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Multisite Magnetization Transfer Studies of Metal Migration in (η^3-C_7H_7)Re(CO)$_4$, (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$, (η^3-C_7H_7)Re(CO)$_3$PMe$_3$, (η^5-C_7H_7)Re(CO)$_3$, (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$, (η^5-C_7H_7)Os(CO)$_2$SnPh$_3$, and (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$[†]

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Multisite magnetization transfer (MMT) studies of metal migration around the C_7H_7 rings in (η^3-C_7H_7)Re(CO)$_4$ (**1**), (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (**2**), (η^3-C_7H_7)Re(CO)$_3$PMe$_3$ (**3**), (η^5-C_7H_7)Re(CO)$_3$ (**4**), (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**), (η^5-C_7H_7)Os(CO)$_2$SnPh$_3$ (**6**), and (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$ (**7**) are reported. The possible presence of 1,2-, 1,3-, and/or 1,4-metal shifts in the ring fluxionality was investigated in all compounds, and it was shown that both 1,2- and 1,3-shifts occur concurrently in **5** and **6**, but that only 1,2-shifts occur in **1**, **2**, **3**, and **4**, and only 1,3-shifts in **7**. Several of the compounds exist as mixtures of isomers, and the application of MMT was crucial in unraveling the fluxionality of one isomer in the presence of the other. Thus, MMT experiments allowed the study of the rate of metal migration in the symmetric isomer of **2**, which occurs in the presence of more rapid exchange in the asymmetric isomer. The symmetric isomer of **3** was found to exchange faster than the asymmetric isomer. MMT study of the exchange between symmetric and asymmetric isomers of **7** at low temperatures showed that the two enantiomers of the asymmetric isomer exchange directly with the symmetric isomer, but not with each other. MMT experiments allowed the study of metal migration in **7** in the presence of the isomer interchange process. The rate constants and free energies of activation for the metal shifts and for the isomer interchange are reported. It was concluded that orbital symmetry considerations do not provide useful predictions about the mechanisms of metal migration in compounds containing η^1-, η^3-, or η^5-C_7H_7 rings.

Introduction

Multisite magnetization transfer (MMT) methods[1−4] have been used widely to study the rates and mechanisms of slow intra- and intermolecular exchange processes in organic,[5−16] inorganic,[17−21] organometallic,[4,12,22−53] and biochemical systems.[54−57] The organic applications have involved determination of the rates of the inversion process in [8.8.7] (1,4,2) cyclophanes,[5] rates of exchange between different conformations of molecules via rotations about C−N[6,7,9,12,14,16] and C−C[8,10,11] bonds, an elegant demonstration that the

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clockwise and counterclockwise restricted rotations in 1-triptycyl[4]helicene occur at identical rates,[13] and the determination of the rates of interconversion of five isomers of a 10-membered ring containing a disulfide and two amide bonds.[15] MMT investigations of inorganic systems have included studies of the rates of Berry pseudorotation and ligand rotation in a five-coordinate phosphorus tetrafluoride complex,[17] ligand exchange in Rh(I) and Rh(II) complexes,[18] a very elegant study of Xe atom hopping between eight cages with different Xe occupancies in a zeolite matrix,[19] ligand substitution and isomerization in Pt(II) complexes,[20] and kinetics of Si exchange between aqueous silicate species in highly alkaline solution.[21] With organometallic compounds, the most widespread studies by far have been aimed at the elucidation of the mechanisms and rates of carbonyl migration and/or isomer exchange in bimetallic[29,31,35,36,39,40,50] and metal cluster compounds,[24,26,27,30,32,38,43] and studies of the modes of metal migration and the rates of isomer interchange in compounds containing indenyl and related ligands.[37,41,42,45,47,48,51,52] Investigations of the pathways for metal migration in organometallic compounds have been reported for molecules containing cycloheptatrienyl,[4] cyclooctatetraenyl,[22,46] cyclooctatrienyl,[28] cyclooctadienyl,[22] and norbornadienyl[22] ligands and include a very incisive demonstration of hapticity interchange in $(\eta^6\text{-}C_8H_8)Ru(\eta^4\text{-}C_8H_8)$.[46] Other organometallic applications of MMT include studies of intramolecular hydride transfer,[23] intramolecular hydride−methylene proton exchange,[49,53] intermolecular hydrogen atom transfer,[33] enantiomer interchange in a chiral allylpalladium complex,[25] hindered rotation about the Mn−C bond in a manganese diphosphine tricarbonyl complex,[44] and *exo*−*endo* isomer interchange in a cyclohexadienyliridium complex.[44] The biochemical applications of MMT[54−57] were concerned with alkali metal ion transport across membranes.

The effects of spin−spin coupling on MMT results have been investigated,[5,10,15] and it was found that weak coupling does not affect the magnetization transfer provided the selective inversion uniformly inverts all of the peaks associated with a particular site. Attempts to optimize the nature of the inversion step in MMT and thereby increase the sensitivity of the measured magnetizations to the values of the rate constants have been made,[35,58] but their use has not been widespread since the selective inversion of the resonance(s) associated with a particular site is close to optimal. The use of weighted least squares procedures in the analysis of MMT data[59,60] has been suggested, but has not been widely adopted.

Fluxional organometallic molecules, particularly "ring whizzers", have captivated the imagination of the chemical community ever since Piper and Wilkinson[61] made the initial observation of fluxionality in $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$. A very important milestone in the investigation of fluxionality of such molecules was the recognition[62] that differential changes in the widths of the NMR lines associated with the ring protons or carbon atoms of polyene and polyenyl rings contained important information about the details of the rearrangement process when the rate of exchange is slow. In this slow exchange regime, the width of the line associated with a particular set of equivalent sites on the ring is proportional to the rate at which magnetiza-

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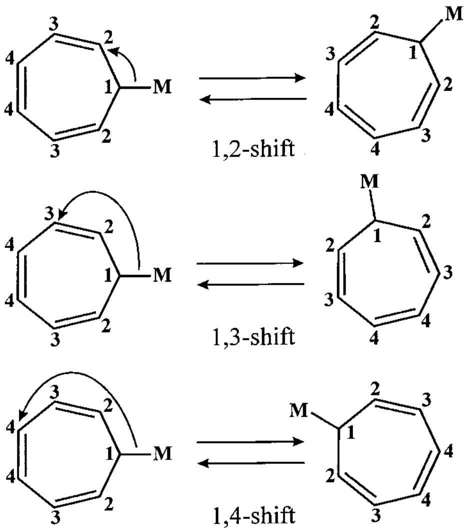

Figure 1. Metal migration processes in $(\eta^1\text{-}C_7H_7)$-M. Only the counterclockwise shifts are shown.

tion is exchanged out of those sites. For example, focusing on a $(\eta^1\text{-}C_7H_7)$-M system in a symmetrical environment, which has relevance to the current study, Figure 1 shows that movement of the metal from site 1 to site 2 (a 1,2-metal shift) will result in only half the rate of increase in the width of the resonance due to site 4 compared to those associated with the other sites because the magnetization from one of the sites labeled 4 is not exchanged. If, instead, the fluxionality were due to 1,3- (or 1,4-) metal shifts the lines associated with site 2 (or site 3) would remain sharper than the other lines because the magnetization at only one of the sites labeled 2 (or 3) is exchanged by the metal shift process. A theoretical framework within which the mechanisms of metal migrations may be discussed was afforded with the advent and successful application of the Woodward–Hoffmann orbital symmetry arguments to pericyclic reactions[63] and the extension of these ideas to σ-bonded polyenyl–metal complexes[64–67] and ultimately by Mingos[68] to π-bonded polyene– and polyenyl–metal complexes. Mann[69] has made an important contribution to the understanding of metal migrations in polyene– and polyenyl–metal complexes by showing that, under symmetry control, metal migrations must be accompanied by specific exchange of the other ligands attached to the metal.

Metal migrations in organometallic molecules containing $\eta^3\text{-}C_7H_7$ and $\eta^5\text{-}C_7H_7$ have been studied in relatively few cases.[4,70–81] Metal migrations in organometallic molecules containing $\eta^3\text{-}C_7H_7$ ligands include $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}\eta^3,\eta^4\text{-}C_7H_7)Fe(CO)_3$,[70] $(\eta^3\text{-}C_7H_7)Mo(\eta^5\text{-}C_5H_5)(CO)_2$,[71,72] $(\eta^3\text{-}C_7H_7)Co(CO)_3$,[71] $(\eta^3\text{-}C_7H_7)Fe(\eta^5\text{-}C_5H_5)(CO)$[73] and $(\eta^3\text{-}C_7H_7)Mo\{(C_3H_3N_2)BEt_2\}(CO)_2$,[74] $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ and $(\eta^3\text{-}C_7H_7)Fe(CO)_3PbPh_3$,[75,76] $(\eta^3\text{-}C_7H_7)Re(CO)_3PMe_3$,[77] $(\eta^3\text{-}C_7H_7)Mn(CO)_3PMe_3$,[77] and $(\eta^3\text{-}C_7H_7)Os(CO)_3SnPh_3$.[4,78] In all cases, the NMR evidence was consistent with 1,2-metal migrations around the cycloheptatrienyl ring, and most of the kinetic results are summarized by Mann.[69] Organometallic molecules containing the $\eta^5\text{-}C_7H_7$ moiety that have been reported are $(\eta^5\text{-}C_7H_7)Mn(CO)_3$,[79] $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]^+$,[79] $(\eta^5\text{-}C_7H_7)Ru(\eta^5\text{-}C_7H_9)$,[80] and $(\eta^5\text{-}C_7H_7)Fe(\eta^5\text{-}C_7H_9)$.[81] Again, 1,2-metal migrations are believed to predominate in the fluxional processes in these compounds.[69] In this paper, we report MMT studies of metal migration in three organometallic compounds containing the η^3-cycloheptatrienyl moiety, $(\eta^3\text{-}C_7H_7)Re(CO)_4$ (**1**), $(\eta^3\text{-}C_7H_7)Os(CO)_3SnPh_3$ (**2**), and $(\eta^3\text{-}C_7H_7)Re(CO)_3PMe_3$ (**3**), and four compounds containing $\eta^5\text{-}C_7H_7$, $(\eta^5\text{-}C_7H_7)Re(CO)_3$ (**4**), $(\eta^5\text{-}C_7H_7)Fe(CO)_2SnPh_3$ (**5**), $(\eta^5\text{-}C_7H_7)Os(CO)_2SnPh_3$ (**6**), and $(\eta^5\text{-}C_7H_7)Ru(CO)_2SnPh_3$ (**7**).

Theory

The theoretical basis of the MMT method has been described previously.[2–4] MMT experiments involve the selective inversion of the magnetization at a particular site and measurement of the *z*-magnetizations at all sites at various times from the point of inversion until thermal equilibrium is reestablished. The magnetizations associated with the exchanging sites follow the differential equation

$$\frac{d}{dt}[\mathbf{M} - \mathbf{M}(\infty)] = \mathbf{A}\cdot[\mathbf{M} - \mathbf{M}(\infty)] \qquad (1)$$

where **M** is a column vector containing the magnetization at each of the sites at time *t*, **M**(∞) is a column vector of thermal equilibrium magnetizations, and **A** is the exchange-relaxation matrix whose elements are given by

$$A_{ij} = \begin{cases} \sum_\alpha k_\alpha \Pi_{ji}^{(\alpha)}, & i \neq j, \\ -R_{1i} + \sum_\alpha k_\alpha \Pi_{ii}^{(\alpha)}, & i = j, \end{cases} \qquad (2)$$

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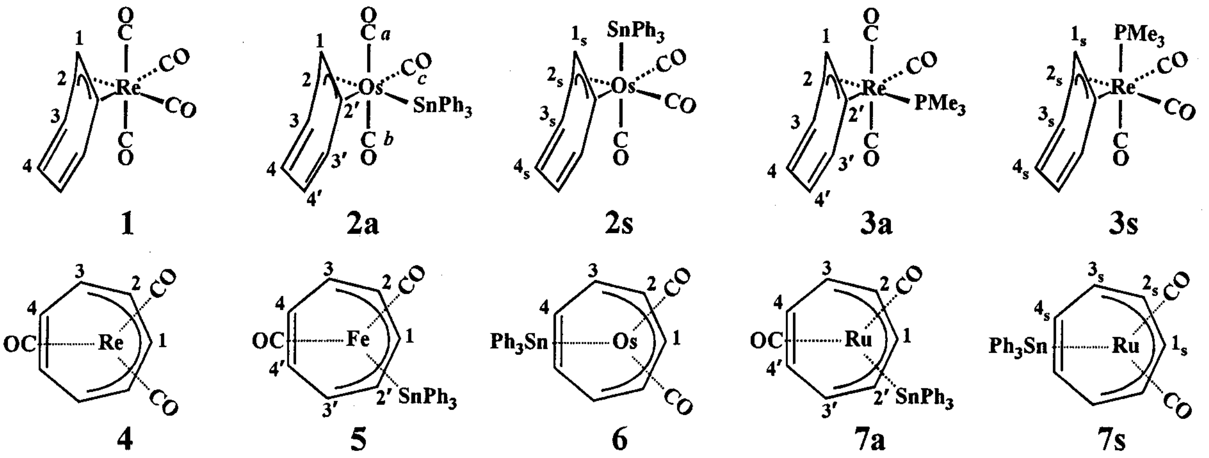

Figure 2. Schematic diagrams showing the structures of compounds **1**−**7**.

