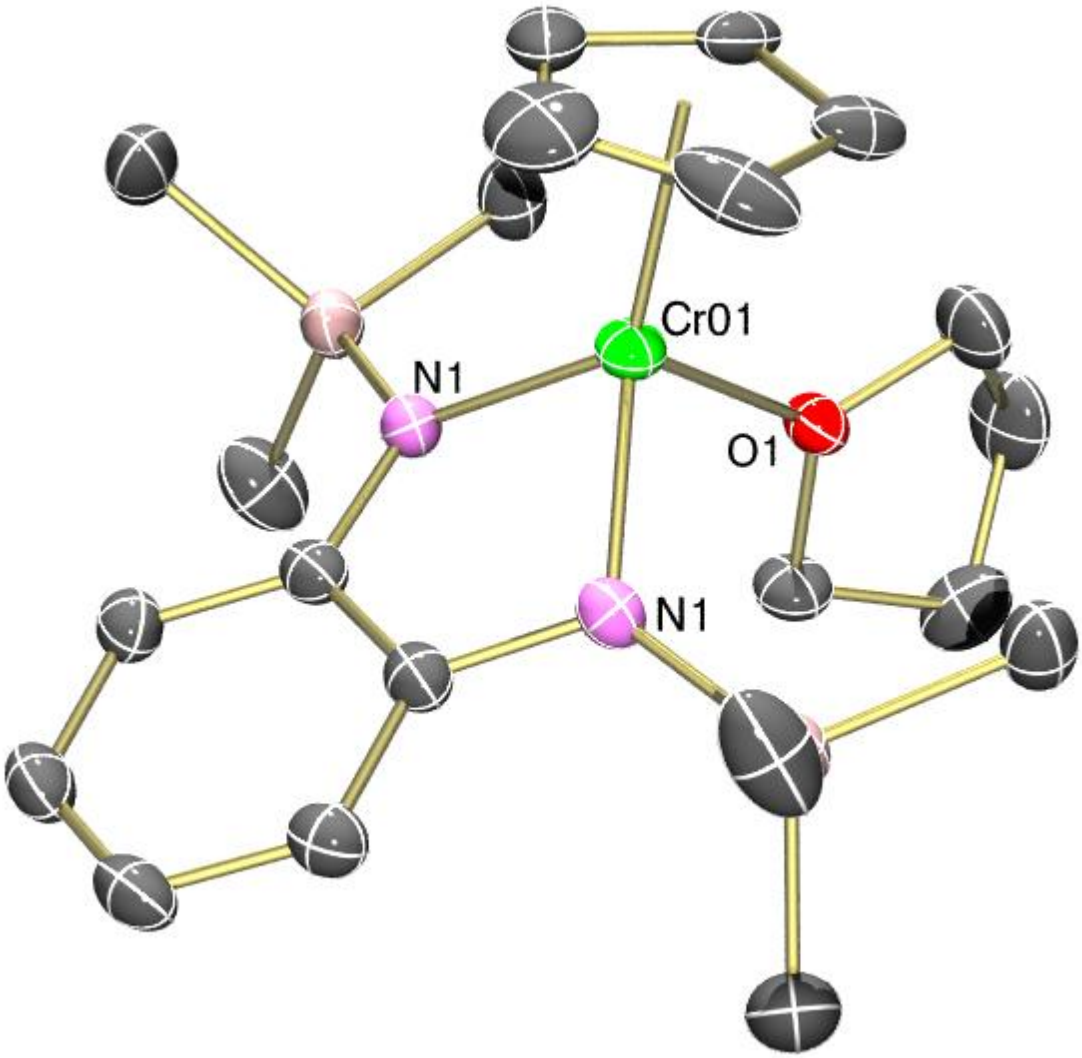


Figure S2. Thermal ellipsoid diagram (50%) of **5** (CCDC 1001254). All hydrogen atoms have been removed for clarity.

