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FURTHER EVIDENCE FOR THE “PIANO STOOL” TRANSITION STATE IN η^6 -CYCLOOCTATETRAENEMETAL FLUXIONAL MOLECULES

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Summary

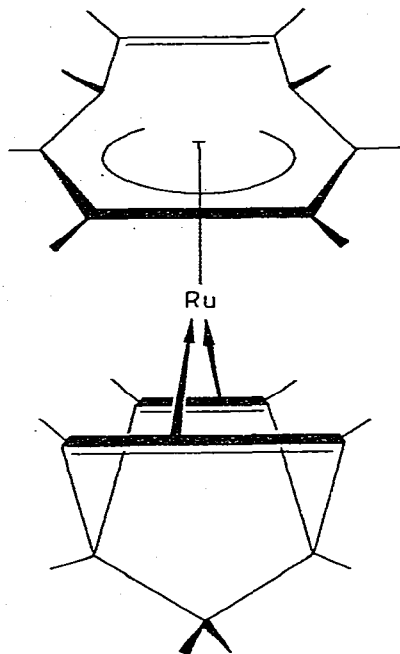
The fluxional behavior of the molecule $(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-norbornadiene})\text{Ru}$ has been studied by carbon-13 NMR spectroscopy in the temperature range -72 to $+60^\circ\text{C}$ and by proton NMR in the range -90 to $+95^\circ\text{C}$. The spectrum in the slow exchange limit is in accord with the presumed structure provided rapid rotation (or accidentally equivalent chemical shifts) is assumed for the norbornadiene ligand. In the slow exchange limit the C_8H_8 ligand has four ^{13}C signals at 127.3, 93.5, 92.3, and 66.8 ppm (vs. TMS). As the temperature is raised these all broaden and collapse at the same rate. This behavior rigorously rules out the occurrence of 1,2 shifts and is consistent only with the occurrence of a symmetrical, “piano stool” transition state or with a series of 1,3 shifts. It is argued that the former is the correct choice. Proton spectra are also reported and shown to be consistent with the mechanistic conclusion. The norbornadiene ligand rotates rapidly in such a way as to average environments of the olefinic carbon atoms (and the attached protons) though the ^{13}C spectrum shows evidence for slowing of this motion at -72°C .

Introduction

It has recently been shown [1] that for the molecules $(\eta^6\text{-C}_8\text{H}_8)\text{M}(\text{CO})_3$, where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, the process responsible for NMR equivalence of all ring carbon atoms and all ring hydrogen atoms at higher temperatures is not 1,2 shifts (as is, definitely, the case with $(\eta^4\text{-C}_8\text{H}_8)\text{M}(\text{CO})_3$ molecules [2,3]) but, instead, a process which has as a transition state a symmetrical intermediate with a structure resembling that of a piano stool. According to the explanation proposed for the particular cases studied, such a pathway should be expected in all cases which are similar structurally and electronically, regardless of the exact identity of the metal, the ring or the other ligands.

In order to test the generality of the pathway, we have studied other molecules which differ in several obvious respects from the $(\eta^6\text{-C}_8\text{H}_8)\text{M}(\text{CO})_3$ case but still have the features considered necessary and sufficient to make the "piano stool" pathway operative.

The first of these, whose behavior we report here, is $(\text{C}_8\text{H}_8)(\text{C}_7\text{H}_8)\text{Ru}$, a compound prepared and shown to be fluxional (but not mechanistically characterized) by Schrock and Lewis [4]. The suggested structure of this compound has not been confirmed crystallographically, but the only reasonable possibilities in accord with spectroscopic data are I or the closely related



(I)

arrangement in which the norbornadiene ligand, C_7H_8 , is turned by 90° about its internal C_2 symmetry axis. However, as shown by the NMR spectra, the C_7H_8 unit presumably rotates much more rapidly than the $\text{C}_8\text{H}_8\text{Ru}$ group rearranges. Therefore, this detail is of no importance in relation to the rate or mechanism of $\text{C}_8\text{H}_8\text{Ru}$ rearrangement. The important point about I with respect to the question of rearrangement pathway is that $\text{Ru}(\text{norbornadiene})$, though superficially quite different from $\text{Cr}(\text{CO})_3$, has the same qualitative electronic structure, binds to C_8H_8 in the same way to give I which should, according to our previous ideas [1], be expected to execute the same type of rearrangement as the $(\eta^6\text{-C}_8\text{H}_8)\text{Cr}(\text{CO})_3$ species and its Mo and W homologs.

