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# NMR Investigation into the Relative Stabilities and Rates of Exchange of Chelating Dienes Coordinated Towards Monovalent Rhodium

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*The relative stabilities and rates of exchange of chelating dienes (1-9) coordinated towards monovalent rhodium ($Rh_2(diene)_2Cl_2$) have been investigated by NMR. The complexes of bicyclo[2.2.2]octa-2,5-diene (2) and bicyclo[2.2.1]hepta-2,5-diene (1) appeared to be thermodinamically the most stable and kinetically the most labile. The rate of exchange was at least $10^3$-$10^4$ times faster than for the other dienes. The kinetic lability is accounted for by a strong π-backbonding character of (1) and (2), favouring pentacoordination. Geometry of the diene, electronic (π-backbonding) and steric effects account for the relative order of stabilities.*

## Introduction

Previously we reported on the NMR kinetic investigation of the system bicyclo[2.2.1]hepta-2,5-diene (1) and μ-dichloro-bis-(bicyclo[2.2.1]hepta-2,5-diene)-dirhodium (Rh(1))* in the temperature range of −90°to +100°.[1] The study revealed a surprisingly rapid exchange of the chelating diene via the intermediate formation of a five-coordinate rhodium-bis(bicyclo[2.2.1]hepta-2,5-diene)chloride. This species was detected below −40°.

It seemed of interest to investigate how the rate of the exchange is affected by the structure of the chelating diene. To this end we extended our investigation to systems containing the following chelating « dienes » with their corresponding dimeric complexes $Rh_2(diene)_2Cl_2$:

bicyclo[2.2.2]octa-2,5-diene (2)

2,3,5,6-tetramethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (3)

hexamethylbicyclo[2.2.0]hexa-2,5-diene (4)

cycloocta-1,5-diene (5)

cycloocta-1,3,5,7-tetraene (6)

2,3-dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene (7)

1,4-dimethyl-2,3-dicarbomethoxy-7-oxa-bicyclo[2.2.1]hepta-2,5-diene (8)

endo-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (9).

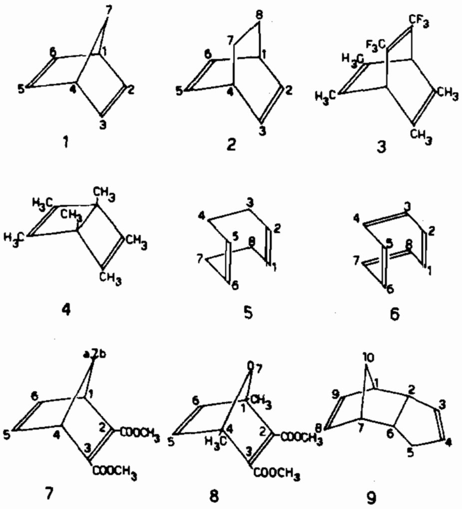

Figure 1. Chelating Olefins

In addition, the order of coordination ability of the chelating dienes was established by determining the equilibrium constants for

$$Rh_2(diene)_2Cl_2+2\ diene^* \rightleftharpoons Rh_2(diene)_2^*Cl_2+2\ diene \tag{1}$$

The results are discussed in terms of the thermodynamic and kinetic stabilities of the complexes with respect to the geometry of the diene and the effect of substituents on the strength of the rhodium-olefin bond.

## Results

A. *Preparation of the $Rh_2(diene)_2Cl_2$ complexes.* Addition of the appropriate diene to a suspension of rhodium-bis(butadiene)chloride in n-pentane at room temperature in a nitrogen atmosphere gave an almost quantitative yield of very pure diene complexes $Rh_2(diene)_2Cl_2$. The displacement occurred readily, since the volatility of butadiene tends to drive it to completion:

$$2\ Rh(C_4H_6)_2Cl+2\ diene \rightarrow Rh_2(diene)_2Cl_2+4C_4H_6 \tag{2}$$

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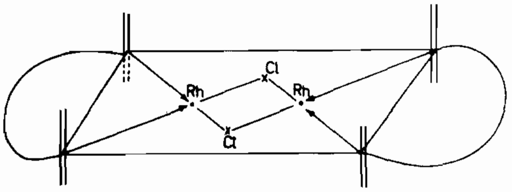
(*) $Rh_2(diene)_2Cl_2$ complexes will be denoted as Rh(1)—Rh(9).

