J|A|C|S
COMMUNICATIONS

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

Wesley H. Monillas, Glenn P. A. Yap, Leonard A. MacAdams, and Klaus H. Theopold*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received April 12, 2007; E-mail: theopold@udel.edu

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.

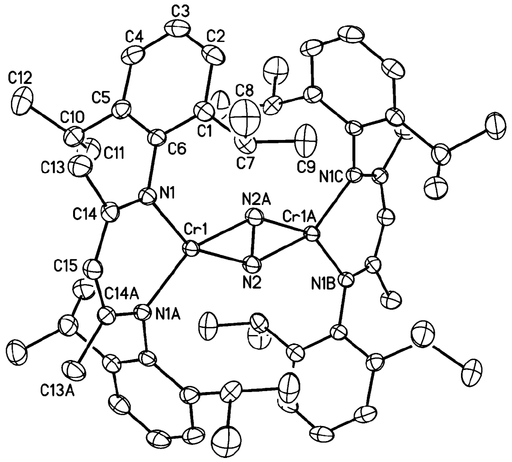
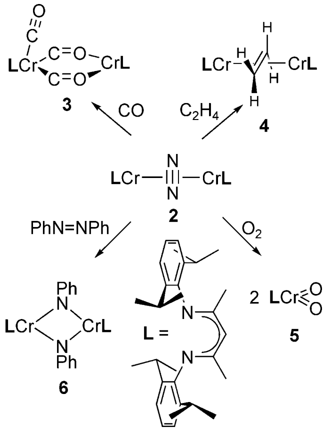


Figure 1. The molecular structure of **2** (30% probability level); all six N and two Cr atoms are approximately coplanar. Selected interatomic distances (Å) and angles (deg): N2−N2A, 1.249(5); Cr1−N1, 2.0264(16); Cr1−N2, 2.0209(9); Cr1−N2−Cr1A, 144.00(13); Cr1−N2−N2A, 72.00(6).

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.

