# A Weak, Short Metal−Metal Bond in a Chromium(II) Amidinate Complex

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Dinuclear chromium(II) complexes containing metal−metal bonds have been the subject of intense investigation.[1] Of particular interest are complexes with chromium−chromium distances of ≤2.0 Å.[1,2] Such complexes have been proposed to contain chromium−chromium quadruple bonds, which are formed upon overlap of metal $\sigma$, 2 $\pi$, and $\delta$ orbitals.[3] Molecular orbital calculations support the idea of the quadruple bonds,[4] but severe electron correlation problems have limited the amount of information that can be obtained. An open question relates to the strength of the chromium−chromium quadruple bond.[1,5] A majority of the complexes with short chromium−chromium bond lengths adopt a "lantern" structure, with four three-atom bridging ligands holding the two chromium atoms in close proximity.[2] In most cases, treatment of the lantern complexes with neutral Lewis bases leads to adducts that retain chromium−chromium bonds,[1] which is consistent with the idea of a strong metal−metal bond. However, several complexes with short chromium−chromium bonds have been demonstrated to undergo reversible cleavage to monomeric complexes upon treatment with neutral Lewis bases. For example, treatment of [(tetraazaannulene)Cr]$_2$ (Cr−Cr 2.096 Å) with pyridine leads to a monomeric pyridine adduct.[6] [Li(L)]$_4$[Me$_8$Cr$_2$] (Cr−Cr = 1.98 Å) is dimeric when L = THF or Et$_2$O but is cleaved to [Li(TMEDA)]$_2$-[CrMe$_4$] upon addition of TMEDA.[7] Dinuclear chromium(II) acetate is in equilibrium with the aquated monomer in water/acetic acid mixtures.[8] These experiments imply that the strength of the chromium−chromium bonds cannot exceed combined energies of the new metal−ligand bonds in the monomeric species. Finally, Gambarotta has examined the role of ligand-substituent steric bulk in determining the existence of a chromium−chromium bond with amidinate ligands of the formula [RNC(R′)NR]⁻ (R = C$_6$H$_{11}$, SiMe$_3$; R′ = H, Me, Ar).[9] Only when R = C$_6$H$_{11}$ and R′ = H is a dimeric lantern-type complex obtained; when R′ = CH$_3$ or Ar, monomeric bis(amidinate) complexes were observed.

Herein we describe the synthesis of monomeric and dimeric chromium complexes containing amidinate ligands of the formula [RNC(CH$_3$)NR′]⁻. When R = R′ = tBu or iPr, monomeric complexes result. However, a novel dimeric complex is obtained when R = tBu and R′ = Et. The X-ray crystal structure of this complex reveals a short chromium−chromium bond, with two $\mu_2$- and two $\eta^2$-amidinate ligands within each dimer. Despite the presence of the short chromium−chromium bond, NMR spectra and solution molecular weight experiments demonstrate that this dimeric complex dissociates to monomers in cyclohexane and benzene solutions. This is the first example of chromium−chromium bond cleavage in the absence of an added Lewis base and implies that the chromium−chromium bond in the dimeric complex is weak.

Treatment of chromium(II) chloride with 2 equiv of Li[tBuNC-(CH$_3$)NtBu], Li[iPrNC(CH$_3$)NiPr], or Li[tBuNC(CH$_3$)NEt] (prepared from the corresponding carbodiimides and methyllithium) afforded Cr[tBuNC(CH$_3$)NtBu]$_2$ (**1**, 50%), Cr[iPrNC(CH$_3$)NiPr]$_2$ (**2**, 54%), and [Cr(tBuNC(CH$_3$)NEt)$_2$]$_2$ (**3**, 58%) as deep blue,