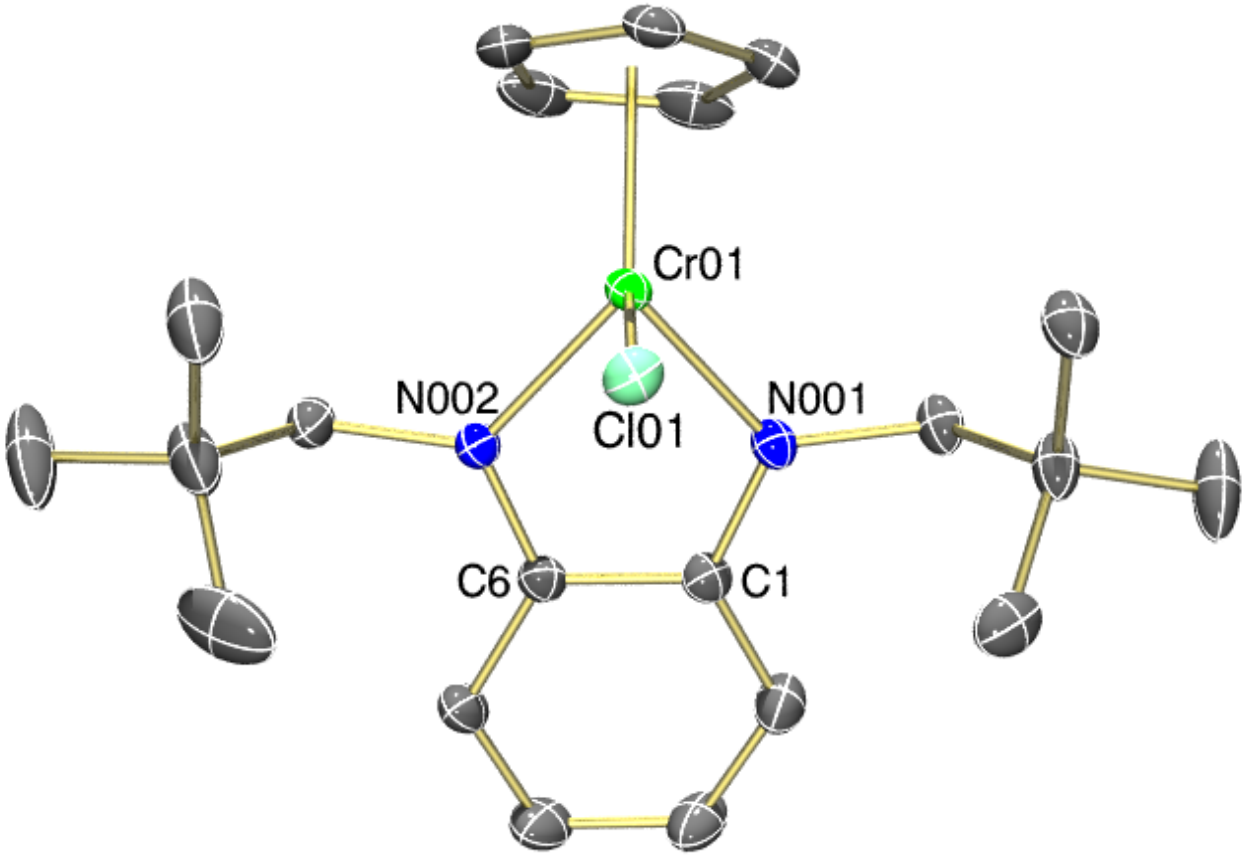


Figure S3. Thermal ellipsoid diagram (50%) of **6** (CCDC 1001255). All hydrogen atoms have been removed for clarity.

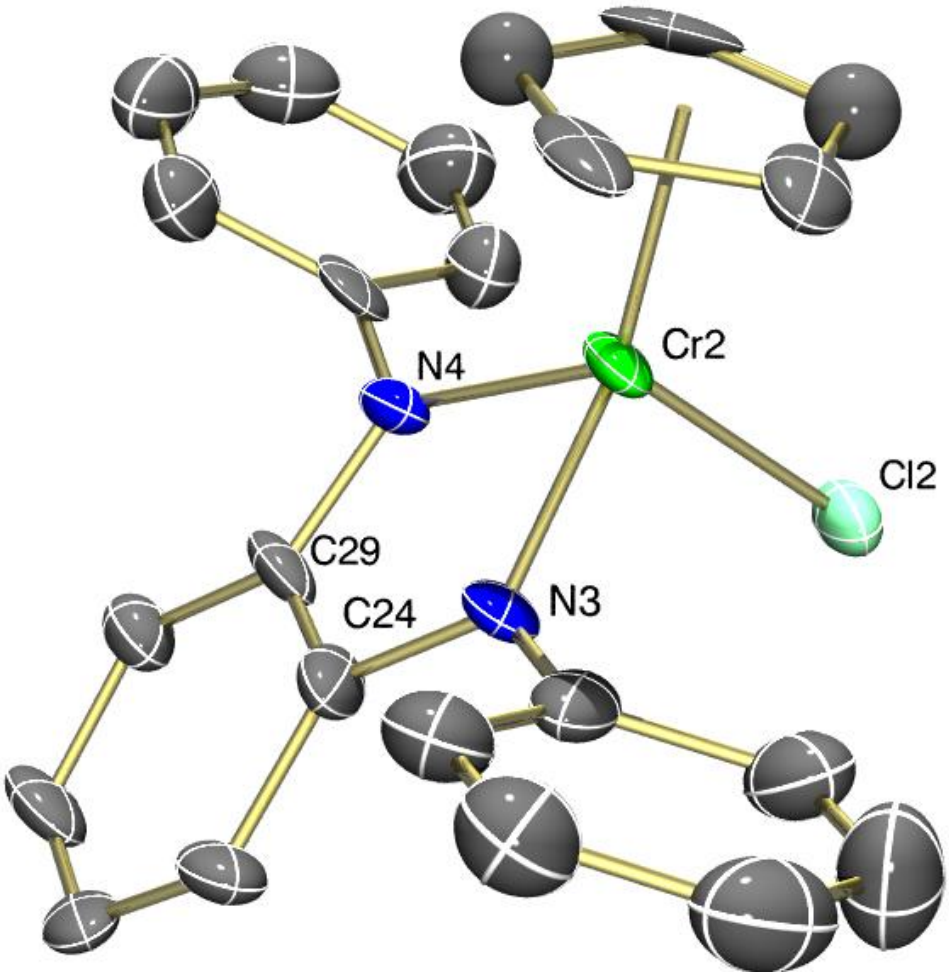


Figure S4. Thermal ellipsoid diagram (50%) of **7a**. (CCDC 1001256) All hydrogen atoms have been removed for clarity.

