Electronic Supplementary Information for Dalton Transactions

Cyclopentadienyl mesityl complexes of chromium(II) and chromium(III)

Wen Zhou,[a] Jeffrey A. Therrien,[a] D. Lee K. Wence,[a] Emily N. Yallits,[a] Julia L. Conway,[a] Brian O. Patrick[b] and Kevin M. Smith*[a]

[a]*Department of Chemistry, University of British Columbia Okanagan, 3333 University Way, Kelowna, BC, Canada V1V 1V7*

[b]*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

Table of Contents

Experimental Section:

General Considerations: All reactions were carried out under nitrogen using standard Schlenk and glove box techniques. Hexanes, Et_2O, THF and toluene 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. Iodine was purified by sublimation and stored under nitrogen. $PbCl_2$ (Aldrich, 98%) was dried at 120 ºC prior to use. NaCp (2.0M in Et_2O), $CrCl_2$ (99% anhydrous), $CrCl_3$ (anhydrous), 1,4-dioxane (anhydrous), MesMgBr (1.0 M in Et_2O) and benzoylacetone were purchased from Aldrich and used as received. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich 98%) was distilled under vacuum, degassed with three freeze-pump-thaw cycles, and stored under nitrogen. Anhydrous DBU·HCl was prepared by the reaction of DBU in dry Et_2O under N_2 with anhydrous HCl (1.0 M in Et_2O, Aldrich), followed by isolation and storage in a glove box. 1,3-Dimethylimidazolium iodide (Me-NHC·HI), [1] 1,3-diisopropylimidazolium chloride (iPr-NHC·HCl),[1] and chromocene (Cp_2Cr),[2] were prepared according to the literature procedures. [Cp_2Cr][X] (X = I or OTf)[3] were prepared by oxidation of Cp_2Cr in THF with iodine or AgOTf. 1,3-diisopropylimidazolium chloride was washed with acetone and dried prior to use.[4] Salicylaldimine[5] and β-ketoimine[6] ligands were prepared according to the literature procedures by condensation of substituted anilines with salicylaldehyde and benzoylacetone, respectively. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, ON,

Canada or by the UBC Department of Chemistry microanalytical services. UV-visible spectra were obtained on a VARIAN Cary 50 Bio UV-vis spectrophotometer using air-tight cells sealed with Kontes Teflon valves. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer in C_6D_6 with chemical shifts referenced to the solvent peak.

CpCr(^{i}Pr-NHC)Cl (**1**). To a mixture of solid 1,3-diisopropylimidazolium chloride (295 mg, 1.56 mmol) and Cp_2Cr (283 mg, 1.55 mmol) was added 18 mL of THF. The initially orange-red solution slowly turned purple, and was allowed to stir at room temperature overnight. The solvent was removed in vacuo, the bright purple solid was extracted with aliquots of 3:1 Et_2O:THF and filtered through the Celite. The purple solution (total volume 15 mL) was cooled to –35 °C to yield bright purple crystals of **1** (268 mg, 57%) after three days. ^{1}H NMR (C_6D_6, 400 MHz): δ 16.9 (br, $\omega_{1/2}$ = 560 Hz, 12 H, CH(C*H*$_3$)$_2$), –11.0 (br, $\omega_{1/2}$ = 280 Hz, 2 H, NCH). Anal. Calcd for $C_{14}H_{21}N_2CrCl$: C, 55.17; H, 6.94; N, 9.19. Found: C, 55.29; H, 6.62.; N, 9.05. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 517 (150).

CpCr(^{i}Pr-NHC)Mes (**2**). Purple crystals of **1** (97 mg, 0.318 mmol) were suspended in 15 mL Et_2O and stirred until most of the crystals had dissolved. Slow addition of MesMgBr (0.4 mL, 1.0 M in Et_2O, 0.4 mmol) led to a rapid colour change from purple to orange-brown. After stirring at room temperature for 2 h, 1,4-dioxane (0.4 mL, 4.7 mmol) was added, resulting in the immediate formation of a large quantity of white precipitate. After stirring for an additional 20 min, the suspension was filtered through Celite, and the insoluble residue was washed with

additional 3 × 4 mL Et_2O. The solvent was removed in vauco, and the brown residue was extracted with aliquots of first hexanes and then Et_2O, which were filtered again through Celite. The resulting orange-brown solution (total volume 16 mL, 3:1 hexanes:Et_2O) was cooled to –35 °C overnight to yield **2** as small, shiny black crystals (67 mg, 54%). ^{1}H NMR (C_6D_6, 400 MHz): δ 48.6 (br, $\omega_{1/2}$ = 530 Hz), 16.7 (br, $\omega_{1/2}$ = 670 Hz), –14.1 (br, $\omega_{1/2}$ = 400 Hz). Anal. Calcd for $C_{23}H_{33}N_2Cr$: C, 70.92; H, 8.54; N, 7.19. Found: C, 69.78; H, 8.63; N, 7.11. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 462 (320).

CpCr(^{i}Pr-NHC)(Mes)I, (**3**) *Method A: from **2***. Black crystals of **2** (73.3 mg, 0.189 mmol) were dissolved in 1:1 THF:Et_2O (10 mL total volume), and to the resulting solution was added I_2 (26.3 mg, 0.104 mmol) dissolved in 3 mL Et_2O. After stirring for 20 h, the solvent was removed in vacuo, the residue was extracted with 8 mL Et_2O and 2 mL THF and then filtered through Celite. The deep purple solution was cooled to –35 °C to yield black crystals of **3** (48.7 mg, 50%) in two fractions. ^{1}H NMR (C_6D_6, 400 MHz): δ 26.6, 19.1, 10.3, 5.4, –7.8, –23.1. Anal. Calcd for $C_{23}H_{33}N_2CrI$: C, 53.49; H, 6.44; N, 5.42. Found: C, 50.22; H, 5.95; N, 5.04. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 536 (490).

