Hydrolytic Cleavage of the Cr–Cr Triple Bond in $(C_5Me_5)_2Cr_2(CO)_4$. The Formation and Crystal Structure of $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$, an Adamantane Analogue

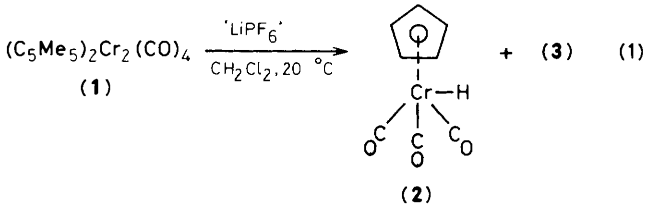
D. Wormsbächer,[a] **K. M. Nicholas,***[a†] **and A. L. Rheingold***[b]

[a] Department of Chemistry, Boston College, Chestnut Hill, MA 02167, U.S.A.
[b] Department of Chemistry, University of Delaware, Newark, DE 19716, U.S.A.

$(C_5Me_5)_2Cr_2(CO)_4(Cr{\equiv}Cr)$ reacts with moist $LiPF_6$ in CH_2Cl_2 at room temperature, or with H_2O directly in refluxing toluene, to produce the mononuclear hydride $(C_5Me_5)Cr(CO)_3H$; the latter reaction also produces a salt $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6][(C_5Me_5)Cr(CO)_3]_2$ whose BF_4^- derivative, $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$, has been characterized by *X*-ray crystallography.

The structure and reactivity of complexes containing metal–metal multiple bonds have been major themes in modern inorganic and organometallic chemistry.[1] A class of complexes receiving considerable attention in this context has been the group 6 species $(cp)_2M_2(CO)_4$ (M≡M) (cp = C_5H_5 or C_5Me_5), especially the Mo derivatives.[2] In the course of seeking Lewis acid-promoted reactions of $(C_5Me_5)_2Cr_2(CO)_4$ with carbon dioxide, we have uncovered a series of novel and rapid reactions involving hydrolysis of the Cr–Cr triple bond.

Stirring a dark green CH_2Cl_2 solution of (**1**) with excess of $LiPF_6$[3] under CO_2, N_2, or Ar results in a gradual colour change to deep blue over a period of 24—78 h and the appearance of new i.r. absorptions at 1995 and 1910 cm^{-1}. The species responsible for these absorptions can be isolated as golden, air sensitive crystals (43%) upon sublimation (60 °C/0.1 mmHg) and has been identified as the hydride complex $(C_5Me_5)Cr(CO)_3H$ (**2**) on the basis of its spectroscopic properties‡ and alternative synthesis *via* protonation of $(C_5Me_5)Cr(CO)_3Na$[4] with acetic acid or treatment of $(MeCN)_3Cr(CO)_3$ with C_5Me_5H.§ An incompletely characterized, blue paramagnetic cyclopentadienyl derivative (**3**) was also obtained which was found (by i.r.) to be devoid of carbonyl ligands.¶



The formation of hydride (**2**), the high oxygen content of (**3**), and the hygroscopicity of $LiPF_6$ led us to suspect the involvement of water in this reaction. Indeed, treatment of (**1**) with aqueous HPF_6 in CH_2Cl_2 also produced (**2**). Moreover, (**1**) reacts with H_2O directly (no acid catalyst) in refluxing aqueous toluene (24 h) to afford (**2**) again (25—35% yield) along with a violet, CH_2Cl_2-soluble pyrophoric solid formulated as $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6][(C_5Me_5)Cr(CO)_3]_2$ (**4**), equation (2).

$$(1)\xrightarrow[\text{toluene}]{H_2O}(2)+\underset{(4)}{[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6][(C_5Me_5)Cr(CO)_3]_2}\quad(2)$$

The structure of (**4**) was established as follows. The presence of the $(C_5Me_5)Cr(CO)_3^-$ ion was indicated by i.r. absorptions (CH_2Cl_2) at 1875, 1760, and 1715 cm^{-1} ‖ and the metathesis of (**4**) with $HBF_4{\cdot}Me_2O$ to give hydride (**2**) [equation (3)]. Also produced in this reaction was a blue paramagnetic salt, $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6](BF_4)_2$, (**5**), ‖ whose structure has been determined by *X*-ray crystallography.

$$(4)\xrightarrow{HBF_4}(2)+\underset{(5)}{[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6](BF_4)_2}\quad(3)$$

