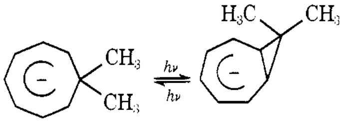
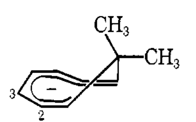
the potassium salt. Solutions of anion **4** were stable at room temperature for at least 2 hr and, when kept at low temperature and quenched into pentane–water, produced (in low yield) a mixture containing 6,6-dimethyl-1,3,5-cyclooctatriene (**5**) as the major (97%) component.[10]

Of particular interest is the observation that **4** is also produced by disrotatory opening upon photolysis[11] of the (potassium) 8,8-dimethylbicyclo[5.1.0]octadienyl anion[12] (**6**) in liquid ammonia. A photoequilibrium appeared to be established since the ratio of the nmr signals for **4** and **6** remained constant at *ca.* 1:3 on prolonged irradiation. This was confirmed by the observation that the same solution of **4** and **6** is produced by irradiation of **4** (in ammonia-d_3). This is the first example of a reversible photochemical electrocyclization of a carbanion and is also the first case in which both reactant and product have been directly observed in a photochemical electrocyclization of a carbanion.[13]

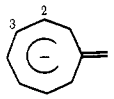


4 6

Whereas minimization of antibonding interactions between the π orbitals at C_1 and C_7 may be best achieved in a planar conformation of **4**,[14] this will introduce bond angle strain which might be more detrimental energetically than any increase in antihomoaromaticity expected in a folded conformation (**7**).[15] The observation of a six-proton singlet for the methyl protons at $-77°$ is compatible with either a planar conformation or a rapidly flipping folded conformation where $\Delta G^{\ddagger}$ is estimated to be <10 kcal/mol.[16] However, the fact that J_{23} in **4** (9.0 Hz) is significantly smaller than J_{23} in the methylenecyclooctatrienyl anion **8** (10.5 Hz),[17] despite the near identity of the corresponding self-consistent HMO π-bond orders (0.55 and 0.57, respectively), suggests that the former anion may be folded, as in **7**. Finally, although the signals for H_1 and H_7 appear at a lower field than usual for protons on negatively charged carbons, the question of whether **4** displays any "antihomoaromatic" behavior cannot be answered without detailed reference to appropriate model compounds.



7



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(10) Nmr (CCl_4): three two-proton multiplets centered at δ 6.02, 5.72, and 5.45 (olefinic), a multiplet at 2.23 (2 H, methylene), and a singlet at 1.05 (6 H, methyl); uv (hexane) λ_{max} 261 nm (ϵ 3850).

(11) A 0.1 *M* solution of **6** was irradiated through Pyrex with a 275-W GE sunlamp.

(12) Anion **6** was prepared by reaction of potassium amide in liquid ammonia with 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene. The latter was prepared from 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (from an extension of the procedure of A. P. ter Borg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1217 (1961)) by methylation with lithium dimethylcopper (E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967)).

(13) H. Kloosterziel and G. M. Gorter-la Roy (*J. Chem. Soc., Chem. Commun.*, 352 (1972)) have postulated the intermediacy of the cyclooctatrienyl anion in the photochemical conversion of the (potassium) bicyclo[5.1.0]octadienyl anion to the cyclooctatetraene dianion in liquid ammonia.

(14) M. Feldman and W. C. Flythe, *J. Amer. Chem. Soc.*, **93**, 1547 (1971).

(15) Cyclononatrienyl anions have recently been shown to be significantly bent; S. W. Staley and N. J. Pearl, manuscript submitted for publication.

(16) This value of $\Delta G^{\ddagger}$ was calculated by assuming a difference of 0.65 ppm in the chemical shifts of the methyl groups in the hypothetical conformation **7**. This is the chemical-shift difference for the methyl protons in **6** and is probably a high estimate. (See F. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter VII.)

(17) S. W. Staley and G. M. Cramer, manuscript submitted for publication.

Structural Study of a Ruthenium Hydride Cluster by Nematic-Phase Proton Magnetic Resonance

Sir:

The difficulties in establishing hydride proton positions in transition metal hydrides are well known.[1] We wish to report the structural information obtained from a study of the proton magnetic resonance of the recently synthesized[2] compound $H_3Ru_3(CO)_9CCH_3$ (I) dissolved in the nematic phase of a liquid crystal.

