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CONFORMATIONAL ISOMERISM IN η^5-CYCLOPENTADIENYL-η^3-ALLYLRUTHENIUM CARBONYL COMPLEXES

DOROTHY H. GIBSON *, WEN-LIANG HSU, ALAN L. STEINMETZ,
Department of Chemistry, University of Louisville, Louisville, Kentucky 40292 (U.S.A.)

and BRYCE V. JOHNSON *
Research and Development, Amoco Chemicals Corporation, Naperville, Illinois 60566 (U.S.A.)

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Summary

Phase transfer catalysis provides a high yield synthetic route to *endo*- and *exo*-η^5-cyclopentadienyl-η^3-allylruthenium carbonyl and the corresponding η^3-2-methallyl derivatives. In both cases, the *endo* isomer thermally isomerizes to the more stable *exo* isomer. Activation parameters for the isomerizations are substantially greater than those for the corresponding iron compounds, but a similar mechanism involving $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformations is implied. Prolonged photolysis of the η^3-allyl or 2-methallyl complexes leads to photostationary states in which the *exo* isomer is predominant.

Introduction

Interconversion of stereoisomeric η^3-allyl-metal complexes is well documented [1]. In the case of η^5-cyclopentadienyl-η^3-allyl-molybdenum and -tungsten dicarbonyl complexes, equilibrium is established between *endo* and *exo* η^3-allyl configurations, as evidenced by NMR spectral studies of the complexes over a broad range of temperatures [2]. The mechanism for *endo-exo* interconversion with these systems is believed to involve pseudorotation of the η^3-allyl group about the allyl—metal bond axis [1]. Studies of η^5-cyclopentadienyl-η^3-allyl-iron carbonyl complexes have been somewhat more difficult to do because of the thermal lability of the *endo* isomers. However, Rosenblum and his coworkers [3] have done an extensive study of the iron complexes and have suggested that the isomerization behavior in these complexes involves $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformations, since *syn* → *anti* conversions take place in the iron complexes but not with their molybdenum and tungsten analogs.

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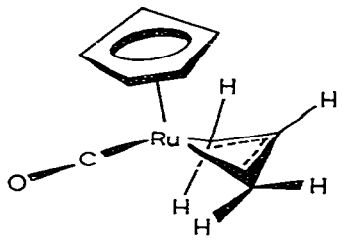
The η^5-cyclopentadienyl-η^3-allylruthenium carbonyl complexes have been less well studied, however, and *endo* isomers have generally been elusive. Previous preparations of η^5-C_5H_5-η^3-C_3H_5RuCO have led predominantly [4], or exclusively [5], to a single conformational isomer which has been assigned [5a] the *exo* configuration shown below:



(Ia, *exo*)

Two synthetic routes have involved photolytic decarbonylation of the η^1-allyl complex as the means of generating η^3-product(s), followed by elution chromatography on alumina; such methods have provided very low product yields [4,5a]. Using phase transfer catalysis (PTC), we have prepared, separated and characterized *exo* and *endo* isomers of both the parent (Ia, Ib) and the 2-methallyl (IIa, IIb) complexes and have determined activation parameters for their thermal isomerizations.

Results and discussion

Synthesis and structural assignments

Treatment of either η^5-cyclopentadienylruthenium dicarbonyl chloride or bromide with the allylic halide (allyl bromide or 2-methallyl chloride) under PTC conditions provides roughly equal amounts of the *endo* and *exo* η^3-allyl products. The combined yields of products, in both cases, approach 90%. Unlike the related iron and molybdenum halides, for which PTC conditions can be varied to provide either η^1 or η^3 product [6], the ruthenium halides yield η^3 complexes as the principal products under all conditions tried thus far (see Experimental).

Although it is stable in CH_2Cl_2 or hexane solutions, *endo* isomer Ib is destroyed on chromatography columns containing florisil or silica gel. This behavior on chromatography, combined with its lability upon photolysis (see discussion below), probably accounts for the predominance of the *exo* isomer in previous preparations. *Endo* and *exo* isomers were, in each case, separated by fractional crystallization from pentane. The physical and spectral properties of the four compounds are summarized in Table 1; with the 2-methyl complexes, also, the more stable isomer is assigned the *exo* configuration (IIa) for the reasons discussed below. The PMR spectra are shown in Figures 1 and 2.

