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Electronic Effects in the Oxidative Addition of Iodomethane with Mixed-Aryl β-Diketiminate Chromium Complexes

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The Cr^{II} complexes CpCr[DppNC(Me)CHC(Me)NC_6H_4Y] (**1**; Dpp = 2,6-$(Me_2CH)_2C_6H_3$) were used to prepare the corresponding Cr^{III} iodo (**2**) and methyl (**3**) mixed-aryl β-diketiminate compounds with Y = OMe (**a**), CH_3 (**b**), H (**c**), CF_3 (**d**). Oxidation of the Cr^{II} precursors with iodine gave CpCr[DppNC(Me)CHC(Me)NC_6H_4Y](I) (**2a**−**d**). The Cr^{III} methyl compounds **3a**−**d** were prepared by reaction of the Cr^{II} complexes with iodomethane followed by MeMgI. The Cr^{III} chloride complexes **4a**−**d** were synthesized by salt metathesis of isolated $CpCrCl_2$(THF) with the appropriate deprotonated mixed-aryl β-diketiminate. The structures of the paramagnetic complexes **1b**,**c**, **2a**,**b**, **3a**−**d**, and **4a**−**d** were determined by single-crystal X-ray diffraction. The rate constants for the single-electron oxidative addition of iodomethane with **1a**−**d** were determined by monitoring the reaction by UV−vis spectroscopy. The rate constants correlated well with the electronic parameters of the Y substituents ($\rho = -0.36$). The rate constants for **1a**−**d** were an order of magnitude greater than those previously obtained for the same reaction with CpCr[$(DppNCMe)_2CH$] and related ortho-disubstituted symmetric β-diketiminate complexes.

Introduction

The reaction of Cr^{II} with organic halides is a critical feature of chromium-catalyzed carbon−carbon bond-forming reactions for organic synthesis.[1] Single-electron oxidative addition is also intimately connected mechanistically to transition-metal-mediated radical polymerization.[2] We have been interested in the single-electron oxidative addition reaction of organic halides (R−X) with well-defined CpCr[$(ArNCMe)_2CH$] complexes, as shown in Figure 1.[3] The initial slow step is the halogen atom abstraction of R−X with Cr^{II} to generate the Cr^{III}−X compound and an alkyl radical.[4] The energy difference between **A** and **C** is determined by the strength of the R−X bond that is broken compared to the weaker Cr^{III}−X bond that is formed. The subsequent fast step relies on the remarkable ability of Cr^{II} to efficiently trap carbon-based radicals.[5] The strength of the Cr−R bond formed dictates the energy difference between **C** and **E**.

The reaction coordinate shown in Figure 1 also illustrates the energetics for the use of these complexes for controlled radical polymerization.[2] With well-defined complexes in the absence of halide sources as the starting point, the reversible Cr−R homolysis forms the basis of organometallic mediated radical polymerization (OMRP).[2,6] Alternatively, the concentration of $R^{\bullet}$ can also be minimized via an atom-transfer radical polymerization (ATRP) mechanism if halides are available.[2,6b,7] For the current system, we have demonstrated that a well-defined Cr^{III} neopentyl complex can serve to both initiate and control polymerization of vinyl acetate by OMRP.[8] However, the barrier between **C** and **B** was determined to be prohibitively high in this system: both experimental and computational studies indicated that the ATRP mechanism was not competitive with OMRP.[9]

The ease with which the steric and electronic properties of the β-diketiminate ligand can be varied has contributed to its widespread use over the past decade.[10] Certain aspects of the reaction coordinate shown in Figure 1 appear to be amenable to control through ancillary ligand steric effects. Increasing the size of the NAr substituents raises the relative energy of the CpCr[$(ArNCMe)_2CH$](R) complex through increased

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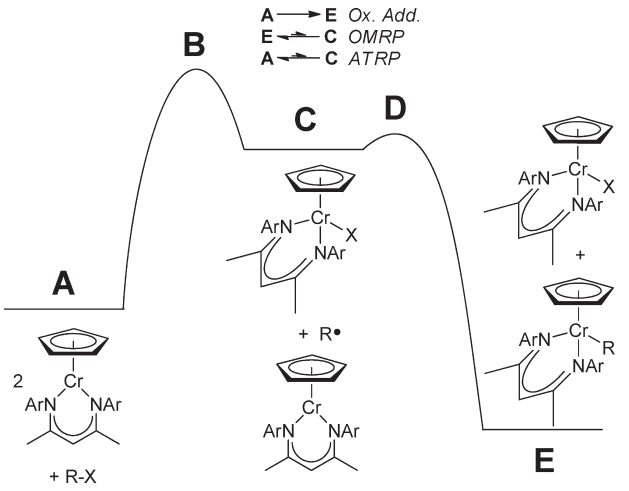
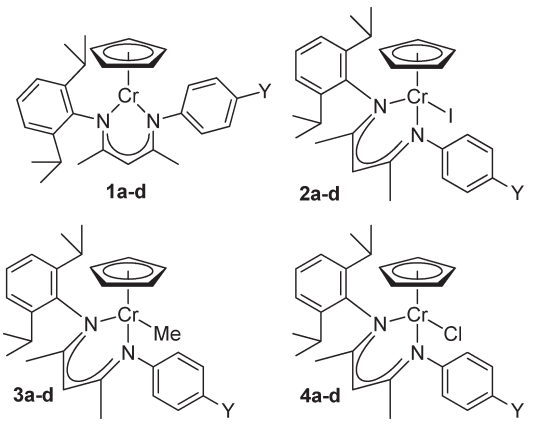


Figure 1. Schematic energy diagram for single-electron oxidative addition of R−X by CpCr[(ArNCMe)$_2$CH].