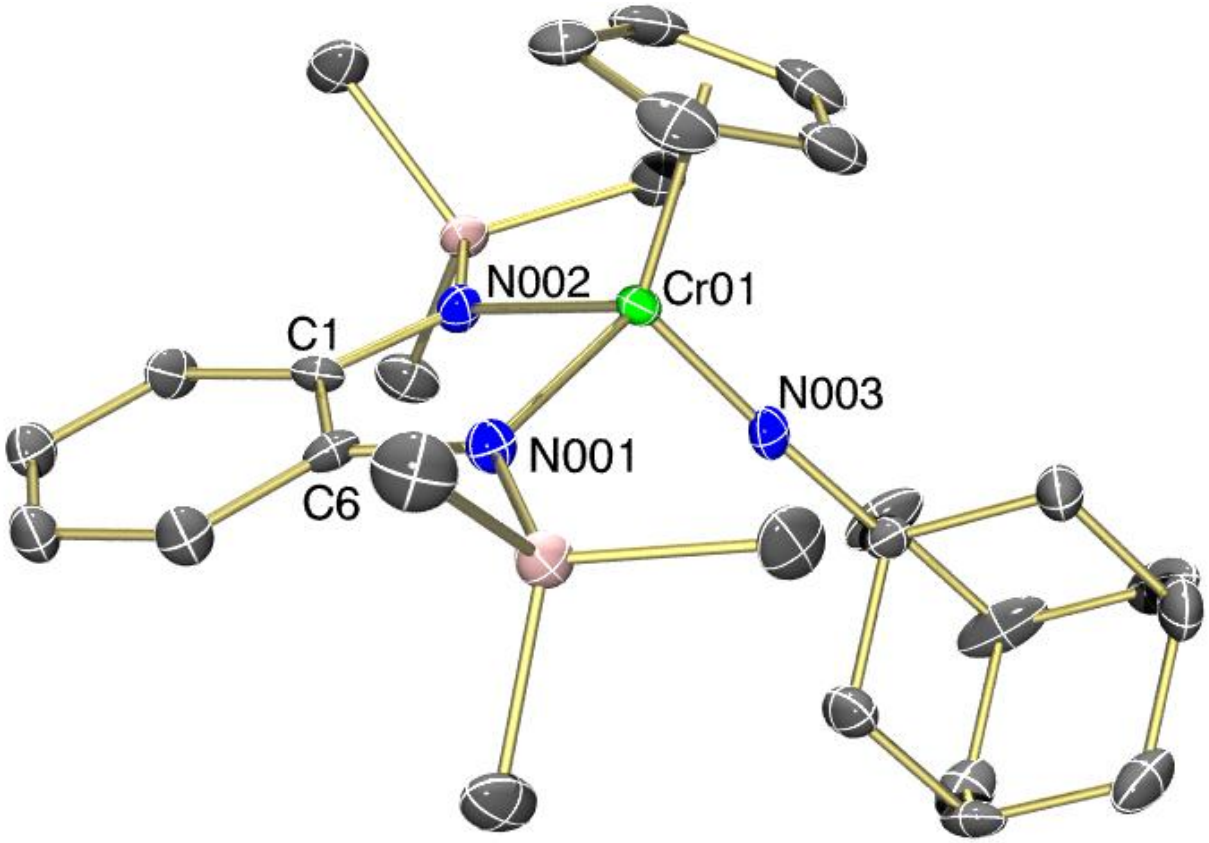


Figure S5. Thermal ellipsoid diagram (50%) of **7b** (CCDC 1001257). All hydrogen atoms have been removed for clarity.

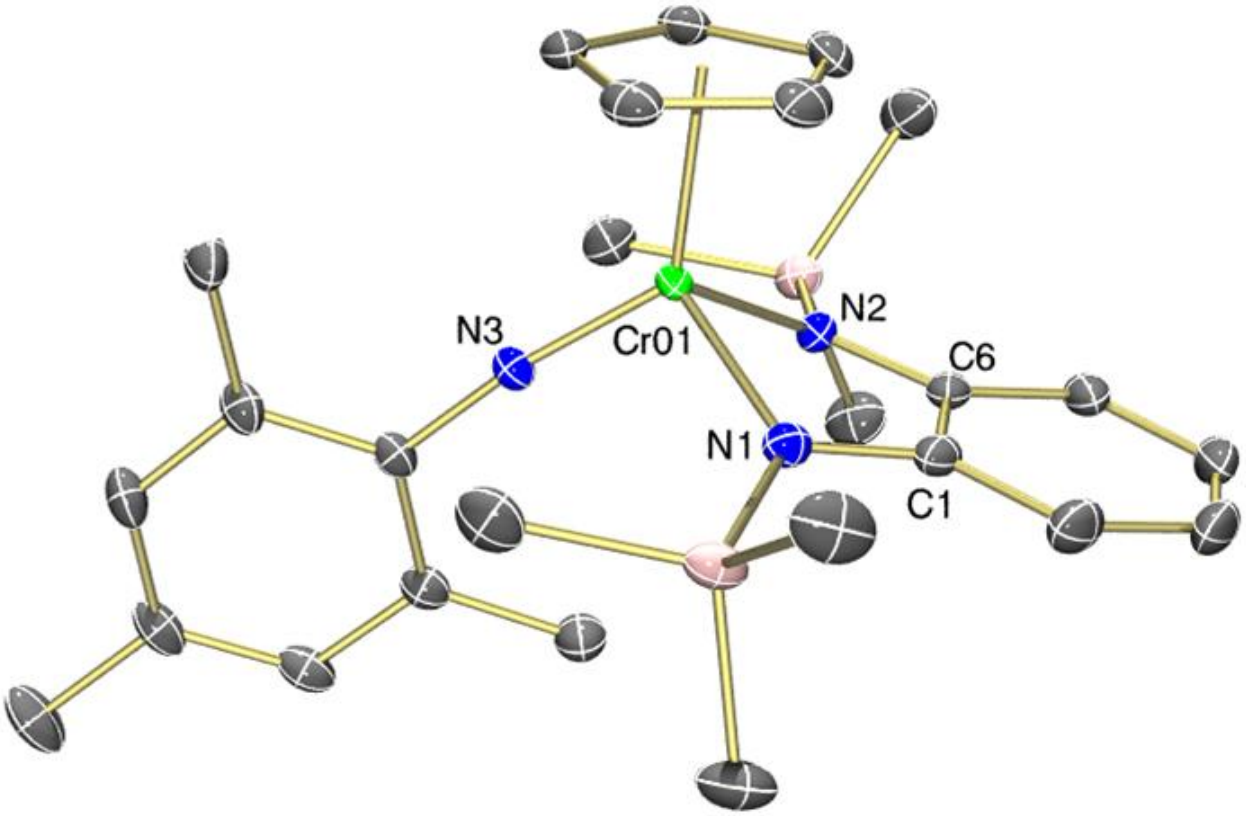


Figure S6. Thermal ellipsoid diagram (50%) of **8** (CCDC 1001260). All hydrogen atoms have been removed for clarity.

