

Synthesis and Reactivity of Chromium Cyclopentadienyl β -Diketiminato Compounds

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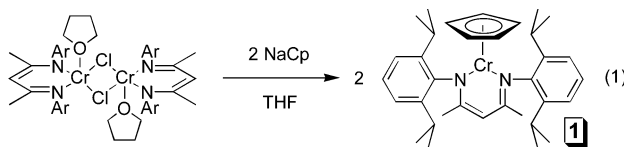
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Summary: The activation of iodomethane by the Cr(II) complex **1** to form the Cr(III) iodide and Cr(III) methyl compounds **2** and **3** was monitored by UV–visible spectroscopy. The Cr(III) halide species were independently synthesized by oxidation of **1** with lead(II) halides, the Cr(III) methyl compound was prepared via salt metathesis of the Cr(III) triflate, and their structures were determined by single-crystal X-ray diffraction.

Activated organic halides have long been known to react with Cr(II) reagents to form Cr(III) organometallic complexes.¹ While interest in this process has been renewed by its recent application in Cr-based catalytic asymmetric coupling reactions,² there has been a lack of well-defined Cr(II) compounds to model this single-electron-transfer reactivity.³ We wish to understand how the ancillary ligands control the reactivity of the paramagnetic chromium complexes in the fundamental reactions of importance to these synthetic organic applications. In this work we have developed new synthetic approaches to structurally characterized, sterically protected CpCr^{II} and CpCr^{III} complexes and use UV–visible spectroscopy to monitor the reaction of a Cr(II) compound with iodomethane.

β -Diketiminato complexes of Cr(III) have recently been reported as catalyst precursors for olefin polymerization.^{4,5} In 2001, Gibson and co-workers prepared {Cr[(ArNCMe)₂CH](μ -Cl)}₂ by reduction of the Cr(III) β -diketiminato complex {Cr[(ArNCMe)₂CH]Cl(μ -Cl)}₂ by

PhCH₂MgCl (Ar = 2,6-(CHMe₂)₂C₆H₃).^{4c} As shown in eq 1, {Cr[(ArNCMe)₂CH](μ -Cl)}₂ reacts with NaCp to



form CpCr[(ArNCMe)₂CH] (**1**) in good yield.⁶ While a recent review suggested that then-unknown coordinatively unsaturated CpCr^{II} complexes would likely require highly substituted C₅R₅ derivatives to prevent dimerization,⁷ the bulky β -diketiminato ligand allows **1** to be prepared as a monomer using merely the parent C₅H₅ ligand. The Cr(II) complex **1** is green to incident light and magenta to transmitted light in both solution and the solid state and crystallizes readily from pentane at –30 °C. The favorable solubility properties and relatively low air sensitivity of **1** was a welcome contrast to CpCr[(Me₃SiN)₂CPh], while the μ_{eff} value of 4.94 μ_{B} for **1** (Evans' method, C₆D₆, 300 K) is consistent with the quintet spin state previously calculated for the related Cr(II) amidinato complex.³ The molecular structure of **1** was determined using single-crystal X-ray diffraction (Figure 1).⁸ The six-membered ring containing Cr, N(1), N(2), C(2), C(3), and C(4) is planar and is roughly perpendicular to the plane defined by the cyclopentadienyl ligand. The aryl groups are perpendicular to the diketiminato ligand backbone, with the

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(6) CpCr[(ArNCMe)₂CH] (**1**). A solution of NaCp(THF)_{0.48} (102 mg, 0.823 mmol) in 5 mL of THF was added dropwise at room temperature to a solution of {Cr[(ArNCMe)₂CH](μ -Cl)}₂·3THF^{4c} (499 mg, 0.411 mmol) in 30 mL of THF. The green solution immediately became magenta to transmitted light. After 3 h, the solvent was removed in vacuo, the residue was extracted with 20 mL of pentane, and the extract was filtered through Celite. The solvent was again removed in vacuo, the solution was extracted with 10 mL of pentane, and the extract was cooled to –30 °C. After 1.5 h, 211 mg of dark green crystals was isolated, with the supernatant solution providing an additional 142 mg of product in two crops upon further cooling to –30 °C (Yield: 353 mg, 80%). IR (KBr): 3057 (w), 2962 (m), 2868 (w), 1526 (m), 1464 (w), 1435 (m), 1394 (s), 1317 (m), 1266 (w), 1251 (w), 1175 (w), 1099 (w), 1054 (w), 1018 (w), 934 (w), 854 (w), 795 (m), 777 (m). μ_{eff} = 4.94 μ_{B} . Anal. Calcd for C₃₄H₄₆CrN₂: C, 76.37; H, 8.67; N, 5.24. Found: C, 76.13; H, 8.90; N, 5.19. UV–vis (pentane): λ_{max} (e) 430 nm (5565 M⁻¹ cm⁻¹). Mp: 180–185 °C.