Experimental section

$(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-C}_7\text{H}_8)\text{Ru}$ was prepared according to the literature procedure [4]. All samples were handled under an atmosphere of prepurified argon.

Solvents were dried over Na-K benzophenone and distilled immediately prior to use. In case of solvents used in NMR studies, trap-to-trap distillation and freeze-thaw degassing preceded their use. Sample manipulations conformed to accepted Schlenk techniques [5].

Instrumental measurements.- The proton NMR spectra were measured on a Varian Associates HA-100 spectrometer. Temperature calibrations for the variable temperature spectra were obtained from either methanol or ethylene glycol standards and are expected to be accurate to $\pm 3^\circ$.

Carbon-13 NMR spectra were recorded on a JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer operating at 25.033 MHz. The temperatures were measured with a copper constantan thermocouple and a Leeds and North-up Model 913 digital thermometer. The thermocouple was inserted into a regular NMR sample tube containing a solvent system identical to that employed for the measurements of spectra. The temperature of the cryostat was adjusted to a desired value with the thermocouple and dummy sample tube in the probe and was confirmed after each run in the same way. The two values always agreed to within $\pm 1^\circ$. Chemical shifts were measured relative to internal tetramethylsilane.

The carbon-13 and proton NMR spectra were computer simulated for purposes of line shape analysis. A locally modified version of the computer program EXCHSYS by G.M. Whitesides and J.K. Krieger was used for this simulation. These simulations and computations were performed on an IBM 360/65 computer at the Texas A & M University Data Processing Center.

Results

Carbon-13 NMR spectra for the compound $(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-C}_7\text{H}_8)\text{Ru}$ have been recorded at various temperatures ranging from -72°C to the decomposition point of the compound in solution, i.e., somewhere between the temperatures of 50°C and 60°C . This decomposition manifests itself not by plating out of black decomposition material as is so frequently the case in temperature-sensitive organometallics but by a change in color from yellow-orange to deep red. This solution behavior parallels the solid state behavior [6].

Figure 1 presents representative carbon-13 spectra of the $\eta^6\text{-C}_8\text{H}_8$ ligand as the temperature is raised from a slow exchange limit spectrum at 8°C where the four separate sharp resonances assignable to the four sets of two carbons in η^6 -cyclooctatetraene are observed, to just below the decomposition point, 50°C . The spectra were run on a saturated solution in tetrahydrofuran with 20% CDCl_3 for internal locking and 5% TMS as an internal standard. Although a complete spectrum will not be illustrated here the η^4 -norbornadiene ligand has resonances at 48.2, 39.4 and 27.2 ppm assigned, respectively, to the methylene, bridgehead and olefinic carbon atoms.

It is unfortunate that here, just as in the case of the $(\text{COT})\text{M}(\text{CO})_3$ complexes [1], a definite assignment of the ring peaks cannot be made. From previous data [7] we can be reasonably certain that the ring resonance at 127.3 ppm is due to those carbon atoms containing the free olefin. While individual assignments for the other carbon atoms cannot be made, mechanistic informa-