[1] H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.* 86, 1066 (1967).

Particularly the synthesis of the cyclooctatetraene complex by this method was more convenient and led to a considerable improvement of the yield reported in the literature*.[2] Cyclohexa-1,4-diene could not be coordinated to monovalent rhodium.

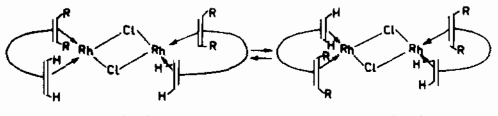
Tetraethylene or tetracarbonyldirhodium dichloride complexes can also be used as starting materials; the complexes obtained from the tetraethylene compound, however, were in general impure.

The complexes thus synthesized are dimeric and diamagnetic; the rhodium has a planar four-coordinate $dsp^2$ hybridized state. This is concluded from the X-ray structure of $Rh_2$(cycloocta-1,5-diene)$_2Cl_2$[3] and by analogy with isoelectronic divalent palladium complexes of bicyclo[2.2.1]hepta-2,5-diene[4] in which the double bonds of the chelating diene are located perpendicularly to the plane formed by the two metal atoms and the two chlorine atoms.



Coordination is not accompanied by isomerization; on treatment with potassium cyanide the original dienes were recovered quantitatively.

B. *Spectroscopic properties of the complexes $Rh_2$(diene)$_2Cl_2$.* The NMR spectra of solutions of the chelating dienes and those of the diene complexes in $CDCl_3$ were independent of the temperature between –80° and +100°**. The only exception appears to be Rh (7), whose NMR spectrum showed at –40° two broad signals for the olefinic protons at 5.77 and 4.50 ppm in the ratio of about 1 : 2. When the temperature is raised the signals broaden and finally coalesce to one sharp signal at 4.84 ppm at +60°. The line broadening was not affected by addition of the parent diene. The temperature-dependent behaviour is attributed to the occurrence of an interconversion process between two configurational isomers Rh ($7^A$) and Rh ($7^B$):



Rh(7A) Rh(7B)

The different environment of the olefinic hydrogens in Rh ($7^A$) and Rh ($7^B$) should give rise to the two signals. Opening of one of the chloride bridges by a solvent molecule would effect the interconversion of Rh ($7^A$) and Rh ($7^B$). A similar bridge splitting reaction is proposed to explain the rapid exchange between 1 and Rh (1)*.[1] An alternative explanation, involving alternating coordination of 7 as a bidentate and a monodentate (involving the carbomethoxy-substituted double bond) seems less likely.

The table lists NMR data for the chelating dienes and the complexes; in addition, some relevant IR data are given. The table shows that coordination of dienes results in general in a decrease in the double bond stretching frequency and in an upfield shift of the olefinic protons.

Considerable upfield shifts were also observed for the bridge methylene protons in bicyclo[2.2.2]octa-2,5-diene (2) and in bicyclo[2.2.1]hepta-2,5-diene (1). It is noteworthy that the chemical shifts of the methylene protons in the complex are present even at higher fields than in the corresponding saturated alkanes.[6]

2,3,5,6-Tetramethyl-7,8-bis(trifluoromethyl)bicyclo-[2.2.2]octa-2,5,7-triene (3) acts as a bidentate by coordination via the methyl-substituted double bonds.** The four methyl groups in the coordinated « diene » absorb at one frequency, 0.40 ppm upfield from the corresponding signal due to the free diene. Hence the methyl groups are magnetically and chemically equivalent. The doublet splitting of 1.1 c/s arises from rhodium coupling. The proposed coordination is supported by fluorine resonance, which shows the same chemical shift for the $CF_3$ group in the coordinated and the free ligand***.

C. *Exchange of dienes with $Rh_2$(diene)$_2Cl_2$.* NMR spectra of solutions of the chelating dienes (1 - 9) and the corresponding dimeric rhodium complexes in deuterochloroform in a molar ratio of 2 : 1 — in order to obtain equal intensities for the signals of the corresponding protons — were investigated in the temperature range –90° to +100°.