Scheme 1. Mixed-Aryl β-Diketiminate Cr^{II} and Cr^{III} Complexes (Y = OMe (a), CH_3 (b), H (c), CF_3 (d))



steric hindrance. The resulting decrease in energy between **E** and **D** is evident in an increased rate measured for the Cr^{III}−R homolysis.[11] The same decrease in Cr^{III}−R homolytic bond dissociation energy can be achieved by increasing the steric requirements of the R group,[11] as previously observed for aqueous Cr^{III} alkyl complexes.[5]

Currently, Cr-mediated coupling reactions of R−X and aldehydes use nickel cocatalysts to activate aryl or alkenyl halides,[1,12] and alkyl halides require cobalt or iron cocatalysts.[1,13] Lowering the barrier from **A** to **B** through ancillary ligand modification would extend the range of R−X substrates that can react directly with Cr, simplifying catalyst design. Unlike the Cr−R BDE, however, the rate-determining step for R−X activation did not display any significant sensitivity to steric modification of the β-diketiminate ligand. We previously reported that the rate of oxidative addition of iodomethane with CpCr[(ArNCMe)$_2$CH] is relatively constant for Ar = Dpp (diisopropylphenyl, 2,6-$(Me_2CH)_2C_6H_3$), Dep

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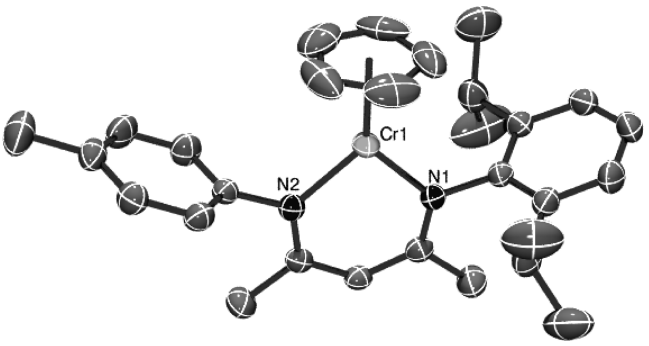

Figure 2. Thermal ellipsoid diagram (50%) of Cr^{II} complex **1b**.

(diethylphenyl, 2,6-$(CH_3CH_2)_2C_6H_3$), Xyl (xylyl, 2,6-Me_2-C_6H_3), Mes (mesityl, 2,4,6-$Me_3C_6H_2$).[14]

We now report the use of mixed-aryl β-diketiminate ligands[15] to explore electronic effects in the single-electron transfer reactivity of Cr^{II} complexes.[3b] In these ligands, one bulky Dpp subsituent is retained to afford steric protection to the paramagnetic Cr^{II} and Cr^{III} complexes in Scheme 1. The absence of ortho substituents is intended to allow the second aryl moiety to more readily align with the Cr[(NCMe)$_2$CH] plane, enhancing electronic effects transmitted to the chromium center from the para group (Y = OMe (**a**), CH_3 (**b**), H (**c**), CF_3 (**d**)). We previously reported the synthesis of the three Cr^{II} complexes CpCr[DppNC(Me)CHC(Me)NC_6H_4Y] (**1a**,**c**,**d**), the X-ray crystal structures of two of these compounds (**1a**,**d**), and their use in the controlled radical polymerization of vinyl acetate initiated by V-70.[16] In this contribution, we report the independent synthesis of the corresponding Cr^{III} iodo, methyl, and chloro complexes (**2a**−**d**, **3a**−**d**, and **4a**−**d** in Scheme 1, respectively). Kinetic measurements of the oxidative addition of iodomethane with **1a**−**d** demonstrate a clear electronic influence of the para group. The significant increase in the rate constants measured for all four mixed-aryl Cr^{II} complexes in comparison to the previously reported symmetric β-diketiminate analogues appears to be an unanticipated steric consequence of removing the ortho substituents to enhance electronic effects.

Results and Discussion

Synthesis of Chromium(II) Complexes. In the initial 2004 communication,[3a] the symmetric CpCr[(DppNCMe)$_2$CH] was prepared by treatment of Gibson's {Cr[(DppNCMe)$_2$-CH]}$_2$(μ-Cl)$_2$ dimer[17] with NaCp. Subsequent syntheses of CpCr[ArNCMe)$_2$CH] complexes relied on the sequential addition of NaCp and Li[(ArNCMe)$_2$CH] to $CrCl_2$ in THF.[8] The latter route was employed for the previously reported Cr^{II} mixed-aryl complexes **1a**,**c**,**d**,[16] as well as for the new *p*-methyl-substituted variant **1b** (eq 1). The X-ray crystal

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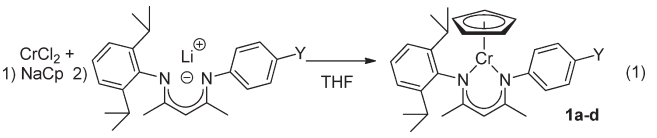
structure of **1b** is shown in Figure 2, and the newly determined structure of **1c** is included in the Supporting Information.



(1)

The success of the apparent cyclopentyldienide displacement reaction from Cp_2Cr had previously been attributed to the ability of the bulky NAr substituents to preclude the formation of Cr^{II} bis(β-diketiminate) complexes.[14] Indeed, by using an even more sterically demanding ligand, Mindiola and co-workers have prepared three-coordinate Cr[(DppNCtBu)$_2$CH](X) complexes.[18] However, it was recently demonstrated that Cr[(RNCMe)$_2$CH]$_2$ complexes can be prepared and structurally characterized not only for R = C_6H_5, $CH_2C_6H_5$ but also for the bulkier R = 2-(Me$_2$CH)C_6H_4, 2-(Me$_3$C)C_6H_4, $C_{10}H_7$ derivatives.[19−21] Similarly, CpCr(C_6H_4-CH_2NMe_2),[22] CpCr[(Me$_3$SiN)$_2$CPh],[23] and CpCr(Mes)(L) (L = DBU, N-heterocyclic carbene)[24] compounds have all been prepared, despite the stability of the known Cr($C_6H_4CH_2$-NMe_2)$_2$,[25] Cr[(Me$_3$SiN)$_2$CPh]$_2$,[26] and Cr(Mes)$_2$(L)$_2$ complexes.[27] The factors that favor the synthesis of CpCr(LX) compounds instead of the corresponding Cr(LX)$_2$ species remain to be explored.[28]

Synthesis of Chromium(III) Iodo Complexes. Single-electron oxidation of well-defined Cr^{II} precursors with iodine is a common route to Cr^{III} iodo complexes.[24,29] Reaction of **1a**−**d** with I_2 did give the expected iodo complexes **2a**−**d** (eq 2), although the mixed-aryl β-diketiminate compounds did not crystallize as readily as the more symmetric CpCr-[(ArNCMe)$_2$CH](I) analogues.[14] Complex **2c** (Y = H), in particular, displayed a tendency to precipitate as a powder rather than form crystals. The lower yields for compounds **2a**−**d** are presumed to be due to the difficulties in recrystallizing these chiral-at-metal complexes, rather than an inherent problem with the synthetic route in eq 2 or a lack of stability of the Cr^{III} iodo species. The X-ray crystal structure