*Method B from **1**.* Purple crystals of **1** (77.2 mg, 0.253 mmol) were dissolved in 10 mL Et_2O, and then MesMgBr (0.3 mL, 1.0 M in Et_2O, 0.3 mmol) was added, leading to a rapid colour change from bright purple to orange. After 40 min, 1,4-dioxane (0.3 mL, 3.5 mmol) was added inducing the immediate precipitation of white powder. The solution was filtered through Celite and washed with Et_2O.

Addition of I_2 (32.4 mg, 0.255 mmol) dissolved in 3 mL Et_2O led to a colour change from orange to deep purple. After for an additional 45 min, solution filtered through the Celite and cooled to –35 °C overnight to yield black crystals of **3** (47 mg, 36%).

CpCr(^{i}Pr-NHC)Cl$_2$ (**4**). To a mixture of solid **1** (101 mg, 0.331 mmol) and $PbCl_2$ (166.1 mg, 0.643 mmol) was added 15 mL of THF. Over 1 h, the colour of the solution changed from bright purple to a darker blue purple, and the white precipitate turned to a metallic grey. The THF solution was filtered through the Celite, the residue was washed with 4 mL Et_2O, and the resulting solution was cooled to –35 °C. Black crystals of **4** (48.2 mg, 43 %) were isolated in three fractions. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.1, –10.8. Anal. Calcd for $C_{14}H_{21}N_2CrCl_2$: C, 49.42; H, 6.22; N, 8.23. Found: C, 50.18; H, 6.33; N, 8.18. UV/vis (THF; λ, nm (ε, $M^{-1}cm^{-1}$)): 578 (890).

CpCr(Me-NHC)I$_2$ (**5**). To a brown yellow suspension of [Cp_2Cr][I] (414.6 mg, 1.341 mmol) in 30 mL THF was added solid 1,3-dimethylimidazolium iodide (299.4 mg, 1.336 mmol). After 30 min stirring, the supernatant had turned a dark green colour. The suspension was left to stir for 3 days, after which it was a dark, homogeneous teal solution. The solution was concentrated in vacuo then filtered through the Celite. Cooling the teal solution to –35 °C yielded black blocks of **5** (277 mg, 44%) isolated in three different fractions. Anal. Calcd for $C_{10}H_{13}N_2CrI_2$: C, 25.72; H, 2.81; N, 6.00. Found: C, 26.10; H, 2.45; N, 5.72. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 580 (1100).

CpCr[OC$_6$H$_4$CHN(2,6-^{i}Pr$_2$C$_6$H$_3$)]I (**6b**). To an orange-red solution of Cp_2Cr

(123 mg, 0.676 mmol) in 15 mL of Et_2O was added I_2 (105 mg, 0.406 mmol), resulting in the precipitation of yellow $[Cp_2Cr][I]$. The solvent was removed in vacuo and the salicylaldimine ligand $[OC_6H_4CHN(2,6\text{-}iPr_2C_6H_3)]$ (211.1 mg, 0.749 mmol) was added. To the solids was added 15 mL Et_2O and 2 mL CH_2Cl_2, and the reaction mixture was stirred overnight. After 20 h the solvent was removed in vacuo, and the residue was extracted with 10 mL of hexane and 5 mL of CH_2Cl_2 then filtered through the Celite. The Celite was washed with 2 × 5 mL hexanes and the combined filtrates were crystallized at –35 °C to give black crystals of **6b** (156.8 mg, 44%) in three different fractions.

The complexes CpCr[OC(Ph)CHC(Me)O]I (**6a**) and CpCr[OC(Ph)CHC(Me)N(3,5-$Me_2C_6H_3$)](O_3SCF_3) (**6c**) were prepared by analogous protonolysis reactions of $[Cp_2Cr][I]$ and $[Cp_2Cr][OTf]$ with benzoylacetone and Ph(O)CHC(Me)NH(3,5-$Me_2C_6H_3$), respectively.

CpCr(DBU)Cl (**7**). To an orange-red solution of Cp_2Cr (487.8 mg, 2.68 mmol) in 30 mL THF, solid DBU·HCl (505.8 mg, 2.68 mmol) was added and the suspension was stirred at room temperature for 20 h. The solvent of the resulting purple solution was removed in vacuo. The purple residue was triturated with Et_2O and the solvent was again removed in vauco. The residue was extracted with toluene, filtered through Celite and cooled to –35 °C. Purple **7** (458 mg, 56%) was isolated in two fractions. Anal. Calcd for $C_{14}H_{21}N_2CrCl$: C, 55.17; H, 6.95; N, 9.19. Found: C, 55.17; H, 6.64; N, 8.90. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 547 (110).

CpCr(DBU)Mes, (**8**) *Method A: from $CrCl_2$.* To a suspension of $CrCl_2$

(150.1 mg, 1.22 mmol) in 20 mL THF, NaCp (0.63 mL, 2.0 M in THF, 1.26 mmol) was added dropwise. After stirring for 30 min, DBU (0.90 mL, 6.02 mmol) was added, resulting in a colour change from orange-brown to a very dark purple-red. Dropwise addition of MesMgBr (1.30 mL, 1.0 M in Et_2O, 1.30 mmol) resulted in a further darkening of the solution. After stirring for 16 h, 1,4-dioxane (1.0 mL, 12 mmol) was added. The solvent was removed in vacuo, and the residue was extracted with aliquots of Et_2O and filtered through Celite until the washings were colourless. The filtrate was concentrated in vacuo to 15 mL, and the resulting solution was cooled to –35 °C. After four days, black crystals of **8** (277.8 mg, 59%) were isolated in one fraction. ^{1}H NMR (C_6D_6, 400 MHz): δ 75.6, 43.7, 11.5. Anal. Calcd for $C_{23}H_{32}N_2Cr$: C, 71.11; H, 8.30; N, 7.21. Found: C, 69.18; H, 8.18; N, 7.40. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 496 (160), 358 (790).

