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The Fluxional Behaviour of η^6(Bicyclo[6.2.0]deca-2,4,6-triene) Hexacarbonyl Diruthenium (Ru–Ru) by ^{1}H and ^{13}C NMR Techniques

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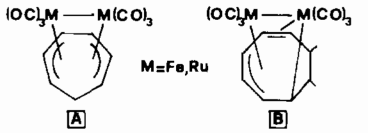
The variable temperature ^{1}H NMR spectra of $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ ($C_{10}H_{12}$ = bicyclo[6.2.0]-deca-2,4,6-triene) shows that this molecule undergoes the fluxional behaviour previously reported for $[M_2(CO)_6(\eta^6\text{-polyolefin})]$ complexes (M = Fe, Ru) which have in the solid an asymmetric skew-type structure. The use of ^{13}C NMR techniques, employed for the first time for a diruthenium complex of the above type, allows a comparison of the mechanism of the fluxional process with that of the diiron analog. Although the observed line shape changes of the carbonyl resonances in the two complexes are somewhat different the processes are basically the same. In the case of the diruthenium complex, however, the simple twitching process, the local scrambling of the carbonyl groups on the allyl bound ruthenium atom, and the local scrambling on the other ruthenium atom, are all well separated and allow a direct proof of the correctness of the predicted changes. The activation energies of the three processes have a higher value than those of the diiron analog and this appears to be a general trend.

Introduction

Several complexes of the type $[M_2(CO)_6(\eta^6\text{-polyolefin})]$* (M = Fe, Ru, Os) have been synthesized and an impressive number of articles have appeared dealing with their characterization both in the solid state and in solution [1].

These complexes may be classified in three cathegories [2]: the first differentiation can be made on the basis of their X-ray structure. The two different configurations are reported in Scheme 1; the symmetric structure (A) was found in cycloheptatriene)hexacarbonyldiiron [3] and it is likely to be present in the diruthenium analog [4]. The skew-type structure (B) was established for all the other complexes investigated. It is worth noting that no bis-allyl configuration has been reported so far for complexes having a C_8 polyolefinic ring.



Scheme 1

Variable temperature NMR techniques support the above distinction between A and B type complexes and introduce a new effect in the derivatives of type B. Although most complexes B show fluxional behaviour some do not*. The latter group occur with asymmetric substitution in the C_8 ring. This eliminates the two energetically equivalent forms which is necessary for the fluxional behaviour (Scheme 2) [5–7] to be possible.

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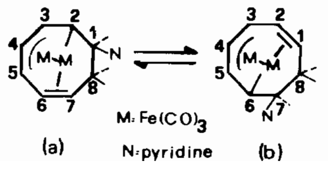
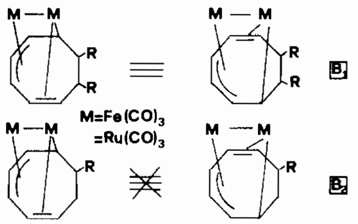
*In this paper the discussion of $[M_2(CO)_6(\eta^6\text{-polyolefin})]$ is limitated to those complexes having the two carbonyl metal groups linked together and coordinated to the same polyolefinic ring.

*Cationic complexes of the type $\{[Fe_2(CO)_6(\eta^6\text{-}C_8H_9N)]^+\}$ (N = pyridine or phosphine) are also known [5]. They show a mutual rearrangement of the enantiomers a and b, *via* a 1,3 shift of N (Scheme 1′).

