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Cyclopentadienyl benzamidinato chromium complexes as models for alkyl halide activation by chromium reagents†

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Cyclopentadienyl complexes of Cr(II) and Cr(III) are stabilized by bis(trimethylsilyl)benzamidinato ligands, allowing the resulting well-defined compounds to serve as models for alkyl halide activation by mid-valent Cr-based reagents.

While $CrCl_2$ has been used in C–C bond forming reactions for many years, additional incentive to develop ancillary ligands for these systems has been provided by the recent discovery of catalytic[1] and asymmetric catalytic[2] Cr-based reactions. The systematic investigation of the relevant Cr(II) and Cr(III) species is hindered by their paramagnetism, which reduces the utility of NMR. Recent work in the rational design of related paramagnetic Cr(III) olefin polymerisation catalysts has relied extensively on X-ray crystallographic and density functional theoretical techniques.[3] It is the goal of our research program to apply this approach to synthetic organic applications of Cr-based reagents, using well-defined compounds to model the individual reactions of the proposed catalytic cycles. We would like to communicate our first results in this area, involving the synthesis, structural determination, computational investigation and preliminary reactivity studies of cyclopentadienyl benzamidinato complexes of Cr(II) and Cr(III) as models for alkyl halide activation by Cr reagents.

$CpCrCl_2(THF)$ has previously been demonstrated to be an effective precatalyst for coupling organic halides and aliphatic aldehydes.[1] We chose to modify this structure by incorporating *N*-silylated benzamidinato groups, as these readily modified ligands have previously been shown to stabilize an impressive array of transition metal and main group complexes.[4] As shown in Scheme 1, the blue Cr(III) chloro complexes $CpCr[(Me_3SiN)_2CAr]Cl$, (**1a**, Ar = Ph; **1b**, Ar = 4-$C_6H_4CF_3$) are synthesized by the reaction of $Li[(Me_3SiN)_2CAr](tmeda)$[5] with $CpCrCl_2(THF)$.† Both **1a** and **1b** react with $PhCH_2MgCl$ to give the corresponding purple Cr(III) benzyl complexes, $CpCr[(Me_3SiN)_2CAr](CH_2Ph)$, (**2a**, Ar = Ph; **2b**, Ar = 4-$C_6H_4CF_3$). The structures of **1a**, **2a**, and **2b** have been confirmed by single crystal X-ray diffraction, as shown in Fig. 1.‡

The Cr(III) chloro compounds **1a** and **1b** are reduced to Cr(II) by treatment with allyl magnesium bromide. The red–brown products $CpCr[(Me_3SiN)_2CAr]$, (**3a**, Ar = Ph; **3b**, Ar = 4-$C_6H_4CF_3$) are highly pentane soluble and are very air sensitive, which has hindered their isolation and characterization. However, crystals of **3a** were structurally characterized by X-ray diffraction (Fig. 1).‡ The formation of **3a** and **3b** presumably proceeds *via* the Cr(III) intermediate $CpCr[(Me_3SiN)_2CAr](allyl)$ that then decomposes to Cr(II) by formal loss of allyl radical.[6] These Cr(II) compounds are apparently stable with respect to ligand exchange to form Cp_2Cr and $Cr[(Me_3SiN)_2CAr]_2$,[7] in contrast to the instability of CpCrCl.[8]

Density functional theory was employed to investigate this system, using Gaussian 98 for Windows[9] with the B3LYP

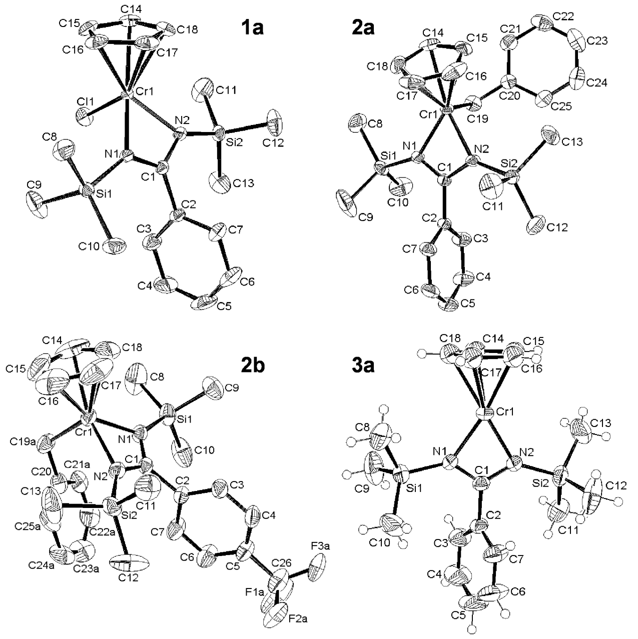
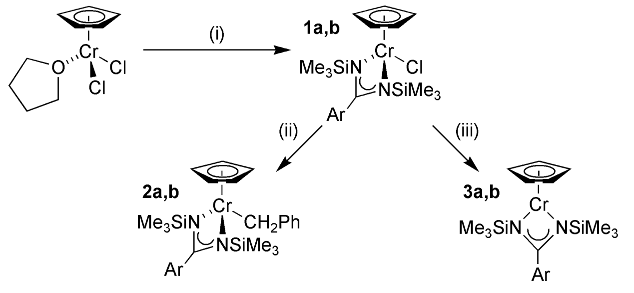


