The Mechanism of Hydrogen Migration in Cyclohexadienylmanganese Tricarbonyl

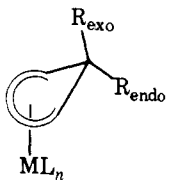
W. Lamanna and M. Brookhart*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received October 1, 1979*

Abstract: The thermal isomerization of 6-*exo*-^{1}H-cyclohexadienyl-d_6-manganese tricarbonyl (VIII) was carried out at 145 °C in octane-d_{18}. The single 6-exo hydrogen (^{1}H) isomerizes to vinylic ring sites by a unimolecular process with first-order rate constant $k = 1.1 \times 10^{-5}$ s^{-1} at 145 °C, $\Delta G^{\ddagger} = 34$ kcal/mol. The *initial* (first 20% reaction) ratios of H incorporation into ring sites (1,5), (2,4), and 3 were 1.1:1.2:1.0, respectively. No ^{1}H incorporation into the 6-endo position is noted. Based on these results, the mechanism proposed for hydrogen migration involves insertion of manganese into the endo C–D bond to form an intermediate η^4-benzenemanganese tricarbonyl deuteride, Xa. At competitive rates, this intermediate can collapse to cyclohexadienylmanganese tricarbonyl or undergo 1,2 manganese shift which results in scrambling of ^{1}H to new sites in the η^4-benzene intermediate. Estimation of the activation energy for 1,2 manganese migration of ca. 15–20 kcal/mol establishes the free-energy difference between the cyclohexadienylmanganese tricarbonyl complex and the intermediate η^4-benzenemanganese tricarbonyl hydride as ca. 14–19 kcal/mol.

Introduction

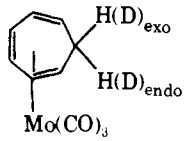
Cyclic polyolefin transition metal complexes of general structure I exhibit thermally induced hydrogen migrations.[1] A common feature of these isomerizations is that H_{endo} mi-



I

grates to other carbon sites always remaining endo, which results in scrambling of R_{exo} to other ring positions without R_{exo}–C bond cleavage. Most mechanistic schemes which have been advanced to account for specific H_{endo} migration invoke formation of metal hydride intermediates or, at the least, strong metal–H_{endo} interaction during migration.

Cycloheptatriene-7-d_1-molybdenum tricarbonyl (II, 50:50 mixture of D_{exo} and D_{endo}) is reported[1e] to show scrambling of H_{exo} at equal rates to all olefinic ring positions. $H(D)_{endo}$



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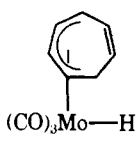
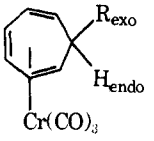