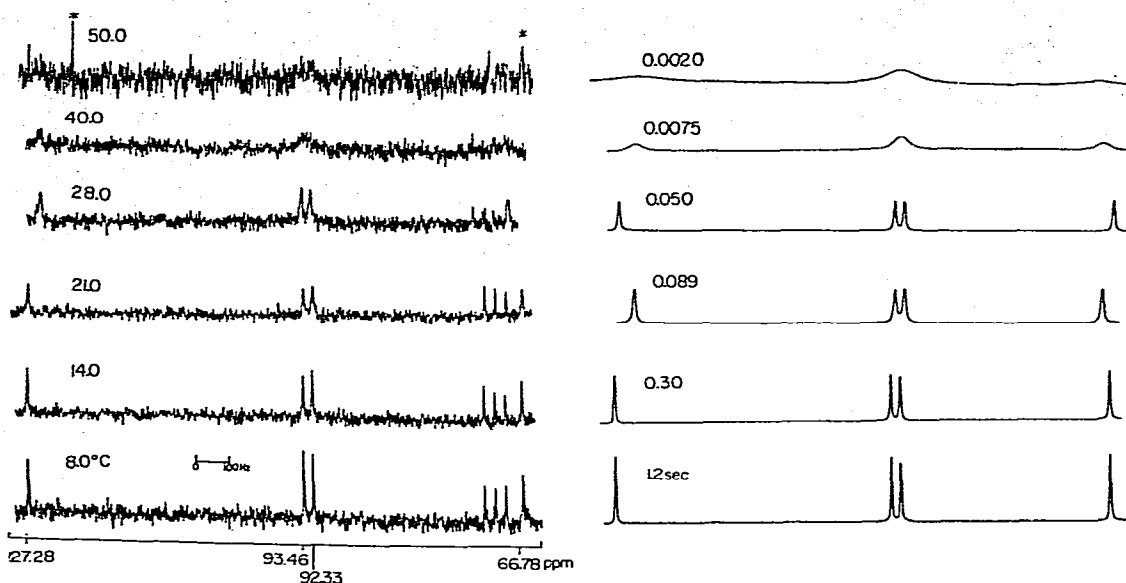


Fig. 1. Measured and computed carbon-13 NMR spectra in the ring carbon region of $(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-C}_8\text{H}_8)\text{Ru}$. The solvent system is 80% THF/20% CDCl_3 with a trace of TMS as an internal reference. The triplet immediately left of the carbon resonance at 66.8 ppm is due to CDCl_3 . Temperatures ($^\circ\text{C}$) and mean preexchange lifetimes (sec) are indicated. Asterisks indicate resonances due to thermal decomposition products.

tion may be gleaned from temperature dependence of the spectrum, as will be shown presently.

The spectrum was also recorded at several temperatures below 9°C , the lowest being -72°C , where sample crystallization was extensive. The four cyclooctatetraene resonances, the methylene resonance and the bridgehead resonances were unchanged from those present at 9°C . However, the olefinic resonance collapsed. Presumably, it would reappear in a one to one pattern in accord with the structure I, if spectra could be obtained at still lower temperatures.

Proton NMR spectra were run at temperatures ranging from -90 to 95°C . Thermal instability did not interfere with measurements from 50 – 95°C as in the ^{13}C spectra, because the proton spectra could be measured much more quickly. For the ^{13}C spectra at least 2000 pulses were required to give an acceptable carbon-13 spectrum above 50°C , and this required approximately forty minutes.

Both the measured proton spectra in the ring proton region as well as computer simulated spectra are presented in Fig. 2. The sample was dissolved in toluene- d_6 utilizing TMS as both an internal standard and an internal lock signal. The resonance positions for the four sets of ring protons were 4.19, 4.99, 5.04 and 5.41 ppm downfield from TMS and the corresponding linewidths 8, 4, 10 and 8 Hz, respectively. Because of the inherent ambiguity in line widths due to proton-proton coupling the activation parameters derived from the proton spectra are subject to considerable inaccuracy. Again the norbornadiene