NMR and IR spectral properties

Comparisons of the chemical shift values of the allylruthenium compounds with those of the iron complexes [3] (all in CS_2 solution) provide support for the structural assignments of the ruthenium systems and also show some

TABLE 1

PHYSICAL, PMR AND IR DATA FOR η^5-CYCLOPENTADIENYL-η^3-ALLYLRUTHENIUM COMPLEXES

Compound	Color	Crystalline form	m.p. (°C)	NMR (δ [a])						IR ν(CO) [b]
				C_5H_5	H_c	CH_3	H_s (H_c, H_s) [c]	H_a (H_c, H_a) [c]	N [d] (H_a, H_s) [d]	
endo-η^5-C_5H_5-η^3-C_3H_5RuCO (Ib)	yellow	needles	71—71.5	5.17s [e]	4.08m	—	3.03d (6.3)	1.80d (11.0)	(<1.0)	1937
				5.01s [f]	3.83m	—	2.93d	1.69d		
exo-η^5-C_5H_5-η^3-C_3H_5RuCO (Ia)	pale yellow	needles	52—53	5.04s [e]	4.07m	—	2.92dt (6.9)	1.28dt (10.6)	(2.4)	1958
				4.88s [f]	3.92m	—	2.78m	1.15m		
endo-η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO (IIb)	yellow	plates	65	5.14s [e]	—	1.97s	2.94s	1.90s	(<1.0)	1931
				4.97s [f]	—	1.87s	2.80s	1.78s		
exo-η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO (IIa)	pale yellow	plates	50—50.5	4.95s [e]	—	1.91s	2.99t	1.32t	(2.2)	1956
				4.79s [f]	—	1.87s	2.87m	1.19m		

[a] Chemical shifts are given in ppm downfield from TMS; s = singlet, d = doublet, dt = doublet of triplets, m = multiplet, t = triplet. [b] In hexane solution, in cm^{-1}. [c] Splittings measured directly from NMR spectrum, in Hz. [d] The parameter $N = |J_{as} + J_{as'}|$ is given for the AA'BB' set (corresponding to the separation of outer lines of the apparent triplet) in Hz. [e] In $CDCl_3$ solution. [f] In CS_2 solution.

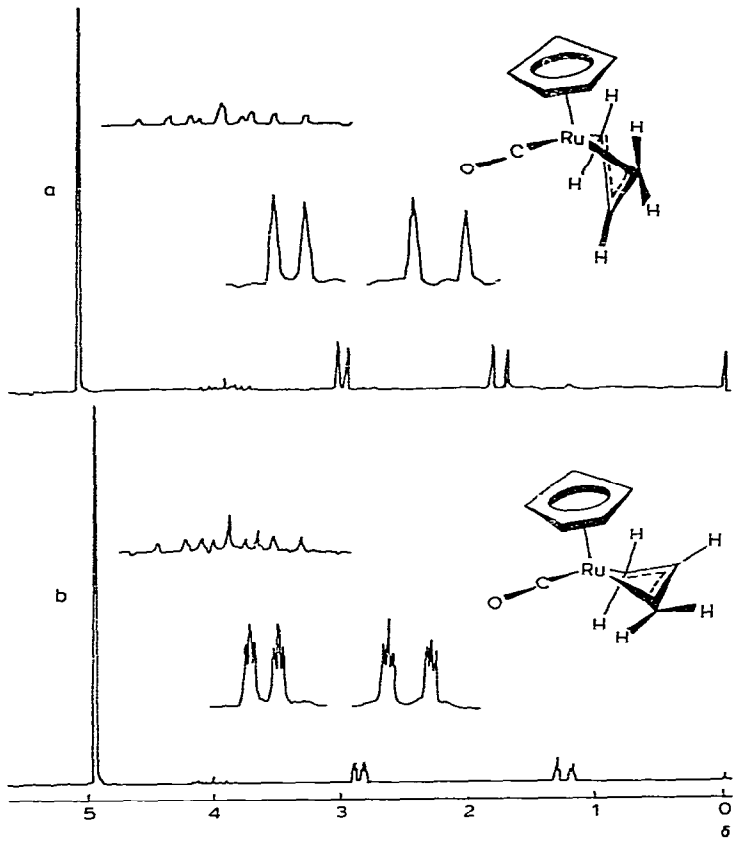


Fig. 1. 90 MHz PMR spectra of (a) *endo*- and (b) *exo*-η^5-C_5H_5-η^3-C_3H_5RuCO in $CDCl_3$ at 20°C.

interesting differences. The cyclopentadienyl resonances of Ia, b and IIa, b are deshielded relative to their iron analogs by about 0.50 ppm; the resonances for H_c and H_s are similarly deshielded (0.06—0.41 ppm). There is a marked difference in deshielding of *anti* hydrogens in the ruthenium systems relative to the iron complexes when *endo* and *exo* isomers are compared; H_a in the *endo* ruthenium complexes are deshielded by about 0.20 ppm, but *anti* protons (H_a) in the *exo* ruthenium complexes appear at about 0.70 ppm to lower field than in the iron complexes. With the complexes of both metals, H_a appears at substantially higher field in the *exo* isomers and the geminal splittings are also greater with these isomers. The difference in shielding of the *anti* protons in the *endo* and *exo* isomers has been attributed to the anisotropy of the cyclopentadienyl ring [2b]. For the unsubstituted allyl complexes, at least, the differences between iron and ruthenium compounds are somewhat greater than those between molybdenum and tungsten complexes.

