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DYNAMIC PROCESSES IN AN OCTANO-BRIDGED 3-OXAQUADRICYCLANE AND A FREE AND RHODIUM-COMPLEXED 7-OXANORBORNADIENE

H. HOGEVEEN * and B.J. NUSSE

Department of Organic Chemistry, The University, Nijenborgh, 9747 AG Groningen (The Netherlands)

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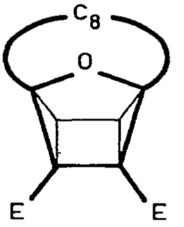
Summary

The octamethylene chains in [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane and in [8](1,4)-7-oxanorbornadiene both undergo two dynamic processes, which have been identified by NMR spectroscopy. The slower process involves a swinging of the octano bridge over the ether-oxygen atom, the faster one a conformational change within the octano bridge. The octamethylene chains in di-[8](1,4)-7-oxanorbornadienerhodium chloride show the same processes. In addition, two other processes are observed in this complex: a degenerate one, involving a rotation of the 7-oxanorbornadiene ligands around the rhodium—oxygen axes, and a non-degenerate one, involving an exchange of free and coordinated 7-oxanorbornadiene.

Introduction

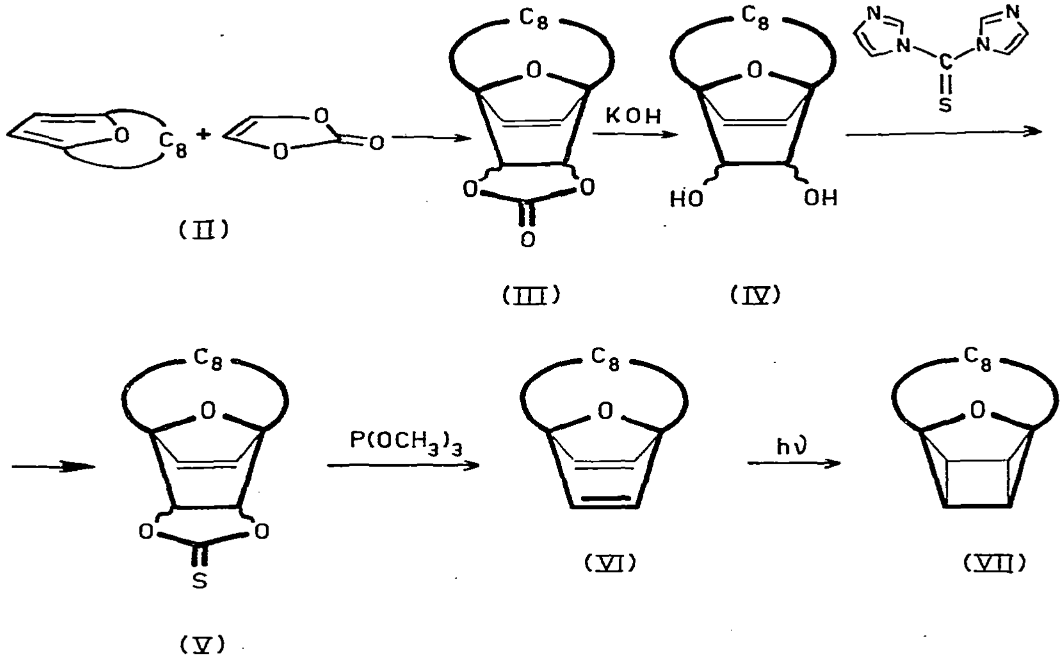
We have recently become interested in transition metal catalyzed reactions of quadricyclanes [1] and 3-oxaquadricyclanes [2]. The reactions of 3-oxaquadricyclanes are of special interest because of the presence in the molecule of two different reaction sites, a cyclopropyl ring and an ether-oxygen atom. It has been found that the presence of the octamethylene chain in [8](2,4)-1,5-



(I)

$E = CO_2CH_3$

SCHEME 1



dicarbomethoxy-3-oxaquadricyclane (I) markedly affects both the thermal stability of I and the course of transition metal catalysed reactions of I when compared with those of 1,5-dicarbomethoxy-2,4-dimethyl-3-oxaquadricyclane [2]. In order to provide insight into these effects, the structure of compound I was determined by X-ray analysis [3]. Special attention was paid to the spatial relationship between the octamethylene chain and the ether-oxygen atom, as well as to the detailed conformation in the octamethylene chain [3]. A preliminary communication has dealt with the conformational mobility of the octamethylene chain of I in solution [4] *.

In order to reduce the number of possible sites of attack of the catalyst on 1,5-dicarbomethoxy substituted 3-oxaquadricyclanes [2], the compounds without the ester substituents were needed, and so [8](2,4)-3-oxaquadricyclane (VII) was prepared, as in Scheme 1 **.

The tetracoordinated rhodium complex X was then prepared from [8](1,4)-7-oxanorbornadiene (VI) according to literature procedures [9,10] (Scheme 2). The interest in complex X arises from its possible use as a catalyst in the isomerization of 3-oxaquadricyclanes and/or 7-oxanorbornadienes [11]. However, during the initial attempts to synthesize complex X it was observed that another complex, to which the pentacoordinated structure XI was assigned, is also formed if a small excess (10%) of 7-oxanorbornadiene (VI) is used. Complex XI

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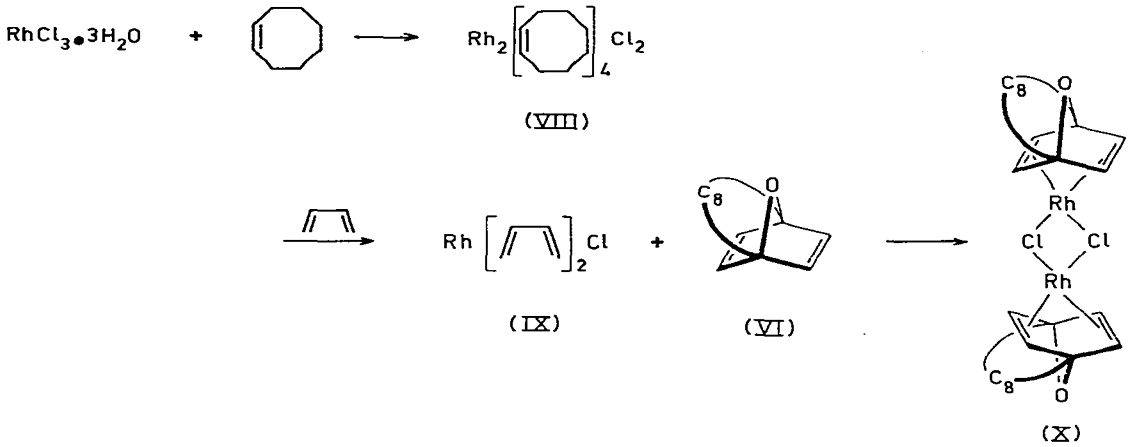
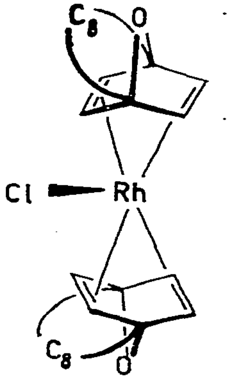
* Similarly, the behaviour of the polymethylene chain has been studied in [8](2,5)-furanophane [5], [8](1,4)-2,3-dicyano-7-oxanorbornadiene [6] and [*n*](1,3)-cyclophanes [7].

** This route is based upon that described in ref. 8 for the synthesis of unsubstituted 3-oxaquadricyclane.

SCHEME 2



is formed quantitatively with instantaneous evolution of CO on adding 5 mol% of $Rh_2(CO)_4Cl_2$ to a solution of VI in chloroform *. The formation of XI results from an exchange between free (VI) and complexed 7-oxanorbornadiene (X). Such a ligand exchange between free and complexed norbornadiene has been previously described [12] (Scheme 3); however, in the analogous complex of 2,3-dicarbomethoxy-1,4-dimethyl-7-oxanorbornadiene such a ligand exchange has not been observed [10].



(XI)

We describe below the characteristics of four dynamic processes which have been studied by NMR spectroscopic techniques: the swinging of the octamethylene chain and the conformational change in it (compounds I, VI and XI), the exchange of VI and the rotation of the ligands (VI) around the rhodium—oxygen axes in complex XI. Some results from the X-ray analysis of 3-oxaquadricyclane (I) [3] are also included to permit a detailed explanation to be offered for the dynamic processes undergone by compound I.