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(8) Crystal data for **1**: C₃₄H₄₆CrN₂, *M*_r = 534.73, triclinic, space group P $\bar{1}$, *a* = 9.2659(8) Å, *b* = 12.556(1) Å, *c* = 13.740(1) Å, α = 74.733(3)°, β = 87.446(4)°, γ = 78.980(3)°, *V* = 1513.6(2) Å³, *Z* = 2, Rigaku/ADSC CCD using Mo K α radiation (λ = 0.710 69 Å), *T* = 173(2) K, full-matrix least-squares refinement, 35 996 reflections measured, 7375 unique, *R*₁ = 0.053 (for 5989 reflections with *I* > 2 σ (*I*)), *wR*₂ = 0.145 (refined on *F*², all data).

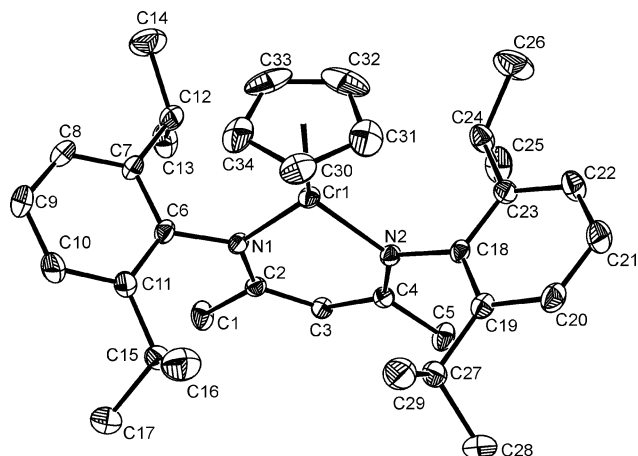
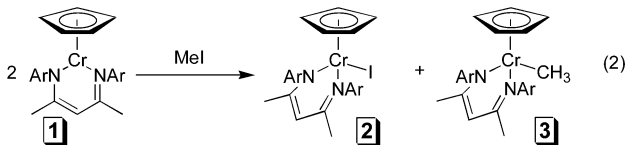


Figure 1. ORTEP diagram of $\text{CpCr}[(\text{ArNCMe})_2\text{CH}]$ (**1**; 50% ellipsoids).

ortho ^iPr substituents positioned to protect the open coordination sites of the Cr(II) center.

Despite the steric bulk of the β -diketiminato ligand, **1** reacts readily with MeI at room temperature in pentane (eq 2). This reaction is particularly notable,



