

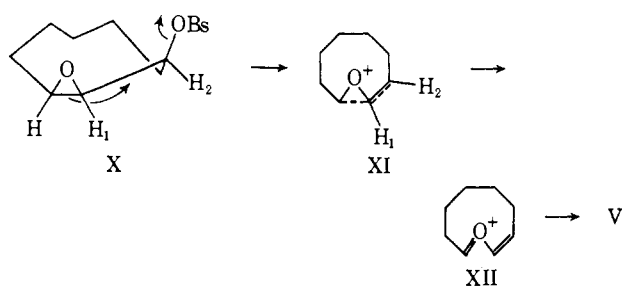
Table II. First-Order Rate Constants^a and Activation Parameters^a for Solvolysis of IIb and IIIb in 80% Ethanol-Water

Compd	Temp, °C	10 ⁶ k, sec ⁻¹	ΔH [‡] , kcal/mol	ΔS [‡] , kcal/mol
IIb	59.8	22.7 ± 0.5	25.3 ± 0.4	0.7 ± 1.3
	49.8	6.64 ± 0.26		
	40.1	1.82 ± 0.07		
	25.0	0.23 ^b		
IIIb ^c	100.3	12.2 ± 0.18	27.3 ± 0.1	-3.7 ± 0.4
	90.2	4.26 ± 0.004		
	80.1	1.40 ± 0.003		
	25.0	0.00089 ^b		

^a Calculated by nonlinear regression analysis. The reactions were monitored spectrophotometrically. ^b Extrapolated from data at higher temperatures. ^c Triethylamine was used as a buffer.

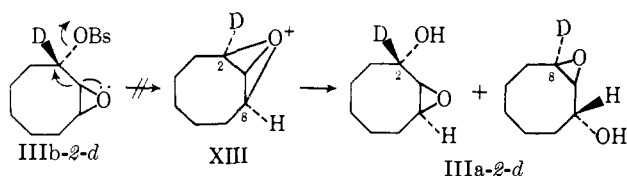
The mechanism by which IIIb solvolyzed to yield IIIa was investigated by solvolysing IIIb-2-d.⁶ The major

Scheme I



product possessed identical infrared and nmr spectra as IIIa-2-d. Therefore, participation by the nonbonding electrons of oxygen in the solvolysis of IIIb, which would lead to oxabicyclobutonium ion XIII, was ruled out as a major solvolytic pathway.⁷ Intermediate XIII, if formed, would lead to scrambling of deuterium between C-2 and C-8 of the product IIIa because of the chemical equivalency of C-2 and C-8 in XIII (Scheme II).

Scheme II

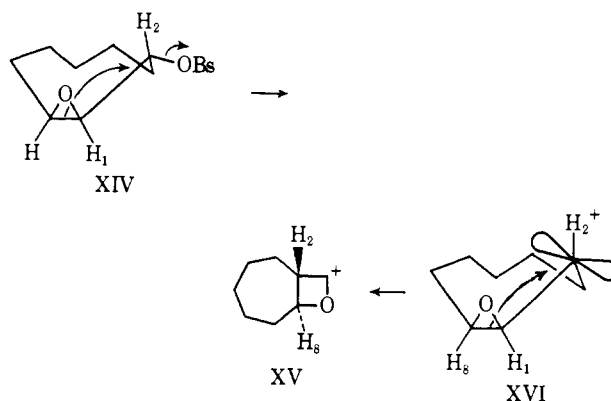


A plausible intermediate in the formation of 17% of cycloheptenecarboxaldehyde (VI) from IIIb is the trans-fused bicyclic oxonium ion XV, formed either by concurrent ionization-bond migration or ionization followed by migration of the C-C bond of the oxirane ring to the backside of the vacant p orbital at C₂ (Scheme III).⁸ The low reactivity of IIIb and formation of significant amounts of retained, inverted, and hydride-shift alcohols from IIIb indicate that anchimeric assistance to ionization by the oxirane ring is at best a minor

(6) *anti*-Alcohol IIIa-2-d was prepared by sodium borodeuteride reduction of 2-cyclooctenone, followed by epoxidation of 2-cyclooctenol-1-d with *m*-chloroperbenzoic acid.

