Communication

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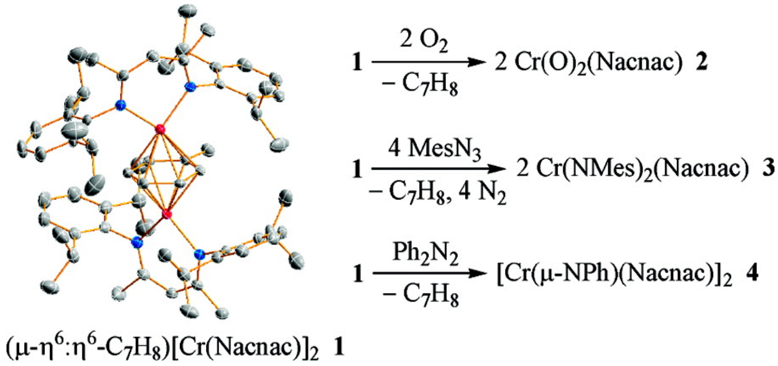
J. Am. Chem. Soc., **2007**, 129 (26), 8066-8067• DOI: 10.1021/ja072003i • Publication Date (Web): 13 June 2007



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Inverted-Sandwich Dichromium(I) Complexes Supported by Two β-Diketiminates: A Multielectron Reductant and Syntheses of Chromium Dioxo and Imido

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Low-coordinate mononuclear transition-metal complexes are interesting not only in the structural motifs, but also in the reactivity toward small molecules.[1] For instance, Cummins et al. have demonstrated the remarkable three-coordinate complex $Mo(N[R]Ar)_3$ capable of splitting dinitrogen and thus forming the nitride $Mo(N)(N[R]Ar)_3$ under mild conditions.[2] Recently, β-diketiminates have received considerable attention as ancillary ligands for metal complexes.[3] Of particular interest is their ability in stabilizing unusual low-coordinate univalent transition metals.[4−6] Our interest in β-diketiminato complexes focuses on the synthesis and reactivity of Cr(I) complexes. In this communication, we describe the reduction of a β-diketiminato−Cr(II) complex in toluene. The resulting product has been characterized and its reactivity examined with dioxygen, organoazide, and azobenzene to provide a family of structurally diverse Cr(V) dioxo and imido complexes. It thus reveals that this compound is a useful reagent for the generation of the "Cr(Nacnac)" species, which acts as a four-electron reductant.

Reduction of $[Cr(\mu\text{-}Cl)(Nacnac)]_2$ (Nacnac = $HC(C(Me)NC_6H_3\text{-}i\text{-}Pr_2)_2$)[7] with KC_8 in toluene affords an inverted sandwich compound in which a toluene molecule bridges two Cr(Nacnac) fragments in an η^6,η^6 fashion.[8] Compound **1**, $(\mu\text{-}\eta^6{:}\eta^6\text{-}C_7H_8)[Cr(Nacnac)]_2$, is obtained in 88.2% yield as a dark-purple crystalline substance. The compound is paramagnetic between 50 and 300 K and exhibits a solid-state magnetic moment of ca. 6.75 μ_B, as measured by SQUID magnetometry, consistent with an $S = 3$ ground state. To facilitate assignment of the NMR spectrum of **1**, the deuterated variant **1**-d_8 was prepared by carrying out the synthesis in toluene-d_8. The four resonances for the bound toluene were thereby identified at 17.8, 14.2, 12.9, and 12.4 ppm in the ^2H NMR spectrum of the compound; the high-field resonances are assigned to the aryl deuterons, and the downfield signal signifies the deuteriomethyl group. It was found also that benzene-bridged dichromium compound could be obtained by carrying out the KC_8 reaction in C_6D_6, and a single resonance peak was observed at 13.7 ppm in the ^2H NMR spectrum of $(\mu\text{-}C_6D_6)[Cr(Nacnac)]_2$, in accord with the chemical shift assignments for **1**.