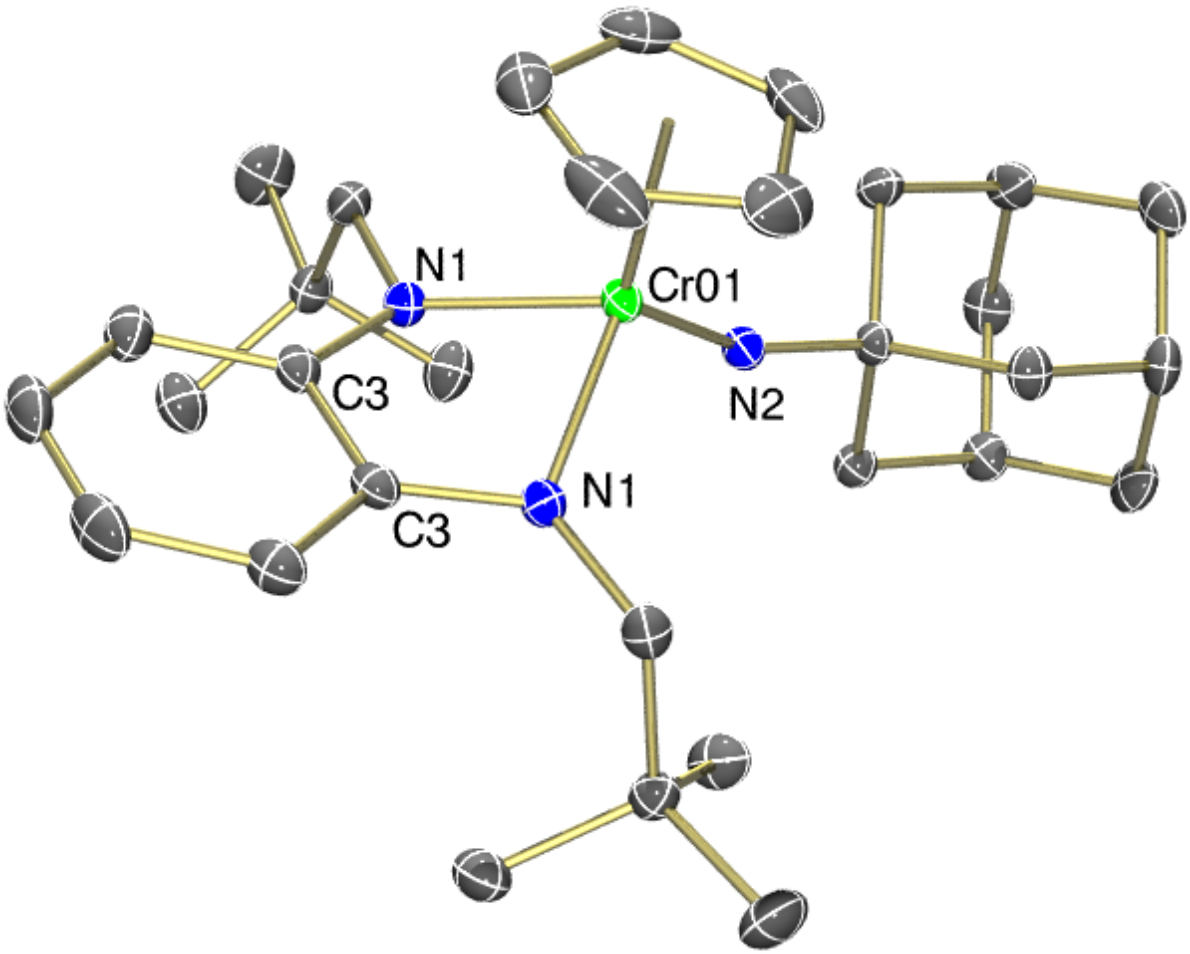


Figure S7. Thermal ellipsoid diagram (50%) of **9** (CCDC 1001261). All hydrogen atoms have been removed for clarity.