purple, and amber or metallic green crystals, respectively (eq 1). The structural assignments for **1**−**3** were based on spectral and analytical data, and X-ray crystal structure determinations.[10] Complexes **1** and **2** were paramagnetic, with magnetic moments of 4.78 and 4.93 $\mu_B$. These values are close to the expected spin-only values for four unpaired electrons (4.90 $\mu_B$). X-ray crystal structure determinations revealed monomeric structures with tetrahedral geometry for **1** and square planar geometry for **2**. Complex **3** crystallized as a mixture of amber blocks and metallic green plates from hexane at −20 °C. X-ray crystal structure determinations determined that these two types of crystals are different crystallographic forms of the same chemical species, [Cr(tBuNC(CH$_3$)-NEt)$_2$]$_2$.[10] The crystal and molecular structure of the metallic green modification is described below. Complex **3** was further characterized by spectral and analytical data, as detailed below.
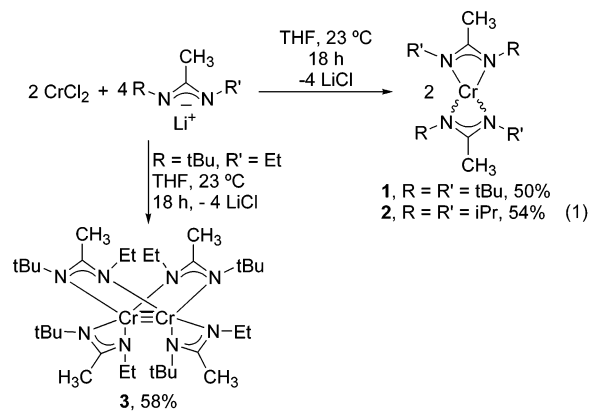


Figure 1 contains a perspective view of **3** (metallic green crystals), along with selected bond lengths and angles. The chromium atoms occupy two alternate sets of positions in a 50:50 ratio. Each chromium atom is bonded to the nitrogen atoms of one amidinate ligand in a terminal, chelating $\eta^2$-fashion and to the nitrogen atoms of two amidinate ligands with $\mu_2$-interactions. The $\mu_2$-ligands are cis within the dimer, apparently to make room for the $\eta^2$-ligands. The $\eta^2$-interactions are characterized by chromium−nitrogen bond lengths of 2.0439(16) (Cr(1)−N(1)) and 2.0479(17) Å (Cr(1)−N(2)). The $\mu_2$-amidinato interactions have chromium−nitrogen bond lengths of 2.1154(17) (Cr(1)−N(1)′) and 2.1673(17) Å (Cr(1)−N(2)′). The chromium−chromium distance is 1.9601(12) Å. The geometry around each chromium atom can be viewed as distorted square pyramidal with the chromium atom being the axial bond of each square pyramid. The distorted square pyramidal distortion is characterized by N(1)−Cr(1)−N(2), N(1)−Cr(1)−N(2)′′, N(1)′-Cr(1)−N(2)′′, and N(1)′−Cr(1)−N(2) angles of 66.04(7), 96.25(6), 97.57(7), and 97.76(6)°. The Cr−Cr−N angles have an average value of 99.63°. The N−Cr−Cr−N torsional angle within the $\mu_2$-amidinate ligands is 17.9°, while the corresponding value for the $\eta^2$-amidinate ligands is 19.1°. Thus, the CrN$_4$ fragments are twisted slightly from being perfectly eclipsed along
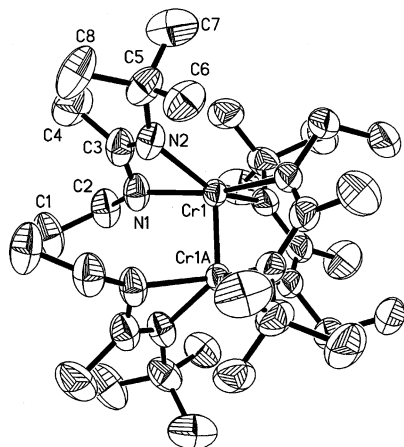
**Figure 1.** Perspective view of **3**. Selected bond lengths (Å) and angles (deg): Cr(1)−N(1) 2.0439(16), Cr(1)−N(2) 2.0479(17), Cr(1)−N(1)′ 2.1154(17), Cr(1)−N(2)′ 2.1673(17), Cr(1)−Cr(1A) 1.9601(12), N(1)−Cr(1)−N(2) 66.04(7), N(1)−Cr(1)−N(2)′ 96.25(6), N(1)′−Cr(1)−N(2)′ 97.57(7), N(2)−Cr−N(1)′ 97.76(6), N(1)−Cr(1)−N(1)′ 163.80(7), N(2)−Cr(1)−N(2)′ 145.09(6).

the chromium−chromium axis, apparently due to steric interactions involving the *tert*-butyl groups.

