Therefore, we assume that the reactions proceed via a common labile intermediate which upon workup decomposes to give adducts I or, alternatively, reacts further with alkyne to afford rhenapyrans III.

Supplementary Material Available: Details of the analytical and spectroscopic results (3 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Polynuclear Chromium(III) Alkyls. Crystal Structure of a Paramagnetic μ_3-Methylidyne Complex with Short Nonbonded Cr–Cr Contacts

Darrin S. Richeson, Shih-Wen Hsu, Natalie H. Fredd, Gregory Van Duyne, and Klaus H. Theopold*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received August 27, 1986

Organometallic chemistry is dominated by diamagnetic molecules. Recently, however, appreciation has been growing for the importance of radical reactions and metallaradicals in this area of chemistry.[1] Herein we describe some paramagnetic chromium(III) alkyls and the facile conversion of a methyl ligand into a μ_3-methylidyne fragment.

Addition of 1 equiv of TlCp to a stirred Et_2O solution of $MeCrCl_2(THF)_3$[2] at room temperature resulted in a rapid color change from green to dark red. After 30 min the solution was filtered, the solvent evaporated, and the solid residue recrystallized from Et_2O to yield dark red crystals of bis(μ-chloro)dimethylbis(η^5-cyclopentadienyl)dichromium (**1**) in 90% yield (Scheme I).[3] In an analogous reaction of $EtCrCl_2(THF)_3$ the corresponding ethyl dimer **2** was formed in 78% yield.

The molecular structure of **1** was determined by X-ray diffraction (Figure 1).[4] The dimeric molecule has crystallographic C_i symmetry and features the pseudooctahedral coordination geometry of a three-legged piano stool around chromium. Two bridging chloride ligands hold the dimer together, and the methyl groups stand trans to each other. The Cr–Cr distance of 3.29 Å is too long to allow for metal–metal bonding, giving each chromium a 15-electron configuration. The magnetic susceptibility of **1** was measured in the temperature range 3–300 K, and the temperature dependence of χ_m is characteristic of an antiferromagnetically coupled dimer (μ_{eff}(300 K) = 3.58 μ_B). The data were fitted by using the Heisenberg–Dirac–Van Vleck (HDVV) model for a dimer of two $S = {}^3/_2$ ions giving $J = -72$ cm^{-1}.[5]

Alkyl dimers **1** and **2** are air sensitive both in solution and in the solid state. They dissolve readily in common organic solvents, and such solutions are stable at room temperature for several hours. Added nucleophiles rapidly cleave the dimers, forming a series of mononuclear chromium(III) alkyl complexes (see Scheme I).[6]

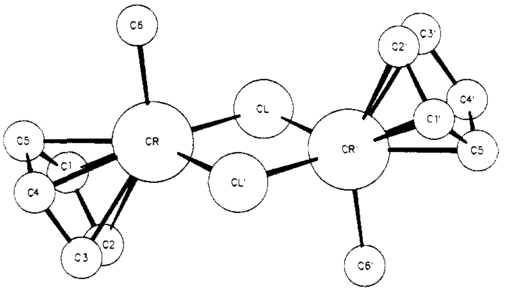


Figure 1. Molecular structure of **1**. Selected bond distances: Cr–Cr', 3.287 (1); Cr–C6, 2.073 (3); Cr–Cl, 2.355 (1); Cr–Cl', 2.357 (1) Å. Interatomic angles: Cr–Cl–Cr', 88.5 (1)°; Cl–Cr–Cl', 91.5 (1)°; Cl–Cr–C6, 94.2 (1)°; Cl'–Cr–C6, 95.0 (1)°.