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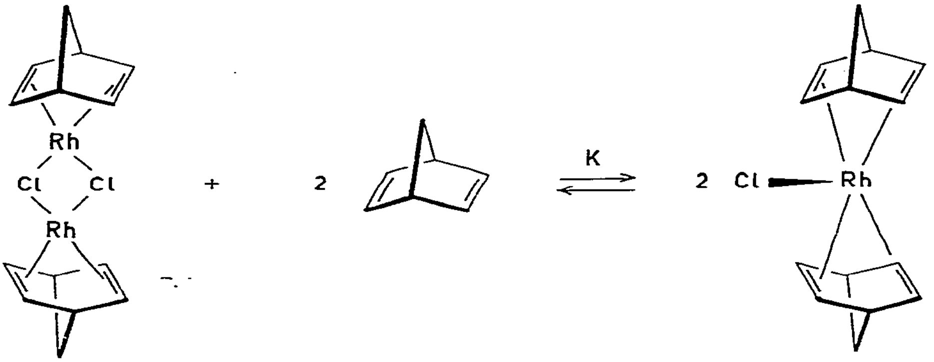
* The excess of VI slowly disappears (over 24 h at room temperature) and is converted into an unstable unidentified compound.

SCHEME 3



Results and discussion

A. Conformation of [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane in the solid state

In the crystalline state compound I consists of two conformers (A and B in Fig. 1) which are arranged alternately *. A side view of the octamethylene chain of conformer B is depicted in Fig. 2, in which some of the C—H···O distances (in Å) are given, the hydrogen atoms being located on calculated positions. The fact that the *syn*-conformer (B) and the *anti*-conformer (A) of 3-oxaquadricyclane (I) occur in equal amounts indicates that there is no significant steric interaction between the two ester groups and the octamethylene chain in B, in agreement with the representation of B in Fig. 1 **. When a Dreiding model of compound I, incorporating the data of Fig. 2, is inspected it reveals that the ether-oxygen atom at the top of the molecule is completely shielded on one side. This indicates that the transition metal catalyzed reactions of I at this oxygen atom will be sterically hindered, and this agrees with the observed relatively low rates for I in these reactions [2]. The explanation that a transannular effect in the eleven-membered ring, formed by the rigid C—O—C fragment and the octamethylene chain is responsible for the relatively fast thermal decomposition of I as compared with the dimethyl derivative [2] is consistent with the data of Fig. 2. The distances between three hydrogen atoms and the ether-oxygen atom are 2.33, 2.35 and 2.38 Å, respectively. These distances are smaller than the sum of the Van der Waals radii of hydrogen and oxygen (1.2 and 1.40 Å, respectively [13]), and so this situation is energetically unfavourable.

B. Dynamic processes

1. [8](2,4)-1,5-Dicarbomethoxy-3-oxaquadricyclane (I). At +35°C the ^{1}H NMR spectrum of I (0.6 M in CS_2) consists of two singlets at δ 3.66 (6 H) and 2.55 ppm (2 H) due to the ester hydrogen atoms and the tertiary hydrogen

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* The question of whether all ester groups, or all octamethylene chains, are arranged on the same side in the crystal has not been investigated [3].

** The distances between the ester group and the octamethylene chain have not been calculated [3].

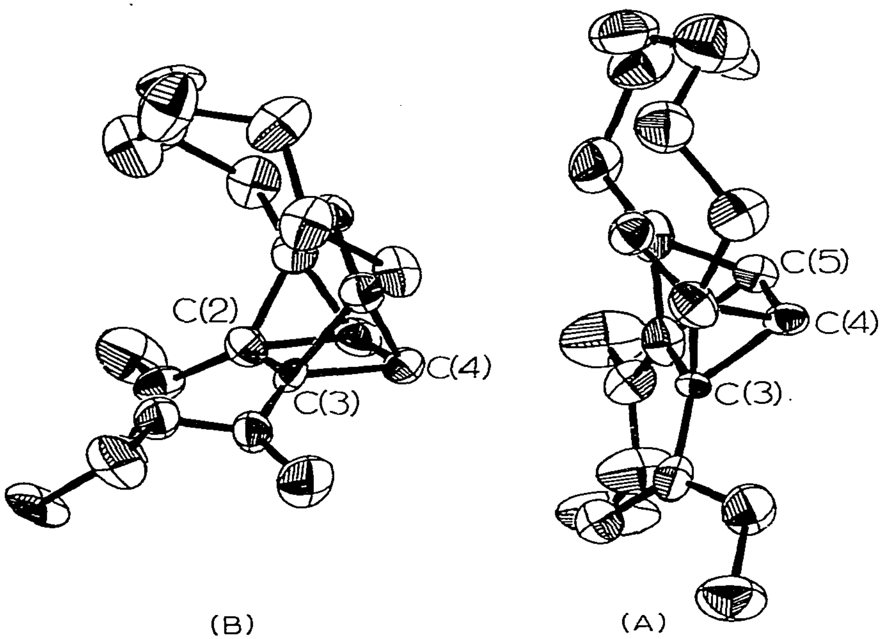

Fig. 1. Two conformers of I in the crystalline state.

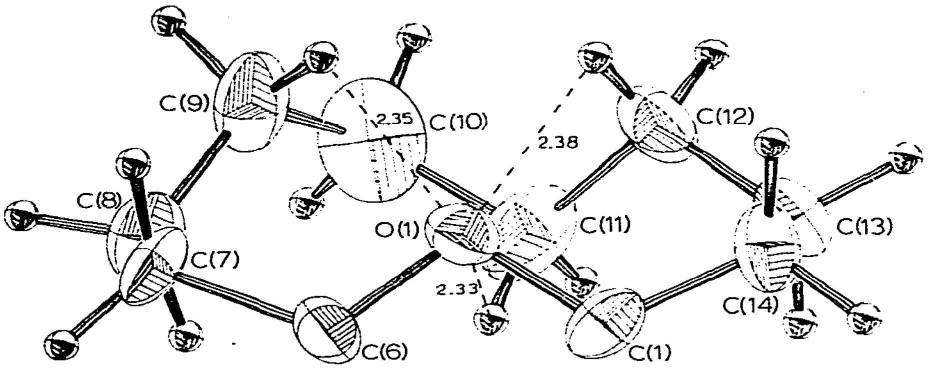

Fig. 2. Side view of the octamethylene chain in conformer B.

atoms, respectively, and three multiplets at δ 1.95—2.10 (4 H), 1.45—1.84 (8 H) and 1.19—1.45 ppm (4 H) due to the hydrogen atoms of the octamethylene chain. The line shape of the signal around δ 2.55 ppm at various temperatures is shown in Fig. 3 *.

From Fig. 3a one sees that the signal for the two tertiary hydrogen atoms (at C(4) and C(5), Fig. 1), which is still a sharp singlet at —52° C, broadens on further cooling. At —74° C two broadened signals are observed at δ 2.59 and 2.52 ppm, the signal at δ 2.59 ppm becoming sharper on further cooling. The signal

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* The three multiplets are also temperature dependent, but the changes are such that no definite conclusions about conformational changes can be drawn.

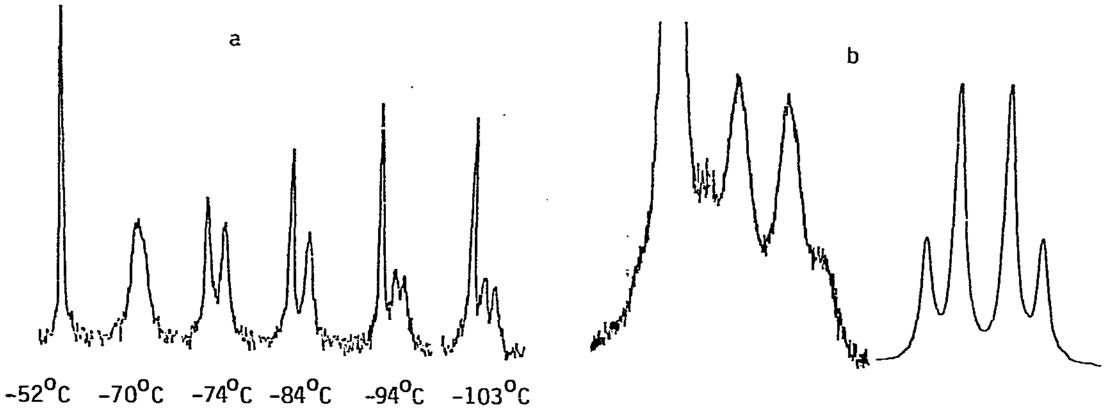

Fig. 3. (a) 100 MHz ^{1}H NMR signal of I centered around δ 2.55 ppm at various temperatures; (b) expanded signal at −103°C and computer-simulated AB-pattern (J 2.6 Hz); CS_2-solution.

at δ 2.52 ppm shows line-broadening on cooling below −74°C culminating in an AB-pattern at −103°C (Fig. 3b), $\delta(A) - \delta(B)$ being 0.066 ppm and $J(AB)$ being 2.6 Hz *. These two line-broadenings are explained in terms of two dynamic processes that occur in compound I. The free enthalpies of activation for both processes are calculated at the coalescence temperatures using the formulas [15]: $k(\text{coal}) = \pi\delta\nu/\sqrt{2}$ ((−70°C), $k(\text{coal}) = \pi\sqrt{(\nu_A - \nu_B)^2 + 6J^2(AB)}/\sqrt{2}$ (−90°C) and $\Delta G^{\ddagger}_{T(\text{coal})} = 4.57\ T(\text{coal})\ [10.32 - \log k(\text{coal})/T(\text{coal})]$. This has led to the following values: $\Delta G^{\ddagger}_{203} = 10.6$ kcal/mol and $\Delta G^{\ddagger}_{183} = 9.4$ kcal/mol.