Method B: from Cp_2Cr. To an orange-red solution of Cp_2Cr (49.9 mg, 0.274 mmol) in 10 mL of THF was added solid DBU·HCl (51.9 mg, 0.275 mmol) and a few drops of neat DBU. After stirring for 18 h, the colour changed from orange to bright purple. The solvent was removed in vacuo to remove the cyclopentadiene byproduct. The residue was dissolved in 20 mL THF, MesMgBr (0.30 mL, 1.0 M in Et_2O, 0.30 mmol) was added dropwise, and the solution was stirred for 24 h. 1,4-dioxane (0.3 mL, 3.5 mmol) was added and the solution was stirred for 15 min. The solvent was removed in vacuo, the residue was extracted with Et_2O, filtered through Celite and the resulting solution was concentrated and filtered through Celite again. The UV-visible spectra of a diluted aliquot of this solution was identical to that of **8**

prepared by the preceding method.

CpCr(DBU)(Mes)I (**9**). To a solution of **8** (199.5 mg, 0.514 mmol) in 20 mL of Et_2O, I_2 (67.8 mg, 0.267 mmol) was added as a solution in 2 mL THF, resulting in a colour change to blue-violet. After stirring for 4 h, the solution was filtered through Celite and cooled to –35 °C overnight. Black crystals of **9** (119.9 mg 45%) were isolated the next day. ^{1}H NMR (C_6D_6, 400 MHz): δ 20.1, 16.9, 3.9, –0.1. Anal. Calcd for $C_{23}H_{32}N_2CrI$: C, 53.60; H, 6.26; N, 5.43. Found: C, 53.83; H, 6.18; N, 5.52. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 574 (1150), 357 (2500).

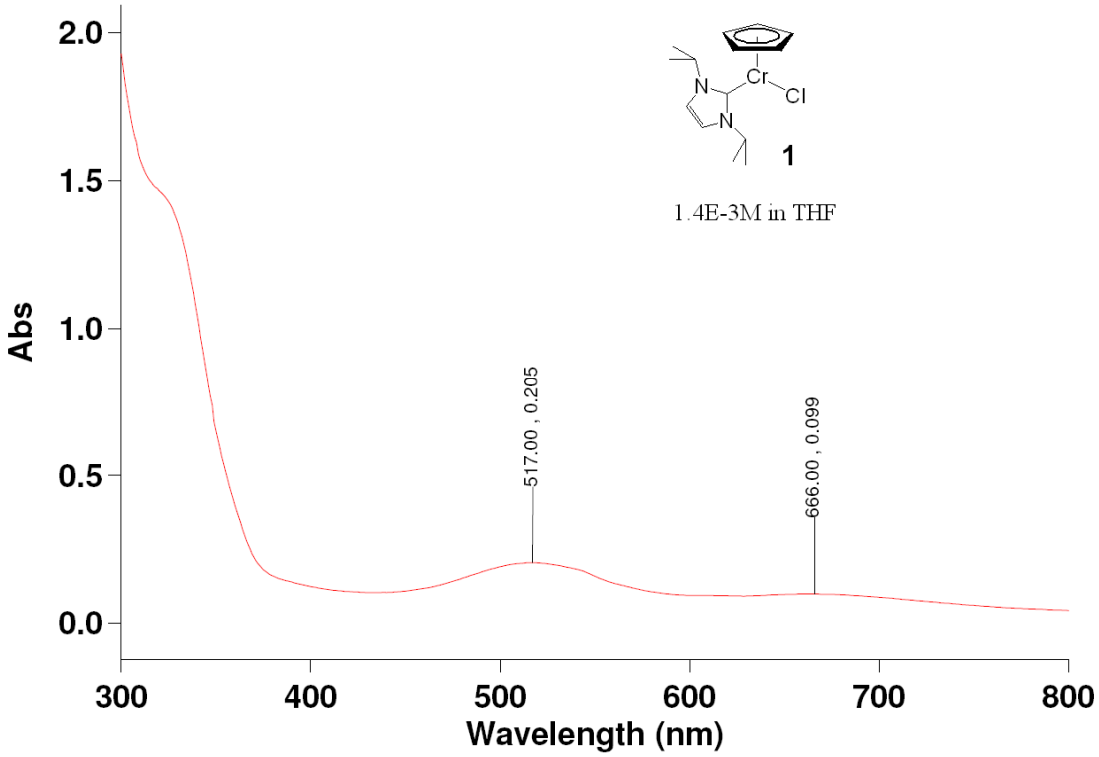
[CpCr(μ-Mes)]$_2$ (**10**).To a suspension of $CrCl_2$ (508.9 mg, 4.141 mmol) in 50 mL of THF was added NaCp (2.10 mL, 2.0 M in THF, 4.20 mmol). After stirring for 30 min, MesMgBr (4.6 mL, 1.0 M in Et_2O, 4.6 mmol) added by syringe. After stirring at room temperature for 24 h, the solvent was removed in vacuo, and the residue was extracted with toluene and filtered through Celite. The filtrate was concentrated in vacuo to ~30 mL and filtered through Celite again. The dark purple solution was cooled to –35 °C. After four days, black crystals of **10** (397.7 mg, 41%) were isolated. ^{1}H NMR (C_6D_6, 400 MHz): δ 19.6 (br, $\omega_{1/2}$ = 340 Hz), 10.1, 9.92. Anal. Calcd for $C_{28}H_{32}Cr$: C, 71.17; H, 6.83. Found: C, 71.17; H, 6.49. UV/vis (THF; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 583 (750).

