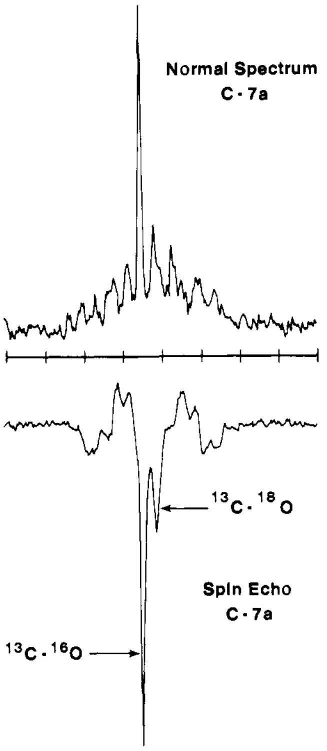

Figure 2. 100.6-MHz ^{13}C NMR spectral expansions of C-7a of griseofulvin (**1**) derived from sodium [1-^{13}C,^{18}O$_2$]acetate (0.05 ppm/division). The spin-echo experiment (5684 scans) has τ = 0.109 s.

Table I. ^{13}C NMR Data of Griseofulvin (1) Derived from Sodium [1-^{13}C,^{18}O$_2$]Acetate[a]

carbon	chemical shift, ppm	$\Delta\delta\,^{16}$O–^{18}O (ppm × 100)[b]	isotope ratio[c] ^{16}O/^{18}O
4'	196.8	4.2	68:32
3	192.4	4.0	75:25
2'	170.8	2.0	83:17
6	169.7	1.5	78:22
7a	164.7	1.7	75:25
4	157.9	1.6	71:29

[a] Fourier transform spectra were measured on a Bruker WH400 spectrometer at 100.6 MHz by using ca. 0.1 M solutions of **1** in CDCl$_3$ with Me$_4$Si internal standard. Assignments agree with those reported in ref 5c. Signals for carbons bearing oxygens were first expanded by using 32K data block/2000 Hz, 80–1200 scans, 16.4-s acquisition time, and 45° pulse angle. Subsequent spin-echo expansions (vide infra) employed 32K data block/2000 Hz, 650–5700 scans, and 8.2-s acquisition time. [b] ^{18}O upfield shift values are ±0.1 (ppm × 100). [c] Approximate values obtained from relative peak heights of ^{13}C–^{16}O and ^{13}C–^{18}O inverted signals in the spin-echo experiments.

to **1**. The use of spin-echo Fourier transform (SEFT) techniques for separation of ^{18}O-induced isotope shifts from long-range carbon–carbon couplings has already proved advantageous in other biosynthetic work in our laboratories and should be widely applicable.

Acknowledgment. We are grateful to Professor D. E. Cane (Brown University) and Professor R. L. Van Etten (Purdue University) for providing copies of their manuscripts[10f,11e,f] prior to publication. Valuable discussions with Professor D. L. Rabenstein (University of Alberta) about his spin-echo NMR research were central to this work. We thank the Stable Isotopes Resource of Los Alamos National Laboratory for generous gifts of [^{18}O]water and the Natural Sciences and Engineering Research Council of Canada for financial support (Grant A0845 and NSERC summer studentship to M.P.L.).

A Fluxional η^1-Cycloheptatrienyl Derivative of Ruthenium Exhibiting Both 1,2 and 1,4 Metal Migrations

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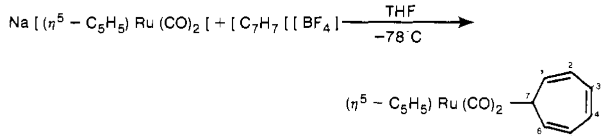
The fluxional behavior of a large number of compounds in which a cyclopentadienyl ring is bonded in monohapto fashion to a metal has been studied.[1,2] In all cases where the pathway has been determined, the metal migrates to the adjacent carbon atom of the five-membered ring; that is, a 1,2 migration occurs. In no case has an alternate pathway been detected, although the possibility of two or more concurrent processes was recognized at an early stage.[3]

We recently prepared the first η^1-cycloheptatrienyl derivative of a transition metal, (OC)$_5$Re(7-η^1-C$_7$H$_7$) (**1**),[4] and showed that it was fluxional by 1,2 migration of the metal. In further investigations, we have now prepared the ruthenium derivative (η^5-C$_5$H$_5$)Ru(CO)$_2$(7-η^1-C$_7$H$_7$) (**2**).[5] Remarkably, this monohapto compound displays two concurrent fluxional pathways, 1,2 *and* 1,4 migration.