The results for the bicyclo[2.2.1]hepta-2,5-diene (1) system — the occurrence of a rapid exchange reaction above –40° via a penta-coordinate intermediate Rh-$(C_7H_8)_2Cl$, detectable below –40° — have been reported previously.[1] Of the remaining systems only that of bicyclo[2.2.2]octa-2,5-diene (2) shows a similar NMR spectroscopic behaviour: the spectra for the other systems were exactly a superposition of those of the complex and the corresponding diene over the whole temperature range. The life time of the dienes (3 - 9) has to be at least 1 second at 100°. For cycloocta-1,5-diene (5) line broadening was observed

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(*) Recently a similar preparation of the cyclooctatetraene complex has been reported by Bennett and Saxby.[2a]

(**) $Rh_2$(hexamethylbicyclo[2 2.0]hexa-2,5-diene)$_2Cl_2$ (Rh(4)) was stable in $CDCl_3$ for at least 24 hours at 100°. The observed catalysis of the valence isomerization of the parent diene into hexamethylbenzene by this rhodium complex cannot be ascribed to decomposition of the complex.[5]

(2) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.* 3178 (1959). J. Chatt and. L. M. Venanzi, *J. Chem. Soc.* 4735 (1957).

(2a) M. A. Bennett and J. D. Saxby, *Inorg. Chem. 7,* 321 (1968).

(3) J. A. Ibers and R. G. Snyder, *J. Am. Chem. Soc. 84,* 495 (1962). *Acta Cryst. 15,* 923 (1962).

(4) N. C. Baenziger, J. R. Doyle, and C. Carpenter, *Acta Cryst. 14,* 303 (1961).

(*) On the contrary, the rhodium complex of the asymmetric diene 8 does not exhibit two signals for the olefinic protons. This may be due to the large preference for one of the isomers or to a rapid interconversion even at low temperature.

(**) A similar mode of coordination is observed in $(C_{14}H_{14}F_6)Fe(CO)_3$: however, in $(C_{14}H_{14}F_6)Co(C_5H_5)$ the « diene » is coordinated asymmetrically via the trifluoromethyl-substituted and one of the methyl-substituted double bonds.[7]

(***) In $(C_{14}H_{14}F_6)\{(C_6H_5)_3P\}RhCl$, the $CF_3$ group absorbs at the same frequency (60.7 ppm) as observed for Rh(3) and (3); $CH_3$ groups 0.96 and 1.88 ppm.

(5) H. C. Volger and H. Hogeveen, *Rec. Trav. Chim. 86,* 830 (1967). H. C. Volger and M. M. P. Gaasbeek, *Rec. Trav. Chim. 87,* 1290 (1969).

(6) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem. 42,* 926 (1964).

**Table I.** NMR and IR data of chelating dienes (1 - 9) and of the π-dichlorobis(diene)dirhodium complexes; solvent $CDCl_3$; chemical shifts in ppm from TMS.