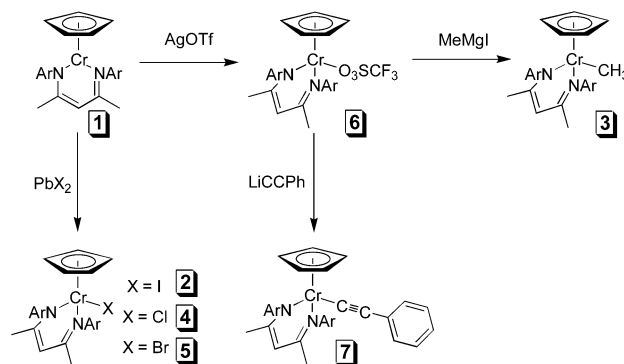
since the Cr(II) salts typically used for synthetic organic applications require donor solvents and elevated temperatures to activate less reactive organic halides.¹ Primary alkyl halides are known to be particularly unreactive with Cr(II) in aprotic solvents and usually require the addition of a cobalt catalyst to generate the desired Cr(III) alkyl species.^{2c,9} The enhanced reductive power of **1** compared to other Cr(II) sources is consistent with the electron-donating ability of the cyclopentadienyl and β -diketiminato ligands. The reaction between **1** and at least a 10-fold excess of MeI was monitored by UV–visible spectroscopy, following the reduction of the absorption band of **1** at 430 nm. Plots of k_{obs} vs [MeI] were linear under the pseudo-first-order conditions that were used, consistent with the bimolecular halogen atom abstraction that has been shown to be the rate-determining step for the activation of organic halides with Cr(II) species.¹⁰ The second-order rate constant was calculated to be $k = (5.7 \pm 0.5) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. This value is very similar to that obtained from the reaction of MeI with the Cr(II) complex with the macrocyclic ligand [15]aneN₄, where k was found to be $(4.6 \pm 1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.¹¹ Remarkably, the value for the reaction between MeI and $\text{CpCr}(\text{CO})_3$ is considerably smaller at $(8.75 \pm 2.13) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$,^{10b} despite the lower formal Cr oxidation state and smaller ancillary ligands of $\text{CpCr}(\text{CO})_3$. Further studies are evidently required to determine the factors responsible for the

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Scheme 1



dramatic difference in reducing ability between **1** and $\text{CpCr}(\text{CO})_3$.

The identities of the products shown in eq 2 were confirmed by the independent synthesis of $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{I})$ (**2**) and $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{CH}_3)$ (**3**). The Cr(III) halide complexes $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{X})$ (X = I (**2**), Cl (**4**), Br (**5**)) are readily obtained by treating **1** with the corresponding PbX_2 species (Scheme 1).¹² Related $\text{Cp}^*\text{Cr}^{\text{III}}$ complexes with β -diketiminato ligands bearing H substituents on the N donor atoms have also previously been prepared by nitrile insertion and alkane elimination reactions from $[\text{Cp}^*\text{Cr}(\text{R})(\mu\text{-Cl})_2]$ compounds.¹³ Lead(II) halides have previously been used as single-electron oxidants to synthesize Ti(IV) halides from paramagnetic $\text{Cp}^*_2\text{Ti}^{\text{III}}$ complexes.¹⁴ A similar one-electron-oxidation reaction using AgOTf provides $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{OTf})$ (**6**; Scheme 1). The Cr(III) methyl complex **3** can be prepared from the Cr(III) triflate **6** and MeMgI (Scheme 1).¹⁵ The low isolated yields of the salt metathesis reaction products are likely at least partially due to the enhanced solubility of **3** and **7** in pentane, but competing side reactions^{4d} (e.g. reduction to **1**, displacement or deprotonation of the β -diketiminato ligand) may also be occurring. The UV–visible

(12) $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{I})$ (**2**). A suspension of PbI_2 (22 mg, 0.048 mmol) in 5 mL of Et_2O was added to a solution of **1** (50 mg, 0.094 mmol) in 10 mL of Et_2O . After it was stirred overnight, the solution was filtered through Celite to remove Pb and was concentrated by slow evaporation to yield 48 mg of green crystals of **2** (78%). IR (KBr): 3057 (w), 2963 (w), 2861 (w), 1524 (s), 1463 (m), 1432 (m), 1379 (s), 1310 (m), 1256 (m), 1170 (m), 1114 (w), 1099 (m), 1058 (w), 1016 (m), 934 (m), 853 (w), 808 (m), 791 (m), 760 (m), 705 (w). $\mu_{\text{eff}} = 3.69 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{34}\text{H}_{46}\text{CrIN}_2$: C, 61.72; H, 7.01; N, 4.23. Found: C, 62.00; H, 7.14; N, 4.24. UV–vis (pentane): $\lambda_{\text{max}}(\epsilon)$ 435 nm ($4392 \text{ M}^{-1} \text{ cm}^{-1}$). Mp: 249–251 °C. $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{Cl})$ (**4**) and $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{Br})$ (**5**) were prepared similarly by reacting **1** with 0.5 equiv of PbCl_2 and PbBr_2 , respectively.