Synthesis of **2** followed the same anion plus tropylium route (reaction 1) used previously.[4] Infrared spectroscopy indicated nearly quantitative formation of **2**, but isolated yields were 70% or less due to the very high solubility in pentane from which it was crystallized at −78 °C.[6,7]



(1)

2

The fluxionality of **2** was studied by applying the spin saturation transfer technique of Forsén and Hoffman[9] to the ^{13}C NMR spectrum[10] at 279.0 K.[11] Spectra acquired with saturation at

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[5] Compound **2** is an orange crystalline solid, mp 47 °C. Anal. Calcd for C$_{14}$H$_{12}$RuO$_2$: C, 53.67; H, 3.86. Found: C, 53.63; H, 3.86. Mass spectrum (14 eV, 25 °C), M$^+$, (M − CO)$^+$, (M − 2CO)$^+$, C$_7$H$_7$$^+$ (base peak); IR (cyclohexane, ν_{CO}, cm^{-1}) 2015 (s), 1961 (s), 1958 (sh); ^{1}H NMR (cyclohexane-d_{12}, 20 °C) δ 5.40 (s, C$_5$H$_5$), 5.64 (m, H$_{3,4}$), 5.22 (m, H$_{1,6}$), 5.10 (m, H$_{2,5}$), 4.02 (t, H$_7$, $^3J_{1-7}$ = 7.8 Hz); olefinic proton resonances (cf. Figure 1 for numbering system) assigned by decoupling experiments. ^{13}C NMR (THF-d_8, 20 °C) δ 202.7 (CO), 140.8 (C$_{1,6}$), 134.9 (C$_{3,4}$), 122.8 (C$_{2,5}$), 89.9 (C$_5$H$_5$), 19.5 (C$_7$); assignments derived from ^{1}H NMR by selective decoupling.

[6] Compound **2** in solution slowly forms ditropyl and the ruthenium dimer; it is slightly less stable thermally than **1**. The ruthenium anion was obtained by a published procedure.[8]

[7] The result for ruthenium may be contrasted with the analogous reaction involving iron in which mainly [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$ was obtained with a very low yield (4%) of a compound ultimately formulated as (η^5-C$_5$H$_5$)Fe(CO)(η^3-C$_7$H$_7$): Ciappenelli, D.; Rosenblum, M. *J. Am. Chem. Soc.* **1969**, *91*, 3673, 6876. In our hands, this reaction gives the iron dimer quantitatively.

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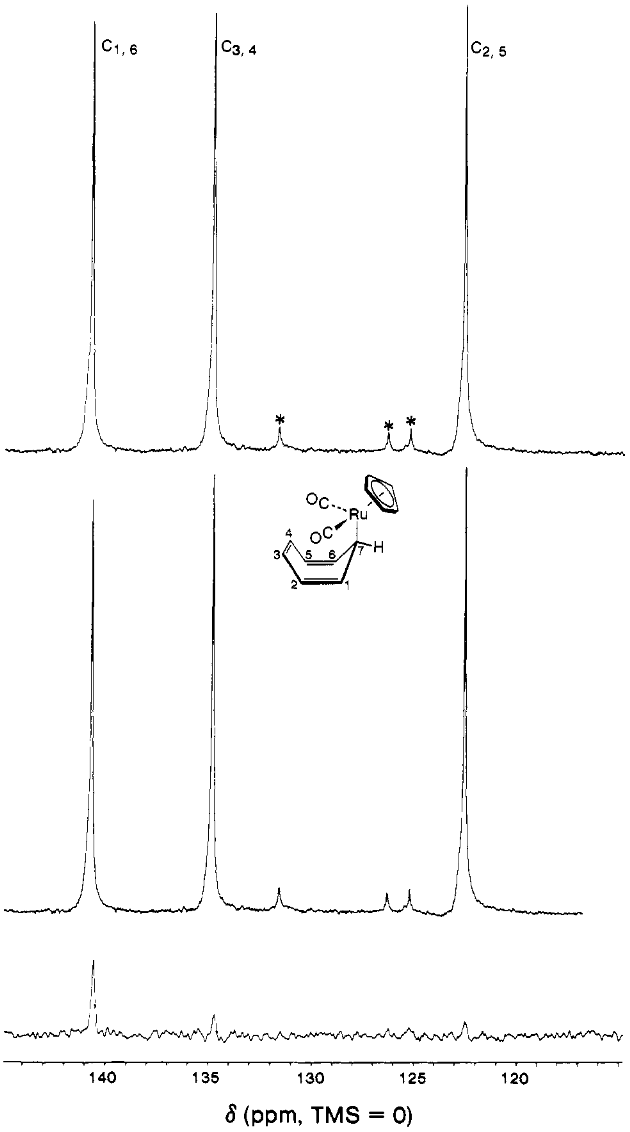