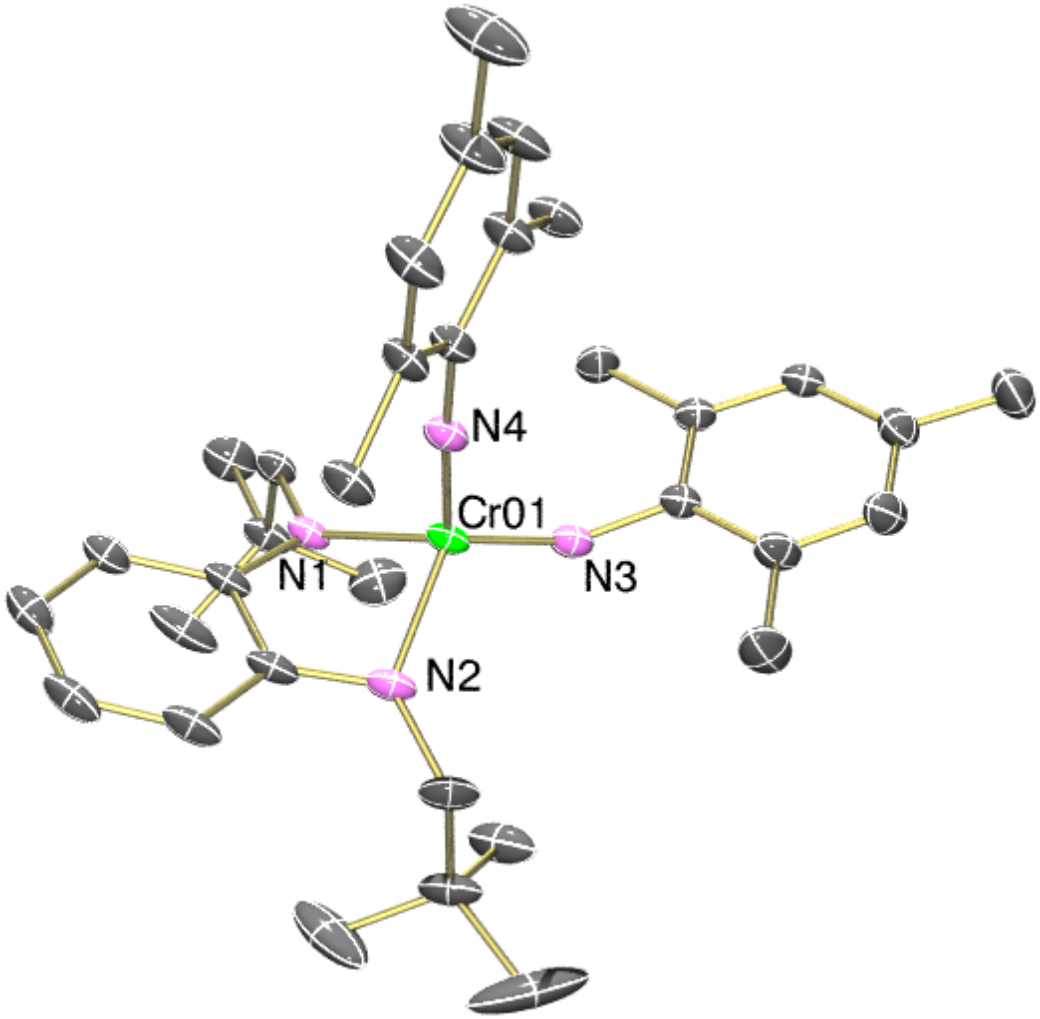


Figure S8. Thermal ellipsoid diagram (50%) of **11** (CCDC 1001262). All hydrogen atoms have been removed for clarity.

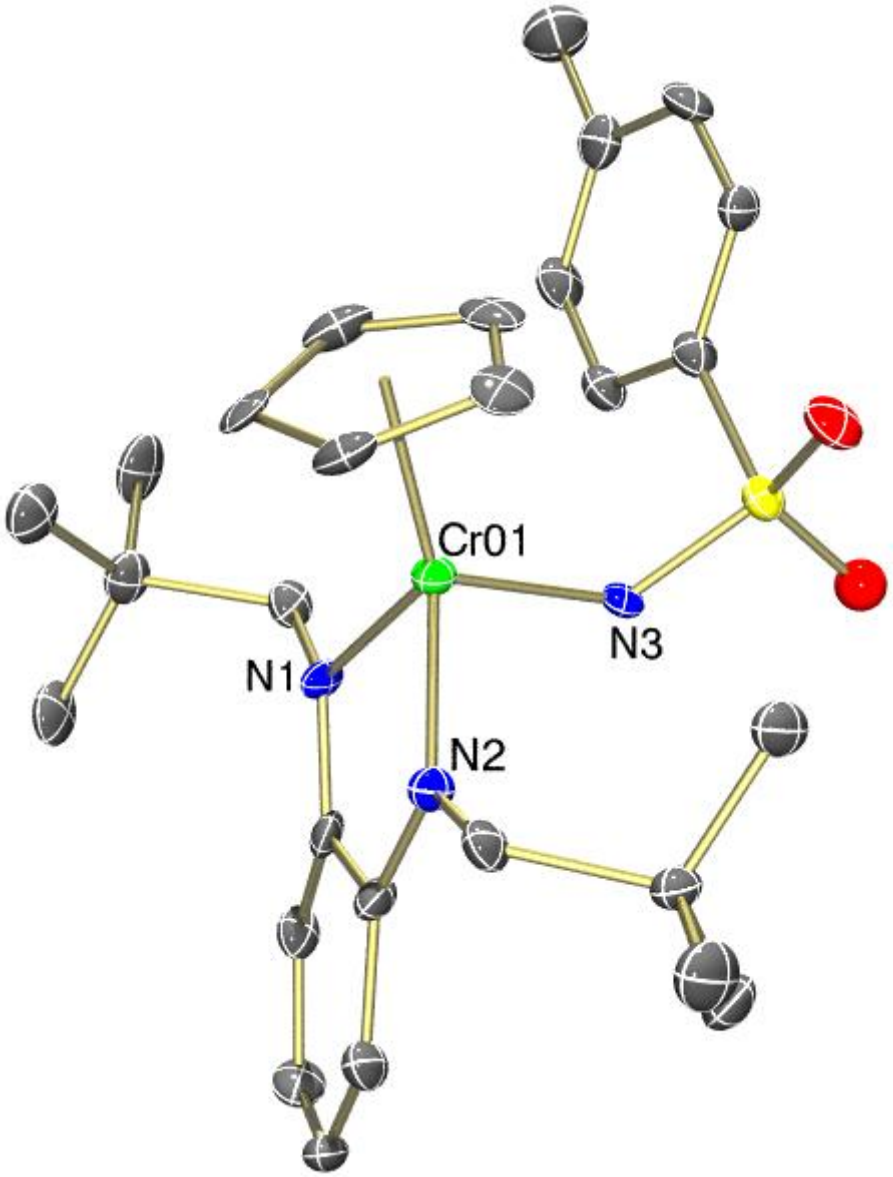


Figure S9. Thermal ellipsoid diagram (50%) of **12** (CCDC 1001263). All hydrogen atoms have been removed for clarity.