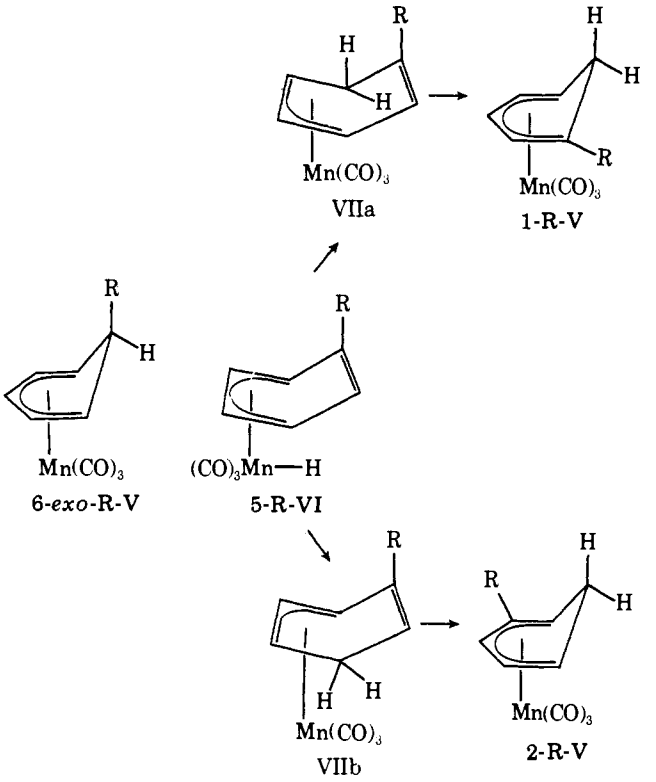
III



IV

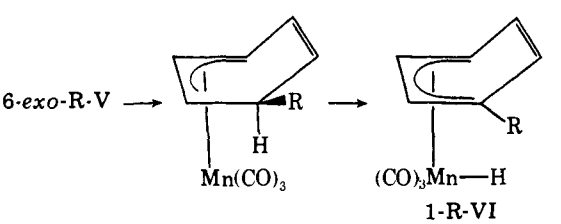
migration to metal with formation of a cycloheptatrienylmolybdenum tricarbonyl hydride in which all ring positions can equilibrate was proposed to account for the observed data. In view of more recent work on cycloheptatrienylmetal complexes,[2] the most likely structure for such an intermediate would be a rapidly fluxional 18-electron η^5-cycloheptatrienylmolybdenum tricarbonyl hydride, III. In contrast, for the structurally similar 7-exo-substituted cycloheptatrienechromium tricarbonyl systems, IV (R = CH_3, C_6H_5), Pauson has observed[1d] not random scrambling of R_{exo} to other ring positions but sequential 1,5 migration. These results were rationalized by a Cr-assisted endo-H migration without formation of a discrete Cr–H intermediate.

The thermal isomerizations of 6-exo-substituted cyclohexadienylmanganese tricarbonyl systems, 6-*exo*-R-V (R = CH_3, C_6H_5), have been examined by Pauson[1a] and shown to undergo endo-H migration. In the case of R = CH_3 equal ratios of the 1- and 2-methyl isomers are initially formed, while for R = C_6H_5 the 1 isomer predominates over the 2 isomer. The 3 isomers are unobserved. The intermediate proposed to account for formation of the 1 and 2 isomers was 5-R-VI, which may form coordinately unsaturated intermediates VIIa and VIIb



by metal hydride migration to either terminus of the η^4 fragment. Coordination of the free olefin results in formation of the 1- and 2-R-V isomers.

The difficulty with this mechanism is that, applying microscopic reversibility, intermediate 5-R-VI cannot be formed



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directly from 6-*exo*-R-V; species 1-R-VI would be expected, as indicated below. Direct collapse of 1-R-VI would result in regeneration of 6-*exo*-R-V or the unobserved 3 isomer.

The complex 1,2,5,6-η^4-cycloheptatriene-7-d_1-rhodium acetylacetonate has been shown[1c] to undergo endo-H migration, but ^{1}H integrals were not sufficiently accurate to allow any conclusions regarding the initial sites to which the 7-exo-D migrates.

The currently available data clearly point to certain problems associated with determining the detailed mechanism of hydrogen migration in systems of general structure I. In most cases examined, the structure of the plausible intermediate metal hydrides is such that fluxional metal migration, which could be competitive with collapse, must be considered in analyzing data. For exo-substituted systems (R_{exo} = alkyl, aryl) the case is quite complex in that the potentially fluxional intermediates may exist as several isomers, and as we and others have demonstrated[3,4] substituents often exhibit strong site perferences. Thus products could result from collapse of one predominant isomer and mechanistic conclusions based on R_{exo} as a "well-behaved" label could be incorrect. Such a possibility may account for the differences observed in the unsubstituted and substituted cycloheptatriene-M(CO)$_3$ (M = Mo, Cr) systems (II and IV)[1d,e] and the absence of the 3 isomer (3-R-V) in the initial thermal isomerization of the 6-exo-substituted cyclohexadienylmanganese systems.[1a]

Clearly the best systems for determining the basic mechanistic features of the isomerization are the specifically deuterated systems where fluxional intermediates are not biased by substituents. However, the systems labeled with a single deuterium on the methylene position, although synthetically readily accessible, are far from ideal in that assessing *initial* ratios of deuterium incorporation (first 20% reaction) into various (protio) ring sites relies on accurate measurement of quite small decreases in the ^{1}H integrals. Measurement of initial ratios is critical to prevent biasing of the data from multiple shifts which eventually results in random scrambling. The ideal systems for examination are then those in which the olefinic and endo positions have been completely deuterated and the exo position is "labeled" with ^{1}H. In isomerizations of such systems, the ratios of *initial* ^{1}H incorporation into various ring sites may be readily and accurately measured and these ratios are not biased by substituent site preferences. We have undertaken examination of several systems labeled in this fashion[5] and wish to report here results obtained with 6-*exo*-^{1}H-cyclohexadienyl-d_6-manganese tricarbonyl (VIII), which allows a detailed description of the isomerization mechanism and provides interesting insight into the structure and behavior of the metal-hydride intermediate.