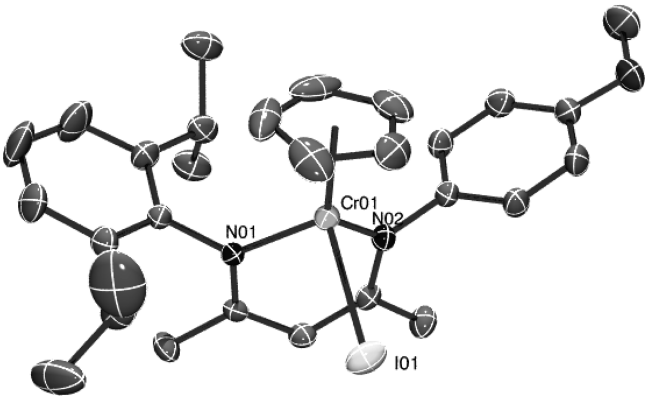
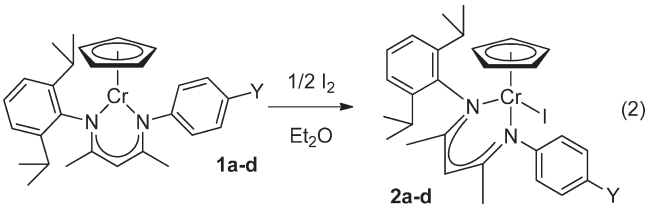


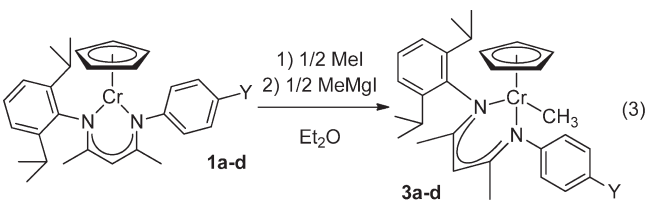
Figure 3. Thermal ellipsoid diagram (50%) of Cr^{III} iodo complex **2a**.

of **2a** is shown in Figure 3; the structure of **2b** is included in the Supporting Information.



(2)

Synthesis of Chromium(III) Methyl Complexes. The optimal choice of RMgX and Cr^{III} precursor to prepare CpCr-[(ArNCMe)$_2$CH](R) complexes by salt metathesis depends on the steric demands of the NAr and R groups.[3a,14,8,11] Both the Cr^{III} iodide and Cr^{III} chloride mixed-aryl β-diketiminate complexes reacted readily with MeMgI. However, synthesis of Cr^{III} methyl compounds **3a**−**d** directly from the corresponding Cr^{II} precursors, as shown in eq 3, capitalized on the ease of synthesis of **1a**−**d**. Addition of iodomethane to CpCr-[(DppNC(Me)CHC(Me)NC$_6$H$_4$Y] produced a mixture of Cr^{III} iodo and Cr^{III} methyl species, which were converted to **3a**−**d** by subsequent addition of MeMgI. Complexes **3b**,**d** were also prepared by reaction of the appropriate Cr^{II} complex with MeI and SmI_2.[30] As was observed for CpCr[(DppNCMe)$_2$-CH](CH$_3$),[3a] the high solubility of the Cr^{III} methyl complexes limited the yield of products **3b**−**d** as crystalline solids. The comparatively high yield of **3a** may be due to a slight reduction in lipophilicity imparted by the polar methoxy substituent.



(3)

Synthesis of Chromium(III) Chloro Complexes. In light of the problems encountered in recrystallization of the Cr^{III} iodo complexes **2a**−**d**, routes were investigated to prepare Cr^{III} chloro compounds as potential precursors for the

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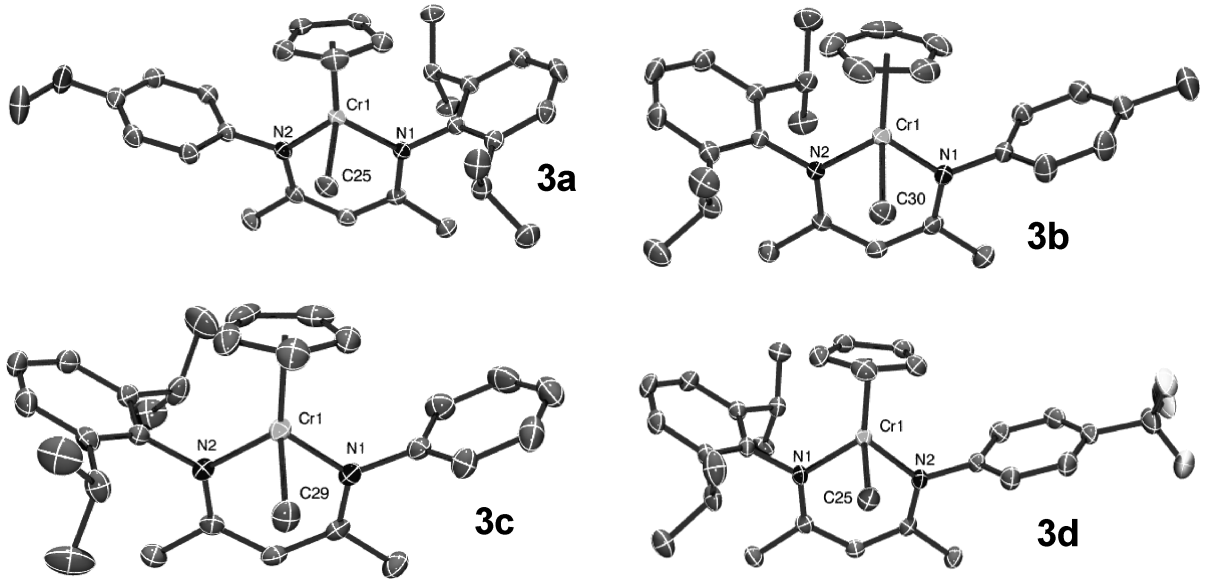
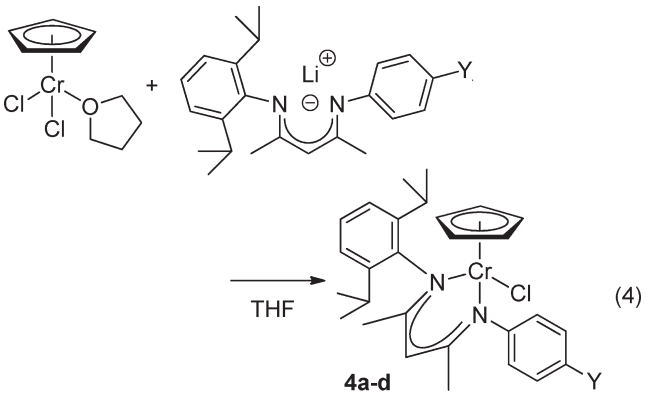


