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π-CYCLOHEXADIENONE DERIVATIVES OF RHODIUM(I) ACETYLACETONATE. CRYSTAL AND MOLECULAR STRUCTURE OF RHODIUM (η^4-4-METHYL-4-*exo*-TRICHLOROMETHYL-2,5-CYCLOHEXADIENE-1-ONE)(PENTANE-*O,O′*-2,4-DIONATE)

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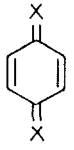
Summary

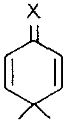
By means of the ligand exchange reactions of Rh(acac)(C_2H_4)$_2$ (VII) with *para*-semiquinoid cyclohexadienone ligands (4,4-dimethyl- (VI), 4-methyl-4-n-butyl- (IX), 4-methyl-4-dichloromethyl- (X), 4-methyl-4-trichloromethyl- (XIII) -cyclohexadiene-2,5-ones-1) the corresponding π-diene derivatives of Rh(acac)(η^4-dienone) have been obtained and characterized by ^{1}H NMR and IR spectra. In reactions with the ligands IX and X, mixtures (1/1) of diastereomeric complexes with *exo*- and *endo*-configuration are formed. Reaction with the ligand (XIII) is stereospecific and results in the formation of a complex with only *exo*-configuration, whose crystal and molecular structure have been determined by an X-ray structural study. The crystals are monoclinic with space group $P2_1/c$, a 7.673(3), b 10.794(4), c 18.38(1) Å, β 100.89(4)°, $Z = 4$. Stereospecificity of the ligand exchange reaction is evidently due to the preferable direction of the metal atom attack from the sterically less crowded *exo*-site of the semiquinoid ligand.

Introduction

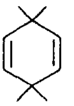
The alkylidenecyclohexadienes Ia and the cyclohexadienones Ib, because of the peculiarities of their structures, (particularly the presence of a diene system of π-bonds in the ring, active *exo*-unsaturated moiety and saturated geminal site) can be treated as a quite broad class of semiquinoid (SQ) π-ligands [1], occupying an intermediate position between the well investigated quinoid (Q) [2–6] and the dehydrobenzoid (DHB) [7,8] systems.



(Q)



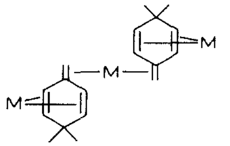
(I, SQ)



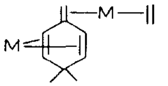
(DHB)

(a; X = CR_2,
b; X = O)

The organoelement chemistry of the alkylidenecyclohexadienes Ia is extremely diverse and presents examples of various types of reactions and rearrangements [9]. In particular, it has been recently shown that trienes of the Ia type react with Rh^I derivatives to form bi- and trinuclear complexes II and III with a mixed $\eta^2 + \eta^4$-type of metal coordination by a *para*-semiquinoid system. From this point of view, the simpler cyclohexadienone compounds of the Ib type are of special interest as they make it possible to investigate separately the effect of the η^4-coordination of the transition metal by the π-diene moiety of the semiquinoid system. It should be noted here that the π-diene type of coordination (especially in the chemistry of Rh^I derivatives) is at present one of the most wide-spread and interesting types of π-bonding, playing a very important role in our understanding of the nature of mutual influence and the characteristic spatial features of the molecules of organoelement compounds [10–14]. This is also of great importance for the understanding of the mechanisms of a number of homogeneous metal-complex catalysis processes [15–17].