In eq 2, R_{1i} is the longitudinal relaxation rate for the *i*th site, k_α is the rate constant for the αth exchange process, and $\Pi^{(\alpha)}$ is the matrix of exchange coefficients for this exchange. The off-diagonal element $\Pi_{ji}^{(\alpha)}$ represents the number of exchanges in the αth exchange process which result in magnetization transfer from site *j* to site *i*, and the diagonal element $\Pi_{ii}^{(\alpha)}$ is related to the off-diagonal elements by

$$\Pi_{ii}^{(\alpha)} = -\sum_{l \neq i} \Pi_{il}^{(\alpha)} \tag{3}$$

and represents the number of exchanges that transfer magnetization out of site *i*.

The solution to eq 1 is obtained by direct diagonalization of matrix **A** and the magnetization at site *l* at time *t* after the selective inversion is given by[4]

$$M_l(t) = M_l(\infty) + \sum_{i,j=1}^{N} \exp(\Lambda_i t) U_{li} U_{ij}^{-1}[M_j(0) - M_j(\infty)] \tag{4}$$

where *N* is the number of sites in the exchange network, Λ and **U** are the eigenvalues and eigenvectors of matrix **A**, and $\mathbf{U}^{-1}$ is the inverse of **U** such that $\mathbf{U}^{-1}\cdot\mathbf{A}\cdot\mathbf{U} = \Lambda$, $M_j(0)$ is the *z*-magnetization for site *j* immediately after the inversion, and $M_j(\infty)$ is the equilibrium magnetization for site *j*. The rate constants k_α, which describe the kinetics of the exchange process, are obtained by iterative least squares fitting[82] of the observed magnetizations from the MMT experiment to the magnetizations calculated using eq 4. In the least squares procedure, the relaxation rates, R_{1i}, are fixed at the values determined from a nonselective inversion−recovery experiment, while the variables $\{M_j(\infty), [M_j(0) - M_j(\infty)]\}_{j=1}^{N}$ and k_α are varied as the fit is improved iteratively.

There are a number of features in the analysis of MMT data that warrant discussion.

i. There is no explicit or implicit requirement that the experimental MMT magnetization data set contain magnetization for all of the *N* sites in order to obtain information about the exchange process. If the magnetizations of one or more sites cannot be measured precisely because the resonances overlap with other peaks, the least squares analysis can be applied to the observed magnetizations from those sites that are measurable.

ii. The important variable in eq 1 is $[\mathbf{M}(t) - \mathbf{M}(\infty)]$, *not* simply $\mathbf{M}(t)$. This means that, if there is overlapping of the *l*th peak in an exchanging system with a resonance from the solvent, an impurity, or any other molecule present, one may determine the magnetization at site *l* by simply integrating the pair of overlapping peaks because the contributions to $M_l(t)$ and $M_l(\infty)$ from the spurious peak will be identical, and $M_l(t) - M_l(\infty)$ will be independent of the intensity of the spurious peak provided its intensity is the same at times *t* and ∞.

iii. It is possible to reformulate eq 1 so that one or more of the magnetizations is the sum of the magnetizations at two sites and use the modified equations as the basis for a fit of magnetization data where the peaks of two sites of the exchanging system are significantly overlapped.

iv. One may fit the measured magnetizations for several different selective inversion experiments (e.g., an experiment with selective inversion of site 1 and an experiment with selective inversion of site 3) together by expanding the dimensions of the **A** matrix. This has the advantage of reducing the estimated errors in the rate constants.

Before proceeding to a presentation of the results, it is instructive to consider the construction of the exchange coefficient matrixes $\Pi^{(\alpha)}$, which describe the magnetization transfers associated with each of the metal shift processes shown in Figure 1. The compounds studied in this work are shown schematically in Figure 2. As shown in Figure 2, compounds **2**, **3**, and **7** exist as mixtures of symmetric and asymmetric isomers. In these asymmetric isomers, all seven ring positions in the η^3- or η^5-C_7H_7 moiety are nonequivalent and the metal migration process may involve 1,2-, 1,3-, and/or 1,4-metal shifts as shown in Figure 1. Since the rate of the metal shifts must be independent of the shift direction,[13] the analysis of the MMT data for these compounds will provide values for the rate constants k_{1-2}, k_{1-3}, and k_{1-4}, for the 1,2-, 1,3-, and/or 1,4-metal

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[82] Marquardt, D. W.; Bennett, R. G.; Burell, E. J *J. Mol. Spectrosc.* **1961**, *7*, 269.

shift processes. The respective exchange coefficient matrices are

$$\Pi^{(1-2)} = \begin{pmatrix} -2 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -2 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & -2 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & -2 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & -2 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & -2 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 & -2 \end{pmatrix} \qquad (5)$$

$$\Pi^{(1-3)} = \begin{pmatrix} -2 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & -2 & 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & -2 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & -2 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & -2 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 & -2 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & -2 \end{pmatrix} \qquad (6)$$

and

$$\Pi^{(1-4)} = \begin{pmatrix} -2 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & -2 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & -2 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & -2 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & -2 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 & -2 \end{pmatrix} \qquad (7)$$

In eqs 5−7, the columns and rows of the Π matrices are associated with ring positions in the order 1, 2, 2′, 3, 3′, 4, 4′. Thus, in the analysis of the fluxional process in **2a** and **3a**, $N = 7$ in eq 4 and the sum over α includes terms for the 1,2-, 1,3-, and 1,4-metal shifts.

In the symmetric isomers **2s**, **3s**, and **7s** and in compounds **1**, **4**, and **6**, the cycloheptatrienyl ring is in a more symmetrical environment so that the ring positions 2 and 2′, 3 and 3′, and 4 and 4′ are pairwise equivalent, and the sites can be designated 1_s, 2_s, 3_s, 4_s in **2s**, **3s**, and **7s** and simply 1, 2, 3, 4 in compounds **1**, **4**, and **6**. The exchange coefficient matrices associated with the 1,2-, 1,3-, and 1,4-metal migration processes with respective rate constants k_{1-2}, k_{1-3}, and k_{1-4} are

$$\Pi^{(1-2)} = \begin{pmatrix} -2 & 1 & 0 & 0 \\ 2 & -2 & 1 & 0 \\ 0 & 1 & -2 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}, \qquad (8)$$

$$\Pi^{(1-3)} = \begin{pmatrix} -2 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 2 & 0 & -2 & 1 \\ 0 & 1 & 1 & -2 \end{pmatrix}, \qquad (9)$$

and

$$\Pi^{(1-4)} = \begin{pmatrix} -2 & 0 & 0 & 1 \\ 0 & -2 & 1 & 1 \\ 0 & 1 & -1 & 0 \\ 2 & 1 & 0 & -2 \end{pmatrix}, \qquad (10)$$

respectively. In eqs 8−10, the order of rows and columns in the Π matrices is 1_s, 2_s, 3_s, 4_s (or simply 1, 2, 3, 4). Therefore, in the analysis of the fluxional process in **1**, **2s**, **3s**, **4**, **6**, and **7** when **7a** and **7s** are averaged, $N = 4$ in eq 4 and the sum over α includes terms for the 1,2-, 1,3-, and 1,4-metal shifts.

In eqs 1 and 2, the contribution to magnetization transfer due to cross-relaxation between exchanging nuclei is ignored. If motional modulation of intramolecular dipole−dipole interactions is an important mechanism for relaxation of the protons in the cycloheptatrienyl group, these dipolar interactions also provide a mechanism for transfer of magnetization between the protons on the C_7H_7 ring because cross-relaxation always accompanies dipolar relaxation.[83,84] Following the approach described in earlier work on strongly coupled systems,[10] one can show that the cross-relaxation associated with motional modulation of intramolecular dipole−dipole interactions between neighboring ring protons manifests itself as a 1,2-metal shift around the C_7H_7 ring with a negative rate constant of $-(1/6)\ \bar{R}_1^{(\mathrm{dipolar})}$, where $\bar{R}_1^{(\mathrm{dipolar})}$ is the average dipolar relaxation rate for the ring protons. Unfortunately, this result is valid only in the fast motional modulation limit where $\omega_H{}^2\tau_\theta{}^2 \ll 1$ (ω_H is the proton resonance frequency in s^{-1} and τ_θ is the reorientational correlation time for the molecule). The effects of cross-relaxation when rotational modulation is slower may be somewhat larger, but are not easily estimated. Nevertheless, we have assumed that the fast modulation result gives a useful guideline for estimating the dipolar contributions to the rates of magnetization transfer. Hence, the values of k_{1-2} reported here have been corrected for dipolar cross-relaxation by assuming that dipolar relaxation is the dominant relaxation mechanism for the protons on the cycloheptatrienyl ring in all compounds studied, so that

$$k_{1-2}^{(corrected)} = k_{1-2}^{(least\ squares\ fit)} + \frac{1}{6}\bar{R}_1 \qquad (11)$$

It should be emphasized that the corrections described in eq 11 are the maximum corrections expected if the fast motion condition is met and no other relaxation processes (such as interactions with paramagnetic impurities in the sample, or motional modulation of dipolar interactions between ring protons and those on the $SnPh_3$ or PMe_3 ligands in **2**, **3**, **5**, **6**, and **7**) contribute to the relaxation rate. Since the corrections to the rate constants determined from eq 11 are small in all cases, it is unlikely that the application of this equation leads to large systematic errors in k_{1-2}.

Results

We have studied the fluxional behavior of the cycloheptatrienyl (C_7H_7) moiety in a number of organometallic compounds: (η^3-C_7H_7)Re(CO)$_4$ (**1**), the asymmetric and symmetric isomers of (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (**2a** and **2s**), the asymmetric and symmetric isomers of (η^3-C_7H_7)Re(CO)$_3$PMe$_3$ (**3a** and **3s**), (η^5-C_7H_7)Re(CO)$_3$ (**4**), (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**), (η^5-C_7H_7)Os(CO)$_2$SnPh$_3$ (**6**), and the asymmetric and symmetric isomers of (η^5-

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[83] Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961; p 295.

[84] Werbelow, L. G.; Grant, D. M. *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: San Diego, 1977; Vol. 9, p 189.

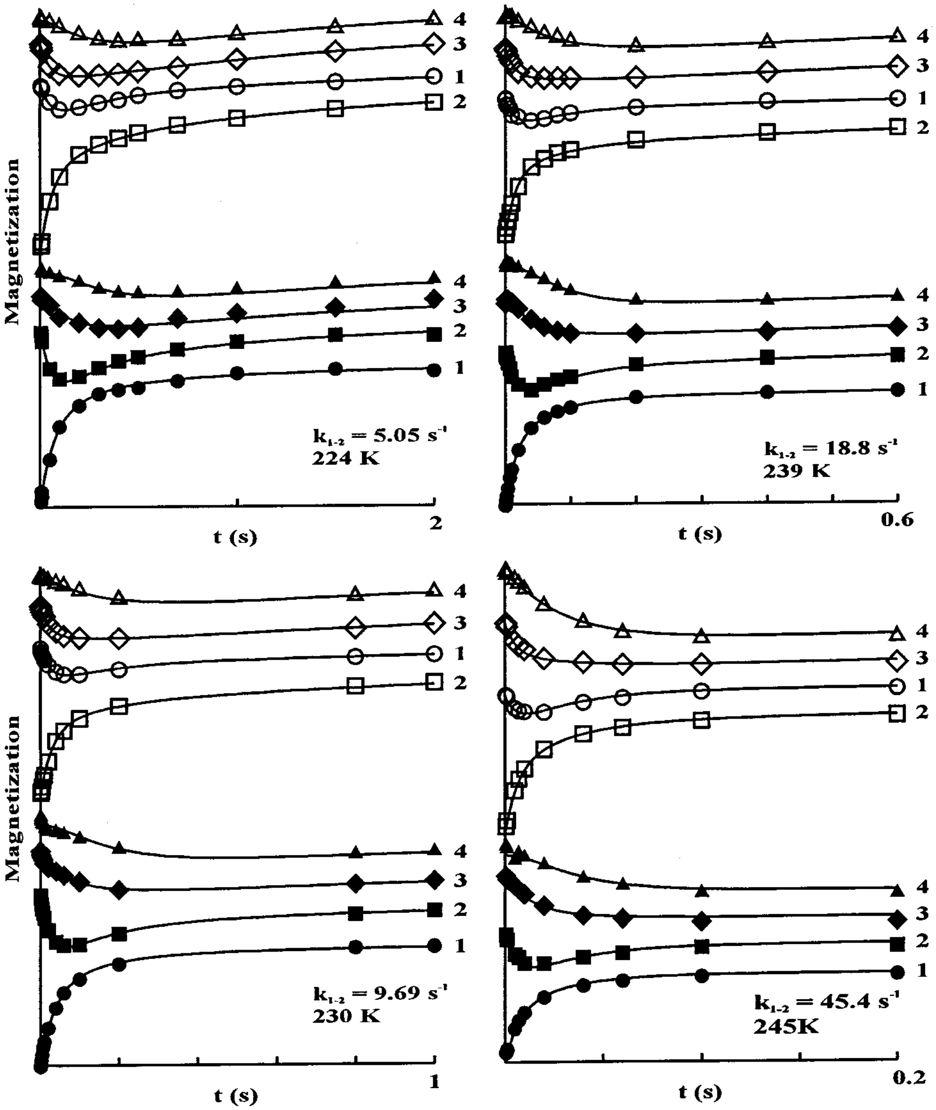

Figure 3. ^{1}H (200 MHz) MMT results for (η^3-C_7H_7)Re(CO)$_4$ (**1**) in methylcyclohexane-d_8 at temperatures indicated. Filled symbols: observed magnetizations for experiments in which site 1 is selectively inverted. Open symbols: observed magnetizations for experiments in which site 2 is selectively inverted. Lines: least squares fit of the combined data set. The values of k_{1-2} obtained are shown.