Figure 4. Thermal ellipsoid diagrams (50%) of Cr^{III} methyl complexes **3a**−**d**.

independent synthesis of **3a**−**d** by salt metathesis. Although the symmetric CpCr[(DppNCMe)$_2$CH](Cl) could be prepared by oxidation with $PbCl_2$, it was not readily accessible by salt metathesis reactions from $CpCrCl_2(THF)$.[3a] This observation was confirmed by Jin and co-workers, although this route served well for their preparation of CpCr[(PhNCMe)$_2$CH](Cl) and related β-keto iminate complexes.[31] For CpCr[(XylNCMe)$_2$CH](Cl), sequential reaction of $CrCl_3$ with deprotonated β-diketiminate followed by NaCp had proved optimal.[8]

The preparation of CpCr[(DppNC(Me)CHC(Me)NC$_6$H$_4$Y](Cl) (**4a**−**d**) was achieved using isolated $CpCrCl_2(THF)$, as shown in eq 4, rather than reacting the $CrCl_3$ with the mixed-aryl Li β-diketiminate. Schaper and co-workers demonstrated that attempts to prepare bis(β-diketiminate) Cr^{III} complexes by reaction of Li[(XylNCMe)$_2$CH] with $CrCl_3$(THF) yielded only the monosubstituted compound.[20] Although inadvertent formation of Cr(LX)$_2$Cl complexes by salt metathesis is not an issue even for the smallest symmetric 2,6-disubsituted β-diketiminate, it was a recurring problem for the synthesis of Cr[(PhNCMe)$_2$CH]X$_2$ derivatives.[19,32] Adding the mixed-aryl β-diketiminate to a well-defined Cr^{III} precursor that already has a cyclopentadienyl ligand presumably helps avoid such difficulties in the synthesis of **4a**−**d.**



(4)

X-ray Crystal Structures of Cr^{III} Methyl and Chloro Complexes. X-ray crystal structures were obtained for all four mixed-aryl β-diketiminate complexes for both the Cr^{III} methyl and Cr^{III} chloro species. The thermal ellipsoid diagrams for compounds **3a**−**d** and **4a**−**d** are shown in Figures 4 and 5, respectively, and the Cr−X (X = Cl, CH_3) bond lengths are collected in Table 1. In the symmetric CpCr[(ArNCMe)$_2$CH](R) alkyl complexes, the Cr−CH_3 species had shorter bonds (between 2.0645(17) and 2.076(2) Å)[3a,14] than were found for substituted primary alkyl Cr−CH_2R complexes (typically between 2.10 and 2.13 Å).[11] The mixed-aryl Cr^{III} methyl complexes **3a**−**d** follow the same trend, with two compounds (**3a**,**d**) having Cr−CH_3 bond lengths less than 2.06 Å. However, no clear connection was evident between the Cr−CH_3 or Cr−Cl bond lengths in Table 1 and the electronic properties of the NC_6H_4Y substituents for **3a**−**d** or **4a**−**d**.

The differing steric demands of the N-aryl groups are displayed in the Cr−N bond lengths for **3a**−**d** and **4a**−**d** (Table 2). With the exception of the anomalously long Cr−N(Dpp) bond of 2.134(3) Å in **4b**, the Cr−N(Dpp) bond lengths are similar to those observed for the corresponding symmetric CpCr[(ArNCMe)$_2$CH]X compounds.[3a,8,14] In all cases, the Cr−N(C_6H_4Y) bond is significantly shorter, presumably reflecting the reduced steric requirements of the smaller aryl group. Once again, however, no correlation between the electronic properties of the Y group and the Cr−N(C_6H_4Y) bond length could be discerned.

Kinetic Measurements of Iodomethane Activation. The reaction of the mixed-aryl Cr^{II} complexes **1a**−**d** with at least 10 equiv of MeI in pentane was monitored by UV−vis spectroscopy at 530 nm (eq 5).[14] The second-order rate constants were obtained by running the pseudo-first-order reactions with different concentrations of excess iodomethane and then plotting k_{obs} vs [MeI]. The rate constants were calculated to be $k = (9.80 \pm 0.3) \times 10^{-1}\ M^{-1}\ s^{-1}$ for **1a** (Y = OMe), $k = (8.94 \pm 0.4) \times 10^{-1}\ M^{-1}\ s^{-1}$ for **1b** (Y = Me), $k = (7.48 \pm 0.2) \times 10^{-1}\ M^{-1}\ s^{-1}$

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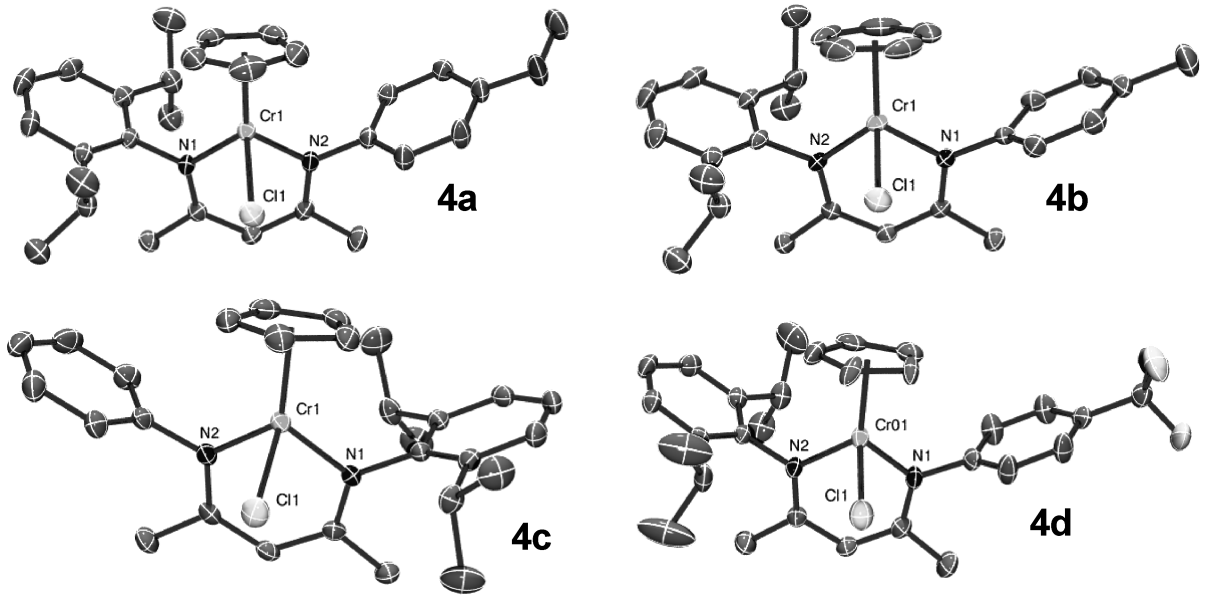


Figure 5. Thermal ellipsoid diagrams (50%) of Cr^{III} chloro complexes **4a**−**d**.

