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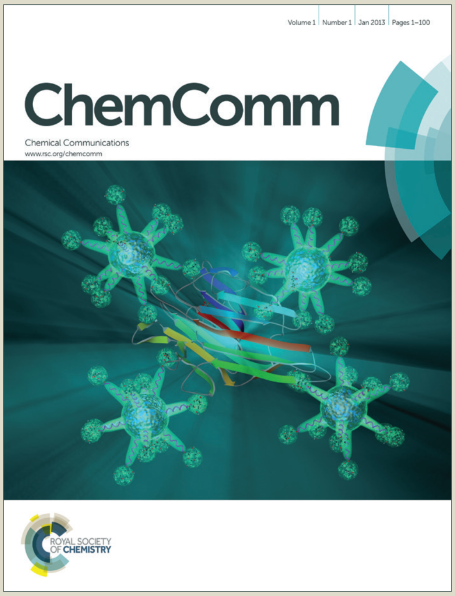

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Influence of redox non-innocent phenylenediamido ligands on chromium imido hydrogen-atom abstraction reactivity

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Paramagnetic $CpCr[(RN)_2C_6H_4]$ compounds (R = $SiMe_3$, CH_2CMe_3 and Ph) were treated with $R'N_3$ azides to generate chromium imido complexes, $CpCr[(RN)_2C_6H_4](NR')$, with R' = adamantyl, aryl or SO_2Ar. The H-atom abstraction reactivity of the imido complexes differed as the R and R' substituents were varied.

Redox-active ancillary ligands have been used to suppress unwanted single-electron reactivity in first-row transition metal catalysts.[1] However, metal-mediated radical processes often result in useful and complementary reactivity modes compared to the two-electron pathways typically observed for heavier transition metal catalysts.[2] The hydrogen atom abstraction and N-group transfer reactivity of first-row metal imido complexes has been attributed to the electronic structure of high spin M(NR') species generated by treatment of well-defined metal complexes with organic azides (N_3R').[3]

In a new strategy for using non-innocent ligands in catalyst design,[4] van der Vlugt and co-workers recently reported how redox-active ancillary ligands can facilitate generation of reactive palladium-bound nitrene radicals.[5] We have pursued a similar approach, using phenylenediamido complexes that can be oxidized to form ligand-based radicals.[6] As shown in Fig. 1, reaction of $CpCr[(RN)_2C_6H_4]$ intermediates with azides can potentially produce either Cr^V d^1 imido complexes, or Cr^{III} species with radical ancillary and reactive ligands.[7]

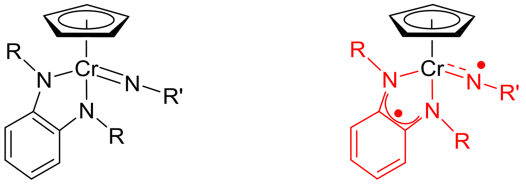
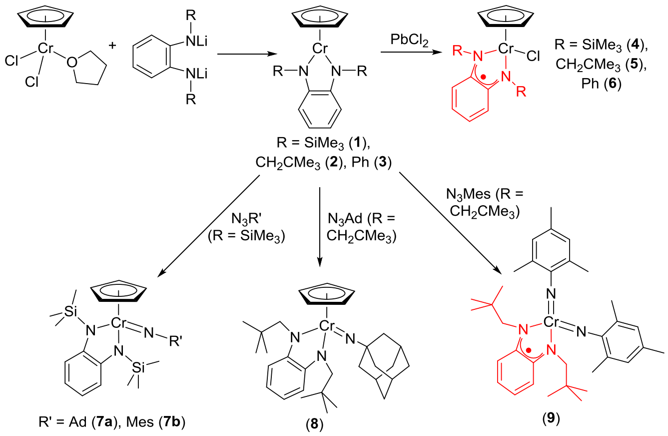


Fig. 1 Two possible electronic structures of $CpCr[(RN)_2C_6H_4](NR')$ intermediates.