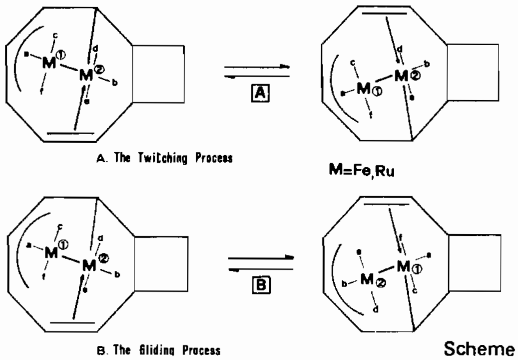


Scheme 1′



Scheme 2

In some cases complexes of the type B_2 are obtained as racemates [5]. The interconversion of compounds of type B_1 can be completely rationalized in terms of metal–olefin bond change by ^1H NMR techniques, which however can give no information about the mechanism of interconversion. The direct consequence of this is the impossibility of discrimination between the most plausible mechanism pathways of the fluxional behaviour, considered by Cotton *et al.* [8, 9]: the twitching and the gliding processes (Scheme 3). The twitching process involves only a partial rotation of the $(OC)_3M–M(CO)_3$ moiety while the two carbonyl metal groups maintain their η^3- and η^1, η^2-type of coordination to the polyolefin, respectively. The gliding process involves a complete rotation of the $(OC)_3M–M(CO)_3$ moiety about the axis perpendicular to the M–M bond and the mean plane of the C_1, C_6 atoms. The two basic processes can be distinguished by variable temperature ^{13}C NMR spectroscopy*. So far the following complexes have been investigated by this technique: $[Fe_2(CO)_6(\eta^6\text{-}C_7H_8]$ [11] [C_7H_8 = Cycloheptatriene), $[Fe_2(CO)_6(\eta^6\text{-}C_8H_{10})]$ [8] (C_8H_{10} = Cycloocta-1,3,5-triene), $[Fe_2(CO)_6(\eta^6\text{-}C_9H_{10})]$ [12] (C_9H_{10} = Bicyclo[6.1.0]nona-2,4,6-triene), and $[Fe_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ [9] ($C_{10}H_{12}$ = Bicyclo [6.2.0] deca-2,4,6-triene). In each case the carbonyl groups appear to move, and changes in the metal–olefin bonds occur in all complexes except for the cycloheptatriene derivative [11].



Scheme 3

In our opinion two further experiments are necessary to obtain a general picture of these complexes: the ^{13}C NMR study of a diruthenium derivative of type B_1 and of a dimetal derivative of type B_2*. We present here the variable temperature ^1H and ^{13}C NMR studies of $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ [13] and compare its behaviour with those of previously investigated diiron complexes [8, 9, 12].

Experimental

The compound $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ was prepared as previously described [13].

^1H NMR spectra were recorded on a Varian NV-14 60 MHz spectrometer and the temperature was monitored by a Varian 60 HO temperature control. The sample was dissolved in a mixture of CS_2/TMS (95/5 v/v), degassed in vacuum line, and purged with nitrogen.

The solubility of the compound was insufficient for recording good ^{13}C NMR spectra in the carbonyl peaks region. Attempts to exchange the carbonyl groups with ^{13}CO were unsuccessful since decomposition of the sample occurred both in the thermal as well as in the photochemical reaction. Therefore the sample was prepared directly by reaction of ^{13}CO enriched $Ru_3(CO)_{12}$ and bicyclo[6.2.0]deca-2,4,6-triene. Procedures as in ref. 13 were used for the separation and purification of the sample which resulted in a 10–15% ^{13}CO enrichment. About 20 mg of this sample were dissolved in CD_2Cl_2 for the spectra recorded between –90 °C and –50 °C. The sample was dissolved in $CD_3C_6D_5$ for the spectra between –40 °C and +90 °C, and in 1,3,5-triethylbenzene (with a d^6DMSO insert for locking) for the spectra between +100 °C and +170 °C. A small amount of Cr(acac)$_3$ was added as relaxation agent in the –40 °C–+170 °C experiments. Less than 2,000 pulses were necessary for low temperature experiments whilst up to 4,000 and 7,000 pulses were used for the –40 °C–+90 °C and +100 °C–+170 °C spectra, respectively. Chemical shifts were referenced against a peak of the solvent and then calculated (in ppm) downfield from TMS.