Figure 1. Olefinic region of the ^{13}C NMR spectra of $(\eta^5\text{-}C_5H_5)Ru(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)$ (**2**), 100.6 MHz, 0.71 M in THF-d_8, 279.0 K. Upper spectrum: normal spectrum with intensities equal to $M_z(0)$; C_7 off scale at 19.5 ppm; asterisks mark 2% ditropyl impurity. Middle spectrum: taken with saturation at C_7; intensities of ring carbons reduced, equal to $M_z(\infty)$. Lower difference spectrum $[M_z(0) - M_z(\infty)]$: 300 scans with saturation field off resonance minus 300 scans with saturation at C_7, followed by Fourier transformation.

C_7 showed decreases in the intensities of the other signals which are most sensitively shown on the difference spectrum of Figure 1. Here, peak intensity is proportional to the decrease caused by saturation transfer from C_7. The difference spectrum values[12] at $C_{1,6}$, $C_{2,5}$, and $C_{3,4}$ are 0.0466, 0.0064, and 0.0095, respectively. Qualitatively,[13] the intensity decrease is greatest at the 1,6 positions, implying that 1,2 migration is an important process. The intensity decrease at $C_{2,5}$ could result from two consecutive 1,2 migrations, but if this were the only pathway, the decrease at $C_{3,4}$ should be smaller still. Instead, the $C_{3,4}$ decrease is greater, which suggests that a 1,4 migration is occurring.

A more certain evaluation of the three possible migration pathways and their rates (k_{12}, k_{13}, k_{14}) requires a solution of the Bloch equations modified to take account of transfer of magnetization among the nuclei.[9] The results are as follows:[14] $k_{12} = 1.7 \pm 0.4 \times 10^{-2}\ s^{-1}$; $k_{13} = 0.1 \pm 0.1 \times 10^{-2}\ s^{-1}$; $k_{14} = 0.3 \pm 0.1 \times 10^{-2}\ s^{-1}$.

The numerical results support the qualitative indication that more than one pathway is operative. A 1,2 migration is the major pathway, at a rate five or six times faster than that of the 1,4 migration. The rate of 1,3 migration is zero within the estimated errors, and we shall take it to be zero or extremely small. The conclusion, however, that there are two significant migration pathways in **2** seems inescapable.

It is reasonable to regard these migrations as sigmatropic shifts[15] and to discuss them in terms of orbital symmetry concepts.[16,17] We accordingly change to the alternative nomenclature under which 1,2 and 1,4 migrations become sigmatropic [1,7] and [1,5] shifts, respectively.

In substituted cycloheptatrienes, 7-XC_7H_7, the nature of X determines which sigmatropic shifts are allowed.[18] For the simplest case, X = H, only a [1,5] shift is allowed; for X = CH_3 or other group with an accessible p orbital, [1,7] or [1,6] shifts are also allowed with inversion at X. The case of X = $Sn(C_6H_5)_3$ is especially interesting, since a [1,5] pathway was observed.[19] The main group metal tin thus behaved in the "ordinary" way, in the sense of following hydrogen in its migratory behavior.