X-ray crystallography was used to confirm the dinuclear nature of compound **1** as shown in Figure 1. Interestingly, the two (Nacnac)Cr six-member rings are arranged in an orientation with a N(1)−Cr(1)−Cr(2)−N(4) torsion angle of 57.3°. Whereas Cr(2)−C distances to the toluene ring are approximately equal and average to 2.264(4) Å, corresponding Cr(1)−C distances range from 2.221(4) to 2.471(3) Å, the longest distance being to one of the methyl group substituted carbon atoms of the ring. Both chromium atoms tend toward the same edge, C(62)−C(63), and as a result the whole molecule is distorted. The average C−C distance for the bridging toluene molecule was determined to be 1.431(5) Å. The six-membered rings of **1** adopt a planar conformation. The arene thus undergoes a slight (ca. 0.04 Å) increase in d_{C-C} upon complexation, relative to free toluene.[9]

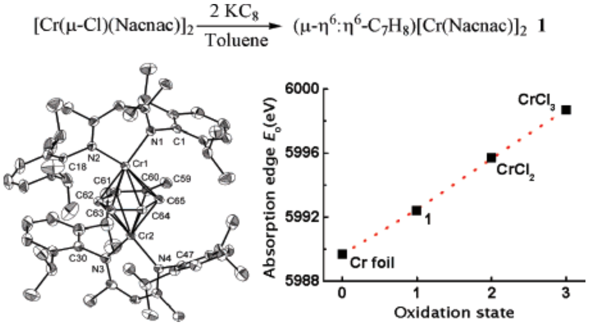

Figure 1. Synthesis and molecular structure of **1** with thermal ellipsoids at the 30% probability level and a plot of X-ray absorption edge energy E_0 vs oxidation states of Cr.

Formulation of compound **1** as $(\mu\text{-}C_7H_8)[Cr(Nacnac)]_2$ implies various possibilities for the chromium valency. One extreme requires a formally univalent chromium center. To clarify the detailed electronic structure of the chromium ions in **1**, the X-ray absorption measurements were undertaken. The Cr K-edge absorption spectra of Cr foil, **1**, $CrCl_2$, and $CrCl_3$ are displayed in Figure S2 (Supporting Information). A plot of X-ray absorption edge E_0 versus various oxidation states of Cr displays a linear relationship (Figure 1), suggesting an oxidation state of I for Cr in **1**. The chemical reactivity of compound **1** is also consistent with the formality of univalent chromium, inasmuch as **1** behaves as an 8-electron reductant, giving rise to chromium(V) derivatives and extruding neutral toluene upon reaction with appropriate substrates.

Metal complexes in which benzene or toluene bridges two metal centers in an η^6,η^6 fashion are rare.[10−13] Inspired by Cummins and Evans' arene-bridged diuranium complexes displaying remarkable reactivity,[11,12] we were also interested in exploring the reactivity of **1**. Noteworthy is that **1** readily undergoes arene exchange reactions with retention of the inverted sandwich structure. The dissolution of **1** in C_6D_6 results in the formation of $(\mu\text{-}C_6D_6)[Cr(Nacnac)]_2$ as well, and **1** is thus believed to act as two Cr(Nacnac) synthetic equivalents. Addition of several equivalents of dry oxygen to **1** in ether at room-temperature elicits a rapid color change from purple to orange-brown, signaling the formation of the mononuclear dioxo complex $Cr(O)_2(Nacnac)$ (**2**) that may be isolated in 53.4% yield as dark-brown crystals. The X-ray structure of **2** consists of two terminal oxo atoms attached to a tetrahedral chromium center (Figure 2).

Compound **2** is subjected to a detailed EPR study as a result of its solution magnetic moment of 1.71 μ_B at room temperature. The room-temperature EPR spectrum of **2** in toluene displays a sharp isotropic signal at $g_{iso} = 1.9779$. It features an intense central

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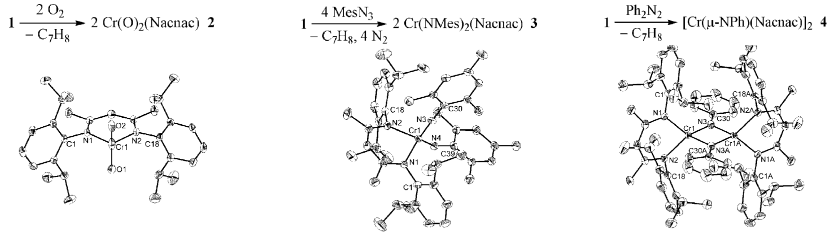
10.1021/ja072003i CCC: $37.00 © 2007 American Chemical Society



$$1 \xrightarrow[-\ C_7H_8]{2\ O_2} 2\ Cr(O)_2(Nacnac)\ \mathbf{2}$$

$$1 \xrightarrow[-\ C_7H_8,\ 4\ N_2]{4\ MesN_3} 2\ Cr(NMes)_2(Nacnac)\ \mathbf{3}$$

$$1 \xrightarrow[-\ C_7H_8]{Ph_2N_2} [Cr(\mu\text{-}NPh)(Nacnac)]_2\ \mathbf{4}$$