Fig. 1 Molecular structures of $CpCr[(Me_3SiN)_2CPh]Cl$ **1a**, $CpCr[(Me_3SiN)_2CPh](CH_2Ph)$ **2a**, $CpCr[(Me_3SiN)_2CC_6H_4CF_3](CH_2Ph)$ **2b**, and $CpCr[(Me_3SiN)_2CPh]$ **3a**.



Scheme 1 Synthesis of **1**, **2** and **3** (**a**, Ar = Ph; **b**, Ar = 4-$C_6H_4CF_3$). *Reagents and conditions*: i, $[(Me_3SiN)_2CAr]Li(tmeda)$, THF; ii, $PhCH_2MgCl$, THF; iii, C_3H_5MgBr, THF.

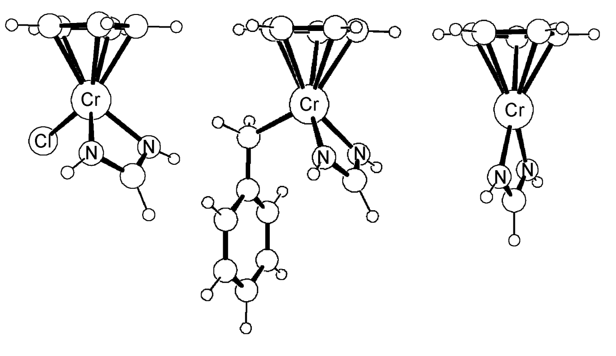


Fig. 2 Optimised structures of $CpCr[(HN)_2CH]Cl$ (left), $CpCr[(HN)_2CH](CH_2Ph)$ (middle) and $CpCr[(HN)_2CH]$ (right).

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† Electronic supplementary information (ESI) available: experimental and computational details. See http://www.rsc.org/suppdata/cc/b2/b207710h/

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functional and the LANL2DZ basis set.† The optimised geometries of the spin quartet CpCr[$(HN)_2CH$]Cl and CpCr[$(HN)_2CH$](CH_2Ph) and spin quintet CpCr[$(HN)_2CH$] model compounds (Fig. 2) agreed relatively well with the corresponding structures obtained from X-ray diffraction. The calculated bond lengths were within 0.035 Å, except for the cyclopentadienyl Cr–C bonds that were all nearly 0.1 Å too long. The major variations in R–N–Cr bond angles between the calculated (R = H) and experimental (R = $SiMe_3$) structures are most likely due to lack of appropriate steric interactions in the simplified model system. These parameters improved when the model was expanded to include SiH_3 substituents on the amidinato nitrogens.†

The nature of the putative allyl intermediate was also examined computationally. The coordination mode of the allyl ligand depends on the spin state of the molecule. Starting from similar initial geometries for CpCr[$(HN)_2CH$](allyl), the spin quartet optimised with a monodentate C_3H_5 group while the allyl ligand in the spin doublet system is bound through all three carbon atoms (Fig. 3). The high spin quartet configuration was calculated to be 21.2 kcal mol^{-1} more stable than the doublet. While hybrid functionals such as B3LYP are known to favour high spin states due to inclusion of Hartree–Fock exchange,[10] reoptimising both geometries using the pure DFT method BP86 still left the doublet species higher in energy than the quartet.

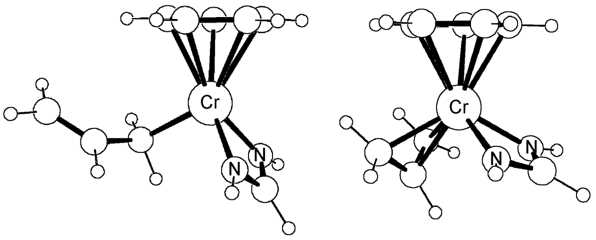

Fig. 3 Optimised structures of spin quartet (left) and spin doublet (right) CpCr[$(HN)_2CH$](C_3H_5).