(7) Oxabicyclobutonium ions have been proposed as intermediates in the solvolysis of several simple epoxycarbonyl derivatives: H. Morita and S. Oae, *Tetrahedron Lett.*, 1347 (1969); H. G. Richey, Jr. and D. V. Kinsman, *ibid.*, 2505 (1969).

Scheme III



reaction pathway, and that an intermediate with charge residing mainly on C-2 must exist.

The solvolytic reactivity of 9-oxabicyclo[6.1.0]non-2-yl system Ib ($n = 6$) can be estimated to be a factor of *ca.* 10⁶–10⁷ less than the corresponding bicyclo[6.1.0]non-2-yl system Ia ($n = 6$).⁹ These data indicate that the nonbonding electrons on oxygen, in the absence of participation by the nonbonding electrons on oxygen, are not nearly as effective as cyclopropane rings in stabilizing developing positive charge on adjacent carbon atoms. In the solvolysis of IIIb, where only 17% of VI is formed, the product distribution indicates that the oxirane ring exhibits a destabilizing effect.

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(8) Stereospecific bond migration in *anti*-2-bicyclo[6.1.0]nonyl *p*-nitrobenzoate solvolysis leads to a trans-fused cyclobutane ring.^{1b}

(9) The solvolytic reactivity of 2-bicyclo[*n*.1.0]alkyl brosylates was estimated to be *ca.* 10⁹ times greater than that of 2-bicyclo[*n*.1.0]alkyl *p*-nitrobenzoates.^{1b} The rates of solvolyses of IIb, IIIb, and Ia ($n = 6$) were extrapolated to common solvents and temperature.

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Establishment of Absolute Configuration in Tris-β-diketonate-Chelate Complexes by X-Ray Methods. The Structure of Λ(+)₆₈₉-trans-Tris[(+)-3-acetylcamphorato]chromium(III)

Sir:

Of chiral coordination compounds, tris complexes of bidentate ligands comprise an important and much studied subclass. Despite considerable interest in this area, only a small number of absolute configurations have been put on a firm basis *via* X-ray analysis.¹ Surprisingly, tris-β-diketonate complexes, which have occupied a prominent position in the development of coordination chemistry, are among the types of complex for which absolute configurations have not been

(1) For a recent review, see R. D. Gillard and P. R. Mitchell, *Struct. Bonding (Berlin)*, 7, 46 (1970).

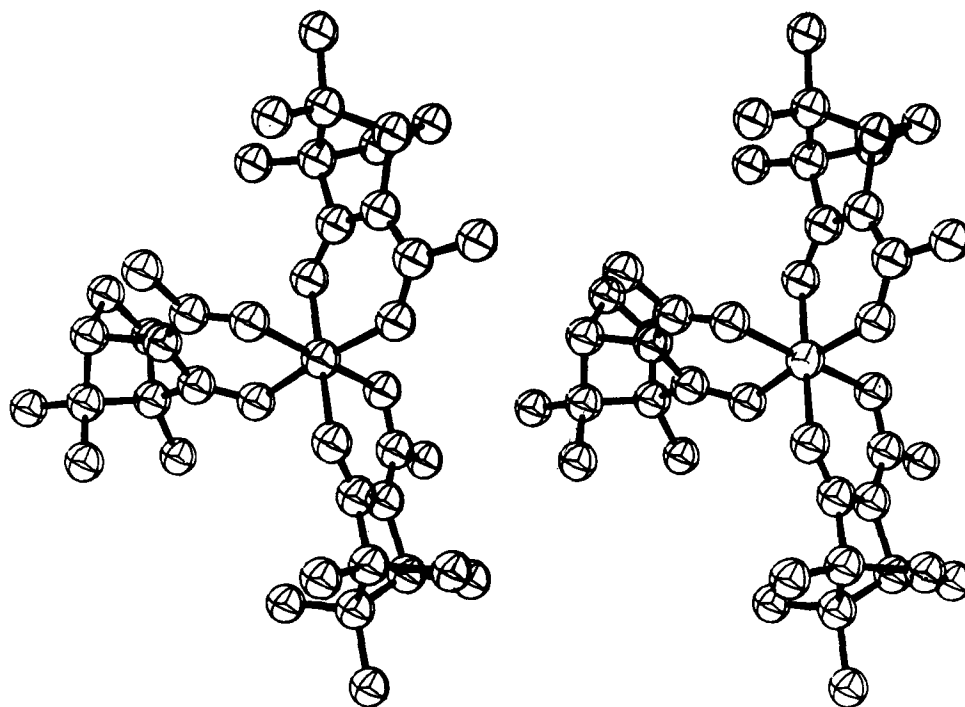
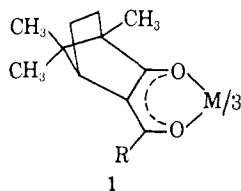


