ORGANOMETALLICS

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Oxidatively Induced Reductive Elimination from a Chromium(III) Bis(aryl) Complex

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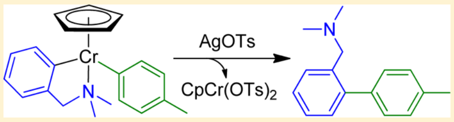
Supporting Information



ABSTRACT: The previously reported high-spin Cr(II) compounds CpCr($C_6H_4CH_2NMe_2$) (**1**) and CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$] (**2**) were investigated as precursors to CpCr(III) complexes. Single-electron oxidation of **1** was used to prepare CpCr($C_6H_4CH_2NMe_2$)(X) for X = I (**3**), OTs (**4**), O_2CPh (**5**), $OCMe_2Ph$ (**6**), SPh (**7**). Similarly, CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$](X) for X = I (**8**), SPh (**9**) were obtained from **2**. Reactions of **4** with $PhCH_2MgCl$ or Mg(C_6H_4Me)$_2$ reagents gave the Cr(III) benzyl (**10**) and *p*-tolyl (**11**) complexes, respectively. The corresponding reaction of **4** with Mg(CH_2CMe_3)$_2$ led to isolation of **12**, a bimetallic complex with a bridging neopentylidene group. While the reaction of **7** or **10** with AgOTs gave Cr(III) tosylate complex **4**, the reaction of **11** and AgOTs led to the product of reductive elimination. The structures of **1**, **2**, **6**−**8**, **11**, and **12** were elucidated using single-crystal X-ray diffraction.

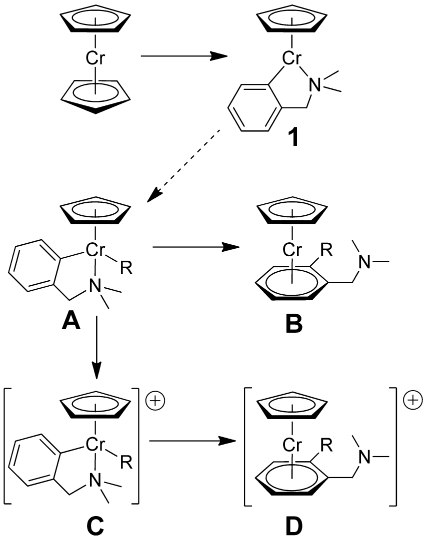
INTRODUCTION

Some of the most significant recent advances in palladium-catalyzed reactions can be traced back to mechanistic studies involving well-defined, structurally characterized complexes.[1] This strategy is arguably even more valuable for the investigation of new first-row transition-metal catalysts for C−C bond formation, particularly if the overall mechanism is not clearly understood and one or more of the intermediates may be paramagnetic.[2] Fürstner and co-workers provided an exceptional demonstration of this approach, using highly reactive nonstabilized low-valent iron complexes originally prepared by Klaus Jonas as well-defined catalyst precursors for cross-coupling reactions.[3]

We have recently employed cyclopentadienyl and β-diketiminate ancillary ligands to explore the single-electron reactivity of well-defined paramagnetic Cr(II) and Cr(III) complexes.[4] The CpCr(Nacnac) framework proved useful for investigating the rates of oxidative addition of iodomethane,[5] the controlled radical polymerization of vinyl acetate,[6] the radical cyclization of haloacetals,[7] and the catalytic formation of C(sp^3)−P bonds from cyclohexyl halides and Ph_2P−X reagents.[8] However, this system is not amenable for studying cross-coupling reactions, as the Cr^{III}−R complexes cannot accommodate an additional alkyl ligand.[9]

As illustrated in Scheme 1, CpCr($C_6H_4CH_2NMe_2$) (**1**) was an attractive precursor for the synthesis of well-defined paramagnetic organochromium complexes with potential for cross-coupling reactivity. Like the iron complexes utilized by Fürstner,[3] the high-spin Cr(II) complex **1** was prepared by Jonas and co-workers three decades ago in the investigation of cyclopentadienide displacement reactions from 3d metallocenes. The synthesis[10] and X-ray structure[11] of **1** were reported in two review articles published in 1985, as well as its reactivity with CO, ethylene, lithium metal, organolithium reagents, and alkynes.[10] We postulated that the synthetic strategies previously used to prepare CpCr(Nacnac)(R) complexes[9] might be employed to generate $CpCr^{III}$ bis(hydrocarbyl) complexes (**A**) from CpCr($C_6H_4CH_2NMe_2$). Reductive elimination from **A** would generate Cr(I) η^6-arene complexes (**B**).[12] Alternatively, single-electron oxidation of **A** to

Scheme 1. Potential Use of CpCr($C_6H_4CH_2NMe_2$) (1) as a Precursor for Mid-Valent Organochromium Complexes



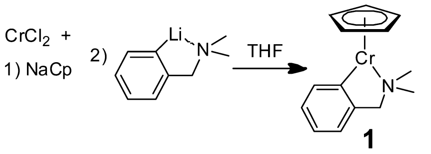
Received: August 6, 2012
Published: September 12, 2012

the cationic $CpCr^{IV}$ species **C** might induce reductive elimination to the cationic Cr(II) η^6-arene intermediates **D**.

In this paper, we report an alternative synthetic route to complex **1** directly from $CrCl_2$ and the structural characterization of the Cr(II) product resulting from insertion of PhC≡CPh into the Cr−aryl bond of **1**. Both complex **1** and its alkyne insertion product were treated with single-electron oxidants to produce new $CpCr^{III}$ three-legged piano-stool complexes. The Cr(III) benzyl and tolyl derivatives of **1** were then synthesized, characterized, and oxidized with AgOTs, leading to loss of benzyl ligand and oxidatively induced reductive elimination, respectively.

■ RESULTS AND DISCUSSION

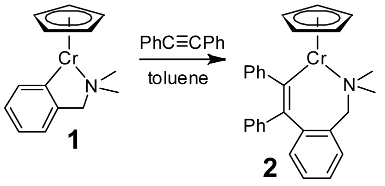
Synthesis of Previously Reported Cr(II) Complexes 1 and 2. $CpCr(C_6H_4CH_2NMe_2)$ (**1**) had been prepared by Jonas by reaction of chromocene (Cp_2Cr) with $Li[C_6H_4CH_2NMe_2]$ in THF at 55−60 °C in 70−80% yield.[10] A more facile synthesis of compound **1** is now reported directly from $CrCl_2$, analogous to the previously reported synthesis of Cr(II) CpCr(Nacnac) complexes.[5,6] Compound **1** was prepared by sequential addition of NaCp and $Li[C_6H_4CH_2NMe_2]$ at room temperature to a suspension of $CrCl_2$ in THF (eq 1). The solid-state molecular structure of **1** prepared in this manner has the same space group and unit cell parameters as in the previous report[11] and has Cr−N and Cr−C(1) bond lengths of 2.110(2) and 2.056(2) Å, respectively (Figure 1).