| | | | | |
|---|---|---|---|---|
| **Bicyclo[2.2.1]hepta-2,5-diene (1)** | | | | |
| δ | 1 | | Rh (1) | |
| H(2,3,5,6) | 6.82 (t) | Spacing 1.9 c/s* | 3.92 (t) | spacing 2.3 c/s* |
| H(1,4) | 3.60 (m) | | 3.85 | |
| H(7) | 2.00 (t) | J(1-7) 1.7 c/s | 1.17 | J(1-7) 1.4 c/s |
| ν(C=C) | 1550 $cm^{-1}$ | | 1449 $cm^{-1}$ | |
| **Bicyclo[2.2.2]octa-2,5-diene (2)** | | | | |
| | 2 | | Rh (2) | |
| H(2,3,5,6) | 6.32 (m)* | | 3.55 (m)* | |
| H(1,4) | 3.60 (m) | | 4.13 (m) | |
| H(7,8) | 1.24 (t) | J(1-7) 1.4 c/s | 0.96 (t) | |
| ν(C=C) | 1630 $cm^{-1}$ | | 1430 $cm^{-1}$ | ($CH_3SOCH_3$) |
| **2,3,5,6-Tetramethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (3)** | | | | |
| | 3 | | Rh (3) | |
| $CH_3$(2,3,5,6) | 1.73 | | 1.43 (d) | J(Rh—$CH_3$) 1.1 c/s |
| H(1,4) | 4.21 | | 4.67 | |
| $CF_3$*** | 61.2 | | 61.1 | |
| ν(C=C—$CH_3$) } | 1673 $cm^{-1}$ | | } 1492 $cm^{-1}$ | |
| ν(C=C—$CF_3$) } | 1705 $cm^{-1}$ | | } 1668 $cm^{-1}$ | |
| **Hexamethylbicyclo[2.2.0]hexa-2,5-diene (4)** | | | | |
| | 4 | | Rh (4) | |
| $CH_3$(C=C) | 1.65 | | 1.60 | |
| $CH_3$(tert. C) | 1.08 | | 0.87 | |
| ν(C=C) | 1685 $cm^{-1}$ | | 1505 $cm^{-1}$ | |
| **Cycloocta-1,5-diene (5)** | | | | |
| | 5 | | Rh (5) | |
| H(1,2,5,6) | 5.58 | | 4.20 | |
| H(2,4,7,8) | 2.49 | | 2.46; 1.71 | |
| ν(C=C) | 1660 $cm^{-1}$ | | | |
| **Cycloocta-1,3,5,7-tetraene (6)** | | | | |
| | 6 | | Rh (6) | |
| H | 5.73 | | 5.79 (non-coordinate double bonds)<br>4.26 (coordinated double bonds) | |
| ν(C=C) | 1640 $cm^{-1}$ | | 1412 $cm^{-1}$ | |
| **2,3-Dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene (7)** | | | | |
| | 7 | | Rh (7) | |
| H(5,6) | 6.88 (t) | Spacing 2.0 c/s | +60° 4.84 | −40° 4.50, 5.77 |
| H(1,4) | 3.89 | | 4.13 | 4.15 |
| H(7a) | 2.07 | AB pattern J(7a-7b) 7.2 c/s | 1.44 | } broad signal |
| H(7b) | 2.23 | J(1 -7b) 1.7 c/s | 1.66 | } |
| $COOCH_3$ | 3.74 | J(1 -7a) 1.6 c/s | 3.74 | 3.79 |
| **1,4-Dimethyl-2,3-dicarbomethoxy-7-oxa-bicyclo[2.2.1]hepta-2,5-diene (8)** | | | | |
| | 8 | | Rh (8) | |
| H(5,6) | 6.93 | | 4.72 (d) | J(Rh-H) 2.6 c/s |
| $CH_3$(1,4) | 1.69 | | 1.76 | |
| $COOCH_3$ | 3.69 | | 3.72 | |
| **Endo-tricyclo([5.2.1.$0^{2,6}$]deca-3,8-diene (9)** | | | | |
| | 9 | | Rh (9) | |
| H(3,4) | 5.25** | | 5.96, 4.06 | |
| H(8,9) | 5.70 | | 4.50 | |
| H(1,7) | 2.94 | | 3.18, 2.72 | |

* AA' pattern of AA'XX' spectrum  ** Assignment as given in API spectrum 244.  *** $^{19}F$ NMR relative to $CFCl_3$.

only from 130° onwards; for hexamethylbicyclo[2.2.0]hexa-2,5-diene (4) a slow irreversible valence isomerization of the diene into hexamethylbenzene was observed from 80° onwards.[5]

For bicyclo[2.2.2]octa-2,5-diene (2) the penta-coordinate species was detected below –90°. One broad signal of this species was present at 4.4 - 4.2 ppm. The amount of this species at –107° was estimated at 20-30%. The signals of the diene itself had a much lower intensity. We were not able accurately to determine the constant of the equilibrium between the three species. From –90° upwards line broadening of the signals was observed. At 70° three signals were present: two broad signals at 5.54 and 3.67 ppm of the olefinic protons and of the bridgehead protons, respectively, and one sharp signal at 1.16 ppm owing to the bridge methylene groups.