In contrast, the pathway in the case of X = $Re(CO)_5$ (**1**) was [1,7].[4,20] How the [1,7] shift is achieved is not known. There have been suggestions that d orbitals at accessible energies might play a part,[1] but we are unaware of any theoretical considerations of the problem.[21]

The importance of the ruthenium derivative **2** is its demonstration that *both* [1,7] and [1,5] pathways are open to transition-metal migrating groups, in the sense that activation energies for both processes may be similar and small. While the [1,5] sigmatropic shift is readily accommodated under present symmetry rules (an invariant metal σ orbital interacting with the triene), the [1,7] shift remains, as it was in **1**, a feature that poses interesting problems.

For **2**, the suggestion might be advanced that inversion at the pseudotetrahedral ruthenium center is occurring in the [1,7]

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[10] A magnetically dilute nucleus is advantageous in these experiments since nuclear Overhauser effects are eliminated. It is worth noting that the more familiar line-shape analysis procedure is not applicable to **2**; as the temperature is increased, thermal decomposition becomes rapid before migration becomes fast enough to affect line shape.

[11] At this temperature intensity changes are small but easily interpreted qualitatively because consecutive shifts can be ignored. Measurements have been made at intervals to 304 K and the rate constants (k_{12} and k_{14}) derived from them give good Eyring plots. Above 304 K thermal decomposition of **2** was significant.

[12] Values quoted, in the usual nomenclature, are $\{M_z(0) - M_z(\infty)\}/M_z(0)$ for the equivalent pairs of nuclei. It is convenient to designate this quantity *S*, which we term the relative saturation parameter.

[13] Qualitative discussion is simplified when the relaxation times of all nuclei are similar as they are in **2**. At 279.0 K, $T_1^{1,6} = 3.11$, $T_1^{2,5} = 3.16$, $T_1^{3,4} = 3.23$ s.

[14] Estimation of error limits in these rate constants is difficult. The limits shown are the calculated cumulative effects of the following errors in the input parameters:[12] 10% in $S^{1,6}$; 20% in $S^{2,5}$ and $S^{3,4}$; 10% in each of the T_1 values. The *k*'s are defined as the rate of leaving one site in either direction.

[15] Since a sigmatropic reaction is rather precisely defined (ref 16, p 242; ref 17, p 114), it may be appropriate to restate that it is an uncatalyzed, intramolecular process involving a cyclic transition state in which an atom or group is simultaneously joined to both termini of a π electron system. We are concerned only with thermal processes.

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[21] Another aspect of the problem has been pointed out by a referee, who observes that the energy difference between allowed and forbidden pathways might vary considerably with the group X. This is because the choice of frontier orbitals to define the sigmatropic rules is based on an energy difference between otherwise degenerate orbitals and the assumption of an early transition state.[17b] The exact meaning of the latter concept in a degenerate sigmatropic shift requires clarification, however.

pathway. We are reluctant at present to accept this facile explanation, since its application to the [1,7] pathway in **1** is by no means clear. Since [1,7] pathways in both **1** and **2** have the same activation energy ($\Delta G^{\ddagger} \simeq 19$ kcal mol^{-1}), a similar rationale might be expected for both octahedral and tetrahedral metal centers.

We are continuing our efforts to establish an understanding of the fluxional behavior of compounds of this class.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Professor R. E. D. McClung for valuable discussions of the spin saturation transfer experiments.

Registry No. **2**, 80387-87-7; Na[(η^5-C_5H_5)Ru(CO)$_2$], 42802-20-0.