(1)

We have previously found UV−visible spectroscopy to be a useful tool for monitoring the reactivity of paramagnetic cyclopentadienyl Cr(II) and Cr(III) complexes.[4,7b,9] The UV−vis spectrum of compound **1** contains two strong absorption bands at 325 and 374 nm and a weaker absorption at 467 nm. Given the lack of steric protection in **1**, it is notable that the complex does not undergo ligand redistribution[13] to form Cp_2Cr and $Cr(C_6H_4CH_2NMe_2)_2$.[14]

Treatment of compound **1** with 1 equiv of PhC≡CPh caused a rapid color change from orange to burgundy (eq 2).



(2)

Recrystallization of the resulting product provided the compound $CpCr[C(Ph)C(Ph)C_6H_4CH_2NMe_2]$ (**2**) in high yield and sufficient purity to be used in subsequent reactions. The solid-state molecular structure of **2**, shown in Figure 1, confirmed the structure proposed by Jonas for this reaction.[10] The Cr−N (2.134(3) Å) and Cr−C(17) (2.088(3) Å) bond lengths in compound **2** are slightly longer than those of **1**. The N−Cr−C(17) bond angle of the chelating ligand (94.27(8)°) in compound **2** is also significantly larger in comparison to the angle in compound **1** (83.32(6)°), due to the larger ring size of the resulting metallacycle. The UV−vis spectrum of **2** displays an absorption band at 509 nm. Although PhC≡CPh insertion results in an expanded chelate ring size for compound **2**, it is stable at room temperature in solution for days, and solid samples of **2** can be stored for up to 2 years under an inert atmosphere with no signs of decomposition.

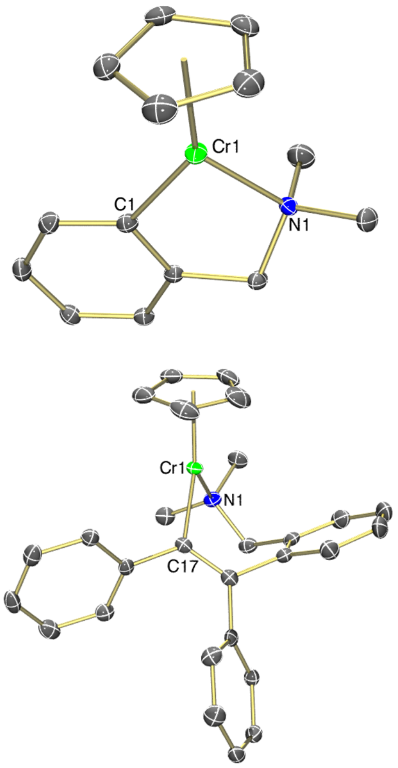


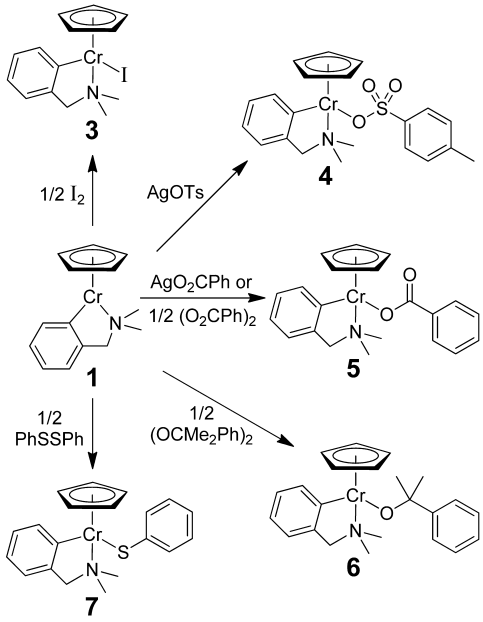
Figure 1. Molecular structures (50% thermal ellipsoids) of compounds **1** (top) and **2** (bottom). Hydrogen atoms have been removed for the sake of clarity.

Single-Electron Oxidation of $CpCr(C_6H_4CH_2NMe_2)$ (1). The synthesis of Cr(III) $CpCr(C_6H_4CH_2NMe_2)(X)$ compounds was targeted in order to examine their stability with respect to reductive coupling and to prepare synthetic precursors that could be used to prepare $CpCr(C_6H_4CH_2NMe_2)(R)$ compounds, where R = alkyl, aryl. Compound **1** reacted cleanly with 0.5 equiv of I_2 to provide the Cr(III) iodide compound **3** (Scheme 2).[15] The UV−vis spectrum of compound **3** displays absorption bands at 512 and 696 nm and two shoulder bands at 378 and 430 nm.

The oxidation of compound **1** with the appropriate silver reagents provided $CpCr(C_6H_4CH_2NMe_2)(OTs)$ (**4**) and $CpCr(C_6H_4CH_2NMe_2)(O_2CPh)$ (**5**) (Scheme 2). The benzoate compound **5** was also readily prepared by reaction of compound **1** with 0.5 equiv of benzoyl peroxide. The UV−vis spectra of compounds **4** and **5** were similar to that of the iodide compound **3**, with absorption bands at 365, 418, and 499 nm for **4** and 414 and 504 nm for **5**. The band at ∼415 nm has a smaller extinction coefficient in comparison to the 500 nm band for all three compounds (**3**−**5**). These two absorption bands appear to be characteristic of $CpCr(C_6H_4CH_2NMe_2)(X)$ compounds, where X = halide, pseudohalide.

Compound **1** reacted with dicumyl peroxide to form the Cr(III) alkoxide compound $CpCr(C_6H_4CH_2NMe_2)(OCMe_2Ph)$ (**6**) (Scheme 2). The Cr−N (2.135(2) Å) and Cr−C(1) (2.051(3) Å) bond lengths in compound **6** are

Scheme 2. Synthesis of Cr(III) $CpCr(C_6H_4CH_2NMe_2)(X)$ Compounds 3−7 by Single-Electron Oxidation of 1



similar to those of compounds **1** and **2** (Figure 2). The Cr−O bond length (1.828(2) Å) of compound **6** is slightly shorter and the Cr−O−C angle (140.2(2)°) is smaller than those observed in comparable $CpCr^{III}$ alkoxide compounds.[7b,16] Presumably these geometric differences are a result of the decreased steric bulk of the benzylamine ligand of **6** in comparison to larger ancillary ligands. Compound **6** contains a distorted three-legged piano-stool geometry with the O−Cr−N bond angle (87.25(7)°) being significantly smaller compared to the O−Cr−C(1) bond angle of 99.66(8)°.

