

## The Shortest Metal–Metal Bond Yet: Molecular and Electronic Structure of a Dinuclear Chromium Diazadiene Complex

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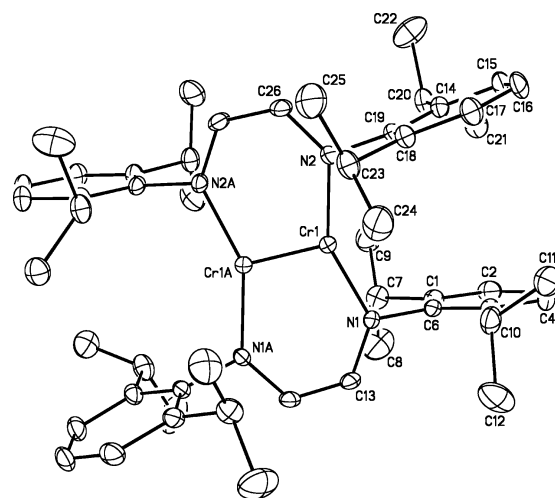
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Dinuclear chromium complexes have played a special role in the history of multiple metal–metal bonding,<sup>1</sup> featuring “supershort” quadruple bonds ( $d_{M-M} < 1.9 \text{ \AA}$ ) of questionable strength.<sup>2</sup> Recent synthetic work by Power et al. and computational investigations by others have even broached the notion of metal–metal bond orders exceeding 4, resulting from extremely sparing coordination of low-valent metals (i.e., those with  $d^5$  and  $d^6$  configurations).<sup>3</sup> For various reasons, we have been exploring the chemistry of chromium coordinated by diazadienes (or  $\alpha$ -diimines). In the course of these investigations, we have discovered a dinuclear compound that exhibits a very short chromium–chromium distance. Indeed, in terms of Cotton’s “formal shortness ratio” (FSR), this compound features the shortest chemical bond presently known (FSR(2) = 0.760, compare with FSR(N<sub>2</sub>) = 0.786).<sup>2a</sup>

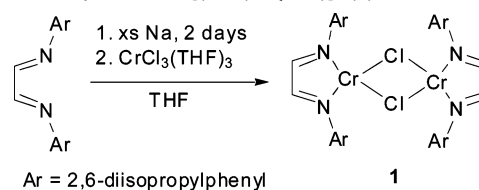
The chemistry of this system began with the synthesis of dark green  $[(^H\text{L}^{\text{iPr}})\text{Cr}(\mu\text{-Cl})_2]$  (**1**,  $^H\text{L}^{\text{iPr}} = N,N'$ -bis(2,6-diisopropylphenyl)-1,4-diazadiene) by slow addition of a THF solution of  $\text{Na}_2[{}^H\text{L}^{\text{iPr}}]$  to  $\text{CrCl}_3(\text{THF})_3$  according to Scheme 1 (see Supporting Information for full characterization). **1** is an antiferromagnetically coupled dimer ( $\mu_{\text{eff}}(300 \text{ K}) = 3.4(1) \mu_B$  per Cr,  $J = -17 \text{ cm}^{-1}$ ) with a Cr–Cr distance of 3.431(1) Å. Reduction of **1** with 2 equiv of  $\text{KC}_8$  in  $\text{Et}_2\text{O}$  gave a green solution after stirring overnight. A  $^1\text{H}$  NMR spectrum in toluene- $d_8$  of the product after workup revealed a diamagnetic spectrum with sharp resonances between 0 and 8 ppm, which showed negligible temperature dependence of the chemical shifts from 0 to 70 °C. Crystallization from a dilute  $\text{Et}_2\text{O}$  solution at  $-30 \text{ }^\circ\text{C}$  gave dichroic, red/green plates of  $(\mu\text{-}\eta^2\text{-}^H\text{L}^{\text{iPr}})_2\text{Cr}_2$  (**2**) that were characterized by X-ray diffraction (see Figure 1). The geometry around each chromium atom in **2** can best be described as trigonal planar with each metal being coordinated by two N atoms from two different diazadiene ligands as well as by the neighboring Cr atom. The Cr–N distances are unexceptional at 1.913(2) and 1.914(2) Å with a N(1)–Cr(1)–N(2) angle of 150.58(9)°. The most striking feature of **2** is the extremely short Cr–Cr distance of 1.8028(9) Å, making it the shortest metal–metal distance reported to date.<sup>4</sup>

