is in some way involved (for in its absence cyclobutene is the product), and since a mechanism must explain *both* the stereochemistry of the product and the intramolecular transfer of a proton from one carbon to another, the mechanism shown in Scheme I is suggested. Conventionally, the proton is placed at carbon in acid-catalyzed reactions of diazoalkanes. However, there appears to be no reason to believe that the carbon should be more basic than nitrogen. A mechanism of this sort may have other applications to reactions of diazoalkanes.

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Structure of and Bonding in $HCr_2(CO)_{10}^-$. The First Known Linear Electron-Deficient X–H–X Molecular System Stabilized by a Three-Center, One-Electron-Pair Bond[1]

Sir:

We wish to report that a detailed investigation by X-ray, infrared, and nmr methods has revealed the structure of the $HCr_2(CO)_{10}^-$ anion which represents the first known example of a *linear* X–H–X molecular system (where X in this case is the $Cr(CO)_5$ fragment) stabilized by a three-center, one-electron-pair bond (Figure 1).[2]

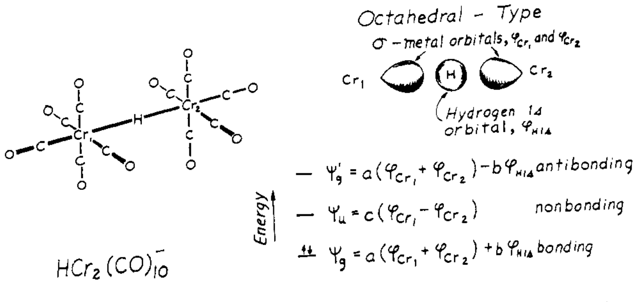

Figure 1. Molecular configuration and MO's for a symmetrical three-center, electron-pair Cr–H–Cr bond. The weighting coefficients *a*, *b*, *c* are taken as positive parameters. The use of such a delocalized three-center bond by which the two electrons in the bonding orbital are distributed over both chromium atoms (as well as the hydrogen atom) results in a closed-shell, electronic configuration for each chromium atom.

The salt $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ was isolated as the major product in the reduction of $Cr(CO)_6$ by $(C_2H_5)_4NBH_4$ in THF when the gross reaction products were extracted into and crystallized from ethanol. The salt also was isolated from the reaction product of $NaBH_4$ and $Cr(CO)_6$ in THF on addition of an ethanolic solution of $(C_2H_5)_4NBr$. *Anal.* Calcd for $C_{18}H_{21}NO_{10}Cr_2$: C, 41.9; H, 4.1; N, 2.7; O, 31.1; Cr, 20.2. Found: (C, 42.4; H, 4.2; N, 2.7; O, 31.0; Cr, 19.6)[3] and (C, 41.2; H, 4.1; N, 3.1; O, 30.2).[4]

Behrens and Klek[5] first synthesized the dimeric hydrogen decacarbonyldichromate monoanion by oxidation of $Na_2Cr(CO)_5$ with water. Later Behrens and Haag[6] obtained $HCr_2(CO)_{10}^-$ by hydrolysis of $Cr_2(CO)_{10}^{-2}$ which was prepared from the reaction of $Cr(CO)_6$ with $NaBH_4$ in liquid ammonia. These authors[7] reported that the same reactants in THF yielded $Cr_3(CO)_{14}^{-2}$. Haworth and Huff[8] also showed the reduction of $Cr(CO)_6$ with $NaBH_4$ in diglyme to give solutions containing carbonyl chromates.

The infrared spectrum of $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ in KBr pellet form shows three distinct absorption bands in the terminal carbonyl region at 2033 (m), 1943 (vs), and 1881 (s) cm^{-1}. Since these absorption maxima are essentially unaltered in the infrared spectra of the tetraethylammonium and sodium salts in THF solutions, the molecular configuration of the monohydrogen anion is preserved on dissolution. The observed infrared carbonyl pattern is consistent with a $(OC)_5Cr–H–Cr(CO)_5^-$ system having D_{4h} (or D_{4d}) symmetry. The presence of a chromium-coordinated hydrogen atom was established from the nmr spectrum of $[(C_2H_5)_4N^+][HCr_2(CO)_{10}^-]$ in THF solution which gives a sharp singlet resonance line at τ 29.47 ppm[9] in the region expected for transition metal bonded hydrogen atoms.[10]

A three-dimensional single crystal X-ray investigation of the salt revealed the coordinates of all nonhydrogen atoms. The present isotropic least-squares refinement, based on 829 reflections collected photographically with Mo $K\alpha$ radiation, gives an unweighted reliability index of 9.8%. The yellow crystals are triclinic with symmetry P1 and with reduced cell parameters a = 6.82, b = 8.91, c = 10.13 Å, α = 78.0°, β = 86.3°, γ = 78.4°; ρ_{obsd} 1.50 g cm^{-3} *vs.* ρ_{calcd} = 1.45 g cm^{-3} for one formula species per unit cell. Although the tetrahedral configuration of the one tetraethylammonium cation (which arbitrarily was placed at the origin of the unit cell with fixed nitrogen coordinates of 0, 0, 0) requires the noncentrosymmetric space group P1, to a first approximation the dinuclear chromium carbonyl anion is disposed about the midpoint of the unit cell with the two halves of the anion related to each other by a center of symmetry.