Several spectra of width 5000 Hz were obtained on a Varian XL-100-15 spectrometer in Fourier-transform mode at probe temperature (37°) using a saturated solution of I in the Vari-Light liquid crystal VL-3268-N (less than 10 mg of solute/0.5 ml of solvent). The 5-mm sample tube was placed coaxially inside a 12-mm tube (nonspinning) containing D_2O as a heteronuclear lock. Resultant line widths at half-height were approximately 10 Hz.

Assuming I has C_{3v} symmetry (Figure 1), as deduced by Canty, *et al.*,[2] only one orientation parameter S_{zz} is required to characterize its orientation.[3] The nearly first-order spectra display the expected two groups of triplets of quartets (Figure 2). The dipolar couplings T_{ij}, defined by

$$T_{ij} = -\frac{\hbar\gamma_i\gamma_j}{2\pi r_{ij}^3}(3\cos^2\beta_{ij} - 1)\,S_{zz} \qquad (1)$$

where r_{ij} is the distance between nuclei i and j, γ_i and γ_j are magnetogyric ratios, and β_{ij} is the angle between the internuclear vector and the z axis (the symmetry axis), were obtained from a modified version of the LAOCOON2 nmr program.[4] This program iterates on dipolar couplings and chemical shifts to give the best agreement with weighted experimental frequencies and calculates the corresponding uncertainties in the computed dipolar couplings. The best fit values are given in Table I. Indirect couplings between methyl protons and hydride protons were taken to be zero,[2] and the indirect couplings between fully equivalent nuclei

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(1) B. A. Frenz and J. A. Ibers, "The Hydrogen Series," Vol. 1, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971, p 33.

(2) A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 1331 (1972).

(3) A. D. Buckingham and K. A. McLauchlan, *Progr. Nucl. Magn. Res. Spectrosc.*, **2**, 63 (1967).

(4) D. Bailey, A. D. Buckingham, M. C. McIvor, and A. J. Rest, *Mol. Phys.*, **25**, 479 (1973).

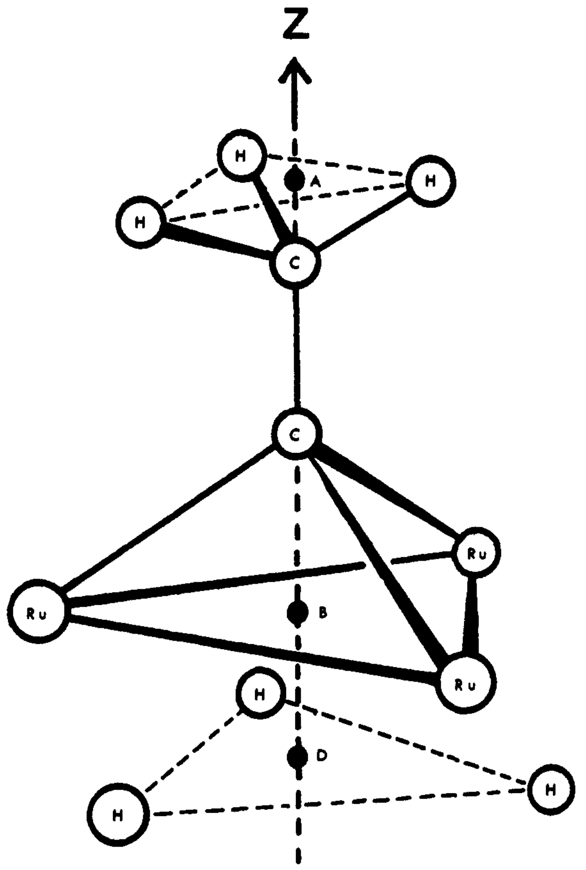

Figure 1. Schematic diagram of $H_3Ru_3(CO)_9CCH_3$ (I) not showing carbonyl groups.