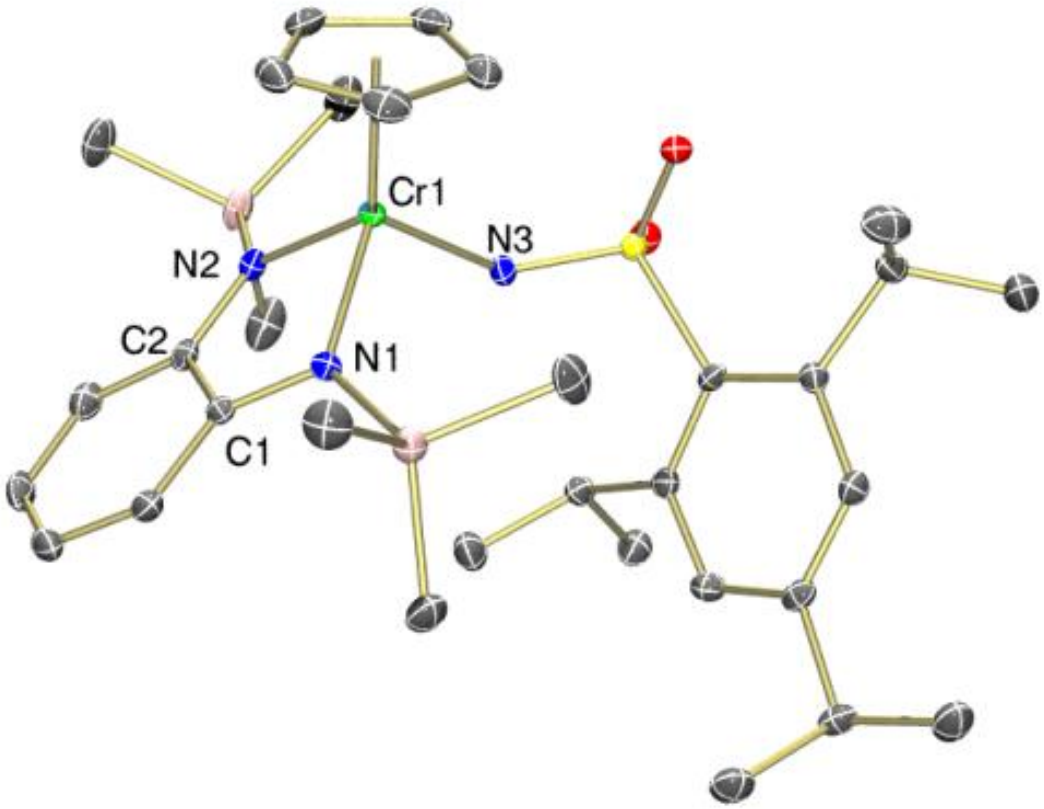
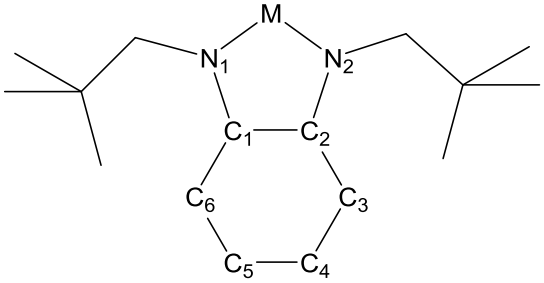


Table S4. Bond Lengths (in Å) for $(Me_3CCH_2N)_2C_6H_4$ ligand in **2a-c**, **5**, **8**, **9**, **11**.



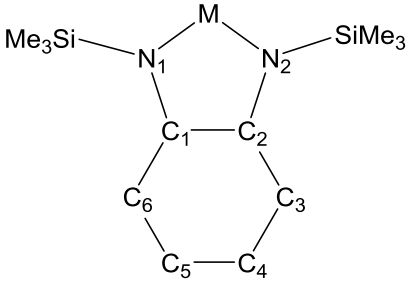
entry	#	N1–C1	N2–C2	C1–C2	C4–C5	Ox. Level
1	Zr(pda)	1.412(2)	1.411(2)	1.365(3)	1.380(3)	X_2
2	Zr(disq)	1.346(2)	1.347(2)	1.467(2)	1.421(3)	LX•
3	Zr (ave)	1.379	1.379	1.416	1.4005	
4	**5** Cl	1.360(2)	1.353(2) C(6)–N(2)	1.439(3) C(1)–C(6)	1.407(3) C(3)–C(4)	LX•
5	**8** NAd	1.379(2) C(3)–N(1)	*a*	1.439(3) C(3)-C(3)#	1.392(4) C(1)-C(1)#	?
6	**9** NMes	1.369(2) C(6)–N(1)	1.362(3) C(1)–N(2)	1.449(3) C(1)–C(6)	1.408(3) C(3)–C(4)	LX•
7	**11** NHTs	1.363(7) C(1)–N(1)	1.367(7) C(6)–N(2)	1.439(7) C(1)–C(6)	1.390(8) C(3)–C(4)	LX•

[a] Both ligand N–C bond lengths are identical due to crystallographic mirror plane.

For the four $(Me_3CCH_2N)_2C_6H_4$ complexes that were structurally characterized by single crystal X-ray diffraction, the oxidation level of the ancillary ligand was assigned by comparison with the structural parameters reported by Heyduk and co-workers for $Zr[(Me_3CCH_2N)_2C_6H_4]_2(THF)$ (X_2 ligand, entry 1) and $Zr[(Me_3CCH_2N)_2C_6H_4]_2(Cl)_2$ (LX• ligand, entry 2).[2] Following the analysis used by Brown for related catecholate and 2-amidophenoxide ligands,[8] the four most significant bond lengths were compared for all complexes. Entry 3 lists the midpoint between the two limiting structures reported by Heyduk: this value was used as the cut-off to distinguish between the dianionic and monoanionic ligand oxidation levels.

For all of the chromium complexes, the C1–C2 bond length (the two carbons bound to the N-donor atoms) were found to be closer to the monoanionic diiminosemiquinonate LX• form than the phenylenediamide X_2 form. For most of the complexes, however, the other bond lengths were indicative of the oxidation level of the ligand. The exception was the adamantyl imido complex **8**, which also displayed unusual Cr–NAd bonding parameters, with a long Cr–NAd bond (1.658(2) Å) and a Cr–N–Ad angle that deviated from linearity (159.76(18)°).

Table S5. Bond Lengths (in Å) for $(Me_3SiN)_2C_6H_4$ ligand in **1a**, **7a-d**, **12**.

