ketone **10**[13,24] occurred, somewhat to our surprise, mainly from the side of the imine substituent. Chromatographic purification allowed the crystalline amino alcohol **12**,[13,25] mp 91–91.5 °C, to be isolated in 62% yield, together with 10% of recovered ketone **10** and 20% of a mixture of amino alcohol **11**, the corresponding oxazolidine, and a small amount of an unknown material. The formation of both amino alcohol isomers in reasonable amounts provided an opportunity to examine the stereoselectivity of the hydroindolone synthesis with both cyclopentane stereoisomers. Reduction of **11** with $NaCNBH_3$ in acidic ethanol gave, after chromatographic purification, pure **13**[13] in 77% yield. Amino alcohol **13** showed a characteristic intramolecular hydrogen-bonded OH absorption at 3460 cm^{-1} (CCl_4) in the infrared spectrum. Treatment of secondary amine **13** at 70 °C in Me_2SO[26] with 1 equiv of paraformaldehyde and 0.9 equiv of *d*-10-camphorsulfonic acid, afforded *cis*-octahydroindolone **15**,[13,27] mp 157.5–158.5 °C, in 91% yield. In a similar fashion, imine **12** was reduced with $NaCNBH_3$ to give the crystalline secondary amine **14**,[13] mp 98.5–99 °C, in 88% yield. The reaction of **14** with 1 equiv of paraformaldehyde and a sulfonic acid catalyst in benzene or ethanol was less clean than that of stereoisomer **13** and gave **15** together with varying amounts of the corresponding *trans*-octahydroindolone.[27,28] However, when Me_2SO was used as the solvent,[28] the cis isomer was formed with high stereoselectivity (cis/trans > 30:1, 250-MHz ^1H NMR analysis)[27] and pure *cis*-octahydroindolone **15** could be isolated in 65% yield. The diphenylmethyl group of **15** was easily removed by transfer hydrogenation[29] (Pd/C, cyclohexene, ethanol, 1 N HCl) to give *cis*-octahydroindolone **16**,[13] in 95% yield after chromatographic purification. The *N*-acetyl derivative of **16** melted at 126–127 °C (lit.[23b] 126.5–127.5 °C), and **16** showed spectroscopic properties identical with those reported[23b] for an authentic sample, thereby completing a formal total synthesis of *dl*-crinine (**9**). This efficient four-step sequence afforded *cis*-octahydroindolone **16** in 47% overall yield from protected amino ketone **10** and 24% overall yield from *trans*-2-aminocyclopentanol.

The results described here provide a further illustration of the use of "directed" aza-Cope rearrangements in organic synthesis. The ring-enlarging pyrrolidine annulation reaction proceeds in excellent yield under mild conditions and allows *cis*-3a-aryl-octahydroindolones to be assembled in a stereoselective fashion in 3–4 steps from a 2-aminocyclopentanone precursor. It is significant that cyclopentanols **7** and **13** which have the amine and vinyl groups oriented trans were converted with *complete stereoselectivity* to *cis*-octahydroindolone products (see eq 2). Also important for future applications of this chemistry is the demonstration that cyclopentanols with the opposite orientation of vinyl and amine groups may also be transformed with high stereoselectivity to *cis*-octahydroindolones. Further extensions of this chemistry, for example, for the preparation of *Aspidosperma* alkaloids,[30] will be described in future publications from this laboratory.

Acknowledgment. The support of the National Institutes of Health (NS-12389) and the Camille and Henry Dreyfus Foundation is gratefully acknowledged. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF departmental instrumentation grants.

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(24) Prepared in 52% yield from *trans*-2-aminocyclopentanol[15b] by reaction with benzophenone followed by oxidation.[16]

(25) The structure of this amino alcohol was confirmed by single-crystal X-ray analysis. Details will be published in a subsequent full account.

(26) This conversion occurs similarly in other solvents such as benzene.

(27) The 250-MHz ^1H NMR spectrum of **15** showed a characteristic narrow multiplet (half-height width = 5 Hz) for the angular H_{7a} hydrogen at δ 3.51 and a singlet at δ 5.18 for the diphenylmethyl hydrogen. No trace of the trans isomer (δ 4.76, s, C*H*Ph_2; δ 3.0–3.2, m, C_{7a}-H) was seen in the 250-MHz ^1H NMR spectrum of the crude reaction product.

(28) Although **15** was always the major product, the stereoisomer ratios varied considerably with solvent and other reaction details. This aspect of the reaction will be treated in detail when a full account of the work is published.