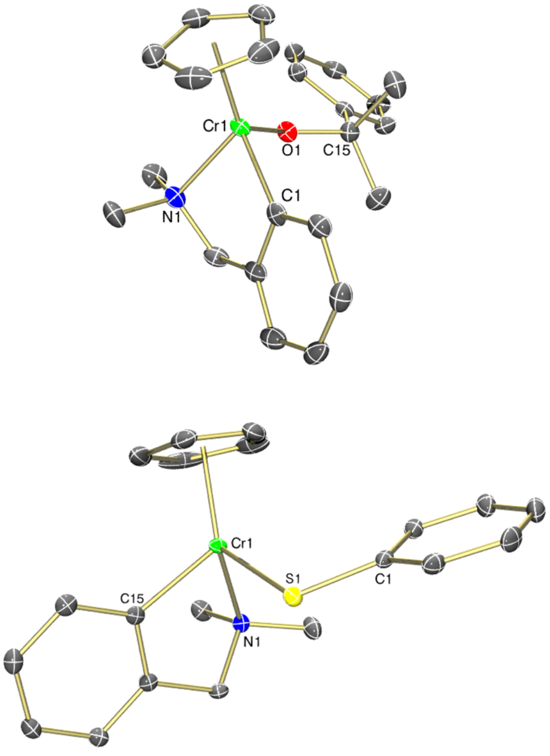


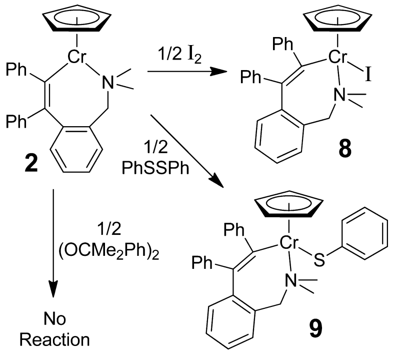
Figure 2. Molecular structures (50% thermal ellipsoids) of compounds **6** (top) and **7** (bottom). Hydrogen atoms have been removed for the sake of clarity.

The Cr(II) compound **1** also underwent rapid reaction with PhSSPh, forming the Cr(III) complex $CpCr(C_6H_4CH_2NMe_2)(SPh)$ (**7**) (Scheme 2). The solid-state molecular structure of **7** displays a typical Cr^{III}−S bond length of 2.3479(5) Å and Cr−S−C bond angle of 113.05(6)°.[9,17] The structure of **7** is similar to that of the alkoxide compound **6** with Cr−N and Cr−C(1) bond lengths of 2.131(2) and 2.050(2) Å, respectively. The major difference in compound **7** is that the three-legged piano-stool geometry is not distorted like that of compound **6**. The S−Cr−N and S−Cr−C(1) bond angles are very similar to one another. In fact, the S−Cr−N angle (94.93(5)°) is actually slightly larger than the S−Cr−C(1) angle (92.05(5)°), the opposite trend in bond angle size in comparison to the alkoxide **6**.

The UV−vis spectrum of the alkoxide **6** displays absorption bands at 432 and 579 nm. The Cr^{III}−SPh complex **7** has an absorption band at 533 nm and two shoulder bands at 341 and 400 nm. The UV−vis spectra of **6** and **7** contain distinctive absorption bands that allow for easy distinction from the Cr(II) starting material and the Cr(III) halide analogues, providing a useful characterization technique for these paramagnetic complexes when analyzing reaction products.[7,9] While lower than expected results were repeatedly obtained for C and H in the elemental analysis of **6**, the identity of the impurity in these samples has yet to be determined.

Single-Electron Oxidation of $CpCr[C(Ph)C(Ph)C_6H_4CH_2NMe_2]$ (2). The single-electron oxidation of the Cr(II) compound **2** was examined for comparison with compound **1**. Treatment of **2** with 0.5 equiv of I_2 provided the iodide complex $CpCr[C(Ph)C(Ph)C_6H_4CH_2NMe_2](I)$ (**8**) in high yield (Scheme 3). Compound **8** has a strong absorption band at 555 nm and a weaker absorption at 725 nm, which is significantly different from the spectrum of the Cr(III) iodide compound **3**. The solid-state molecular structure of compound **8** contains Cr−C(17) (2.097(5) Å) and Cr−N (2.194(4) Å) bond lengths that are the longest of the compounds reported herein (Figure 3). The Cr−I bond length of 2.6877(9) Å is similar to that in the CpCr *β*-diketiminate Cr(III) iodide complexes.[5] Similar to alkoxide compound **6**, the Cr(III) iodide **8** has a slightly distorted geometry with I−Cr−N and I−Cr−C(17) bond angles of 96.9(1) and 101.2(2)°, repectively. The N−Cr−C(17) bond angle in **8** (91.6(2)°) is slightly smaller compared to that in the Cr(II) precursor **2**, presumably to

Scheme 3. Synthesis of Cr(III) Compounds 8 and 9 by Single-Electron Oxidation of 2



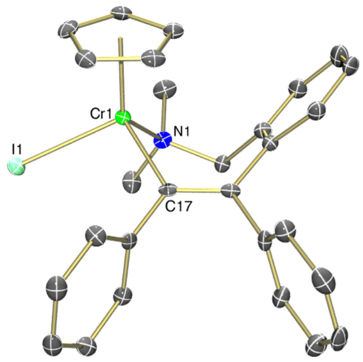


Figure 3. Molecular structure (50% thermal ellipsoids) of compound **8**. Hydrogen atoms have been removed for the sake of clarity.

accommodate the additional iodide ligand. Perhaps the most interesting structural feature of compound **8** is the orientation of the chelating ligand backbone, which is clearly bent up toward the Cp ligand to form a boatlike conformation of the metallacycle. This orientation is similar to that of the Cr(II) precursor **2** but is much more pronounced in the Cr(III) iodide complex **8**, likely due to the increased coordination number of the metal center.