$CpCr[(Me_3SiN)_2C_6H_4]$ (**1**) was prepared in Et_2O from $CpCrCl_2(THF)$ either by sequential addition of $(Me_3SiNH)_2C_6H_4$ and 2 equiv Me_3SiCH_2MgCl,[8] or by direct reaction with $Li_2[(Me_3SiN)_2C_6H_4]$ (Scheme 1).[9] The magnetic moment of 3.49 μ_B for $CpCr[(Me_3SiN)_2C_6H_4]$ (Evans, C_6D_6), was consistent with either a Cr^{III} d^3 complex with a dianionic phenylenediamido ligand, or with antiferromagnetic coupling between Cr^{II} d^4 and a monoanionic diiminosemiquinonate ligand radical.[6] The N-neopentyl (**2**) and N-phenyl (**3**) derivatives were also generated by analogous routes.[10]



Scheme 1 Synthesis of $CpCr[(RN)_2C_6H_4]$ complexes **1–9**.

When **1** was recrystallized in the presence of THF, the THF adduct $CpCr[(Me_3SiN)_2C_6H_4](THF)$ (**1a**) was isolated (Figure 2). Coordination of THF to **1** appeared to be reversible as judged by UV-vis spectroscopy. Reversible THF binding was previously observed for $Cp^*Cr(CH_2SiMe_3)_2$.[11]

Monoanionic, bidentate ligand-based radicals (LX•) can be generated by coordination of neutral ligands (L_2)[12] such as diimines to $CrCl_2$.[13] Our previously reported synthesis of CpCr(LX•)(Cl) compounds from sequential treatment of $CrCl_2$ with diimine or pyridine-imine L_2 ligands followed by NaCp relied on this electron transfer reaction from Cr^{II} to the ligand π^* orbital.[14] The reactions shown in Scheme 1 employed a complementary strategy, where the ligand-based radical was generated by single-electron oxidation of a bidentate, dianionic (X_2) ligand coordinated to a Cr^{III} centre. Treatment of **1**–**3** with

PbCl$_2$ gave the corresponding CpCr[(RN)$_2$C$_6$H$_4$](Cl) complexes (R = SiMe$_3$ (**4**), CH$_2$CMe$_3$ (**5**), or Ph (**6**)).[15]

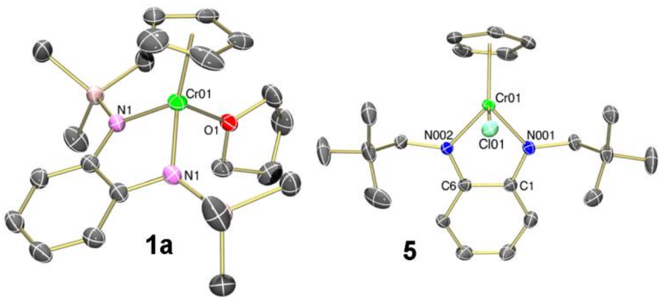


Fig. 2 Molecular structures (50% probability ellipsoids) of **1a** (left) and **5** (right).

The chloride complexes **4**–**6** were all hexanes soluble, forming very dark green solutions with two or more strong absorbance bands (ε ≥ 1500 M^{-1} cm^{-1}) at wavelengths longer than 500 nm. The magnetic moments of 2.73 μ_B, 2.62 μ_B, and 2.53 μ_B for complexes **4**, **5**, and **6**, respectively (Evans, C$_6$D$_6$) indicated a ground spin state of S = 1, consistent with either a dianionic phenylenediamide (X$_2$) ligand coordinated to Cr^{IV} d^2, or a monoanionic radical antiferromagnetically coupled to a Cr^{III} d^3 centre. The molecular structures of **5** (Figure 2) and **6** (ESI)[10] both displayed the regular three-legged piano stool geometries commonly observed for CpCr^{III} complexes.[16] While twinning problems rendered the detailed structural parameters of **6** unreliable, the N–C and C–C bond lengths of **5** were consistent with those observed by Heyduk for the monoanionic radical (Me$_3$CCH$_2$N)$_2$C$_6$H$_4$ ligand.[6] Complexes **4**–**6** are therefore best considered as CpCr(LX•)(Cl) Cr^{III} complexes with oxidized radical ligands.