Results and Discussion

Deuterium Labeling. The 6-*exo*-^{1}H-hexadeuteriocyclohexadienylmanganese tricarbonyl complex (VIII) was prepared by reduction of the hexafluorophosphate salt of η^6-$C_6D_6Mn(CO)_3^+$ with lithium aluminum hydride. Hydride attack is exclusively exo and the resulting cyclohexadienyl-d_6 complex exhibited an exo ^{1}H resonance at δ 2.08 (triplet, J_{HD} = 3.8 Hz) with low-intensity signals δ 2.59, 2.91, 4.77, and 5.85 corresponding to residual ^{1}H in the 6-endo, (1,5), (2,4), and 3 positions, respectively. The random distribution of protio material in the latter positions originates from residual protons in the benzene-d^6 used in the preparation of this complex and corresponds to ca. 1% protio material in each position.

Thermal Isomerization. A detailed description of the preparation of ^{1}H NMR samples and the thermal isomerization procedure is given in the Experimental Section. In 5-mm NMR tubes, samples of 6-*exo*-^{1}H-cyclohexadienyl-d_6-manganese tricarbonyl were dissolved in octane-d_{18} solvent under a nitrogen atmosphere. The solutions were degassed by several freeze–pump–thaw cycles and the tubes were sealed under high vacuum. Thermal isomerization was accomplished by heating NMR samples at 145.0 ± 0.5 °C for ca. 1-h intervals. The reaction was quenched by cooling to 25 °C and the progress of the isomerization was monitored by ^{1}H NMR. Detailed studies were carried out at two concentrations, ca. 0.1 and 0.4 M in labeled complex.

Table I.[a] Distribution of $C_6D_6HMn(CO)_3$ Isomers[b] as a Function of Time

h[c]	% 6-*exo*-^{1}H-VIII	% 3-^{1}H-VIII	% 2-^{1}H-VIII	% 1-^{1}H-VIII
0	96.0	0.8	1.5	1.7
1.48	91.8	2.1	3.1	2.9
2.48	85.2	3.8	5.5	5.5
3.62	82.0	4.7	7.2	6.1
5.17	77.4	6.0	8.6	8.0
6.85	73.4	7.4	9.6	9.6
7.73	68.7	8.4	12.1	10.8
8.80	67.3	8.5	12.6	11.6
12.13	60.2	10.6	15.4	13.7
16.28	53.7	11.9	17.1	17.3
29.53	38.8	14.7	23.2	23.2
>45.73	17.3	16.9	33.3	32.6

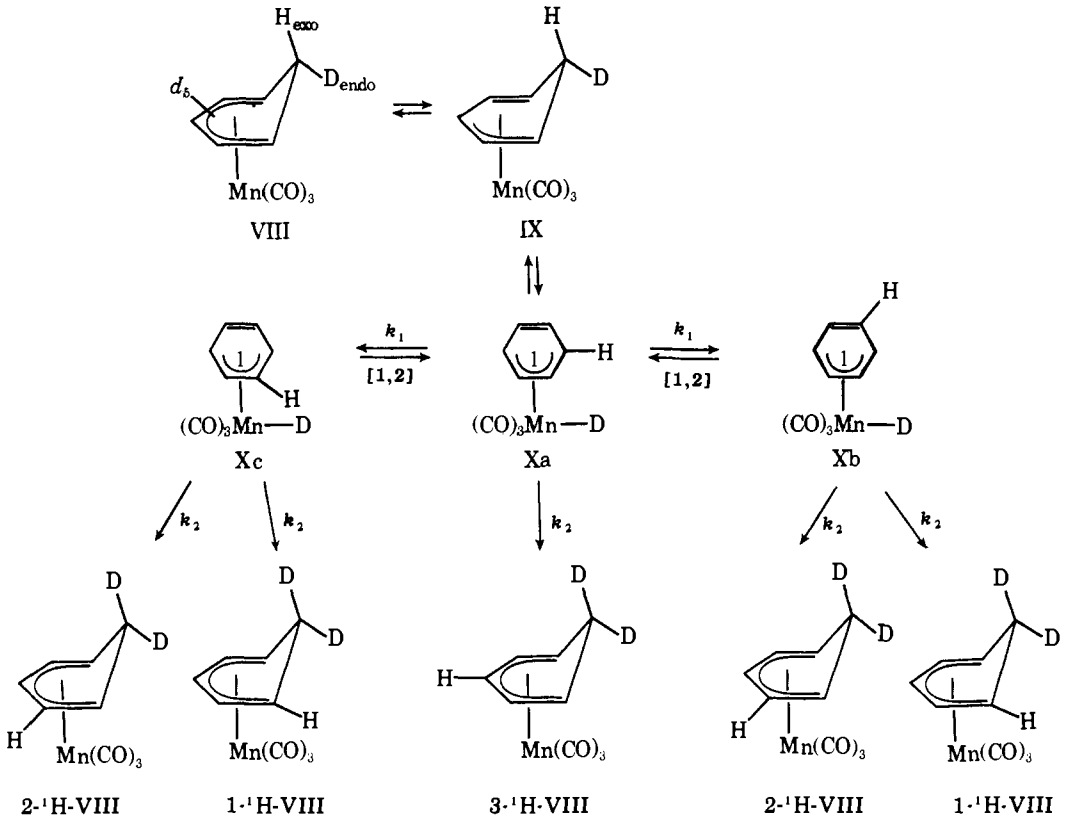
[a] Data obtained by integration of NMR spectra of thermolyzed sample of VIII (ca. 0.1 M). [b] Endo-^{1}H isomer not included since H_{endo} resonance remains unchanged. [c] Hours at 145 °C.