As can be seen from the summary of ^{13}C NMR data in Table 2, there is a marked difference (15.5—21.0 ppm) in the shielding of the central carbon atoms of the η^3-allyl ligands in the ruthenium complexes with C_2 in the *endo* isomers being strongly deshielded. A difference of this magnitude (18.3 ppm) has also been seen with the related η^3-allylmolybdenum complexes studied by

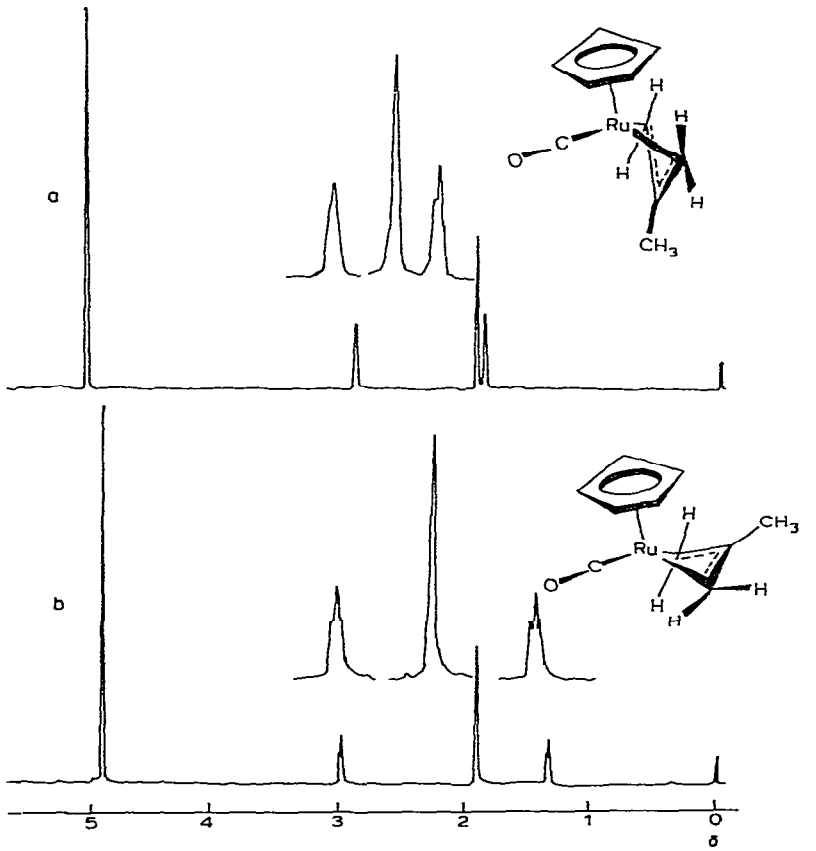


Fig. 2. 90 MHz PMR spectra of (a) *endo*- and (b) *exo*-η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO in $CDCl_3$ at 20°C.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS [a] OF η^5-CYCLOPENTADIENYL-η^3-ALLYL-RUTHENIUM COMPLEXES

Compound	C(1)	C(2)	C_5H_5	CO	CH_3
Ia	30.9	67.7	81.4	207.8	—
	(153.0)	(157.3)	(176.5)		
Ib	32.0	88.7	83.5	202.0	—
	(155.9)	(160.3)	(178.0)		
IIa	33.4)	89.6	82.9	207.8	27.1
	(157.4)		(176.6)		(126.5)
IIb	34.0	105.1	83.7	203.2	25.3
	(154.8)		(178.0)		(125.0)

[a] Determined in benzene-d_6 at 20°C relative to internal TMS in ppm, coupling constants are in brackets in Hz.

Faller [2b]; again, strong deshielding of C_2 is observed. It now appears that the relative chemical shifts of C_2 may be useful in establishing the *exo* or *endo* nature of the allyl ligands in this series of compounds.

As with the corresponding iron complexes, it is the *endo* ruthenium isomer in each case which exhibits the lower frequency IR carbonyl band; the values are closely analogous to the related iron complexes.

Thermal isomerizations

Prolonged heating of the *endo* ruthenium isomers (or mixtures containing *endo* and *exo*) leads to a product mixture containing less than 2% of the *endo* isomer rather than an equilibrium mixture containing comparable amounts of the two conformers, as is observed with the cyclopentadienyl-molybdenum and -tungsten complexes [2b]. This behavior thus parallels that of the iron complexes studied by Rosenblum [3]. The rates of isomerization of the *endo* isomers were determined by measuring the change in the integrated cyclopentadienyl resonances (in the PMR spectrum) against time when samples of the complexes were heated in nitrobenzene-d_5; kinetic data are reported in Table 3. It was not possible to do the kinetic runs in $CDCl_3$ as Rosenblum did with the iron complexes since the ruthenium compounds are much less labile. Both of the iron compounds have $\Delta G^{\neq}$ values of approximately 24 kcal/mol whereas the allylruthenium complex has $\Delta G^{\neq} = 28.9 \pm 0.6$ and the 2-methyl derivative has $\Delta G^{\neq} = 31.4 \pm 1.6$ kcal/mol (see Table 3).