(II)



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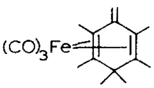
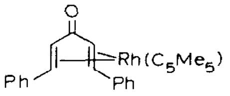


(IV)



(V)

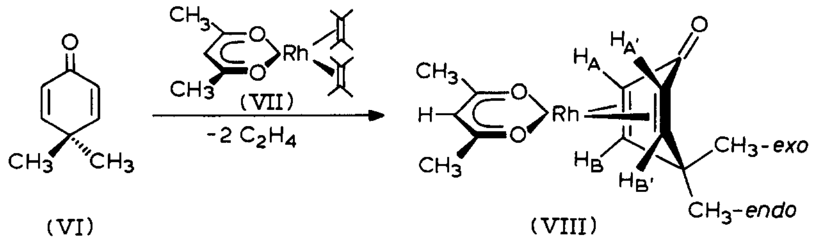
M = Rh(acac)

Among the derivatives of cyclohexadienones Ib, the iron-tricarbonyl diene complexes of the IV type are well known [18,19]. They can be obtained by different methods [20] and, in their turn, can be regarded as closed analogues of open dienone complexes of transition metals, such as V [21] (see the structure in ref. 22).

In continuing our investigations in the organoelement chemistry of semiquinoid systems [1,9] we studied the possibility for η^4-diene rhodium(I) complexes syntheses with a number of 4,4-disubstituted 2,5-cyclohexadienones and compared their structural parameters with those of the related organometallic compounds with quinoid (Q) [5,6] and dihydrobenzoid (DHB) [8] ligands.

Results and discussion

In the present work a typical semiquinoid dienone VI has been found to readily form a π-complex with Rh^I. This complex was obtained by substitution of ethylene ligands in diethylene(acetylacetonato)rhodium (VII) [11]. The reaction was conducted by adding equimolar quantities of complex VII and dienone VI to a benzene solution at room temperature (eq. 1):



(1)

According to elemental analysis data, positive ion [23] and negative ion [24] mass spectrometry and ^1H NMR spectroscopy, the crystalline orange-yellow substance obtained is a typical rhodium(I) diene complex VIII. Comparison of the ^1H NMR spectral characteristics (Table 1) of the initial dienone VI and its rhodium derivative VIII indicates considerable structural changes of the semiquinoid molecule on its coordination by the transition metal atom. While vinyl protons in the spectrum of the dienone VI give rise to a four-spin AA'BB' system (which is also typical of other similar structures [25]), in the molecule of complex VIII they correspond already to an AB quartet owing to the visible disappearance of the distant ^4J(H–H) and ^5J(H–H) spin–spin interaction with a simultaneous decrease of the ^3J(H–H) constant from 10 to 7 Hz. The π-coordination in the molecule causes in this case, firstly, a substantial enhancement of the shielding of the above protons and, secondly, additional splitting of each signal of the observed AB quartet into a doublet, caused by the spin–spin interaction of the ring protons with the ^{103}Rh nucleus. Similar values for these constants ($J(^1H–^{103}Rh)$ 1 Hz) were previously observed in cyclooctatetraene [26] and pentadiene [21] complexes of rhodium(I).

TABLE 1

^1H NMR SPECTRAL DATA OF THE COMPOUNDS INVESTIGATED (C_6D_6), CHEMICAL SHIFTS (δ ppm)[a]

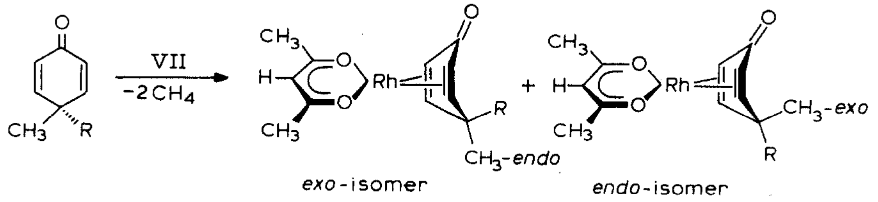
Compound	Cyclohexadienone moiety				Acatylacetonate moiety		J(AB) (Hz)
	CH_3	R	$H_A,H_{A'}$	$H_B,H_{B'}$	CH_3	H	
VI	0.75	–	6.14	6.24	–	–	10.0
VIII	1.65 0.54	–	3.83^{b}	4.50^{b}	1.80	5.16	7.5
IX	0.78	0.8–1.9	6.10	6.32	–	–	10.0
exo-XI	1.69	$0.7–1.0^{c}$	3.95^{b}	4.50^{b}	1.82	5.13	7.3
endo-XI	0.58	$0.7–1.1^{c}$	3.97^{b}	4.54^{b}	1.80	5.08	7.3
X	0.83	4.82	6.19	6.23	–	–	10.0
X^{d}	1.40	5.72	6.48	6.92	–	–	10.0
exo-XII	1.85	4.81	3.80^{b}	4.43^{b}	1.76	5.12	7.0
endo-XII	0.70	6.30	4.12^{b}	4.47^{b}	1.77	5.11	7.0
exo-XII[d]	2.05	4.87	4.10^{b}	4.40^{b}	1.97	5.47	7.0
endo-XII[d]	0.99	6.91	4.34^{b}	4.37^{b}	1.96	5.44	7.0
XIII	1.14	–	6.25	6.55	–	–	10.0
exo-XIV	2.35	–	3.87^{b}	4.59^{b}	1.79	5.14	7.3