Compound **2** also reacted with 0.5 equiv of PhSSPh to form the CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$](SPh) complex **9** (Scheme 3). The UV−vis spectrum of **9** displays an absorption band at 591 nm and two shoulder bands at 360 and 400 nm. The low-energy absorption at 591 nm is shifted significantly in comparison to the SPh compound **7** (533 nm), making the two compounds easily distinguishable from one another. Interestingly, CpCr($C_6H_4CH_2NMe_2$)(SPh) (**7**) did not react with PhC≡CPh to generate **9**. Even at 90 °C, no reaction was observed with **7** and a large excess of PhC≡CPh (20 equiv) over a 48 h period.

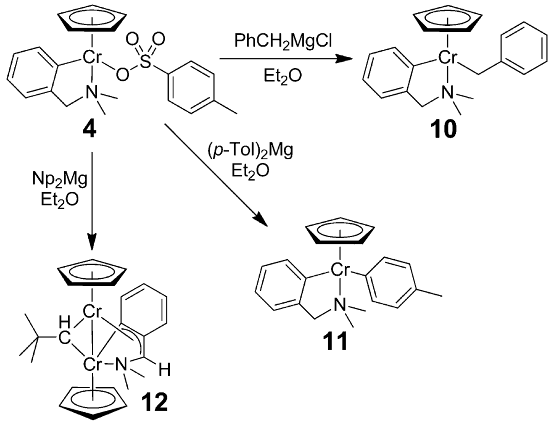
Unlike the CpCr benzylamine compound **1**, compound **2** did not react with dicumyl peroxide to form a Cr(III) alkoxide. The difference in reactivity is attributed to the metal center in compound **2** being more sterically protected compared to compound **1**. The $CpCr^{II}$ diimine and β-diketiminate compounds are also unreactive toward dicumyl peroxide, despite the fact that the desired Cr(III) alkoxide product is readily prepared by other methods.[7b,16b] This is consistent with the previous report that Cr(II) reacts with peroxides via an inner-sphere electron transfer mechanism, which is dependent on steric considerations of both the metal center and the peroxide substrate.[18]

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(R) Complexes. Given the demonstrated reactivity of related Cr(III) tosylate complexes with RMgCl and R_2Mg reagents,[6b,8,9] tosylate compound **4** was chosen as a precursor for testing salt metathesis reactions in the synthesis of CpCr($C_6H_4CH_2NMe_2$)(R) compounds, where R = hydrocarbyl. A Cr(III) benzyl compound was prepared by reaction of compound **4** with $ClMgCH_2Ph$ to provide the compound CpCr($C_6H_4CH_2NMe_2$)(CH_2Ph) (**10**) in high yield (Scheme 4). Solutions of compound **10** are red, with an absorption band at 575 nm and a shoulder at 390 nm.

Reaction of the tosylate compound **4** with Mg(C_6H_4Me)$_2$ caused a rapid color change to purple (Scheme 4). Recrystallization from hexanes provided compound **11** in good yield. The Cr−N (2.131(1) Å) and Cr−C(1) (2.040(1) Å) bond lengths (Figure 4) are similar to those of the other Cr(III) CpCr benzylamine complexes. The three-legged piano-stool geometry of **11** is distorted slightly, with C(15)−Cr−C(1) and C(15)−Cr−N bond angles of 97.58(6) and 93.84(5)°, although to a lesser extent than the alkoxide compound **6**. The Cr−C(15) bond length of 2.075(1) Å is slightly shorter compared to that in the sterically crowded CpCr[(XylNCMe)$_2$CH](Ph) complex.[9] The UV−vis spectrum of **11** displays two strong absorption bands at 378 and 393 nm and a weaker band at 538 nm. As observed for complex **6**, lower than expected results were repeatedly obtained for C and H in the elemental analysis of **11**, presumably due to contamination with some impurity. Attempts to prepare Cr(III) alkyl complexes by reacting iodide complex **8** with organomagnesium reagents were unsuccessful.

Synthesis of a Cr(III) neopentyl complex was also attempted by reaction of compound **4** with the dialkyl Grignard reagent

Scheme 4. Reactions of Cr(III) Tosylate 4 with RMgCl and R_2Mg Reagents



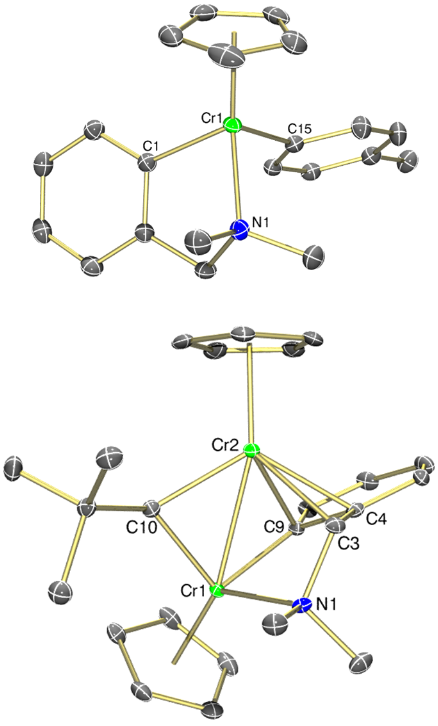


Figure 4. Molecular structures (50% thermal ellipsoids) of compounds **11** (top) and **12** (bottom). Hydrogen atoms have been removed for the sake of clarity.

$Mg(CH_2CMe_3)_2$ (Scheme 4). Upon workup, a first fraction of black crystals was isolated, followed by the isolation of a second small fraction of black crystals. Characterization of the first fraction (X-ray and UV−vis) identified the material as the Cr(II) compound **1** (19% yield), while the mother liquor displayed a significantly different UV−vis spectrum with an absorption band at 535 nm and a shoulder at 400 nm. X-ray diffraction of a single crystal isolated from a second fraction identified the material as the unexpected bimetallic compound $(CpCr)_2(\mu\text{-}CHCMe_3)(\mu\text{-}\eta^3{:}\kappa^2\text{-}C_6H_4CHNMe_2)$ (**12**) in low yield (Figure 4). The structure of **12** contains two CpCr groups with a bridging neopentylidene and a bridging $C_6H_4CHNMe_2$ ligand that has been deprotonated at the benzylic position, C(3). The Cr−Cr distance in **12** of 2.6416(5) Å and the Cr−C(10) bond lengths of 2.036(2) and 2.054(2) Å are similar to those of other Cr μ-alkylidene compounds.[19] The $C_6H_4CHNMe_2$ ligand has κ^2N,C coordination to Cr(1) and is bound in an η^3-benzyl bonding interaction to Cr(2). The Cr(2)−C(3) (2.118(2) Å), Cr(2)−C(4) (2.206(2) Å), and Cr(2)−C(9) (2.185(2) Å) bond lengths are all relatively short, comparable to those in previously reported Cr(III) η^3-benzyl complexes.[20] The Cr(1)−N bond length of 2.128(2) Å and Cr(1)−C(9) bond length of 2.028(2) Å are similar to those of the other CpCr benzylamine compounds reported herein. The geometry at the two Cr atoms can be described as three-legged piano-stool Cr(III) centers.