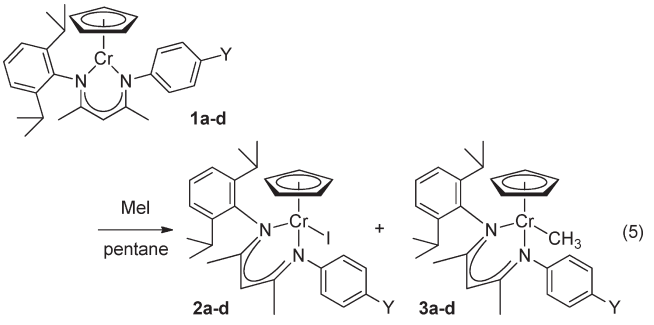
Table 1. Cr−X Bond Lengths (Å) in CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$Y](X) Complexes (X = CH$_3$ (3a−d), Cl (4a−d))

Cr−X	Y = OMe	Y = CH_3	Y = H	Y = CF_3
Cr−CH_3	2.0563(15) (**3a**)	2.0608(17) (**3b**)	2.0799(18) (**3c**)	2.052(2) (**3d**)
Cr−Cl	2.3046(4) (**4a**)	2.3173(10) (**4b**)	2.2984(5) (**4c**)	2.2947(2) (**4d**)

Table 2. Cr−NAr Bond Lengths (Å) in CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$Y](X) Complexes (X = CH$_3$ (3a−d), Cl (4a−d))

Cr−NAr	Y = OMe	Y = CH_3	Y = H	Y = CF_3
Dpp	2.0262(12) (**3a**)	2.0254(12) (**3b**)	2.0391(13) (**3c**)	2.0274(19) (**3d**)
C_6H_4Y	2.0128(12) (**3a**)	2.0175(14) (**3b**)	2.0109(13) (**3c**)	2.0177(19) (**3d**)
Dpp	2.0274(12) (**4a**)	2.134(3) (**4b**)	2.0285(11) (**4c**)	2.024(2) (**4d**)
C_6H_4Y	2.0067(12) (**4a**)	2.011(3) (**4b**)	1.9993(12) (**4c**)	2.000(2) (**4d**)

for **1c** (Y = H), and $k = (4.96 \pm 0.3) \times 10^{-1}\ M^{-1}\ s^{-1}$ for **1d** (Y = CF_3).



As demonstrated by the Hammett plot in Figure 6, the observed rate constants for the single-electron oxidative addition of MeI fit well with the electronic parameters (σ) for the NC_6H_4Y substituents.[33] The observed electronic effect of the Y group is relatively modest ($\rho = -0.36$), corresponding to about a 2-fold decrease in rate constant from the most electron-donating (**1a**, Y = OMe, $\sigma = -0.27$) to the most electron-withdrawing substituent (**1d**, Y = CF_3, $\sigma = +0.54$). The ability of electron-donating groups to accelerate the oxidative addition of iodomethane can be understood in terms of the potential energy surface discussed above. Increasing the electron-donating ability of the β-diketiminate ligand stabilizes the Cr^{III} iodo compound with respect to the Cr^{II} species, thereby lowering the barrier between **A** and **C** (Figure 1). The correlation is especially remarkable given the absence of obvious structural differences in the X-ray structures attributable to any electronic influence of the Y group. In all of the mixed-aryl X-ray structures, the NC_6H_4Y groups are aligned roughly perpendicular to the Cr[$(NCMe)_2CH$] plane. However, in solution the absence of

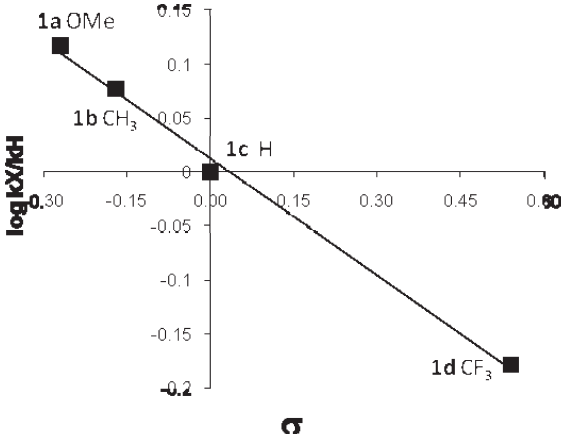


Figure 6. Hammett plot showing the correlation between the Y group and the rate constant for MeI oxidative addition for **1a**−**d**.

(33) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

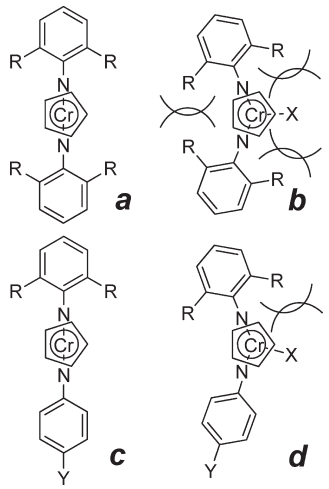


Figure 7. Relative steric repulsion in CpCr(LX) and CpCr(LX)(X) complexes with symmetric and mixed-aryl β-diketiminate ligands.

ortho substituents may allow the NC_6H_4Y group to access a planar conformation where the electronic influence of the Y group may more readily be transmitted to the chromium center.[34]

The observed sensitivity to electronic effects is in marked contrast to the absence of pronounced steric effects on the rate of MeI oxidative addition by symmetric CpCr[(ArNCMe)$_2$CH] Cr^{II} complexes.[14] Surprisingly, even the least reactive mixed-aryl Cr^{II} complex, **1d**, has a rate constant that is *an order of magnitude larger* than all of those previously determined for the symmetric complexes, which ranged from 1.9×10^{-2} to 2.8×10^{-2} M^{-1} s^{-1}.[14]

