

MIXED ($\eta^2:\eta^4$)-COORDINATION OF *para*-SEMIQUINOID TRIENE LIGANDS (1-METHYLENE-4,4-DIALKYL-2,5-CYCLOHEXADIENES) WITH TWO TRANSITION METAL CENTRES IN BI- AND TRI-NUCLEAR RHODIUM(I) COMPLEXES

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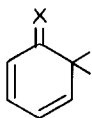
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Summary

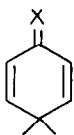
The reaction between $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and 1-methylene-4-methyl-4-R-2,5-cyclohexadienes (RC_8H_9) leads to binuclear complexes $[\text{Rh}(\text{acac})_2(\text{C}_2\text{H}_4)(\text{RC}_8\text{H}_9)]_2$, where $\text{R} = \text{CH}_3$, CHCl_2 and $n\text{-C}_4\text{H}_9$, in which triene ligands show a mixed ($\eta^2:\eta^4$) mode of coordination. The possibility of conversion of the binuclear complex ($\text{R} = \text{Me}$) into the trinuclear species $[\text{Rh}(\text{acac})]_3(\text{CH}_3\text{C}_8\text{H}_9)_2$ has been demonstrated. The reported ^1H NMR spectral evidence suggests an *anti*-stereospecific nature for all the reactions studied. Possibilities for both geometrical and optical stereoisomerism of the new semi-quinoid organometallics are discussed on the basis of the spectral data.

Introduction

Among unsaturated compounds, capable of coordinating transition metal centres, ligands with different (with respect to coordination) alkene fragments are of considerable interest. Triene *ortho*- and *para*-semi-quinoid molecules, such as I and II [1], having a diene ring system, exocyclic unsaturated fragments and a saturated geminal site can be classified in this group of ligands.

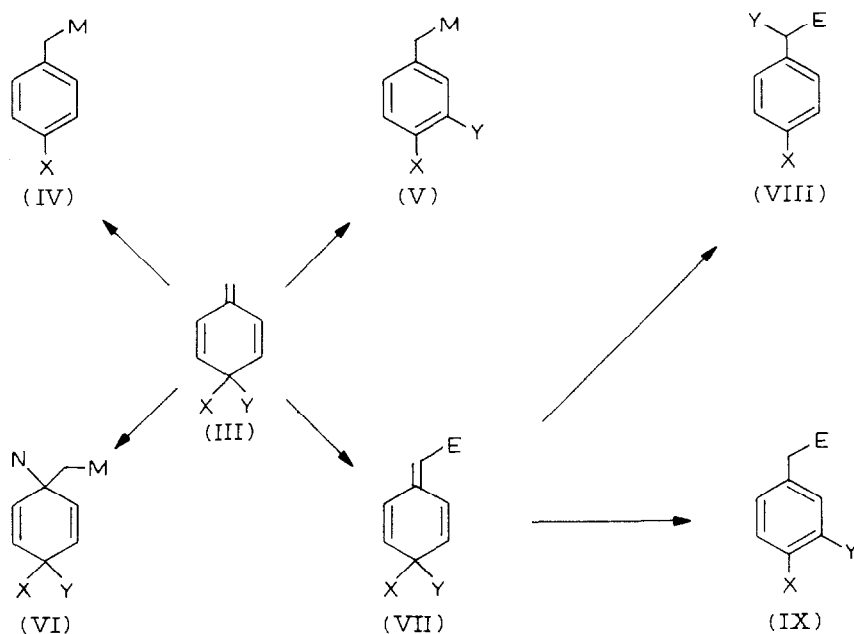


(I)



(II)

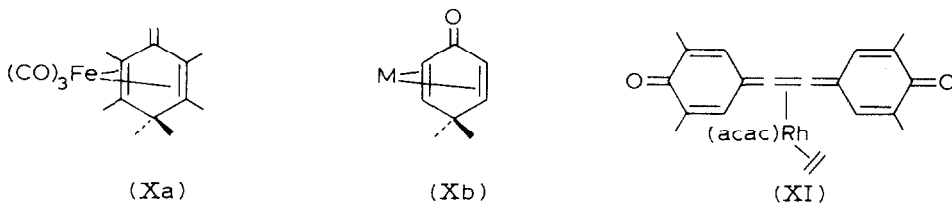
($\text{X} = \text{O}, \text{CR}_2, \dots$)



SCHEME 1

It has been shown earlier, Scheme 1, that the semiquinoid compounds (III), having H and Alk substituents of the geminal site, are capable of reacting with Hg, Sn, Ge and Au derivatives to give arylmethyl-organometallic compounds (IV) via electrophilic aromatization (the reaction of aromatizational metallation) [2-6]. When trienes of type III possess two geminal alkyl groups, they can, under the action of mercury or phosphorus containing reagents, undergo skeletal rearrangements (V) [7] or solvometallation (VI) [8], respectively. They may also undergo *exo*-metallation to afford *exo*-element-substituted *para*-semiquinoid systems (VII) [8]. Phosphorus derivatives of VII [9] were found to undergo subsequent skeletal isomerisations forming structures of the types VIII and IX [11].