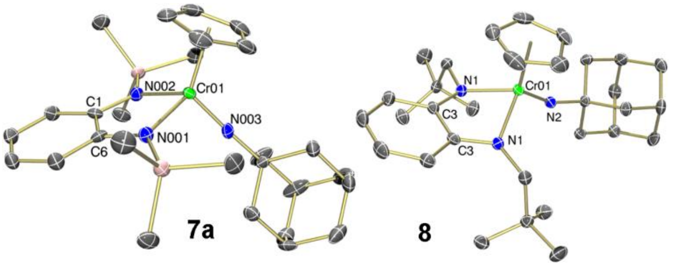
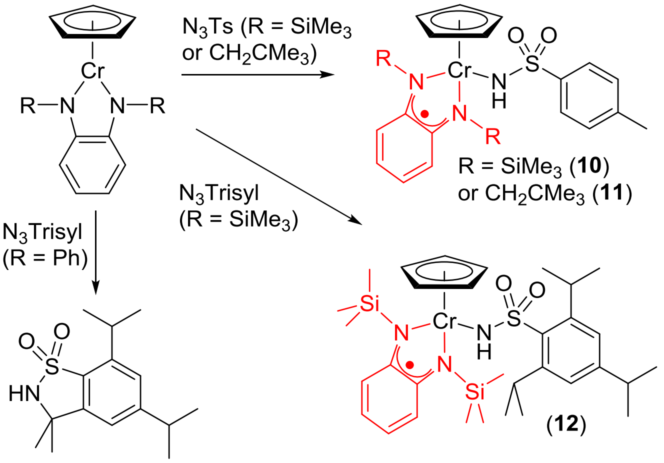


Fig. 3 Molecular structures (50% probability ellipsoids) of adamantyl imido complexes **7a** (left) and **8** (right).

Whether the CpCr[(RN)$_2$C$_6$H$_4$] intermediates were isolated (R = SiMe$_3$ **1**) or generated *in situ* (R = Me$_3$CCH$_2$ **2**) both species reacted with alkyl and aryl azides to form chromium imido compounds.[17] Two CpCr[(Me$_3$SiN)$_2$C$_6$H$_4$](NR') complexes (R' = Ad **7a**, Mes **7b**) were isolated as X-ray quality crystals (**7a** is shown in Figure 3). Based on their solution magnetic moments of 2.09 to 1.69 μ_B, their short Cr–N imido bonds (1.632(4) to 1.676(1) Å) and phenylenediamide bond lengths, complexes **7ab** both appeared to be Cr^{V} d^1 complexes bound to non-radical ligands. The electronic structure of CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NAd) (**8**) (Figure 3) was more difficult to assign based on the observed structural parameters, as described in the ESI.[10] The unexpectedly diamagnetic product resulting from treatment of **2** with N$_3$Mes was determined to be the bis(imido) complex Cr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NMes)$_2$ (**9**), as shown in Scheme 1. Related π-loaded[18] CpCr(NR)$_2$(X) complexes have previously been shown to be unstable with respect to net loss of a cyclopentadienyl radical.[19] Based on the ancillary ligand N–C and C–C bond lengths, the S = 0 ground spin state was tentatively attributed to an LX• radical antiferromagnetically coupled to a Cr^{V} d^1 centre. However, Brown has recently demonstrated that similar structural distortions are observed when related dianionic catecholate and amidophenoxide ligands act as π-donors to d^0 metal centres,[20] and so the alternative of X$_2$ bound to Cr^{VI} cannot be ruled out.



Scheme 2 Reactions of CpCr[(RN)$_2$C$_6$H$_4$] (**1**–**3**) with tosyl and trisyl azide.