Photochemical isomerizations

Rosenblum [3] has determined that the η^3-2-methallyliron complexes are photochemically labile; mixtures initially enriched in the *exo* isomer yield product mixtures in which the amount of *endo* isomer has been greatly increased. Photochemical equilibrium is attained eventually and when photolysis is carried out at 300 or 254 nm, the *endo* isomer predominates at equilibrium. Whether the η^3-allyliron complexes can also be isomerized photochemically is not clear; the *endo*—*exo* isomer distribution does not change during the photochemical preparation of these complexes from the corresponding η^1-allyl compound and the complexes were apparently not studied further.

All four of the η^3-allylruthenium complexes show UV absorption maxima

TABLE 3

RATES OF THERMAL ISOMERIZATIONS [a] OF Ib and IIb

Compound	Temp. (°C)	$k \times 10^4$ (sec^{-1})	$t_{1/2}$ (min)
endo-C_5H_5-C_3H_5RuCO (Ib)	119.5	5.60 ± 0.08	20.6
	113.0	3.48 ± 0.25	33.2
	103.0	1.23 ± 0.04	94.0
$\Delta G^{\neq} = 28.9 \pm 0.6$ kcal/mol, $\Delta H^{\neq} = 26.5 \pm 0.6$ kcal/mol, $\Delta S^{\neq} = -6.5 \pm 1.5$ e.u.			
endo-C_5H_5-2-CH_3-C_3H_4RuCO	140.5	2.39 ± 0.23	48.4
(IIb)	134.0	1.20 ± 0.06	96.1
	129.5	0.72 ± 0.02	159.8
$\Delta G^{\neq} = 31.4 \pm 1.6$ kcal/mol, $\Delta H^{\neq} = 34.6 \pm 1.6$ kcal/mol, $\Delta S^{\neq} = 7.9 \pm 2.3$ e.u.			

[a] Determined in nitrobenzene-d_5.

TABLE 4

STEREOISOMER PRODUCT RATIO FROM PHOTOLYSIS OF η^3-ALLYLRUTHENIUM COMPLEXES

Complex (*endo*/*exo*), solvent	Irradiation time (h)	Product ratio [a] (*endo*/*exo*)
Ib/Ia (31/69), benzene-d_6	1.0	22/78
	2.5	10/90 [b]
Ib/Ia (79/21), benzene-d_6	1.0	49/51
	2.0	26/74
	6.0	10/90 [b]
Ib/Ia (56/44), cyclohexane-d_{12}	2.0	30/70
	6.0	13/87
	11.0	3/97 [b]
IIb/IIa (78/22), benzene-d_6	2.0	59/41
	4.0	48/52
	8.0	34/66 [b]
IIb/IIa (81/19), cyclohexane-d_{12}	4.0	51/49
	10.0	35/65
	22.0	22/78 [b]

[a] Determined from PMR spectra. [b] Apparent equilibrium ratio.

at about 220 nm; the *endo* isomers also show a less intense absorption band at about 316 nm whereas the *exo* isomers exhibit a shoulder at about 280 nm. UV photolysis of mixtures containing both *endo* and *exo* η^3-allyl or η^3-2-methallyl complexes lead to photostationary states in which the *exo* isomer strongly predominates (see Table 4). The parent allyl complexes establish equilibrium at a much faster rate than the 2-methyl compounds, and Ia is more strongly favored at equilibrium than IIa. The lability of Ib under photolysis is probably the major reason for the previous difficulties in isolating this isomer. The predominance of IIa at photochemical equilibrium contrasts sharply with the results obtained for the corresponding iron compound where photolyses conducted in petroleum ether solution led to mixtures in which the concentration of the *endo* isomer had become predominant (300 or 254 nm) or was greatly enriched (350 nm).

Mechanism

The compounds we have examined do not allow an unambiguous determination of the isomerization mechanism, but the pattern of behavior in the case of the thermal isomerizations is clearly analogous to the corresponding iron compounds and not to those of molybdenum and tungsten. Dissimilarities observed in these two systems have been discussed previously within the context of pseudorotation (Mo, W) [2a] vs. η^3—η^1—η^3 interconversion (Fe) [3]. The two mechanisms can be distinguished by their effect on protons or other substituents in the *syn* or *anti* allyl positions. While these positions retain their identity during the course of rotation or pseudorotation, they become interchanged when the allyl reverts to a σ-bonded intermediate during η^3—η^1—η^3 interconversion.

A convincing method for assigning allyl isomerization mechanisms has been developed by Faller through the use of spin saturation transfer (SST) [7]. Studies of the molybdenum system show that for η^5-C_5H_5-η^3-2-CH_3-$C_3H_4Mo(CO)_2$, conformer interconversion occurs by pseudorotation since spin saturation of

the *anti* proton absorption in one isomer is transferred only to the *anti* proton of the other conformer of the pair [7]. On the other hand, in the asymmetric electronic environment found in η^5-$C_5H_5(\eta^3$-$C_3H_5)Mo(I)(NO)$ [8], η^3—η^1—η^3 conversion occurs, since spin saturation is transferred from *anti* protons of one isomer to both *syn* and *anti* protons of the other isomer.