On the other hand, interaction between trienes (III) and transition metals gave η^4 -bonding of the π -diene ring as in Xa [12a-c]. Similar bonding is observed in the case of *para*-semiquinoid dienones (Xb) [1,12d], while monoalkene η^2 -coordination



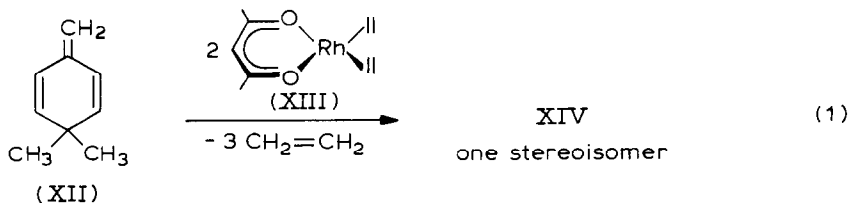
(M = Fe(CO)₃, Rh(acac))

through the central π -bond is realised for related diquinoethylene systems [13a]. The above-mentioned presence of *exo*-monoalkene and π -diene functions in trienes such as III could provide formation of polynuclear complexes, in which simultaneous bonding of both the functions with transition metals could occur. To study this

possibility, derivatives of monovalent rhodium [13b] have been chosen as model reagents, since they are known to form η^2 - as well as η^4 -type complexes readily.

Results and discussion

It has been found that the complex $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ (XIII) [14a] reacts with 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (XII) on gentle heating (36°C , pentane, 5 h) to produce the orange crystalline compound XIV, the process being practically independent of the ratio of the reagents (eq. 1). Analytical and ^1H NMR



spectral data (see Table 1, Fig. 1) of the compound are in full accord with a dual coordination mode of the triene, which appears to be an η^4 -coordinated ligand with respect to the first acetylacetonatorhodium fragment (cf. [1]) and at the same time, an η^2 -coordinated ligand with respect to the second rhodium fragment; the remaining coordination site of the latter is occupied by an ethylene molecule.

The AA'BB'XX' spin system of the starting triene XII treated in terms of an AMX approximation is given in Table 1. For its rhodium derivative XIV, nonequivalence of all four vinylic ring protons and both exomethylene protons is observed (Fig. 1). An evident similarity of chemical shifts of the two latter protons (δ 1.98 and 3.51 ppm) with corresponding signals from *i*-H (inner) and *o*-H (outer) protons of the coordinated 1,5-hexadiene in the known complex $\text{Rh}(\text{acac})(\text{C}_6\text{H}_{10})$ (δ 1.8 and

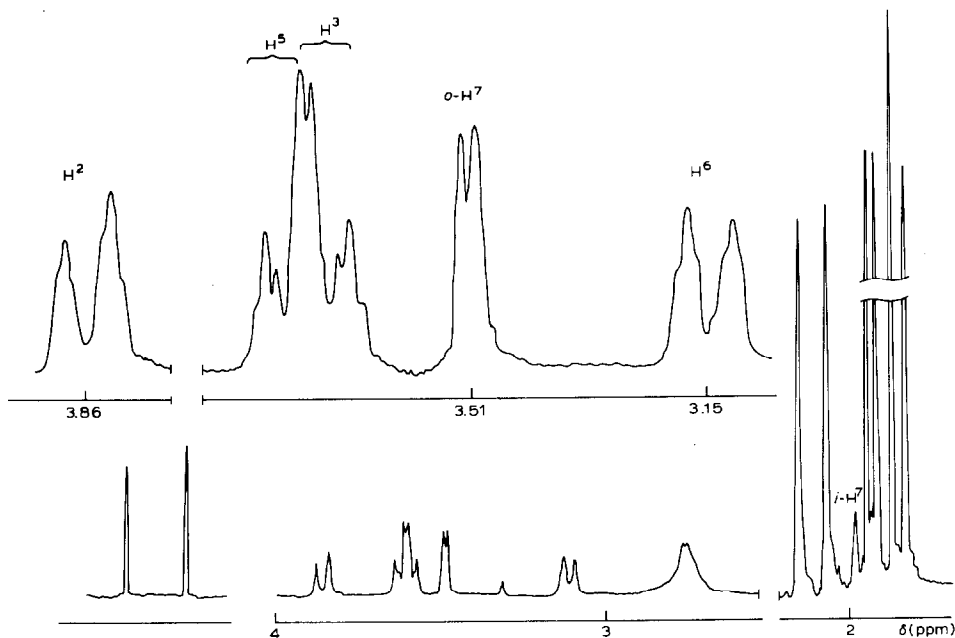
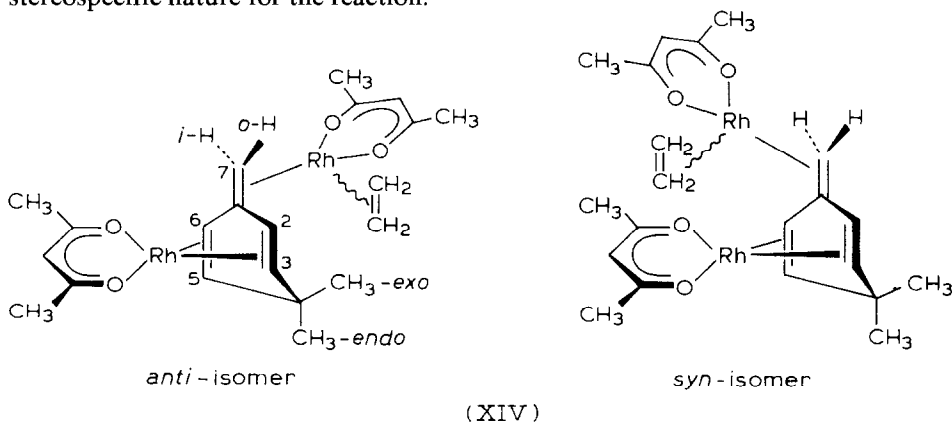