The first process (conversion of one into two singlets) is ascribed to a swinging of the octamethylene chain over the ether-oxygen atom, i.e. the interconversion of conformers A and B (Fig. 1). The occurrence of analogous swinging processes has been previously assumed to explain the temperature dependence of the ^{1}H NMR spectra of [8](2,5)-furanophane [5], [8](1,4)-2,3-dicyano-7-oxanorbordiene [6] and [n](1,3)-cyclophanes [7]. The line-broadening that arises from the first process is caused by the reversible interconversion of the two (mutually equivalent) H(1) atoms of conformer A and the two (mutually equivalent) H(2) atoms of conformer B (Scheme 4). On cooling below −74°C this interconversion occurs so slowly that the singlets for the H(1) and H(2) atoms can be observed separately in the ^{1}H NMR spectrum. The fact that these two singlets are of virtually equal intensity shows that conformers A and B are of equal free-enthalpy, and that therefore there is no significant steric interaction between the octamethylene chain and the two ester groups in conformer B.

The second process (conversion of the singlet at δ 2.52 ppm into the AB-pattern) is ascribed to a conformational change within the octamethylene chain of conformer A, the details of which are shown by the interconversion of conformers C and D (Scheme 5). (The same conformational change will also occur within the octamethylene chain of conformer B; however, that change is not

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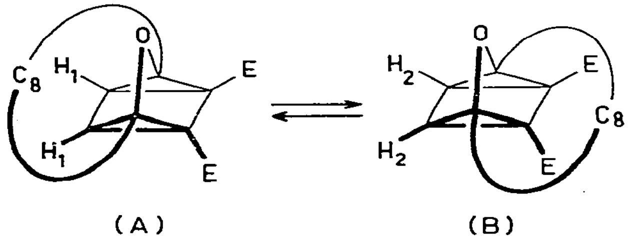
* A similar coupling constant (J 2.8 Hz) was found for 1,5-dicarbomethoxy-2-methyl-3-oxaquadricyclane [14].

SCHEME 4

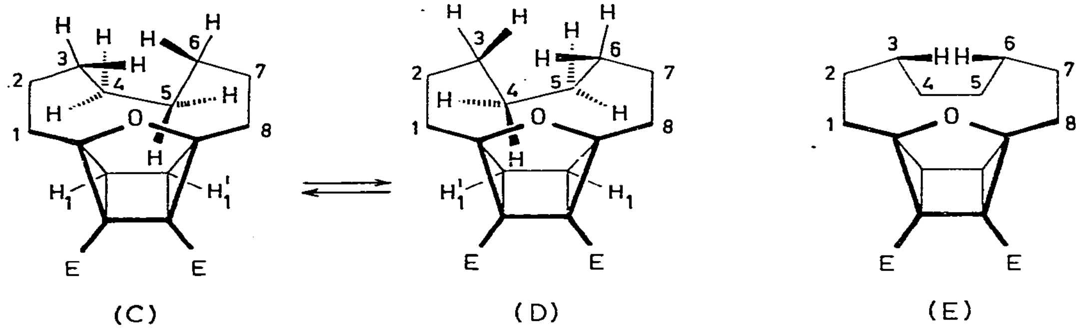


$\Delta G^{\ddagger}_{203}$ 10.6 kcal/mol

manifest in the signal at δ 2.59 ppm). The conformers C and D can be viewed as the two *gauche*-conformations of the butane-moiety formed by C(3)—C(4)—C(5)—C(6) of the octamethylene chain. As a consequence, the interconversion of the conformers C and D is in essence the interconversion of the *gauche*-conformations of the butane-moiety, which occurs via the eclipsed conformation E. From Scheme 5 it can be seen that in both of the conformers C and D the hydrogen atoms H(1) and H(1′) are magnetically different as a result of the spatial arrangement of the octamethylene chain. The interconversion of these H(1) and H(1′) atoms causes the line-broadening associated with the second process. Even at —70° C the interconversion of H(1) and H(1′) is still very fast, so that these atoms are equivalent on the NMR time scale. However, on cooling below —94° C the interconversion of H(1) and H(1′) is sufficiently slow to permit separate observation of the corresponding signals.

Some of the factors which contribute to the energy barriers of both processes are worth mentioning. For the first process (the interconversion of conformers A and B) it can be assumed that the energy barrier is mainly caused by the strong repulsion in the transition state between the four hydrogen atoms on C(3) and C(6) of the octano-chain and the ether-oxygen atom. On this basis it is easy to see that the energy barrier of the analogous swinging process in [8](2,5)-furanophane is smaller than that in [8](2,5)-thiophenophane [5], as a result of the smaller Van der Waals radius of oxygen than of sulfur (1.40 and

SCHEME 5

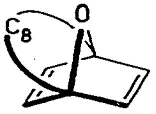


$\Delta G^{\ddagger}_{183}$ 9.4 kcal/mol

1.85 Å, respectively [13]), and the combined effect of the differences in bond angles and bond lengths (CSC 92°; COC 106°; C—S 1.71 Å; C—O 1.36 Å [16]). A second contribution to the energy barrier of the swinging process may be provided by desolvation of the ether-oxygen atom in the transition state.

At least two factors contribute to the energy barrier of the second process (the interconversion of conformers C and D). First, the butane moiety becomes eclipsed during this degenerate process. Second, as a Dreiding model indicates, there is a strong repulsion between two hydrogen atoms on C(3) and C(6), which come very close as indicated in structure E (Scheme 5). In this connection it is noteworthy that the previously unexplained difference between the temperature dependent ^{1}H NMR signals of the octamethylene chain hydrogens in [8](2,5)-furanophane and [8](2,5)-thiophenophane at —97° C (a signal of intensity 2 H at δ 0.0 ppm for the furanophane and a signal of intensity 1 H at δ —1.5 for the thiophenophane [5]) can be accounted for by assuming that in these compounds an analogous degenerate process takes place. As a consequence of the freezing-out of the conformational change process in the octamethylene chain, one of its hydrogen atoms becomes located above the aromatic ring, as can be seen from a Dreiding model. This results in a strong shielding of that hydrogen atom, which is manifest in its chemical shift of δ —1.5 ppm. In fact the process is frozen out at —97° C for the thiophenophane but not for the furanophane, as indicated by the appearance of a one-hydrogen signal for the former and a two-hydrogen signal for the latter at —97° C. The observed rate difference between the furanophane and the thiophenophane must be related to the difference between oxygen and sulfur with regard to bond angles, bond lengths and Van der Waals radii.

2. *[8](1,4)-7-oxanorbornadiene (VI).* It is plausible that the 7-oxanorbornadiene (VI) should undergo the dynamic processes similar to those observed for the 3-oxaquadricyclane (I). It is of interest to see whether the difference in geometry between a 3-oxaquadricyclane and a 7-oxanorbornadiene molecule is reflected in the energy barriers for these processes *. With that purpose the line shape of the signals due to the four olefinic hydrogen atoms in the ^{1}H NMR spectrum was recorded at various temperatures. The following results were obtained: —49.5° C, singlet at δ 6.87 ppm (line width 1.8 Hz); this singlet is very broad at —76.2° C (line width 12.2 Hz); —86.5° C, two broadened singlets at δ 6.81 and 6.96 ppm (both line widths 4.0 Hz); —93.2° C, one singlet at δ 6.81 ppm (line width 1.7 Hz) and an AB-pattern, the centres of the doublets at δ 6.94 and 7.01 ppm, J 5.2 Hz ** (line width 1.7 Hz). The conversion of one into two singlets is ascribed to the swinging of the octamethylene chain over



(VI)

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* The presence or absence of the two ester groups will have no affect, see section B1.