Crystal data for (**5**): $C_{40}H_{66}B_2Cr_4F_8O_6$, M = 1024.5, tetragonal, space group $I\bar{4}$, $a = b$ = 12.424(2), c = 15.320(2) Å, U = 2364.5 Å^3, Z = 2, D_c = 1.44 g cm^{-3}, $F(000)$ = 1160, μ(Mo-K_α) = 9.79 cm^{-1}. A deep blue crystal (0.26 × 0.28 × 0.32 mm) was grown from CH_2Cl_2–Et_2O. The structure was solved by direct methods and difference Fourier techniques. Corrections for absorption and a 9% linear decay in reflection intensity were applied to the data. Refinement by a blocked-cascade routine using 929 observed reflections [$F_0 \geqslant 2.5\sigma(F_0)$] and anisotropic temperature factors for the non-hydrogen atoms, with the exception of the atoms of one of the BF_4^- fluorine atoms, led to R_F = 0.066, R_{wF} = 0.072 and GOF = 1.645. One of the two independent BF_4^- ions was unresolvably disordered. Hydrogen atoms were incorporated as fixed contributions after at least one hydrogen atom in each methyl group had been reliably located. No crystallographic evidence for the hydroxy hydrogen atoms was found; their probable positions would suggest two-fold disorder.**

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† Present address: Department of Chemistry, University of Oklahoma, Norman, OK 73019, U.S.A.

‡ (**1**) I.r.(pentane) ν(CO) 2010, 1933, and 1927 cm^{-1}; ^1H n.m.r.(CD_2Cl_2) δ 1.97(s,15H) and 5.68(s,1H); ^{13}C (CD_2Cl_2) δ 238(CO), 101(C_5Me$_5$), and 11(C_5*Me*$_5$). Satisfactory elemental analysis was obtained. Hydride (**2**) has been mentioned previously (ref. 4) but no properties or method of preparation were given, H. G. Alt, K. A. Mahmoud, and A. J. Rest, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 544.

§ $(C_5Me_5)Cr(CO)_3H$ (**2**) displays unusual reactivity towards oxygen. Momentary exposure of a solution of (**2**) to air (or pure O_2) immediately produces a dark red transient species whose spectroscopic properties [i.r. (pentane): ν(CO) 1982, 1930, 1907, and 1890 cm^{-1}; ^1H n.m.r. (C_6D_6) δ 1.48; ^{13}C (CD_2Cl_2) δ 256.1, and 102.9] are distinctly different from those reported for the expected dimer, $(C_5Me_5)_2Cr_2(CO)_6$ (ref. 5). When deprived of air the red species decomposes over several minutes to regenerate (**2**) and dimer (**1**).

¶ Crystals of (**3**) from pentane–CH_2Cl_2 had approximate composition $(C_5Me_5)CrP_{0.8}F_{3.2}O_7$ but thus far have resisted attempts to determine their *X*-ray structure owing to microtwinning.

‖ Solutions of $(C_5Me_5)Cr(CO)_3Na$ (ref. 4) in tetrahydrofuran exhibit i.r. bands at 1833, 1783, and 1732 cm^{-1}; (**5**) i.r. (KBr) 3400(OH), 2980, and 2920(Me), 1485, 1450, 1430, 1382, and 1075(BF_4) cm^{-1}.

** The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

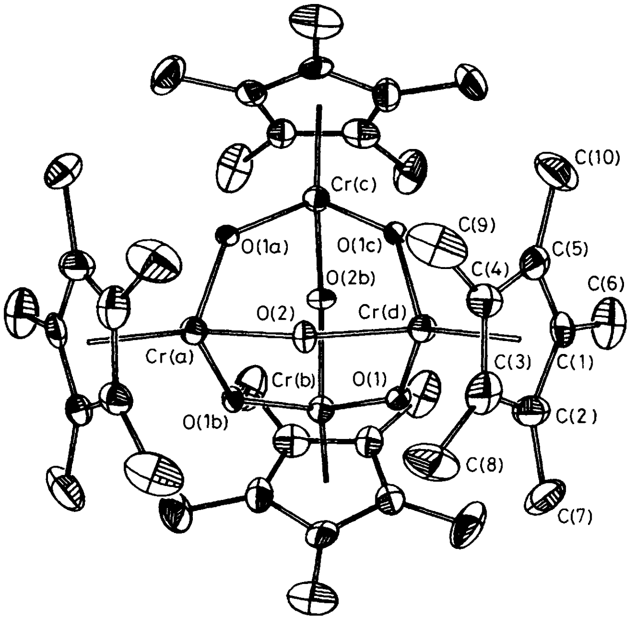

Figure 1. Thermal ellipsoid diagram of the cation of (**5**). Hydrogen atoms have been deleted for clarity.