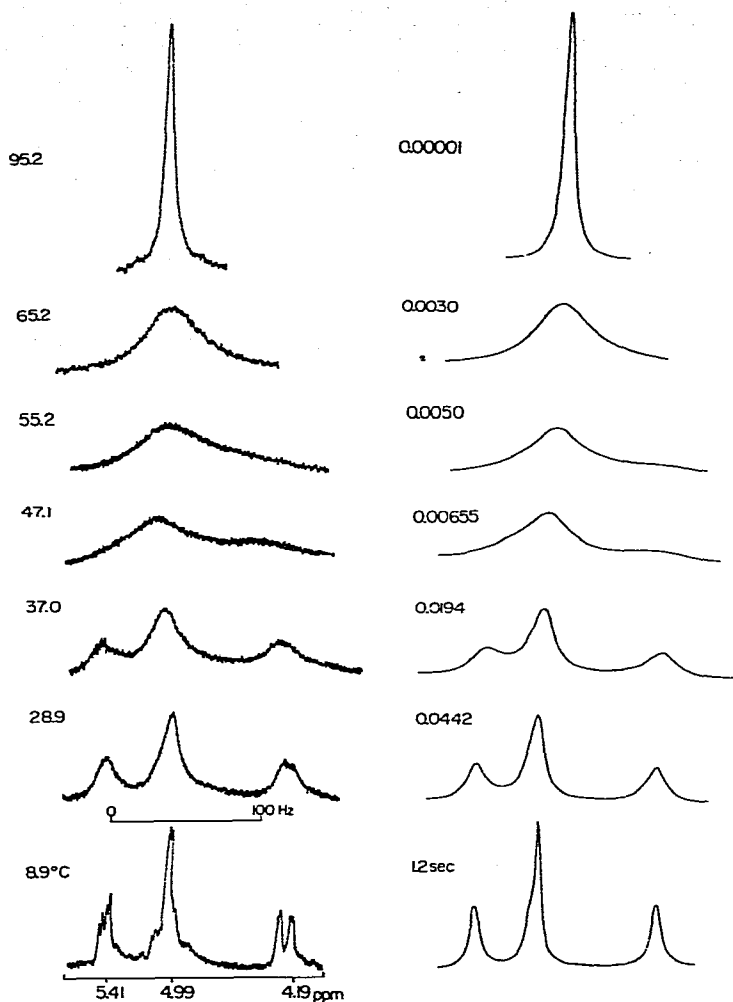


Fig. 2. Proton NMR spectra and corresponding computer simulations of the ring proton region of $(\eta^6\text{-C}_8\text{H}_8)(\eta^4\text{-C}_7\text{H}_8)\text{Ru}$. Spectra were run in toluene- d_8 with a lock and internal reference signal of TMS. Temperatures ($^{\circ}\text{C}$) and mean preexchange lifetimes (sec) are indicated.

portion of the spectrum is not presented. While the slow exchange limit spectrum for η^6 -cyclooctatetraene was reached at 9°C , even at -90°C the norbornadiene signals remained unchanged from their room temperature shapes.

A close comparison of Figs. 1 and 2 will reveal that the preexchange lifetimes at certain temperatures are not identical for the ^{13}C and ^1H spectra. The differences, which never exceeded a factor of 2 and could contribute only small errors to estimates of activation parameters, arise because the two sets of measured spectra were matched independently of each other. The existence of these small discrepancies is actually useful and we have made no attempt to eliminate them, since they give a practical estimate of the precision attainable in matching computed spectra to observed spectra.

Discussion

This work was undertaken to test the generality of the "piano stool" intermediate in the rearrangement of *hexahapto*-cyclooctatetraene-metal systems. The only prior mechanistic carbon-13 NMR studies of η^6 - C_8H_8 ligand systems dealt with the $(\eta^6-C_8H_8)M(CO)_3$ ($M = Cr, Mo$ and W) molecules, where it was found that the only mechanisms consistent with the experimental data were random or 1,3-shifts, and the 1,3-shift mechanism was rejected. Extension of such studies to other transition metal triads containing *multihapto* cyclic polyene ligands is necessary to test the generality of this conclusion.

The work of Schrock and Lewis [4] provided the first practicable η^6 -cyclooctatetraene complexes of Group VIII metals, in particular, ruthenium and osmium. * While $(\eta^4-C_8H_8)Fe(CO)_3$ and $(\eta^4-C_8H_8)Ru(CO)_3$ have been studied in detail [3,9] and the mechanism of rearrangement proven to be 1,2 shifts [3,9] no compound of this triad which was experimentally and spectroscopically tractable containing a $\eta^6-C_8H_8$ ligand had yet been synthesized. The complex $(\eta^6$ -cyclooctatetraene) $(\eta^4$ -norbornadiene)ruthenium appeared to be well suited to our purpose.