The ancillary ligand effects in the reaction of CpCr(LX) with alkyl halides may be attributable to the difference in steric demands between crowded Cr^{III}–X and open Cr^{II} complexes. Figure 7a,b illustrates the Cr^{II} and Cr^{III}–X species, respectively, for the symmetric ortho-disubstituted β-diketiminate system. The steric demands of the N(2,6-$R_2C_6H_3$) groups are more acutely felt in CpCr(LX)(X) than in CpCr(LX), resulting in the relative destabilization of the Cr^{III} product. For the mixed-aryl β-diketiminate system (Figure 7c,d), the relative destabilization of Cr^{III} is lessened due to reduced steric repulsion. Increasing the relative stability of CpCr(LX)(X) results in a diminished barrier between **A** and **C** in Figure 1, corresponding to the observed enhancement in the rate of oxidative addition of MeI for **1a**–**d**.

Conclusions

Paramagnetic Cr^{III} CpCr[DppNC(Me)CHC(Me)NC_6H_4Y](X) complexes with mixed-aryl β-diketiminate complexes were prepared from $CpCrCl_2$(THF) (X = Cl) or by single-electron oxidation of the corresponding Cr^{II} species (X = I, CH_3). Despite the absence of structural differences in the Cr^{III} complexes as Y was varied, a distinct electronic effect on the rate of oxidative addition of iodobenzene was observed. The rate constants ranged from $k = (9.80 \pm 0.3) \times 10^{-1}$ M^{-1} s^{-1} for **1a** (Y = OMe) to $k = (4.96 \pm 0.3) \times 10^{-1}$ M^{-1} s^{-1} for **1d** (Y = CF_3) and correlated well with the σ_p substituent constants for the Y groups. The substantial rate enhancement for **1a**–**d** compared to CpCr[(DppNCMe)$_2$CH] and related symmetric ortho-disubstituted β-diketiminate complexes was attributed to differences in steric congestion between the Cr^{II} and Cr^{III} complexes in the two systems. It remains to be determined if continued steric reduction will lead to yet further enhancement of single-electron oxidative addition reactivity for CpCr(LX) complexes.

Experimental Section

General Considerations. All reactions were carried out under nitrogen using standard Schlenk and glovebox techniques. Hexanes, pentane, Et_2O, CH_2Cl_2, 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. Iodine was purified by sublimation before use. *n*-BuLi (1.6 M in hexanes), NaCp (2.0 M in THF), $CrCl_2$, $CrCl_3$ (anhydrous), iodomethane (2.0 M in MTBE), 1,4-dioxane (anhydrous), SmI_2 (0.1 M in THF), and methylmagnesium iodide (3.0 M in Et_2O) were purchased from Aldrich and used as received. The β-diketiminate ligands were prepared according to the literature procedure.[15a,16] $CpCrCl_2$(THF) was prepared by treatment of Cp_2Cr with excess anhydrous HCl (1.0 M in Et_2O) in THF at 0 °C.[35] The Cr^{II} β-diketiminate compounds **1a**, **c**,**d** were prepared as described in the literature.[16]

UV/vis spectroscopic data were collected on a Varian Cary 100 Bio UV–visible spectrophotometer in pentane or hexanes 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.

Synthesis of CpCr[DppNC(Me)CHC(Me)NC_6H_4Me] (1b). A solution of NaCp (1.9 mL, 2.0 M in THF, 3.8 mmol) was added dropwise to a suspension of $CrCl_2$ (418.2 mg, 3.4 mmol) in 25 mL of THF, and the resulting mixture was stirred at room temperature for 2 h. In a separate reaction vessel, a solution of *n*-BuLi (2.4 mL, 1.6 M in hexanes, 3.8 mmol) was added dropwise to a −30 °C solution of DppNHC(Me)CHC(Me)NC_6H_4Me (1.18 g, 3.38 mmol) in 15 mL of THF, and the yellow solution was warmed to room temperature and stirred for 1 h. The ligand solution was then added to the Cr^{II} reaction mixture. After this mixture was stirred overnight, the solvent was removed in vacuo, the residue was extracted with hexanes, and the extract was filtered through Celite and cooled to −30 °C. **1b** (1.279 g, 81%) was isolated in three crops over several days. Anal. Calcd for $C_{29}H_{36}N_2Cr$: C, 74.97; H, 7.81; N, 6.01. Found: C, 71.59; H, 6.15; N, 8.71. UV/vis (hexanes; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 306 (10 300), 428 (5800), 557 (1080).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC_6H_4(OMe)](I) (2a). To a solution of **1a** (100 mg, 0.208 mmol) in 5 mL of Et_2O was added a solution of I_2 (27.9 mg, 0.110 mmol) in 3 mL of Et_2O. After the mixture was stirred for 20 h, the solvent was removed in vacuo, the residue was extracted with 3 mL of Et_2O, and the extract was filtered through Celite and cooled to −30 °C. **2a** (50 mg, 40%) was isolated after 2 days. Anal. Calcd for $C_{29}H_{36}N_2O$CrI: C, 57.34; H, 5.97; N, 4.61. Found: C, 57.62; H, 6.04; N, 4.82. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 432 (5500).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC_6H_4Me](I) (2b). To a solution of **1b** (200 mg, 0.431 mmol) in 10 mL of Et_2O was added a solution of I_2 (60.1 mg, 0.237 mmol) in 4 mL of Et_2O. After the mixture was stirred for 20 h, the solvent was removed in vacuo, the residue was extracted with 5 mL of Et_2O, and the extract was filtered through Celite and cooled to −30 °C. **2b** (103 mg, 40%) was isolated after 2 days. Anal. Calcd for $C_{29}H_{36}N_2$CrI: C,

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(35) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.