Results and Discussion

Variable Temperature ^1H NMR and ^{13}C NMR Spectra of the Ring Carbon Atoms of $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$

The occurrence of a fluxional process in $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ has been reported in a preliminary

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*The gliding process has been ruled out in favour of the twitching one, on the basis of ^1H NMR spectra, in the case of $[Rh_2(\eta^5\text{-}C_5H_5)_2(\eta^6\text{-}C_8H_{10})]$ [10], which can be related to the complexes of type B_1 in having a $Rh_2(\eta^5\text{-}C_5H_5)_2$ unit replacing $M_2(CO)_6$. In that case indeed the two cyclopentadienyl signals remain sharp and never coalesce. However, the fact that $M_2(CO)_6$ is not isostructural with $Rh_2(\eta^5\text{-}C_5H_5)_2$ must be considered.

*A variable temperature ^{13}C NMR study of the complex $\{[Fe_2(CO)_6(C_8H_9N)]^+(BF_4)^-\}$ (N = pyridine) [5] appears also to be of interest.

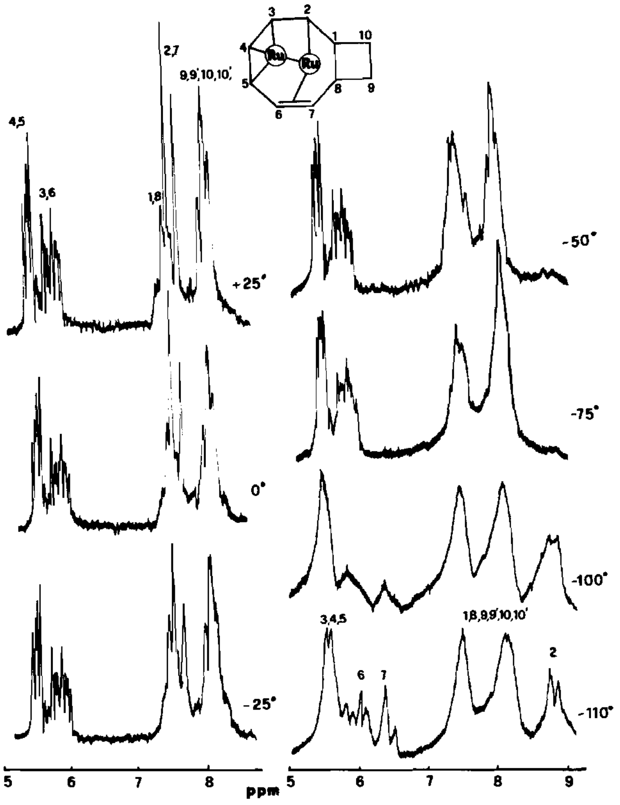


Figure 1. The 60 MHz variable temperature ^{1}H NMR spectra of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$] in CS_2.

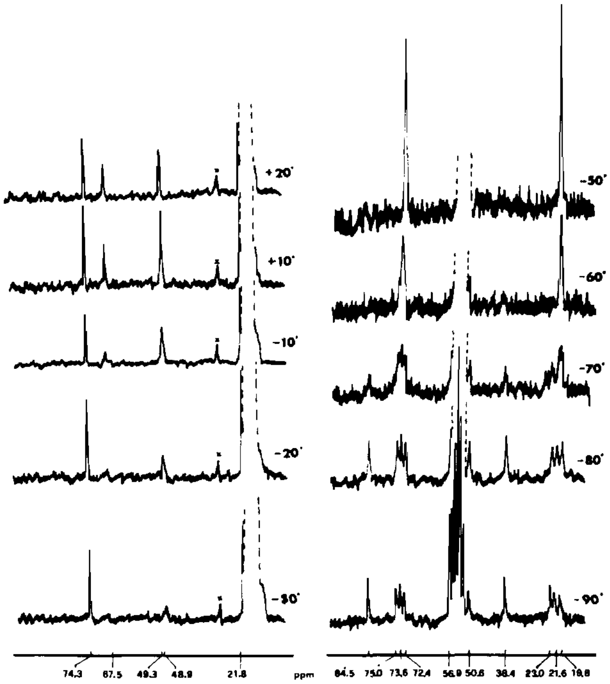
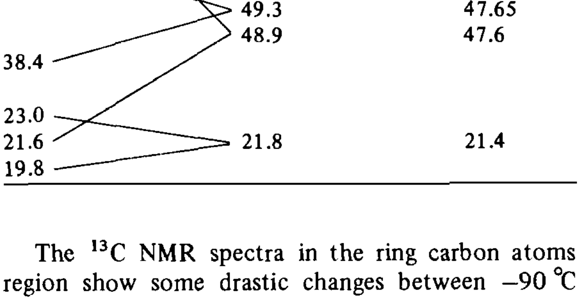