Although SST experiments were not reported for the iron complexes studied by Rosenblum, *anti*—*syn* isomerizations were observed in the 1-substituted systems. However, the activation energies for that process were clearly higher than those required for *endo* → *exo* conversion. Since proof of a η^3—η^1—η^3 process requires simultaneous *anti*—*syn* and *endo*—*exo* isomerization, the observation that *anti*—*syn* exchange (which must involve the more hindered intermediate 1-substituted η^1 complex) takes place at a slower rate does not clarify the mechanistic choice in these compounds.

The ruthenium systems we have studied do not bear substituents at the 1 position so *anti*—*syn* exchange was not directly observable. Application of the spin saturation transfer method to the system was considered and familiarity with the technique was gained by successfully performing a SST experiment on the parent η^3-allylmolybdenum complexes in the manner that Faller treated the corresponding η^3-2-methallyl derivative (see Experimental). However. for the Ru compounds, a comparison of the maximum *endo* → *exo* isomerization rate ($k = 5.6 \times 10^{-4}$ sec^{-1} at 120°C) and the T_1 values determined for *syn* and *anti* protons (2.78 sec) indicated that measurable magnetization transfer was unlikely (intensity changes upon saturation are proportional to $\tau_A/\tau_A + T_1$ where τ_A is the reciprocal of the first order rate constant for leaving the site [9]). This was confirmed by saturation experiments at 125°C in which irradiation of protons in either isomer failed to produce any detectable spin transfer. The ruthenium compounds also differ from allyl systems exhibiting SST in that the isomerization is best described as *endo* → *exo* conversion rather than attainment of a dynamic equilibrium; The conversion is thermally irreversible, leaving no spectroscopically detectable *endo* population. Increasing the temperature to obtain a rate sufficient for magnetization transfer would be impractical since *endo* → *exo* conversion would be very rapid.

Attempts to distinguish Group VI and Group VIII behavior based on simplified molecular orbital diagrams appear to be inconclusive. A simple rotational mechanism in the Group VI compounds has been discounted by Hoffman, et al., [10] whose careful examination of orbital interactions accompanying such rotation reveals a significant loss of favorable orbital interaction. Diagrams of the Group VIII cyclopentadienyl system that show a reduction in metal—allyl bonding in the intermediate [3] apply equally as well to the η^3-$C_3H_5Fe(CO)_3I$ system in which a rotation (or pseudorotation) has been demonstrated by SST [9].

Although definitive mechanistic evidence is lacking for both iron and ruthenium systems, the η^3—η^1—η^3 pathway suggested by Rosenblum appears to us to be the most reasonable particularly in view of the high activation energies of the ruthenium complexes. *Endo* → *exo* isomerization of the 2-methallyl-ruthenium compound, for example, requires nearly 15 kcal more energy than interconversion of the corresponding molybdenum complex. This increase, occurring in spite of the reduction in steric interaction resulting from the

decrease in coordination number, argues strongly for a difference in mechanism in the two systems.

Comparisons of activation energy changes resulting from Fe → Ru or Mo → W substitution are also worth noting. The Group VI system, in which a low energy rotation or pseudorotation path is available is characterised by nearly identical free energy barriers for analogous molybdenum or tungsten complexes. However, we believe the 5—7 kcal/mole increases over iron activation energies that occur in ruthenium allyls conform more appropriately to an η^3—η^1—η^3 mechanism (based on a bonding reduction and hence on relative *d* orbital energy levels) rather than to one typically dominated by steric factors (a rotation/pseudorotation mechanism).

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen. Hexane, allyl bromide and 2-methallyl chloride were distilled before use; dichloro methane, reagent grade, was used directly. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl under nitrogen. Sodium cyclopentadienide (in THF; Alfa), ruthenium trichloride hydrate (Matthey-Bishop), chlorine gas (Matheson) and benzyltriethylammonium chloride (Aldrich) were used as received without further purifications. η^5-$C_5H_5Ru(CO)_2I$ was prepared as described previously [11].

NMR spectra were obtained using a Bruker WH90-DS spectrometer with a B-ST 100/700 Variable temperature accessary. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotomer and calibrated against DCl. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The elementary analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

$[Ru(CO)_3Cl_2]_2$ *

$RuCl_3 \cdot nH_2O$, 35.0 g (42.1% Ru), was dissolved in 350 ml of 90% formic acid and 265 ml concentrated hydrochloric acid. The solution was then refluxed for 2 days after which it was bright yellow in color. Removal of solvents, in vacuo, afforded the crude product (yellow) which was used directly in the preparation of the cyclopentadienyl dimer described below.