** A comparable coupling constant (J 5.5 Hz) has been found for 2,3-dicarbomethoxy-1-methyl-7-oxanorbornadiene [17].

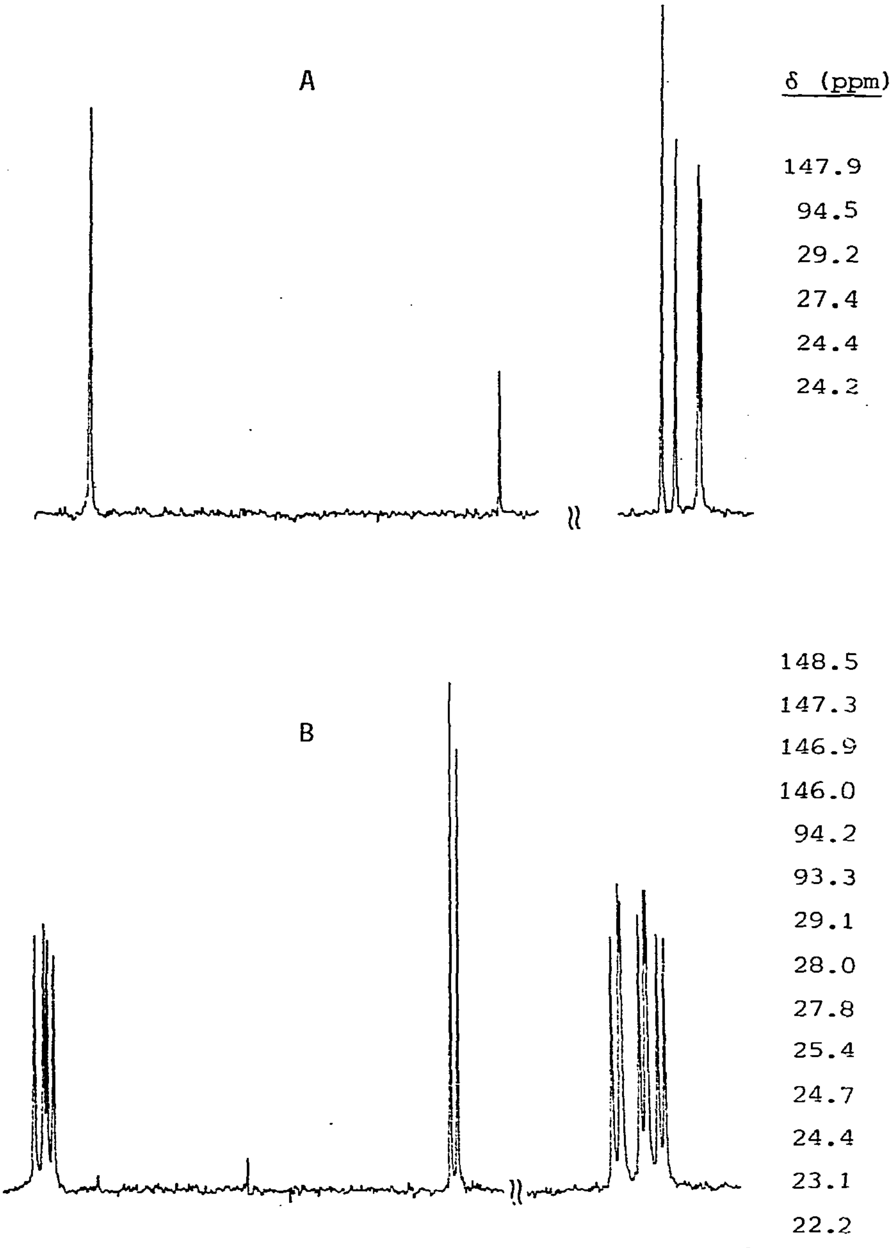


Fig. 4. ^{13}C NMR spectra of VI (CD_2Cl_2; 0.6 *M*) at —20°C (A) and —92°C (b).

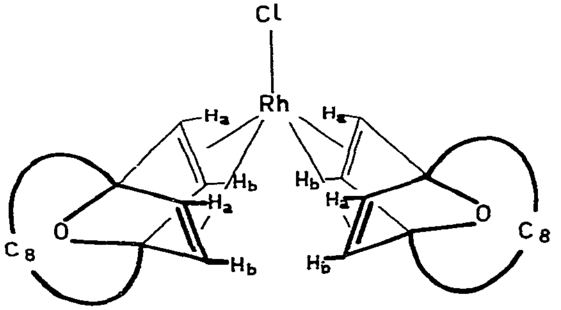
the oxygen atom while the conversion of one of these two singlets into the AB-pattern is ascribed to the conformational change within the octamethylene chain (see section B1). The free enthalpy of activation of the swinging process at —76.2°C has been calculated [15] to be $\Delta G^{\ddagger}_{196.8}$ 10.0 kcal/mol. The conformational change process is frozen out over a relatively small temperature range (—86.5 till —93.2°C) and so the activation parameter for that process were determined by ^{13}C NMR line-broadening. In the ^{13}C NMR spectrum of VI at

—20° C (Fig. 4A) there is one signal for the four olefinic carbon atoms and one for the two bridge-head carbon atoms next to the oxygen atom at δ 147.9 and 94.5 ppm, respectively. However, at —92° C (Fig. 4B) there are four signals for the olefinic carbon atoms (δ 146.0, 146.9, 147.3 and 148.5 ppm) and two signals for the bridge-head carbon atoms (δ 93.3 and 94.2 ppm). It will be clear that the observation of four signals for the four sp^2 carbon atoms at —92° C indicates that both processes have been frozen out on the NMR time scale at that temperature. Also, that the occurrence of two signals for the two bridge-head carbon atoms is due to the conformational change process (and not the swinging process) being slow. From the changes in line shape of the signal(s) due to the bridge-head carbon atoms as function of the temperature, and by use of eq. 1, in which k equals $\pi\Delta$ (slow exchange) and $4\pi P_A P_B{}^2\,(\delta\nu)^2/\Delta$ (fast exchange) [15], the activation parameters of the conformational change process have been obtained: $\Delta H^{\neq} = 9.8\ (\pm 0.2)$ kcal/mol and $\Delta S^{\neq} = -1\ (\pm 1)$ e.u.

$$\log k/T = 10.32 - \Delta H^{\neq}/4.57T + \Delta S^{\neq}/4.57 \qquad (1)$$

A comparison of the free enthalpies of activation for the swinging process in VI ($\Delta G^{\ddagger}_{196.8}$ 10.0 kcal/mol) and in I ($\Delta G^{\ddagger}_{203}$ 10.6 kcal/mol) as well as for the conformational change process in VI ($\Delta G^{\ddagger}_{183}$ 10.0 kcal/mol) and in I ($\Delta G^{\ddagger}_{183}$ 9.4 kcal/mol) reveals that the difference in geometry between VI and I hardly affects the energy barrier of either process.

3. *Di-[8](1,4)-7-oxanorbornadienerhodium chloride (XI).* It is expected that at room temperature the two dynamic processes of the octamethylene chains in complex XI, viz. the swinging and the conformational change process, should be fast on the NMR time scale, as is the case in the free ligand VI (compare section B2). On the basis of the structure of complex XI * one would therefore expect two ^{1}H NMR signals for the olefinic hydrogen atoms, one for the H_a and one for the H_b atoms. However, Fig. 5 shows that this is not the case: at —15.5° C only one signal is observed at δ 4.69 ppm (doublet; J(Rh—H) 1.5 Hz). On lowering the temperature line broadening takes place, resulting in two signals of equal intensity at δ 4.56 and 4.84 ppm at —49.0° C. On further cooling another line-broadening takes place of both signals (at δ 4.56 and 4.84 ppm);



(XI)

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* The structure of this complex is based upon analogy with dibutadienerhodium chloride [18].

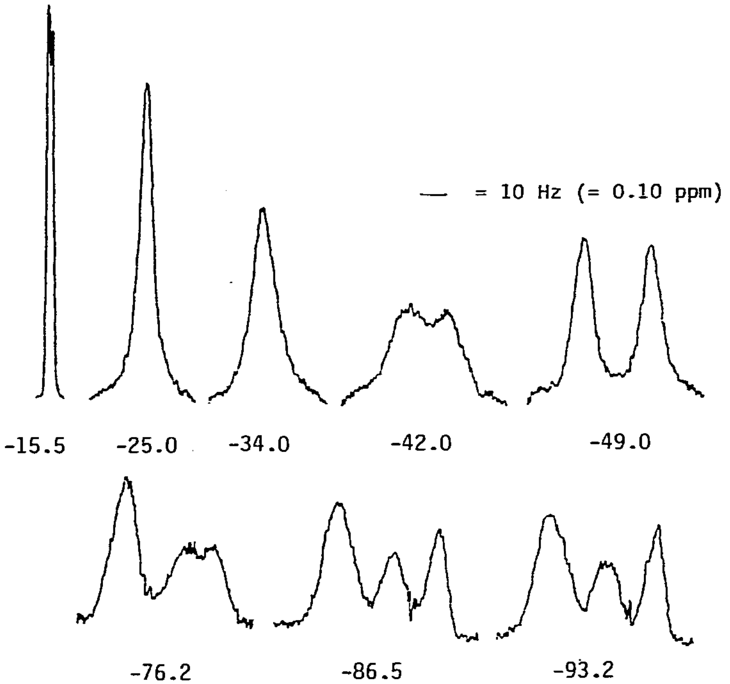

Fig. 5. Temperature dependent line shape of the 100 MHz ^1H NMR signal at δ 4.69 ppm due to the olefinic hydrogen atoms in XI, formed in a solution of VI (0.6 *M*) and $Rh_2(CO)_4Cl_2$ (5 mol%) in $CDCl_3/CS_2$; *J*(Rh—H) 1.5 Hz.

the line shape of the signals at —76.2, —86.5 and —93.2° C are also shown in Fig. 5.