The relative energies of reactants and products for benzyl chloride and allyl chloride activation by the Cr(II) species was also evaluated, assuming the accepted two step, single electron transfer mechanism for this process.[1,11] Reaction of CpCr[$(HN)_2CH$] with Cl–R to give R$^{\cdot}$ and CpCr[$(HN)_2CH$]Cl was calculated to be exothermic in both cases, with ΔH values of −4.2 and −7.1 kcal mol^{-1} for R = CH_2Ph and C_3H_5, respectively. Inclusion of N–SiH_3 groups varied the energies only slightly, to −6.1 kcal mol^{-1} for $PhCH_2Cl$ and −9.0 kcal mol^{-1} for C_3H_5Cl. Combination of R$^{\cdot}$ and a second equivalent of CpCr[$(HN)_2CH$] was found to be exothermic, with ΔH values of −14.6 and −12.9 kcal mol^{-1} for R = CH_2Ph and C_3H_5, respectively.

Red–brown solutions of CpCr[$(Me_3SiN)_2CAr$] in pentane or C_6D_6 react rapidly with $PhCH_2Cl$ to give violet solutions. For **3b**, the paramagnetic products of this reaction can be observed using ^{19}F NMR.[12] The spectrum consists of two singlets, assigned to the Cr(III) chloro and benzyl complexes, by comparison to the ^{19}F NMR spectra of independently synthesised **1b** and **2b** (−62.2 and −62.8 ppm, respectively, C_6D_6, referenced to $PhCF_3$ δ = −63.72 ppm).[13]

In conclusion, we have shown that the bis(trimethylsilyl)benzamidinato ligand can be used to prepare a range of well-defined organometallic chromium complexes. Computational and preliminary reactivity studies show that these compounds can act as models for the critical alkyl halide activation step in Cr-based reagents for organic synthesis. We are currently investigating how selectively modifying the amidinato substituents changes the Cr(II)/Cr(III) redox potentials and the ability of the Cr(II) species to activate organic halides, as well as other stoichiometric and catalytic reactions of importance to mid-valent chromium-mediated organic synthesis.

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Notes and references

‡ *Crystal data* for $C_{18}H_{28}ClCrN_2Si_2$ **1a**: M = 416.05, monoclinic, space group = $P2_1/n$, a = 10.1145(3), b = 12.0381(3), c = 18.5467(9) Å, β = 104.055(2)°, V = 2190.6(1) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 7.56 cm^{-1}, 19652 reflections measured, 4729 unique, (R_{int} = 0.039), final residuals $R1$ = 0.027 [for 3677 reflections with $I > 3\sigma(I)$], $wR2$ = 0.082 [all data]. *Crystal data* for $C_{25}H_{35}CrN_2Si_2$ **2a**: M = 471.73, monoclinic, space group = $P2_1/n$, a = 11.3146(4), b = 21.3320(7), c = 11.9997(6) Å, β = 113.493(3)°, V = 2656.2(2) Å^3, T = 173 K, Z = 4, μ(Mo-Kα) = 5.34 cm^{-1}, 22678 reflections measured, 6271 unique, (R_{int} = 0.049), final residuals $R1$ = 0.035 [for 4106 reflections with $I > 3\sigma(I)$], $wR2$ = 0.101 [all data]. *Crystal data* for $C_{26}H_{34}CrF_3N_2Si_2$ **2b**: M = 539.73, monoclinic, space group = $C2/c$, a = 16.205(2), b = 9.982(2), c = 35.488(3) Å, β = 97.757(4)°, V = 5688(1) Å^3, T = 173 K, Z = 8, μ(Mo-Kα) = 5.22 cm^{-1}, 17818 reflections measured, 9796 unique, (R_{int} = 0.038), final residuals $R1$ = 0.057 [for 4160 reflections with $I > 2\sigma(I)$], $wR2$ = 0.141 [all data]. *Crystal data* for $C_{18}H_{28}CrN_2Si_2$ **3a**: M = 380.60, orthorhombic, space group = $Pbca$, a = 9.5040(5), b = 20.006(2), c = 22.638(2) Å, V = 4304.3(5) Å^3, T = 298 K, Z = 8, μ(Mo-Kα) = 6.44 cm^{-1}, 30407 reflections measured, 4284 unique, (R_{int} = 0.087), final residuals $R1$ = 0.036 [for 1858 reflections with $I > 3\sigma(I)$], $wR2$ = 0.099 [all data]. CCDC 191563–191566. http://www.rsc.org/suppdata/cc/b2/b207710h/ for crystallographic data in CIF or other electronic format.

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