C_7H_7)Ru(CO)$_2$SnPh$_3$ (**7a** and **7s**). It is useful to describe the behavior of the compounds containing η^3-C_7H_7 and of those containing η^5-C_7H_7 in separate subsections.

Fluxional Behavior of Compounds Containing η^3-C_7H_7. Compound **1** is formally six-coordinate with pseudo-octahedral geometry and has a perpendicular mirror plane which passes through the C_7H_7 ring so that atoms on opposite sides of the ring are chemically equivalent. Hence the low-temperature ^{1}H and ^{13}C NMR spectra of **1** show four cycloheptatrienyl resonances with intensity ratio 1:2:2:2 and three carbonyl resonances with intensity ratio 1:1:2.[77] However, low-temperature ^{1}H and ^{13}C NMR studies of compounds **2**[78] and **3**[77] show the existence of two noninterconverting isomers for each compound: a *mer* or asymmetric isomer in which there are seven distinct cycloheptatrienyl peaks and three distinct CO peaks, and a *fac* or symmetric isomer in which a perpendicular mirror plane passes through the C_7H_7 ring so that there are only four cycloheptatrienyl resonances and two carbonyl resonances. The structures of the isomers of these compounds are shown in Figure 2.

(η^3-C_7H_7)Re(CO)$_4$ (1). Heinekey[77] has studied the ^{13}C NMR line shapes of the C_7H_7 resonances in **1** over the temperature range 265−311 K. He concluded that 1,2-metal shifts were the dominant mode of fluxionality of the cycloheptatrienyl ring in **1** and found activation parameters $\Delta H^{\ddagger}_{1-2} = 61 \pm 0.8$ kJ mol^{-1} and $\Delta S^{\ddagger}_{1-2} = 31 \pm 3$ J K^{-1} mol^{-1} for this exchange process. The results of MMT experiments on **1** in which magnetization at site 1 and at site 2 were selectively inverted are shown in Figure 3 for temperatures 224−245 K. The observed magnetizations in Figure 3 show the dominance of 1,2-metal shifts since inverted site 1 magnetization is transferred most rapidly to site 2, and inverted site 2 magnetization is transferred at equal rates to sites 1 and 3, but more slowly to site 4. Furthermore, the depth of the minimum in the site 2 magnetization versus *t* curve for each of the experiments in which site 1 magnetization was selectively inverted is deeper than the minimum in the site 1 magnetization versus *t* curve for the corresponding experiment in which site 2 is selectively inverted. Since 1,2-shifts from site 1 always

Table 1. Rate Constants for "Ring Whizzing" in Compounds Containing η^3-C_7H_7

compound	temperature (K)	k_{1-2} (s^{-1})^{a,b}	$\bar{R}_1$ (s^{-1})
1	215	1.28 (0.28)	1.1
	224	5.05 (0.86)	0.66
	230	9.69 (1.47)	0.48
	239	18.8 (1.68)	0.48
	245	45.4 (9.80)	0.43
	265	200^c	
	274	500^c	
	283	1200^c	
	292	3000^c	
	311	14000^c	
2a	180	4.21 (0.76)	0.40
	186	5.17 (0.63)	0.47
	187	5.96 (0.59)	0.50
	188	8.15 (0.77)	0.60
	191	11.1 (0.97)	0.60
	196	16.3 (1.9)	0.64
2s	203	1.12 (0.19)	0.80
	214	2.55 (0.26)	1.0
	224	6.86 (1.46)	1.1
	233	26.2 (10.4)	1.15
3s	223	0.54 (0.11)	1.26
	239	3.01 (0.16)	0.80
	244	4.74 (0.41)	0.72
	258	23.1 (2.66)	0.50
	264	44.0 (9.0)	0.43

[a] Numbers in parentheses are the nonlinear errors in the rate constants from the least squares analyses. [b] Values of rate constants include corrections for dipolar cross-relaxation (see eq 11). [c] Rate constants obtained in Heinekey's line shape studies.[77]

transfer magnetization from site 1 to site 2, but only half of the 1,2-shifts transfer magnetization to site 2 from site 1, the inverted site 1 magnetization is transferred more rapidly to site 2 than the inverted site 2 magnetization can be transferred to site 1. Least squares analyses of the MMT data in which k_{1-2} and k_{1-3} and/or k_{1-4} were allowed to vary freely always gave values for k_{1-3} and k_{1-4} that were significantly smaller than the estimated errors in these parameters. For example, analysis of the data for 230 K with all rate constants varying freely gave $k_{1-2} = 8.9 \pm 2.2$ s^{-1}, $k_{1-3} = 0.32 \pm 2.1$ s^{-1}, and $k_{1-4} = 0.06 \pm 1.3$ s^{-1}. Thus, we conclude, as Heinekey did,[77] that only 1,2-metal shifts are important in **1** and that 1,3- and 1,4-shifts can be ignored. The values of k_{1-2} obtained from the MMT experiments on **1** are given in Table 1 along with the proton relaxation rates. For comparison, the values of the rate constants reported by Heinekey[77] are also included in Table 1. Since the relaxation rates did not show significant site dependence, only the average relaxation rates, $\bar{R}_1$, are given. The dipolar corrections to the rate constants (see eq 11) were smaller than the estimated errors in k_{1-2} at all temperatures. The value of the free energy of activation, $\Delta G^{\ddagger}_{1-2}$, is 51.7 ± 0.3 kJ mol^{-1} and is tabulated in Table 2 along with those for the other compounds studied. This value is consistent with the activation parameters obtained in Heinekey's line shape analysis.[77]

Table 2. Free Energies of Activation for "Ring Whizzing" in Compounds Containing η^3- and η^5-C_7H_7

compound	temperature range (K)	$\Delta G^{\ddagger}_{1-2}$ (kJ mol^{-1})^a	$\Delta G^{\ddagger}_{1-3}$ (kJ mol^{-1})^a
1	215−245	51.7 (0.3)	
2a	180−196	42.0 (0.2)	
2s	203−233	50.0 (0.4)	
3s	223−264	55.9 (0.3)	
4	253−294	63.9 (0.3)	
5	258−283	65.6 (0.4)	64.6 (0.3)
6	268−298	67.3 (0.5)	71.4 (2.4)
7	221−234		48.9 (0.3)

[a] Numbers in parentheses are the estimated errors in $\Delta G^{\ddagger}$ derived from the nonlinear errors in the rate constants obtained from least squares analysis of MMT data.

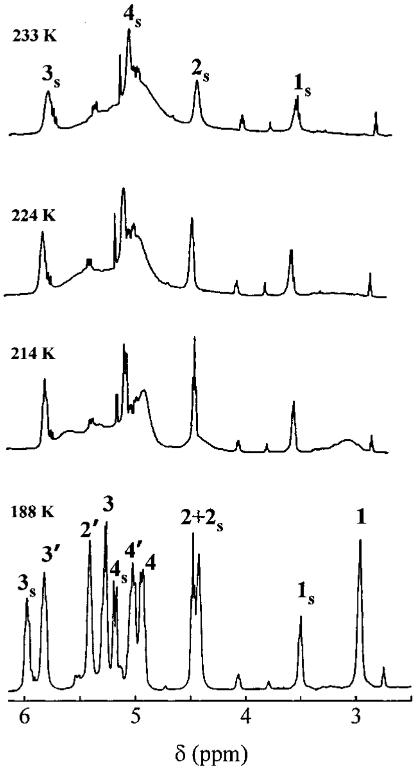

Figure 4. Variable-temperature ^{1}H NMR spectra (400 MHz) for the C_7H_7 region of (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (**2**) in CD_2Cl_2.

(η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (2a and 2s). The variable-temperature ^{1}H NMR spectra of **2** are shown in Figure 4. The presence of the two isomers is clearly visible in the low-temperature (188 K) limiting spectrum, which shows 11 cycloheptatrienyl proton signals. The resonances can be sorted into two subsets: one for each of the two accessible geometrical isomers of this formally six-coordinate pseudo-octahedral molecule (see Figure 2). The more intense set of seven signals is assigned to the asymmetric meridional isomer, **2a**, and the other four peaks to the symmetric facial isomer, **2s**. The assignments given in Figure 4 are based on intensity data, chemical shift considerations, and homonuclear decoupling experiments and are in accord with previous studies on η^3-C_7H_7 compounds.[75] The identification of **2s** as the *fac-exo* arrangement, as shown in Figure 2, rather than the *fac-endo* one with the SnPh$_3$ group placed near the C_7H_7 ring, is based on arguments presented in discussing the analogous iron compound.[75] We cannot rule out the presence of a small amount of the *fac-endo* symmetrical isomer since Figure 4 does contain additional small "impurity" peaks, and the signals near δ 2.8 and 4.1 ppm could be due, respectively, to the H(1) and H(2) protons of *fac-endo* **2s**. The room-temperature ^{1}H NMR spectrum shows two averaged C_7H_7 signals. The C_7H_7 signal at δ 4.40 ppm is sharp, whereas the peak at δ 4.63 ppm is broad, and the ratio of their integrated intensities is approximately 3:1. At higher temperature, the broad signal sharpens noticeably, but the relative intensities of the two peaks remain virtually unchanged. Thus compound **2** exists as a mixture of two fluxional isomers which do not interconvert on the NMR time scale.

Before describing our detailed analysis of the fluxional behavior of **2a** and **2s**, an important qualitative observation from Figure 4 should be pointed out. The signals assigned to the asymmetric isomer, **2a**, broaden and then coalesce at much lower temperatures than those of the symmetric isomer, **2s**. Thus, interestingly, "ring whizzing" in **2a** must be faster than in **2s**, an observation that is certainly not intuitively obvious from the subtle differences in their molecular structures.

Preliminary MMT work[4] on the asymmetric isomer **2a** indicated that this isomer exhibits exclusively 1,2-metal shifts at 188 K. The dominance of the 1,2-metal migration process is confirmed by this more extensive report. The data for selective inversion experiments in which the resonances at sites 1, 2′, and 3 were selectively inverted were analyzed separately including only the 1,2-metal shift process, and rate constants, k_{1-2}, with respective values 7.60 ± 0.53, 8.48 ± 0.89, and 8.31 ± 1.24 s^{-1} were obtained. Fitting the MMT results from the three separate experiments simultaneously gave $k_{1-2} = 8.05 \pm 0.77$ s^{-1}. The resonances for site 2 of **2a** and site 2s of **2s** strongly overlap, so we have analyzed the data by two methods: (1) the total integral over the 2 and 2s peaks was taken to be a reliable quantitative measure of the site 2 magnetization, and (2) site 2 magnetization was excluded completely from the analysis. Both methods gave essentially identical values of k_{1-2}, but method (1) gave slightly smaller least squares estimates of the errors in k_{1-2}. MMT measurements on the asymmetric isomer **2a** have been made over the temperature range 180−196 K, and the rate constants are given in Table 1. $\Delta G^{\ddagger}_{1-2} = 42.0 \pm 0.2$ kJ mol^{-1} for the 1,2-metal shifts in **2a**. The average proton relaxation rates are also included in Table 1. The values of $\bar{R}_1$ at all temperatures were too small to give significant dipolar corrections to the rate constants k_{1-2} (see eq 11).