Oxidatively Induced Reductive Elimination. The 1914 report that biphenyl was produced when stoichiometric anhydrous $CrCl_3$ was added to PhMgBr in Et_2O has been cited as one of the key early discoveries on the road to palladium-catalyzed cross-coupling reactions.[21] While the underlying organometallic chemistry in this process remained obscure for several decades,[22] the propensity of chromium(III) aryl compounds to engage in alkyne insertion and reductive elimination reactions was eventually recognized.[23]

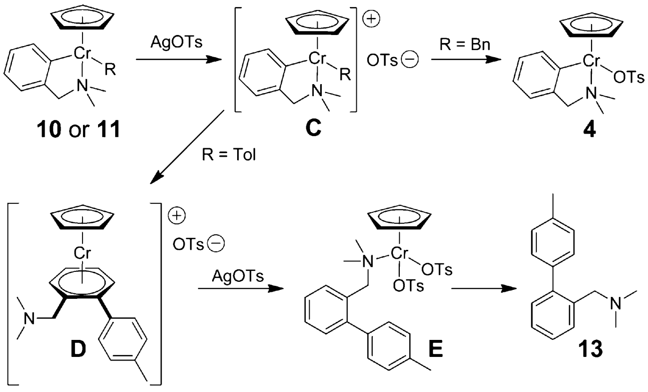
The Cr(III) alkoxide (**6**) and SPh (**7**) compounds were remarkably thermally robust, displaying no signs of decomposition by UV−vis spectroscopy when heated in solution (toluene) at 90−100 °C for 24 h. The benzyl (**10**) and aryl (**11**) compounds were also stable at elevated temperatures (90 °C), showing no changes in their UV−vis spectra.

Sanford and co-workers have examined the effect of single-electron oxidation for inducing reductive elimination from the Pd(II) complex $(^t\text{Bubpy})Pd(Me)_2$.[24] The reaction was reported to proceed by initial single-electron oxidation of the Pd(II) to form a Pd(III) intermediate that undergoes disproportionation to form a Pd(IV) intermediate, which reductively eliminates ethane. The single-electron oxidation of Ni(II) compounds has also been examined for carbon−halogen bond formation by reductive elimination from a Ni(III) intermediate.[25] In both cases chemical oxidants have been used for oxidation of the organometallic complexes. Cationic silver was an effective oxidant for the Pd(II) system[24] and has been used extensively herein for the single-electron oxidation of Cr(II) species. We were therefore interested in the potential for Ag(I) to induce oxidation of the highly stable Cr(III) compounds reported herein.

Upon treatment of the Cr(III)−SPh complex **7** with a stoichiometric amount of AgOTf, a rapid color change was observed and the UV−vis spectrum of the reaction mixture closely resembled that of the tosylate compound **4**. This suggested that a metathesis reaction with the silver reagent had occurred, in order to form the $CpCr(C_6H_4CH_2NMe_2)(OTf)$ species, instead of the desired oxidation to form a Cr(IV) species.

Treatment of the Cr(III) benzyl complex **10** with 2 equiv of AgOTs resulted in formation of the Cr^{III}−OTs complex. As illustrated in Scheme 5, a possible mechanism for the conversion of **10** to **4** is the generation of the cationic Cr(IV) intermediate **C**. Instead of the desired reductive elimination reaction, homolysis of the $Cr{-}CH_2Ph$ bond generates the Cr(III) tosylate **4** and benzyl radical. In a related process, Jordan and co-workers have generated cationic Zr(IV) and Ti(IV) alkyl species by one-electron oxidation of d^0 $Cp_2M(CH_2Ph)_2$ complexes with $Ag[BPh_4]$.[26]

Scheme 5. Possible Mechanism for Reactions of Cr(III) Benzyl (10) and Tolyl Complexes (11) with AgOTs



A rapid reaction was also observed between the tolyl compound **11** and 2 equiv of AgOTs to produce a black precipitate (presumably metallic silver) and a blue solution with absorption bands at 463 and 608 nm, characteristic of $CpCr(X)_2(L)$ compounds, where X is a halide and L is a neutral donor ligand.[27,28] Treatment of the Cr(III) dimer complex $[CpCrCl(\mu\text{-}Cl)]_2$ with a stoichiometric amount of $PhCH_2NMe_2$ resulted in a rapid color change from turquoise to blue, with the UV−vis spectrum of the resulting product displaying absorption bands at 522 and 668 nm, similar to the case for the monomeric $CpCrCl_2(THF)$. Additionally, sequential reaction of $CpCrCl_2(THF)$ with 2 equiv of AgOTs followed by 1 equiv of $PhCH_2NMe_2$ provided a blue powder with a UV−vis spectrum identical with that of the reaction of compound **11** with AgOTs. The blue species is therefore tentatively assigned as $CpCr(OTs)_2(NR_3)$ (**E**), where NR_3 = **13**. Treatment of the $CpCr(OTs)_2(NR_3)$ species with HCl to protonate the tertiary amine, followed by neutralization of the resulting mixture, allowed for isolation of the desired reductive elimination product **13** in 90% yield (Scheme 5).

One mechanistic possibility is that outer-sphere oxidation of Cr(III) tolyl complex **11** generates the cationic Cr(IV) intermediate **C**, as proposed for the benzyl complex **10**. Reductive elimination to form the Cr(II) η^6-arene intermediate **D** instead of formation of Cr(III) tosylate **4** is consistent with the relative instability of the phenyl radical in comparison to the benzyl radical.[9] Oxidation of Cr(II) η^6-arene **D** with another 1 equiv of AgOTs produces the spectroscopically observed intermediate **E**: related CpCr(III) trialkylamine complexes $CpCrCl_2(NEt_3)$ and $Cp^*CrF_2(NEt_3)$ have been observed by Köhler and co-workers.[28a]