Table I summarizes the data obtained for a run which was 0.1 M in complex. The H_{endo} signal remained unchanged in intensity throughout the course of the isomerization and is not entered in the table. The integrals for the H_{exo}, H_1, H_2, and H_3 signals have been normalized to 100 for each point. Qualitative inspection of the data reveals that H_{exo} does not migrate initially to a single site, but neither is completely random scrambling (i.e., H_1:H_2:H_3 = 2:2:1) observed. Quantitatively, the first-order rate constants for initial disappearance of H_{exo}, calculated for the first 25% reaction to avoid problems with multiple shifts, were $k = 1.1 \times 10^{-5}$ (0.1 M) and 1.2×10^{-5} s^{-1} (0.4 M) at 145 °C corresponding to $\Delta G^{\ddagger} = 34.0$ kcal/mol. (Good first-order plots are obtained for the first 25% reaction; first-order kinetics is demonstrated by invariance of k with concentration of the complex.) The rates of initial ^{1}H incorporation into the olefinic ring positions were also determined, the average relative rates being 1.1:1.2:1.0 for the (1,5), (2,4), and 3 positions, respectively. As is evident from the table, at long times ^{1}H becomes randomly distributed, as expected, over all ring sites excluding the endo position.

Isomerization Mechanisms. The lack of ^{1}H incorporation into the 6-endo position confirms Pauson's observations and conclusions that it is solely the 6-endo hydrogen (deuterium) which undergoes migration.[1a] However, the behavior of 6-*exo*-methyl and -phenyl substituted systems which rearrange predominantly to the 1 and 2 isomers is in contrast to VIII, which shows incorporation of ^{1}H into all three ring sites with incorporation at the 3 position favored if statistical corrections are made.

Shown in Scheme I is what we believe to be a reasonable and complete description for isomerization of VIII. Certain features are similar to those earlier proposed by Pauson[1a] and have many analogies to the mechanisms of hydrogen migrations in in iron diene complexes studied by Whitesides.[6] Dissociation of an olefinic unit from VIII produces the 16-electron unsaturated π-allyl complex IX. Insertion of the metal into the endo C–D bond will then yield the η^4-benzenemanganese deuteride Xa with the single ^{1}H at position 1. C_1 is equivalent to C_4 in this intermediate and collapse will lead either back to starting VIII or to 3-^{1}H-VIII. However, in analogy with other η^4-arene complexes,[7,8] intermediate Xa is capable of fluxional metal migration around the ring. The first shift, assuming 1,2 metal

Scheme I

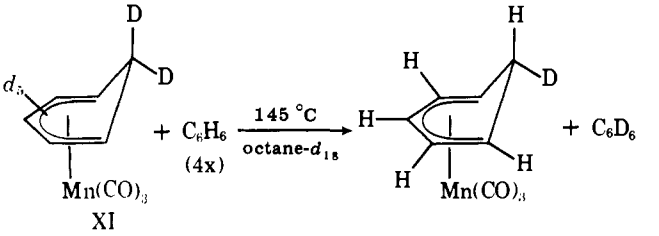


migration, will give rise to either Xb or Xc, both of which collapse through π-allyl intermediates to 50:50 mixtures of 1-^{1}H-VIII and 2-^{1}H-VIII products.