To investigate the mode of "ring whizzing" further, all MMT data sets were fit allowing k_{1-2} and k_{1-3} and/or k_{1-4} to vary. In all cases, the values of k_{1-3} and k_{1-4} obtained from such fits were smaller than the estimated errors in these rate constants. For example, the rate constants $k_{1-2} = 5.46 \pm 1.58$ s^{-1}, $k_{1-3} = 0.37 \pm 1.50$ s^{-1}, and $k_{1-4} = 0.0 \pm 0.90$ s^{-1} were obtained by allowing all rate constants to vary in fitting the MMT data at 187 K. This firmly establishes that only 1,2-metal shifts are important in the cycloheptatrienyl ring fluxionality in **2a**.

The large differences in the chemical shifts of protons at sites 2 and 2′ of **2a** attest to a significant asymmetry in the η^3-bonding between the metal and the C_7H_7 ring. In view of the asymmetry, one might propose that metal migration in one direction (clockwise or counterclockwise) might be more facile than migration in the opposing direction. However, as Kelly et al.[13] have pointed out, internal rotation in a preferred direction would defy the Second Law of Thermodynamics. Their MMT studies of 1-triptycyl[4]helicene detected no preference for the direction of the internal rotation.[13] Attempts to fit the MMT data for **2a** using independent rate constants for clockwise and counterclockwise 1,2-metal shifts gave values for these rate constants that were equal within the estimated errors.

The ^1H NMR spectrum shows no evidence of fluxionality of the symmetric isomer **2s** below 196 K. Above 203 K, the ^1H resonances from the asymmetric isomer **2a** broaden considerably and approach coalescence above 213 K, while the resonances from **2s** remain distinct and narrow as shown in Figure 4. Isomer **2s** begins to show observable fluxional behavior above 203 K. Since the metal migration in this isomer is still in the slow exchange limit over the temperature range 203−233 K, its fluxional behavior may be studied by MMT in this temperature range, even in the presence of the now rapidly exchanging **2a**. Since the site 1_s peak is the only resonance free of overlap (see Figure 4), all MMT experiments involved the selective inversion of site 1_s magnetization. Since this resonance does not overlap significantly any signal from the asymmetric isomer, selective inversion should not perturb any resonances from **2a** significantly, and hence those broad signals, which underlie the other resonances, should not show any temporal response during the experiment. Thus the time dependence of the intensities of the peaks of **2s** is governed only by magnetization transfer between the sites in this isomer. The precision of the measurements of peak intensities of the resonances of **2s** which appear as sharp resonances superimposed on the broad **2a** peaks was somewhat lower than the precision obtained in the measurements of peak intensities in the MMT experiments on **2a** described above, but were sufficiently precise to afford unambiguous analysis of the mode of metal migration in isomer **2s**.

The results of the MMT experiments on **2s** are shown in Figure 5. Following the selective inversion of site 1_s magnetization, the observed magnetization at site 2_s rapidly decreases to a minimum at short times and then slowly increases to its equilibrium value at long times. The decrease in the magnetization at site 3_s is considerably slower than that at site 2_s, and the decrease at site 4_s is still slower. The rapid decrease in magnetization at site 2_s following the selective inversion of magnetization at site 1_s indicates rapid transfer of magnetization due to a direct 1,2-metal shift. The slower decrease at sites 3_s and 4_s indicates that the inversion may be transferred to these sites simply by successive 1,2-shifts. This temporal behavior of the magnetizations indicates qualitatively that 1,2-metal shifts provide the dominant exchange mechanism in the symmetric isomer **2s**. Least squares analyses of the MMT data in which k_{1-2} and k_{1-3} and/or k_{1-4} were allowed to vary freely always gave values for k_{1-3} and k_{1-4} that were smaller than the errors in these parameters. For example, the fit of the MMT data for 214 K with all rate constants varying freely gave $k_{1-2} = 2.95 \pm 0.74$ s^{-1}, $k_{1-3} = 0.0 \pm 0.49$ s^{-1}, and $k_{1-4} = 0.04 \pm 0.31$ s^{-1}. Thus, we conclude that only 1,2-metal shifts occur in **2s** and that 1,3- and 1,4-shifts are not important. The agreement between the observed magnetizations and those calculated from the least squares fits is very good at the lower temperatures, as shown in Figure 5. The poorer agreement at 233 K and the larger errors in the rate constants at the higher temperatures are due to increased difficulty in measur-

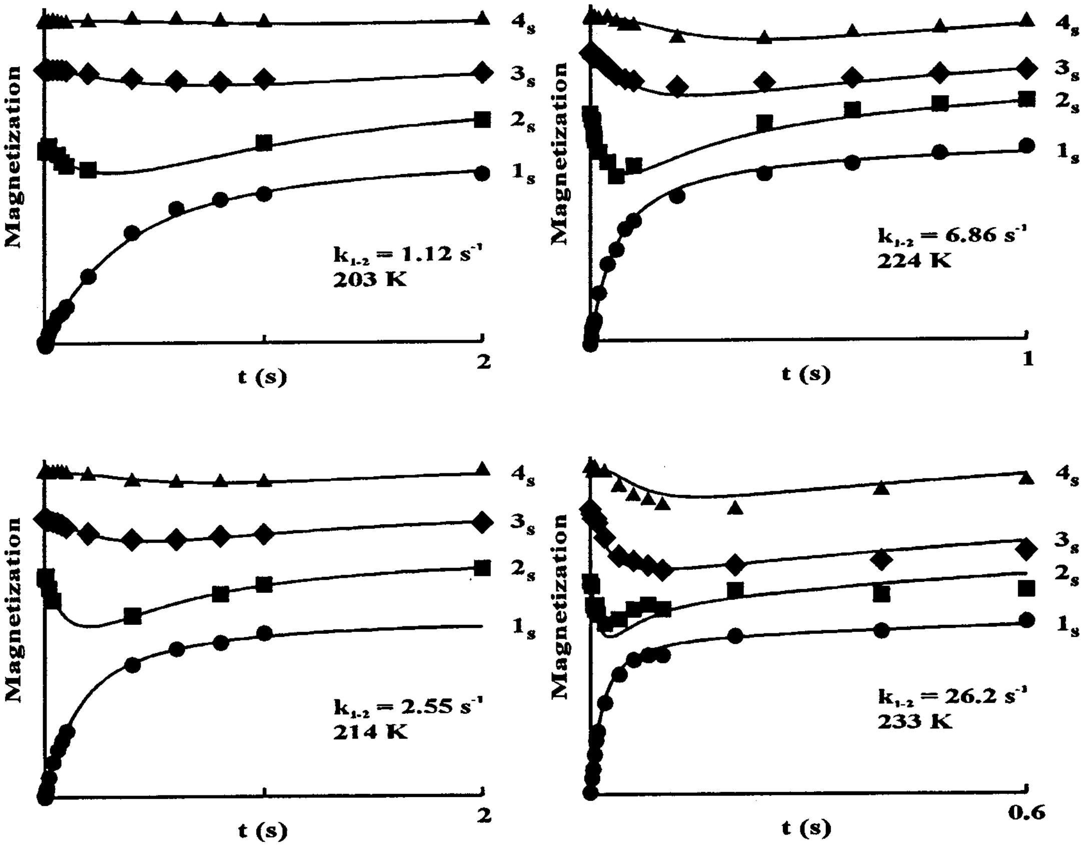

Figure 5. ^{1}H (400 MHz) MMT results for the symmetric isomer of (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (**2s**) in CD_2Cl_2 at temperatures indicated. Symbols: observed magnetizations. Lines: least squares fit of the data. The values of k_{1-2} obtained are shown.

ing precise peak integrals as the peaks become broader. This is not too surprising due to the distorted baseline produced by the underlying broad resonances of the asymmetric isomer **2a**. Even under such unfavorable conditions with severe baseline distortions and the presence of another rapidly exchanging isomer, it was possible to delineate the mode of exchange and to obtain reliable rate constants for the 1,2-metal shift process using the MMT method. The values of k_{1-2} obtained from the MMT experiments on **2s** are given in Table 1. $\Delta G^{\ddagger}_{1-2} = 50.0 \pm 0.4$ kJ mol^{-1} for the 1,2-metal shifts in **2s**. The average proton relaxation rates are also given in Table 1. The dipolar corrections to the rate constants were smaller than the estimated errors in k_{1-2} at all temperatures.

(η^3-C_7H_7) Re (CO)$_3$PMe$_3$ (3a and 3s). Heinekey's infrared and NMR studies[77] of (η^3-C_7H_7)Re(CO)$_3$PMe$_3$ (**3**) showed that this compound, like (η^3-C_7H_7)Os(CO)$_3$-SnPh$_3$ (**2**), exists as a pair of nonexchanging geometrical isomers with the symmetric and asymmetric isomers present with a **3s**:**3a** ratio of about 7:1 at 203 K. He concluded that Re-migration in **3s** occurs via 1,2-metal migration around the cycloheptatrienyl ring, on the basis of observations of differential line-broadening in the ^{1}H NMR spectra in the slow exchange region. MMT experiments were performed on the symmetric isomer **3s** over the temperature range 223−264 K. As in the other η^3-cycloheptatrienyl systems, the time dependence of the magnetizations after a selected inversion suggested that 1,2-metal shifts are dominant. Least squares analyses of the MMT data in which k_{1-2} and k_{1-3} and/or k_{1-4} were allowed to vary freely always gave values for k_{1-3} and k_{1-4} that were significantly smaller than the errors in these parameters. For example, analysis of the data for 239 K with all rate constants varying freely gave $k_{1-2} = 2.79 \pm 0.19$ s^{-1}, $k_{1-3} = 0.05 \pm 0.19$ s^{-1}, and $k_{1-4} = 0.02 \pm 0.13$ s^{-1}. As expected from the results on **2a**, **2s**, and **1**, we can ignore 1,3- and 1,4-metal migrations in **3s**. The values of k_{1-2} obtained from the analysis of the MMT data are given in Table 1, together with the average relaxation rates, $\bar{R}_1$. $\Delta G^{\ddagger}_{1-2} = 55.9 \pm 0.3$ kJ mol^{-1} for 1,2-metal shifts in **3s**. In the MMT experiment on **3s** at 223 K, the rate of exchange, k_{1-2}, obtained from the least squares fitting of the data was found to be 0.33 ± 0.08 s^{-1}, which is significantly smaller than the relaxation rate $\bar{R}_1 = 1.26 \pm 0.16$ s^{-1}. At temperatures below 239 K, the estimated dipolar cross-relaxation contributions to the rate of 1,2-shifts are larger than the estimated errors in k_{1-2} obtained from the least squares analysis, but the corrections are not significant at temperatures above 239 K.

The asymmetric isomer, **3a**, is less prominent than the symmetric isomer, **3s**, and the ^{1}H resonances for ring protons at positions 4 and 4′ overlap the 4_s resonance of the symmetric isomer. In fact, the intensities for site 4_s used in the analysis of the magnetization data for **3s** described above included the underlying 4 and 4′ resonances of **3a**. MMT experiments on **3a** were much more difficult than those on **3s** because of the higher noise level and overlap. We found that we could obtain reliable integrals only for sites 1, 2, and 2′ and were forced to analyze truncated MMT data sets which included only magnetizations from these sites. The rate constants, k_{1-2}, obtained from these fits, which assumed that only 1,2-metal shifts are important in **3a**, had large errors ($k_{1-2} = 1.7 \pm 0.96$ s^{-1} at 245 K, 3.9 ± 1.1 s^{-1} at

252 K, 5.7 ± 5.3 s^{-1} at 259 K) and were significantly smaller than the corresponding rate constants for **3s** (see Table 1).

Fluxional Behavior of Compounds Containing η^5-C_7H_7. Organometallic compounds containing the η^5-cycloheptatrienyl ligand offer more diversity in structure and dynamics than those containing an η^3-C_7H_7 ligand. Although the fluxional behavior of a vast number of transition metal organometallic compounds has been investigated,[69] only a very few studies of compounds containing η^5-C_7H_7 have been reported.[76–81] Heinekey[77] studied the ^{13}C NMR line shapes of (η^5-C_7H_7)Re(CO)$_3$ (**4**) over the temperature range 268−313 K and found that the line shape variation was consistent with 1,2-metal migration. These measurements gave activation parameters $\Delta H^{\ddagger}_{1-2} = 61.9 \pm 0.8$ kJ mol^{-1} and $\Delta S^{\ddagger}_{1-2} = -5 \pm 3$ J K^{-1} mol^{-1}.

