Table III. Energy of COT as a Function of Bond Angle

Bond angle, deg	Unsymmetrical structures Bond lengths, Å	Unsymmetrical structures ΔH_f, kcal/mol	Symmetrical structures Bond lengths, Å	Symmetrical structures ΔH_f, kcal/mol
135.0	1.355; 1.475	73.7	1.410	87.6
132.575	1.353; 1.471	66.1	1.408	79.6
130.15	1.353; 1.471	60.9	1.407	74.2
127.725	1.353; 1.471	57.8	1.407	71.3
125.3	1.355; 1.473	56.7	1.408	70.3

shift in fact takes place *via* a symmetrical nonplanar structure as transition state; the difference in energy between this and COT would then be ΔE, rather than ΔE *plus* the energy required to flatten the COT ring. The nonplanar transition state could indeed correspond to the "crown" structure considered earlier[7] as a possibility for COT itself.

(7) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.*, 73, 3370 (1951).

(8) Robert A. Welch Postdoctoral Fellow.

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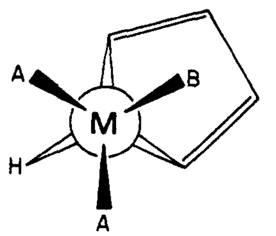
New Evidence for the 1,2-Shift Pathway in Fluxional *Monohapto*cyclopentadienylmetal Compounds[1]

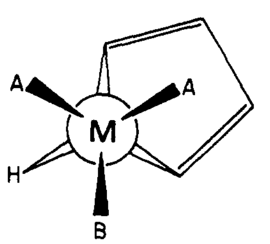
Sir:

A pmr study of $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_5H_5)^2$ (**1**) showed conclusively that rearrangement of the $(h^1\text{-}(C_5H_5)$ ring occurs predominantly by 1,2 *or* 1,3 shifts as opposed to any process causing random site exchanges. On the available evidence 1,2 shifts were preferred. Further, but indirect, evidence[3] supported 1,2 shifts. Still, this fundamental point merits further attention.

a



b



1 M=Fe; A=CO; B=$\underline{h}^5$-C_5H_5
2 M=Ru; A=CO; B=$\underline{h}^5$-C_5H_5
3 M=Mo; A=C_5H_5; B=NO

We therefore report two studies which strengthen the case for 1,2 shifts.[4]

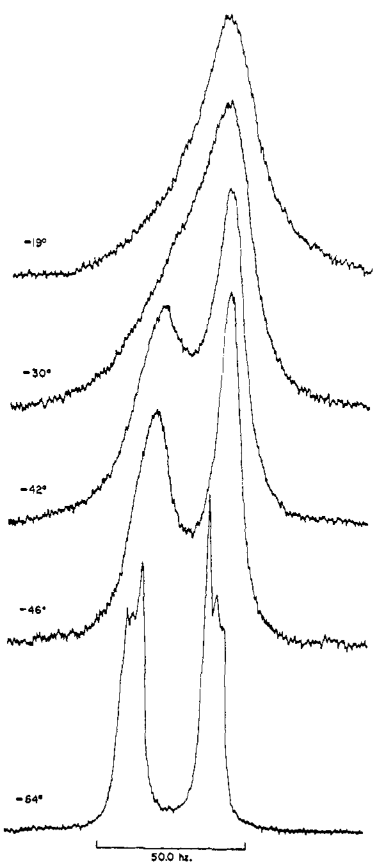


Figure 1. Spectra of the olefinic multiplet of $(h^5\text{-}C_5H_5)\text{-}Ru(CO)_2\text{-}(h^1\text{-}C_5H_5)$ recorded at several temperatures in 3:1 (v/v) CS_2–$C_6D_5CD_3$ at 100 MHz.