Table I. Nmr Parameters for I Dissolved in VL-3268-N at 37°

$T_{\text{intra-Me}}$	±801.4 ± 1.1 Hz
$T_{\text{intra-hydride}}$	±294.2 ± 1.2 Hz
T_{inter}	∓82.4 ± 0.8 Hz
Rms error in fitting spectrum	2.2 Hz
S_{zz}	±0.03764 ± 0.00005[a]

[a] Assuming $r_{\text{intra-Me}}$ from Table II is exact.

do not affect the spectrum when anisotropies in these couplings are negligible. Both $T_{\text{intra-Me}}$ and $T_{\text{intra-hydride}}$ must be of like sign since β in eq 1 is 90° for both; T_{inter}, the dipolar coupling between methyl and hydride protons, was found to be of opposite sign (see below).

Because the experimental dipolar couplings can yield only ratios of internuclear distances (neglecting vibrational corrections), estimates of internuclear distances were made (Table II). S_{zz} was computed from eq 1 using $r_{\text{intra-Me}}$ and the observed $T_{\text{intra-Me}}$. Both $r_{\text{intra-hydride}}$ and r_{AD} (Figure 1) were then calculated, the latter from a numerical integration program which evaluated T_{inter} from eq 1 for a rapidly rotating methyl group at constant distance from the plane of the hydride protons (two other values of this distance which reproduced $|T_{\text{inter}}|$ were less than 0.5 Å and were thus rejected as unreasonable).

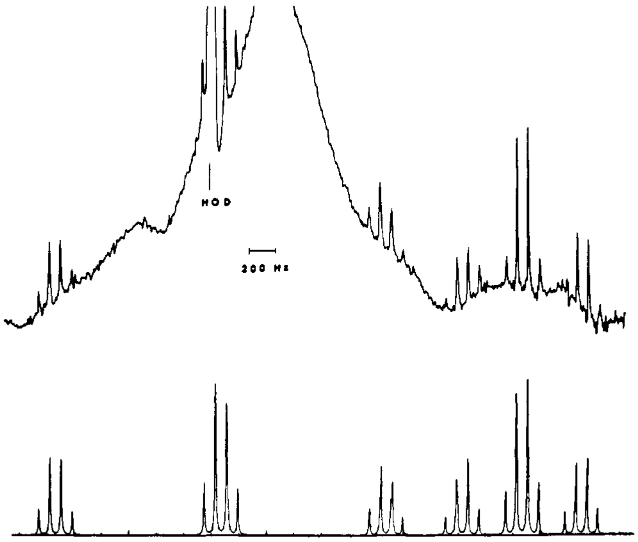

Figure 2. Experimental nematic-phase spectrum of I and calculated spectrum without liquid crystal background absorption.

Table II. Assumed and Calculated Geometrical Parameters

$r_{\text{intra-Me}}$	1.780 Å[a]	assumed
$r_{\text{C-CH}_3}$	1.520 Å[b]	
$r_{\text{Ru-C(apical)}}$	2.050 Å[c]	
$r_{\text{Ru-Ru}}$	2.930 Å[d]	
$r_{\text{intra-hydride}}$	2.486 ± 0.004 Å[e]	calcd
r_{AD} (Figure 1)	4.115 ± 0.020 Å[e]	
r_{BD} (Figure 1)	1.065 ± 0.020 Å	
$r_{\text{Ru-H}}$	1.905 Å[f]	
Ru-H-Ru	101°[f]	