58.89; H, 6.13; N, 4.74. Found: C, 58.55; H, 6.37; N, 5.04. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 433 (6300), 579 (700).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_5$](I) (2c). To a solution of **1c** (100 mg, 0.222 mmol) in 3 mL of Et_2O was added a solution of I_2 (24.0 mg, 0.0946 mmol) in 4 mL of Et_2O. After the mixture was stirred for 20 h, the solvent was removed in vacuo, the residue was extracted with 10 mL of Et_2O, and the extract was filtered through Celite and cooled to −30 °C. **2c** (10 mg, 8%) was isolated after several days. Anal. Calcd for $C_{28}H_{34}N_2CrI$: C, 58.24; H, 5.93; N, 4.85. Found: C, 57.85; H, 6.20; N, 4.82. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 431 (4200), 577 (620).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$CF$_3$](I) (2d). To a solution of **1d** (115 mg, 0.222 mmol) in 6 mL of Et_2O was added a solution of I_2 (45 mg, 0.177 mmol) in 4 mL of Et_2O. After the mixture was stirred for 20 h, the solvent was removed in vacuo, the residue was extracted with 3 mL of Et_2O, and the extract was filtered through Celite and cooled to −30 °C. **2d** (48.3 mg, 34%) was isolated after several days. Anal. Calcd for $C_{29}H_{33}N_2F_3CrI$: C, 53.96; H, 5.15; N, 4.34. Found: C, 54.04; H, 5.44; N, 4.21. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 431 (5600).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$(OMe)](CH$_3$) (3a). To a solution of **1a** (200 mg, 0.416 mmol) in Et_2O was added a solution of MeI (0.12 mL, 2.0 M in MTBE, 0.24 mmol). After the reaction mixture was stirred for 1 h, MeMgI (0.08 mL, 3.0 M in Et_2O, 0.24 mmol) was added. After this mixture was stirred overnight, excess 1,4-dioxane (0.3 mL, 3.3 mmol) was added and the reaction mixture was stirred for an additional 2 h. The solvent was removed in vacuo, the residue was extracted with 18 mL of hexanes, the extract was filtered through Celite, and the solvent was again removed in vacuo. The purple solid was extracted with 15 mL of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3a** (170 mg, 82%) was isolated after 2 days. Anal. Calcd for $C_{30}H_{39}N_2OCr$: C, 72.70; H, 7.32; N, 5.65. Found: C, 72.50; H, 7.66; N, 5.52. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 417 (4600), 542 (1300).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$Me](CH$_3$) (3b). Method A. To a solution of **1b** (250 mg, 0.538 mmol) in 15 mL of Et_2O was added a solution of MeI (0.15 mL, 2.0 M in MTBE, 0.30 mmol). After the reaction mixture was stirred for 1 h, MeMgI (0.10 mL, 3.0 M in Et_2O, 0.30 mmol) was added. After this mixture was stirred overnight, excess 1,4-dioxane (0.3 mL, 3.3 mmol) was added and the reaction mixture was stirred for an additional 2 h. The solvent was removed in vacuo, the residue was extracted with 20 mL of hexanes, the extract was filtered through Celite, and the solvent was again removed in vacuo. The purple solid was extracted with 10 mL of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3b** (67 mg, 26%) was isolated after several days.

Method B. To a solution of **1b** (86 mg, 0.185 mmol) in 10 mL of THF was added a solution of MeI (0.10 mL, 2.0 M in MTBE, 0.20 mmol), followed by a solution of SmI_2 (2.24 mL, 0.1 M in THF, 0.224 mmol). After the reaction mixture was stirred for 3 h, the solvent was removed in vacuo, the residue was extracted with 5 mL of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3b** (39 mg, 44%) was isolated after several days.

Anal. Calcd for $C_{30}H_{39}N_2Cr$: C, 75.13; H, 8.20; N, 5.84. Found: C, 74.98; H, 8.44; N, 5.49. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 417 (5700), 541 (1700).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_5$](CH$_3$) (3c). To a solution of **1c** (200 mg, 0.444 mmol) in Et_2O was added a solution of MeI (0.13 mL, 2.0 M in MTBE, 0.26 mmol). After the reaction mixture was stirred for 1 h, MeMgI (0.09 mL, 3.0 M in Et_2O, 0.27 mmol) was added. After this mixture was stirred overnight, excess 1,4-dioxane (0.3 mL, 3.3 mmol) was added and the reaction mixture was stirred for an additional 2 h. The solvent was removed in vacuo, the residue was extracted with hexanes, the extract was filtered through Celite, and the solvent was again removed in vacuo. The purple solid was extracted with a minimum amount of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3c** (50 mg, 24%) was isolated after several days. Anal. Calcd for $C_{29}H_{37}N_2Cr$: C, 74.81; H, 8.01; N, 6.02. Found: C, 75.20; H, 7.63; N, 6.21. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 417 (5100), 541 (1500).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$CF$_3$](CH$_3$) (3d). Method A. To a solution of **1d** (200 mg, 0.386 mmol) in 15 mL of Et_2O was added a solution of MeI (0.11 mL, 2.0 M in MTBE, 0.22 mmol). After the reaction mixture was stirred for 1 h, MeMgI (0.07 mL, 3.0 M in Et_2O, 0.21 mmol) was added. After this mixture was stirred overnight, excess 1,4-dioxane (0.3 mL, 3.3 mmol) was added and the reaction mixture was stirred for an additional 2 h. The solvent was removed in vacuo, the residue was extracted with hexanes, the extract was filtered through Celite, and the solvent was again removed in vacuo. The purple solid was extracted with a minimum amount of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3d** (63 mg, 31%) was isolated after several days.

Method B. To a solution of **1d** (70 mg, 0.135 mmol) in 10 mL of THF was added a solution of MeI (0.075 mL, 2.0 M in MTBE, 0.15 mmol), followed by a solution of SmI_2 (1.5 mL, 0.1 M in THF, 0.15 mmol). After the reaction mixture was stirred for 3 h, the solvent was removed in vacuo, the residue was extracted with 5 mL of hexanes, and the extract was filtered through Celite and cooled to −30 °C. **3d** (37 mg, 52%) was isolated after several days.