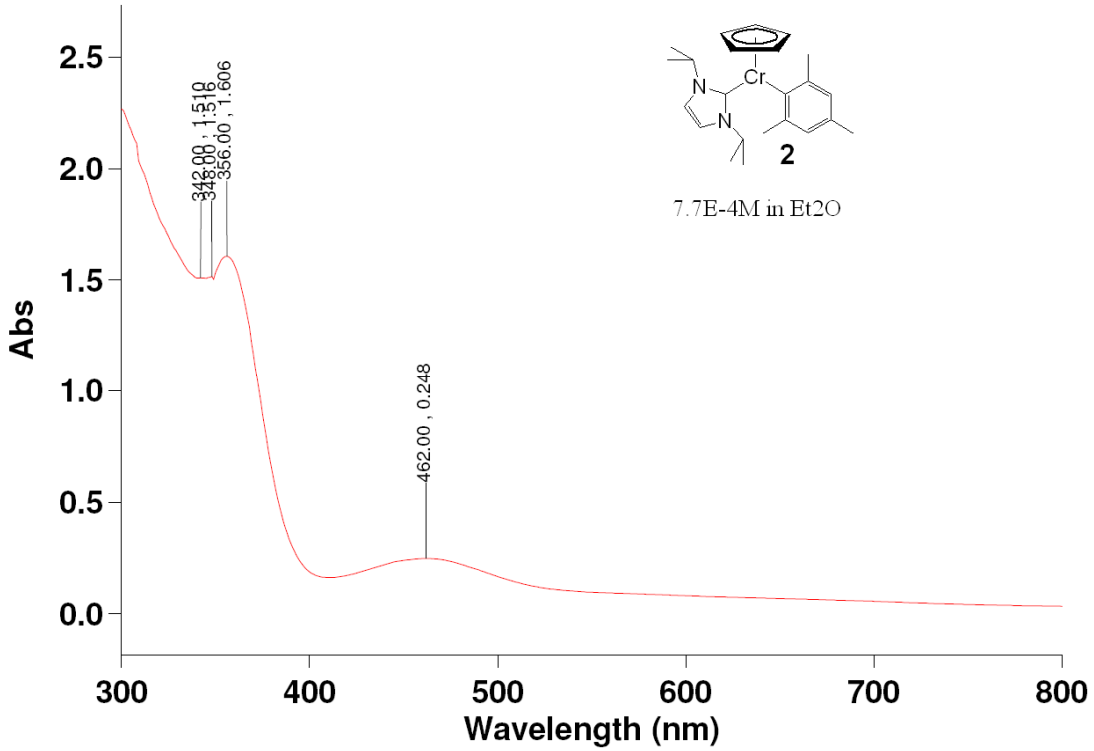
Table 1. Crystal data and refinement parameters for X-ray structures of **2**, **8, 9** and **10**.