[a] Groups designations see eqns. 1 and 2. [b] Components of these signals are additionally split into doublets $J(^1H–^{103}Rh)$ 1 Hz. [c] The low-field portion of the multiplet is obscured by neighbouring signals. [d] Solvent $CDCl_3$.

Important structural information can also be inferred from the positions of the methyl signals in the ^1H NMR spectrum of complex VIII. While both CH_3 groups in the dienone VI give rise to a singlet (which is under ambient conditions indicative of the planar structure), in the spectrum of VIII there are two kinds of CH_3 groups in position 4, which is caused by their different (i.e. *exo-* and *endo-*) orientation. Based on conventional spectral assignments in analogous (containing a geminal site) organometallic systems [10,27] the high field signal should belong to the *exo*-CH_3 group, while the low field one should belong to the *endo*-CH_3 group.

For semiquinoid ligands which contain two different substituents in the geminal cross-site one could have already expected the formation of two stereoisomeric compounds on complexation with rhodium. This assumption was in fact confirmed with the ligands IX and X (eq. 2) which formed the products XI and XII, each representing a mixture of two diastereomeric complexes (*exo-* and *endo*-XI and *exo-* and *endo*-XII *) according to ^1H NMR spectroscopy (Table 1). Those stereoisomers of compounds XI and XII whose methyl signals are observed to be deshielded as a result of the resonance absorption of geminal CH_3 groups, which agrees with their *endo*-orientation should be assigned to the *exo*-configurational series. The corresponding isomers for which one observes the shielding of the above groups, consistent with their *exo*-orientation in the molecule (Table 1**) should be assigned to the *endo*-configurational series.

The control of the dienone IX reaction in an NMR spectrometer ampoule (C_6D_6, 0.5 h, 50% conversion) and preparative product isolation (under conditions excluding the possibility of alteration of isomeric composition) of dienones IX and X reactions with a 100% conversion allows us to conclude that in both cases the stereoisomeric complexes are being formed in practically equal ratios, which corresponds to the non-stereoselectivity of the studied transformations (eq. 2).



(2)

(R = n-C_4H_9(IX) ;
R = $CHCl_2$ (X))

(R = n-C_4H_9(XI) ;
R = $CHCl_2$ (XII))

At the same time, the *para*-semiquinoid ligand XIII with CH_3 and CCl_3 substituents in the geminal site (Scheme 1) proved to be highly stereoselective and, according to the data of ^1H NMR spectroscopy, resulted in the formation of only the *exo*-stereoisomeric complex XIV with the low field CH_3-group signal in its NMR spectrum. Direct proof of the *exo*-orientation of the CCl_3 substituent was obtained