(1) $(h^5\text{-}C_5H_5)Ru(CO)_2(h^1\text{-}C_5H_5)$ (**2**) has been prepared.[5a] Pmr spectra of both **1** and **2** have been studied at low temperatures. Both show unsymmetrical collapse of the olefinic multiplet (Figure 1), with the low-field side collapsing more rapidly.[5b] As explained before, assignment of this part of the multiplet to H(2), H(2′) proves 1,2 shifts, while assigning it to H(3), H(3′) proves 1,3 shifts. Strong evidence for its assignment to H(2), H(2′) comes from the limiting low-temperature spectra, as shown in Figure 2 for **2**. The very similar limiting spectra of **1** and **2** are well reproduced by computer-simulated spectra, obtained after iterative refinement of coupling constants[6] to the values of Table I. These sets of J values, which the comparisons in Table I show to be very plausible, assume that the low-field part of each multiplet is due predominantly to H(2), H(2′). Because the H(1) resonance (a broadened triplet, well reproduced in the simulated spectra) is ~250 Hz upfield, the profile of the olefinic multiplet is negligibly altered by reversing the assignment and simultaneously the values of J_{12} and J_{13}. However, the values $|J_{12}| \approx 0$ and $|J_{13}| \approx 1.2$ are not acceptable.[7] Thus only the assignment leading to 1,2 shifts is acceptable.

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(1) Stereochemically Nonrigid Organometallic Molecules. XXVI. Previous paper in this series: F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, **19**, 237 (1969). The present study was supported in part by the Petroleum Research Fund administered by the American Chemical Society, and the National Science Foundation under Grant No. 7034X.

(2) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(3) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

(4) 1,2 shifts may not predominate in *all* such molecules, as for example those with nontransitional or borderline metals.

(5) (a) Made in yields of 1–5% by treating $Ru(CO)_2Cl_2$ or $Ru(CO)_2I_2$ with NaC_5H_5 in 1,2-dimethoxyethane. *Anal.* Calcd for $C_{12}H_{10}O_2Ru$: C, 50.17; H, 3.52. Found: C, 50.2; H, 3.55. (b) For **1**, $E_a = 9.8 \pm 0.1$ kcal mol^{-1} and $\log A = 11.7 \pm 0.1$; for **2**, $E_a = 10.3 \pm 0.3$ kcal mol^{-1} and $\log A = 11.2 \pm 0.2$.

(6) NMRPLOT, a modified version of the computer program LAOCN3 by A. A. Bothner-By and S. M. Castellano, was kindly supplied by Professor G. M. Whitesides of this department.

(7) (a) H. Günther, *Z. Naturforsch*, **24b**, 680 (1969), shows that J_{13} varies from +1 to −1.8 Hz with dihedral angle, γ, being 0 for $\gamma \approx 60°$. (b) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**,

Table I. Proton–Proton Coupling Constants (Hz)

Compound	J_{12}	J_{13}	J_{23}	$J_{23'}$	$J_{22'}$	$J_{33'}$	Source
C_5H_6	+1.36	−1.52	+5.06	+1.09	+1.98	+1.90	*a*
1	±1.17	±0.01	+4.66	+1.15	+2.02	+2.02	*b*
2	±1.22	±0.10	4.64	1.17	2.06	2.12	*b*
Indene	2.02	−1.98	5.58				*c*
$(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_9H_7)$	~2.3	~0	5.5				*d*

[a] S. L. Manatt, personal communication. [b] This work. [c] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962). [d] Reference 3.

(2) To reconcile solution pmr data[8] and the crystal structure[9] of $(C_5H_5)_3MoNO$, it has been proposed[9] that in solution the conformers **3a** and the enantiomorphous forms of **3b** cease to be rapidly interconverted and, for any given molecule, one enantiomorph of **3b** increasingly predominates below about −60°. This explains why two C_5H_5 rings which are equivalently bonded to the Mo atom become nonequivalent in the pmr spectrum, while the olefinic multiplet of the $(h^1\text{-}C_5H_5)$ group *simultaneously* breaks up into a more complex pattern.[8] The details of this breakup provide support for 1,2-shifts by confirming the assignment of the signal at lower field to H(2), H(2′). Thus, it is the low-field side which again collapses *below* −50°, ultimately giving rise to two signals each of intensity appropriate to one proton. This can be attributed to the molecule settling into one of the **3b** configurations (both are found in the crystal[9]), in which the H(2), H(2′) protons sense their different environments strongly due to their proximity to the $(C_5H_5)_2MoNO$ moiety, while the H(3), H(3′) protons are much further away and sense the differences much less. Assignment of the low-field signal to H(2), H(2′) is thus required.