Figure 1. Stereoscopic pair showing Δ -*trans*-Cr(+ atc)₃ viewed down the pseudo-C₃ axis.

established by X-ray methods. We report here the absolute configuration of a member of this class, namely, $\Lambda(+)$ ₅₈₉-*trans*-tris[(+)-3-acetylcamphorato]chromium(III) (**1**, M = Cr, R = CH₃), one of four diastereoisomers of this compound (Δ -*trans*, Λ -*trans*, Λ -*cis*, Δ -*cis*).² The ligand (+)-3-acetylcamphorate, +atc, is derived



from (+)-3-bromocamphor, a chiral molecule of known absolute configuration.³ Partial separations have been reported^{4,5a} for diastereoisomers of the related tris complexes of hydroxymethylenecamphor, hmc (**1**, M = Cr, Co; R = H) by column chromatography. Quite recently, complete separation of diastereoisomers has been achieved for Co(+atc)₃^{5b,6} and Cr(+atc)₃^{5b} by column⁶ and thin layer chromatographic,^{5b} tlc, techniques. Of special relevance is the fact that King and Everett have established,^{5b} by tlc and X-ray powder photography, the correspondence between the four diastereoisomers of the Cr(+atc)₃ and Co(+atc)₃ series, enabling the structure of a single member to establish the absolute stereochemistries of all members of both

groups. Particular importance may be attached to the present determination since the spectral criterion, wherein a positive CD band for the E_a component of the lowest energy ligand-field transition of d³ and d⁶ (spin paired) complexes is associated with a Λ configuration, has been shown⁷ to be invalid in the case of Λ - (+)₅₈₉-tris(1,3-diaminopropane)cobalt(III) cation and questioned in another case.⁸ The above spectral criterion, with corroborative evidence from molecular models,⁴ has previously been used to assign the absolute configurations of tris-hmc^{4,5a} and -atc^{5,6} complexes.

Cr(+atc)₃ was prepared and separated into four diastereoisomers, A–D (in order of decreasing R_p, *i.e.*, isomer A moves most rapidly on the tlc sorbent⁹), as described elsewhere.^{5b} Brown tabular crystals were grown by vapor-phase diffusion of water into an ethanolic solution of isomer B at room temperature. This sample is characterized^{5b} by the following CD maxima and minima [ν ($\epsilon_1 - \epsilon_2$): 16.3 (−1.8), 18.6 (+3.7), 27.5 (−19), 29.4 (+48), 32.2 (−36), 36.2 (+17), 38.2 (−8), 40.2 (+12) cm^{−1} × 10^{−3} (l. mol^{−1} cm^{−1}). The crystals are monoclinic, space group P₂₁, as required by systematic absences observed on Weissenberg films and in the diffractometer data. The measured density of 1.17 (3) g/cm³ (floatation in aqueous potassium iodide solution) compares favorably with that calculated, 1.19 (2) g/cm³, for Z = 2. The cell dimensions are: a = 12.915 (18), b = 7.790 (11), c = 17.590 (6) Å; β = 93.06 (1)°. Intensity data were taken on a Syntex computer-controlled automatic diffractometer using nickel-filtered Cu K α radiation. The structure was

(2) The designation of chirality conforms to the IUPAC recommendations, *Inorg. Chem.*, **9**, 1 (1970). The notations *cis* and *trans* are sometimes referred to as *facial* or (1,2,3) and *meridional* or (1,2,6), respectively.