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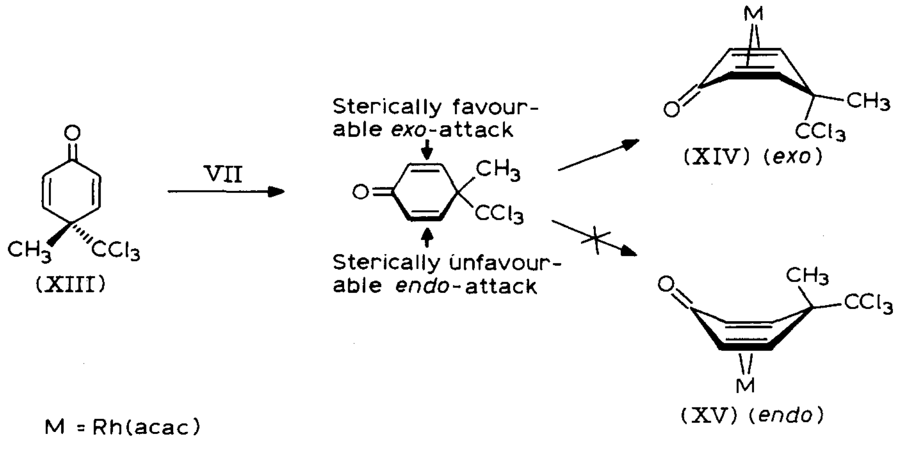
* The reaction of dienone X with $Rh(acac)(CO)_2$ (obtained by the method described in [28]) proceeds in a similar way, though in more severe conditions and with a smaller yield. The interaction of semiquinoid ligands with complex VII is, in principle, reversible, which has been proved by converting complex XII into a mixture of X and VII on treatment with ethylene (see Experimental).

** Configurational designations for the stereoisomeric complexes in question are based upon the relative arrangement of R and Rh(acac) groups.



SCHEME 1

by an X-ray diffraction study (see the following section). This result, of general interest to organometallic stereochemistry, is, in our opinion, because of the two possible directions of the metal atom attack from two diastereotopic sides of the planar dienone molecule XIII the sterically more favourable direction is that in which the rhodium atom approaches the molecule from the side opposite to the bulky CCl_3 group.

This kind of stereochemical effect must apparently have a sufficiently general nature and might also play an important role in other organometallic reactions of ligand exchange if the participating ligands have more than one side capable of coordination with approximately the same electronic properties, but strongly different steric requirements. It can be assumed, in particular, that a stereochemical mechanism similar to that shown in Scheme 1 also controls the ligand exchange reaction between the $[RhCl(C_2H_4)_2]_2$ complex and 1-carbethoxy-2,5-cyclohexadiene [8], in this case a cyclohexadiene compound with *exo*-orientation of the bulky COOR substituent (XVI) is also preferably formed.

At the same time, it should be noted that steric overcrowding in the reaction studied caused by $CHCl_2$ and C_4H_9 groups does not seem to be so significant in comparison with CCl_3 groups *. Therefore, in the reactions of ligands IX and X with the rhodium complex VII, coordination of the metal on both sides of the dienone molecules is in fact equally probable and they do not manifest any noticeable stereoselectivity (eq. 2).

The crystal and molecular structure of (η^4-4-methyl-4-exo-trichloromethyl-2,5-cyclohexadiene-one-1)rhodium-2,4-O,O'-pentanedionate

An X-ray diffraction study of compound XIV was of interest for three reasons. Firstly, it was necessary to confirm unambiguously the correctness of the ^1H NMR spectral assignments of its *exo*-configuration, discussed above, which was important

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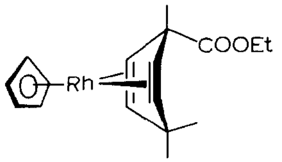
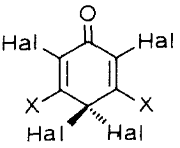
* This can be explained, e.g., by the presence of these substituents in the conformations where the bulky chlorine atoms in $CHCl_2$ or the propyl group in C_4H_9 are directed towards the side opposite to the approaching rhodium atom.