Deuteron NMR Study of Molecular Order and Motion in a Liquid Crystalline Polymer

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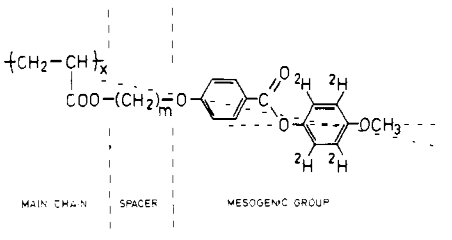
A variety of liquid crystalline polymers has systematically been synthesized recently, following the model[1,2] of decoupling the molecular motions of the mesogenic side groups and the main chain by inserting a flexible spacer. Nematic, smectic, and even cholesteric phases have been obtained.[3,4] In certain cases, both nematic and smectic phases could be generated simply by varying the length of the spacer. An example of this behavior is provided by the systems depicted schematically in Figure 1, involving phenyl benzoates as mesogenic groups. These materials show properties of polymers, e.g., a glass transition where molecular motions are frozen in. Their glass transition temperature T_g is influenced by the length of the spacer (Figure 1) and the mesogenic group. As to be expected, T_g also depends on the nature of the main chain.[4] In addition and as already described, these polymers also show properties of liquid crystals at temperatures above T_g, e.g., they can be oriented in electric[5,6] and magnetic fields. In contrast to low molecular weight liquid crystals, these polymeric systems do not crystallize when cooled below T_g. Thus the liquid crystalline structure can be frozen in, allowing the investigation of glassy liquid crystalline systems. Unknown so far are any details about the influence of the spacer on the behavior of the mesogenic groups; especially there is no information about possible motions and the molecular order of the mesogenic units below T_g. The question to what extent the side group is decoupled from the main chain can be tackled, in principle, by a variety of techniques which can be employed to study liquid crystalline systems.[9] In this communication we wish to give a preliminary report of a detailed study of molecular order and motion using ^{2}H NMR spectroscopy, concentrating on the system with a spacer length of $m = 6$, which shows both nematic and smectic phases. Deuteron NMR spectroscopy is especially appealing since it allows direct observation of the mesogenic group.[10-15] Moreover, substantial changes are expected to show up in the ^{2}H spectra at T_g. While in the liquid crystalline phase the quadrupole coupling experienced by the ^{2}H nucleus is partially averaged due to molecular motion,[9,10-15] leading



m	Transition Temperatures [K]
2	g 325 n 376 i
6	g 305 s 365 n 383 i

Figure 1. Structure and phase transitions of selectively deuterated liquid crystalline polymers. The molecular axis (- - -) of the mesogenic group as revealed by ^{2}H NMR line-shape analysis as well as the local C_2 axis (-··-) of the phenyl ring are shown. g denotes glass transition; *s*, *n*, *i* = transition to liquid crystalline *s*mectic or *n*ematic phase or to *i*sotropic melt (determined by DSC).

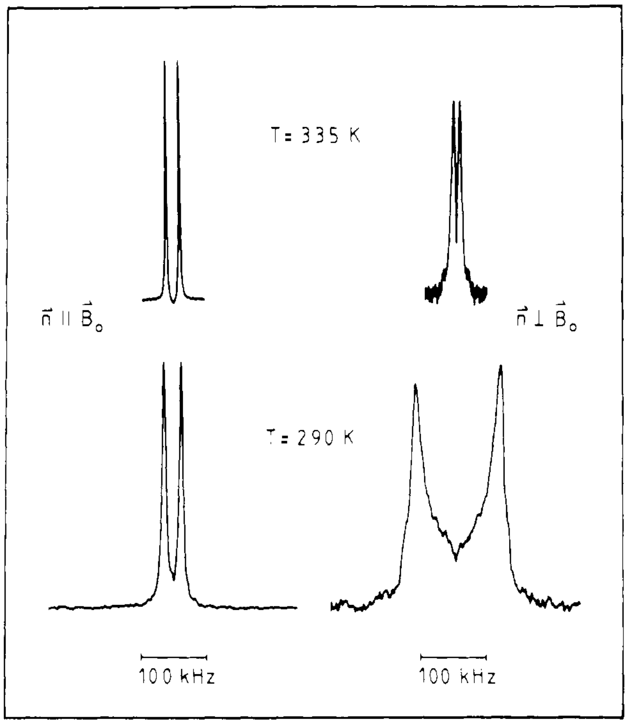


Figure 2. ^{2}H NMR spectra of the smectic liquid crystalline polymer (Figure 1), oriented in its nematic phase by the magnetic field (8.5*T*) of the NMR spectrometer, at 335 (above T_g) and 290 K (below T_g) with director n parallel (left) and perpendicular (right) to the magnetic field.

[†] Institut für Physikalische Chemie.

[‡] Institut für Organische Chemie.

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