Figure 2. The variable temperature ^{13}C NMR spectra of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$] in the ring carbon atoms region. In the right part of the spectra the solvent is $CD_3C_6D_5$; peak marked x is an impurity of the solvent. In the left part of the spectra the solvent is CD_2Cl_2. The chemical shifts are expressed in ppm from TMS and differ in the two solvents by less than 0.3 ppm.

communication [13]. At room temperature the ^{1}H NMR spectrum is consistent with that of a molecule having a plane of symmetry bisecting the metal–metal bond and the C_4–C_5, C_1–C_8, and C_9–C_{10} bonds (Figure 1). Consequently the signals of the room temperature spectrum are assigned in the following sequence: τ = 5.49 ($H_{4,5}$), 5.84 ($H_{3,6}$), 7.48 ($H_{1,8}$), 7.56 ($H_{2,7}$: J = 8.2 Hz), 8.05 ($H_{9,9'}$, $H_{10,10'}$) in CS_2. On cooling down the doublet due to $H_{2,7}$ begins to broaden at ≅–10 °C and collapses at ≅–60 °C. At –75 °C the peaks due to $H_{1,8}$ and $H_{9,9'}$, $H_{10,10'}$ broaden, followed shortly after by the other signals. At –100 °C a new spectrum originates which is resolved at ≅–110 °C. The assignments in the "frozen" configuration are considered to be τ = 5.50 ($H_{3,4,5}$), 5.85 (H_6), 6.4 (H_7), 7.3–8.3 ($H_{1,8}$, $H_{9,9'}$, $H_{10,10'}$) and 8.83 (H_2) These assignments, however, must be considered as tentative owing to superimposition of several peaks (Figure 1). The –110 °C spectrum is consistent with the skew-type structure found for the analogous diiron derivative [14] and is similar to the "frozen" spectrum registered at –129 °C for that complex. Therefore it is reasonable to suggest that the skew-type configuration is also pertinent to the complex in the crystal, analogously with all the other complexes of type B_1.

TABLE I. Chemical shifts (in ppm from TMS) for the Ring Carbon Atoms of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$].



–90 °C	+20 °C	Calculated
84.5		
75.0	74.3	73.7
73.6		
72.4		
	67.5	67.55
56.9		
50.6		
	49.3	47.65
	48.9	47.6
38.4		
23.0		
21.6	21.8	21.4
19.8		

The ^{13}C NMR spectra in the ring carbon atoms region show some drastic changes between –90 °C and –50 °C (Figure 2). The original ten signals (spectrum at –90 °C) which are consistent with an asymmetric configuration of the molecule in the "frozen"