Fig. 1. ^1H NMR spectrum of the binuclear rhodium complex XIV.

3.19 ppm, respectively) [14a] (cf. [14b]) allowed assignment of these to the nonequivalent *exo*-methylene *i*-H⁷-*o*-H⁷ protons of XIV, the relative integral intensities of these signals being also in accord with the assumption. One may assume that the signal from H⁶ of the four nonequivalent ring protons, which is close to the shielded *i*-H⁷ proton, should be also observed in the highest field, while the signal from H² (close to *o*-H⁷) should be observed in the lowest field (see Fig. 1). However, assignment of additional splittings of all the protons to either coupling between themselves or with the ¹⁰³Rh nuclei (as well as an assignment of the H³ and H⁵ resonances) could not be explained in such simple terms. Therefore, experiments using the double homonuclear resonance technique have been carried out. Irradiation of the sample at the frequency of the H² proton (δ 3.86 ppm) proved its spin coupling with H³ (δ 3.61 ppm, J 6.7 Hz) and the absence of such coupling (within 0.5 Hz accuracy) with other protons of the molecule. Irradiation of H⁶ (δ 3.15 ppm) showed that this proton is coupled with H⁵ (J 6.7 Hz). Irradiation of both H⁵ and H³ (δ 3.65 and 3.61 ppm) provided additional support that these are coupled (J 6.7 Hz) with the protons H⁶ and H², respectively. Finally, irradiation of the signals from *o*-H⁷ and *i*-H⁷ (δ 3.51 and 1.98 ppm) did not lead to any perceptible spectral changes.

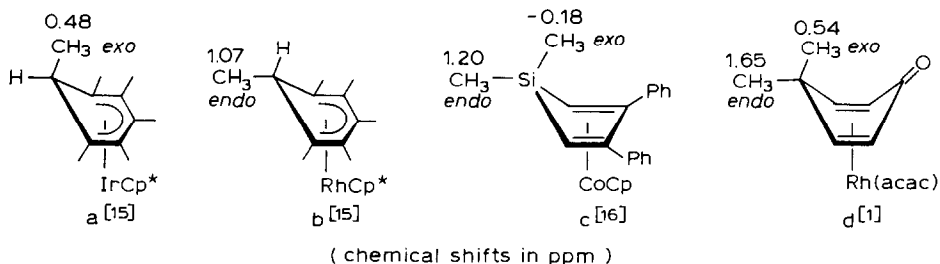
Since in all cases the signals from the ring vinyl protons retained their triplet-like form unchanged ($J \approx 1$ Hz) and those from *o*-H⁷ remained characteristic doublets (J 2.3 Hz) the experiment proved that all the ring protons were coupled with both ¹⁰³Rh nuclei, while *o*-H⁷ was only coupled with a single Rh nucleus (probably, with the η^2 -coordinated one). The absence of visible *i*-H⁷-Rh (η^2) coupling may arise from different Rh-C⁷-*o*-H and Rh-C⁷-*i*-H bond angles.

The positions of methyl resonances in the ¹H NMR spectra of the compounds in Table 1 are noteworthy. Since for all compounds obtained the possibility for geometric isomerism exists, arising from a *syn*- or *anti*-arrangement of the two rhodium atoms with respect to the semi-quinoid "plane" (see structure XIV)*, it should be noted that observation in the spectrum of XIV of only two, not four, methyl resonances indicates the presence of an individual isomer and indicates a stereospecific nature for the reaction.



