Communication

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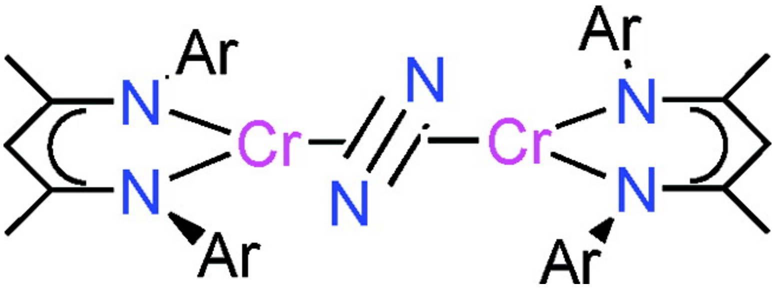

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Binding and Activation of Small Molecules by Three-Coordinate Cr(I)

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Continuing our exploration of chromium chemistry enabled by "nacnac" (i.e., β-diketiminate) ligands,[1] we have turned our attention to low formal oxidation states. More specifically, we wish to explore the structure and reactivity of monovalent chromium (Cr(I)), a relatively rare oxidation state of said metal. Herein we report the synthesis of a versatile precursor molecule—namely an unusual Cr(I) dinitrogen complex—and its reactions with various small molecules of interest.

Reaction of CrI_2 with (i-$Pr_2Ph)_2$nacnacLi yielded the dinuclear iodide [(i-$Pr_2Ph)_2$nacnacCr(μ-I)$]_2$ (**1**) as green crystals in high yield (87%). Magnesium reduction of **1** in THF under a nitrogen atmosphere resulted in a color change to brown within 24 h. Crystallization of the reaction product from pentanes produced [(i-$Pr_2Ph)_2$nacnacCr$]_2$(μ-N_2) (**2**) in 67% yield. The structure of **2** has been determined by X-ray diffraction, and the result is shown in Figure 1. Chromium dinitrogen complexes are rare,[2] and **2** is the only example featuring side-on bonding of N_2 in the μ_2-η^2:η^2 coordination mode.[3] The N−N distance of 1.249(5) Å implies a modest degree of reduction of the N_2 molecule. The facile ligand substitution chemistry exhibited by **2** (vide infra) suggests a description as a Cr(I) complex containing a dinitrogen ligand that is not "activated" with respect to hydrogenation to ammonia,[3] but a formal oxidation state of Cr(II) with a N_2^{2-} ligand could also be considered. **2** features isotropically shifted and broadened ^{1}H NMR resonances, and its effective magnetic moment (μ_{eff}(293 K) = 3.9(1) μ_B) suggests antiferromagnetic coupling between the two Cr atoms.

The reactivity of **2** is marked by ready displacement of the N_2 ligand by a variety of molecules, such as π-acids or potential oxidants. Scheme 1 shows some representative and interesting examples. The molecular structures of **3** and **4** are shown in Figure 2; some relevant observations follow.

2 reacts rapidly with molecules that are stronger back-bonders than N_2. Thus, exposure of a THF solution of **2** to CO (1 atm) produced carbonyl complex [(i-$Pr_2Ph)_2$nacnacCr$]_2$(CO)(μ-η^1:η^1-CO$)_2$ (**3**) as green crystals in 63% isolated yield. Remarkably, **3** is neither symmetric nor diamagnetic. One terminal carbonyl and two μ-isocarbonyls are C-bonded to square pyramidal Cr1, whereas the square planar coordination environment of Cr2 is completed by a nacnac ligand and two carbonyl oxygens. The IR spectrum of **3** features CO stretching bands at 1919, 1616, and 1577 cm^{-1}. **3** is best thought of as a mixed-valent (Cr^0Cr^{II}) complex, and its magnetism (μ_{eff}(293 K) = 4.8(1) μ_B) is consistent with such a description, in which Cr1 is diamagnetic (low-spin d^6) and Cr2 has four unpaired electrons (high-spin d^4).