$[\eta^5$-C_5H_5-$Ru(CO)_2]_2$ **

The ruthenium chlorocarbonyl dimer, 38.5 g (0.08 mol) was dissolved in 500 ml of freshly dried and distilled THF and placed in a 1 l three necked flask. Sodium cyclopentadienide (1/2 mol in THF) was then added dropwise during $2\frac{1}{2}$ hours. The solution, now deep orange in color, was refluxed overnight. The resulting bright yellow-orange solution was then concentrated on a rotary evaporator. The orange residue was triturated repeatedly with benzene and the combined benzene extracts (ca. 3 l) were filtered through celite; the

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* This procedure represents a modification of a literature method [12].

** This procedure represents a modification of the method given in ref. 13.

filtrate was then concentrated on a rotary evaporator. The residue was then slurried with cold petroleum ether and the product collected by filtration. Yields of crude product were typically 17—29 g (53—71% based on the ruthenium chloride hydrate).

η^5-C_5H_5-Ru(CO)$_2$X (X = Cl, Br)

These compounds were prepared by slightly modified literature procedures [11]. An equimolar amount of chlorine (0.48 g), or bromine (1.08 g), dissolved in 180 ml of solvent (CCl_4 for the chlorine reaction, CH_2Cl_2 for the bromine reaction) was added dropwise to a stirred solution of $[\eta^5\text{-}C_5H_5\text{-}Ru(CO)_2]_2$ (3.0 g, 0.675 mmol) in 180 ml of dichloromethane at 0°C. The resultant solution was stirred for another 30 min and then filtered; solvent was removed from the filtrate on a rotary evaporator at reduced pressure. The brownish yellow residue was purified by column chromatography on florisil (Fisher F-100) with CH_2Cl_2/hexane (1 : 1 V/V). Yield and m.p. for $\eta^5\text{-}C_5H_5Ru(CO)_2Cl$: 2.93 g (85%), 101—101.5°C and $\eta^5\text{-}C_5H_5Ru(CO)_2Br$: 3.67 g (90%), 88.5—88.8°C.

η^5-C_5H_5-η^3-C_3H_5RuCO (mixture of isomers)

(a) Synthesis from η^5-C_5H_5-Ru(CO)$_2$Br. Benzyltriethylammonium chloride, 3.42 g (15 mmol) dissolved in 100 ml of 5 *N* NaOH was added rapidly to a mechanically stirred solution containing 1.31 ml (15 mmol) of allyl bromide and 1.51 g (5 mmol) of $\eta^5\text{-}C_5H_5Ru(CO)_2Br$ in 100 ml of CH_2Cl_2. After reaction was complete (15 min as evidenced by disappearance of the ν(CO) bands of the ruthenium bromide complex), the dichloromethane layer was separated and the solvent was removed on a rotary evaporator at reduced pressure to leave a brownish-yellow residue. Trituration of the residue with three 50 ml portions of hexane (extraction of the CH_2Cl_2 solution with water in the usual way [6] leads to destruction of the *endo* isomer); the combined extracts were dried (over $MgSO_4$), filtered and the solvent was removed from the filtrate on a rotary evaporator to give a yellow solid which consisted of a 50 : 50 mixture of *endo*- and *exo*-η^5-C_5H_5-η^3-C_3H_5RuCO. The mixture was further purified by sublimation at 0.1 mm/40°C (1.05 g, 89%).

(b) Comparison of the reactivities of chloro-, bromo- and iodo-η^5-cyclopentadienyl ruthenium dicarbonyl. When 0.5 eq of benzyltriethylammonium chloride (to 1 eq of $\eta^5\text{-}C_5H_5Ru(CO)_2Br$) was used, reaction was complete in 1 hour and gave a 50 : 50 mixture of *endo* and *exo* isomers. In the same manner, the corresponding chloro and iodo compounds required 30 min and 90 min, respectively, for completion of the reaction; the chloride provided an 80% yield of *endo* and *exo* (50 : 50) isomers, but the iodide provided a 20 : 80 mixture of *endo* and *exo* isomers (yield not determined).

η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO (mixture of isomers)

This compound was prepared using procedure (a) described above for the η^3-allyl isomers except that 2-methallyl chloride was substituted for allyl bromide. A yellow solid which consisted of a 50 : 50 mixture of *endo* and *exo* isomers was obtained in 90% yield after 10 min reaction time.

Reducing the amount of phase transfer catalyst (while keeping the rest, including work-up procedures, constant) changed both reaction time and yield.

Thus, when 0.5 eq of benzyltriethylammonium chloride (to 1 eq of η^5-$C_5H_5Ru(CO)_2Br$) was used, reaction was complete in 30 min and gave a 50 : 50 mixture of *endo* and *exo* isomers; the combined yield was 85%. Under the same conditions, η^5-$C_5H_5Ru(CO)_2Cl$ also gave a 50 : 50 mixture of isomers after 20 min and the combined yield was 84%.