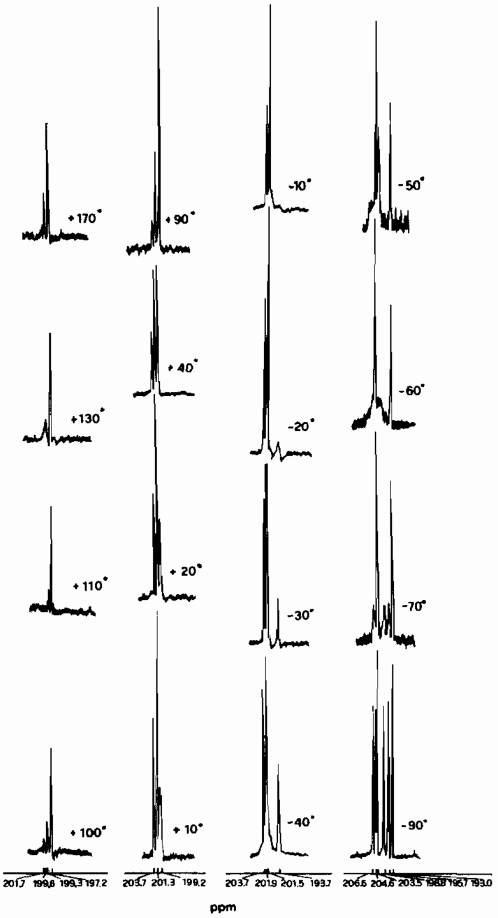
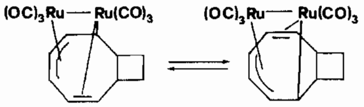


Figure 3. The variable temperature ^{13}C NMR spectra of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$] in the carbonyl region. Spectra from −90 °C to −50 °C are in CD_2Cl_2; spectra from −40 °C to +90 °C are in $CD_3C_6D_5$ with a small amount of $Cr(acac)_3$; spectra from +100 °C to 170 °C are in 1,3,5-triethylbenzene with a small amount of $Cr(acac)_3$. Chemical shifts are in ppm from TMS (see note in Table II for solvent dependence).

state progressively collapse and at −50 °C practically all have disappeared in the base line except for two peaks at 74.3 and 21.8 ppm from TMS. At 0 °C a new spectrum corresponding to a time averaged interconversion is resolved. At +10 °C all the new five peaks expected for a symmetric molecule are sharp (Figure 2). Table I presents a possible pairing of the ten peaks at −90 °C to give the five peaks at +20 °C. The comparison between the calculated (from the −90 °C spectrum) and the observed values (at +20 °C) is reasonably good once the shift due to the change of the temperature is considered. It is too speculative with these data to attempt an assignment to the signals which is anyway not essential to the discussion. The ^{13}C NMR data for the ring carbon atoms and those previously obtained from ^1H NMR spectra are completely in agreement with a fast exchange at higher temperatures between two enantiomorphs (Scheme 4).



Scheme 4

A part from activation parameters which will be discussed later no further information can be obtained by variable temperature NMR spectra of the organic ligand.

Variable temperature ^{13}C NMR Spectra of the Carbonyl Groups of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$]

The ^{13}C NMR spectrum of [$Ru_2(CO)_6(\eta^6$-$C_{10}H_{12})$] at −90 °C shows six distinct signals for the carbonyl groups, as anticipated for a structure of type B (Figure 3). Although we have not registered spectra at temperatures lower than −90 °C, it is reasonable to suppose that at about −110 °C all the peaks should have a relative intensity 1. On raising the temperature four carbonyl signals broaden and eventually collapse at about −60 °C. The four collapsed peaks then emerge as two very close singlets which are detectable at −60 °C and more clearly at −80 °C. The second and fourth peaks (from the left in the −80 °C spectrum) at higher temperature rapidly collapse and at −10 °C disappear in the base line. At +10 °C a new singlet grows and progressively sharpens up. At +50 °C the other two peaks of the original four-line spectrum at −30 °C start to collapse and the process is complete at about 115 °C. At 130 °C a new singlet appears which is still growing at +170 °C, the highest temperature reached in this study.