Reaction of **2** with ethylene formed another unusual organometallic molecule, namely, [(i-$Pr_2Ph)_2$nacnacCr$]_2$(μ-η^2:η^2-C_2H_4) (**4**). Binuclear **4** features a single ethylene ligand symmetrically coordinated to two metal centers. The C−C distance of 1.482(6) Å is consistent with binding of neutral ethylene to two electron-rich π-basic Cr(I) centers. While the Dewar−Chatt−Duncanson model can certainly be adapted to fit this situation, the μ-η^2:η^2 bonding mode of ethylene is rare.[4] The ^{1}H NMR spectrum of **4** did not change upon exposure to excess ethylene (1 atm), providing no evidence for a reversible dissociation into mononuclear ethylene complexes. We look forward to an investigation of analogues of **4** and their reactivity.

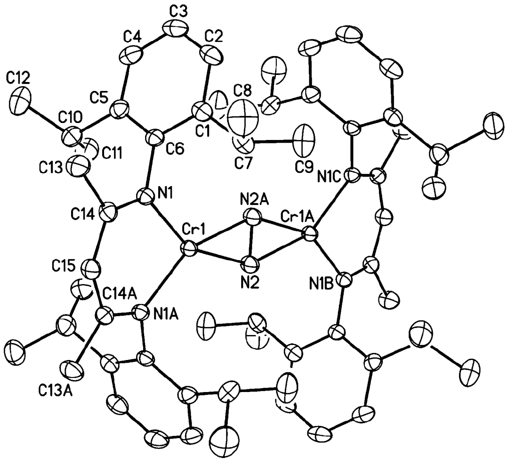
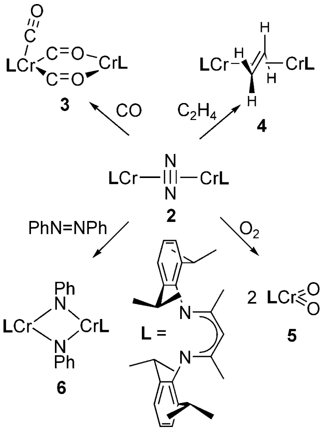


Figure 1. The molecular structure of **2** (30% probability level); all six N and two Cr atoms are approximately coplanar. Selected interatomic distances (Å) and angles (deg): N2−N2A, 1.249(5); Cr1−N1, 2.0264(16); Cr1−N2, 2.0209(9); Cr1−N2−Cr1A, 144.00(13); Cr1−N2−N2A, 72.00(6).

Scheme 1. Reactions of **2** with CO, C_2H_4, O_2, and PhN═NPh



Potential oxidants replace the N_2 ligand of **2**, resulting in products of oxidative addition. For example, dioxygen—a molecule of some interest to us[5] and many others,[6] in the context of aerobic oxidation catalysis—reacted with **2** to yield (i-$Pr_2Ph)_2$nacnacCr(O$)_2$ (**5**), that is, a mononuclear Cr(V) dioxo complex (μ_{eff}(293 K) = 1.8(1) μ_B, consistent with a d^1 configuration). This reaction is of note as a rare example of a four-electron oxidative addition of O_2 to a single metal center. The detailed mechanism of this transformation, probably involving bi- or mononuclear superoxide and peroxide intermediates, will be interesting to unravel.