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(15) $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{CH}_3)$ (**3**). A solution of AgOTf (99 mg, 0.387 mmol) in 5 mL of THF was added to a solution of **1** (204 mg, 0.381 mmol) in 40 mL of THF, resulting in a rapid color change to yellow-brown with the formation of a dark precipitate. After it was stirred for 1 h, the solution was filtered, and MeMgI (0.14 mL of 3 M solution in Et_2O , 0.42 mmol) was added by syringe. The solution changed color from red-orange to purple. After 30 min, the solvent was removed in vacuo, and the residue was extracted with 15 mL of pentane and the extract filtered through Celite. The solvent was again removed in vacuo, and the residue was extracted with 5 mL of pentane. After the filtered solution was cooled to -30°C overnight, 42 mg of dark purple crystals was isolated (yield: 42 mg, 20%). IR (KBr): 3058 (w), 2958 (s), 2869 (m), 1575 (w), 1541 (m), 1521 (s), 1465 (m), 1435 (m), 1389 (s), 1384 (m), 1339 (w), 1313 (m), 1260 (m), 1173 (m), 1112 (w), 1099 (w), 1019 (m), 934 (w), 851 (w), 797 (m), 761 (m). $\mu_{\text{eff}} = 4.62 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{35}\text{H}_{49}\text{CrN}_2$: C, 76.46; H, 8.98; N, 5.10. Found: C, 71.91; H, 8.39; N, 4.76. UV–vis (pentane): $\lambda_{\text{max}}(\epsilon)$ 422 nm ($6303 \text{ M}^{-1} \text{ cm}^{-1}$). Mp: 209–212 °C.

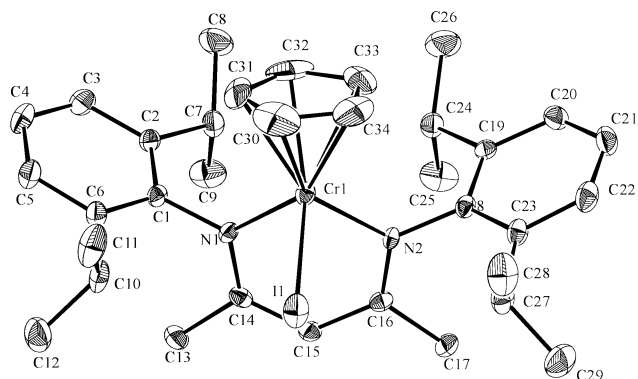


Figure 2. ORTEP diagram of $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{I})$ (**2**; 50% ellipsoids).

absorbance spectrum of a 1:1 mixture of isolated iodide **2** and methyl **3** is identical with the final spectrum obtained from reacting $\text{CpCr}[(\text{ArNCMe})_2\text{CH}]$ and MeI.

Preliminary reactions indicated that chloride **4** was not readily accessible by salt metathesis of CpCrCl_2 (THF) and that **4** reacted quite slowly with Grignard reagents. These synthetic difficulties, which are presumably due to the sterically demanding nature of the $(\text{ArNCMe})_2\text{CH}$ ligand, are neatly circumvented by the reactions in Scheme 1. The stability of the Cr(II) complex **1** allows the quantitative study of the key alkyl halide activation step important for synthetic organic reactions mediated by mid-valent Cr reagents.^{1,2} Single-electron oxidation with Pb(II) and Ag(I) species makes **1** a useful precursor to Cr(III) compounds, with the triflate **6** being particularly amenable to further salt metathesis reactions. This route also provides access to the phenyl alkynyl complex **7**.¹⁶ However, initial attempts to prepare analogous compounds with bulkier hydrocarbyl ligands have so far been unsuccessful.