In principle the twitching process, starting from the limiting spectrum of six lines, should give collapse of four signals, namely *c, f, d,* and *e* to give a spectrum of two lines due to *b* and *a*; then *c* and *f*, and *d* and *e*, should emerge as two singlets of intensity 2, so that the spectrum should appear as a sequence of four lines of relative intensity 1(*b*): 2(*c, f*):2(*d, e*):1(*a*). All the data so far available on the diiron derivatives [8, 9, 12] never reach this spectrum since rotation around the allyl bound iron atom starts to occur before, thus complicating the interpretation of the spectra. In the case of the diruthenium complex the pure twitching process can be followed almost completely before the above mentioned rotation takes place, as shown by the four signal spectrum at −30 °C (Figure 3). The four signals, however, are not in the anticipated 1:2:2:1 intensity ratio. This finding is in agreement with the ^1H and ^{13}C NMR spectra registered for the ring carbon atoms region, in which the interconversion of the two enantiomorphs (Scheme 4) or the twitching process (Scheme 3) are observed in their fast exchange limit only at about 0 °C. It is therefore reasonable to expect that the above correct relative intensity 1:2:2:1 should be found at about 0 °C. The fact that already at −30 °C four signals are evident is just a fortuitous circumstance and represents

TABLE II. Observed and Calculated (in parenthesis) Chemical Shifts for the Carbonyl Peaks of $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ from ^{13}C NMR Spectra at Various Temperatures

−90 °C	*d,e* 206.6	*c,f* 204.6	*b* 203.5	*f,c* 198.8	*e,d* 195.7	*a* 193.0
−30 °C		*b* 203.7 (203.5)	*c, f* 201.9 (201.7)	*d, e* 201.5 (201.1)		*a* 193.7 (193.0)
+40 °C		*b* 203.7 (203.5)		*d, e* 201.3 (201.1) *a, c, f* 199.2 (198.8)		
+150 °C			*b, d, e* 201.6* (202.1)	*a, c, f* 199.2* (198.8)		

*The observed chemical shifts at 150 °C are corrected. They appear in 1,3,5-triethylbenzene at 199.6 and 197.2, respectively. Comparison with the chemical shifts at +90 °C in $CD_3C_6D_5$ shows for each signal a downfield shift of 2.0 ppm in triethylbenzene, according to the correction.

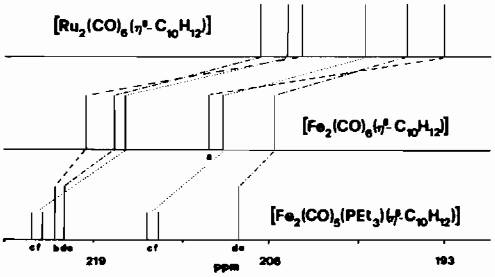
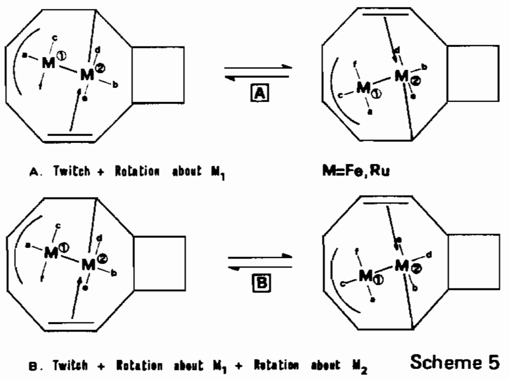


Figure 4. Assignment and comparison of the chemical shifts of the carbonyl groups in *hexahapto*-bicyclo [6.2.0]deca-2,4,6-triene derivatives of carbonyldiruthenium and -diiron derivatives, by ^{13}C NMR spectroscopy in the "frozen" configuration.

the first case in which the twitching process is nearly not contaminated by other processes.