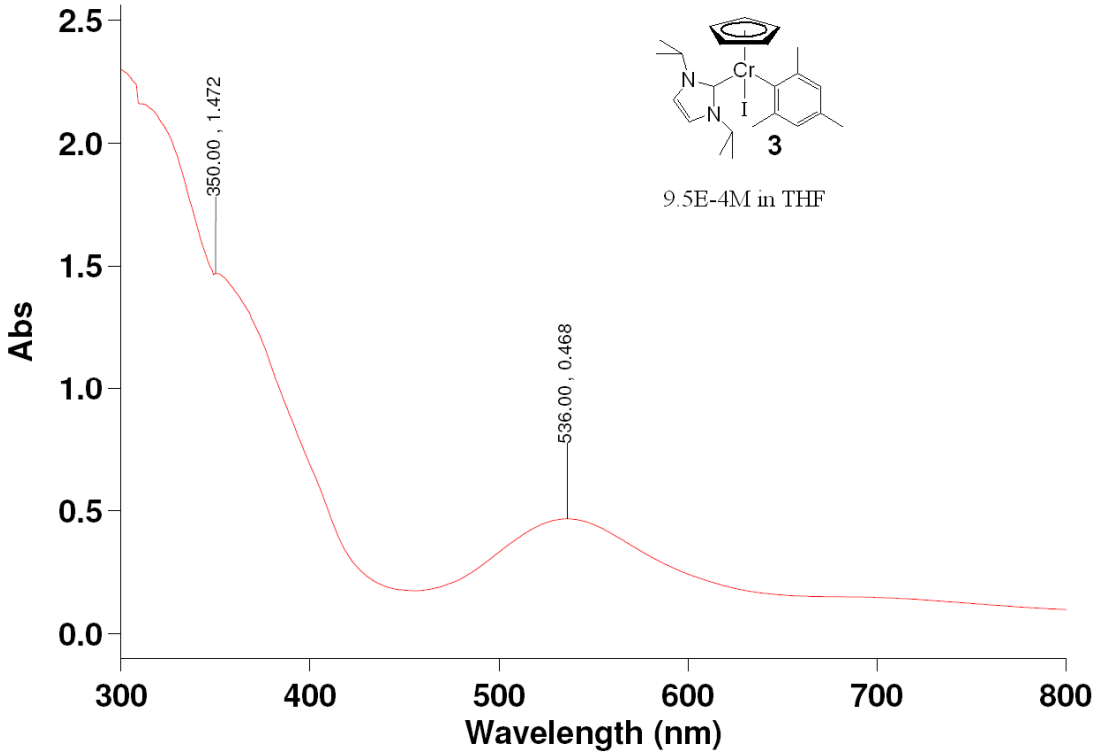
	2	**8**	**9**	**10**
Chemical formula	$C_{23}H_{32}CrN_2$	$C_{23}H_{32}N_2Cr$	$C_{23}H_{32}N_2ICr$	$C_{56}H_{64}Cr_4$
Formula weight (g/mol)	388.51	388.51	515.41	945.12
Crystal size (mm)	0.10 X 0.25 X 0.35	0.18 X 0.32 X 0.40	0.24 X 0.35 X 0.52	0.16 X 0.35 X 0.40
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Unit-cell dimensions				
a, Å	8.3577(2)	14.3796(11)	11.5521(5)	8.3398(8)
b, Å	8.4155(2)	15.9373(12)	13.9206(5)	11.8870(12)
c, Å	18.1329(5)	18.4488(13)	14.6207(6)	12.6085(12)
α, deg	97.0890(10)	90	90	94.928(5)
β, deg	98.1880(10)	90	110.507(1)	93.544(4)
γ, deg	118.4210(10)	90	90	108.619(5)
V, $Å^3$	1083.10(5)	4227.9(5)	2202.2(2)	1174.86(23)
T (K)	173(2)	173(2)	173(2)	173(2)
Space group	*P* -1	*P* bca	*P 21/n*	*P* -1
Z	2	8	4	2
F(000)	416	1663.7	1044	495.9
μ, ($mm^{-1)}$	0.536	0.549	1.931	0.937
Reflections measured,	17616	26292	31129	16929
Indep reflections, R_{int}	5028, 0.0164	5111, 0.0366	5314, 0.025	5590, 0.0235
θ, range (deg)	2.817-27.8275	2.2065-17.522	2.38-28.01	1.63-28.07
Absorp, T_{min},T_{max}	0.857, 0.948	0.7648, 0.9059	0.485, 0.629	0.797, 0.861
DC (calc) (Mgm^{-3})	1.19	1.22	1.555	1.34
Obsd data(*I*>2.00σ*(I)*)	4383	3446	4798	4831
R1,wR2 (F^2,all data)	0.0375, 0.0761	0.0726, 0.1059	0.025, 0.054	0.0466, 0.1025
R1,wR2 (*F,I*>2.00σ*(I)*)	0.0294, 0.0715	0.0371, 0.0885	0.022, 0.052	0.0394, 0.0996
Goodness-of-fit (S)	1.023	1.035	1.06	1.186
No. data/rest/params	5028/0/238	5111/0/238	5214/0/245	5590/0/275
Max.,min. $peak^3$, ($e^-Å^3$)	0.318, -0.356	0.285, -0.379	0.86, -0.38	0.394, -0.318

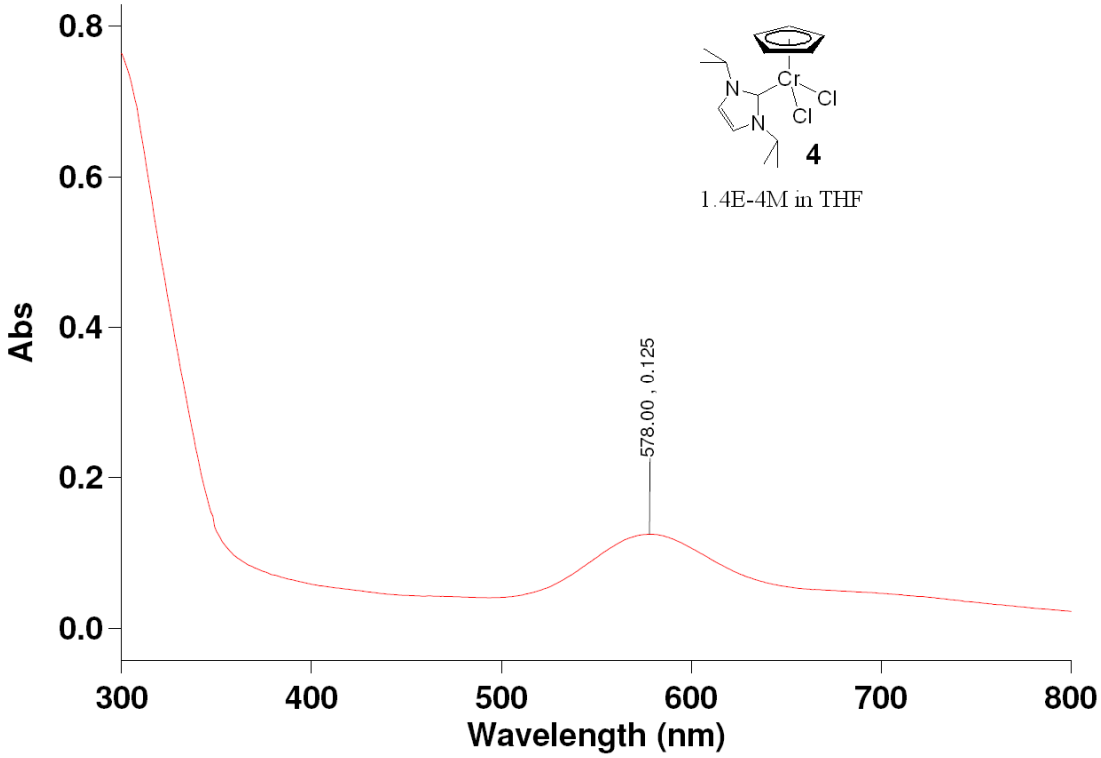
Table 2. Crystal data and refinement parameters for X-ray structures of **6a**, **6b** and **6c**.