(3) F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966).

(4) J. H. Dunlop, R. D. Gillard, and R. Ugo, *J. Chem. Soc. A*, 1540 (1966).

(5) (a) Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968); (b) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, submitted for publication.

(6) C. S. Springer, Jr., R. E. Sievers, and B. Feibush, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, INORG-106, submitted for publication.

(7) R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

(8) G. R. Brubaker and L. E. Webb, *J. Amer. Chem. Soc.*, **91**, 7199 (1969).

(9) Precoated, preparative tlc plates with a 2-mm layer of silica gel, F-254 (Brinkmann Instruments, Inc.), were used employing the multiple development, ascending technique with a 95:5 (by volume) chloroform-acetone solvent mixture.

solved by conventional Patterson and Fourier techniques. At the present stage of isotropic full-matrix least-squares refinement $R = 0.094$ using 1482 reflections for which $I \geq 4\sigma(I)$. The anomalous dispersion of the chromium atom has been included.

The results show, by internal comparison with the known absolute configuration of the camphor moiety,³ that sample B of $\text{Cr}(+\text{atc})_3$ is the Λ -trans isomer, in agreement with previous assignments based on spectroscopic^{4,5,10} and steric⁴ arguments. This result is confirmed by a Bijvoet analysis of several Friedel pairs employing the anomalous dispersion of the chromium atom. Furthermore, employing the correlations of King and Everett,^{5b} the correspondence of diastereoisomers of both $\text{Cr}(+\text{atc})_3$ and $\text{Co}(+\text{atc})_3$ is definitely established as follows: A, Δ -trans; B, Λ -trans; C, Λ -cis, D, Δ -cis. The Λ configuration and trans geometry of isomer B are clearly evident in the stereoview provided by Figure 1.

The Cr-O distances are all identical to within experimental error and average 1.97 (1) Å. The O-Cr-O angles within the individual chelate rings average 91.9 (1)°. The three carbon and two oxygen atoms defining each chelate ring are quite accurately coplanar with no atom deviating more than 0.04 Å from the least-squares plane in any instance. These chelating planes are inclined to the planes defined by the chromium and two oxygen atoms by angles of 17.6, 16.3, and 15.5° for each of the three bidentate ligands. Dihedral coordination of this type by β -diketonate ligands has been noted before.¹¹

Single-crystal electronic spectroscopy has shown that for the lowest energy ligand-field transition in $\text{Cr}(\text{acac})_3$,¹² ${}^4A_2 \rightarrow ({}^4E_a + {}^4A_2)$, and $\text{Co}(\text{acac})_3$,¹³ ${}^1A_1 \rightarrow ({}^1E_a + {}^1A_2)$, the E_a component lies at higher energy in each case. This result, coupled with the CD data^{5b} for the present tris-atc complexes, demonstrates that a positive CD band for the E_a component is diagnostic of the Λ absolute configuration in tris- β -diketonate complexes of chromium and cobalt. The assignment¹⁴ of absolute configuration of diastereoisomers of the tris- β -diketonate complexes of cobalt(III) derived from the chiral natural products carvone and pulegone recently made on this basis is thus supported.

A complete description of this structure and an analysis of the factors governing stereoselectivity in this class of complex will be presented in a subsequent publication.

Acknowledgments. We thank Professor G. W. Everett, Jr., of the University of Kansas for supplying us with separated diastereoisomers, and the College of Science, The Pennsylvania State University, for an allocation of funds for computer time.