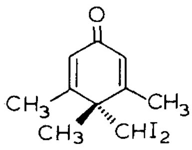
in order to check the validity of similar assignments for the compounds VIII, XI and XII and also to understand the nature of the stereospecificity of ligand exchange in the case of compound XIII (Scheme 1). Secondly, it seemed important to compare the geometrical parameters of XIV with similar parameters known from the literature for non-coordinated alkyl- and halogen-substituted cyclohexadiene-2,5-ones-1 XVII (X = H [29], X = Hal [30]) and XVIII [31] so as to elucidate the nature of structural changes introduced into the molecules of this type on coordination by transition metal atom. Thirdly, it was interesting to compare the results of an X-ray diffraction study of XIV with earlier published structural parameters of the quinone XIX [5,6], 1,4-cyclohexadiene, XVI [8] and dibenzylideneacetone, V [21,22] complexes of Rh^I with respect to which the semiquinoid system XIV, from a structural point of view, occupies in some sense an intermediate position.



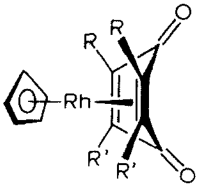
(XVI)



(XVII)



(XVIII)



(XIX)

(XIXa, R = R' = CH_3, XIXb, R = $(CH_3)_3C$, R' = H)

The structure of *exo*-XIV is shown in Fig. 1, bond lengths and angles are listed in Tables 2 and 3, respectively, and the atomic coordinates and their temperature factors are listed in Table 4 (see Experimental). The rhodium atom in the molecule investigated is symmetrically coordinated by the two oxygen atoms of the bidentate acetylacetonate ligand and the two double bonds of the cyclohexadienone ring. The chelate cycle plane is approximately perpendicular to the plane of the double bonds C(7)=C(8) and C(10)=C(11) (dihedral angle 87.9(2)°), which results in a square-planar coordination of the metal atom, typical for Rh^I complexes. The Rh–C(olefin) bond lengths observed in XIV show good agreement with similar values found in most of the η^2-olefin rhodium complexes [32–34]. It should be noted, however, that the presence of a bulky trichloromethyl substituent in the geminal site gives rise to some important structural peculiarities for XIV. This substituent is in a pseudo-axial orientation relative to the cyclohexadiene ring and causes a considerable steric strain in the cyclohexadiene ligand. Notwithstanding the almost ideally staggered conformation around the C(9)–C(13) bond (the C(12)C(9)C(13)Cl(2) torsion angle is equal to 179.6(7°)), repulsion of the Cl atoms from the environment of the C(9) atom remains quite significant (the Cl(1) · · · C(12) and Cl(3) · · · C(12) distances (3.083(7) and 3.110(7) Å) are substantially shorter than the sum of the Van der Waals radii of Cl and C atoms (3.5 Å)) [35] and cause, along with other possible reasons, a noticeable elongation of the axial C(9)–C(13) bond up to 1.570(8) Å in comparison with the equatorial C(9)–C(12) bond length of 1.523(9) Å. At the same time, the staggered conformation of substituents around the C(9)–C(13) bond results in a strong repulsion of the Cl(2) from the carbonyl C(6) atom. This repulsion seems to be the reason for a considerable increase in the C(9)C(13)Cl(2) (113.6(4)°), C(8)C(9)C(13) (113.2(5)°) and C(10)C(9)C(13) (114.0(5)°) bond angles as compared with the ideal tetrahedral value of 109.5°. However, despite the above mentioned

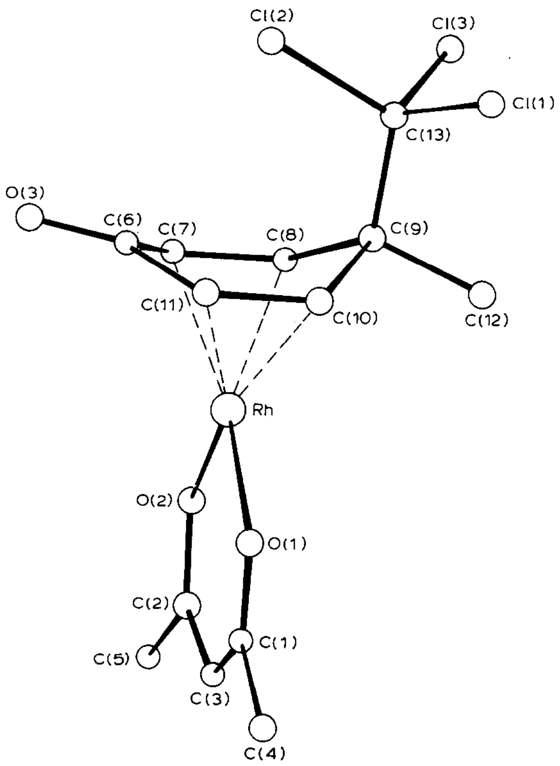


Fig. 1. The molecular structure of *exo*-XIV.