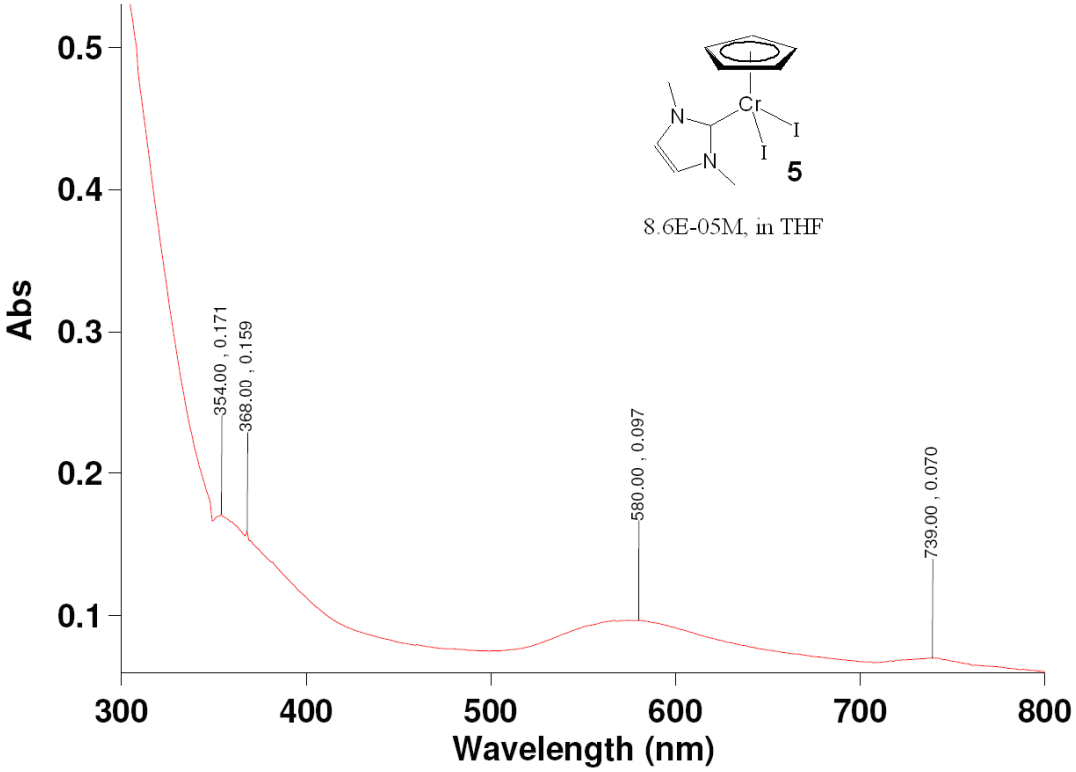
	6a	**6b**	**6c**
Chemical formula	$C_{15}H_{14}O_2CrI$	$C_{24}H_{27}NOCrI$	$C_{24}H_{23}O_4F_3NSCr$
Formula weight (g/mol)	405.16	524.37	530.5
Crystal size (mm)	0.10 X 0.12 X 0.24	0.12 X 0.25 X 0.25	0.16 X 0.36 X 0.44
Crystal system	Monoclinic	Triclinic	Orthorhombic
Unit-cell dimensions			
a, Å	19.6228(14)	8.9810(8)	13.518(9)
b, Å	7.4584(6)	10.4430(9)	16.712(8)
c, Å	20.531(2)	12.6068(11)	21.148(16)
α, deg	90	92.002(4)	90
β, deg	98.570(4)	107.735(4)	90
γ, deg	90	91.342(5)	90
V, $Å^3$	2971.3(4)	1124.77(17)	4778(5)
T (K)	173(2)	173(2)	173(2)
Space group	*P* $2_1/c$	*P* -1	*P* bca
Z	8	2	8
F(000)	1576	526	2184
μ, ($mm^{-1)}$	2.842	1.895	0.621
Reflections measured,	32094	26216	33379
Indep reflections, R_{int}	7098, 0.037	8161, 0.048	5769, 0.027
θ, range (deg)	2.4-27.72	1.7-27.94	2.73-27.93
Absorp, T_{min}, T_{max}	0.628, 0.753	0.49, 0.797	0.816, 0.905
DC (calc) (Mgm^{-3})	1.811	1.548	1.475
Obsd data(I>2.00σ(I))	5357	7372	4501
R1,wR2 (F^2,all data)	0.051, 0.064	0.033, 0.076	0.050, 0.087
R1,wR2 (F,I>2.00σ(I))	0.030, 0.058	0.027, 0.072	0.032, 0.077
Goodness-of-fit (S)	1.01	1.11	1.06
No. data/rest/params	7098/0/345	8161/0/258	5769/0/310
Max.,min. $peak^3$, ($e^-Å^3$)	0.69, -0.69	0.65, -0.62	0.41, -0.35