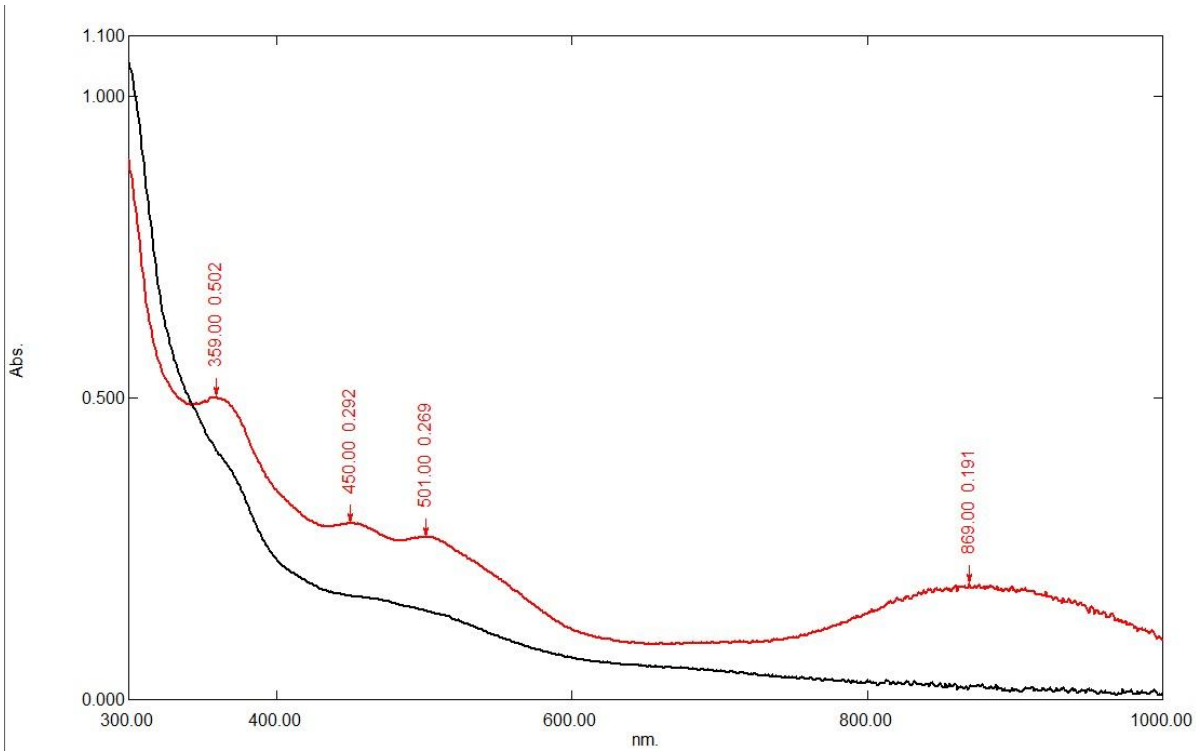


entry	#	N1–C1	N2–C2	C1–C2	C4–C5	Cr-N imido	Ox. Level
1	Zr(pda)	1.412(2)	1.411(2)	1.365(3)	1.380(3)		X_2
2	Zr(disq)	1.346(2)	1.347(2)	1.467(2)	1.421(3)		LX•
3	Zr (ave)	1.379	1.379	1.416	1.4005		
4	**1a** THF	1.407(3) C(1)–N(1)	*a*	1.415(5) C(1)–C(1)#	1.377(5) C(3)–C(3)#		X_2
5	**7a** NAd	1.387(6) C(6)–N(1)	1.396(6) C(1)–N(2)	1.420(6) C(1)–C(6)	1.386(7) C(3)–C(4)	1.632(4)	X_2
6	**7b** NMes	1.388(2) C(1)–N(1)	1.382(2) C(6)–N(2)	1.428(2) C(1)–C(6)	1.382(2) C(3)–C(4)	1.660(1)	X_2
7	**12** NHTrisyl	1.361(2)	1.360(2)	1.439(3)	1.405(3)	2.027(2)	LX•

[a] Both ligand N–C bond lengths are identical due to crystallographic mirror plane.

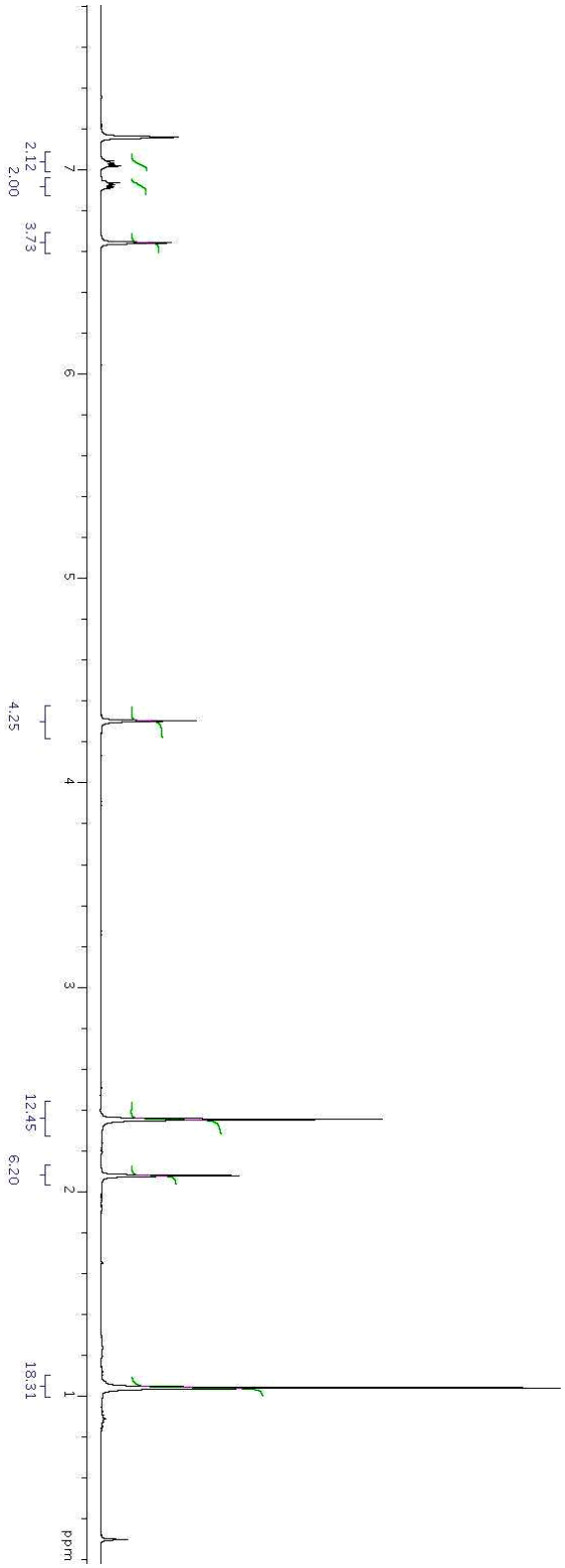
As in Table S6, the table above is an attempt to tentatively assign the oxidation level of the $(Me_3SiN)_2C_6H_4$ ligand by comparison of the key ligand bond lengths to the zirconium complexes reported by Heyduk and co-workers.[2] Both of the imido complexes **7ab** showed bond lengths consistent with a dianionic X_2 ligand, with the C1–C2 length again being closer to the radical LX• form in both cases.