Attempted preparations of η^5-C_5H_5-η^1-2-CH_3-$C_3H_4Ru(CO)_2$

Reactions of η^5-$C_5H_5Ru(CO)_2X$ (X = Cl, Br) with 2-methallyl chloride under PTC conditions which had provided the η^1-allyl iron and molybdenum complexes [6], gave only the η^3-2-methallylruthenium complexes. However, when benzyltriethylammonium chloride, 0.342 g (1.5 mmol) dissolved in 10 ml of 0.5 *N* NaOH (5 mmol) was added rapidly to a mechanically stirred solution containing 0.15 ml (1.5 mmol) of 2-methallyl chloride and 0.129 g (0.5 mmol) of η^5-$C_5H_5Ru(CO)_2Cl$ in 10 ml of CH_2Cl_2, the reaction mixture showed (IR) the presence of additional compounds. After η^5-$C_5H_5Ru(CO)_2Cl$ was completely consumed (30 min), the reaction mixture was worked up in the manner described above for η^5-C_5H_5-η^3-C_3H_5RuCO, procedure (a), to leave a brownish-yellow oily residue which appeared to consist of a mixture containing 25% of η^5-C_5H_5-η^1-2-CH_3-$C_3H_4Ru(CO)_2$ [ν(CO) (hexane) 2020s, 1963vs cm^{-1}] *, 10% of $[\eta^5$-$C_5H_5Ru(CO)_2]_2$, 34% of *exo*- and 31% of *endo*-η^5-C_5H_5-η^5-2-CH_3-C_3H_4-RuCO as estimated from the IR spectrum. The η^1-complex was not isolated.

In the same manner, when 1 eq of benzyltriethylammonium chloride (to 1 eq of η^5-$C_5H_5Ru(CO)_2Cl$) was used, the reaction required 1 hour to go to completion but the distribution of products remained unchanged.

Separation and characterization of the endo and exo isomers

Endo isomers of both allyl- and 2-methylallylruthenium complexes decomposed on fluorisil (Fisher F-100) and silica gel (MCB grade 12) columns. Sublimation at 0.1 mmHg and 25—45°C lead to incomplete separation. The separation of *endo* and *exo* isomers in both cases was achieved by repeated crystallization (via triangulation [14]) at —20°C from pentane. The spectral properties of all four compounds are listed in Table 1. All these compounds are soluble in organic solvents and stable in air at room temperature for several days.

η^5-C_6H_5-η^3-C_3H_5RuCO

exo isomer (Ia): m.p. 52—53°C (lit. 44—45°C [4], 45°C [5a], 50°C [5b]. The spectral properties of this isomer are identical to those reported previously.

endo isomer (Ib): m.p. 71—71.5°C. Analysis. Found: C, 45.72; H, 4.36; O, 6.70. Calcd for $C_9H_{10}ORu$: C, 45.95; H, 4.28; O, 6.80%.

η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO

exo isomer (IIa): m.p. 50—50.5°C. Analysis. Found: C, 48.08; H, 4.75; O, 6.33. Calcd: for $C_{10}H_{12}ORu$ C, 48.18; H, 4.85; O, 6.42%.

endo isomer (IIb): m.p. 65°C. Analysis. Found: C, 48.14; H, 4.94; O, 6.07. Calcd: C, 48.18; H, 4.85; O, 6.42%.

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* η^5-C_5H_5-η^1-$C_3H_5Ru(CO)_2$ has ν(CO) (cyclohexane) 2015vs, 1970vs cm^{-1}; see ref. 4.

Thermal isomerizations

(a) Attempted isomerization of η^5-C_5H_5-η^3-C_3H_5RuCO. A 45 : 55 mixture of *endo* and *exo* isomers was refluxed in $CHCl_3$ for 3 hours. Infrared spectra indicated no evidence of isomerisation.

(b) Attempted isomerizations of η^5-C_5H_5-η^3-2-CH_3-C_3H_4RuCO. a 42 : 58 mixture of *endo* and *exo* isomers was dissolved in CH_3CN and half of this solution was left standing at room temperature for 7 days and the other half was heating at 50°C for 5 days. Infrared spectra showed no isomerization in either case; however, the sample which had been heated showed some decomposition of the 2-methyl complexes as evidenced by darking of the solution and formation of a solid residue. On the other hand, a mixture having the same ratio of *endo* and *exo* isomers (42 : 58) gave a 20 : 80 mixture of *endo* and *exo* isomers after refluxing in octane (b.p. 125°C) for 21 hours and the same mixture gave a 12 : 88 mixture of *endo* and *exo* isomers after heating in decalin at 140°C for 4 hours.

