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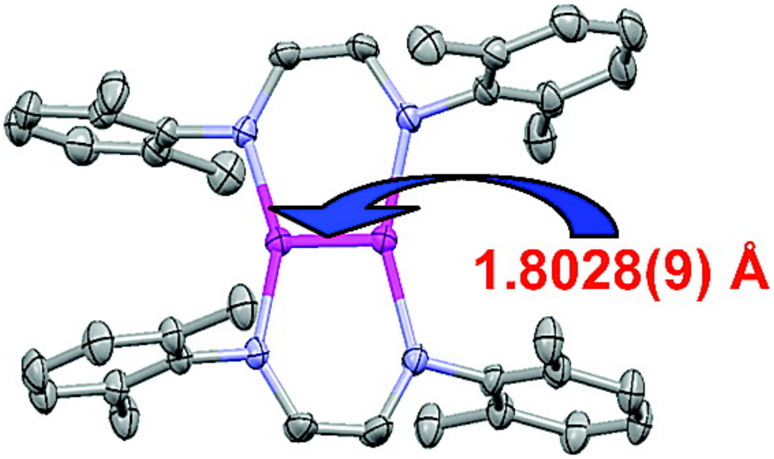

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COMMUNICATIONS

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

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Dinuclear chromium complexes have played a special role in the history of multiple metal−metal bonding,[1] featuring "supershort" quadruple bonds ($d_{M-M} < 1.9$ Å) of questionable strength.[2] 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).[3] For various reasons, we have been exploring the chemistry of chromium coordinated by diazadienes (or α-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_2) = 0.786).[2a]

The chemistry of this system began with the synthesis of dark green $[(^{H}L^{iPr})Cr(\mu\text{-}Cl)]_2$ (**1**, $^{H}L^{iPr}$ = *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diazadiene) by slow addition of a THF solution of $Na_2[^{H}L^{iPr}]$ to $CrCl_3(THF)_3$ according to Scheme 1 (see Supporting Information for full characterization). **1** is an antiferromagnetically coupled dimer (μ_{eff}(300 K) = 3.4(1) μ_B per Cr, $J = -17$ cm^{-1}) with a Cr−Cr distance of 3.431(1) Å. Reduction of **1** with 2 equiv of KC_8 in Et_2O gave a green solution after stirring overnight. A ^{1}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 Et_2O solution at −30 °C gave dichroic, red/green plates of $(\mu\text{-}\eta^2\text{-}^{H}L^{iPr})_2Cr_2$ (**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.[4]

Due to the nonplanar structure of the N_4Cr_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}H NMR spectrum. However, at room temperature, only two ^{i}Pr−CH$_3$ and one CH ^{i}Pr−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}H NMR time scale. Accordingly, low-temperature ^{1}H NMR spectra in the −70 to 25 °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 ^{i}Pr−CH$_3$ resonances are accidentally degenerate and show no significant temperature dependence.

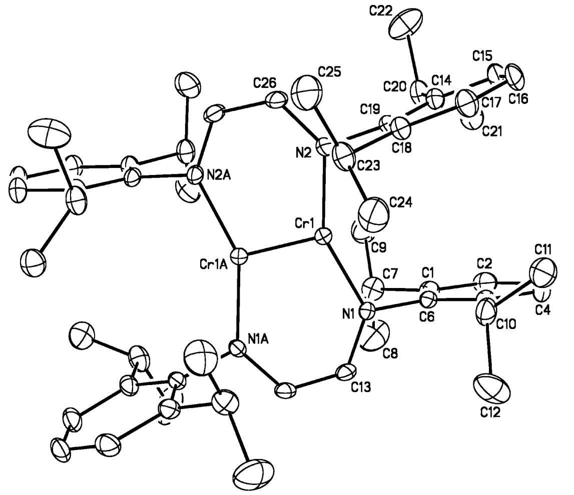
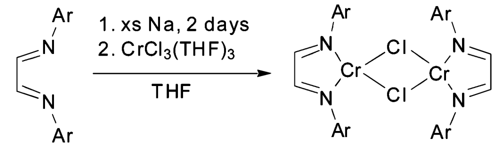


Figure 1. The molecular structure of **2** (30% probability level). Selected interatomic distances (Å) and angles (deg): Cr(1)−Cr(1A), 1.8028(9); Cr(1)−N(1), 1.914(2); Cr(1)−N(2), 1.913(2); N(1)−C(13), 1.373(3); N(2)−C(26), 1.362(3); C(13)−C(13A), 1.345(5); C(26)−C(26A), 1.354(5); N(1)−Cr(1)−N(2), 150.58(9); 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 $[(^{H}L^{iPr})Cr(\mu\text{-}Cl)]_2$ (**1**)



Ar = 2,6-diisopropylphenyl

1

Because of the redox ambiguity of diimine and other imine containing ligands,[5] 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.[6]

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′**).[7] 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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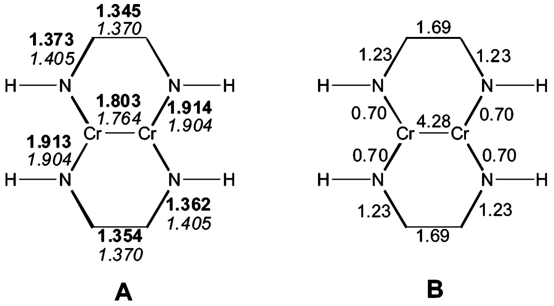

Figure 2. Bond lengths (Å) for **2** (bold) and **2′** (italics) (**A**) and effective bond orders from NRT analysis of **2′** (**B**).

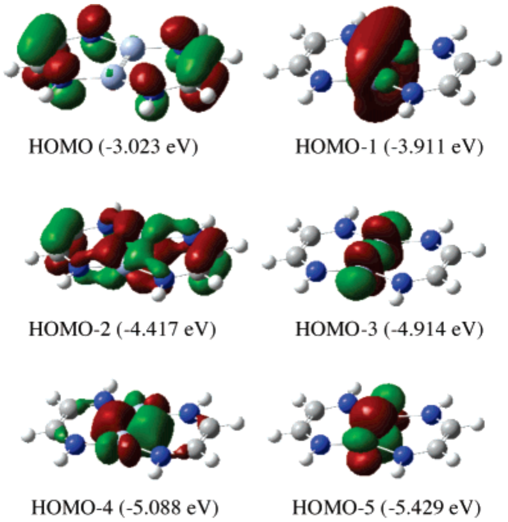
HOMO (-3.023 eV)
HOMO-1 (-3.911 eV)
HOMO-2 (-4.417 eV)
HOMO-3 (-4.914 eV)
HOMO-4 (-5.088 eV)
HOMO-5 (-5.429 eV)

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°, reasonably close to the average of the two measured angles in **2** (16.8°) and a Cr−Cr distance of 1.790 Å.

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 π-bonding and C−N π-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 σ-bonding character is displayed by HOMO-3, whereas HOMO-4 and HOMO-5 exhibit dπ-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).[8] The fifth Cr−Cr bonding interaction (HOMO-2) is highly delocalized but otherwise takes the form of a dδ 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.[9]

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 δ-like orbital. To gain a more nuanced perspective on the issue of effective bond order, natural resonance theory (NRT) analysis was performed.[9,10] 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.[8]

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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