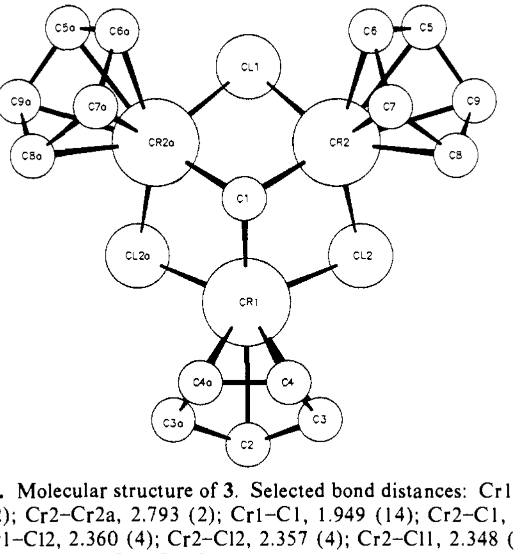
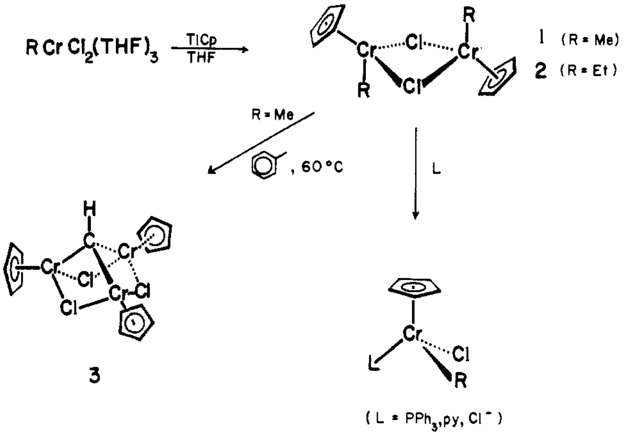


Figure 2. Molecular structure of **3**. Selected bond distances: Cr1–Cr2, 2.837 (2); Cr2–Cr2a, 2.793 (2); Cr1–C1, 1.949 (14); Cr2–C1, 1.935 (10); Cr1–Cl2, 2.360 (4); Cr2–Cl2, 2.357 (4); Cr2–Cl1, 2.348 (4) Å. Interatomic angles: Cr1–C1–Cr2, 93.8 (5)°; Cr2–C1–Cr2a, 92.4 (6)°; Cr1–Cl2–Cr2, 73.9 (1)°; Cr2–Cl1–Cr2a, 73.0 (1)°.

Scheme I



(L = PPh_3, py, Cl^-)

When a toluene solution of **1** was heated to 60 °C for several hours, the color of the solution changed from dark red to purple. At the same time methane, ethane, and ethylene were evolved. Filtration, removal of solvent, and extraction of the residue with THF yielded purple needles of the trinuclear chromium complex **3** in 24% yield.[7] The nature of this compound became clear only as the result of a crystal structure determination (Figure 2).[8] the molecule exhibits crystallographic C_s symmetry only (Cl1, C1,

---

(1) (a) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (b) Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, 80. (c) Halpern, J. *Angew. Chem.* **1985**, *97*, 308. (d) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

(2) Nishimura, K.; Kuribayashi, H.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1972**, *37*, 317.

(3) **1**: IR (Nujol) 3080 (wk), 1108 (m), 1017 (m), 1003 (m), 839 (m), 827 (s), 812 (s), 802 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 112 (br), 90 (br) ppm. Anal. Calcd for $C_{11}H_{16}Cl_2Cr_2$: C, 43.00; H, 4.81. Found: C, 42.60; H, 4.76. **2**: IR (KBr) 2945 (s), 2846 (s), 1450 (m), 1364 (m), 1117 (s), 1018 (s), 1006 (s), 843 (m), 821 (vs), 797 (vs), 473 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{20}Cl_2Cr_2$: C, 46.30; H, 5.55, Cl, 19.52. Found: C, 46.42; H, 5.63; Cl, 19.60.

(4) Dark red crystals from Et_2O; orthorhombic *Pccn*; $a = 15.667$ (3) Å, $b = 11.421$ (3) Å, $c = 7.858$ (2) Å; $Z = 4$; $R = 0.034$, $R_w = 0.049$.

(5) (a) Martin, R. L. In *New Pathways in Inorganic Chemistry*; Ebsworth, Maddock, Sharp, Eds.; Cambridge University: Cambridge, 1968; Chapter 9. (b) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; Chapter 5. (c) Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

(6) Satisfactory analytical data have been obtained on all complexes. Details of the characterization will be published in a full paper.

(7) **3**: IR (KBr) 3117 (wk), 1606 (wk), 1432 (s), 1355 (wk), 1116 (m), 1014 (s), 808 (s), 804 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 31.0 (br) ppm, μ_3-CH not detected. Anal. Calcd for $C_{16}H_{16}Cl_3Cr_3$: C, 40.83; H, 3.43; Cl, 22.60. Found: C, 40.85; H, 3.53; Cl, 22.85.