The carbon-13 and proton NMR spectra, illustrated in Figs. 1 and 2, respectively, show that here, just as in $(\eta^6-C_8H_8)M(CO)_3$ systems, the process which interconverts ring sites is one that causes each of the four sets of ring carbon resonances to collapse at the same rate. This immediately eliminates both 1,2 and 1,4 shifts as possibilities. The proton NMR results eliminate 1,5 shifts, because at high temperatures this mechanism would lead to two equally intense resonances, whereas a single line is observed.

According to the analysis presented in earlier papers [1-3] the only remaining possibilities are 1,3 shifts and some process which scrambles the sites randomly. For the reasons previously given [1] we reject the 1,3 shift process and propose instead an intimate mechanism in which the eight-membered ring becomes flat, or nearly so, while at the same time the metal atom assumes a position equidistant from all of the carbon atoms. In a compound where the other ligands are three CO groups, the shape of the molecule at this point is very similar to that of an old fashioned piano stool and we have therefore referred to it as the "piano stool" intermediate or transition state. This designation is retained here, for the sake of consistency, even though the pictorial appositeness is lacking when there is no resemblance between the other ligand(s) and the legs of a piano stool.

Neither the ^{13}C nor the proton NMR spectra are well suited to the evaluation of activation parameters since the former were obtainable only below the coalescence temperature while the latter exhibit spin-spin couplings that strongly affect the apparent line widths. Consequently, only crude estimates have been made. The reciprocal rates and temperatures for the ^{13}C spectra are too limited and uncertain to warrant an Arrhenius plot, but for the proton

* We are aware of the existence of the catalytically important molecule $(\eta^6-C_8H_8)(\eta^4-C_8H_8)Fe^0$, but problems associated with assignment of individual resonances, as well as the insurmountable problem of ring interchange occurring at a temperature ($-50^\circ C$) where eccentric rotation of the $\eta^6-C_8H_8$ ring is only commencing [8] make this unsuitable for our purposes.

spectra such a plot gave a reasonably good straight line and from a least squares fitting the following Arrhenius parameters were obtained: $\log A = 11.6 \pm 0.9$ and $E_a = 14.1 \pm 0.70$ kcal/mole. The value of A corresponds to a ΔS^\ddagger of about -6 eu. While a negative ΔS^\ddagger seems reasonable in view of the proposed transition state, the magnitude may be too large. If, instead, we assume that $\Delta S^\ddagger = 0$, which corresponds to $\log A = 13.2$, then for each of the five proton spectra and three ^{13}C spectra in which the lines are fairly broad (i.e., those in the intermediate exchange rate range) we calculate an activation energy of 16.2 ± 0.2 kcal/mole. We conclude that $\log A = 12.4$ (i.e., $\Delta S^\ddagger = -3 \pm 3$ e.u.) and $E_a = 14.0 \pm 1.5$ kcal/mol are the best estimates of activation parameters obtainable from the data at our disposal.

Finally we note that tentative evidence is obtained in the ^{13}C spectrum for deceleration of the rotation of the norbornadiene group relative to the C_8H_8 portion of the molecule. In either the rotamer shown in I or that obtained by an internal rotation by 90° , the four olefinic carbon atoms of the norbornadiene form two nonequivalent pairs, but internal rotation averages their environments. We assume that the collapse of the resonance for these carbon atoms that is observed at -72°C indicates that rotation is becoming too slow to average them on the NMR time scale. The fact that the resonance for the two bridgehead carbon atoms remains sharp might indicate that the preferred rotamer is that shown in I, where these carbon atoms are equivalent, but the possibility that the orthogonal rotamer is preferred cannot be conclusively ruled out since, in that case, there might be only a small difference in the chemical shifts.

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