Due to the nonplanar structure of the  $\text{N}_4\text{Cr}_2$  core, chiral **2** is expected to exhibit resonances of four unique methyl groups and two unique methine protons associated with the isopropyl groups in its  $^1\text{H}$  NMR spectrum. However, at room temperature, only two  $^{\text{iPr}}\text{Pr}-\text{CH}_3$  and one  $\text{CH}^{\text{iPr}}\text{Pr}-\text{CH}$  resonances were observed. This is presumably due to a low barrier, fluxional process whereby a twist about the metal–metal bond interconverts the two enantiomers on the  $^1\text{H}$  NMR time scale. Accordingly, low-temperature  $^1\text{H}$  NMR spectra in the  $-70$  to  $25 \text{ }^\circ\text{C}$  temperature range showed a decoalescence phenomenon resulting in three methyl resonances (in a 1:1:2 ratio) and two methine signals. Presumably, two of the  $^{\text{iPr}}\text{Pr}-$



**Figure 1.** The molecular structure of **2** (30% probability level). Selected interatomic distances (Å) and angles (deg): Cr(1)–Cr(1A), 1.8028(9); Cr(1)–N(1), 1.914(2); Cr(1)–N(2), 1.913(2); N(1)–C(13), 1.373(3); N(2)–C(26), 1.362(3); C(13)–C(13A), 1.345(5); C(26)–C(26A), 1.354(5); N(1)–Cr(1)–N(2), 150.58(9); N(1)–Cr(1)–Cr(1A), 104.78(6); N(2)–Cr(1)–Cr(1A), 104.63(6); N(1)–Cr(1)–Cr(1A)–N(1A), 17.74(6); N(2)–Cr(1)–Cr(1A)–N(2A), 15.82(6).

### Scheme 1. Preparation of $[(^H\text{L}^{\text{iPr}})\text{Cr}(\mu\text{-Cl})_2]$ (**1**)



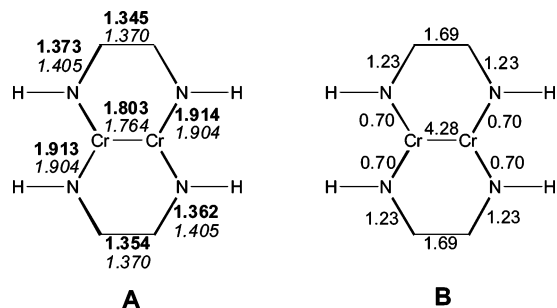
$\text{CH}_3$  resonances are accidentally degenerate and show no significant temperature dependence.

Because of the redox ambiguity of diimine and other imine containing ligands,<sup>5</sup> the Cr atoms in **2** could formally be assigned as Cr(II) coordinated by dianionic enediamide ligands, Cr(I) with monoanionic ligand-centered radical ligands, or Cr(0) with neutral diimine ligands. The long C–N distances (1.373(3) and 1.362(3) Å) and short C–C distances (1.345(5) and 1.354(5) Å) are consistent with a reduced diimine ligand.<sup>6</sup>