The slow exchange method was applied for the signal at 6.32 ppm to obtain $1/\tau$ values. A plot of log $(1/\tau)$ versus the reciprocal of the absolute temperature appears to be linear; the activation parameters were calculated to be 3.8 kcal.mole$^{-1}$ and $10^{5.0}$ sec$^{-1}$ (pseudo-first-order frequency factor). (For bicyclo-[2.2.1]-hepta-2,5- diene these values were 4.6 kcal.mole$^{-1}$ and $10^{6.2}$ sec$^{-1}$)[1]. Hence bicyclo[2.2.2]-octa-2,5-diene (2) exchanges at about the same rate as bicyclo[2.2.1]hepta-2,5-diene (1); for both systems the rates are at least $10^3$-$10^4$ times faster than for all other systems (3 - 9). The large similarity with the bicyclo-[2.2.1]hepta-2,5-diene (1) system renders it likely that the same mechanism is involved in the exchange process of 2.

D. *Displacement reactions.* Addition of an appropriate amount of a chelating diene to a solution of a rhodium complex of a different diene gives rise to a displacement according to:

$$2\ \text{diene}^* + \text{Rh}_2(\text{diene})_2\text{Cl}_2 \rightleftharpoons 2\ \text{diene} + \text{Rh}_2(\text{diene})^*_2\text{Cl}_2 \qquad (1)$$

The extent of the displacement was measured by integration of suitable NMR signals of the four components in the reaction mixtures. Equilibration was generally rapid at room temperature. The integration was carried out at –60° in order to avoid the complications of the rapid exchange reactions when 1 or 2 is involved.

The decreasing order of chelating dienes with respect to their coordination ability towards monovalent rhodium is as follows:

$$K = \begin{array}{l} \text{C}_7\text{H}_8(1) \underset{3}{>} \text{C}_8\text{H}_{10}(2) \underset{2}{>} \text{C}_{14}\text{H}_{14}\text{F}_6(3) \geqslant \text{C}_8\text{H}_{12}(5) \underset{80}{>} \\ \underset{80}{>} \text{C}_{11}\text{H}_{12}\text{O}_4(7) \geqslant \text{C}_{10}\text{H}_{12}(9) \underset{100}{>} \text{C}_{12}\text{H}_{18}(4) \underset{10}{>} \text{C}_{12}\text{H}_{14}\text{O}_5(8) \underset{6}{>} \text{C}_8\text{H}_8(6) \end{array}$$

The constant $K = \dfrac{[\text{diene}]^2[(\text{Rh}_2(\text{diene})^*_2\,\text{Cl}_2]}{[\text{diene}^*]^2[(\text{Rh}_2(\text{diene})_2\text{Cl}_2]}$ denotes the equilibrium between the next nearest neighbours.

The displacement of hexamethylbicyclo[2.2.0]hexa-2,5-diene (4) from the rhodium complex by bicyclo-[2.2.1]hepta-2,5-diene (1) was kinetically studied by NMR at –5°. For the secondorder rate constant we found the value $0.2 \times 10^{-2}$l . mole$^{-1}$sec$^{-1}$. The displacement clearly occurred in two stages via the intermediate formation of the mixed complex $\text{Rh}_2(\text{C}_7\text{H}_8)(\text{C}_{12}\text{H}_{18})\text{Cl}_2$. This was evidence by the appearance of a signal at 0.90 ppm, ascribed to the bridgehead methyl groups of $\text{C}_{12}\text{H}_{18}$, which after an initial increase in intensity completely disappeared. The maximum concentration of the mixed complex was estimated to be 30%.

## Discussion

We will first discuss the thermodynamically controlled coordination stability of the chelating dienes and subsequently the kinetically controlled exchange.

The relative order in coordination stabilities of the rhodium complexes of the chelating dienes (1 - 9) is thought to be due to (i) the geometry of the diene and (ii) the nature of the substituents. Both factors will be important in creating conditions favourable for bond formation, *i.e.* maximum overlap between and matching of the energy levels of the molecular orbitals involved in the bonding*. Lack of quantitative data on the bond angles and distances for most of the dienes — coordinated and uncoordinated — renders it difficult to discuss the effect of the geometry on a quantitative basis. However, some general remarks can be made.