During the first line-broadening (cooling to —49.0° C) the signal at δ 6.87 ppm, due to the olefinic hydrogens of the free ligand VI present in solution, remains sharp (compare also section B2). The chemical shift of the signal for the olefinic hydrogens of complex XI does not change, and remains at δ 4.69 ppm. It is concluded that the free ligand VI is not involved in the line-broadening process, and also that this line-broadening is not caused by the swinging process of the octamethylene chains in XI. The latter conclusion is based on the following considerations. In section B2 it was noted that the difference in geometry between 7-oxanorbornadiene and 3-oxaquadricyclane does not significantly affect the energy barrier of the swinging process. Because it is unlikely that in XI the geometry of the complexed 7-oxanorbornadiene (VI) will differ much from that of the free 7-oxanorbornadiene (VI) * no significant difference in energy barrier can be expected for the swinging process of the octamethylene chain in the free and (in XI) complexed 7-oxanorbornadiene (VI).

The observed line-broadening in which the olefinic H_a and H_b atoms become identical can be ascribed in principle to : (a) a unimolecular dissociation of the

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* The geometry of π-complexed norbornadiene in $Pd(NOR)_2Cl_2$ differs very little from that of free norbornadiene [19].

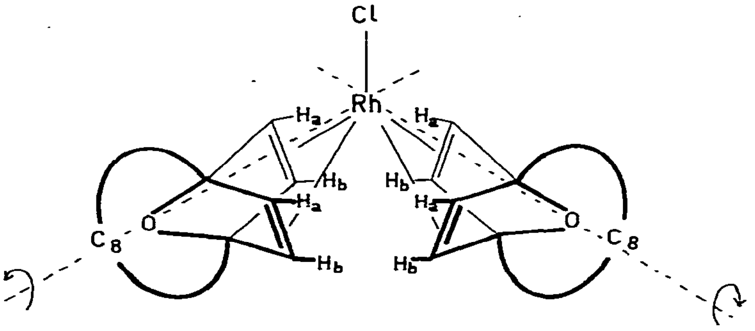

Fig. 6. Rotation of the 7-oxanorbornadiene ligands in rhodium complex XI.

rhodium—chlorine bond, the chloride ion departing from the front side and recombining with the rhodium atom from the back side; (b) a dissociation leading to decomplexation of the 7-oxanorbornadiene ligands, followed by a recombination after rotation of the ligands; (c) a rotation of the 7-oxanorbornadiene ligands within the molecule around axes through the rhodium and oxygen atoms (Fig. 6), without dissociation *. If the explanation (a) or (b) were correct a large positive entropy of activation would be expected because there is an increase in the number of the entities **. However, from the Eyring-plot in Fig. 7 a $\Delta S^{\ddagger}$ of 3.0 (±2.0) e.u. has been calculated *** ($\Delta H^{\ddagger}$ being 12.4 ± 0.3 kcal/mol). Therefore, explanations (a) and (b) are both unlikely. An additional argument which rules out explanation (b) is found in the observation of a doublet in the ^{1}H NMR spectrum of XI at —15.5° C (Fig. 5). The occurrence of this doublet, due to Rh—H coupling, during the fast interconversion of the H_a and H_b atoms, shows that the rhodium is continuously complexed to the C=C bonds; in case of a rapid reversible complexation—decomplexation mechanism no Rh—H coupling would be observed [22]. In summary, it seems reasonable that the broadening of the signal due to the olefinic hydrogen atoms in complex XI, observed on cooling from —15.5 to —49.0° C, is caused by a rotation of the 7-oxanorbornadiene ligands around axes through the rhodium and oxygen atoms, as shown in Fig. 6. This conclusion is further supported by the fact that analogous rotations of ethylene ligands occur in the following rhodium complexes [23]): $C_5H_5Rh(C_2H_4)_2$ (E_a 15.0 kcal/mol; log A = 12.52), $C_5H_5Rh(SO_2)C_2H_4$ (E_a 12.2 kcal/mol; log A = 12.26) and $C_5H_5Rh(C_2F_4)C_2H_4$ (E_a 13.6 kcal/mol; log A = 13.6). In all three complexes Rh—H coupling is observed during the fast interconversion of the olefinic hydrogen atoms of the ethylene ligands. The calculated $\Delta S^{\ddagger}$ values (—3.0, —4.1 and +2.0, respectively) are comparable to that of the rotation process in XI.

Fig. 5 shows another line-broadening and splitting of the signals on cooling

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* An alternative mechanism not involving a dissociation of a ligand is pseudorotation. The motions in rotation and in pseudorotation are similar but not identical. There is no conclusive way of discriminating between these possibilities in the present case.

** Investigation of the dynamic behaviour of tetramethylcyclobutadienealuminum trichloride has revealed a $\Delta S^{\ddagger}$ of +12 e.u. for the dissociation of a chloride ion from the complex [20].

*** Compare the value of $\Delta S^{\ddagger}$ (3.0 ± 2.0 e.u.) for the unimolecular inversion at the sulphur atom in chromium pentacarbonyl sulphide complexes [21].

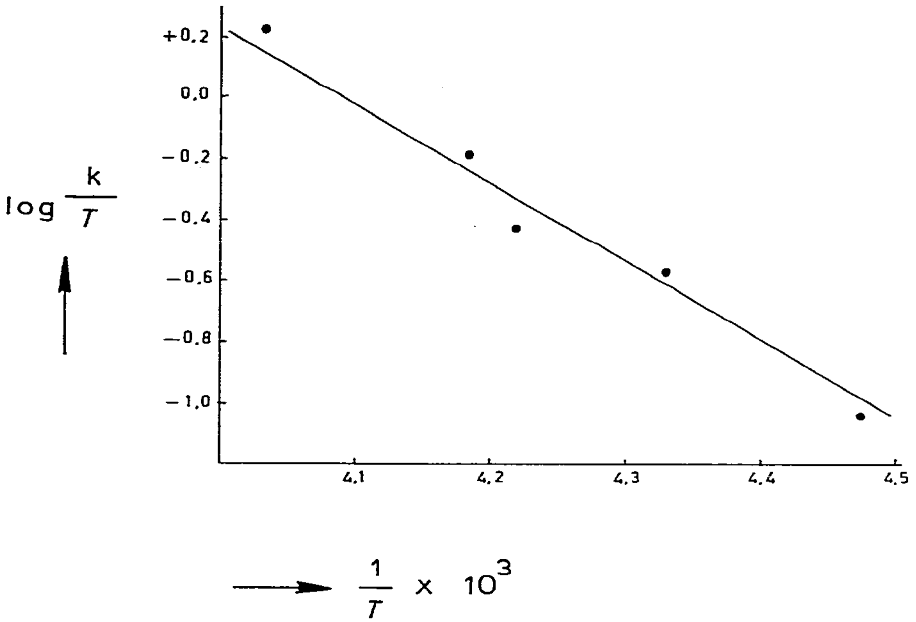
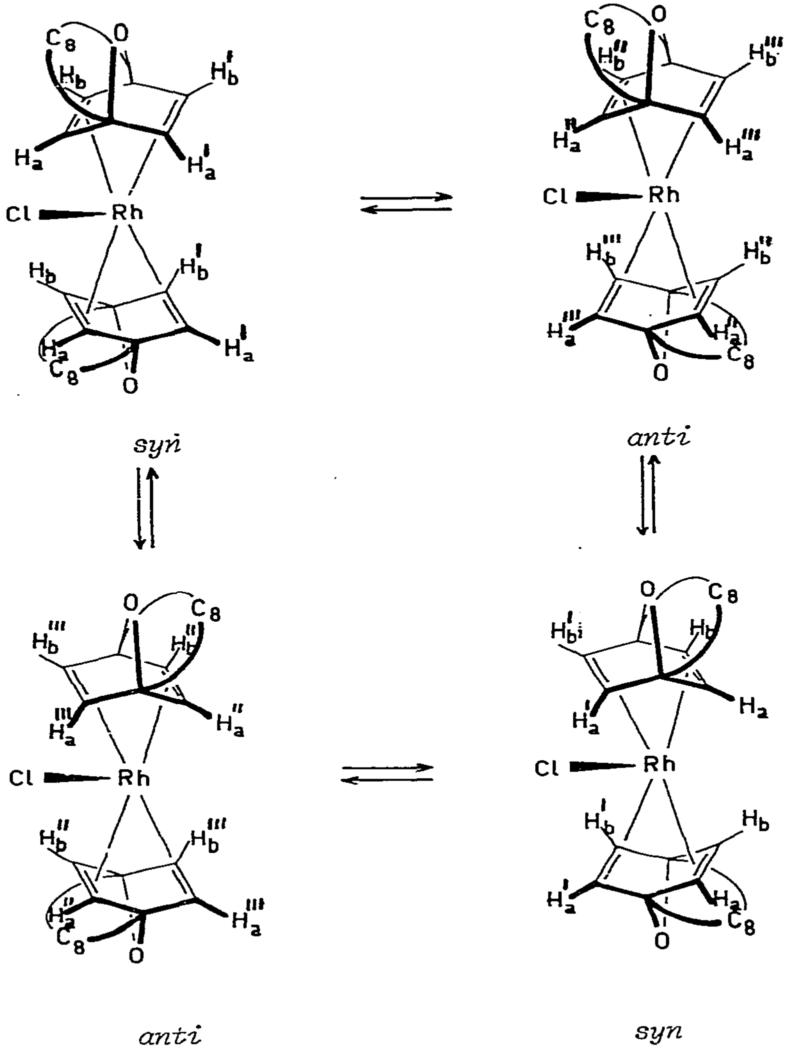