The rapid collapse of the second and fourth signals (from the left) in the spectrum at −30 °C and the singlet coming out at 201.5 ppm on raising the temperature, is that expected for a process which, in addition to the twitching one, involves rotation of the carbonyl groups around one ruthenium atom (Scheme 5). The choice between rotation around Ru(1) or Ru(2) depends on the assignement of the carbonyl signals. Once $CO_{(b)}$ is assigned to the third peak in the spectrum at −90 °C the rotation must occur around Ru(1), *i.e.* the allyl bound metal atom. All the complexes of type B_1 have been shown to behave similarly and the correct assignment of $CO_{(b)}$ at the peak which is sharp during the two processes under discussion is demonstrated by the comparative study carried out by a combination of X-ray structural analysis and variable temperature ^{13}C NMR experiments on $[Fe_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ and $[Fe_2(CO)_5(PEt_3)(\eta^6\text{-}C_{10}H_{12})]$ [9]. Only $CO_{(a)}$ is substituted by the phosphine. The similar behaviour of the two complexes of bicyclo[6.2.0]deca-2,4,6-triene (Fe and Ru) supports our assignment of $CO_{(b)}$. Comparison with the carbonyl peaks of the diiron analog shows in the diruthenium complex a general shift of all the signals toward the right part of the spectrum (Figure 4). This is not surprising if one compares the I.R. spectrum of the two complexes in the carbonyl stretching region*. The shift toward higher frequencies in the ruthenium complex may be an indication of a less strong M–C bond which produces the shift found in the ^{13}C NMR spectra. We also note that the relative shift is more pronounced for the *b* and *a* carbonyl signals. We have no explanation for this point.



Scheme 5

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*The I.R. spectrum of the diruthenium derivative in the carbonyl stretching region shows bands at 2072, 2036, 2008, 1997 and 1980 cm^{-1} [13], the diiron analog shows bands at 2063, 2013, 1992, 1978, and 1961 cm^{-1} [15].

TABLE III. Energies of Activation[a] for the Twitching Process of $[M_2(CO)_6(\eta^6\text{-polyolefin})]$ Complexes.

Complex	T_c°K	^{1}H NMR $(H_2–H_7)$	^{13}C NMR (c, f)	(d, e)	Ref.
$[Fe_2(CO)_6(C_8H_{10})]$	220	10.3^b			
	238		10.9	10.8	
			(11.6)	(11.4)	8
$[Ru_2(CO)_6(C_8H_{10})]$	248	11.3			18
$[Fe_2(CO)_6(C_9H_{10})]$	163	7.4		7.3	
	158		7.2		
	163	(7.4)		(7.3)	
	158		(7.4)		12
	163		(7.9)	(7.8)	9
$[Fe_2(CO)_6(C_{10}H_{12})]$	183	8.3			
	185		8.5	8.3	
	185		(9.0)	(8.8)	9
$[Ru_2(CO)_6(C_{10}H_{12})]$	215	10.0	10.0	9.8	

[a]These values have been obtained from the approximate formula [16] $\Delta G^{\ddagger}_{T_c} = -RT_c \ln \pi h \Delta\nu/\sqrt{2}kT_c$; data in parenthesis have been reported by other formulae. [b]The value is tentative since the spectrum is not well resolved [19].

TABLE IV. Energies of Activation[a] for the Rotation Processes of $[M_2(CO)_6(\eta^6\text{-polyolefin})]$ Complexes

Complex	T_c°K	Rotation about M_1	T_c°K	Rotation about M_2
$[Fe_2(CO)_6(C_8H_{10})]$	238	14.2	298	17.8
	(263)	(12.8)	(373)	(17.9)
$[Fe_2(CO)_6(C_9H_{10})]$	168	10.3	258	15.4
	(208)	(10.1)	(313)	(15.0)
$[Fe_2(CO)_6(C_{10}H_{12})]$	193	11.7	290	17.3
	(218)	(10.6)	(375)	(18.0)
$[Ru_2(CO)_6(C_{10}H_{12})]$	263	15.6	383	23.9

[a]These values have been obtained from the approximate formula [17] $\Delta G^{\ddagger}_{T_c} = RT_c \ln[(k/h\pi)(T_c/\Delta\nu)X/(1 + \Delta P)]$; data in parenthesis have been reported by Cotton *et al.* by other formulae [9].