(8) Purple crystals from THF/pentane; orthorhombic $Pmn2_1$; $a = 14.743$ (1) Å, $b = 9.5695$ (7) Å, $c = 6.3521$ (5) Å, $Z = 2$; $R = 0.053$, $R_w = 0.043$.

0002-7863/86/1508-8273$01.50/0 © 1986 American Chemical Society

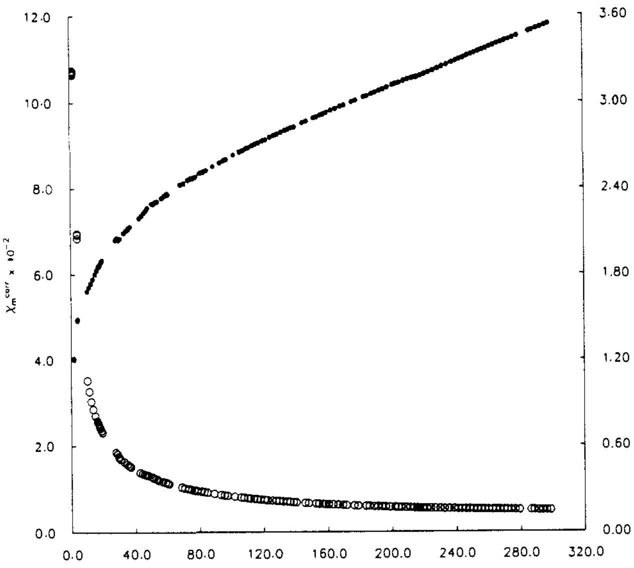


Figure 3. Molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, filled circles) of chromium trimer **3**.

Cr1, and C2 lie on the mirror plane), but the three chromium atoms form an almost perfect equilateral triangle. Sitting atop this triangle is a μ_3-CH group, presumably formed by multiple abstraction of hydrogen from a methyl ligand. Three chloride ligands, each bridging between two chromium atoms, and three cyclopentadienyl groups complete the molecule.

Common to both **1** and **3** is a pseudooctahedral coordination environment around Cr(III) consisting of a cyclopentadienyl ring, two chloride ligands, and an alkyl group. Edge sharing of two such fragments generates **1**, and condensation of three of these units in a doubly edge sharing arrangement results in **3**. Despite these similarities, the structures are remarkably different. Whereas **1** exhibits a Cr–Cr distance of 3.29 Å, that distance decreases to an average value of 2.82 Å in **3**. This is well within the range of distances typical of Cr–Cr single bonds (2.65–2.97 Å).[9] Another manifestation of this shortening is the decrease in the Cr–Cl–Cr angle from 88.5° in **1** to an average value of 73.6° in **3**.[10] The question then arises whether **3** is a true chromium cluster. Does it contain M–M bonds, or is it merely a polynuclear complex with unusually short M–M contacts?

Metal–metal bonding implies spin pairing, and we have therefore studied the magnetic behavior of **3** (Figure 3). The effective magnetic moment of **3** is temperature dependent, indicating an antiferromagnetic interaction between the chromium atoms.[5,11] The phenomenon of molecular antiferromagnetism does not depend on direct metal–metal bonding, as the observation of such interaction in **1** demonstrates. However, in a recent series of papers, Pasynskii et al. have proposed the occurrence of antiferromagnetism in Cr–Cr bonded systems.[12] Their sole criterion for the presence of such bonding seems to be the observed metal–metal distance. We prefer to think of these systems as weakly interacting, i.e., occupying an intermediate position in the spectrum ranging from isolated metal centers to true metal–metal bonds.[13]

There remains the question what, if not metal–metal bonding, is the cause of the drastic contraction of the Cr–Cr distance in **3**? A comparison with other structurally characterized μ_3-CH complexes provides a possible clue.[14] The M–C–M angles in this—albeit small—sample are typically smaller than 90° (ranging from 81.5 to 87.5°). The corresponding average angle of 93.3° in **3** represents a deviation from the preferred hybridization of the μ_3-CH ligand. It may be this structural "clamp" that is responsible for the short Cr–Cr contacts. It remains to be seen whether this situation affects the reactivity of the μ_3-CH group.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (CHE-8451670 and CHE-8512710), the Camille and Henry Dreyfus Foundation, the Atlantic Richfield Foundation, Dow Chemical Co., Rohm and Haas Co., and Cornell University.