Fig. 7. Eyring-plot of the process by which the olefinic H_a and H_b atoms in complex XI become identical.

below —49.0° C. The signal at δ 4.56 ppm is just split at —76.2° C, whereas the signal at δ 4.84 ppm is only broader relative to that at —49.0° C; at —86.5° C the original signal at δ 4.56 ppm has been split into two signals, whereas that at δ 4.84 ppm has continued to broaden. In the same temperature range broadening of the singlet at δ 6.87 ppm, due to the olefinic hydrogen atoms of free 7-oxanorbornadiene (VI) present in solution, is observed: at —76.2° C a very broad singlet, at —86.5° C two broadened singlets (compare section B2). It is concluded that the broadening of the signals at δ 4.56 and 4.84 ppm is connected with the swinging process of the octamethylene chains; as the swinging is "frozen out", the H_a and the H_b atoms become different on the NMR time scale. From a stereochemical point of view it is interesting that by the swinging process of the two octamethylene chains in complex XI *syn*- and *anti*-conformers are interconverted, as shown in Scheme 6 (the *syn*-conformers are identical and the *anti*-conformers are enantiomeric conformations). In prinxiple, the corresponding hydrogen atoms in the *syn*- and *anti*-conformers (H_a—H_a''' and H_b—H_b''') are different from each other. These differences are not large enough, however, to allow for separate observation of the various hydrogens, not even in the 360 MHz ^{1}H NMR spectrum.

On cooling from —86.5 to —93.2° C hardly any changes are observed in the signals due to the olefinic hydrogen atoms in the 100 MHz ^{1}H NMR spectrum of XI (Fig. 5). However, from the 360 MHz spectrum a further splitting of the three signals can be seen (Fig. 8). From the fact that at —93.2° C an AB-pattern and a singlet are observed for the olefinic hydrogen atoms in free 7-oxanorbornadiene (VI) (compare section B2), it is concluded that the splitting observed in the 360 MHz spectrum at —94° C results from a freezing-out of the conformational change process within the octamethylene chains of XI. As a conse-

SCHEME 6



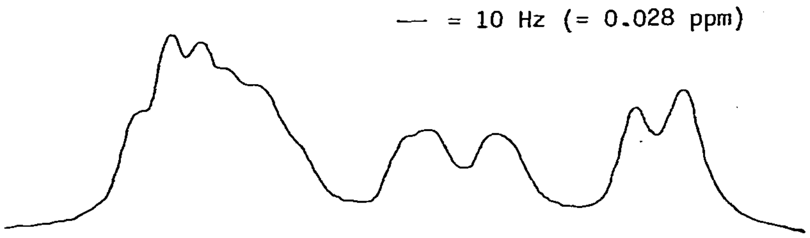
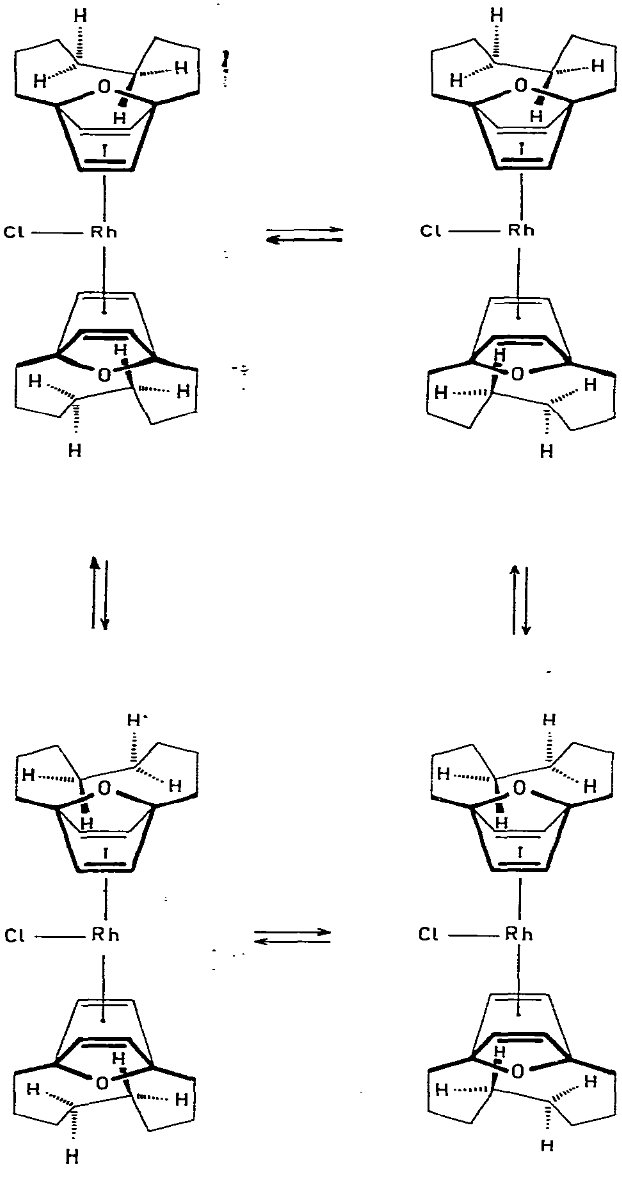


Fig. 8. 360 MHz ^{1}H NMR signals of the olefinic hydrogen atoms in complex XI at −94°C ($CDCl_3/CS_2$).

SCHEME 7

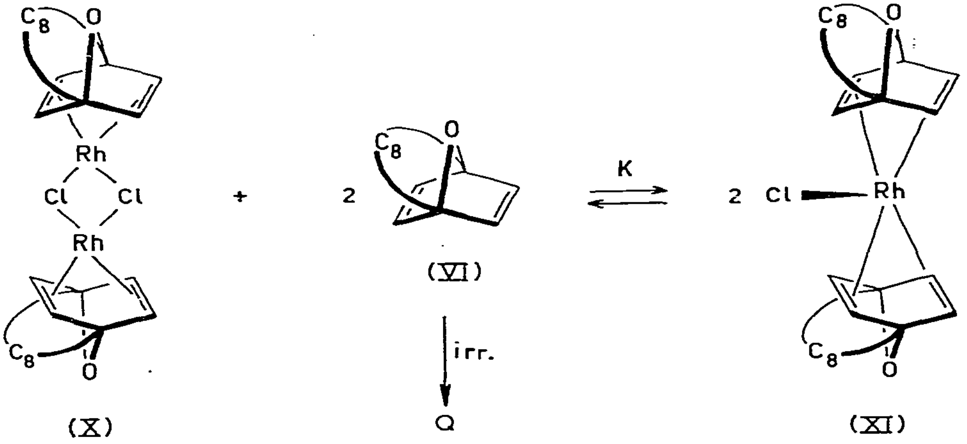


quence of this freezing-out four conformations are possible for the *syn*- as well as for each of the two *anti*-conformers; in Scheme 7 this is shown for the *syn*-conformer.

C. Exchange between free and rhodium-complexed [8](1,4)-7-oxanorbornadiene (VI)

In the Introduction it was mentioned that the pentacoordinated rhodium complex XI is formed during the synthesis of the tetracoordinated complex X if 10% excess of the 7-oxanorbornadiene VI is used and also upon adding 5

SCHEME 8



mol% $Rh_2(CO)_4Cl_2$ to a solution of VI *. Complex XI is also formed almost quantitatively (based on X) if 5 mol% of complex X is added to a solution of the 7-oxanorbornadiene (VI). If an excess (10—20%) of complex X is added to the solution of VI, the ^1H NMR spectrum of the solution obtained shows that VI has been converted completely, and both the complexes X and XI are present. From these results it is concluded that there is a reversible and an irreversible reaction involving VI, X and XI (Scheme 8).

The complexes X and XI (Scheme 8) were characterized by mass spectrometry (X: M^+ 684; XI: $(M - HCl)^+$ 510) and by comparison of their ^1H NMR spectra with those of the corresponding norbornadiene complexes $Rh_2(NOR)_2Cl_2$ and $Rh(NOR)_2Cl$, respectively (Scheme 3; relevant are the chemical shifts of the olefinic hydrogen atoms: X δ 4.21 ppm and $Rh_2(NOR)_2Cl_2$ δ 3.92 ppm [12], XI δ 4.69 and $Rh(NOR)_2Cl$ δ 4.38 ppm [12]).

From the data obtained the equilibrium constant $K = [XI]^2/[VI]^2 \cdot [X]$ (Scheme 8) is calculated ** to be $K > 5000\ M^{-1}$ at —18°C. This value is much larger than that for the equilibrium between norbornadiene, $Rh_2(NOR)_2Cl_2$ and $Rh(NOR)_2Cl$ (Scheme 3), which amounts to about $2\ M^{-1}$ at the same temperature [12]. Comparison of the two K values suggested that it should be possible to isolate complex XI, in contrast to $Rh(NOR)_2Cl$ which has resisted isolation [12]. We were indeed able to isolate complex XI although not analytical pure (see Experimental). A qualitative explanation for the large difference between the two K values can be given as follows. There are known to be two contributions to the rhodium—diene bonding, a σ- and a π-interaction. In the σ-interaction there is an "electron-flow" from the diene to rhodium, whereas the reverse is true in the π-interaction (Fig. 9).