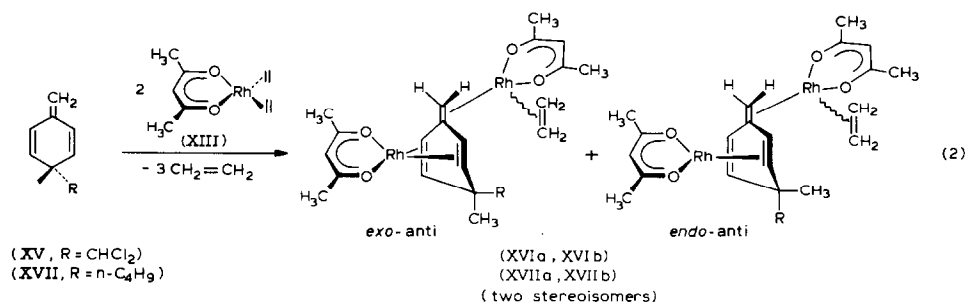
* Configurational designation of the stereoisomeric complexes discussed is accepted on the basis of mutual array of Rh(acac) and Rh(acac)(C₂H₄) moieties. For the present, the schematic representation of this complex (and others below) will not specify in detail the geometry of the *exo*-methylene fragment relative to the ring plane.

There is a common feature in the ^1H NMR spectra of mononuclear organometallic compounds having differently oriented methyl groups in the geminal site (a–d). This is manifested in definite deshielding of their *endo*-methyl groups which is accompanied by pronounced shielding of *exo*-methyl groups. The absence of such



nonequivalence of the methyl groups in the binuclear complex XIV, where they both appear to be deshielded, Table 1, is in better agreement with *anti* configuration for the compound, since only in the case electronic and steric factors, affecting from opposite sides of the semiquinoid "plane", can compensate the spectral differences of the *exo*- and *endo*-methyl. It also should be pointed out that the *anti* configuration of the complexes is also favoured for steric reasons, since in this case steric constrain might be much lower than in the case of *syn* isomers. This steric factor may account for the stereospecificity of the reaction.

The general occurrence of this reaction, leading to organorhodium species with a mixed coordination mode, was confirmed by going to semiquinoid trienes with dichloromethyl XV and *n*-butyl XVII groups in their geminal site. Complexes XVI and XVIII isolated in these cases also contain one molar equivalent of both triene and ethylene and two molar equivalents of acetylacetonatorrhodium(I) (eq. 2).



It has been found by ^1H NMR spectroscopy that compounds XVI and XVIII are mixtures of two stereoisomers (Table 1). This follows from the characteristic doubling of all resonances (Fig. 2) and seems to result from different arrangements of two different geminal substituents. Fractional crystallization of XVI and XVIII from hexane gave less soluble dark-red crystals of the individual isomers XVIa and XVIIIa. Since in all the spectra of these stereoisomers the signals from the methyl groups as well as CHCl_2 and CH_2Pr fragments are considerably deshielded compared to the free trienes XV and XVII, one can suggest *anti*-configuration for these compounds, as in XIV, stereoisomers XVIa, b and XVIIIa, b being different in the *exo*- and *endo*-arrangements of the CH_3 and R groups with respect to the η^4 -rhodium atom.

TABLE 1. ¹H NMR SPECTRAL DATA FOR COMPOUNDS XII AND XIV-XIX (δ (ppm), J (Hz))

Compound	Solvent	Triene fragment		CH ₃	H ⁵ , H ³ -quartet / (J(H ² H ³))	H ⁵ , H ⁶ -quartet (J(H ⁵ H ⁶))	<i>i</i> -H ⁷ /	<i>o</i> -H ⁷ ^g	Acac-fragment		CH ₂ =CH ₂ (br)
		R	CH ₃						CH ₃	H	
XII	C ₆ D ₆	-	1.05	5.16-6.14 (10.0)	4.88	-	-	-	-	-	-
XIV	CDCl ₃	-	2.07	3.15-3.65 (6.7)	1.98	3.61-3.86 (6.7)	1.88	3.51	1.84	1.88	5.18
XIV	C ₆ D ₆	-	2.15	3.27-3.70 (6.7)	2.06	3.92-4.40 (6.7)	1.95	3.88	1.93	1.95	5.36
XVII	C ₆ D ₆	1.35 ^a	1.04	5.59-6.36 (10.0)	4.95	-	-	-	1.76	1.78	5.10
XVIIIa	CDCl ₃	2.64-3.12 ^a	2.16	3.18-3.64 (6.7)	1.83	3.58-3.88 (6.7)	1.88	3.45	1.82	1.88	5.18
XVIIIb	C ₆ D ₆	2.72-3.38 ^a	2.21	3.29-3.80 (6.7)	1.89	3.86-4.34 (6.7)	1.95	3.78	1.93	1.95	5.36
XVIIIb	CDCl ₃	^b	2.15	3.15-3.69 (6.7)	^b	3.65-3.88 (6.7)	1.75	3.49	1.72	1.75	5.10
XV	C ₆ D ₆	5.36	1.20	5.65-6.12 (10.5)	4.80	-	1.85	-	1.84	1.85	5.25
XVIa	CDCl ₃	9.61	2.33	3.24-3.90 (6.7)	2.13	3.86-3.97 (6.7)	1.88	3.62	1.88	1.90	5.22
XVIa	C ₆ D ₆	10.10	2.48	3.24-3.83 (6.7)	2.02	3.93-4.38 (6.7)	1.98	3.69	1.95	1.98	5.40
XVIIb	CDCl ₃	7.79	2.37	3.26-3.72 (6.7)	2.02	3.68-3.97 (6.7)	1.86	3.51	1.84	1.86	5.22
XVIIb	C ₆ D ₆	7.80	2.59	3.84-4.10 (6.7)	1.96	4.25-4.43 (6.7)	1.98	3.85	1.96	1.98	5.40
XIX	CDCl ₃	-	2.15 ^c	3.31 ^d -3.64 ^d (6.5)	1.88 ^d	3.53 ^d -3.64 ^d (6.5)	1.72	3.15 ^d	1.84 ^c	1.72	5.04
XIX	C ₆ D ₆	-	2.21 ^c	3.48 ^d -3.85 ^d (6.5)	2.04 ^d	3.85 ^d -4.15 ^d (6.5)	1.89 ^k	3.54 ^d	1.72 ^c	1.85 ^c	5.34 ^d
			2.28 ^c				1.67 ^c		1.93 ^c	1.85 ^c	5.26 ^d
										1.85 ^c	5.02