The ratios of initial ^{1}H incorporation into positions (1,5), (2,4), and 3 will depend on the relative magnitude of the rates of collapse of Xa to the dienyl complex, k_2, and the rate of fluxional metal migration, k_1. If $k_1 \gg k_2$ (metal migration faster than collapse), then ^{1}H incorporation into positions (1,5), (2,4), and 3 will occur in a statistical 2:2:1 ratio, respectively. If $k_1 \ll k_2$, then initially ^{1}H incorporation will occur only at site 3. At long reaction times incorporation of ^{1}H at sites (1,5) and (2,4) will occur at equal rates. If $k_1 \simeq k_2$, then initial incorporation at all sites will occur, with site 3 showing greater than statistical incorporation and sites (1,5) and (2,4) less than statistical incorporation. In addition, sites (1,5) and (2,4) will also show *equal* rates of ^{1}H incorporation. These latter conditions are precisely what is observed and thus we propose that the mechanism shown in Scheme I obtains where $k_1 \simeq k_2$.

There is a second mechanism which is plausible and which must be conclusively ruled out. The observed results could be explained by the mechanism in Scheme I where $k_1 \ll k_2$ (specific ^{1}H incorporation at site 3) coupled with a mechanism which would exhibit statistical incorporation of ^{1}H into sites (1,5), (2,4), and 3. Such a randomizing process could occur by exchange of traces of free benzene (in this case benzene-d_5) generated by slight decomposition of VIII with the η^4-bound arene in Xa. This exchange process would clearly randomize ^{1}H in VIII and only low concentrations of free benzene-d_5 would be required to allow its operation. The feasibility of this mechanism is reinforced by Pauson's observations that the η^4-arenemanganese hydride intermediates do exchange with free arenes and by the fact that during thermal isomerization of VIII we do observe low concentrations of benzene-d_5 from trace decomposition.

The conclusive experiment which rules out this mechanism is the demonstration that exchange is a much slower process than thermal isomerization. The perdeuterated complex XI (prepared by lithium aluminum deuteride reduction of $[C_6D_6Mn(CO)_3](PF_6)$ was treated with a *fourfold* molar excess of C_6H_6 in octane-d_{18} under thermal isomerization conditions (145 °C) and the following exchange was observed:

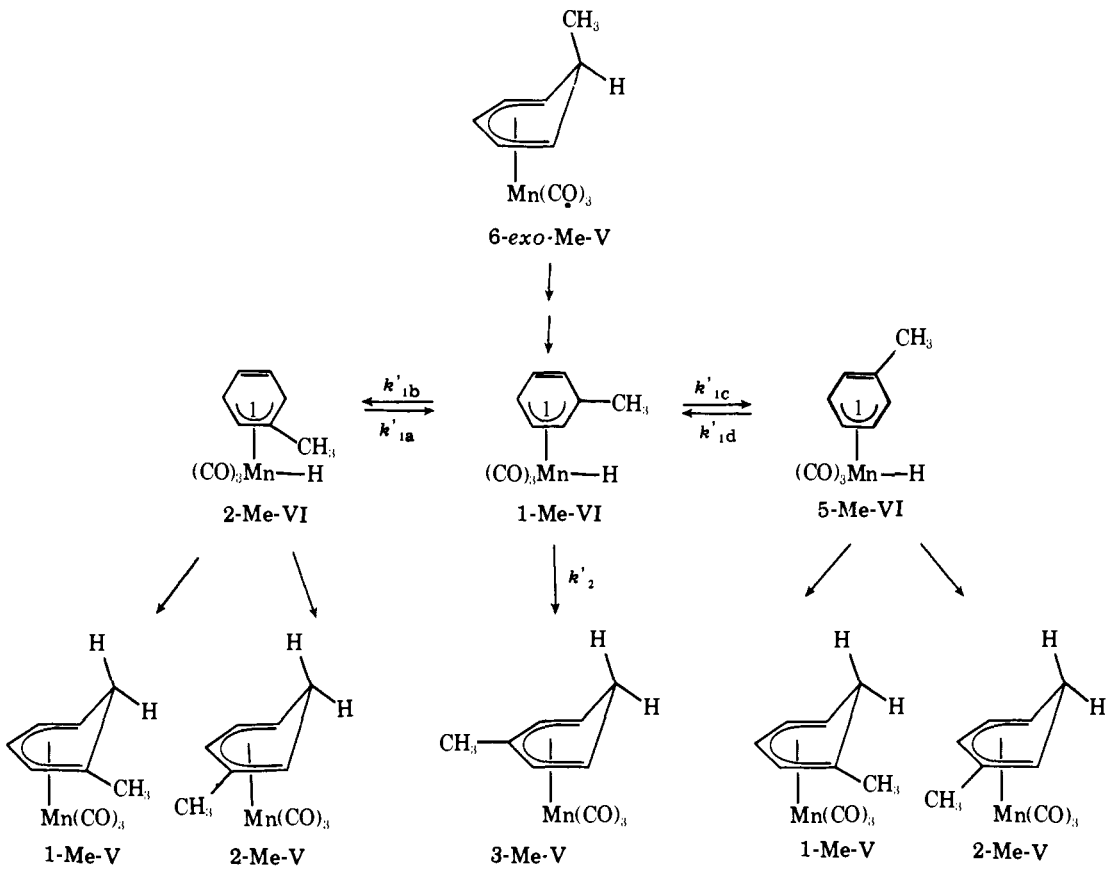


The lack of incorporation of ^{1}H into the endo site confirms Pauson's conclusions[1a] that exchange occurs through an η^4-arenemanganese hydride (deuteride) intermediate where the endo-H(D) is the source of the Mn-H(D). The rate of exchange, even with a fourfold excess of benzene present, is very much slower than hydrogen migration. After 32 h at 145°C only ca. 1.2% C_6H_6 had been incorporated into the dienyl complex, while the half-life for hydrogen migration in VIII is only 17 h. Thus the exchange of the η^4-arene in Xa is not competitive with collapse and exchange mechanisms can be eliminated from consideration in the hydrogen-migration process.

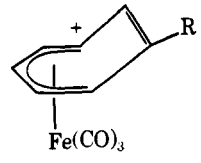
The results for the 6-exo-substituted systems, V, must now be examined in light of the mechanistic features observed for the parent system. Using the 6-exo-methyl isomer as an illustration, Scheme II seems most plausible for generating the 1- and 2-methyl isomers.

The lack of the 3-methyl isomer in the initial products could be explained if isomers 2-Me-VI and/or 5-Me-VI were favored thermodynamically over 1-Me-VI and if k'_2 were less than k'_{1a} and/or k'_{1c}. Given the delicate balance of the rates of collapse and fluxional shift in the parent system and the marked effect

Scheme II



of substituents on equilibria of the type 2-Me-VI ⇄ 1-Me-VI ⇄ 5-Me-VI,[3,4] such conditions seem quite plausible. In fact, based on the monosubstituted $C_7H_6RFe(CO)_3^+$ systems[2] in which both methyl and phenyl prefer the free olefinic site (isomer XIV most stable), we suggest that the 5-methyl



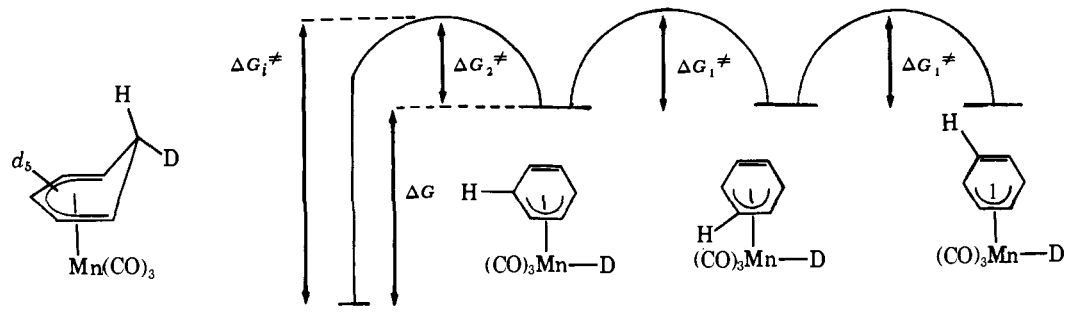
XIV

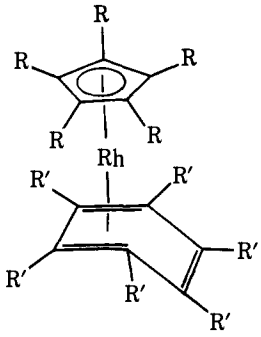
(phenyl)-VI isomer is probably favored. Thus, in accord with Pauson's suggestion, products most likely arise from collapse of 5-R-VI which is, however, formed as indicated in Scheme II. Based on the fact that the hybridization of the terminal carbons, $C_{1,4}$, of the η^4 fragment are closer to sp^3 than $C_{2,3}$ or $C_{5,6}$ and in analogy with the isomer preferences of the iron system, 1-Me-VI is likely the *least* stable isomer. This further supports the idea that the absence of 3-R-V products is due to more rapid fluxional isomerization than collapse in 1-R-VI.