Highly reactive M(NSO$_2$Ar) intermediates are widely used in catalytic applications for organic synthesis.[21] While these reactive species are often prepared using isolated or *in situ* generated PhI=NSO$_2$Ar reagents, the corresponding N$_3$SO$_2$Ar azides have also been employed.[22] Reaction of complexes **1** or **2** with N$_3$Ts resulted in new products **10** and **11** with significantly different colours and UV-vis spectra than those of the Cr^{V} imido compounds **7** and **8** (Scheme 2). The molecular structure of **11** is shown in Figure 4. Based on the Cr–NTs bond length (2.013(4) Å), the Cr–N–S bond angle (135.2(3)°), and the solution magnetic moment (2.49 μ_B), **11** appeared to be the S = 1 complex CpCr[(Me$_3$CCH$_2$N)$_2$C$_6$H$_4$](NHTs) **11**, the product resulting from addition of a hydrogen atom to the expected Cr=NTs intermediate. The solvent is a likely H-atom source in this process, although this has not yet been verified. Crystals of **10** that were also examined crystallographically were found to be extensively disordered, but the Cr–NHTs portion of the molecule appeared similar to **11**, indicating that the Me$_3$Si-substituted complex **10** also underwent a H-atom abstraction reaction.

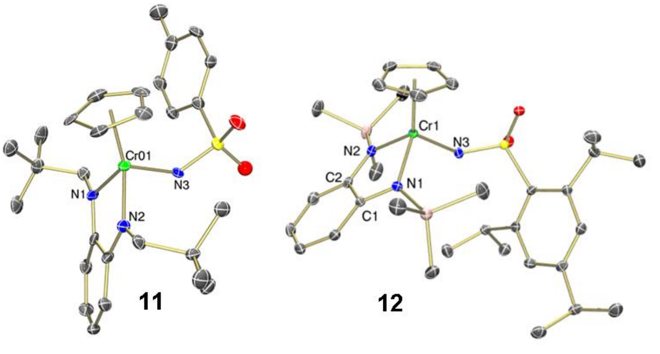


Fig. 4 Molecular structures (50% probability ellipsoids) of **11** (left) and **12** (right).

Zhang and co-workers have used trisyl azide [NTrisyl = $NSO_2(2,4,6\text{-}^iPr_3C_6H_2)$] as a substrate for cobalt-catalyzed radical H-atom abstraction and cyclization.[23] When **1** was reacted with N_3Trisyl, the overall colour change to dark green was similar to that observed with N_3Ts but was qualitatively much more rapid, consistent with the expected rate increase for an intramolecular H-atom abstraction process (Scheme 2). However, crystals isolated from the reaction of **1** with N_3Trisyl showed that the product $CpCr[(Me_3SiN)_2C_6H_4](NHTrisyl)$ (**12**) had not undergone cyclization to form the desired benzosultam (Figure 4). The structural parameters and magnetic moment of **12** are again consistent with a Cr^{III} amido complex with a monoanionic diiminosemiquinonate radical ligand. Despite the qualitatively faster reaction, the isopropyl substituents of the trisyl amido ligand in **12** remain intact. It is possible that for the reaction of **1** with N_3Trisyl, H-atom abstraction from the ^{i}Pr methine carbon was followed by a bimolecular H-atom transfer to generate the structurally characterized product and a second organochromium complex with a $H_2C{=}C(Me)$-substituted ligand that did not crystallize with **12**.

In contrast, the stoichiometric reaction of $CpCr[(PhN)_2C_6H_4]$ (**3**) with N_3Trisyl in C_6D_6 at ambient temperature overnight gave the ^1H NMR spectrum of the expected benzosultam product. The organic product was obtained in > 80% isolated yield after chromatography by treating N_3Trisyl with 20 mol% of **3** after 6 days at room temperature, or 65 h at 70 °C. Investigation of the steric and electronic factors responsible for the successful intramolecular C–H amination of N_3Trisyl with phenyl-substituted **3** as catalyst while **1** fails to cyclize will be the subject of upcoming computational studies.

Conclusions

The solid state molecular structures and hydrogen-atom abstraction reactivity of $CpCr[(RN)_2C_6H_4](NR')$ imido complexes were found to depend on both the R substituents on the phenylenediamido nitrogen donor atoms as well as the imido R' group. Improving the C–H functionalization catalysis observed for **3** with N_3Trisyl will require further mechanistic, computational and spectroscopic investigation in order to understand how modifying the redox-active ancillary ligand controls the electronic structure of the Cr(NR') group.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and crystallographic details and CIF files of **1a**, **5**, **6**, **7a, 7b**, **8**, **9**, **11** and **12** (CCDC 1001249, 1001254-1001257, 1001260-1001263). See DOI: 10.1039/c000000x/

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