An electron-transfer series of octahedral \( \alpha \)-diimine complexes [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{Cr} \)]\( \text{BARF} \)\( \text{BARF} \), \( n = 2, 1, 0 \) has been synthesized and crystallographically characterized. Cyclic voltammetry indicated additional formation of [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \)\( \text{BARF} \). The molecular structures suggested that all redox processes were ligand-based. Magnetic moments were consistent with spin ground states of \( S = 0 \) for [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \), \( S = 1/2 \) for [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \), and \( S = 1 \) for [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \). The experimental data is consistent with chromium maintaining the +III oxidation state throughout, while being coordinated by varying numbers of neutral diimines [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)] and diimine radical anions [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)].

As part of our wide-ranging exploration of open-shell chromium organometallics,\(^1\) we have recently employed \( \alpha \)-diimines (aka 1,4-diadiazidines) as ancillary ligands.\(^2\) We were particularly attracted by the redox activity of these ligands, which might be expected to ameliorate the strictures imposed by oxidation state changes during catalytic cycles (e.g. \( \text{Cr}^{3+}/\text{Cr}^{4+} \) in the selective oligomerization of ethylene).\(^3\) Three oxidation states of the \( \alpha \)-diimine ligands have been identified, namely the neutral diimine \( \text{L} \), the radical monoanions \( \text{L}^- \), and the two-electron-reduced enediamide \( \text{L}^2- \). The assignment of ligand oxidation states is informed by their detailed structural parameters, which change in a predictable way; however, spectroscopic and computational techniques are also often employed.

The electronic flexibility of \( \alpha \)-diimine ligands enables the preparation of molecules with unusual atomic and electronic structures. A representative example from our laboratory was the serendipitous discovery of dinuclear [(\( \text{L}^{\text{PP}} \))\( \text{Cr} \)]\( \text{BARF} \)\( \text{BARF} \)\( \text{BARF} \), which features a rather short Cr–Cr quintuple bond between Cr(i) (d\(^3\)) ions coordinated by two singly reduced bridging \( \alpha \)-diimines [(\( \text{L}^{\text{PP}} \))\( \text{Cr} \)] and exhibits notable reactivity with a wide variety of small molecules.\(^6\) In an extension of this chemistry, we encountered the deceptively simple octahedral complex [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)], which might have exhibited similar reactivity with a wide variety of small molecules.\(^6\) In an extension of this chemistry, we encountered the deceptively simple octahedral complex [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)], which might have exhibited similar reactivity with a wide variety of small molecules.\(^6\) In an extension of this chemistry, we encountered the deceptively simple octahedral complex [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)].

The synthesis and characterization of 1 has been described,\(^8\) it is an air sensitive material that can easily be oxidized (see Scheme 1). Thus treatment of a brown Et\(_2\)O solution of 1 with 1.0 equivalent of FeBARF (Fc\(^+=\) ferricenium, BARF\(^-\) = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) yielded a deep purple solution, from which [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \)\( \text{BARF} \) was isolated in 92% yield after recrystallization from Et\(_2\)O/toluene. In contrast to 1, solid [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \) appears to be stable in air; its structure has been determined by X-ray diffraction and the result is shown in Fig. 1, with selected bond distances listed in Table 1.

Further oxidation of 1\(^*\) proved feasible. Synthetic access to the green [(\( \text{L}^{\text{C}} \))\( \text{Cr} \)]\( \text{BARF} \)\( \text{BARF} \)\( \text{BARF} \) can be had either by the oxidation of 1 with 2.0 equivalents of FeBARF or by the reaction of 1\(^*\)BARF with 1.0 equivalent of FeBARF in Et\(_2\)O. Recrystallization from methylene chloride at −30 °C afforded

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\(^3\) Electronic supplementary information (ESI) available: Preparative and crystallographic and spectroscopic data. CCDC 1000091 and 1000092. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc03332a

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**Scheme 1** The electron-transfer series for complexes 1–1\(^*\).
13+/12+/11/ are highly chemically reversible under our experimental conditions.

The observation of three reversible redox processes raises the question of the electronic structure and formal oxidation state of chromium of the various members of this electron transfer series. The most reduced compound, 1, has unambiguously been assigned an electronic structure represented by \((\text{L}^+)_3\text{Cr}^{\text{III,8}}\); it seems highly improbable that its oxidation should result in a lowering of the metal’s oxidation state below +III. Accordingly, there remains the question whether the successive oxidations remove electrons from the metal or from the ligands. To answer this question we turn to a consideration of the structural details of these complexes. We note that all three molecules feature octahedral coordination of chromium. Given the pronounced stabilization of the \(d^3\) electronic configuration in an octahedral ligand field, and the known tendency for chromium in higher oxidation states to adopt lower coordination numbers, this is already a hint. Selected interatomic distances for 1, 1+, and 12+ are listed in Table 2.