In most of the studies cited above,[76–81] the mechanism was qualitatively established to be a 1,2-metal shift, with only Heinekey's study of **4**[77] being a quantitative line shape analysis. However, attempts to fit the line shapes of the ^{1}H NMR spectra of (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**) were unsuccessful, and Reuvers[76] was unable to determine the mode of metal migration in this compound.

Compound **5** exists in the solid state as a racemic mixture of two asymmetric enantiomers, and there is rapid exchange between these enantiomers at temperatures where the cycloheptatrienyl group is fluxional.[76] In contrast to the iron complex, the osmium complex,[86] (η^5-C_7H_7)Os(CO)$_2$SnPh$_3$ (**6**), exists as the symmetric isomer since the ^{13}C NMR spectrum shows only a single carbonyl resonance over the temperature range 179−380 K. The ^{1}H NMR spectrum of **6** was found to consist of four resonances for the cycloheptatrienyl group below 320 K, and these resonances broaden over the temperature range 298−318 K and finally collapse to the baseline at 380 K.

Unlike the iron and osmium compounds, **5** and **6**, which exist exclusively as one or the other of the possible isomers, the ruthenium compound, (η^5-C_7H_7)Ru(CO)$_2$-SnPh$_3$ (**7**), exists as an exchanging mixture of asymmetric and symmetric isomers.[86] At low temperatures, the exchange between the symmetric, **7s**, and asymmetric, **7a**, isomers is sufficiently slow that the ^{1}H NMR spectrum shows resolved resonances from each of the protons in the C_7H_7 groups of the two isomers and the ratio of the intensities of the peaks of the isomers **7a**:**7s** is 3.5:1 at 183 K. The rate of isomer exchange is of a suitable magnitude at this temperature to allow study by MMT. At higher temperatures, the ^{1}H NMR spectrum consists of four peaks of varying widths at positions corresponding to the averages of the peak positions in **7a** and **7s**, and metal migration occurs at temperatures above 220 K.

(η^5-C_7H_7)Re(CO)$_3$ (4). A study of the ^{13}C NMR line shapes of (η^5-C_7H_7)Re(CO)$_3$ (**4**) by Heinekey[77] concluded that the fluxionality was due to a 1,2-metal migration process. Since MMT may be more sensitive to the existence of a slow fluxional process in the presence of a more rapid one than spectral line shapes are, we have performed a series of MMT experiments on **4** in an attempt to detect the presence of other fluxional processes. MMT experiments in which magnetization at site 1 was inverted were carried out over the range 253−294 K. It was evident from the MMT data that 1,2-metal shifts are the dominant process giving rise to the fluxionality of **4** because the magnetizations at sites 2, 3, and 4 have initial decreases in the order 2, 3, 4, and these magnetizations go through minima at progressively longer times in this order. This is exactly analogous to the observed behavior of **1** shown in Figure 3. Least squares analysis of the MMT data for **4** at 276 K, in which the rate constants k_{1-2}, k_{1-3}, and k_{1-4} were varied freely, gave rate constants $k_{1-2} = 4.31 \pm 1.34$ s^{-1}, $k_{1-3} = 0 \pm 1.06$ s^{-1}, and $k_{1-4} = 0.12 \pm 0.57$ s^{-1}. Attempts to fit the MMT data at other temperatures all gave values for the rate constants k_{1-3} and k_{1-4} that were much smaller than the estimated errors in these parameters. Hence, in agreement with the line shape analysis,[77] the conclusion is that only the 1,2-metal shift process is involved in the fluxional motion of the C_7H_7 ring in **4**. The values of the rate constants k_{1-2} obtained in fitting the MMT data with k_{1-3} and k_{1-4} fixed at zero are given in Table 3. The values of k_{1-2} reported by Heinekey[77] are also included in Table 3. $\Delta G^{\ddagger}_{1-2} = 63.9 \pm 0.3$ kJ mol^{-1} for the 1,2-metal shifts in **4**, which is consistent with the activation parameters that Heinekey's line shape studies afforded.[77]

Table 3. Rate Constants for "Ring Whizzing" in Compounds Containing η^5-C_7H_7

compound	temperature (K)	k_{1-2} (s^{-1})[a,b]	k_{1-3} (s^{-1})[a]	$\bar{R}_1$ (s^{-1})
4	253	0.37 (0.06)		0.13
	263	1.13 (0.09)		0.12
	268	3[c]		
	276	4.19 (0.51)		0.10
	278	8[c]		
	283	12[c]		
	288	20[c]		
	293	35[c]		
	294	25.4 (3.3)		0.10
	298	50[c]		
	303	70[c]		
	308	120[c]		
	313	200[c]		
5	258	0.22 (0.07)	0.36 (0.07)	0.88
	263	0.49 (0.07)	0.74 (0.08)	0.86
	268	0.88 (0.07)	1.37 (0.07)	0.84
	272	1.54 (0.14)	2.30 (0.15)	0.79
	278	2.95 (0.44)	4.35 (0.46)	0.73
	283	5.38 (0.84)	7.93 (0.86)	0.69
6	268	0.34 (0.07)	0.03 (0.08)	0.77
	273	0.74 (0.10)	0.12 (0.07)	0.60
	282	2.61 (0.47)	0.43 (0.28)	0.52
	291	4.76 (0.85)	1.45 (0.50)	0.42
	298	9.4 (3.7)	2.0 (1.8)	0.40
7	221		13.3 (2.1)	0.91
	227		25.6 (3.3)	0.94
	231		45.9 (7.9)	0.99
	234		58.1 (6.9)	0.97

[a] Numbers in parentheses are the nonlinear errors in the rate constants from the least squares analyses. [b] Values of rate constants after correction for dipolar cross-relaxation (see eq 11). [c] Rate constants obtained in Heinekey's line shape studies.[77]

(η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (5). It has been established that (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**) exists as an enantiomeric pair of asymmetric molecules as shown in Figure 2, with known solid state structure, and because of the asymmetry, all seven protons in the cycloheptatrienyl ring are chemically nonequivalent.[76] The interconversion of the enantiomers of **5** occurs at all temperatures

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(85) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664.
(86) Takats, J.; Kiel, G.-Y. Manuscript in preparation.

accessible to liquid state NMR study and is in the fast exchange limit at temperatures above 258 K. Reuvers[76] has estimated an activation barrier of ∼40 kJ mol^{-1} for the enantiomer interconversion based on a line shape study of the carbonyl resonances in the ^{13}C NMR spectrum. The enantiomer interconversion induces a plane of symmetry in the seven-membered ring with a resulting averaging of the chemical shifts of sites 2 and 2′, 3 and 3′, and 4 and 4′. In the following discussion, we will use the labels 2, 3, and 4, respectively, to designate the averaged (2, 2′), (3, 3′), and (4, 4′) cycloheptatrienyl ring positions. Attempts to elucidate the mode of metal migration in **5** by studying the line shape of the ^{1}H spectrum were unsuccessful.[76] The fluxional behavior of this compound has been investigated using MMT over the temperature range 258−283 K, where the four resonances are reasonably well resolved. To avoid any ambiguities, we carried out sets of MMT experiments in which the magnetization at site 2 (2, 2′) and at site 4 (4, 4′) were selectively inverted. The results of these experiments are shown in Figure 6. Examination of the data in Figure 6 for the MMT experiment in which magnetization at site 2 is selectively inverted at 272 K shows that the site 4 magnetization decreases and reaches a minimum at shorter times than the magnetization at site 3, which indicates the presence of 1,3-metal shifts. The fact that the magnetization at site 3 reaches a minimum before magnetization at site 2 in the corresponding experiment in which magnetization at site 4 is selectively inverted indicates that 1,2-metal shifts are also operative. Least squares analysis of the MMT data for the two experiments at 283 K, in which the rate constants k_{1-2}, k_{1-3}, and k_{1-4} were varied freely, gave rate constants $k_{1-2} = 5.5 \pm 1.2$ s^{-1}, $k_{1-3} = 7.9 \pm 2.5$ s^{-1}, and $k_{1-4} = 0.0 \pm 1.9$ s^{-1}. Attempts to fit the MMT data at other temperatures all gave values for the rate constant k_{1-4} that were smaller than the estimated error in this parameter. Hence the ring fluxionality in **5** is a superposition of 1,2- and 1,3-metal shift processes. To investigate the sensitivity of the least squares fitting to the inclusion of 1,2- and/or 1,3-metal shift processes, we performed fits of the data in which k_{1-4} was fixed at zero, and only k_{1-2}, only k_{1-3}, or both k_{1-2} and k_{1-3} were varied. The results of these fits for the MMT experiments at 283 K are also shown in Figure 7. When either of the rate constants is fixed at zero during the least squares procedure, the variance increases dramatically and the quality of the fit decreases very significantly as the comparison of observed and calculated magnetizations in Figure 7 shows. With k_{1-3} fixed at zero (Figure 7B), the calculated magnetizations at sites 1 and 3, for the experiment when site 2 magnetization is inverted, decrease much more rapidly at short times than do the observed magnetizations because the value of k_{1-2} required to fit the recovery of the site 2 magnetization is too large to accommodate the slower decreases in the observed magnetizations at sites 1 and 3. In the fits where k_{1-2} was set to zero (Figure 7C), the value of k_{1-2} which gave minimum variance was too small to account for the observed rapid recovery of site 2 magnetization, and the calculated magnetizations at all other sites are in poor agreement with the observed ones. These fits show that the least squares analysis is very sensitive to the presence of each of the metal migration processes, and the small nonlinear error estimates in the rate constants obtained from the least squares analyses show that the fits are very sensitive to the values of the rate constants for these processes (see Table 3). Since the values of $\bar{R}_1$ for **5** are larger than the values of k_{1-2} at the lower temperatures, the corrections for dipolar cross-relaxation are larger than the estimated errors in k_{1-2} at temperatures 258−268 K. The free energies of activation for the 1,2- and 1,3-metal shifts in **5** are 65.6 ± 0.4 and 64.6 ± 0.3 kJ mol^{-1}, respectively.

(η^5-C$_7$H$_7$)Os(CO)$_2$SnPh$_3$ (6). In contrast to the Fe complex **5**, the Os complex (η^5-C$_7$H$_7$)Os(CO)$_2$SnPh$_3$ (**6**) exists only as the symmetric isomer.[86] The ^{13}C NMR spectrum showed only a single carbonyl resonance over the temperature range 179−380 K, and the four resonances for the C$_7$H$_7$ ring carbons showed broadening at temperatures 298−318 K and ultimately broadened and collapsed into the baseline at 380 K.[86] We have carried out ^{1}H (200 MHz) MMT studies of the fluxional behavior of **6** over the temperature range 268−298 K. In these experiments, the magnetization at site 1 was selectively inverted at all temperatures, and two experiments in which magnetization at site 3 was inverted were also performed. Cursory examination of the MMT data did not immediately indicate the presence of more than one fluxional process. It was observed that magnetization at site 2 passed through a minimum before magnetization at site 3, so the motion would appear to be dominated by a 1,2-metal shift. However, least squares analysis of the MMT data at 291 K, in which the rate constants k_{1-2}, k_{1-3}, and k_{1-4} were varied freely, gave rate constants $k_{1-2} = 4.69 \pm 0.90$ s^{-1}, $k_{1-3} = 1.50 \pm 0.89$ s^{-1}, and $k_{1-4} = 0.0 \pm 0.63$ s^{-1}, indicating the presence of 1,3-metal shifts. In the least squares analysis of all data sets, the values of k_{1-4} obtained had values much smaller than their estimated errors, so it was concluded that 1,4-metal shifts are absent. To investigate the sensitivity of the data analysis to the presence of both 1,2- and 1,3-metal shift mechanisms in the fluxional motion of **6**, fits were made of the MMT data at 291 K in which k_{1-4} was fixed at zero, and only k_{1-2}, only k_{1-3}, or both k_{1-2} and k_{1-3} were varied. The variance of the fit in which k_{1-3} was fixed at zero and only k_{1-2} was varied was 4 times as large as the variance for the fit when both k_{1-2} and k_{1-3} were varied. The attempt to fit the data by varying only k_{1-3} while k_{1-2} was fixed at zero gave a variance 30 times larger than that for the fit in which both k_{1-2} and k_{1-3} are varied and gave very poor agreement between calculated and observed magnetizations. This is not surprising since 1,2-metal shifts are much more important here than 1,3-shifts in the fluxionality of **6**. The values of k_{1-2} and k_{1-3} obtained from the MMT experiments on **6** are given in Table 3. At 268 K, the estimated error in k_{1-3} is larger than the value k_{1-3}, but the values of this rate constant are larger than their estimated errors at all other temperatures. The corrections to k_{1-2} are larger than the estimated errors at temperatures 268 and 273 K. Although the estimated errors in k_{1-3} are rather high, these results show that the analysis of the MMT experiments does afford measurement of the rate of a slow process in the presence of a more dominant (faster)