^a Signals of α-methylene protons are given; signals of the remaining seven protons fall in the range δ 0.8-1.30 ppm (multiplet). ^b Obscured by neighbouring resonances; relative integral intensities are: ^c 6H, ^d 2H. ^e 12 H. / The components of these signals additionally split into triplets due to coupling with both ¹⁰³Rh nuclei (J ~ 1 Hz). ^g These signals appear as doublets due to coupling with one ¹⁰³Rh nucleus (J ~ 2 Hz).

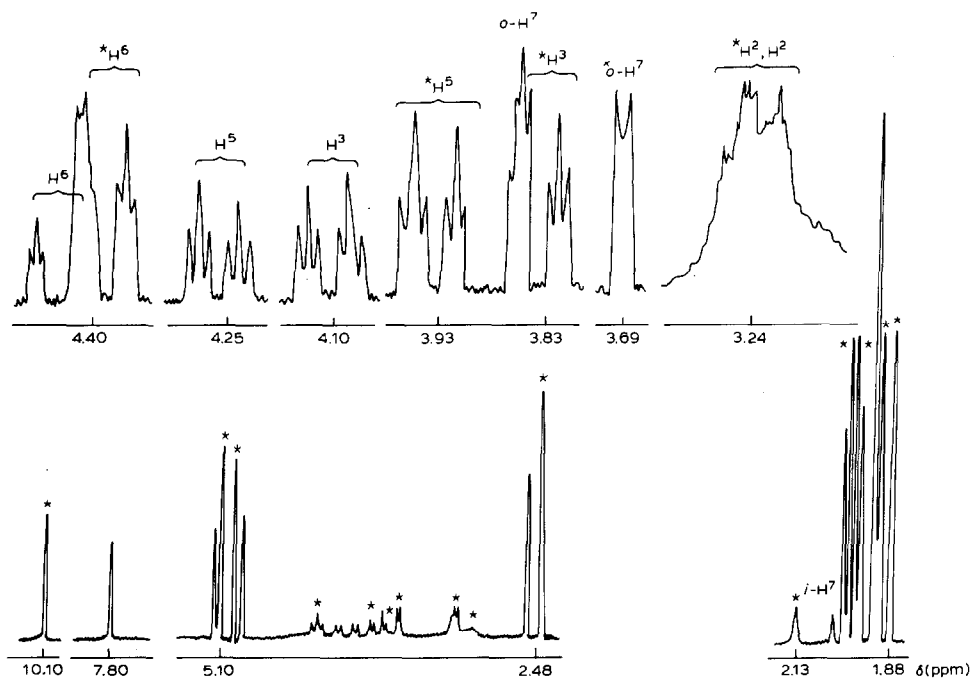


Fig. 2. ^1H NMR spectrum of a mixture (3/2) of the stereoisomers XVIa and XVIb. Signals from the major isomer are indicated with an asterisk.

Another remarkable feature of the new binuclear complexes is their chirality (Fig. 3) providing anisochronicity for all vinylic protons and four methyls of acetylacetonate ligands in the ^1H NMR spectra (Table 1). Complex XVIIIa gives, however, additional independent evidence to support its chiral nature. Using the