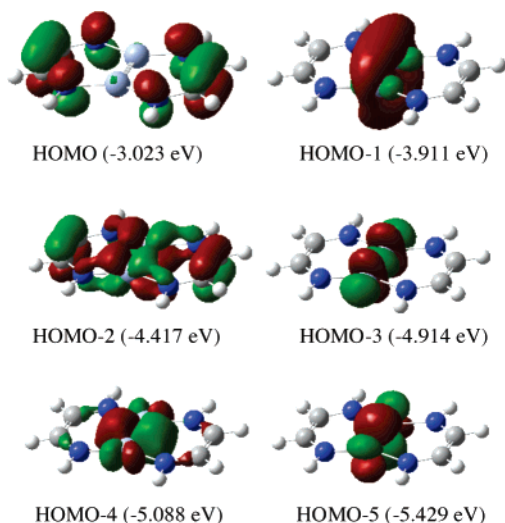
For a more complete description of the electronic structure of **2**, DFT calculations were performed at the BLYP/6-311g level using a model complex where the 2,6-diisopropylphenyl substituents were replaced by hydrogen atoms (i.e., **2'**).<sup>7</sup> Geometry optimizations on the model complex give bond distances that are in good agreement with the X-ray structure in Figure 1 (see structure **A** in Figure 2). Furthermore, spin-restricted and spin-unrestricted calculations suggest a closed shell singlet ground state, consistent with the observed diamagnetic nature of **2** (vide supra). One shortcoming of the computational model is that it is completely planar, whereas the

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**Figure 2.** Bond lengths (Å) for **2** (bold) and **2'** (italics) (A) and effective bond orders from NRT analysis of **2'** (B).



**Figure 3.** A representation of the frontier molecular orbitals of **2'**.

$N_4Cr_2$  core in **2** is not. This deviation is presumably due to the sterically demanding 2,6-diisopropylphenyl groups that are absent in **2'**. Accordingly, an ONIOM optimization of the entire molecule resulted in an N–Cr–Cr–N angle of  $12.2^\circ$ , reasonably close to the average of the two measured angles in **2** ( $16.8^\circ$ ) and a Cr–Cr distance of  $1.790 \text{ \AA}$ .

The calculations showed that the HOMO of **2'** is mostly ligand based and corresponds to an orbital of the diimine ligand that is both C–C  $\pi$ -bonding and C–N  $\pi$ -antibonding (see Figure 3). HOMO-1 through HOMO-5 show considerable metal–metal bonding, whereas the LUMO, LUMO+1, and LUMO+2 appear to be metal–metal antibonding orbitals (see Supporting Information). Cr–Cr  $\sigma$ -bonding character is displayed by HOMO-3, whereas HOMO-4 and HOMO-5 exhibit  $d\pi$ -bond character. The fourth Cr–Cr bonding interaction (HOMO-1) comprises a combination of  $sd$  hybrids oriented such that the main hybrid orbital axes are parallel to one another (such a bonding mode has previously been termed a side-on  $sd-\pi\delta$  bond).<sup>8</sup> The fifth Cr–Cr bonding interaction (HOMO-2) is highly delocalized but otherwise takes the form of a  $d\delta$  metal–metal bond. Natural bond orbital (NBO) and natural localized molecular orbital (NLMO) analyses of the electron density mirror the major features of the Cr–Cr interactions determined from the canonical MO's.<sup>9</sup>

The presence of five occupied molecular orbitals with Cr–Cr bonding character raises the question of metal–metal quintuple bonding. Complexity arises from the highly delocalized nature of the HOMO-2  $\delta$ -like orbital. To gain a more nuanced perspective on the issue of effective bond order, natural resonance theory (NRT) analysis was performed.<sup>9,10</sup> As expected for a system that bears strong delocalization (to the extent of resembling a dimetallanaphthalene), multiple resonance configurations are occupied, some having Cr–Cr quintuple bonds. The effective bond orders are illustrated in Figure 2 (B). This analysis gives slightly higher than 4-fold bonding, 4.28, which is less than the value of 4.64 previously computed for *trans*-bent HCrCrH.<sup>8</sup>

In conclusion, we have prepared a bimetallic chromium complex that features the shortest metal–metal distance measured to date. DFT analysis of its electronic structure indicates high-order metal–metal bonding. Although the highly delocalized nature of the bonding precludes description using a single Lewis structure only, NRT and NBO analyses indicate some degree of quintuple bonding. Further exploration (both experimental and computational) of molecules with metal–metal bonds of high bond order is currently underway in these laboratories.

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**Supporting Information Available:** Synthesis, characterization, and crystallographic details for **1** and **2** as well as the computational details for **2'** and **2** (ONIOM). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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