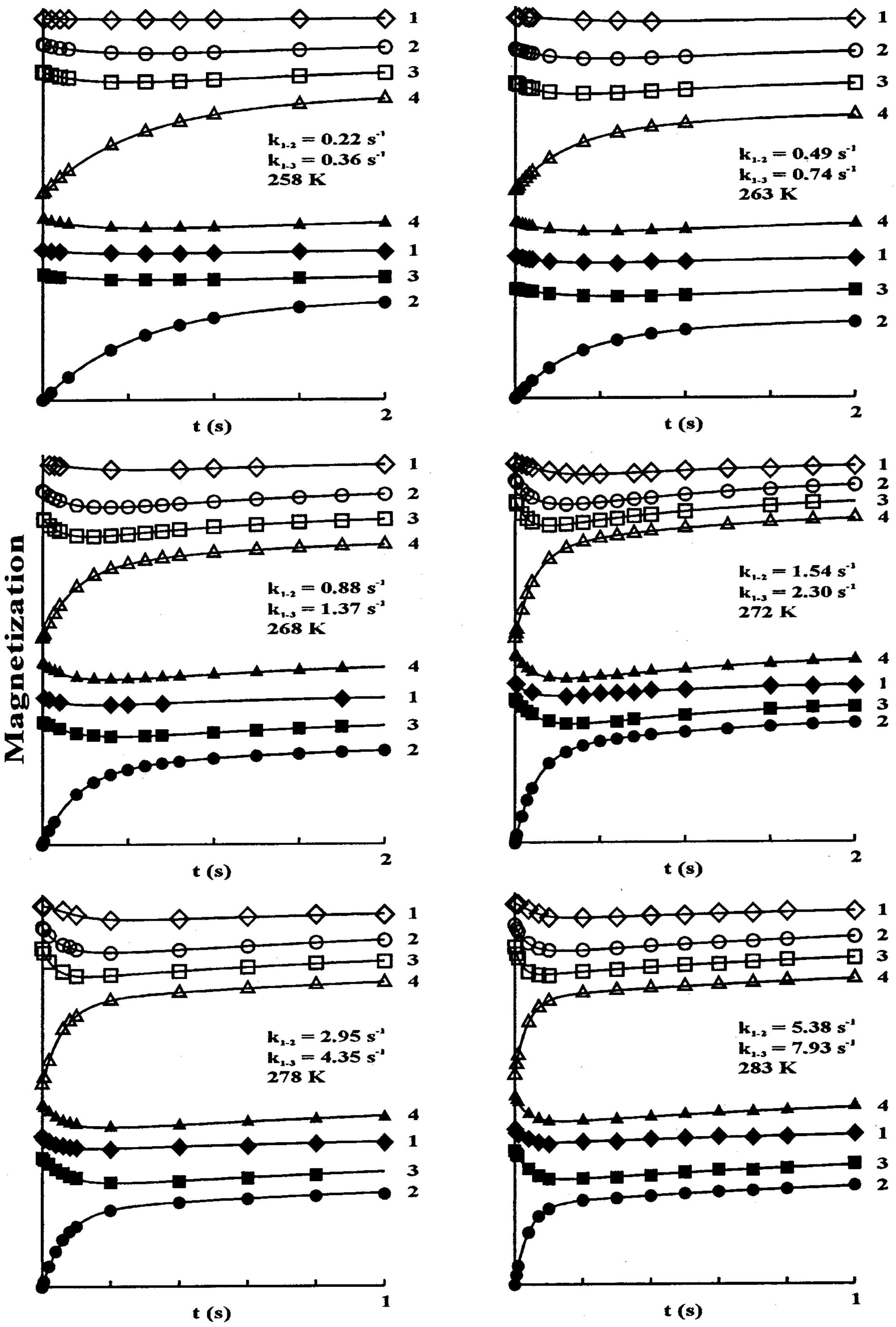


Figure 6. ^{1}H (400 MHz) MMT results for (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**) in THF-d_8 at temperatures indicated. Filled symbols: observed magnetizations for experiments in which site 2 is selectively inverted. Open symbols: observed magnetizations for experiments in which site 4 is selectively inverted. Lines: least squares fit of the combined data set. The values of k_{1-2} and k_{1-3} obtained are shown.

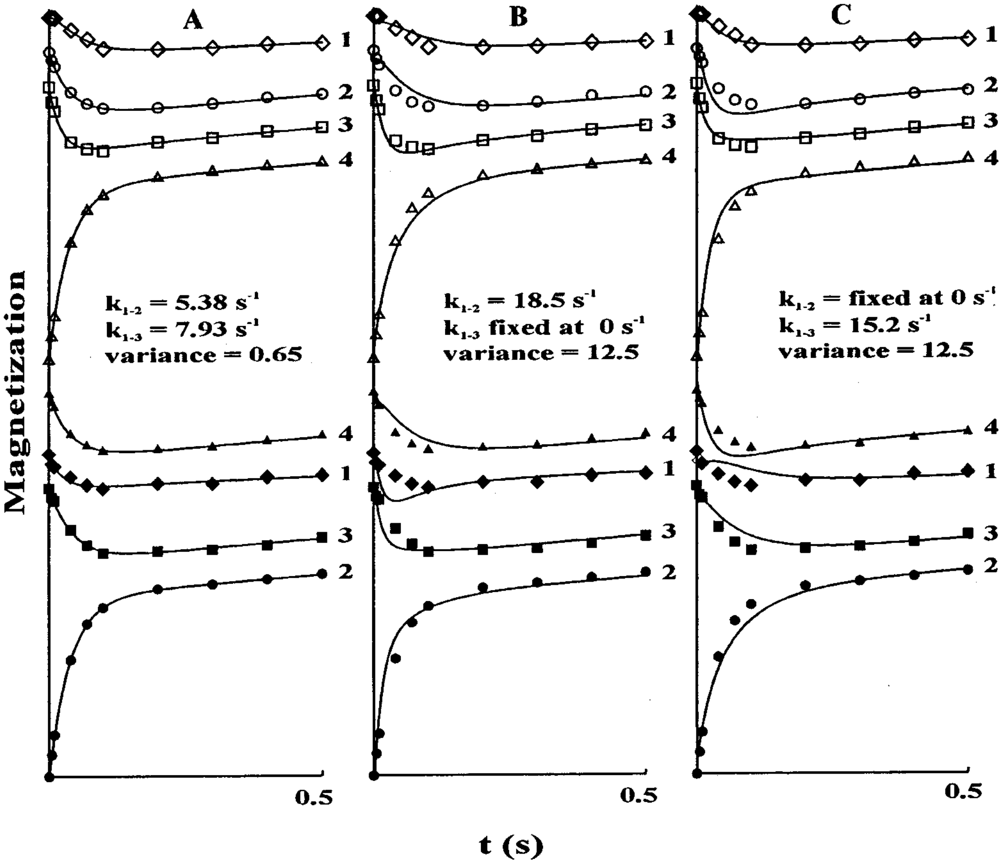


Figure 7. Comparison of least squares fits of ^{1}H (400 MHz) MMT data for (η^5-C_7H_7)Fe(CO)$_2$SnPh$_3$ (**5**) in THF-d_8 at 283 K. A: both k_{1-2} and k_{1-3} varied. B: only k_{1-2} varied with k_{1-3} fixed at zero. C: k_{1-3} varied with k_{1-2} fixed at zero. Filled symbols: observed magnetizations for experiments in which site 2 is selectively inverted. Open symbols: observed magnetizations for experiments in which site 4 is selectively inverted. Lines: least squares fit of the combined data set.

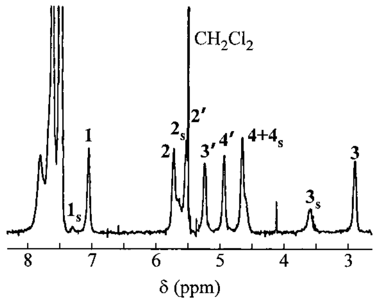


Figure 8. C_7H_7 region of the ^{1}H NMR spectrum (400 MHz) of (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$ (**7**) in CD_2Cl_2 at 183 K.

one. $\Delta G^{\ddagger}_{1-2} = 67.3 \pm 0.5$ kJ mol^{-1} and $\Delta G^{\ddagger}_{1-3} = 71.4 \pm 2.4$ kJ mol^{-1} for the metal shifts in **6**.

(η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$ (7). Unlike the corresponding compounds of iron and osmium, where only one isomeric form of each is present, the complex (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$ (**7**) exists as a mixture of symmetric and asymmetric isomers at low temperatures.[86] It was also observed[86] that the ratio of the ^{13}C NMR intensities for signals due to the symmetric and asymmetric isomers changed between 175 and 190 K, indicating that the two isomers interconvert even at very low temperatures. The low-temperature ^{1}H NMR spectrum (400 MHz) of the C_7H_7 region of compound **7** is shown in Figure 8. The seven lines expected for **7a** and the four lines expected for **7s** are clearly identified, and the assignment of the resonances is based on intensity data, chemical shift considerations, and selective decoupling experiments. An investigation of the **7a**–**7b** isomer interconversion process postulated by Takats and Kiel[86] is described in a later section. When the temperature is raised above 200 K, the C_7H_7 resonances for the two isomers broaden and coalesce, and the spectrum appears to be that of a single symmetric isomer with different line widths for each resonance at temperatures above 220 K, as shown in Figure 9. The four resonances have very different widths because each line originates from two or more lines from sites whose magnetizations are exchanged by the isomer interchange. To emphasize that these lines are exchange averages of the lines in the two isomers, we have used the labels $\bar{1}$, $\bar{2}$, $\bar{3}$, and $\bar{4}$ to indicate the respective exchange averages {1, 1$_s$}, {2, 2′, 2$_s$}, {3, 3′, 3$_s$}, and {4, 4′, 4$_s$}. MMT experiments in which the $\bar{1}$ magnetization was selectively inverted were performed in order to study the fluxional behavior of the C_7H_7 ring in **7** over the temperature range 221–234 K. Accurate MMT measurements outside this rather limited temperature range were precluded because, at lower temperatures the $\bar{3}$ resonance is extremely broad and overlaps the $\bar{4}$ resonance too strongly and at higher temperatures all resonance lines become too broad. In these MMT experiments, site $\bar{3}$ magnetization decreases most rapidly after the site $\bar{1}$ magnetization has been inverted, while site $\bar{4}$ magnetization decreases less rapidly, and site $\bar{2}$ magnetization decreases even more slowly. This indicates that 1,3-metal

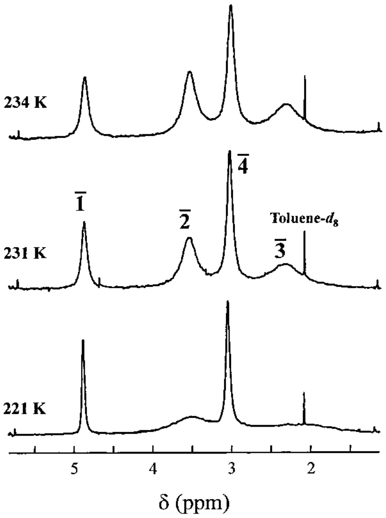
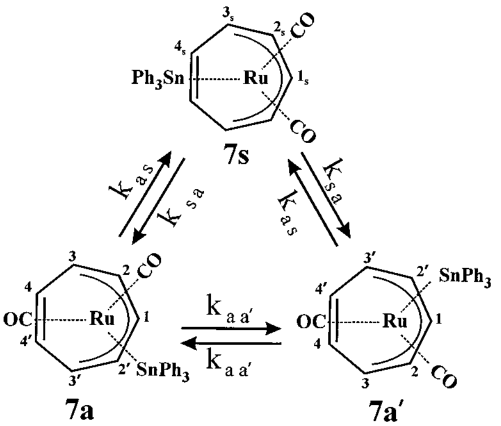


Figure 9. C_7H_7 region of the ^1H NMR spectrum (400 MHz) of $(\eta^5\text{-}C_7H_7)Ru(CO)_2SnPh_3$ (**7**) in toluene-d_8 at temperatures indicated. Peaks labeled $\bar{1}$, $\bar{2}$, $\bar{3}$, and $\bar{4}$ arise from exchange averaging of sites {1, 1_s}, {2, 2′, 2_s}, {3, 3′, 3_s}, and {4, 4′, 4_s}, respectively, in the asymmetric and symmetric isomers of **7**.

shifts are the dominant fluxional process. Least squares analysis of the MMT data for **7** at 221 K, in which the rate constants k_{1-2}, k_{1-3}, and k_{1-4} were varied freely, gave rate constants $k_{1-2} = 0.0 \pm 1.4$ s^{-1}, $k_{1-3} = 8.4 \pm 2.3$ s^{-1}, and $k_{1-4} = 2.9 \pm 2.1$ s^{-1}. Attempts to fit the MMT data at other temperatures all gave values for the rate constant k_{1-2} that were smaller than the estimated error in this parameter. Hence the ring fluxionality in **7** is dominated by the 1,3-metal shift process, but there would appear to be some contribution from 1,4-metal shifts. Analyses of the MMT data at all temperatures, in which the rate constants k_{1-3} and k_{1-4} were varied freely and k_{1-2} was fixed at zero, gave values for k_{1-4} that were slightly larger than the estimated errors in k_{1-4} at 221 and 227 K, but the estimated errors were larger than the values of k_{1-4} obtained at 231 and 234. Furthermore, the value of k_{1-4} obtained from analysis of the data at 234 K was *smaller* than the values of k_{1-4} obtained at 227 and 231 K. Since the overlap between the 3 and 4 resonances is quite substantial at the two lower temperatures where “apparently” significant values of k_{1-4} were obtained, and the values of k_{1-4} obtained at the two higher temperatures, where overlap is less severe, are not significantly different from zero, the presence of a true 1,4-metal shift contribution here is doubtful.