The most stable complexes are those of bicyclo-[2.2.1]-hepta-2,5-diene and bicyclo[2.2.2]octa-2,5-diene; the largely similar coordination ability is due to the similar geometry of the dienes. The dihedral angle** and the distance between the double bonds for bicyclo[2.2.1]hepta-2,5-diene are reported to be 106° and 2.44 Å [9] and are about equal to those in the palladium dichloride complex (103.4° and 2.44 Å).[5] For bicyclo[2.2.2]octa-2,5-diene, the values for the uncoordinated diene may well be a little higher (120° and 2.5 Å, respectively). The failure to prepare a stable complex from cyclohexa-1,4-diene has to be ascribed to the planarity of the molecule;[10] the distance between the double bonds (2.497 Å) is about equal to that in bicyclo[2.2.1]hepta-2,5-diene (1). The instability of the complex of endo-tricyclo[5.2.1.0$^{2,6}$]deca-3,8-diene (9) is probably due to the non-parallel location of — and the large distance (3.12 Å) between — the double bonds.

For cycloocta-1,5-diene (5) and cycloocta-1,3,5,7-tetraene (6) the situation is more complicated. Apart

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(*) Winkhaus and Singer reported a greater stability for the cycloocta-1,5-diene complex compared to the bicyclo [2.2.1] hepta-2,5-diene complex[8]. However, they used thermal-and oxidation stability as their critcria.

(7) R. B. King, *J. Am. Chem. Soc. 84,* 4705 (1962).

(8) G. Winkhaus and H. Singer, *Chem. Ber.* 99, 3602 (1966).

(*) The effect of the increase in negative charge density on the metal (causing an upwards shift of the energy levels of the metal orbitals) on the relative stabilities is illustrated by the fact that cycloocta-1,3,5,7-tetraene (6) forms a more stable complex with zero-valent nickel (Ni(diene)$_2$) than cycloocta-1,5-diene (5).[11]

(**) The dihedral angle mentioned here is not exactly the same as the dihedral angle between the planes of the double bonds in the coordinated diene. The rehybridization, resulting from coordination, would lead to a non-planar arrangement of the substituents with the double bond. Sufficient quantitative data for the deviation from planarity are lacking, however.

(9) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim. 87,* 805 (1968).

(10) G. Dallinga and L. H. Toneman, *J. Mol. Structure 1,* 117 (1967).

from the geometric factors mentioned above, we have also to consider the difference in flexibility between the free and the coordinated diene. On the one hand, coordination will involve a considerable loss in entropy, thus making complex formation relatively unfavourable. On the other hand, flexibility may also favour coordination since the diene can assume an optimal conformation, thus strengthening the bond with the metal. The equal distance between the double bonds in Rh (5) and the free diene (2.87 and 2.8 Å, resp.)[2,3] suggests a relatively strong bond apart from the effect of the dihedral angle and the entropy. The instability of the cyclooctatetraene complex is probably due to the large distance between the non-conjugated double bonds (3.12 Å)[12] combined with the unfavourable entropy effect and the loss of conjugation resulting from coordination of the tetraene.

The effect of substituents on the stability of the monovalent rhodium complexes has already been investigated by Cramer for monoolefins.[13] He found that electron-withdrawing substituents stabilize the complexes; the opposite was found for electron-donating substituents. It was inferred that the contribution of the π-backbond to the overall olefin-rhodium bond strenght is large relative to that of the σ-bond (involving the overlap between the filled π-orbital of the olefin and an empty d or dπ-pπ-hybridized orbital of the metal). In addition, steric-destabilizing effects of the substituents have to be superimposed on the electronic effects.

The above-mentioned destabilizing effect of electron-donating substituents is encountered in the complexes (Rh (3)) (compared with Rh (2)) and Rh (4). The contribution of the geometric factors is estimated to be rather small. The X-ray analysis of $Cr(CO)_3$-$(C_{12}H_{18})$ revealed a dihedral angle of 113° and a distance between the double bonds of 2.54 Å[14] about equal to that in I. The low stability of the asymmetric dienes 7 and 8 is rather surprising, considering the electron-withdrawing character of the carbomethoxy group. It may well be that the favourable effect is entirely counterbalanced by a large steric hindrance of the substituent.