CONCLUSIONS

The synthetic routes used to prepare CpCr(Nacnac)(R) complexes proved useful for the synthesis of CpCr($C_6H_4CH_2NMe_2$)(R) compounds for R = benzyl (**10**), tolyl (**11**). However, unlike the highly reactive Cr(III) tris(phenyl) species, thermolysis of **10** and **11** did not lead to reductive elimination to form Cr(I) η^6-arene compounds. While treatment of **11** with AgOTs induced the desired C−C bond formation process, the corresponding reaction of **10** and AgOTs led to Cr(III) tosylate **4**. This divergent reactivity is attributed to the difference in Cr−C bond strengths (aryl > benzyl) in the postulated common Cr(IV) intermediate **C**.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise indicated, all reactions were carried out under nitrogen using standard Schlenk and glovebox techniques. Hexanes, toluene, Et_2O, and THF were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA). Celite (Aldrich) was dried overnight at 120 °C before being evacuated and then stored under nitrogen. Chromium(II) chloride (anhydrous, 99.9% Cr) was purchased from Strem and stored under nitrogen. NaCp (2.0 M in THF), *n*-BuLi (1.6 M in hexanes), $PhCH_2MgCl$ (1.0 M in Et_2O), diphenylacetylene (98%), silver *p*-toluenesulfonate (99+%), silver trifluoromethanesulfonate (99%), silver benzoate (99%), benzoyl peroxide (97%), dicumyl peroxide (98%), and PhSSPh (99%) were purchased from Aldrich and used as received. *N,N*-Dimethylbenzylamine (Aldrich) was degassed by three freeze−vacuum−thaw cycles and stored under nitrogen prior to use. Iodine was purified by sublimation and stored under nitrogen. Li[$C_6H_4CH_2NMe_2$] was prepared by reacting $PhCH_2NMe_2$ with 1 equiv of *n*-BuLi in Et_2O.[29] Upon stirring overnight, the product was isolated by vacuum filtration, rinsed with hexanes, dried under vacuum, and stored under nitrogen. The Grignard reagents $MgR_2 \cdot x$(1,4-dioxane), where R = CH_2CMe_2, *p*-MeC_6H_4, were prepared on the basis of literature procedures.[30] $CpCrCl_2$(THF) was prepared by addition of HCl (2.0 M in Et_2O, Aldrich) to Cp_2Cr in THF at 0 °C according to the literature procedure.[31]

^1H and ^{13}C spectra (referenced to the residual solvent peak) were recorded on a Varian Mercury Plus 400 spectrometer. UV−visible spectroscopic data were collected on Varian Cary 100 Bio and Shimadzu UV-2550 UV−visible spectrophotometers in a specially constructed cell for air-sensitive samples: a Kontes Hi-Vac Valve with a 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 the UBC Department of Chemistry microanalytical services.

Alternative Synthesis of CpCr($C_6H_4CH_2NMe_2$) (1). This complex was previously prepared by Jonas from Cp_2Cr at elevated temperatures[10] and was structurally characterized by single-crystal X-ray diffraction.[11] A more facile synthesis of **1** directly from commercial $CrCl_2$ at ambient temperature is presented here. $CrCl_2$ (1.243 g, 10.1 mmol) was suspended in THF (45 mL) in a Schlenk flask. NaCp (5.20 mL of a 2.0 M solution in THF, 10.4 mmol, 1.03 equiv) was added dropwise to the $CrCl_2$ with stirring at room temperature, followed by the addition of a THF solution of Li[$C_6H_4CH_2NMe_2$] (1.430 g, 10.1 mmol, 1.00 equiv). The reaction mixture rapidly turned dark orange and was stirred overnight. The solvent was removed under reduced pressure, the residue was extracted with Et_2O (70 mL), and the extract was filtered over Celite and rinsed with Et_2O (4 × 5 mL). The orange-red solution was concentrated to ~70 mL and cooled to −35 °C to yield crystals of **1** (1.48 g, 58%) over several days in two crops. UV−vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 325 (2490), 374 (1430), 467 (200).

Synthesis of CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$] (2). Compound **1** (205 mg, 0.815 mmol) was dissolved in toluene (15 mL). To this solution was added a toluene (2 mL) solution of PhC≡CPh (147 mg, 0.822 mmol, 1.01 equiv) dropwise. The solution rapidly changed color from orange to burgundy. After the mixture was stirred overnight at room temperature, the solvent was removed under reduced pressure, the residue was rinsed with Et_2O and extracted with toluene (15 mL), and the extract was filtered over Celite and cooled to −35 °C to yield crystals of **2** (273 mg, 78%) over several days in three crops. Despite repeated attempts, the elemental analysis for compound **2** was consistently slightly low for carbon. While this may indicate the presence of unidentified impurities, the isolated complex proved to be sufficiently pure for further synthetic reactions (Scheme 3). Anal. Calcd for $C_{28}H_{27}NCr$: C, 78.30; H, 6.34; N, 3.26. Found: C, 76.97; H, 6.54; N, 3.11. UV−vis (THF; λ_{max}, nm): 509.

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(I) (3). Compound **1** (48.9 mg, 0.195 mmol) was dissolved in Et_2O (10 mL) followed by the addition of an Et_2O (3 mL) solution of I_2 (25.6 mg, 0.101 mmol, 0.52 equiv). The color intensity of the solution rapidly increased. Upon stirring for 5 min at room temperature, a maroon precipitate formed and the solution became very pale in color. After the mixture was stirred for 4 days, the precipitate was isolated by vacuum filtration and dried under vacuum to provide compound **3** (61 mg, 83%) as a maroon powder. Anal. Calcd for $C_{14}H_{17}NCrI$: C, 44.46; H, 4.53; N, 3.70. Found: C, 45.70; H, 4.69; N, 3.72. UV−vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 378 (sh), 430 (sh), 512 (740), 696 (200).

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(OTs) (4). Compound **1** (524 mg, 2.09 mmol) was dissolved in Et_2O (30 mL) followed by the dropwise addition of AgOTs (584 mg, 2.09 mmol, 1.00 equiv) suspended in THF (15 mL). The mixture rapidly changed color from orange to purple (orange transmitted) and was stirred at room temperature for 2 days. The solvent was removed under reduced pressure and the residue extracted with toluene (25 mL). The suspension was filtered through Celite to remove a dark gray precipitate (presumably metallic silver), and the filtrate was cooled to −35 °C to yield a burgundy microcrystalline powder of **4** (720 mg, 82%) over several days in two crops. Anal. Calcd for $C_{21}H_{24}O_3SNCr$: C, 59.70; H, 5.73; N, 3.32. Found: C, 59.84; H, 5.80; N, 3.19. UV−vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 365 (650), 418 (470), 499 (910).