[a] Obtained by multiplying the average ratio of $r_{\text{H-H}}/r_{\text{C-H}}$ obtained for methyl cyanide in several liquid crystals by an assumed $r_{\text{C-H}}$ of 1.093 Å: P. Diehl and C. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, Springer-Verlag, Berlin, 1969, pp 40–41; L. Nygaard, *Spectrochim. Acta*, **22**, 1261 (1966). [b] From X-ray results on similar cobalt clusters: P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967); M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, **9**, 362 (1970). [c] Estimated by adding to the Co–C distance of 1.92 Å in similar clusters the increase in metal–carbon distance of 0.13 Å observed in a tetranuclear cluster upon replacing Co by Ru, footnote *b;* F. Klanberg, W. B. Askew and L. J. Guggenberger, *Inorg. Chem.*, 7, 2265 (1968); G. Allegra and S. Valle, *Acta Crystallogr., Sect. B*, **25**, 107 (1969); D. Seyferth, R. J. Spohn, M. R. Churchill, K. Gold, and F. R. Scholer, *J. Organometal. Chem.*, **23**, 237 (1970); L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, **84**, 2450 (1962); R. Mason and K. M. Thomas, *J. Organometal. Chem.*, **43**, C39 (1972). [d] From various X-ray studies of ruthenium clusters with bridging hydrides: M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 545 (1972); A. Cox and P. Woodward, *J. Chem. Soc. A*, 3599 (1971); A. W. Parkins, E. O. Fischer, G. Huttner, and D. Regler, *Angew. Chem.*, **82**, 635 (1970); D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972). [e] Assuming S_{zz} from Table I. If $r_{\text{intra-Me}}$ were actually 1.790 Å, $r_{\text{intra-hydride}}$ would become 2.500 Å and r_{AD} 4.145 Å. [f] An increase of 0.02 Å in r_{AD} increases $r_{\text{Ru-H}}$ from 1.905 to 1.916 Å; the changes in (*e*) increase $r_{\text{Ru-H}}$ to 1.924 Å; an increase of 0.05 Å in $r_{\text{Ru-C}}$ lowers $r_{\text{Ru-H}}$ to 1.858 Å; an increase of $r_{\text{Ru-Ru}}$ by 0.003 Å increases $r_{\text{Ru-H}}$ to 1.907 Å; the angle Ru-H-Ru always remains within 3° of 101°.

In order to determine the position of the hydride protons with respect to the ruthenium framework, we used the values of $r_{\text{C-CH}_3}$, $r_{\text{Ru-Ru}}$, and $r_{\text{Ru-C}}$ in Table II. If the hydride protons are eclipsed with respect to the ruthenium atoms, a ruthenium–hydride proton distance of 1.10 Å is obtained. This is much smaller than any known transition metal–proton bond length.[1] Since the ^{13}C nmr shows that two carbonyl groups on each ruthenium are equivalent,[2] a symmetrically bridged structure is indicated, but an asymmetric arrangement in which the protons jump from one equilibrium position to another is not excluded. Assuming a symmetrical bridge a ruthenium–proton distance of 1.90 Å and a Ru–H–Ru angle of 101° is obtained.

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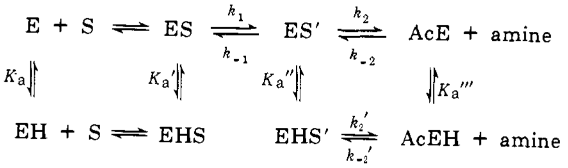
Concerning a Reported Change in Rate-Determining Step in Chymotrypsin Catalysis[1]

Sir:

A pH-induced change in the rate-determining step has been proposed for the chymotrypsin-catalyzed hydrolysis of formylphenylalanine formylhydrazide.[2] The basis of this proposal was a discrepancy between the pK of the Michaelis complex as determined from $V_{\max}$ and K_m measurements; values equal to 6.08 and 6.7, respectively, were determined from these kinetic parameters. The asymmetry of the proposed kinetic mechanism (Scheme I, where ES, ES′, and AcE represent the Michaelis complex, a tetrahedral intermediate and acyl enzyme, respectively, and the site of proton addition is His-57) permits a change in the rate-determining step; at low pH k_2' (EHS′) > k_{-1} (ES′) so that the attack step (k_1) is rate limiting, and at high pH k_{-1} (ES′) > k_2 (ES′) and k_2' (EHS′), so that tetrahedral intermediate breakdown to the acyl enzyme is rate limiting. The change in the rate-determining step presumably makes the pK influencing $V_{\max}$ a "kinetic constant" which is lower than that influencing K_m. This interpretation was supported by studies of proton release associated with substrate binding;[3] as is required by the suggested mechanism no protons were found to be rapidly released. In disagreement with the earlier results[2] we have found the same pK (6.0–6.1) for the Michaelis complex from both $V_{\max}$ and K_m measurements.[4]

Scheme I



The distinctive feature of the proposed mechanism[2] (Scheme I) is the involvement of both imidazole and imidazolium paths in the formation and breakdown of the tetrahedral intermediate from the acyl enzyme: the k_2, k_{-2} and k_2', k_{-2}' reactions in Scheme I. To test this mechanism we have looked for the imidazolium-catalyzed path (k_{-2}') in the attack of formylhydrazine on a formylphenylalanyl enzyme; *i.e.*, the reverse of the reaction previously studied.[2] We have found that there is no reaction involving the imidazole conjugate acid. This result does not appear to be consistent with Scheme I.