Table 2 Librational corrected selected bond distances (Å) for 1–12+

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>1+</th>
<th>12+</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–N3</td>
<td>1.390(3)</td>
<td>1.408(4)</td>
<td>1.444(8)</td>
</tr>
<tr>
<td>C–N9</td>
<td>1.333(2), 1.332(2)</td>
<td>1.314(4), 1.316(4)</td>
<td>1.291(6), 1.300(7)</td>
</tr>
<tr>
<td>Cr–N4</td>
<td>2.0377(16), 2.0418(14)</td>
<td>2.025(3), 2.024(2)</td>
<td>2.088(4), 2.105(4)</td>
</tr>
</tbody>
</table>

Bulk electrolysis experiments carried out in both solvents confirmed the one-electron nature of the reactions and the thermal stabilities of the various redox states. For example, anodic electrolysis of 1+ in dichloromethane/[NBu4][B(C6F5)4] at \(E_{\text{appl}} = 0.1\) V resulted in clean conversion of a purple solution of the monocation to the blue-green solution of 12+. Moving \(E_{\text{appl}}\) to 1.1 V converted 1+ to a yellow-orange solution of 13+. Reversing this sequence regenerated 1+, apparently without loss of the compound. One-electron reduction of 1+ was carried out in THF/[NBu4][PF6] at \(E_{\text{appl}} = -1.7\) V, giving the neutral complex 1, which was subsequently re-oxidized to 1+ at \(E_{\text{appl}} = -1\) V. The three electron-transfer reactions involving
We note that the Cr–N distances in all three compounds vary within a very narrow range (2.019(3)–2.105(4) Å), without any discernable trend. As higher oxidation states tend to engender shorter metal–ligand distances, this too suggests that the oxidation state of the metal is not changing. For this to be true, successive oxidations must remove electrons from the coordinated diimine radical anions, which should result in systematic changes of the C–C and C–N bond distances of the ligand backbones. Although both 1+ and 12+ lack threefold crystallographic symmetry, rendering the ligands inequivalent, their metric data do not support the unambiguous identification of one (or two) neutral diimines in 1+ (or 12+), respectively. In other words, the C–C and C–N distances of the individual ligands in any given compound do not differ significantly. In principle, this may be due to positional disorder in the crystal, or it might indicate effective delocalization of the available electrons over all three ligands. The present structural data cannot distinguish between these two alternatives. Interestingly, DFT calculations on models for 1+ and 12+ are consistent with delocalization in the former (Fig. S12, ESI †) and localization in the latter (Fig. S13, ESI †). In any event, inspection of the average distances (see Table 2, bottom) reveals a gradual lengthening of the C–C bonds and a concomitant foreshortening of the C–N bonds in the order 1 → 1+ → 12+. Thus, in this order the ligands look on average less like radical anions (L∗−) and more like neutral diimines (L). To summarize, the structural data are consistent with formulations of 1+ as [([L∗−]3)Cr III]+ and 12+ as [([L∗−]2L)Cr III]2+. The electronic spectra are shown in Fig. 3. The intense high energy bands are likely π → π* transition of the ligands, while the weak transition in the visible region may be attributed to d → d transitions of the Cr(m) ion. Most conspicuous are the broad bands in the near IR (1389 nm for 1+, 923 and 1006 nm for 12+), which are absent from the spectrum of 1; these are tentatively assigned as ligand-to-ligand intervalence charge-transfer bands associated with the presence of ligands in different redox states on the same metal center.9d

To further characterize the electronic structures of this series of compounds, we have carried out magnetic measurements. The temperature dependencies of the effective magnetic moments of all three complexes are depicted in Fig. 4. Both [1+][BARF] [(1)BF4]3 are simple paramagnets, whose molar magnetic susceptibilities can be fit with Curie–Weiss expressions. Accordingly, their effective magnetic moments are temperature independent over the whole temperature range of 50–350 K. Their respective values are consistent with spin ground states of S = 1/2 for 1+ and S = 1 for 12+. These presumably result from strong antiferromagnetic coupling between the central Cr(m) ion (S = 3/2) and two or one diimide radical anions (S = 1/2), respectively. Extending this rationale to 1 would predict diamagnetism (ground state S = 0) for this complex. However, as can be seen in Fig. 4, 1 actually exhibits a rather small, and temperature dependent magnetic moment. Indeed, this residual paramagnetism was also evident in the 1H NMR spectrum of 1. While its resonances were found in the ‘normal’ shift range (δ 1–10 ppm), the room temperature spectrum (in THF-d8) exhibited a broad resonance at ca. 4.7 ppm, which split into two sharp resonances upon cooling. This apparent ‘coalescence phenomenon’ was ultimately traced to significant temperature dependencies of the chemical shifts of the protons on the backbone of the diimine and the cyclohexyl protons adjacent to the nitrogen, which are accidentally iso-chronous at room temperature (see ESI † for more detail). The residual paramagnetism of 1 can be interpreted as a result of antiferromagnetic coupling between the metal and the ligands that is not strong enough to entirely preclude the occupation of the first excited spin state (S = 1).9d

We have shown that octahedral tris(diimine) chromium complexes form an extensive electron-transfer series of the composition [[(HLCy)3Cr]n+ (n = 3, 2, 1, 0). At least three, and most likely all four of these complexes feature chromium in its highly favored +III oxidation state. The redox processes are wholly ligand based, thus confirming that diimines belong to a growing class of non-innocent ligands that extend the redox capacity of metal complexes. This should prove useful in catalytic cycles involving multi-electron redox processes.

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Notes and references