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(O_2CPh) (5). *Method A.* Compound **1** (76.4 mg, 0.304 mmol) was dissolved in THF (8 mL) followed by the addition of AgO_2CPh (69.4 mg, 0.303 mmol, 1.00 equiv) suspended in THF (6 mL). When it was stirred overnight at room temperature, the solution became burgundy (orange transmitted) and the solvent was removed under reduced pressure. The residue was extracted with Et_2O (10 mL), the extract was filtered over Celite, and the solution was concentrated to a volume of 3 mL before being cooled to −35 °C for 3 days to provide compound **5** (18.4 mg, 16%). Anal. Calcd for $C_{21}H_{22}O_2NCr$: C, 67.73; H, 5.95; N, 3.76. Found: C, 68.00; H, 6.07; N, 3.77. UV−vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 414 (550), 504 (750).

Method B. Compound **1** (30.4 mg, 0.121 mmol) and benzoyl peroxide (16.2 mg, 0.067 mmol, 0.55 equiv) were placed in a Schlenk flask followed by the addition of Et_2O (8 mL). When it was stirred for 5 min at room temperature, the solution became purple (orange transmitted) and was stirred for 2 days. The solvent was removed under reduced pressure, the residue was extracted with toluene (8 mL), and the extract was filtered over Celite and cooled to −35 °C to yield compound **5** (22 mg, 49%) over several days in three crops. The UV−vis spectrum of the product was identical with that of compound **5** prepared by method A.

Synthesis of CpCr($C_6H_4CH_2NMe_2$)($OCMe_2Ph$) (6). Compound **1** (178 mg, 0.706 mmol) and dicumyl peroxide (96.0 mg, 0.355 mmol, 0.50 equiv) were placed in a Schlenk flask followed by the addition of Et_2O (20 mL). When it was stirred overnight at room temperature, the solution became purple; the solvent was removed under reduced pressure, the residue was extracted with hexanes (3 mL), and the extract was filtered over Celite and cooled to −35 °C to yield black crystals of **6** (155 mg, 57%) over several days in two crops. UV−vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 432 (530), 579 (400). Despite repeated attempts, the elemental analysis for compound **6** was consistently low for both carbon and hydrogen. The complex is thus considered to be contaminated with an as yet unidentified impurity.

Anal. Calcd for $C_{23}H_{28}ONCr$: C, 71.48; H, 7.30; N, 3.62. Found: C, 63.12; H, 6.88; N, 3.37.

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(SPh) (7). Compound **1** (104 mg, 0.415 mmol) was dissolved in toluene (3 mL) followed by the dropwise addition of a toluene (1 mL) solution of PhSSPh (45.5 mg, 0.208 mmol, 0.50 equiv). After the solution was stirred overnight at room temperature, Et_2O (2 mL) was added to induce precipitation. The solid was isolated by vacuum filtration, rinsed with Et_2O (3 × 1 mL), and dried under vacuum to provide compound **7** (127 mg, 84%) as an analytically pure brown powder. Single crystals suitable for X-ray crystallography were obtained by Et_2O diffusion into a THF solution of **7**. Anal. Calcd for $C_{20}H_{22}NSCr$: C, 66.64; H, 6.15; N, 3.89. Found: C, 66.72; H, 6.14; N, 3.81. UV–vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 341 (sh), 400 (sh), 533 (550).

Synthesis of CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$](I) (8). Compound **2** (218 mg, 0.508 mmol) was dissolved in toluene (15 mL) followed by the addition of a toluene (2 mL) solution of I_2 (65.0 mg, 0.256 mmol, 0.504 equiv). The color intensity of the reaction mixture rapidly increased upon addition of I_2. After the mixture was stirred overnight at room temperature, the solvent was removed under reduced pressure, the residue wasextracted with toluene (10 mL), and the extract was filtered over Celite and layered with hexanes (4 mL) before cooling to −35 °C to yield compound **8** (17.4 mg). The remaining solution was layered with an additional 4 mL of hexanes and cooled to provide a second crop of **8** (225.2 mg). The remaining solution was concentrated, and single crystals suitable for X-ray diffraction were obtained by vapor diffusion of hexanes into the toluene solution of **8** (28 mg). A total of 271 mg (96%) was isolated in three crops. Anal. Calcd for $C_{28}H_{27}NICr$: C, 60.44; H, 4.89; N, 2.52. Found: C, 60.67; H, 5.07; N, 2.57. UV–vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 555 (1250), 725 (340).

Synthesis of CpCr[C(Ph)C(Ph)$C_6H_4CH_2NMe_2$](SPh) (9). Compound **2** (105 mg, 0.245 mmol) was dissolved in toluene (3 mL) followed by the dropwise addition of a toluene (1 mL) solution of PhSSPh (27.0 mg, 0.124 mmol, 0.51 equiv). After it was stirred at room temperature for 2 days, the reaction mixture was filtered over Celite, rinsed with toluene (3 × 1 mL), and cooled to −35 °C to yield a burgundy-brown powder of **9** (36 mg, 27%). Anal. Calcd for $C_{34}H_{32}NSCr$: C, 75.81; H, 5.99; N, 2.60. Found: C, 75.78; H, 5.96; N, 2.57. UV–vis (toluene; λ_{max}, nm (ε, M^{-1} cm^{-1})): 360 (sh), 400 (sh), 591 (770).

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(CH_2Ph) (10). Compound **4** (140 mg, 0.332 mmol) was placed in a Schlenk flask followed by the addition of Et_2O (30 mL) and $ClMgCH_2Ph$ (0.37 mL of a 1.0 M solution in Et_2O, 0.37 mmol, 1.1 equiv). After the mixture was stirred overnight at room temperature, 1,4-dioxane (300 μL) was added and the mixture was stirred for an additional 1 h before the solvent was removed under reduced pressure. The residue was extracted with hexanes (30 mL), and the extract was filtered over Celite and concentrated to a volume of approximately 8 mL before cooling the red solution to −35 °C to yield a black microcrystalline powder of **10** (87 mg, 77%) over several days in two crops. UV–vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 390 (sh), 575 (620). Despite repeated attempts, the elemental analysis for compound **10** was consistently slightly low for carbon. This discrepancy is tentatively attributed to the loss of benzyl radical from **10** to form **1**, a reactivity mode previously observed for related CpCr(III) benzyl complexes.[9] Anal. Calcd for $C_{21}H_{24}NCr$: C, 73.66; H, 7.06; N, 4.09. Found: C, 72.56; H, 7.01; N, 3.98.