(c) Kinetic measurements from isomerizations in nitrobenzene-d_5. Solutions for kinetic studies were prepared at a concentration of 0.15 *M* in the ruthenium complexes (pure *endo* or a mixture of *endo* and *exo* isomers) and 0.03 *M* in *p*-dichlorobenzene in nitrobenzene-d_5; The NMR samples were then degassed (three freeze-pump-thaw cycles) and sealed in vacuo and then placed in the NMR probe held at the desired temperature (determined from ethylene glycol calibration). Spectra were recorded at appropriate intervals with changes in concentration being obtained by integrating PMR cyclopentadienyl signals of *endo* and *exo* isomers along with the internal reference signal of *p*-dichlorobenzene. The cyclopentadienyl signals in both isomers were sufficiently far apart to allow accurate integrations and the total integration of the mixture of *endo* and *exo* isomers remained constant. Rate constants, k, were obtained from the slope of ln a_0/a_t [where a_0 was initial concentration and a_t was the concentration after time interval t (in min)] versus time plots. Enthalpies of activation, $\Delta H^{\neq}$, were obtained from the equation $\Delta H^{\neq} = E_a - RT$; E_a was obtained by multiplying the slope of the plots of log k against $1/T$ by $-2.303R$ [where R = 1.987 cal deg^{-1} mol^{-1} and T was the middle temperature (in °K)] in the kinetic studies. $\Delta S^{\neq}$ was obtained from the frequency factor, A, the antilogarithm of the intercepts of the plots of log k versus $1/T$, according to the equation [15]

$$\Delta S^{\neq} = R \ln\left(A\frac{N_A h}{eRT}\right)$$

where N_A is Avogadro's constant, h is Planck's constant, and T is the middle temperature from the kinetic studies (in K). Finally, the free energies of activation, $\Delta G^{\neq}$, were obtained from the equation $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ where T again is the middle temperature from the kinetic studies. These slopes and intercepts were determined using the least squares program on a Texas Instruments Model TI-55 calculator. Results are given in Table 3.

Upon standing in nitrobenzene-d_5 at elevated temperature, the solutions slowly darkened; however, there was no solid residue formed and hence no loss of resolution due to paramagnetic broading occurred. Also, the total

integration of cyclopentadienyl protons for the *endo* and *exo* isomers in each case remained constant relative to the internal standard, *p*-dichlorobenzene.

UV spectra and photochemical isomerizations of η^3-allylruthenium complexes

Samples of the complexes dissolved in benzene-d_6 or cyclohexane-d_{12} were placed in thin-wall NMR tubes, and degassed and sealed, in vacuo, as described above. Photolyses employed an Ace-Hanovia 450 W medium pressure quartz mercury-vapor lamp which was cooled by circulating water through a quartz immersion well; the lamp was placed 6 inches from the NMR tubes. The average temperature of the sample in the NMR tube was about 35° C due to the heat produced by the lamp (thermal isomerization of the compounds does not occur under these conditions). The *endo* : *exo* isomer ratios in the starting mixtures and products after irradiation were determined by integrating the cyclopentadienyl resonances (PMR) for *endo* and *exo* isomers at appropriate intervals. Photolysis was stopped when photoequilibrium (i.e. the ratio of isomers remained unchanged) had been reached. Results of these experiments are given in Table 4.

The UV spectra of the complexes were obtained in hexane solution on a Perkin-Elmer Model 571 UV-visible spectrophotometer.

SST experiments

η^5-Cyclopentadienyl-η^3-allylmolybdenum complexes. The decoupler power was 1×10^{-5} W; irradiation for 15 seconds was followed by a 0.1 second delay, then a 90° pulse was applied which was then followed by accumulation of the FID (in the gated decoupling mode). The *anti* proton of the *exo* isomer (at δ 0.89 ppm) was irradiated, causing near collapse of the doublet centered at δ 1.78 ppm (H_a of the *endo* isomer). In the same way irradiating the *endo* isomer (at δ 1.78 ppm) reduced greatly the intensity of H_a of the *exo* isomer. The experiment was performed at 7°C (calibrated against methanol).

η^5-Cyclopentadienyl-η^3-allyl ruthenium complexes. The irradiation time varied between 10 and 20 seconds followed by a delays of either 0.05 or 0.1 second. The decoupler power was varied between 2×10^{-6} and 3×10^{-5} W. When the *anti* proton of the *exo* isomer (at δ 1.38 ppm) was irradiated, no spin saturation had been transferred to either the *anti* proton or the *syn* proton of the *endo* isomer. In the same manner, after irradiating the *anti* proton of the *endo* isomer (at δ 1.99 ppm), no saturation transfer occurred at either the *anti* proton or *syn* proton of the *exo* isomer. There experiments were performed at 125°C in nitrobenzene-d_5.

The relaxation times, T_1, for the *syn* and *anti* protons of both *endo* and *exo* isomers of η^5-C_5H_5-η^3-C_3H_5RuCO in nitrobenzene-d_5 were measured at 20°C by the 180°—τ—90° inversion recovery method. The delay times (τ) ranged from 0.05 to 8 seconds and a 90° pulse (with 15.2 pulse width) was used. The T_1's were obtained from the negative inverse of the slopes of the plots in $\ln\left(1 - \frac{A}{A_0}\right)$ against τ, where A = the measured intensity of the peak for a given τ and A_0 = the intensity of the peak for $\tau >> T_1$. The *syn* and *anti* protons of both isomers have the same relaxation time of 2.78 seconds at 20°C in nitrobenzene-d_5.

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