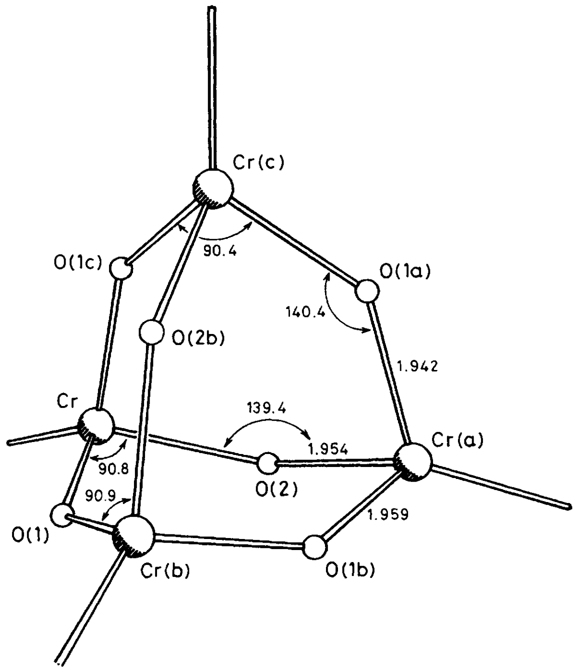

Figure 2. The adamantane cage of the cation of (**5**). E.s.d.'s for Cr–O 0.005 Å, Cr–O–Cr 0.4° and O–Cr–O 0.3°. The Cr · · · Cr distance is non-bonding: 3.669(2) Å.

The structure of (**5**) is ionic; the cation is an unusual adamantane-analogue cage structure formed by four Cr atoms and six (μ-OH) groups (Figure 1). All Cr centres are crystallographically identical (both cation and anion sites have $\bar{4}$ symmetry), capped by η^5-C_5Me_5 groups, and bridged by three μ-OH groups. Although not confirmed by crystallography, the presence of μ-OH groups is supported by the i.r. spectrum || and by electron counting considerations (*vide infra*). Whereas adamantane, $C_{10}H_{16}$, is constructed of tetrahedral carbon atoms (C–C–C angles of *ca.* 109.5°), the cation of (**5**) is constructed of octahedral Cr atoms (O–Cr–O angles of *ca.* 90°) with the η^5-C_5Me_5 rings considered as occupying three co-ordination sites (Figure 2). The angles at the cage oxygen atoms are expanded (Cr–O–Cr *ca.* 140°) to compensate. The Cr–O bond distances in (**5**), 1.952(8) Å, are comparable with two other Cr–(μ-OR) systems: $cp_2Cr_2(\mu$-$OBu^i)_2$, 1.97(1) Å,[6] and $cp_2Cr_2(NO)_2(\mu$-$OMe)_2$, 1.96(1) Å.[7] In the cubane structure, $(cpCrO)_4$, the Cr–O distances are slightly shorter, 1.937(8) Å.[8]

Conventional electron counting schemes permit each Cr atom to be viewed as Cr^{III}, consistent with the observed paramagnetism of (**5**). The cluster complexes (**4**) and (**5**) therefore are electronically related to the mononuclear $cpCrX_3{}^n$ ($X = H_2O$, $n = 2+$[9] and $X = Cl^-$, $n = 1-$[10]) compounds and the recently reported cubane cluster, $(cpCrO)_4$,[8] a growing class of η^6-C_5Me_5 compounds containing metals in high oxidation states.[11]

To our knowledge this constitutes the first example of an organometallic adamantane analogue containing transition metal atoms in the cage framework[12] and the first report of hydrolytic cleavage of a metal–metal multiple bond.

Helpful discussions with Professors B. Foxman (Brandeis) and T. McNeese (Loyola College) are acknowledged. Support was provided by the Office of Naval Research. Funds supporting the purchase of the University of Delaware diffractometer were provided by the National Science Foundation. K. M. N. is an Alfred Sloan Fellow, 1980—84.

Received, 7th January 1985; Com. 039

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