It can be assumed that the relevant MO's of 7-oxanorbornadiene are of lower

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* See also note on p. 239.

** Based upon the following experiment: on adding 65.8 mg (0.096 mmol) of complex X to 13.0 mg (0.064 mmol) of 7-oxanorbornadiene (VI) in 0.8 ml of $CDCl_3$, the ^1H NMR spectrum (at —18°C) of the solution shows that >95% of VI has disappeared, and that complexes X and XI are present in equal amounts. From $K = [XI]^2/[VI]^2 \cdot [X]$, $[VI] < 4 \times 10^{-3}\ M$, and $[X] = [XI] = 8 \times 10^{-2}\ M$, it follows that $K > 5000\ M^{-1}$.

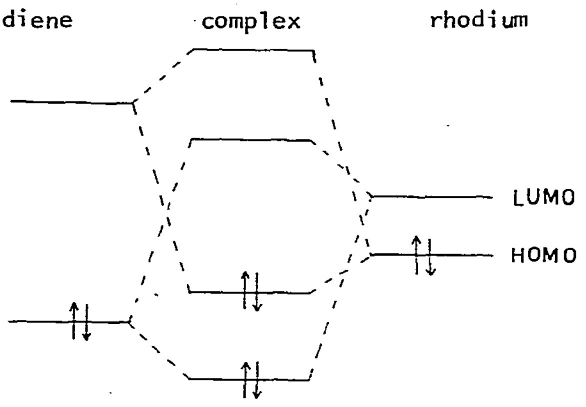

Fig. 9. Interaction diagram of suitable MO's of the diene with HOMO and LUMO of rhodium.

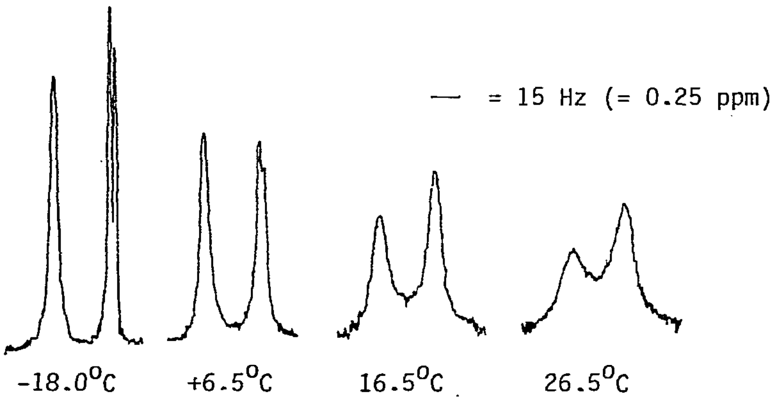

Fig. 10. Temperature dependence of the 60 MHz ^{1}H NMR signals due to the olefinic hydrogen atoms in X (δ 4.21 ppm) and XI (δ 4.69 ppm); J(Rh—H) in complex X is 2.8 Hz; $CDCl_3$ solution (J(Rh—H) in the analogous complex of 2,3-dicarbomethoxy-1,4-dimethyl-7-oxanorbornadiene is 2.6 Hz [10]).

energy than those of norbornadiene because of the electronegative oxygen atom *. This implies that the σ-interaction is smaller but the π-interaction larger for 7-oxanorbornadiene than for norbornadiene. Consequently the rhodium atom in the complex of 7-oxanorbornadiene is more positively charged than that in the complex of norbornadiene. Thus the tendency of the rhodium atom to become pentacoordinated is greater for 7-oxanorbornadiene [10].

To find out wether the forward and backward reactions of the equilibrium in Scheme 8 are so fast that they can be studied by NMR line-broadening, the ^{1}H NMR spectrum of a solution containing VI, X and XI (obtained by dissolving 13.0 mg (0.064 mmol) of VI and 65.8 mg (0.096 mmol) of X in 0.8 ml $CDCl_3$) was recorded at various temperatures. In Fig. 10 the signals due to the olefinic hydrogen atoms in X (δ 4.21 ppm) and XI (δ 4.69 ppm) are shown at various temperatures. On raising the temperature line-broadening is observed, which

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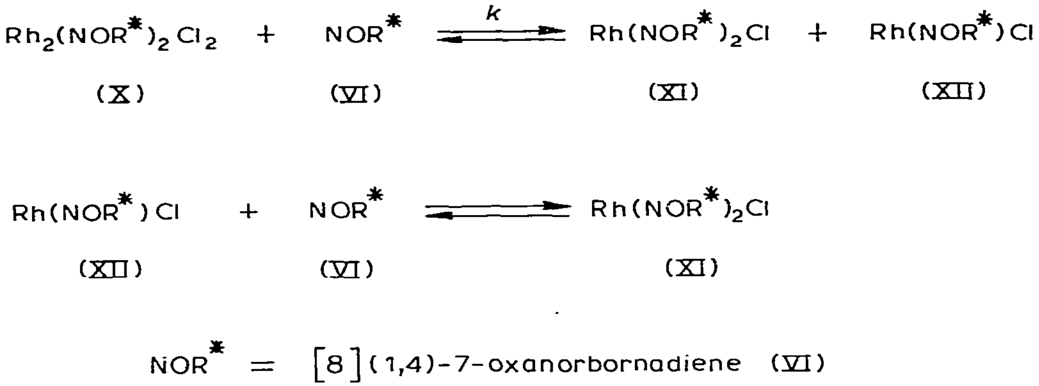
* Compare the difference of ca. 0.5 eV between the highest occupied MO's of 1,5-dicarbomethoxy-3-oxaquadricyclane and 1,5-dicarbomethoxyquadricyclane [24].

SCHEME 9



$$Rh_2(NOR^*)_2Cl_2 \ (X) + NOR^* \ (VI) \xrightarrow{k} Rh(NOR^*)_2Cl \ (XI) + Rh(NOR^*)Cl \ (XII)$$

$$Rh(NOR^*)Cl \ (XII) + NOR^* \ (VI) \longrightarrow Rh(NOR^*)_2Cl \ (XI)$$

$$NOR^* = [8](1,4)\text{-7-oxanorbornadiene} \ (VI)$$

indicates an exchange between free and complexed 7-oxanorbornadiene (VI) as shown in Scheme 8.

The concentration of XI decreases on increasing the temperature; this is probably caused by the irreversible conversion of VI into compound Q (Scheme 8) resulting in a shift of the equilibrium to the left. On lowering the temperature the signals became sharp again, but the concentration of XI becomes smaller. It is assumed that the mechanism of the exchange of free and complexed 7-oxanorbornadiene (VI) is analogous to that of free and complexed norbornadiene [12]: a slow reaction between X and VI leads to XI and a very reactive species XII which reacts very rapidly with a second molecule of VI to afford XI (Scheme 9). On the basis of the assumption that the rate of disappearance of X ($-d[X]/dt$) equals $k[X] \cdot [VI]$ and that the line-width of the signal belonging to X can be expressed as $\tau_X^{-1} = \frac{1}{2}k[VI]$ *, the free-enthalpy of activation can be calculated from eq. 1 (section B2): at +16.5°C $\Delta G^{\ddagger}$ has been found to be <11.9 kcal/mol ($[VI] < 4 \times 10^{-3}$ M; τ_X^{-1} 11.9 Hz).

Conclusions

The octamethylene chains in [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane (I) and in [8](1,4)-7-oxanorbornadiene (VI) undergo two processes. The slower process involves a swinging of the octano bridge over the oxygen atom while the faster involves a conformational change in the octano bridge. The difference in geometry between compounds I and VI has no substantial effect on the energy barrier of either process. For the swinging process: $\Delta G^{\ddagger}_{203}$(I) 10.6 kcal/mol and $\Delta G^{\ddagger}_{196.8}$(VI) 10.0 kcal/mol; for the conformational change process: $\Delta G^{\ddagger}_{183}$(I) 9.4 kcal/mol and $\Delta G^{\ddagger}_{183}$(VI) 10.0 kcal/mol. The same two processes (having similar energy barriers) are shown by the two octamethylene chains in the pentacoordinated di-[8](1,4)-7-oxanorbornadienerhodium chloride (XI). In complex XI another (degenerate) dynamic process has been observed, namely a rotation of the 7-oxanorbornadiene ligands around axes through the rhodium and oxygen atoms ($\Delta H^{\ddagger}$ 12.4 kcal/mol; $\Delta S^{\ddagger}$ +3.0 e.u.).

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* $\tau_{[X]}^{-1} = -d[X]/dt$ [25]. The factor $\frac{1}{2}$ arises from the fact that the concentration of rhodium is twice that of X (cf. [12]).