At about +60 °C the spectrum of the diruthenium derivative consists of three singlets in the ratio 1:2:3, which represents the expected spectrum at the fast exchange limit of the two processes. Apart from the sequence of the signals this three line spectrum was found in all the studies of the ^{13}C NMR of the complexes of type B_1 so far investigated [8, 9, 12].

On raising the temperature the set of two peaks of relative intensity 1:2 starts to collapse whilst the peak of intensity 3 assigned to *a, c, f* carbonyls remains sharp. This last process is attributed to the rotation of the carbonyl groups around Ru(2) which adds to the twitching process and to the roation around Ru(1) (Scheme 5). At 115 °C the two peaks are collapsed. At about 130 °C the new peak corresponding to *b, d, e* carbonyls appear at an intermediate chemical shift. In Table II comparison between calculated chemical shifts (from the signals at –90 °C) and experimental chemical shifts shows an excellent agreement*.

Activation Energies for the Various Processes

A discussion of the activation energies of the processes involved in these fluxional molecules cannot have a general validity, since errors of ±2 Kcal/mol are quite possible. However, the use of the same method of estimation can give a qualitative comparison of the various phenomena, since systematic errors are likely to be cancelled.

On the basis of chemical shift separation between H_2 and H_7 in the ^{1}H NMR spectrum ($\Delta\nu$ = 145 Hz) and the coalescence temperature of the doublet at $\cong$–60 °C, it is possible to calculate [16] the free activation energy for the interconversion of the two enantiomorphs (Scheme 4; Table III). This value (10.0 Kcal/mol) must correlate with that found for the twitching process in the ^{13}C NMR spectra. Assuming that the temperature of coalescence of the *c* and *f* carbonyls is –65 °C, we can calculate it on the basis

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*The chemical shifts in triethylbenzene appear to be affected (see Table II).

of a separation of 145.1 Hz. between *c* and *f*. The same reasoning can be applied to the two peaks *d* and *e*, as shown in Table III. Cotton and Hunter [9] have suggested a relationship between the activation energies and the degree of buckling of the cyclooctatrienyl portion of the polyolefin in each molecule. The order is $[Fe_2(CO)_6(\eta^6\text{-}C_9H_{10})] > [Fe_2(CO)_6(\eta^6\text{-}C_{10}H_{12})] > [Fe_2(CO)_6(\eta^6\text{-}C_8H_{10})]$; in the case of diruthenium complexes the data available cannot give the same information. However, the activation energies calculated for the two complexes studied by ^1H NMR spectroscopy, *i.e.* $[Ru_2(CO)_6(\eta^6\text{-}C_8H_{10})]$ [4] and $[Ru_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$ follow the trend found in the diiron derivatives series.

Comparison with the spectra reported for the diiron analog shows that the two rotation processes also occur at higher temperatures, indicating a larger activation energy for the diruthenium complex. The value of $\Delta G^{\ddagger}$ has been calculated using a formula adapted for processes involving collapse of unequal signals [17] (Table IV). It is also of interest to compare the role of the two metals (Fe and Ru) in terms of activation energies in molecules containing the same polyolefinic ligand. From ^1H NMR data on bicyclo[6.2.0]deca-2,4,6-triene derivatives the activation energy for the interconversion (Scheme 4) of the two enantiomorphs is higher for the diruthenium complex (Table III). Similar results were already found in the other complexes for which a comparison was possible ($[M_2(CO)_6(\eta^6\text{-}C_8H_{10})]$ [18, 19]. This consideration is also substantiated by the ^{13}C NMR data for all the three processes in $[M_2(CO)_6(\eta^6\text{-}C_{10}H_{12})]$. An explanation based on the larger volume and therefore steric hindrance in the ruthenium case might be an oversimplification of the problem; orbital influence and availability are probably more important. The experimental data, however, show that a higher barrier of activation energy is necessary for all the processes involving ruthenium atoms compared with the same complexes of iron. This finding appears of general validity, although further data are probably necessary to support this consideration.

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