Synthesis of CpCr($C_6H_4CH_2NMe_2$)(C_6H_4Me) (11). Compound **4** (81.0 mg, 0.192 mmol) was placed in a Schlenk flask followed by the addition of Et_2O (15 mL). Upon addition of $Mg(C_6H_4Me)_2$·1.89(1,4-dioxane) (39.2 mg, 0.105 mmol, 0.55 equiv) with Et_2O (2 mL), the reaction mixture rapidly turned purple. After the mixture was stirred at room temperature for 3 days, the solvent was removed under reduced pressure, the residue was extracted with hexanes, and the extract was filtered over Celite and concentrated to a volume of approximately 7 mL before cooling the purple (red transmitted) solution to −35 °C to yield compound **11** (49 mg, 75%) over several days in three crops. UV–vis (hexanes; λ_{max}, nm (ε, M^{-1} cm^{-1})): 378 (1210), 393 (1122), 538 (445). Despite repeated attempts, the elemental analysis for compound **11** was consistently low for both carbon and hydrogen. The complex is thus considered to be contaminated with an as yet unidentified impurity. Anal. Calcd for $C_{21}H_{24}NCr$: C, 73.66; H, 7.06; N, 4.09. Found: C, 62.21; H, 6.22; N, 3.84.

Attempted Synthesis of CpCr($C_6H_4CH_2NMe_2$)(CH_2CMe_3). Compound **4** (81.5 mg, 0.193 mmol) was placed in a Schlenk flask followed by the addition of Et_2O (15 mL) and $Mg(CH_2CMe_3)_2$·1.05-(1,4-dioxane) (27.4 mg, 0.106 mmol, 0.55 equiv) with Et_2O (2 mL). After the mixture was stirred overnight at room temperature, the solvent was removed under reduced pressure, the residue was extracted with hexanes, the extract was filtered over Celite, and the solvent was again removed under reduced pressure. The residue was extracted with a minimum of hexanes (2 mL), and the extract was filtered over Celite and cooled to −35 °C to yield black crystals of compound **1** (9.0 mg, 19%). The remaining solution was concentrated and cooled again to obtain a second crop of black crystals, identified as $(CpCr)_2(\mu\text{-}CHCMe_3)(\mu\text{-}\eta^3{:}\kappa^2\text{-}C_6H_4CHNMe_2)$ (**12**) (2.5 mg, 6%).

Oxidatively Induced Reductive Elimination. Compound **11** (99.8 mg, 0.292 mmol) was dissolved in THF (15 mL) followed by the addition of AgOTs (164 mg, 0.586 mmol, 2.01 equiv) with THF (3 mL). When it was stirred for 10 min at room temperature, the solution became blue (UV–vis λ_{max} 463 and 608 nm) and black Ag precipitate formed in the reaction vessel. The reaction mixture was stirred for an additional 1 h before being filtered over Celite. The solvent was removed under reduced pressure. The residue was extracted with 40 mL of Et_2O/H_2O (1/1) followed by the addition of 2 M HCl (2 mL). After it was stirred for 20 min, the pale green mixture was brought to pH 10 by addition of Na_2CO_3. The aqueous layer was washed with Et_2O (2 × 30 mL). The combined organic washings were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Purification by silica gel chromatography with a gradient solvent mixture (5−20% EtOAc in hexanes) afforded **13** (59 mg, 90% yield) as a yellow oil. ^1H NMR (400.1 MHz, $CDCl_3$): δ 2.22 (s, 6H), 2.45 (s, 3H), 3.48 (s, 2H), 7.24−7.40 (m, 7H), 7.62−7.64 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 21.3, 45.2, 60.7, 127.1, 127.4, 128.8, 129.6, 130.1, 130.3, 136.7, 138.5, 142.6.

Reaction of 7 with AgOTf. Compound **7** (4.6 mg, 0.013 mmol) was dissolved in toluene (6 mL) followed by the addition of AgOTf (4.2 mg, 0.016 mmol, 1.3 equiv). The solution rapidly turned orange, and the color intensity decreased significantly. The product was tentatively identified as CpCr($C_6H_4CH_2NMe_2$)(OTf) on the basis of UV–vis analysis of the crude reaction mixture: λ_{max} 360 (sh) and 481 nm.

Reaction of 10 with AgOTs. Compound **10** (10.7 mg, 0.031 mmol) was dissolved in THF (2 mL) followed by the addition of AgOTs (17.9 mg, 0.064 mmol, 2.1 equiv) with THF (1 mL). The reaction mixture turned purple (orange transmitted) upon stirring for 4.5 h at room temperature. The product was identified as compound **4** on the basis of UV–vis analysis of the crude reaction mixture: λ_{max} 365, 420, and 494 nm.

Reaction of $CpCrCl_2$(THF) with $PhCH_2NMe_2$. $CpCrCl_2$(THF) (7.9 mg, 0.030 mmol) was placed in a Schlenk flask followed by the addition of Et_2O (3 mL) with stirring to form a turquoise suspension of $[CpCrCl(\mu\text{-}Cl)]_2$. Upon addition of $PhCH_2NMe_2$ (6.0 μL, 0.040 mmol, 1.3 equiv) the suspension turned blue (UV–vis λ_{max} 522 and 668 nm).

Reaction of $CpCrCl_2$(THF) with AgOTs and $PhCH_2NMe_2$. $CpCrCl_2$(THF) (10.0 mg, 0.038 mmol) was dissolved in THF (2 mL) followed by the addition of AgOTs (21.8 mg, 0.078 mmol, 2.0 equiv) with THF (1 mL). After it was stirred for 0.5 h, the reaction mixture was filtered over Celite and the solvent was removed under reduced pressure. The blue residue was suspended in Et_2O (3 mL) followed by the addition of $PhCH_2NMe_2$ (6.0 μL, 0.040 mmol, 1.0 equiv). The reaction mixture was stirred for 0.5 h before UV–vis analysis (λ_{max} 460 and 607 nm).

X-ray Crystallography. All crystals were mounted on a glass fiber, and measurements were carried out 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[32] and were corrected for absorption effects using the multiscan technique (SADABS).[33] The data were corrected for Lorentz and polarization effects. All structures were solved by direct methods.[34] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but not refined. All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS.[35] The molecular drawings were generated by the use of ORTEP-3[36] and POV-Ray.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving UV−visible spectra and crystallographic data for complexes **1**, **2**, **6**−**8**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation of Innovation, and the University of British Columbia for financial support and Anita Lam (UBC) for collection of single-crystal X-ray diffraction data for complexes **1**, **7**, **8**, **11**, and **12**.

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