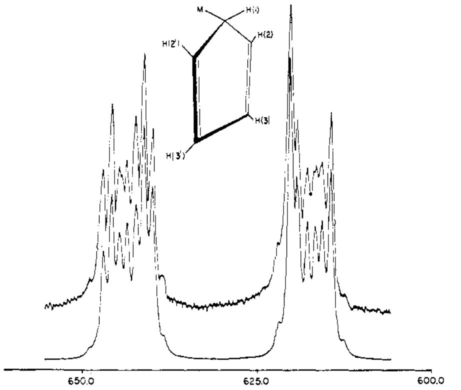

Figure 2. Upper trace: part of the limiting low temperature spectrum of $(h^5\text{-}C_5H_5)Ru(CO)_2(h^1\text{-}C_5H_5)$ recorded at −82° in 3:1 (v/v) CS_2–$C_6D_5CD_3$ at 100 MHz. Abscissa: Hz *vs.* TMS. Lower curve: computer simulated spectrum using *J* values given in Table I.

Relevant to considerations of rotational isomers of types **3a** and **3b** are some observations on **1** and **2**. Under high resolution in cyclohexane, the infrared spectra of **1** and **2** show four CO stretching bands. For **1**: 2022, 2016, 1973, 1966 cm^{-1}; for **2**: 2030, 2023, 1976, 1969 cm^{-1}. The components of each doublet have an intensity ratio of 2 ± 1 which changes by only 5–10% from −65 to +35°. We attribute these observations to approximately equal population of conformers **1a** and **1b**, **2a** and **2b**, with ΔH for **a–b** interconversions <0.5 kcal. In crystalline **1**,[2] **1a** is found.

2870 (1963), correlates J_{12} with ϕ, obtaining $J_{12} \approx$ 2–3 Hz for $\phi \approx 60°$ and $J_{12} \rightarrow 0$ as $\phi \rightarrow 90°$. The actual ϕ in **3** is about 56°, while that in cyclopentadiene (Professor V. Laurie, Princeton University, private communication) is about 55°.

(8) F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, **90**, 6232 (1968), and further studies by the present authors.

(9) J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, **91**, 2528 (1969).

(10) National Science Foundation Predoctoral Fellow, 1966–1970.

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Third-Order Rates of Conversion of Phenylacetylene, a Weak Carbon Acid, by Sodium Hypochlorite to Phenylchloroacetylene and by Sodium Hypobromite to Phenylbromoacetylene

Sir:

It is commonly accepted that the halogenation of weak carbon acids, *e.g.*, ketones, nitriles, nitroalkanes, etc., in basic solution is first order in CH, first order in base, and zero order in halogen (eq 2).[1] We now report

$$\begin{aligned} CH + OH^- &\xrightarrow{\text{slow}} C^- + H_2O \\ C^- + X_2 &\xrightarrow{\text{fast}} CX + X^- \end{aligned} \qquad (1)$$

$$\text{rate} = k[CH][OH^-][X_2]^0 \qquad (2)$$

a third-order rate law (eq 3) for halogenation ($X_2 = Cl_2$

$$\text{rate} = k[C_6H_5C{\equiv}CH][OH^-][XO^-] \qquad (3)$$

or Br_2) of the hydrocarbon phenylacetylene, according to the stoichiometry of eq 4.

$$C_6H_5C{\equiv}CH + OH^- + X_2 \longrightarrow C_6H_5C{\equiv}CX + H_2O + X^- \qquad (4)$$

Some of the kinetic data obtained for reaction 4 are given in Table I. In the range pH >11 and $[OH^-]_0 > 2[X_2]_0$, the equilibrium constants for chlorine and bromine in eq 5 are $K \simeq 10^{15}$ and 10^8, respectively,[2] so that

$$2OH^- + X_2 \rightleftharpoons XO^- + X^- + H_2O \qquad (5)$$

essentially all of the halogen is in the form of hypohalite ions. (In the range $[X_2]_0 \simeq 2[OH]_0$ in which X_2 or HOX are present, competing additions to phenylacetylene complicate this system.) The formation of phenylhaloacetylene was followed spectrophotometrically

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(1) (a) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapters IX, X; (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., Chapter 9.

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 570.