(10) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

(11) F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).

(12) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).

(13) T. S. Piper, *ibid.*, **35**, 1240 (1961).

(14) G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970).

(15) Petroleum Research Fund Predoctoral Fellow, 1969-1970.

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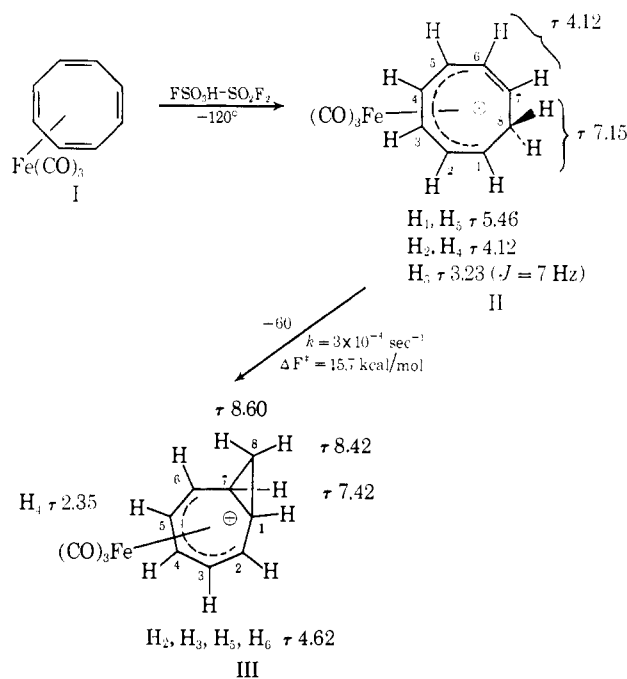
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Direct Observation of the Cyclooctatrienyliron Tricarbonyl Cation and Its Electrocyclic Ring Closure to the Bicyclo[5.1.0]octadienyliron Tricarbonyl Cation

Sir:

There has been much recent interest in metal carbonyl complexes of carbonium ions.¹ Metal carbonyl complexes of the C_8H_9^+ cation generated from protonation of the corresponding cyclooctatetraene complexes have been especially interesting in that the electronic requirements of the metal dictate the structure of the cationic ligand.^{2,3} For example, protonation of cyclooctatetraenemolybdenum tricarbonyl yields the homotropylium complex in which all six π electrons of the homotropylium ion are used in bonding to molybdenum. In contrast, protonation of cyclooctatetraenyliron tricarbonyl² I in sulfuric acid at 0° yields the ring-closed bicyclo[5.1.0]octadienyliron tricarbonyl complex III, in which the cyclopropane ring remains closed⁴ and only the four π electrons of the pentadienyl system are needed for bonding to iron.

In this communication we report the preparation of a new C_8H_9^+ iron tricarbonyl complex, the cyclooctatrienyliron tricarbonyl complex⁴ II, and a study of its electrocyclic ring closure to the bicyclic complex III.



Preparation of complex II is accomplished by low-temperature protonation of I. When I is dissolved in $\text{FSO}_3\text{H}-\text{SO}_2\text{F}_2$ (1:3, v:v) at -120° ion II is formed cleanly. The nmr spectrum⁵ of this ion recorded at

(1) For a review, see E. W. Abel and S. Tyfield, *Advan. Organometal. Chem.*, **8**, 117 (1970).

(2) (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 553 (1961); (b) *J. Chem. Soc.*, 4821 (1962).

(3) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965); (b) R. Aumann and S. Winstein, *Tetrahedron Lett.*, 903 (1970); (c) for a review, see S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(4) Protonation of I was reported to give the cyclooctatrienyliron tricarbonyl complex: G. N. Schrauzer, *J. Amer. Chem. Soc.*, **83**, 2966 (1961). However, work by Davison, *et al.*,² showed the structure to be the bicyclo[5.1.0]octadienyliron tricarbonyl complex, III.

(5) All chemical shifts are in τ relative to internal CH_2Cl_2 taken as τ 4.70.