distortions of bond angles, the observed C(6) · · · Cl(2) distance of 3.016(7) Å still remains rather short.

When comparing XIV with the non-coordinated cyclohexadiene-2,5-ones-1 XVII

TABLE 2

BOND DISTANCES, *d* (Å) FOR COMPOUND *exo*-XIV

Rh–O(1)	2.011(4)	C(6)–C(7)	1.480(9)
Rh–O(2)	2.014(4)	C(6)–C(11)	1.468(9)
Rh–C(7)	2.123(6)	C(7)–C(8)	1.394(9)
Rh–C(8)	2.117(6)	C(8)–C(9)	1.516(8)
Rh–C(7,8) [a]	2.002	C(9)–C(10)	1.520(9)
Rh–C(10)	2.158(6)	C(9)–C(12)	1.523(9)
Rh–C(11)	2.140(6)	C(9)–C(13)	1.570(8)
Rh–C(10,11) [a]	2.034	C(10)–C(11)	1.387(9)
O(1)–C(1)	1.270(7)	C(13)–Cl(1)	1.774(7)
O(2)–C(2)	1.284(7)	C(13)–Cl(2)	1.771(7)
O(3)–C(6)	1.227(8)	C(13)–Cl(3)	1.779(7)
C(1)–C(3)	1.397(9)		
C(1)–C(4)	1.501(9)		
C(2)–C(3)	1.396(9)		
C(2)–C(5)	1.495(9)		

[a] C(7,8) and C(10,11), the midpoints of bonds C(7)=C(8) and C(10)=C(11).

TABLE 3

BOND ANGLES ω (°) FOR COMPOUND *exo*-XIV

O(1)RhO(2)	92.4(2)	RhC(8)C(7)	71.1(4)
O(1)RhC(7,8) [a]	96.2	RhC(8)C(9)	92.9(4)
O(1)RhC(10,11) [a]	167.4	C(7)C(8)C(9)	122.2(5)
O(2)RhC(7,8) [a]	171.4	C(8)C(9)C(10)	101.0(5)
O(2)RhC(10,11) [a]	99.5	C(8)C(9)C(12)	109.3(5)
C(7,8)RhC(10,11) [a]	72.0	C(8)C(9)C(13)	113.2(5)
RhO(1)C(1)	124.8(4)	C(10)C(9)C(12)	109.6(5)
RhO(2)C(2)	124.3(4)	C(10)C(9)C(13)	114.0(5)
O(1)C(1)C(3)	126.0(6)	C(12)C(9)C(13)	109.4(5)
O(1)C(1)C(4)	115.1(6)	RhC(10)C(9)	91.2(4)
C(3)C(1)C(4)	118.9(6)	RhC(10)C(11)	70.5(4)
O(2)C(2)C(3)	125.8(6)	C(9)C(10)C(11)	122.2(5)
O(2)C(2)C(5)	114.7(5)	RhC(11)C(6)	82.5(4)
C(3)C(2)C(5)	119.5(6)	RhC(11)C(10)	71.9(4)
C(1)C(3)C(2)	126.6(6)	C(6)C(11)C(10)	121.9(6)
O(3)C(6)C(7)	124.2(6)	Cl(1)C(13)Cl(2)	107.4(4)
O(3)C(6)C(11)	125.4(6)	Cl(1)C(13)Cl(3)	109.5(4)
C(7)C(6)C(11)	109.0(5)	Cl(1)C(13)C(9)	109.0(4)
RhC(7)C(6)	82.9(4)	Cl(2)C(13)Cl(3)	107.2(3)
RhC(7)C(8)	70.6(4)	Cl(2)C(13)C(9)	113.6(4)
C(6)C(7)C(8)	121.2(5)	Cl(3)C(13)C(9)	109.9(4)