Although not directly established from the X-ray work, stereochemical and bonding considerations are completely consistent with the hydrogen of $HCr_2(CO)_{10}^-$ being collinear with and equidistant from the two symmetry-equivalent chromium atoms.[11] A sym-

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[1] L. B. H. and L. F. D. gratefully acknowledge the financial support of the X-ray work by the National Science Foundation; the use of the CDC 1604 and 3600 computers at the Computing Center was made possible through the partial support of NSF and WARF through the University of Wisconsin Research Committee.

[2] The symmetrical O–H–O hydrogen bonds and the linear HF_2^- anion are examples of three-center, two-electron-pair bonds.

[3] Shell Development Co. from sample prepared by R. G. H.

[4] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., from sample prepared by L. B. H. and P. M. T.

[5] H. Behrens and W. Klek, *Z. Anorg. Allgem. Chem.*, **292**, 151 (1957).

[6] H. Behrens and W. Haag, *Naturforsch.*, **14b**, 600 (1959); *Chem. Ber.*, **94**, 312 (1961).

[7] H. Behrens and W. Haag, *ibid.*, **94**, 320 (1961).

[8] D. T. Haworth and J. R. Huff, *J. Inorg. Nucl. Chem.*, **17**, 184 (1961).

[9] For the corresponding sodium salt in THF solution, τ 29.17 ppm.

[10] *Cf.* (a) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965), and references cited therein; (b) R. J. Doedens and L. F. Dahl, *ibid.*, **87**, 2576 (1965), and references cited therein.

[11] The existence of a symmetrical *bent* hydrogen bridging between two transition metals was ascertained from an X-ray investigation of $HMn_3(CO)_{10}(BH_3)_2$[10a] for which a molecular mirror plane (demanded crystallographically) passes through the hydrogen and relates the two equivalent manganese atoms of the Mn–H–Mn moiety to each other.[12] X-Ray evidence for other similar *bent* three-center electron-pair bonds in which the hydrogen occupies a regular coordination site between two transition metals was acquired for $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$[10b] and

metrically linear bridging hydrogen located on the *idealized* center of symmetry occupies the sixth coordination site about each chromium and thereby enables the molecular geometry of $HCr_2(CO)_{10}^-$ ideally to possess D_{4h} symmetry.[12] Since metal-coordinated hydrogen atoms have been found *without exception* to occupy regular coordination sites about the metal,[10] the coincidence of the principal fourfold axes of the two $Cr(CO)_5$ fragments with each other demands a *linear* Cr–H–Cr bond in order for the hydrogen to be octahedrally coordinated to both chromium atoms; a nonlinear bridging hydrogen octahedrally bonded to both chromium atoms would result in loss of the D_{4h} molecular symmetry. A salient feature is the Cr–Cr distance of 3.41 ± 0.01 Å from which an equidistant bridging hydrogen yields a Cr–H bond length of 1.70 Å; this value is in good agreement with the limited M–H data available for other transition metal hydride complexes.[15]

It is expected that other polynuclear transition metal complexes with direct metal–metal bonds can be protonated to give linear three-center, electron-pair metal–hydrogen–metal bonds. In fact, Hayter[20] has shown that the dimeric monohydridic molybdenum and tungsten carbonyl analogs, $HMo_2(CO)_{10}^-$ and $HW_2(CO)_{10}^-$, are isostructural with that of $HCr_2(CO)_{10}^-$ from the similar infrared and nmr spectral properties of these three anions containing congeneric transition metals. No doubt, the protonated, electron-deficient complex $HFe_2(CO)_8^-$ also contains a linear three-center, two-electron bond.

A stereochemical implication of the structure of $HM_2(CO)_{10}^-$ (where M = Cr, Mo, W) (and the presumed structure of $HFe_2(CO)_8^-$) is that these monohydridic anions cannot be further protonated[21] to give stable dihydridic dimeric complexes without a complete molecular rearrangement or breakdown into monomeric species. Consequently, the nonisolation of such dihydric dimeric complexes is not surprising.

Single crystal X-ray investigations of the other metal carbonyl anions are in progress in order to compare the geometries of the protonated and unprotonated species.

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the $HFe_3(CO)_{11}^-$ anion.[13] For this trinuclear iron carbonyl complex direct substantiation for the bridging hydrogen being equidistant from two iron atoms was given by the anion's Mössbauer spectrum, which shows the two hydrogen-coordinated iron atoms to be equivalent.[14]

(12) The possibility that a symmetrical bridging hydrogen lying on a mirror plane or center of symmetry may be statistically symmetrical (or time-averaged) owing to a double minimum potential function cannot be ruled out but is regarded as much less likely for these monobridging hydrogen–metal complexes. For discussions with references of single- and double-well potentials pertaining to symmetrical hydrogen bonding, see W. C. Hamilton, *Ann. Rev. Phys. Chem.*, **13**, 19 (1962); R. E. Rundle, *J. Phys. Radium*, **25**, 487 (1964).