To investigate the possibility of a contribution from 1,4-metal shifts here, we performed two sets MMT experiments on **7** in CD_2Cl_2 at 232 K: in the first set site $\bar{1}$ magnetization was selectively inverted, and in the second set, site $\bar{2}$ magnetization was selectively inverted. In CD_2Cl_2, resonance $\bar{3}$ is so broad that it resembles the flat baseline, so although we cannot monitor the intensity of this line, its effect on the $\bar{4}$ resonance should be minimal. The results of these two sets of MMT experiments were analyzed simultaneously, ignoring the unmeasurable site $\bar{3}$ magnetization, in a number of ways. When both k_{1-3} and k_{1-4} were allowed to vary freely with k_{1-2} fixed at zero, we obtained $k_{1-3} = 35.8 \pm 22.1$ s^{-1} and $k_{1-4} = 0.0 \pm 9.0$ s^{-1}, while least squares analysis with k_{1-2} and k_{1-4} fixed at zero gave $k_{1-3} = 35.7 \pm 7.3$ s^{-1} with a lower variance. Hence we have concluded that the 1,4-metal shift process does not contribute significantly to the fluxionality of **7**. The values of k_{1-3} obtained from the MMT experiments are given in Table 3. $\Delta G^{\ddagger}_{1-3} = 48.9 \pm 0.3$ kJ mol^{-1} for the 1,3-metal shifts in **7**.

Scheme 1



Isomer Interconversion in $(\eta^5\text{-}C_7H_7)Ru(CO)_2SnPh_3$ (7). From observations of the ^{13}C NMR spectra of **7** in the low-temperature range 175−183 K, it was inferred that the symmetric and asymmetric isomers of this compound are interconverting and that Ru metal migration around the C_7H_7 ring is not important at these temperatures.[86] ^1H MMT experiments were carried out at 178−189 K to elucidate the processes involved in the isomer interconversion. In studies at 178 K, the magnetization at site 3 of the asymmetric isomer (**7a**) was selectively inverted in one set of experiments and that at site 3_s of the symmetric isomer (**7s**) in the other set. The temporal responses of all of the observable resonances due to the C_7H_7 rings were monitored. Following the selective inversion at site 3 of **7a**, the magnetizations at site 3′ of **7a** and at site 3_s of **7s** decreased to minimum values at short times and then recovered to their equilibrium values at longer times in the well-defined manner normally observed in MMT experiments on other systems. The observed magnetizations at all other sites stayed essentially constant and did not show any evidence of metal migration within the two isomers. Similarly, following the selective inversion of site 3_s magnetization of **7s**, only magnetizations at sites 3 and 3′ of **7a** showed the temporal response characteristic of exchanging systems, and the other resonances remained constant throughout. These observations clearly show that magnetization transfer occurs only between the corresponding sites of the two isomers, with no magnetization transfer between the nonequivalent sites of the same isomer as observed in systems with metal migration.

To obtain quantitative information about the isomer interconversion, we propose Scheme 1 to describe the interconversion. In this scheme, we have included **7a** → **7s** conversion with rate constant k_{a-s}, **7s** → **7a** conversion with rate constant k_{s-a}, and the direct enantiomer interconversions **7a** → **7a′** and **7a′** → **7a** with rate constant $k_{a-a'}$. Following a selective inversion in an MMT experiment, magnetization is transferred from site 3_s of **7s** to sites 3 and 3′ of **7a** with rate constant k_{s-a} and exchange coefficient matrix

$$\Pi^{(s-a)} = \begin{pmatrix} 0 & \frac{1}{2} & 0 \\ 0 & -1 & 0 \\ 0 & \frac{1}{2} & 0 \end{pmatrix} \tag{12}$$

from sites 3 and 3′ to site 3_s with rate constant k_{a-s} and exchange coefficient matrix

$$\Pi^{(a-s)} = \begin{pmatrix} -1 & 0 & 0 \\ 1 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix} \tag{13}$$

and from site 3 to site 3′ and from site 3′ to site 3 with rate constant $k_{a-a'}$ and exchange coefficient matrix

$$\Pi^{(a-a')} = \begin{pmatrix} -1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & -1 \end{pmatrix} \tag{14}$$

The order of rows and columns in the exchange coefficient matrices defined in eqs 12−14 correspond to sites 3, 3_s, and 3′.

The results of the MMT experiments at 178 K, in which magnetization at site 3_s of the symmetric isomer **7s** was selectively inverted, and those in which site 3′ of the asymmetric isomer **7a** was inverted are given in Figure 10. In the series of experiments in which site 3_s magnetization is selectively inverted, the temporal responses of sites 3 and 3′ are essentially identical, as one would expect. However, in the set of experiments in which site 3 magnetization is inverted, the magnetization at site 3_s decreases much more rapidly than that at site 3′ and reaches a minimum long before the site 3′ magnetization does. This indicates that the rate of the asymmetric → symmetric isomerization is more rapid than the enantiomer interconversion. Least squares analysis of the combined data sets with all rate constants varied freely gave rate constant values $k_{a-s} = 17.2 \pm 6.7$ s^{-1}, $k_{s-a} = 57.1 \pm 18.2$ s^{-1}, and $k_{a-a'} = 0.4 \pm 4.4$ s^{-1}. One must conclude, therefore, that direct enantiomer interconversion in **7a** is not important: all enantiomer conversion occurs via the two-step process where one enantiomer isomerizes to the symmetric isomer **7s**, which, in turn, isomerizes to the other enantiomer. Least squares analysis of the combined data sets with $k_{a-a'}$ fixed at zero gave a fit with the same variance as the fit when $k_{a-a'}$ was varied freely and gave $k_{a-s} = 17.7 \pm 4.1$ s^{-1} and $k_{s-a} = 58.2 \pm 13.7$ s^{-1}. In the MMT experiments at other temperatures, only selective inversion of site 3 magnetization of **7a** was performed. The rate constants obtained are given in Table 4. The free energies of activation obtained from these rate constants are $\Delta G^{\ddagger}_{a-s} = 41.6 \pm 0.4$ kJ mol^{-1} and $\Delta G^{\ddagger}_{s-a} = 39.8 \pm 0.4$ kJ mol^{-1}.

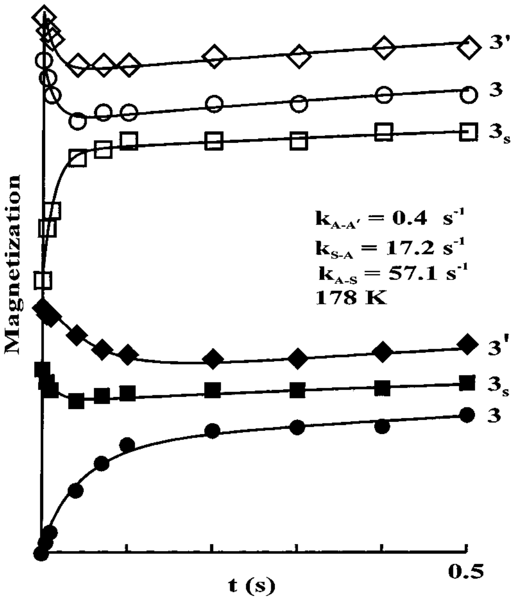


Figure 10. ^{1}H (400 MHz) MMT results for isomer exchange in (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$ (**7**) at 178 K. Filled symbols: observed magnetizations for experiments in which magnetization from site 3 of **7a** is selectively inverted. Open symbols: observed magnetizations for experiments in which magnetization from site 3_s of **7s** is inverted. Lines: least squares fit of the data. The values of the rate constants obtained are shown.

Table 4. Rate Constants for Isomer Interconversion in (η^5-C_7H_7)Ru(CO)$_2$SnPh$_3$

temperature (K)	k_{s-a} (s^{-1})[a]	k_{a-s} (s^{-1})[a]	$\bar{R}_1$ (s^{-1})
178	58 (14)	18 (4)	0.70
183	105 (54)	29 (10)	0.85
189	230 (100)	66 (20)	0.90

[a] Numbers in parentheses are the nonlinear errors in the rate constants from the least squares analyses.

Discussion and Conclusions

In this paper, we have demonstrated the broad applicability of the MMT method in the study of fluxional processes in organometallic molecules. We have shown that the least squares analysis of MMT data allowed the determination of the type(s) of metal shift process(es) that were occurring in each compound and the elimination of others since their rates were much smaller than the corresponding error estimates. The studies of (η^3-C_7H_7)Re(CO)$_4$ (**1**) and (η^5-C_7H_7)Re(CO)$_3$ (**4**) allowed us to corroborate the results of the line shape studies made by Heinekey[77] and to quantitatively confirm his assertion that only 1,2-metal shifts were present in the cycloheptatrienyl ring in these molecules. The study of (η^3-C_7H_7)Os(CO)$_3$SnPh$_3$ (**2**) allowed us to investigate features that could not be attempted with conventional line shape analysis. We were able to determine the mode of cycloheptatrienyl ring fluxionality in the symmetric isomer **2s** in the presence of the much more rapidly exchanging asymmetric isomer **2a**. In this temperature range, the resonance lines of **2a** provide a broad background for the narrower lines of **2s**, as shown in Figure 4, which makes line shape analysis almost impossible. The rate constants for the 1,2-shifts in **2s** were understandably less precise than those obtained for **2a**, but it is doubtful whether line shape analysis could have provided any reliable estimates of the rate constants for 1,2-metal shifts in **2s**. In the study of **2**, we were also able to capitalize on the insensitivity of results obtained by analysis of MMT data to the inclusion of underlying resonance lines from the solvent or other molecules in the determination of the peak integrals and the ability to analyze incomplete MMT data sets when the magnetizations at only some of the sites could be measured reliably. In our studies of the compounds **4**, **5**, **6**, and **7**, which contain the η^5-C_7H_7 group, we were able to investigate quantitatively the possible presence of 1,2-, 1,3-, and/or 1,4-metal shifts in the ring fluxionality and found that both 1,2- and 1,3-shifts occur concurrently in **5** and **6**, but that only 1,2-shifts occur in **4** and only 1,3-shifts in **7**. Line shape analysis does not lend itself to easy and quantitative measurement of exchange rates when two processes occur concurrently.

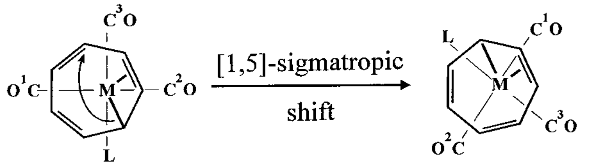
The compound $(\eta^5$-$C_7H_7)Ru(CO)_2SnPh_3$ (**7**) presented our most difficult challenge: the investigation of ring fluxionality in the presence of the relatively rapid interchange between the asymmetric and symmetric isomers **7a** and **7s**, which is fast enough to produce an NMR spectrum appropriate to a symmetrical species, but slow enough that the resonance lines have very different widths. Here again, we were faced with the task of analyzing incomplete MMT data sets since the magnetizations at site 3 could not be measured reliably at all temperatures. The analysis proved possible and allowed us to obtain quantitative estimates of the rate constants and the errors for the various metal shift processes and enabled us to conclude that only 1,3-metal shifts are present. Line shape analysis could not be applied in this case because of the different, temperature-dependent widths of the four cycloheptatrienyl ring resonance lines caused by the rapid isomer interchange. Our MMT study of the **7a**−**7s** isomer interchange process at low temperatures afforded quantitative measures of exchange rates not easily obtained by line shape analysis.