Figure 2. Reactivity of **1** and X-ray molecular structures of **2**−**4**.

resonance of five lines attributable to coupling of the unpaired electron to two magnetically equivalent ^{14}N nuclei of the Nacnac ligand. Successful simulation of the observed spectrum is achieved by specifying two hyperfine couplings: $A_{iso}[^{53}Cr, 9.54\%] = 1.55$ G and $A_{iso}[^{14}N, 99.63\%] = 2.25$ G.

Reaction of **1** with four equivalents of N_3Mes (Mes = 2,4,6-$Me_3C_6H_2$) in ether leads to rapid effervescence and formation of the tetrahedral $Cr(NMes)_2(Nacnac)$ (**3**) which is isolated in 32.6% yield as dark green crystals. Its solution magnetic moment of 2.02 μ_B at room temperature is consistent with an $S = {}^1/_2$. The X-ray structure of **3** (Figure 2) reveals a four-coordinated and crowded Cr center. The critical distances (Å) and angles (deg) are Cr(1)−N(1) = 2.006(3), Cr(1)−N(2) = 1.996(3), Cr(1)−N(3) = 1.663(3), Cr(1)−N(4) = 1.692(3), Cr(1)−N(3)−C(30) = 174.2(2), and Cr(1)−N(4)−C(39) = 154.0(2)°. Complex **3** accordingly features two different imido substituents, one bent and one linear. Having two different imido ligands is common for bis(imido) complexes in the solid state; however, the two imido groups almost invariably equilibrate in solution, based on NMR spectroscopy.[14] In contrast, there are two nonequivalent imido substituents observed in the solution EPR of **3** (Supporting Information). The room-temperature EPR spectrum of **3** in toluene displays an isotropic signal at $g_{iso} = 1.98026$. The spectrum is attributable to coupling of the unpaired electron to two magnetically equivalent ^{14}N nuclei of the Nacnac ligand and two nonequivalent ^{14}N nuclei of the two imido ligands. Successful simulation of the observed spectrum is achieved by specifying four hyperfine couplings: $A_{iso}[^{53}Cr, 9.54\%] = 8.0$ G, $A_{iso}[^{14}N, 99.63\%] = 3.8$ G (two from the Nacnac ligands), $A_{iso}[^{14}N, 99.63\%] = 1.8$ G, and $A_{iso}[^{14}N, 99.63\%] = 1.3$ G. The sterically encumbered Dipp and Mes substituents apparently prohibit equilibration of the two imido groups in solution on the EPR time scale.

Azobenzene reductive cleavage to form bisphenylimido derivatives represents an intriguing N−N bond cleavage process.[11,12,15] Treatment of **1** with 1 equiv of azobenzene in THF leads to a color change to greenish-yellow in 4 h. A yellow crystalline compound is thereby obtained in 23% isolated yield, formulated as the chromium(III) phenylimido-bridged dimmer $[Cr(\mu\text{-}NPh)(Nacnac)]_2$ (**4**) by virtue of a single-crystal X-ray diffraction study. No bonding interaction between N(3) and N(3A) is indicated by the relevant internuclear N···N distance of 2.598(7) Å. Its room temperature solution magnetic moment of 3.87 μ_B implies **4** exhibits an antiferromagnetic behavior.

In conclusion, a remarkable inverted-sandwich dichromium complex **1** is successfully synthesized and fully characterized. Preliminary reactivity studies of **1** establish that the "Cr(Nacnac)" platform will at least support three formal oxidation states (Cr^I, Cr^{III}, Cr^V). Reactions of **1** and other organic functionalities are ongoing and will be reported in due course.

Acknowledgment. We are indebted to the Taiwan, R.O.C. National Science Council for support under Grant NSC 94-2113-M-007-033. Mr. Ting-Shen Kuo (National Taiwan Normal University) is acknowledged for help with crystallographic details. We also thank Professor Daniel J. Mindiola for insightful comments.

Supporting Information Available: Experimental details for the synthesis, X-ray crystallographic data of **1**, **2**, **3**, and **4** including tables and CIF files, X-ray absorption spectrum of **1**, and SQUID data of **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA072003I