The rapid exchange (relative to the NMR time scale) of the bicyclo[2.2.1]hepta-2,5-diene 1 and bicyclo[2.2.2]octa-2,5-diene 2 systems has in common the formation at low temperatures of a penta-coordinate rhodium complex ($Rh(diene)_2Cl$). The mechanism proposed for the exchange comprises the formation of this pentacoordinate rhodium complex:[1]

$$\mathrm{Rh_2(diene)_2Cl_2} \rightleftharpoons \mathrm{(diene)Rh(Cl){-}Cl{-}Rh(diene)} \qquad (3)$$

$$\mathrm{diene + (diene)Rh(Cl){-}Cl{-}Rh(diene)} \overset{+4}{\rightleftharpoons} \mathrm{(diene)Rh(Cl){-}Cl{-}Rh(diene)_2} \qquad (4)$$

$$\mathrm{(diene)Rh(Cl){-}Cl{-}Rh(diene)_2} \overset{+5}{\rightleftharpoons} \mathrm{Rh(diene)Cl + Rh(diene)_2Cl} \qquad (5)$$

$$\mathrm{diene + Rh(diene)Cl} \rightleftharpoons \mathrm{Rh(diene)_2Cl} \qquad (6)$$

The rate-determining step is considered as either (+4) or (+5); the activation parameters are therefore related to $k_{+4}K_3$ or $k_{+5}K_3K_4$.

The rate of the exchange process is affected more by the nature of the coordinated than by that of the free diene. This is evidenced by the fact that bicyclo[2.2.1]hepta-2,5-diene (1) *slowly* displaces hexamethylbicyclo[2.2.0]hexa-2,5-diene (4) from its complex, while with coordinated bicyclo[2.2.1]hepta-2,5-diene (Rh(1) a rapid exchange reaction occurs.

The results can be accounted for by stating that the ability to form penta-coordinated species (reaction steps 4 and 5) is essential for the occurrence of a rapid exchange. Apparently, coordinated 1 and 2 effect a strong withdrawal of electrons from the metal, thus enhancing the actual charge on the metal and favouring penta-coordination Evidence for the stronger π-backbonding character of bicyclo[2.2.1]hepta-2,5-diene (1) relative to that of cycloocta-1,5-diene (5) has also emerged from the difference in reactivity of chloride ion with $(diene)Rh(Cl)(PPh_3)$.[15,16]

## Concluding Remarks

The geometry of the chelating diene and the electronic and steric effects of its substituents primarily determine the coordination ability towards monovalent rhodium. Thermodynamically most stable diene complexes appear to be kinetically the most labile ones.

The strength of the rhodium olefin bond is mainly governed by the π-backbonding character of the diene. Hence, the most strongly coordinated diene induces an increase in the actual charge on the rhodium atom and therefore favours penta-coordination. Formation of penta-coordinate species is thought to be essential to explain the kinetic lability.

## Experimental Part Section

The dienes used were commercially available, except 2,3,5,6-tetramethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (3) and bicyclo[2.2.2]octa-2,5-diene (2), which were prepared according to methods of Krespan[17] and Grob,[18] respectively.

The dimeric rhodium complexes $Rh_2(diene)_2Cl_2$ were prepared as follows. A suspension of $Rh(butadiene)_2$-Cl[19] (0.5 g) in 50 ml of pentane, treated with an equivalent amount of the diene, was stirred under a nitrogen atmosphere at room temperature. The precipitate collected appeared to be pure $Rh_2(diene)_2Cl_2$; yields 85-100%.

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The experimental details on the study of the exchange reaction have been reported previously.[1]

The composition of solutions of the dienes (0.24 molar) and different rhodium diene complexes (0.12 molar) were determined at room temperature by integration of appropriate NMR signals. The equilibrations were approached from both directions in order accurately to establish the composition of the reaction mixture. In the case of bicyclo[2.2.1]hepta-2,5-diene and bicyclo[2.2.2]-octa-2,5-diene the solutions were quenched at –60° in order to avoid overlap of broadened signals.