(29) Cf.: Jackson, A. E.; Johnstone, R. A. W. *Synthesis* **1976**, 685.

(30) Overman, L. E.; Sworin, M. *Tetrahedron*, in press.

Synthesis and Structure of the Distorted Tetrahedral Cluster $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$, the Third Member of the $[(\eta^5\text{-}C_5H_5)_mM_mO_n]$ Series Where *m* and *n* Satisfy Euler's Theorem

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We recently described the synthesis and properties of $Cp_5V_5O_6$ ($Cp = \eta^5\text{-}C_5H_5$), a trigonal-bipyramidal cluster of five vanadium atoms with an oxygen above each of the six faces of the trigonal bipyramid and a Cp ring capping each vanadium atom.[1] Previously Caulton and co-workers described $Cp_6Ti_6O_8$, a cluster with an oxygen atom above each of the eight faces formed by an octahedron of titanium atoms capped by Cp rings.[2] Geometrical considerations (Euler's theorem) alone suggest that $Cp_4Cr_4O_4$, $Cp_3Mn_3O_2$ and $Cp_7Sc_7O_{10}$, each with O atoms above triangular faces of metal atoms, should exist. We have begun a synthetic search for these clusters, using dinitrogen oxide to oxidize Cp_2M derivatives,[1,3-5] and describe here the synthesis, structure, and some properties of the distorted tetrahedral cluster $Cp_4Cr_4O_4$. A compound of this formula was in fact described over 20 years ago by Fischer, Ulm, and Fritz.[6] They considered various structures, including a tetrahedron of chromium atoms, but concluded that a planar eight-membered –Cr–O–Cr– ring was most probable on the basis of infrared spectroscopy.

Treatment of a toluene solution of Cp_2Cr with 1 equiv of N_2O followed by sublimation at 275–300 °C and recrystallization of the sublimate from hexane gave deep blue, very air- and water-sensitive crystals of $Cp_4Cr_4O_4$ in 8% yield. These have the remarkable structure shown in Figure 1.[7] The chromium atoms form an approximate tetrahedron, capped by the Cp rings and with the oxygen atoms above each face, as predicted. All except 1 of the 12 Cr–O distances lie within 2 standard deviations of the average distance of 1.937 (4) Å.[8] The heights of the four oxygen atoms above the triangular faces are essentially identical (average 1.055, range 1.043–1.063 Å), and the four Cr–Cp (ring center) distances are also identical (average 1.920, range 1.912–1.925 Å). However, the Cr–Cr distances are markedly unequal, there being three pairs of similar distances: 2.900 (6) and 2.897 (5), 2.841 (6) and 2.811 (6), and 2.712 (2) and 2.702 (6) Å (see Figure 2). The $Cp_4Cr_4O_4$ molecule therefore has D_2 symmetry within experimental error.

If it is assumed that each oxygen atom donates four of the possible six electrons to the cluster, then $Cp_6Ti_6O_8$ has a total of 86 electrons with which Ti–Cp, Ti–O, and Ti–Ti bonds can be formed; $Cp_5V_5O_6$ has 74, and $Cp_4Cr_4O_4$ 60; $Cp_7Sc_7O_{10}$ would have 96 and $Cp_3Mn_3O_2$ 44. It is clear from the structures of $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$ that the M–O distances are those of a single bond. The average distances are Ti–O 1.973 (3);[2] V–O, 1.861 (6) (axial) and 1.992 (6) (equatorial);[1] Cr–O, 1.937 (4) Å. From the literature Ti^{IV}–O bond distances average close to 1.89[9] and Ti^{III}–O close to 2.13 Å;[10] V^{IV}–O close to 1.93[11] and

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(1) Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 28–29.

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(3) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

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(7) Determined by X-ray crystallography. Crystal data: $C_{20}H_{20}Cr_4O_4$, $M = 532.4$; monoclinic, $P2_1/c$; $a = 10.442$ (3), $b = 20.958$ (8), $c = 11.022$ (3) Å; $\beta = 124.24$ (2)°; $R = 0.030$, $R_w = 0.046$ for 334 variables and 2162 observed reflections out of 2616 measured. Full details will be published elsewhere.

(8) Cr–O = 1.944 (4), 1.929 (3), 1.936 (3), 1.944 (6), 1.939 (3), 1.932 (4), 1.934 (3), 1.936 (3), 1.949 (6), 1.935 (5), 1.944 (4), 1.918 (3) Å.