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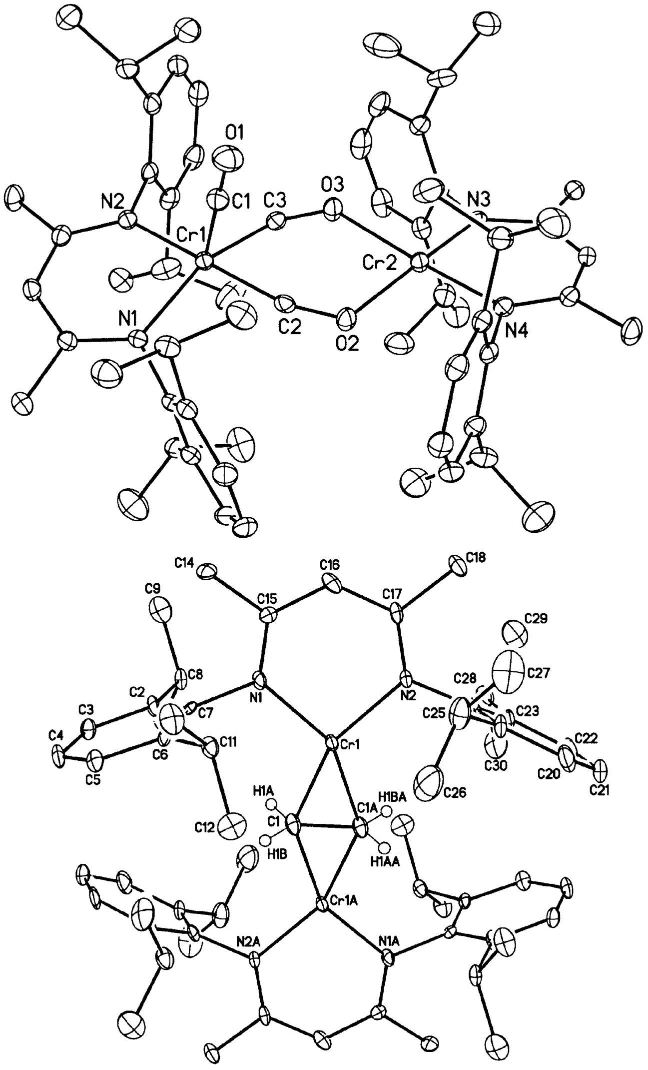

Figure 2. The molecular structures of **3** and **4** (both at 30% probability level); selected interatomic distances (Å) and angles (deg) for **3**: Cr1−C1, 1.833(2); Cr1−C2, 1.797(2); Cr1−C3, 1,797(2); Cr2−O2, 2.0894(15); Cr2−O3, 2.0905(15); C2−O2, 1.203(2); C3−O3, 1.204(2); Cr1−C2−O2, 162.04(16); Cr1−C3−O3, 160.32(16); C2−O2−Cr2, 122.34(12); C3−O3−Cr2, 123.59(13); **4**: Cr1−C1, 2.151(3); Cr1−C1A, 2.168(3); C1−C1A, 1.482(6); Cr1−C1−Cr1A, 139.87(16); Cr1−C1−C1A, 70.6(2).

Intermediate between O_2 (which oxidatively adds) and C_2H_4 (which merely binds) is diimine (N_2H_2). Due to the instability of this simple molecule, we chose its phenyl derivative azobenzene (Ph−N═N−Ph) as a stand-in. Addition of 1 equiv of azobenzene to a THF solution of **2** produced $[(i\text{-}Pr_2Ph)_2\text{nacnacCr}]_2(\mu\text{-NPh})_2$ (**6**). The structure of **6** (see Supporting Information) showed it to be a binuclear Cr(III) complex joined by two bridging phenylimido ligands. Apparently, oxidative addition of the N═N double bond has taken place,[7] halting, in this instance, at the +III formal oxidation state. Like all other molecules described here, **6** is paramagnetic and its magnetic moment ($\mu_{\text{eff}}(293\text{ K}) = 2.6(1)\ \mu_B$) is reasonably attributed to antiferromagnetic coupling of two Cr(III) ions (d^3) mediated by the bridging ligands.

With dinitrogen complex **2**, we have prepared a readily accessible and reactive Cr(I) synthon. The chemistry described here is merely the tip of an iceberg; further studies of Cr(I) compounds are in progress in this laboratory.

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Supporting Information Available: Experimental details regarding the synthesis and characterization of **1**−**6** (pdf) and the X-ray structure determinations of **2**−**6** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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