10.1021/ja0725549 CCC: $37.00 © 2007 American Chemical Society

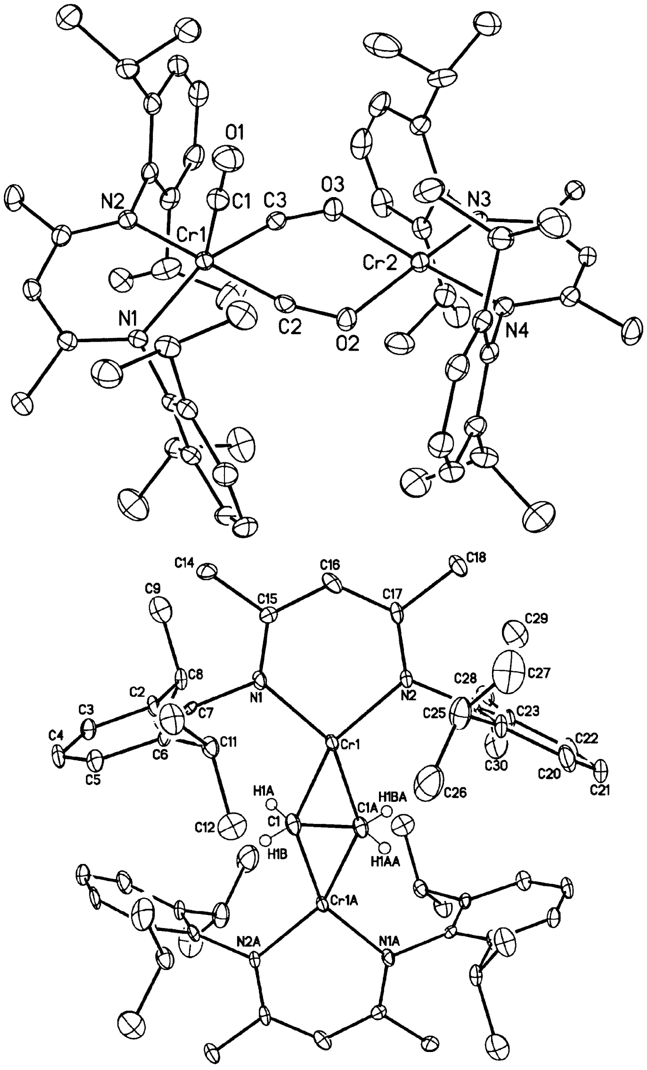


Figure 2. The molecular structures of **3** and **4** (both at 30% probability level); selected interatomic distances (Å) and angles (deg) for **3**: Cr1−C1, 1.833(2); Cr1−C2, 1.797(2); Cr1−C3, 1,797(2); Cr2−O2, 2.0894(15); Cr2−O3, 2.0905(15); C2−O2, 1.203(2); C3−O3, 1.204(2); Cr1−C2−O2, 162.04(16); 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 $[(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}]_2(\mu\text{-NPh})_2$ (**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.

Acknowledgment. This research was supported by NSF (CHE-0616375) and DOE (DE-FG02-92ER14273). We thank P. Tobash and S. Bobev for help with the preparation of chromous iodide.

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.

References

(1) (a) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543. (b) MacAdams, L. A.; Kim, W. K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952−960. (c) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164−1165. (d) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 1082−1083.

(2) (a) Richards, R. L.; Chatt, J.; Fay, R. C. *J. Chem. Soc. A* **1971**, 702−704. (b) Sellmann, D.; Brandl, A.; Endell, R. *J. Organomet. Chem.* **1975**, *90*, 309−318. (c) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954−5956. (d) Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1984**, *23*, 3830−3833. (e) Denholm, S.; Hunter, G.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2789−2791. (f) Zhang, Q.-F.; Chim, J. L. C.; Lai, W.; Wong, W.-T.; Leung, W.-H. *Inorg. Chem.* **2001**, *40*, 2470−2471.

(3) (a) For a recent review, see: MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530−1543.

(4) (a) Cotton, F. A.; Kibala, P. A. *Polyhedron* **1987**, *6*, 645−646. (b) Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 3192−3196. (c) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Taylor, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 5831−5832. (d) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915−917. (e) Takahashi, T.; Kasai, K.; Suzuki, N.; Nakajima, K.; Negishi, E. *Organometallics* **1994**, *13*, 3413−3414. (f) Fischer, R.; Walther, D.; Gebhardt, P.; Goerls, H. *Organometallics* **2000**, *19*, 2532−2540. (g) Dube, T.; Gambarotta S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1432. (h) Shapiro, P. J.; Cotter, W. D.; Schaefer W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (i) Fernandez, F. J.; Gomez-Sal, P.; Manzanero, A.; Royo, P.; Jacobsen, H.; Berke, H. *Organometallics* **1997**, *16*, 1553−1561.

(5) (a) Hess, A.; Hörz, M. R.; Liable-Sands, L. M.; Lindner, D. C.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem. Int. Ed.* **1999**, *38*, 166−168. (b) Hess, J. S.; Leelasubcharoen, S.; Rheingold, A. L.; Doren, D. J.; Theopold, K. H. *J. Am. Chem. Soc.* **2002**, *124*, 2454−2455. (c) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333−2335.

(6) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) Martell, A. E.; Sawyer, D. T. *Oxygen Complexes and Oxygen Activation by Transition Metals*; Plenum Press: New York, 1988. (c) Meyer, F.; Limberg, C. *Organometallic Oxidation Catalysis*; Springer: Berlin, 2007; Vol. 22.

(7) (a) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983−4994. (b) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760−1772. (c) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−248. (d) Aubart, M. A.; Bergman, R. G. *Organometallics* **1999**, *18*, 811−813. (e) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, *122*, 6108−6109. (f) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752−15753. (g) Kilgore, U. J.; Yang, X.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2006**, *45*, 10712−10721.

JA0725549