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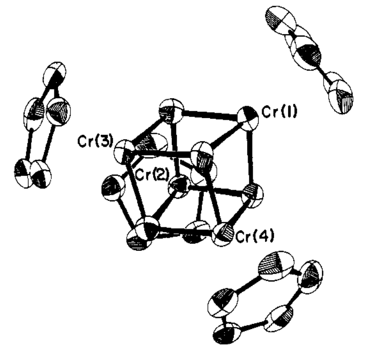

Figure 1. Molecular architecture of $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$.

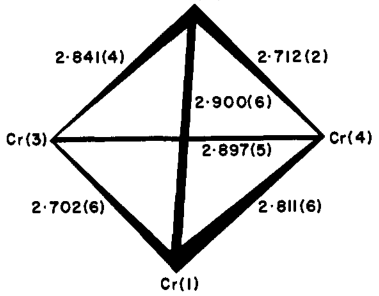

Figure 2. Arrangement of chromium atoms in $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$.

V^{III}–O close to 2.00;[11] and Cr^{III}–O close to 1.96 Å[12] We therefore conclude that each oxygen atom is bonded to the triangle of metal atoms by three M–O single bonds, requiring a total of six electrons. Each M–Cp connection formally also requires six electrons. Therefore the M–O and M–Cp bonding requires in total 84 electrons for $Cp_6Ti_6O_8$, 66 for $Cp_5V_5O_6$, and 48 for $Cp_4Cr_4O_4$; $Cp_7Sc_7O_{10}$ would require 102 and $Cp_3Mn_3O_2$ 30 electrons. We see that $Cp_6Ti_6O_8$ has 2 electrons more than required, $Cp_5V_5O_6$ 8, and $Cp_4Cr_4O_4$ 12; $Cp_3Mn_3O_2$ would have 14 electrons in excess but $Cp_7Sc_7O_{10}$ would be electron deficient by 6 electrons.

The above electron count is important in understanding the magnetic properties of the three clusters $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$. Caulton et al. reported $Cp_6Ti_6O_8$ to be diamagnetic, and this is to be expected by symmetry if the two excess electrons are to be equally shared by the six Ti atoms; preliminary molecular orbital calculations in fact indicate that this pair of electrons is localized in the center of the octahedron in an a_{1g} orbital.[13,14] For $Cp_5V_5O_6$ there are two unpaired electrons per cluster at room temperature.[1] The molecular orbital calculations support the simple view that the eight excess electrons can best be assigned among five vanadium atoms if two unpaired electrons are assigned to the axial and a pair of electrons to each of the equatorial V atoms. This makes the axial V atoms formally V(IV) and the equatorial V(III), which is in agreement with the shorter V(axial)–O distance compared to the V(equatorial)–O distance.

The 12 excess electrons in $Cp_4Cr_4O_4$ could simply be distributed 3 to each Cr atom, which atoms would then be formally 6-coordinated Cr(III) with 3 unpaired electrons. However, the Cr–Cr distances of 2.70–2.90 Å clearly allow antiferromagnetic interaction between the electrons on the individual Cr atoms. The magnetic moment of $Cp_4Cr_4O_4$ shows antiferromagnetism between 80 and 326 K, with no evidence of the Nêel temperature having been reached. At room temperature approximately two unpaired electrons are present. Fischer, Ulm, and Fritz also reported their material to be antiferromagnetic.[6] Molecular orbital calculations give inconclusive results because they depend on the number of unpaired electrons specified as input. However, in all calculations the HOMO and LUMO span the t_1 and a_1 representations of idealized T_d symmetry and are of very similar energies. Hence, one electron occupies the degenerate t_1 orbital, leading to a Jahn–Teller distortion. A similar distortion was observed in $Co_4(NO)_4[\mu_3\text{-}NC(CH_3)_3]_4$.[16]

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Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, bond distances and angles, and a key to the numbering scheme (7 pages). Ordering information is given on any current masthead page.

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Some Geometrical and Electronic Features of the Intermediate Stages of Olefin Metathesis

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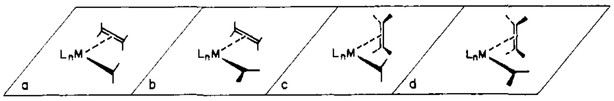
In a theoretical analysis of that microcosm of organometallic and catalytic chemistry, the olefin metathesis,[1] we find the following features:

(1) In a metal–carbene–olefin complex there should be a strong electron count and transition series dependence of the relative orientation of the carbene and ethylene. Only some conformations will be productive in metathesis, e.g., **1a** and not **1b–d**. Attainment of the proper conformation is crucial, for once there the catalysis is essentially done.



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