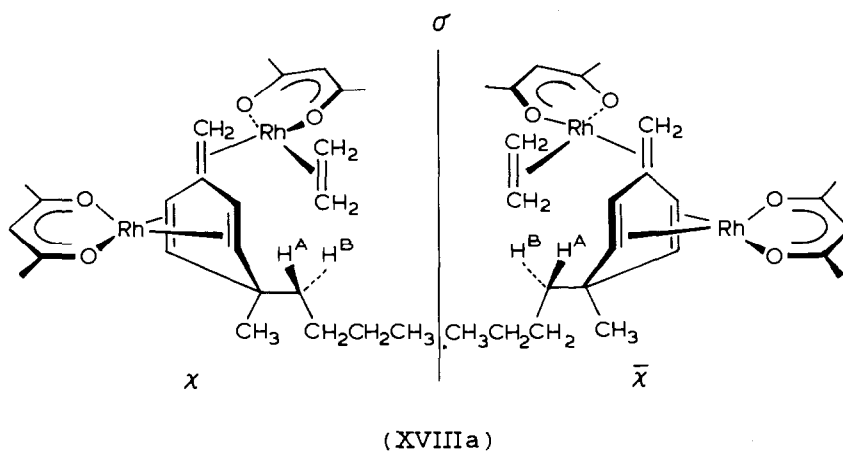


Fig. 3. Chirality in binuclear rhodium complexes with semiquinoid and ethylene ligands (enantiomers XVIIIa are shown as examples).

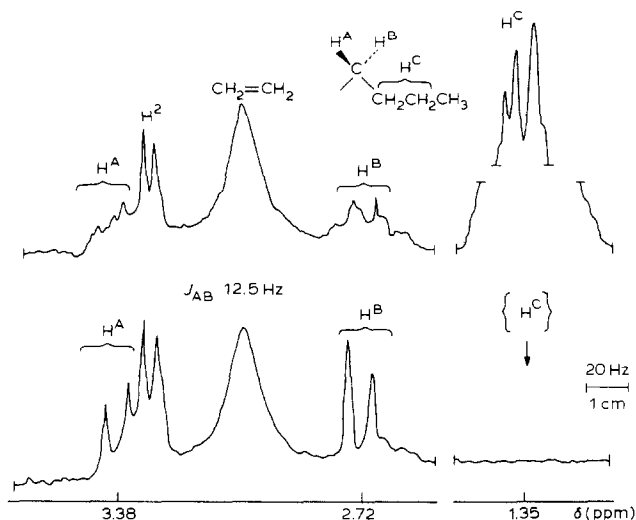


Fig. 4. A study of a high field part of the ^1H NMR spectrum of the binuclear rhodium complex XVIIIa by a double homonuclear resonance technique.

double homonuclear technique it has been (Fig. 4) that two multiplets at δ 3.38 and 2.72 ppm (C_6D_6), with 1H integral intensity each, refer to two nonequivalent α -methylene protons of the n-butyl substituent, which are mutually coupled with 2J 12.5 Hz. It should be noted that a marked difference in the chemical shifts (anisochronicity) of the two diastereotopic protons $\Delta\delta_{\text{AB}}$ 0.66 ppm, which is rather unusual with saturated alkyl chains, may be considered as a definite indication of the fact that the $\text{C}_3\text{H}_7\text{CH}^{\text{A}}\text{H}^{\text{B}}$ group and the chirogenic element of the molecule ($\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)$ substituent) are close thereby suggesting an *anti-exo* configuration for XVIIIa.

All organorhodium compounds obtained are stable in the crystalline state, but decompose on heating in air or in vacuo making their study by mass spectrometry impossible. They possess good solubility in common organic solvents (but are less soluble in saturated hydrocarbons) to afford red solutions. At room temperature (more rapidly on heating) the dissolved complexes decompose, within a few days, liberating free trienes and a rhodium-containing substance of unknown structure which, according to ^1H MNR data, has acac ligand. Free trienes are also produced by treating cooled solutions of XVI and XVIII with an excess of ethylene, demonstrating the reversible nature of the corresponding ligand exchange reaction (eqs. 1, 2).

Further, we have found that on heating a heptane solution of XIV (98°C , 2 h) the formation of a novel violet crystalline product in high yield results, which according to analytical and ^1H NMR spectral data has no ethylene ligand.

The ^1H NMR spectrum of the compound obtained is presented in Fig. 5. There are two singlet resonances with relative integral intensities 1H and 2H in the region of methyne acetylacetonato protons and three singlets each of 6H intensity in the region of methyl-acac signals. Such a pattern is indicative of the presence of three acac ligands in the complex, two of which are equivalent. Further, the intensities of