The structures of complexes **2–4**, **6**, and **7** were determined by single-crystal X-ray diffraction (Figures 2 and 3 and Supporting Information).¹⁷ The conformation of the β -diketiminato ligand is relatively constant in all six structures in this study. The additional ligand in the Cr(III) complexes is accommodated by the Cr atom moving out of the plane defined by the N_2C_3 backbone of the β -diketiminato ligand. The extent of this deformation varies slightly with the size of the anionic

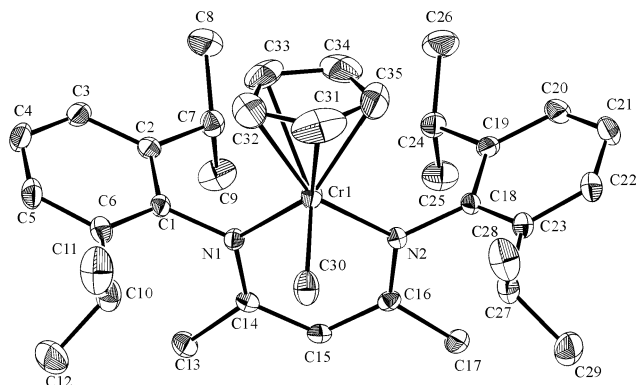


Figure 3. ORTEP diagram of $\text{CpCr}[(\text{ArNCMe})_2\text{CH}](\text{CH}_3)$ (**3**; 50% ellipsoids).

ligand: the Cr lies 0.69 Å out of the ligand plane for methyl **3** and 0.72 Å for both the iodide **2** and chloride **4**, while for the bulkier OTf and CPh groups in **6** and **7**, the Cr is 0.76 and 0.80 Å out of the plane, respectively. Even larger out-of-plane distortions have previously been reported for tetrahedral $(\text{ArNCMe})_2\text{CH}$ complexes of Sc,¹⁸ Ti,¹⁹ and V.²⁰

It is anticipated that the synthetic strategies described here might also be of potential use for preparing sterically hindered Cr(III) alkyl complexes for olefin polymerization applications.⁴ Our initial kinetic study indicates that, even in pentane solution, the CpCr^{II} β -diketiminato complex **1** is considerably more reactive to alkyl halides than the previously studied $\text{CpCr}(\text{CO})_3$ species^{10b} and has activity comparable with that of the most reactive Cr(II) aqueous systems with electron-donating amine ligands.^{10a,11} We are currently developing more general synthetic approaches to well-defined, unsaturated CpCr^{II} complexes and investigating their single-electron-transfer reactivity using electrochemical, spectroscopic, kinetic, and computational techniques.

Acknowledgment. K.M.S. thanks Dr. Brian Wagner for assistance with the iodomethane activation kinetics. This work was supported by the University of Prince Edward Island and the Natural Sciences and Engineering Research Council of Canada (NSERC).

Supporting Information Available: Text and tables giving complete synthetic and characterization data for complexes **1–7** and CIF files containing crystallographic data for complexes **1–4**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) Cr(III) alkynyl species, prepared in situ by reaction of CrCl_2 with alkynyl halides, have previously been shown to add selectively to aldehydes: (a) Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5585–5588. (b) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.

(17) Crystal data for **2**: $\text{C}_{34}\text{H}_{46}\text{CrIN}_2$, $M_r = 661.65$, monoclinic, space group $P2_1/n$, $a = 10.2734(7)$ Å, $b = 25.672(1)$ Å, $c = 12.4415(8)$ Å, $\beta = 106.296(3)^\circ$, $V = 3149.5(3)$ Å³, $Z = 4$, Rigaku/ADSC CCD using Mo K α radiation ($\lambda = 0.71069$ Å), $T = 173(2)$ K, full-matrix least-squares refinement, 27 584 reflections measured, 7098 unique, $R1 = 0.030$ (for 4510 reflections with $I > 3\sigma(I)$), $wR2 = 0.082$ (refined on F^2 , all data). Crystal data for **3**: $\text{C}_{35}\text{H}_{49}\text{CrN}_2$, $M_r = 549.78$, monoclinic, space group $P2_1/n$, $a = 10.1556(7)$ Å, $b = 25.669(2)$ Å, $c = 12.3629(9)$ Å, $\beta = 105.431(3)^\circ$, $V = 3106.7(3)$ Å³, $Z = 4$, Rigaku/ADSC CCD using Mo K α radiation ($\lambda = 0.71069$ Å), $T = 173(2)$ K, full-matrix least-squares refinement, 27 239 reflections measured, 7012 unique, $R1 = 0.039$ (for 4288 reflections with $I > 3\sigma(I)$), $wR2 = 0.115$ (refined on F^2 , all data).

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