In the MMT studies of the isomers of $(\eta^3$-$C_7H_7)Re(CO)_3$-PMe_3 (**3a** and **3s**), we were able to determine the mechanism of fluxionality only for the symmetric isomer **3s** and show that, provided 1,2-metal shifts are dominant in **3a**, the rate of exchange is faster in **3s** than in **3a**. This is in contrast to the results of our studies of the isomers of $(\eta^3$-$C_7H_7)Os(CO)_3SnPh_3$ (**2a** and **2s**) which showed quantitatively that exchange is faster in the asymmetric isomer than in the symmetric isomer.

In our studies of organometallic compounds containing the η^3-C_7H_7 moiety and those of others,[70−75,87] only 1,2-metal shifts have been observed. In the language of the Woodward−Hoffmann analysis of sigmatropic reactions,[63] a 1,2-metal shift in η^3-C_7H_7 complexes corresponds to an allowed [1,5]-suprafacial sigmatropic shift. However, as Mann has carefully pointed out,[69] this [1,5]-shift must be accompanied by simultaneous rearrangement of the other ligands bonded to the metal. In the pseudo-octahedral compounds **1**, **2**, and **3**, this [1,5]-sigmatropic shift would require a 1,2-metal shift around the C_7H_7 ring to be accompanied by the simultaneous interchange of the two axial carbonyl ligands and the interchange of the two equatorial ligands as shown in Scheme 2.

In **1**, the equatorial carbonyl carbon atoms are equivalent, but the axial carbonyls are nonequivalent, so one would expect to observe axial−axial carbonyl exchange at the same rate as the 1,2-metal shifts. However, the ^{13}C NMR spectra of **1** showed that the carbonyl carbon resonances remained sharp at all temperatures studied,[77] indicating the absence of any carbonyl exchange. The three carbonyl carbon atoms in **2a** are nonequivalent and the ^{13}C NMR spectrum shows three sharp lines in the carbonyl region at low temperatures. At higher temperatures, two of the three carbonyl resonances broaden and coalesce to a single line, while the third resonance remains reasonably sharp. The exchange process that produces these effects must involve the interchange of two of the three carbonyls in **2a**, presumably the axial CO's labeled *a* and *b* in Figure 2, which occupy coordination sites that are *trans* to each other, but not the third carbonyl (labeled *c* in Figure 2), which is *trans* to the cycloheptatrienyl ligand. To investigate this exchange process quantitatively, we performed a detailed analysis of the ^{13}C NMR line shapes over the temperature range 263−303 K. We found that it was necessary to include axial−equatorial carbonyl exchange in addition to the more rapid axial−axial exchange in order to obtain satisfactory agreement between observed and calculated line shapes. The carbonyl exchange processes were characterized by $\Delta G^‡ = 61.4 \pm 0.4$ kJ mol^{-1} for the axial−axial carbonyl exchange process and $\Delta G^‡ = 69.5 \pm 0.6$ kJ mol^{-1} for axial−equatorial carbonyl exchange. The rate of axial−axial carbonyl exchange was found to be almost 2 orders of magnitude slower than the 1,2-metal shifts in the cycloheptatrienyl ring in **2a**, and the value of the free energy of activation for axial−axial carbonyl exchange is very different from the value given in Table 2 for "ring whizzing" in this compound. Since the carbonyl ligands in **1** do not exchange and the carbonyls in **2** are not exchanged at the same rate as the 1,2-metal shift around the cycloheptatrienyl ring, the metal shifts and the carbonyl exchange must be independent processes, just as Reuvers[75] has concluded for the Fe analogue of **2**. Hence we must conclude that the observed 1,2-metal shifts in compounds **1** and **2** cannot be viewed as [1,5]-sigmatropic processes.

Scheme 2



The studies of "ring whizzing" in compounds containing the η^5-C_7H_7 ring reported here show that both 1,2- and 1,3-metal shifts contribute concurrently to the "ring-whizzing" process in some of the compounds. Only 1,2-shifts had been reported in earlier studies.[79−81] Here we observed 1,2-metal shifts only in compound **4**. Compounds **5** and **6** exhibited concurrent 1,2- and 1,3-shifts, and the Ru compound **7** only 1,3-shifts. Mann[3] has pointed out that 1,2-metal shifts in η^5-C_7H_7 complexes correspond to forbidden [1,3]-sigmatropic shifts and that the observation of facile 1,2-shifts in such complexes poses a problem with the predictive power of the Woodward−Hoffmann rules as it applies to compounds containing the cycloheptatrienyl ligand.

Studies of the fluxionality of compounds containing the η^1-C_7H_7 ligand have also been reported.[65−67,77] A study of the line shapes of the ^1H NMR spectra of the p-block compound $(\eta^1$-$C_7H_7)SnMe_3$ showed that only 1,4-

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(87) Lewis, C. P.; Kitching, W.; Eisenstadt, A.; Brookhart, M. *J. Am. Chem. Soc.* **1979**, *101*, 4896.

metal migration around the cycloheptatrienyl ring occurs.[65] On the other hand, ^{1}H and ^{13}C spin saturation transfer (SST) experiments on (η^1-C_7H_7)Re(CO)$_5$ and (η^1-C_7H_7)Ru(CO)(PMe$_2$Ph)(η^5-C_5H_5)[66] showed that only 1,2-metal shifts around the cycloheptatrienyl ring occur in these compounds, but ^{13}C SST experiments on (η^1-C_7H_7)Ru(CO)$_2$(η^5-C_5H_5) demonstrated the concurrent occurrence of 1,2- and 1,4-metal shifts.[67] We have performed ^{1}H MMT experiments on both (η^1-C_7H_7)Re(CO)$_5$ and (η^1-C_7H_7)Ru(CO)$_2$(η^5-C_5H_5) and found, in agreement with the earlier work,[67,77] that only 1,2-metal migration is present in (η^1-C_7H_7)Re(CO)$_5$ and that concurrent 1,2- and 1,4-metal shifts are present in (η^1-C_7H_7)Ru(CO)$_2$(η^5-C_5H_5). The rate constants we obtained were also in agreement with those from ^{1}H SST measurements.[67,77] In compounds containing the η^1-C_7H_7 ligand, the 1,2-metal shifts correspond to allowed [1,7]-sigmatropic shifts requiring inversion of configuration at the metal atom, while 1,4-metal shifts correspond to allowed [1,5]-sigmatropic shifts with retention. Larrabee[65] concluded that the observed 1,4-shifts in (η^1-C_7H_7)-SnMe$_3$ were allowed [1,5]-sigmatropic shifts on the basis that the activation energy was much smaller than the Sn−C bond strength. If the ring fluxionality in (η^1-C_7H_7)Re(CO)$_5$ occurs as an allowed [1,7]-sigmatropic shift with inversion, the rate constant, k_{ax-eq}, for the axial−equatorial carbonyl exchange process should be twice as large as the rate constant, k_{1-2}, for the 1,2-metal migration. ^{13}C SST measurements[77] gave $k_{ax-eq} = 0.23 \pm 0.03$ s^{-1} at 304 K, while ^{1}H MMT and SST experiments (after correction for cross-relaxation) gave $2k_{1-2} = 0.17 \pm 0.02$ s^{-1} and ^{13}C SST measurements gave $2k_{1-2} = 0.38 \pm 0.04$ s^{-1} at this temperature. We do not understand the large difference between the rate constant for metal migration obtained from the ^{13}C SST experiments and those obtained from ^{1}H MMT and SST experiments. The value of $2k_{1-2}$ obtained from the ^{1}H MMT and SST experiments is approximately equal to the value of k_{ax-eq}, so one might tentatively conclude that the observed carbonyl scrambling is a consequence of the 1,2-metal migration and that the [1,7]-sigmatropic shift mechanism is operative in this compound. However, in the asymmetric compound (η^1-C_7H_7)Ru(CO)-(PMe$_2$Ph)(η^5-C_5H_5), where Heinekey[77] observed only 1,2-metal migration, there was no evidence for concurrent inversion of configuration at the metal. Hence the 1,2-metal shifts in this compound do not conform to the requirements of a [1,7]-sigmatropic shift.

In conclusion, it is apparent that the application of orbital symmetry to metal migration in compounds containing η^1-, η^3-, or η^5-C_7H_7 ligands is not particularly fruitful. It predicts, in agreement with observation, that compounds containing η^1-C_7H_7 should exhibit 1,2- and/or 1,4-metal shifts and that compounds containing η^3-C_7H_7 should undergo facile 1,2-metal shifts. However, in all cases where detailed analysis of the rearrangement of other ligands attached to the metal was possible, only some of the results obtained for the compound (η^1-C_7H_7)Re(CO)$_5$ appear to be consistent with the predictions of the Woodward−Hoffmann rules. Furthermore, these rules predict that, in direct contradiction to observations in most cases, compounds containing η^5-C_7H_7 should not undergo facile 1,2-metal migrations. The free energies of activation for 1,2-metal migration in molecules **4**, **5**, and **6**, which contain η^5-C_7H_7, are somewhat higher than the corresponding free energies of activation for 1,2-migrations in compounds containing η^3-C_7H_7 (see Table 2) and are comparable to the activation enthalpies for compounds containing η^1-C_7H_7.[65−67,77] The free energy of activation for 1,2-metal shifts in **7**, which also contains η^5-C_7H_7, is slightly smaller than those for **1** and **2s**, which contain an η^3-C_7H_7 ring. There is, therefore, no evidence to support the idea that the metal migrations in compounds with η^5-C_7H_7 are "forbidden" by orbital symmetry and therefore occurring by entirely different mechanisms from those for the "allowed" migrations in compounds containing η^1- or η^3-C_7H_7. Undoubtedly, analysis of the metal shifts using only σ-orbitals is too simplistic, and a more elaborate description including all orbitals on the metal is required. The elucidation of the details of the underlying mechanisms that give rise to the observed 1,2-, 1,3-, and 1,4-metal shifts in organometallic compounds containing the cycloheptatrienyl ligand must await in-depth computational studies of these molecules.

Experimental Section

NMR Studies. ^{1}H NMR spectra were recorded at 200 (compounds **1**, **3**, and **4**) and 400 MHz (compounds **2**, **5**, **6**, and **7**) using Bruker WH-200 and AM-400 spectrometers, respectively. MMT data were collected using a $180°_{selective} - \tau - 90°_{nonselective}$ − Acquire pulse sequence, and longitudinal relaxation times were measured using the standard inversion−recovery technique. Selective inversion was accomplished with DANTE, typically using 15−20 pulses with a flip angle of ~10° and an interpulse spacing of 400−500 μs. The specific values of flip angle and pulse spacing used in each experiment were chosen in order to achieve optimum selectivity. The read pulse was phase-cycled in tandem with the detector using CYCLOPS, and the phases of the DANTE pulses were inverted on alternate scans. Pulse lengths were carefully calibrated before each series of experiments, and the effectiveness of the DANTE selective inversion was optimized before acquiring the MMT data for a series of values of τ. Gaussian line broadening of 0.0−0.25 Hz was used in transforming the FIDs.

The sample temperature was equilibrated for 30 min before data collection, controlled by a Bruker temperature controller, and determined by inserting a thermocouple immersed in toluene in a 5 mm tube into the probe before and after the multisite magnetization transfer or inversion−recovery data sets were collected. The temperature was stable to ±0.5°.

General Synthetic Details. The preparation of the compounds was carried out under purified nitrogen using standard Schlenk techniques and carefully dried solvents. The compounds (η^x-C_7H_7)M(CO)$_y$SnPh$_3$ (M = Fe, Ru, Os; $x = 3$, $y = 3$ and $x = 5$, $y = 2$) (**2**, **5**, **6**, and **7**) were obtained by reacting K[(η^3-C_7H_7)M(CO)$_3$][88] with Ph$_3$SnCl, whereas (η^x-C_7H_7)Re(CO)$_y$ ($x = 3$, $y = 4$ and $x = 5$, $y = 3$) (**1** and **4**) were prepared by treating NaRe(CO)$_5$ with $C_7H_7BF_4$; the initial η^3- or η^1-C_7H_7 bonded materials were decarbonylated either thermally or photochemically. Reaction of (η^5-C_7H_7)Re(CO)$_3$ with PMe$_3$ gave compound **3**. All compounds gave satisfactory elemental analyses.

The preparation and characterization of compounds **2** and **7** have been communicated in a preliminary form.[78,89] Full synthetic and spectroscopic details on these and the other molecules will appear in forthcoming publications.

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Supporting Information Available: Figures showing extensive MMT results for studies of compounds **2a**, **3s**, **4**, **6**, and **7**. This material is available free of charge via the Internet at http://www.pubs.acs.org

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