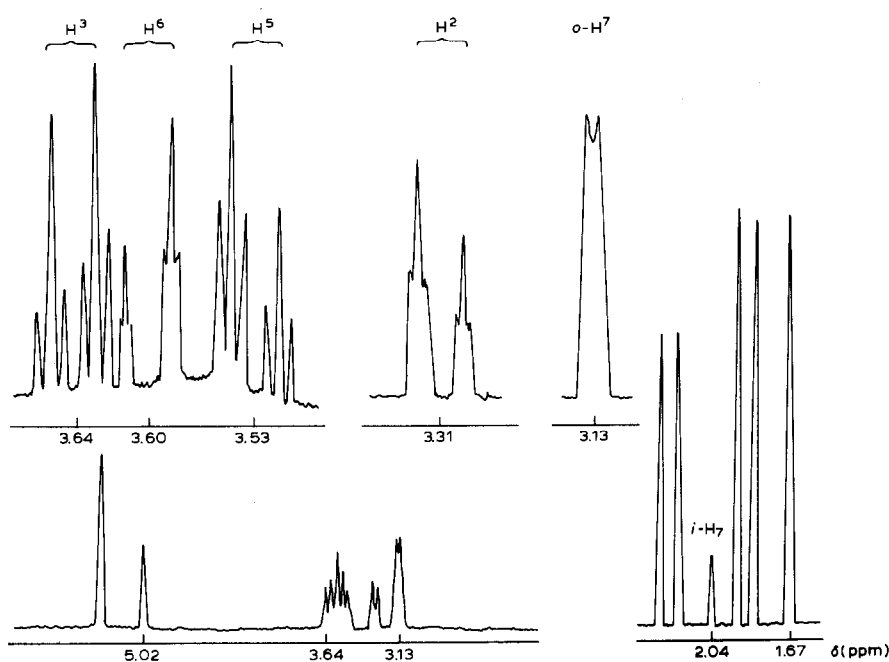
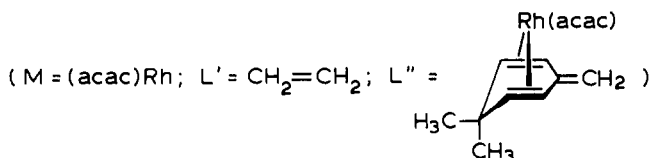
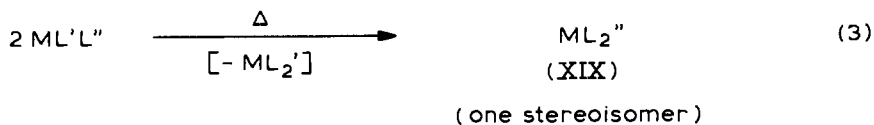


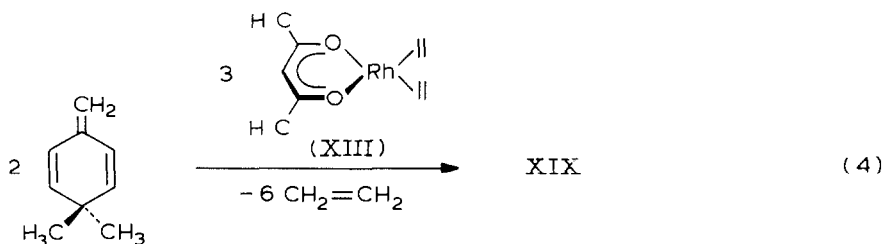
Fig. 5. ^1H NMR spectrum of the trinuclear rhodium complex XIX.

the remaining signals correspond to the presence of two equivalents of triene XII. All the data obtained show that the resulting compound is a trinuclear complex, in which two *para*-semiquinoid ligands are η^4 -bound with acetylacetonatorhodium fragments via π -diene ring systems and, at the same time, η^2 -bound with the central acetylacetonatorhodium fragment via *exo* cyclic methylene groups.

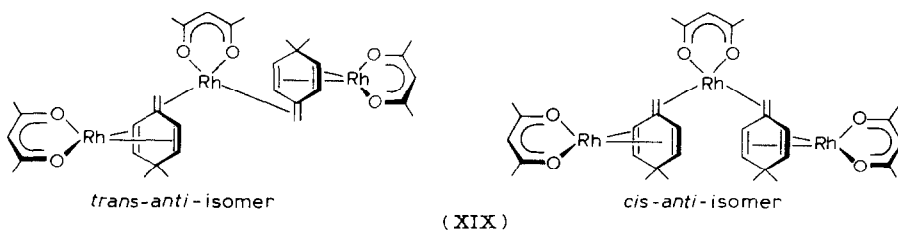
Stoichiometry features of the reactions studied suggest that the process (eq. 3) may be considered as a novel example of the peculiar symmetrization of XIV having two different types of π -ligands (coordinated triene and ethylene), which leads to complex XIX with a coordinated triene as a single type of π -ligands.



A similar result is achieved when a reaction between triene XII and complex XIII is carried out in refluxing heptane, the optimal ratio of the reagents being 2/3 (eq. 4).



Complex XIX might, in principle, possess conformational isomerism due to rotation of two coordinated triene ligands around the metal–ligand bond. However, as in the cases discussed above involving binuclear rhodium complexes (eq. 1), the reaction (eq. 3, 4) also proceeds stereospecifically leading to a single stereoisomer of the trinuclear complex, a less sterically constrained *trans-anti** configuration (XIXa) seems to be more probable.



Experimental

^1H NMR spectra were obtained on a Bruker-WP-200SY spectrometer (200 MHz) in C_6D_6 or CDCl_3 solutions. For measuring chemical shifts the residual signals from $\text{C}_6\text{D}_5\text{H}$ (δ 7.25 ppm) and CHCl_3 (δ 7.27 ppm) of the corresponding solvents were used. Recordings were made with a linewidth not more than 0.2 Hz per channel. To improve the spectral quality an approach involving mathematical line sharpening was used. The delay between impulses during signal storage was 10 s. Thin-layer chromatography was performed using Silufol UV-254 plates (solvent ether/pentane, 1/2).