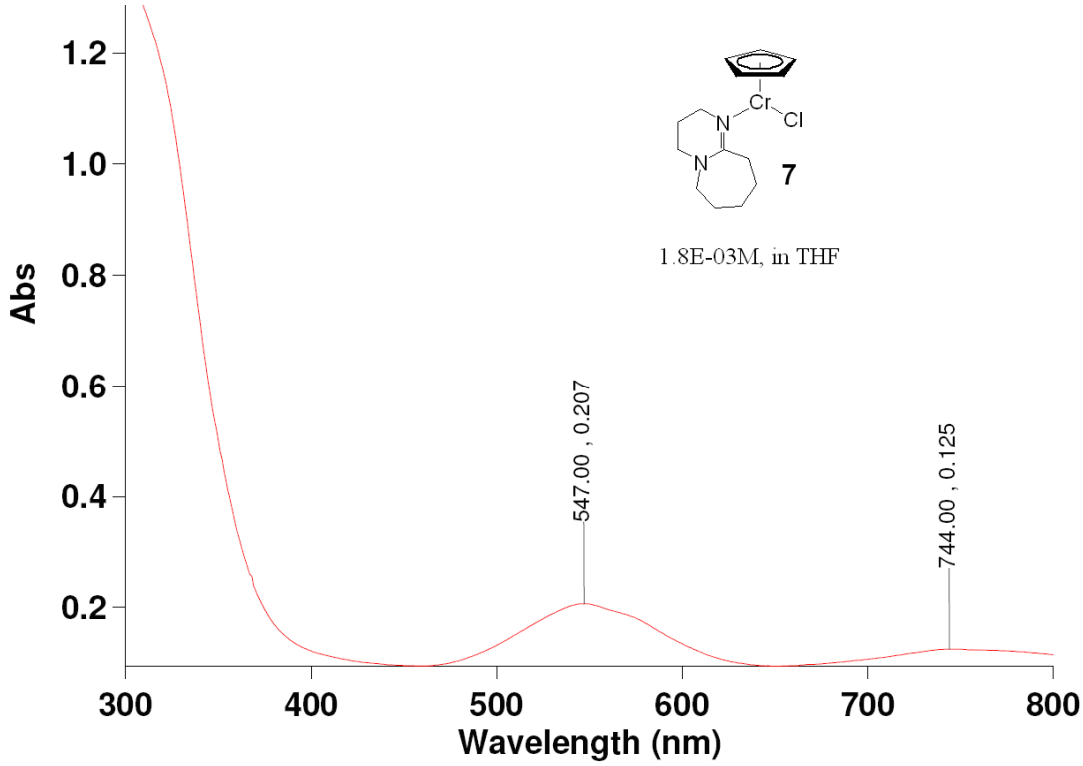


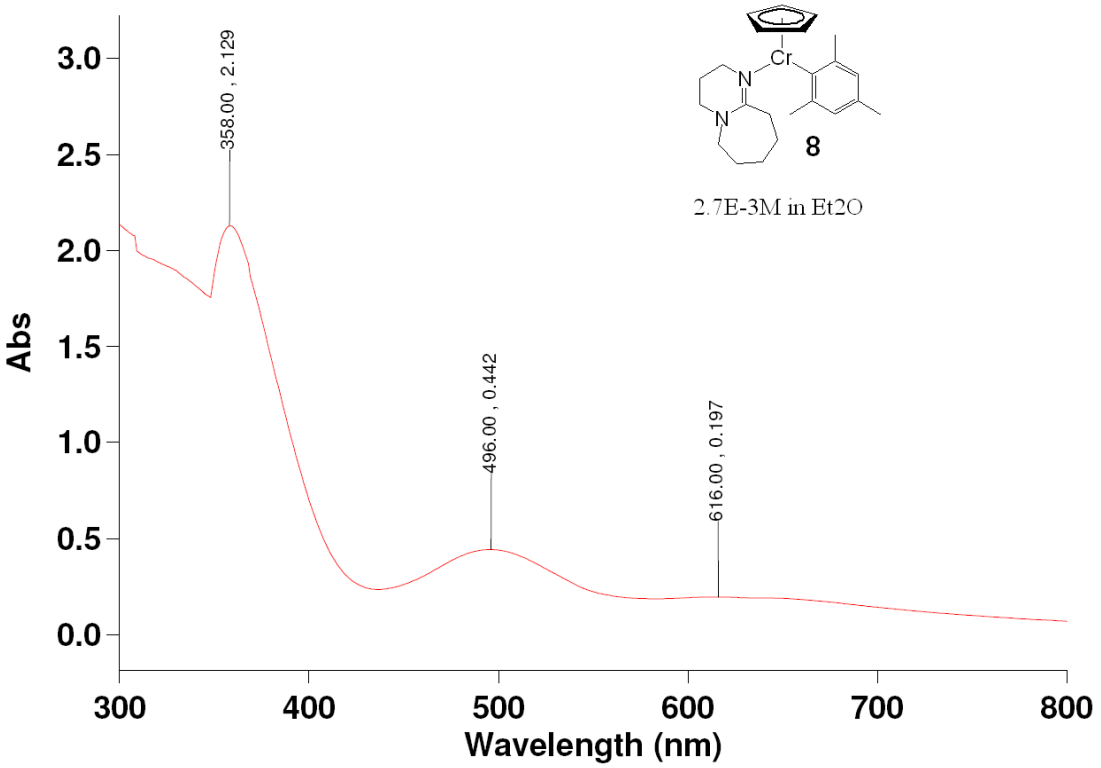


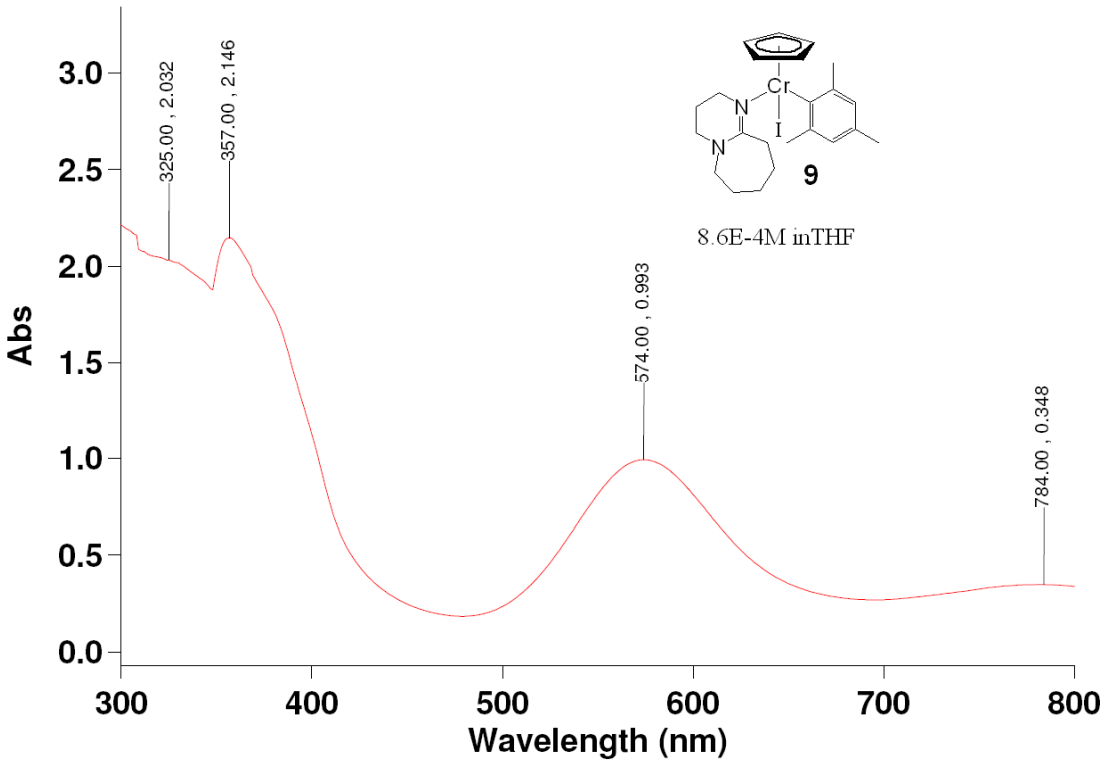


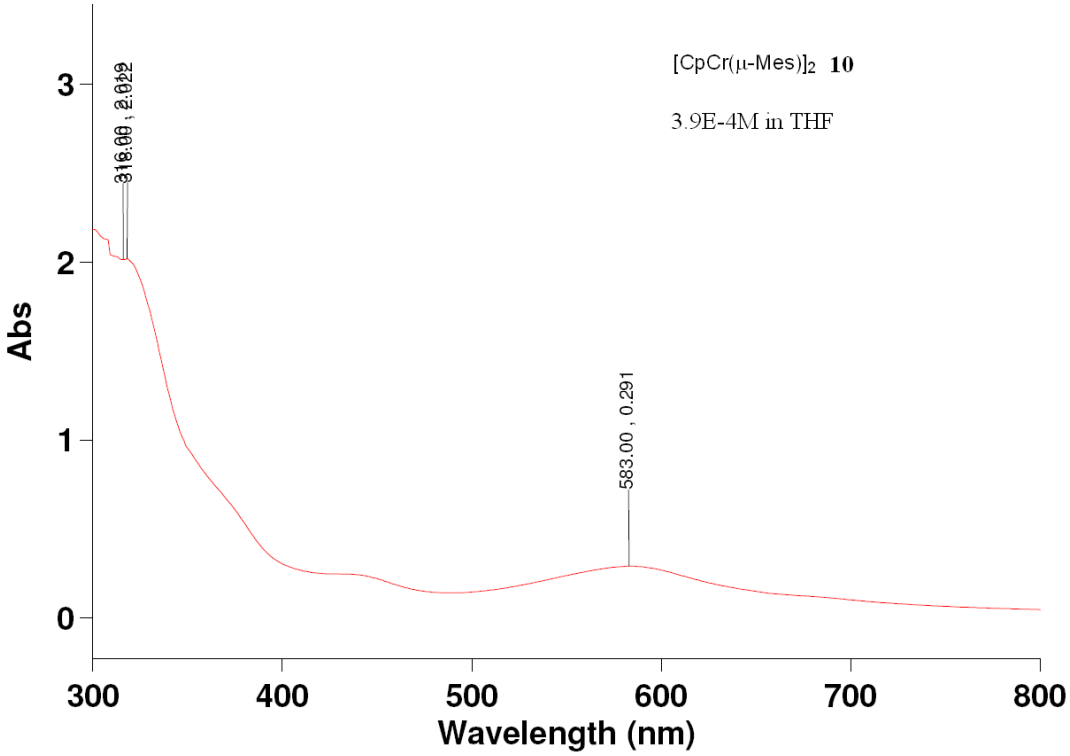












References

(1) T. Schaub, M. Backes and U. Radius, *Organometallics*, 2006, **25**, 4196-4206.

(2) R. B. King, *Organometallic Syntheses: Vol. 1*, Academic Press: New York, NY, 1965; pp 66-67.

(3) E. O. Fischer, K. Ulm and P. Kuzel, *Z. Anorg. Allg. Chem*., 1963, **319**, 253-265.

(4) M. H. Voges, C. Rømming and M. Tilset, *Organometallics*, 1999, **18**, 529-533.

(5) S. Chang, L. Jones II, C. Wang, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 3460-3465.

(6) X. He, Y. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang and Q. Wu, *Organometallics*, 2003, **22**, 4952-4957.