The rate law for formation of formylphenylalanine formylhydrazide from a formylphenylalanyl enzyme (generated from the corresponding methyl ester[5]) is

$$\text{obsd } k_{\text{amine}}/(\text{amine}) = \frac{\dfrac{k_{-1}k_{-2}K_a'''K_a''}{(H)^2k_2'} + \dfrac{k_{-1}k_{-2}'K_a''}{(H)k_2'}}{1 + \dfrac{(k_{-1}+k_2)K_a'''K_a''}{(H)^2k_2'} + \dfrac{k_2'K_a''' + (k_{-1}+k_2)K_a''}{(H)k_2'}} \qquad (1)$$

At high and low pH this reduces to eq 2 and 3, respectively.

$$\text{obsd } k_{\text{amine}}/(\text{amine}) = k_{-1}k_{-2}/(k_{-1}+k_2) \qquad (2)$$

$$\text{obsd } k_{\text{amine}}/(\text{amine}) = k_{-1}k_{-2}'K_a''/(H)k_2' \qquad (3)$$

Hydrolysis of the formylphenylalanyl enzyme follows the rate law

$$\text{obsd } k_{\mathrm{H_2O}} = k_{\mathrm{H_2O}}K_a'''/(K_a''' + (H)) \qquad (4)$$

Measured values of $k_{\mathrm{H_2O}}$ ($V_{\max}$) and pK_a''' were found to be equal to 85 sec^{-1} and 6.85, respectively (ionic strength 0.1, 25°). The apparently "normal" value of the pK for acyl enzyme hydrolysis suggests that this reaction does not involve a pH-dependent change in the rate-determining step (as was suggested for acyl enzyme aminolysis[2]) so that the pK obtained from the kinetics of the hydrolysis reaction is likely to be equal to K_a''' in Scheme I, rather than a complex constant, as was proposed for the acyl enzyme aminolysis.[6] We are not aware of any evidence suggesting a pH-dependent change in the rate-determining step in acyl enzyme hydrolysis. The result of the fact that there is only a single path for acyl enzyme hydrolysis (equiva-

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[1] This investigation was supported by a Public Health Service Research Career Development Award to M. C. (1-K4-GM-10, 010-02) from the National Institutes for General Medical Studies and by a grant (DE03246) from the National Institutes of Health.

[2] A. R. Fersht and Y. Raquena, *J. Amer. Chem. Soc.*, **93**, 7079 (1971).

[3] A. R. Fersht, *ibid.*, **94**, 293 (1972).

[4] E. C. Lucas, M. Caplow, and K. J. Bush, *ibid.*, **95**, 2670 (1973).

[5] (a) That the reactions of the formylphenylalanine methyl ester and formylhydrazide go by the same acyl enzyme path was demonstrated by studying the effect of formylhydrazine on the hydrolysis of the formylhydrazide (see ref 5b for the rationale here). Formylhydrazine decreases the rate of this reaction and the decrease was equal to that predicted from studies of the partitioning of the acyl enzyme formed from the methyl ester; (b) M. Caplow and W. P. Jencks, *J. Biol. Chem.*, **239**, 1640 (1964).

[6] If identical mechanisms are assumed for acyl enzyme aminolysis and hydrolysis, the rate expression for hydrolysis will resemble eq 1. Both aminolysis and hydrolysis will have two kinetic pK's, equal to $[k_2'K_a''' + (k_{-1}+k_2)K_a'']/k_2'$ and $[(k_{-1}+k_2)K_a'''K_a'']/[k_2'K_a''' + (k_{-1}+k_2)K_a'']$, and these will undoubtedly be different for the two reactions. Also, for eq 1 to generate the observed simple sigmoidal pH–rate profile, it is required that in both hydrolysis and aminolysis $K_a''' = K_a''$, $k_{-1} > k_{-2} + k_{-2}'$ and $k_{-2} = k_{-2}'$. It is virtually inconceivable that all of these requirements are met for both reactions. The observation of an identical pH dependence for acyl enzyme hydrolysis and aminolysis would appear to dispose of the notion that Scheme I holds for *both* reactions.