Complex **3** was further characterized by CP/MAS $^{13}$C NMR spectroscopy, magnetic susceptibility measurements, $^{1}$H NMR spectroscopy in solution, and freezing point depression molecular weight measurements. The solid-state $^{13}$C NMR spectra of **3** clearly showed the two different sets of resonances for terminal and bridging amidinate ligands. Moreover, solid **3** was diamagnetic by magnetic susceptibility measurements. However, $^{1}$H NMR spectra in benzene-$d_6$ showed extremely broad resonances and were similar to those of **1** and **2**. A $^{1}$H NMR spectrum of **3** in toluene-$d_8$ at −80 °C still showed extremely broad resonances, ruling out a dynamic process involving interchange of the two amidinate ligand sites. Freezing point depression molecular weight determinations of a 0.096 M solution in benzene revealed molecular weights of 331 and 348, which are within experimental error (±10%) of the molecular weight expected for a monomeric formulation (334). Magnetic moment measurement in benzene using the Evans method[11] afforded a value of $\mu_{eff} = 4.69$, which is close to the values of **1** and **2**. Thus, **3** dissociates into two monomers in benzene solution.

In **1**−**3**, we have progressively lowered the steric profile of the alkyl groups attached to the amidinate nitrogen atoms. Gambarotta previously described the structural effects of changing the steric profile of the group attached to the amidinate core carbon atom in chromium(II) complexes.[9] As in our study, the smallest group (H) promoted the formation of [Cr(C$_6$H$_{11}$NCHNC$_6$H$_{11}$)$_2$]$_2$ with a short chromium−chromium distance (1.913(3) Å), while larger carbon substituents afforded tetrahedral or square planar monomeric species, depending on the steric profile of the groups attached to the nitrogen atoms. In particular, the properties of **1** and **2** mirror those of the monomeric complexes reported by Gambarotta. However, the chemical behavior of **3** is quite distinct from that of [Cr(C$_6$H$_{11}$NCHNC$_6$H$_{11}$)$_2$]$_2$. In contrast to **3**, [Cr(C$_6$H$_{11}$NCHNC$_6$H$_{11}$)$_2$]$_2$ adopted a normal lantern structure with four bridging amidinate ligands. In addition, this complex exhibited a normal $^{1}$H NMR spectrum in benzene-$d_6$, implying retention of the dimeric structure in this medium and concomitant antiferromagnetic coupling between the chromium(II) centers. By contrast, **3** breaks into paramagnetic monomers upon dissolution in benzene-$d_6$ and in the absence of any added neutral Lewis bases. Previous examples of dimer cleavage in chromium(II) complexes have involved the formation

of monomeric complexes containing relatively strong bonds to neutral nitrogen or oxygen donor ligands, which still allows for a relatively strong chromium−chromium bond (i.e., sum of bond energies of the new metal−ligand bonds in monomers). Factors that contribute to the facile dissociation of **3** into monomers include the presence of only two bridging amidinate ligands, the steric bulk of the *tert*-butyl substituents, as well as a lack of perfect orbital alignment along the chromium−chromium axis. Our results imply that the chromium−chromium bond strength in **3** cannot exceed the difference in solvation energies between the dimer and two monomers plus any increase in metal−nitrogen bond strengths in the monomer. While we do not have an exact value for the chromium−chromium bond strength in **3**, it cannot be large and may be on the order of crystal packing forces. In this vein, Gambarotta has proposed that the metal−metal bond in [Li(THF)]$_4$-[Me$_8$Cr$_2$] is stabilized by Li$^+$−CH$_3$ agostic interactions and that the short chromium−chromium bond length may simply correspond to optimization of these agostic interactions.[5b] Previous estimates of metal−metal bond strengths have ranged from 49 kcal/mol in Cr$_2$(O$_2$CCH$_3$)$_4$[5c] to perhaps as low as 10.8 kcal/mol in Cr$_2$(O$_2$-CCH$_3$)$_4$(H$_2$O)$_2$.[8b]

**Supporting Information Available:** Synthetic procedures, analytical and spectroscopic data for **1**−**3** (PDF). An X-ray crystallographic file for **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

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(10) Spectral and analytical data for **1**−**3** are provided in the Supporting Information. We will describe the full structural details of **1**−**3** in a later full paper.

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