Anal. Calcd for $C_{30}H_{36}N_2F_3Cr$: C, 67.53; H, 6.80; N, 5.25. Found: C, 67.37; H, 7.06; N, 5.51. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 417 (5600), 542 (1600).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$(OMe)](Cl) (4a). A solution of *n*-BuLi (0.4 mL, 1.6 M in hexanes, 0.64 mmol) was added dropwise to a −78 °C solution of DppNHC(Me)CHC(Me)NC$_6$H$_4$(OMe) (0.223 g, 0.612 mmol) in 15 mL of THF, and the yellow solution was warmed to room temperature and stirred for 1 h. A solution of $CpCrCl_2$(THF) (150 mg, 0.576 mmol) in 15 mL of THF was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo, the residue was extracted with a total of 10 mL of hexanes and 10 mL of CH_2Cl_2, and the extract was filtered through Celite and cooled to −30 °C. **4a** (158 mg, 53%) was isolated after several days. Anal. Calcd for $C_{29}H_{36}N_2OCrCl$: C, 67.50; H, 7.03; N, 5.43. Found: C, 67.23; H, 7.33; N, 5.25. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 421 (8300), 582 (810).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$Me](Cl) (4b). A solution of *n*-BuLi (2.06 mL, 1.6 M in hexanes, 3.30 mmol) was added dropwise to a −78 °C solution of DppNHC(Me)CHC(Me)NC$_6$H$_4$Me (1.147 g, 3.43 mmol) in THF, and the yellow solution was warmed to room temperature and stirred for 1 h. A solution of $CpCrCl_2$(THF) (781 mg, 3.00 mmol) in THF was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo, the residue was extracted with a total of 10 mL of hexanes and 5 mL of CH_2Cl_2, and the extract was filtered through Celite and cooled to −30 °C. **4b** (555 mg, 37%) was isolated after several days. Anal. Calcd for $C_{29}H_{36}N_2CrCl$: C, 69.66; H, 7.26; N, 5.60. Found: C, 69.30; H, 6.95; N, 5.33. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 421 (5100), 585 (480).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_5$](Cl) (4c). A solution of *n*-BuLi (0.40 mL, 1.6 M in hexanes, 0.634 mmol) was added dropwise to a −78 °C solution of DppNHC(Me)CHC(Me)NC$_6$H$_5$ (0.194 g, 0.581 mmol) in 15 mL of THF, and the yellow solution was warmed to room temperature and stirred for 1 h. A solution of $CpCrCl_2$(THF) (150 mg, 0.576 mmol) in 15 mL of THF was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo, the residue was extracted with a total of 10 mL of hexanes and 10 mL of CH_2Cl_2, and the extract was filtered through Celite

and cooled to −30 °C. **4c** (69 mg, 25%) was isolated after several days. Anal. Calcd for $C_{28}H_{34}N_2CrCl$: C, 69.20; H, 7.05; N, 5.76. Found: C, 69.53; H, 7.39; N, 5.81. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 420 (6100), 585 (570).

Synthesis of CpCr[DppNC(Me)CHC(Me)NC$_6$H$_4$CF$_3$](Cl) (4d). A solution of *n*-BuLi (0.40 mL, 1.6 M in hexanes, 0.634 mmol) was added dropwise to a −78 °C solution of DppNHC-(Me)CHC(Me)$NC_6H_4CF_3$ (0.237 g, 0.588 mmol) in 10 mL of THF, and the yellow solution was warmed to room temperature and stirred for 1 h. A solution of $CpCrCl_2$(THF) (150 mg, 0.576 mmol) in 10 mL of THF was added, and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo, the residue was extracted with a total of 30 mL of Et_2O, and the extract was filtered through Celite and cooled to −30 °C. **4d** (59 mg, 19%) was isolated after several days. Anal. Calcd for $C_{29}H_{33}N_2F_3CrCl$: C, 62.87; H, 6.00; N, 5.06. Found: C, 62.50; H, 6.29; N, 5.33. UV/vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 420 (3700), 584 (430).

Kinetics Measurements. All kinetics measurements were performed according to the same experimental protocol. A typical experiment is described as a representative example with **1a**. In a glovebox, 17.1 mg (0.0356 mmol) of **1a** was dissolved in pentane and diluted to the mark in a 10 mL volumetric flask. An aliquot of 1 mL of this 3.56×10^{-3} M solution was transferred using a pipet to a 25 mL volumetric flask. Pentane was added, and then 80 μL of a 2.0 M solution of MeI in MTBE (0.16 mmol) was added by microliter syringe. Pentane was added up to the mark, and the solution was thoroughly mixed. A portion of the 1.42×10^{-4} M solution was loaded into the UV−visible cell for air-sensitive samples (described above) and transferred from the glovebox to the spectrophotometer, where the absorption at 530 nm was recorded every 0.1 min for 20 min. The resulting kinetics trace was fit to a first-order decay curve to give the rate constant $k_{obs} = 6.24 \times 10^{-3}$ s^{-1}. The pseudo-first-order experiment was repeated three more times with varying excess concentrations of MeI. The second-order rate constant, $k = (4.96 \pm 0.3) \times 10^{-1}$ M^{-1} s^{-1}, for the reaction was extracted from the slope of the straight-line plot of k_{obs} vs MeI concentration ($R^2 = 0.9973$). The reactions with **1b**−**d** were performed in the same manner, with $R^2 = 0.9912$, $R^2 = 0.9985$, and $R^2 = 0.9905$, respectively. The Hammett plot in Figure 6 was generated by graphing $\log(k_Y/k_H)$ (where k_H is the rate constant for **1c**, Y = H) vs the substituent constants taken from ref 33 ($\sigma_p = -0.27, -0.27$, 0, and 0.54 for Y = OMe, CH_3, H, CF_3, respectively) to give $\rho = -0.36$ with $R^2 = 0.9954$.

X-ray Crystallography. Data Collection. All crystals were mounted on a glass fiber, and measurements were made on a Bruker X8 APEX diffractometer with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of -100.0 ± 0.1 °C. Crystal data and refinement parameters are given in the Supporting Information: Table S1 for **1b**,**c** and **2a**,**b**, Table S2 for **3a**−**d**, and Table S3 for **4a**−**d**.

Data Reduction. Data for all complexes were collected and integrated using the Bruker SAINT software package.[36] Data were corrected for absorption effects using the multiscan technique (SADABS).[37] The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement. The structures were solved by direct methods.[38] All non-hydrogen atoms were refined anisotropically (unless otherwise mentioned below). All hydrogen atoms were included in calculated positions but not refined (unless otherwise mentioned below). All refinements were performed using SHELXTL.[39] In complex **2b**, the N(1)−C(17) fragment is disordered and was modeled in two orientations in roughly equal proportions. In complex **3d**, the fluorine atoms of the CF_3 group are disordered and were modeled in two orientations. Complex **4a** crystallizes with disordered solvent in the lattice. No reasonable model of the solvent could be obtained; therefore, the PLATON/SQUEEZE program[40] was used to generate a second, solvent-free data set. In complex **4d**, the Cp ring was disordered and subsequently modeled in two orientations. All non-hydrogen atoms were refined anisotropically except for C25, C26, C27, C28, and C29.

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Supporting Information Available: Tables and CIF files giving complete crystallographic data for complexes **1b**,**c**, **2a**,**b**, **3a**−**d**, and **4a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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