Figure S10. UV-visible spectra indicating reversible binding of THF to $CpCr[(Me_3SiN)_2C_6H_4]$ (**1**).



UV-vis absorption spectra of $CpCr[(Me_3SiN)_2C_6H_4]$ (**1**) in hexane [1.6×10^{-4} M] (red line) and in THF [1.6×10^{-4} M] (black line).

Figure S11. ^{1}H NMR (400 MHz, C_6D_6) spectrum **8**.



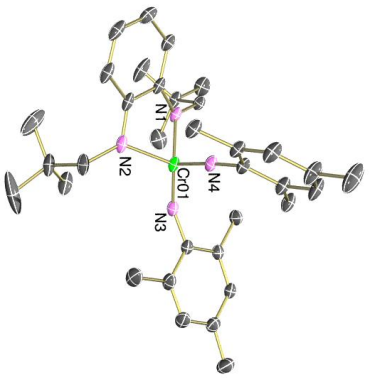
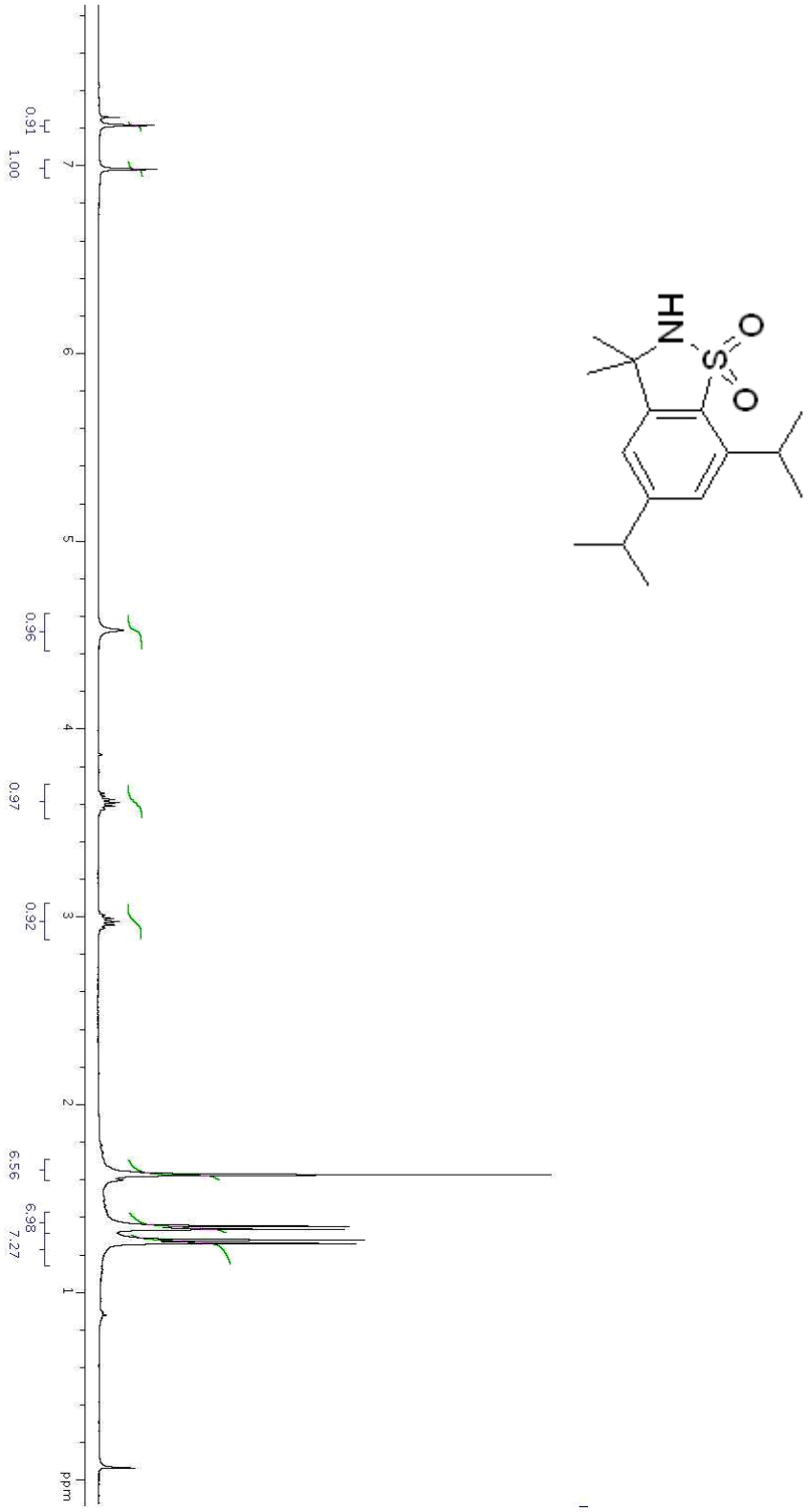


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of product of N_3Trisyl cyclization by 20 mol% **3**.



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