Finally, a rapid exchange has been observed between the 7-oxanorbornadiene ligands in complexes XI and X (chloro-[8](1,4)-7-oxanorbornadienerhodium dimer) and free [8](1,4)-7-oxanorbornadiene (VI) ($\Delta G^{\ddagger}_{289.5} < 11.9$ kcal/mol).

Experimental

Materials and apparatus

The starting materials vinylene carbonate, cyclooctene (Aldrich-Europe), and cyclododecanone (EGA-chemie) were purified by distillation. 1,1′-Thiocarbonyldiimidazole (Aldrich), $RhCl_3 \cdot 3\ H_2O$ (Strem Chemicals Inc.) and butadiene (Baker Chemical Co.) were used without further purification. $Rh_2(CO)_4Cl_2$ (Strem) was crystallized from n-pentane prior to use.

60 MHz ^{1}H NMR spectra were recorded on a Varian A-60D or a Jeol C-60 HL spectrometer; the ^{13}C and 100 MHz ^{1}H NMR spectra on a Varian XL-100 spectrometer (by Ir. P.B.J. Driessen, Drs. W. Mellink, Dr. J. Runsink and Dr. J.H. Wieringa); the 360 MHz ^{1}H NMR spectrum on a Bruker HX-360 spectrometer (by Dr. R. Kaptein). Chemical shifts are relative to TMS. Temperatures were measured by means of a thermocouple. Mass spectra were recorded by A. Kiewiet on an AEI MS 902 apparatus. Melting points were uncorrected and were measured on a Reichert apparatus with microscopic equipment. Elemental analysis were carried out by H. Draayer, J. Ebels, A.F. Hamminga, and J.E. Vos of the Analytical Department.

Syntheses

The synthesis of [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane (I) has recently been reported [2].

[8](1,4)-7-oxanorbornadiene (VI). Starting from cyclododecanone [8](2,5)-furanophane (II) was synthesized by literature procedures [26]. 15.0 g (84.0 mmol) of [8](2,5)-furanophane and 42.0 g (480 mmol) of vinylene carbonate were heated for 8 days to 140°C with stirring *. After cooling, the excess of vinylene carbonate was distilled off (55°C/12 mmHg). The residue, consisting of 85% *exo*- and 15% *endo*-adduct, was crystallized from methylcyclohexane, to give 14.0 g (53 mmol; 63%) of the white crystalline *exo*-adduct III; m.p. 135—136°C. ^{1}H NMR ($CDCl_3$; 35°C): δ 6.24 (s, 2 H); 4.54 (s, 2 H); 0.80—2.16 ppm (m, 16 H). Analysis: Found: C, 68.24; H, 7.67. $C_{15}H_{20}O_4$ calcd.: C, 68.17; H, 7.63%.

13.0 g (49 mmol) of the *exo*-carbonate III was refluxed for 24 h in a mixture of 50 ml of toluene and 300 ml of 1 *N* aqueous KOH. After cooling, the reaction mixture was extracted with toluene. After drying, the toluene was partly distilled off. On cooling to —20°C the (*exo*) *cis*-diol IV crystallized. Yield 10.9 g (46 mmol); 94%); m.p. 139—140°C. ^{1}H NMR ($CDCl_3$, 35°C): δ 6.10 (s, 2 H); 3.70 (m, 2 H); 3.06 (m, 2 H); 0.75—2.34 ppm (m, 16 H). Analysis: Found: C, 70.43; H, 9.21 and O, 19.95. $C_{14}H_{22}O_3$ calcd,: C, 70.54; H, 9.31; O, 20.15%.

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* If the reaction is carried out at 90°C, equal amounts of *exo*- and *endo*-adducts are formed and these can be separated by column chromatography (SiO_2:CH_2Cl_2). *endo*-Adduct, ^{1}H NMR ($CDCl_3$; 35°C): δ 6.33 (s, 2 H); 4.65 (s, 2 H); 0.80—2.16 ppm (m, 16 H).

A mixture of 9.5 g (40 mmol) of the (*exo*) *cis*-diol IV and 10.0 g (56 mmol) of 1,1′-thiocarbonyldiimidazole was refluxed in 250 ml of dry toluene for 1 h. After cooling, the solution was washed with water and dried over anhydrous $MgSO_4$. The toluene was distilled off under reduced pressure. The remaining thiocarbonate V (*exo*-isomer) was crystallized from methylcyclohexane as white crystals. Yield 10.4 g (37 mmol; 90%); m.p. 187—188°C. ^1H NMR ($CDCl_3$; 35°C): δ 6.28 (s, 2 H); 4.82 (s, 2 H); 0.90—2.20 ppm (m, 16 H). Analysis: Found: C, 64.32; H, 7.17 and S, 11.37. $C_{15}H_{20}O_3S$ calcd.: C, 64.26; H, 7.19 and S, 11.43%.

8.3 g (30 mmol) of the *exo*-thiocarbonate V was heated with stirring at 90°C in freshly distilled $P(OCH_3)_3$ for 14 days. After cooling, 400 ml of ether and 300 ml of 2 *N* aqueous NaOH were added and the mixture was stirred at room temperature for 24 h. After separation of the two layers the ether layer was dried over $MgSO_4$ and the ether distilled off. The residue was chromatographed over SiO_2 (n-pentane/CH_2Cl_2 1/1) affording 5.1 g of the 7-oxanorbornadiene (VI) as a slightly yellow oil. This was purified by bulb-to-bulb distillation (80°C/0.15 mmHg), yielding 4.5 g (22 mmol, 73%) of colourless VI. ^1H NMR ($CDCl_3$; 35°C): δ 6.87 (s, 4 H); 2.15—2.30 (m, 4 H); 0.94—2.15 ppm (m, 12 H). ^{13}C NMR (CD_2Cl_2; —20°C): δ 147.9 (d, *J* 176 Hz; 94.5 (s); 29.2 (t, *J* 128 Hz); 27.4 (t, *J* 128 Hz); 24.4 (t, *J* 128 Hz); 24.2 (t, *J* 128 Hz). Analysis: Found: C, 82.35; H, 10.02 and O, 7.98. $C_{14}H_{20}O$ calcd.: C, 82.30; H, 9.86 and O, 7.83%.

Chloro-[8](1,4)-7-oxanorbornadienerhodium-dimer (X). Chlorodicyclooctenerhodium dimer (VIII) was prepared by the published procedure [9]. In a 50 ml two-necked reaction vessel containing 0.5 g (0.7 mmol) of VIII under nitrogen was condensed ca. 10 ml of butadiene at —20°C. After stirring for 1 h at —20°C the brown color of VIII had disappeared and a yellow solid, dibutadienerhodium chloride (IX), had been formed. The excess of butadiene was distilled off at room temperature followed by addition of 25 ml of n-pentane. After cooling the suspension to —10°C, 250 mg (1.2 mmol) of the 7-oxanorbornadiene (VI) was added. The mixture was stirred for 1.5 h at —10°C, then filtered, leaving a yellow solid (X), which was washed three times with n-pentane. Yield 345 mg (0.5 mmol; 83%); decomposition without melting above 180°C. Mass spectrum: M^+ 684. ^1H NMR ($CDCl_3$; 35°C): δ 4.21 (d, 4 H, *J*(Rh—H) 2.8 Hz); 1.79—2.24 (m, 4 H); 1.05—1.79 ppm (m, 12 H). ^{13}C NMR (C_6D_6; 35°C): δ 92.5 (d, *J*(C—Rh) 3.5 Hz); 60.2 (dd, *J* 180 Hz and *J*(C—Rh) 11.2 Hz); 28.6 (t, *J* 128 Hz); 24.6 (t, *J* 128 Hz); 22.9 (t, *J* 128 Hz). Analysis: Found: C, 47.21; H, 5.77; Cl, 10.45. $C_{28}H_{40}O_2Cl_2Rh_2$ calcd.: C, 49.08; H, 5.89; Cl, 10.35%.

Di-[8](1,4)-7-oxanorbornadienerhodium chloride (XI). To a solution of 890 mg (4.4 mmol) of [8](1,4)-7-oxanorbornadiene (VI) in 15 ml of n-pentane under nitrogen was added dropwise a solution of 97 mg (0.25 mmol) of $Rh_2(CO)_4Cl_2$ in 10 ml of n-pentane at —30°C. Immediately a yellow solid precipitated and evolution of carbon monoxide was noted. After stirring for 1 h at —30°C, the mixture was filtered, and the remaining yellow solid (XI) was washed three times with n-pentane. Yield 220 mg (0.4 mmol; 80%); decomposition without melting above 110°C, mass spectrum: $(M - HCl)^+$ 510. ^1H NMR ($CDCl_3$; 35°C): δ 4.67 (br) (s, 4 H); 1.82—2.24 (m, 4 H); 1.01—1.82 ppm (m, 12 H). ^{13}C NMR ($CDCl_3/CS_2$ 1/3; −12°C; dec.): δ 91.8 (br); 73.0 (br); 29.4; 28.1; 24.1; 22.9 ppm. Analysis: Found: C, 59.24; H, 6.99; Cl, 7.08. $C_{28}H_{46}O_2ClRh$ calcd.: C, 61.48; H, 7.37; Cl, 6.48%.

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