The starting trienes XII and XV were obtained by dehydration of the corresponding 1,4-dimethyl-4-alkyl-2,5-cyclohexadienols-1 [17,18] according to ref. 19. The triene XVII was obtained as described in ref. 20. Complex XIII was prepared by a known procedure [14a].

Preparation of XIV, XVI and XVIII

Solutions of 0.2 mmol of the trienes XII, XV or XVII and 0.4 mmol XIII in 50 ml pentane were refluxed. Reaction progress was followed by TLC. After 5 h the solutions turned red with almost complete disappearance of the starting complex XIII (R_f 0.5) and formation of the products XIV, XVI, or XVIII (R_f 0.3–0.4). The resulting solutions were filtered and the filtrates were cooled. The crystalline precipitates were separated, washed with pentane and dried in vacuo. The mother

* Descriptions *cis*- and *trans* refer here to characterize mutual arrangement of two coordinated triene ligands relative to the central rhodium chelate ring plane.

liquors after concentration gave additional portions of the complexes. Total yields were 75–80%.

(η^2 -Ethylene)(4,4-dimethyl-1- η^2 -methylene(2,5- η^4 -cyclohexadiene)rhodium-2,4-*O,O'*-pentadionato)rhodium-2,4-*O,O'*-pentadionato (XIV). M.p. 196°C (dec.). Found: C, 45.75; H, 5.60. $C_{21}H_{30}O_4Rh_2$ calcd.: C, 45.70; H, 5.43%.

(η^2 -Ethylene)(4-methyl-4-dichloromethyl-1- η^2 -methylene)(2,5- η^4 -cyclohexadiene)rhodium-2,4-*O,O'*-pentadionato)rhodium-2,4-*O,O'*-pentadionato (a 3/2 mixture of the stereoisomers XVIa and XVIb by 1H NMR). M.p. 160°C (dec.). Found: C, 41.00; H, 4.61; Cl, 11.44. $C_{21}H_{28}O_4Cl_2Rh_2$ calcd.: C, 40.61; H, 4.51; Cl, 11.43%.

(η^2 -Ethylene)(4-methyl-4-*n*-butyl-1- η^2 -methylene)(2,5- η^4 -cyclohexadiene)rhodium-2,4-*O,O'*-pentadionato)rhodium-2,4-*O,O'*-pentadionato (a 7/3 mixture of the stereoisomers XVIIIa and XVIIIb by 1H NMR). M.p. 146°C (dec.). Found: C, 48.30; H, 6.49. $C_{24}H_{36}O_4Rh_2$ calcd.: C, 48.51; H, 6.06%.

Isolation of individual isomers XVIa and XVIb

100 mg of the above mixture of XVIa and XVIb (or XVIIIa and XVIIIb) were dissolved in 40 ml hexane and after a short reflux filtered. The filtrate was concentrated to 25 ml and allowed to stand at room temperature. Crystals formed were washed with pentane and dried in vacuo. Yield 35–40 mg. M.p.: 151°C (dec.), XVIIIa 168°C (dec.).

Preparation of XIX

(A). A solution of XIV (50 mg) in 15 ml heptane was refluxed. Reaction progress was controlled by TLC. The colour of the solution turned from red to violet with concomitant appearance of traces of XII (R_f 0.5), disappearance of the starting material (R_f 0.35) and formation of the product XIX (R_f 0.2). After 2 h heating was stopped, and an unidentified brown precipitate was filtered off, the filtrate was concentrated and then cooled. Dark violet crystals, that had formed were washed with pentane and vacuum dried. Yield 34.2 mg (90%).

(B). A solution of the triene XII (48 mg, 0.4 mmol) and complex XIII (155 mg, 0.6 mmol) in 40 ml heptane was refluxed for 2 h. The reaction mixture was worked up as described in (A) to yield 127 mg of XIX (75%) bis(4,4-dimethyl-1- η^2 -methylene(2,5- η^4 -cyclohexadiene)rhodium-2,4-*O,O'*-pentadionato)rhodium-2,4-*O,O'*-pentadionato (XIX). M.p. 189°C (dec.). Found: C, 46.85; H, 5.57. $C_{33}H_{45}O_6Rh_3$ calcd.: C, 46.83; H, 5.32%.

Interaction between XVI and XVIII with ethylene

A solution containing 0.01 mmol XVI or XVIII in 10 ml pentane was heated to reflux and cooled down to $-70^\circ C$ under ethylene atmosphere. After 5 min a change in colour of the solution from red to yellow and formation of a yellow crystalline precipitate of XIII was observed. The presence of XIII (R_f 0.5) and free trienes XV and XVIII (R_f 0.3) was detected in the solutions by TLC.

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