Supplementary Material Available: Tables of X-ray structure determinations of **1** and **3** (17 pages); tables of structure factors for **1** and **3** (11 pages). Ordering information is given on any current masthead page.

---

[9] (a) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7312. (b) Vahrenkamp, H. *Chem. Ber.* **1978**, *11*, 3472. (c) Calderon, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W. *J. Organomet. Chem.* **1974**, *64*, C10. (d) McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1858.

[10] Compare with 77.0° in $[Cl_3Cr(\mu\text{-}Cl)_3CrCl_3]^{3-}$: Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; p 466.

[11] (a) Attempts to fit the χ_m data with the HDVV model as applied to an equilateral triangle of $S = {}^3/_2$ ions proved unsatisfactory. However, the room temperature moment of **3** (μ_{eff}(300 K) = 3.55 μ_B) is consistent with $J \approx -110$ cm^{-1}; see ref 11d. (b) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48. (c) Wucher, J.; Gijsman, H. M. *Physica (Amsterdam)* **1954**, *20*, 361. (d) Earnshaw, A.; Figgis, B. N.; Lewis, J. *J. Chem. Soc. A* **1966**, 1656.

[12] (a) Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Yu. V.; Novotortsev, V. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 57. (b) Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Rakitin, Y. V.; Novotortsev, V. M.; Ellert, O. G.; Kalinnikov, V. T. *Inorg. Chim. Acta* **1980**, *39*, 91. (c) Eremenko, I. L.; Pasynskii, A. A.; Gasanov, G. Sh.; Orazsakhatov, B.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *275*, 71 and references therein.

[13] Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

[14] (a) Dimas, P. A.; Duesler, E. N. *J. Am. Chem. Soc.* **1980**, *102*, 7787. (b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (c) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140. (d) Leung, P.; Coppens, P.; McMullan, R. K.; Koetzle, T. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1347. (e) Orpen, A. G.; Koetzle, T. F. *Acta Crystallogr., Sect. B Struct. Sci.* **1984**, *B40*, 606. (f) Vazquez de Miguel, A.; Isobe, K.; Bailey, P. M.; Meanwell, N. J.; Maitlis, P. M. *Organometallics* **1982**, *1*, 1604.

Stereochemistry of the Intramolecular Enamine/Enal (Enone) Cycloaddition Reaction and Subsequent Transformations

Stuart L. Schreiber,* Harold V. Meyers, and
Kenneth B. Wiberg

Sterling Chemistry Laboratory, Department of Chemistry
Yale University, New Haven, Connecticut 06511

Received August 12, 1986

The [4 + 2] cycloaddition reaction of electron-rich olefins with α,β-unsaturated carbonyl compounds is an important transformation in organic synthesis.[1] Enamines are particularly reactive heterodienophiles that often react with heterodienes at room temperature or below. The reaction course is highly dependent on enamine and heterodiene structure and can result in the formation of dihydropyrans, cyclobutanes, and alkylated enamines.[2] We have found the intramolecular reaction of certain enamine/enal (enone) combinations, generated in situ by the action of a secondary alkyl or aryl amine on an aldehyde/enal (enone), proceeds stereoselectively under mild conditions to provide [4 + 2] cycloadducts.[3] Furthermore, the dihydropyran products can

---

[1] Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, 651.

[2] Reviews: (a) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975; (b) Hickmott, P. W. *Ibid.* **1982**, *38*, 3363; (c) Hickmott, P. W. *Ibid.* **1984**, *40*, 2989.

[3] For related studies, see: (a) Clark, K. J.; Fray, G. I.; Jaeger, R. H.; Robinson, R. *Tetrahedron* **1959**, *6*, 217. (b) Snider, B. B.; Roush, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023. (c) Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 3767. (d) Martin, S. F.; Benage, B.; Williamson, S. A.; Brown, S. P. *Tetrahedron* **1986**, *42*, 2903. Professor S. E. Denmark (University of Illinois at Urbana—Champaign) has carried out studies on related reactions that employ thio enol ethers as dienophiles: Denmark, S. E., Sternberg, J. A. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society: Washington, DC, 1985; ORGN 139. See the following paper in this issue.

0002-7863/86/1508-8274$01.50/0 © 1986 American Chemical Society