It is interesting to consider the reaction profile diagram for VIII (Chart I) (η^3 intermediates are not shown). The $\Delta G_i^{\ddagger}$ is 34 kcal/mol calculated from k_{isom} while $\Delta G_1^{\ddagger} \simeq \Delta G_2^{\ddagger}$ since $k_1 \simeq k_2$. If $\Delta G_1^{\ddagger}$, the free energy of activation for 1,2 Mn shift, could be estimated, $\Delta G_2^{\ddagger}$ would be available and ΔG, the difference in free energy between cyclohexadienylmanganese tricarbonyl (VIII) and the intermediate η^4-benzenemanganese hydride (Xa), could be approximated ($\Delta G_i^{\ddagger} - \Delta G_2^{\ddagger}$). The most attractive models for estimating $\Delta G_1^{\ddagger}$ would be other fluxional η^4-arene metal complexes. Complexes of this type are rare[7-11] and only two have been studied in terms of their fluxional behavior.[7,8] The η^4-C_6Me_6-η^6-C_6Me_6Ru system studied by Muetterties[8] is not a suitable model in that it undergoes exchange of all sites by interconversion of the η^4 and η^6 rings; however, η^4-$C_6(CO_2Me)_6RhC_5Me_5$ (XII) examined by Maitlis[7] does show 1,2 Rh migration with $\Delta G^{\ddagger}$ = 20.2 kcal/mol. Another crude model for Xa is the η^5-cycloheptatrienylmanganese tricarbonyl (XIII). From analysis of line shapes, Whitesides[2] estimated $\Delta G^{\ddagger}$ for 1,2 Mn migration as 14 kcal/mol. Assuming that these models indicate the approximate value of $\Delta G_1^{\ddagger}$ then $\Delta G_2^{\ddagger}$ is ca. 15–20 kcal/mol and the difference in free energies between VIII and Xa lines in the range of 14–19 kcal/mol.

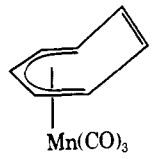
In summary, the unique approach to labeling the cyclohexadienylmanganese tricarbonyl system described here has

Chart I





XII, R = Me
R' = CO_2Me



XIII

allowed a detailed formulation of the hydrogen-migration process in this complex. The involvement of a dienemanganese tricarbonyl hydride which undergoes, at competitive rates, either fluxional manganese migration or collapse to cyclohexadienylmanganese tricarbonyl has been clearly demonstrated. These results clarify the isomerization mechanism of 6-exo-substituted systems which lead initially to formation of specific isomers. Application of these labeling techniques to other systems of general structure I should be straightforward and lead to a firm understanding of the mechanistic details of hydrogen migration in these systems. The thermal isomerizations of appropriately labeled cycloheptatriene and cyclohexadiene transition metal complexes are currently under investigation.

Experimental Section

General. All reactions and manipulations were performed under a dry, oxygen-free, nitrogen atmosphere. ^1H NMR spectra were recorded at 100 MHz using a Varian XL-100 FT NMR spectrometer or 60 MHz using a Perkin-Elmer R24-B CW NMR instrument. Deuterated NMR solvents were distilled under vacuum from 4 Å molecular sieves and degassed by several freeze-pump-thaw cycles prior to use. An insulated oil bath equipped with a direct reading mercury thermoregulator provided constant temperatures (±0.5 °C) for the thermal rearrangement and exchange studies. Manganese pentacarbonyl bromide was prepared from dimanganese decacarbonyl (Strem) according to the procedure of King.[12]

Benzene-d_6-manganese tricarbonyl hexafluorophosphate was prepared using a modification of procedures described previously.[13,14] Manganese pentacarbonyl bromide (9.4 g, 0.0344 mol) and anhydrous, technical-grade aluminum chloride (11.00 g, 0.0825 mol) were refluxed in ca. 50 mL of benzene-d_6 (>99% D, freshly distilled from molecular sieves) for 3 h. Initially carbon monoxide was evolved followed by separation of a brownish bottom layer and yellow upper layer. After cooling (0 °C), 100 mL of ice water was added dropwise with stirring, resulting in formation of a yellow, aqueous layer. The aqueous layer was separated, washed with 100 mL of toluene, filtered through cotton, and collected. This solution was in turn shaken with 120 mL of light petroleum ether (bp 35-60 °C), separated, and then treated dropwise with an excess of 65% aqueous hexafluorophosphoric acid while stirring vigorously. The resulting pale yellow precipitate was filtered through a medium frit, washed with small portions of water and methanol, and dried in vacuo (0.01 mm), giving 8.87 g (70% based on $Mn(CO)_5Br$) of crude benzene-d_6-manganese tricarbonyl hexafluorophosphate. Further purification by recrystallization from acetone/ethanol was possible but led to much lower yields and was unnecessary for our purposes. ^1H NMR (acetone-d_6): δ 6.45 (s).