(13) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(14) N. E. Erickson and A. W. Fairhall, *ibid.*, **4**, 1320 (1965).

(15) To date the only *accurately* known transition metal–hydride distance is the terminal Re–H distance of 1.68 ± 0.01 Å reported from a neutron diffraction study of K_2ReH_9.[16] A three-dimensional X-ray analysis of $HRh(CO)[P(C_6H_5)_3]_3$[17] located the hydrogen at a terminal Rh–H distance of 1.60 ± 0.12 Å, while a three-dimensional X-ray investigation of $HMn_3(CO)_{10}(BH_3)_2$, for which approximate coordinates were obtained for all hydrogen atoms, yielded an average value of 1.65 Å (with esd, 0.1 Å,) for the five independent bridging Mn–H distances.[18] Although not directly established from the X-ray work, a terminal Mn–H distance of 1.5–1.6 Å. was estimated for $HMn(CO)_5$[19] and a bridging Mo–H distance of 1.8 Å was predicted for $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$[10b] from stereochemical considerations.

The approximate *single* bond covalent radii obtained for the earlier members of the transition metal series by the use of one-half the metal–metal bond length[10b] together with an empirical value of 0.2 Å for the hydrogen radius give a reasonably self-consistent set of M–H distances when compared with the values quoted above. The empirically estimated M–H distances (*i.e.*, (M–M) Å/2 + 0.2 Å) are as follows (in Å) Cr–H, 1.7; Mo–H, 1.8; Mn–H, 1.65; Tc–H, 1.7; Re–H, 1.7; Ru–H, 1.65; Os–H, 1.65; Rh–H, 1.55; Ir–H, 1.55. The dependence of covalent radii on such factors as effective metal charge (or valency) and $d\pi$–$d\pi$ electronic repulsion, metal coordination number, and metal hybridization is ignored here along with the fact that a bridged M–H distance is expected to be longer than a terminal M–H distance.

(16) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(17) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

(18) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965, G. R. Wilkes and L. F. Dahl, to be published.

(19) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(20) R. G. Hayter, presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965; to be published.

(21) The possibility that the second proton coordinates to a terminal carbonyl oxygen is excluded on the basis of no definite evidence for such an interaction.

(22) WARF Fellow (University of Wisconsin), 1964–1965; National Science Predoctoral Fellow, 1965–present.

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Active Constituents of Hashish. Synthesis of *dl*-Δ6-3,4-*trans*-Tetrahydrocannabinol

Sir:

"Tetrahydrocannabinol," the active component(s) of hashish (marijuana), the psychotomimetically active resin of the female flowering tops of *Cannabis sativa* L., has long been known to possess the carbon skeleton indicated in structure **1**. Until recently, however, the stereochemistry of the ring fusion (positions 3 and 4), the position of the alicyclic double bond, and, indeed, even the homogeneity of the "active component," were not known. The correct structures of the biogenetic precursor cannabidiol (**2**)[2] and two isomeric tetrahydrocannabinols (**1** and **3**) have recently been established. The major member of the "tetrahydrocannabinol" fraction present in most hemp plants is the Δ^1-3,4-*trans* isomer (**1**),[3] but the isomeric Δ^6-3,4-*trans* isomer (**3**) also occurs naturally and is similar to **1** in physiological potency.[4,5] It has been demonstrated that **1** is formed by acid cyclization of cannabidiol;[3] under more strongly acidic conditions a mixture of **1** and **3** is formed, the latter arising by acid isomerization of the former.[4]

We wish to describe in this communication a simple, one-step synthesis of *dl*-Δ^6-3,4-*trans*-tetrahydrocannabinol (**3**), the racemic modification of one of the physiologically active principles of marijuana, and of two

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(1) This work was supported by a generous grant to Princeton University from the Smith Kline and French Laboratories, Philadelphia, Pa.

(2) R. Mechoulam and Y. Shvo, *Tetrahedron*, **19**, 2073 (1963).

(3) Y. Gaoni and R. Mechoulam, *J. Am. Chem. Soc.*, **86**, 1646 (1964).

(4) R. Hively, F. Hoffmann, and W. A. Mosher, *ibid.*, to be submitted.

(5) R. Mechoulam and Y. Gaoni recently described (*ibid.*, **87**, 3273 (1965)) a total synthesis of *dl*-**1** in 2% over-all yield and stated that this compound was "the active constituent of hashish." The natural occurrence and potency of the Δ^6-3,4-*trans* isomer was apparently unknown to these authors at the time of their publication. It should also be noted that the above statement implies that the natural product is the racemic modification of the Δ^1 isomer, whereas in actuality it is optically active.