6-*exo*-^1H-Cyclohexadienyl-d_6-manganese Tricarbonyl. The methods of Pauson[15] and Wilkinson[13] were modified to prepare the specifically deuterated *exo*-^1H-cyclohexadienyl complex. A stirred suspension of crude benzene-d_6-manganese tricarbonyl hexafluorophosphate (3.30 g, 0.008 97 mol) in anhydrous ether (freshly distilled, 100 mL) at room temperature was treated with lithium aluminum hydride (0.56 g, 0.015 mol) in small portions. The solid dissolved slowly forming a yellow solution. After 3.5 h, water (20 mL) was added dropwise to destroy the excess hydride. Additional ether was added and the layers were separated. The aqueous layer was extracted with 2 × 20 mL of ether, and the ether fractions were combined, dried over sodium sulfate, filtered through Celite, and evaporated to give the crude product. This material was chromatographed on a short column of neutral alumina (activity II) using pentane as eluent. The yellow band which eluted first was collected and the product further purified by evaporation of solvent, recrystallization from pentane at −78 °C, vacuum sublimation (0.01 mm, 45 °C), and recrystallization again from pentane. Bright yellow crystals (1.09 g, 54% based on $C_6D_6Mn(CO)_3PF_6$) of the desired product were recovered as identified by ^1H NMR. ^1H NMR ($CDCl_3$): δ 2.08 (t, $^2J_{D-H}$ = 3.8 Hz, 1 H, H_6-exo), 2.59 (d, $^2J_{H-H}$ = 12 Hz, residual, H_6-endo), 2.91 (s, residual, H_1), 4.77 (s, residual, H_2), 5.85 (s, residual, H_3).

Cyclohexadienyl-d_7-manganese Tricarbonyl. The perdeuteriocyclohexadienyl complex was prepared by the reaction of benzene-d_6-manganese tricarbonyl hexafluorophosphate with lithium aluminum deuteride using the same procedure as outlined for the d_6-6-exo-^1H complex. ^1H NMR spectra revealed residual protons in all the cyclohexadienyl ring positions. Residual ^1H incorporation into each of the non-exo ring positions was random and assumed to be 1% by comparison with the 6-exo-^1H-d_6 complex.

Thermal Isomerization of 6-*exo*-^1H-Cyclohexadienyl-d_6-manganese Tricarbonyl. The 6-*exo*-^1H-cyclohexadienyl-d_6 complex was prepared for thermal isomerization by transfer of 25-50 mg of the complex to a 5-mm NMR tube equipped with a female ground glass joint. The sample was evacuated (0.01 mm) briefly and solvent (octane-d_{18}, 0.5 mL) was added under a nitrogen atmosphere. The solution was degassed by several freeze-pump-thaw cycles and the NMR tube sealed in vacuo. Samples prepared in this manner were wrapped in aluminum foil (to eliminate photochemical reactions) and heated at 145.0 ± 0.5 °C for periods of ca. 1 h. ^1H NMR spectra were recorded periodically at room temperature (Varian XL-100) to monitor the progress of the isomerization. A threefold increase in the delay time between pulses while collecting FT NMR data on partially rearranged samples had no effect on the relative integrals of any of the proton resonances, demonstrating that the observed isomer distributions were real and not merely a manifestation of T_1 differences of various ring protons. ^1H NMR line broadening caused by suspended paramagnetic impurities from trace sample decomposition was eliminated by periodic centrifugation of NMR samples.

Rate of Intermolecular Cyclohexadienyl Exchange with Free Benzene. The preparation and handling of NMR samples for this exchange study were similar to the procedure used in the thermal isomerization experiments. To a 5-mm NMR tube equipped with a female ground glass joint were added 59.1 mg (0.262 mol) of cyclohexadienyl-d_7-manganese tricarbonyl, ca. 88 mg (1.1 mmol) of benzene, and 0.5 mL of octane-d_{18} solvent. The sample was degassed and sealed in vacuo, wrapped in aluminum foil, and heated at 145.0 ± 0.5 °C for 4-15-h periods. ^1H NMR spectra were recorded (Varian XL-100) to quantitatively monitor the progress of the exchange reaction.

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