[a] C(7,8) and C(10,11), the midpoints of bonds C(7)=C(8) and C(10)=C(11).

and XVIII, studied earlier, one should naturally turn to the geometry of the cyclic ligand and its changes resulting from the coordination by the transition metal atom. In a number of studies it has been found [29,30] that the 6-membered rings in various substituted cyclohexadienone derivatives have a planar conformation; deviations from planarity, observed in some cases, are, as a rule, not significant; the largest atomic displacements from the mean plane being less than 0.1 Å *. It is natural, however, that coordination by a transition metal atom should be accompanied by a partial rehybridization ($sp^2 \rightarrow sp^3$) of the olefin carbon atoms, leading to the lengthening of the coordinated double bonds C(7)=C(8) to 1.394(9) Å and C(10)=C(11) to 1.387(9) Å. Thus, as should be expected, these bonds become substantially longer than analogous bonds (1.31–1.34 Å) in the molecules of the non-coordinated cyclohexadienes XVII and XVIII [29–31].

Another consequence of the transition metal coordination and the accompanying rehybridization is a marked distortion of the planarity of the cyclohexadienone ring in XIV, as compared with similar non-coordinated molecules XVII and XVIII. This distortion results in the displacement of the non-coordinated C(6) and C(9) atoms of the ring from the C(7)C(8)C(10)C(11) plane away from the metal atom by 0.315(6) and 0.561(6) Å, respectively. Hence the coordinated cycle acquires the asymmetrical boat conformation shown in Fig. 2. The bend (α_1) of the C(7)C(6)C(11) triangular group with the carbonyl carbon atom at the vertex proves in this case to be substantially smaller than the corresponding bend (α_2) of the opposite C(8)C(9)C(10)

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* This is also true for the 1,4-cyclohexadiene derivatives with α-aminocarboxymethyl [36] or aryl and carboxymethyl [37] substituents.

TABLE 4

ATOMIC COORDINATES ($\times 10^4$, for Rh$\times 10^5$, for H$\times 10^3$) AND TEMPERATURE FACTORS (isotropic for H, equivalent isotropic for other atoms [a]) FOR COMPOUND *exo*-XIV

Atom	x	y	z	B (Å^2)
Rh	18813(6)	3686(4)	13959(2)	1.16(1)
Cl(1)	5990(2)	−1123(2)	3777(1)	2.46(4)
Cl(2)	2304(2)	−822(2)	3808(1)	2.19(4)
Cl(3)	4628(2)	1252(2)	4155(1)	2.58(4)
O(1)	2644(6)	−475(4)	532(2)	1.5(1)
O(2)	1038(5)	1882(4)	790(2)	1.4(1)
O(3)	−1246(6)	−1064(4)	2224(2)	2.0(1)
C(1)	2533(8)	−2(6)	−108(3)	1.5(2)
C(2)	1094(8)	2006(6)	100(3)	1.5(1)
C(3)	1831(8)	1161(6)	−331(3)	1.6(1)
C(4)	3192(10)	−810(7)	−663(4)	1.9(2)
C(5)	243(10)	3160(6)	−250(4)	2.0(2)
C(6)	222(9)	−597(6)	2249(3)	1.5(1)
C(7)	1752(5)	−1249(5)	2040(3)	1.5(1)
C(8)	3458(8)	−754(5)	2208(3)	1.3(1)
C(9)	3923(8)	321(5)	2741(3)	1.3(1)
C(10)	2348(8)	1173(5)	2491(3)	1.4(1)
C(11)	620(9)	733(6)	2317(3)	1.5(1)
C(12)	5610(9)	942(6)	2599(4)	1.7(2)
C(13)	4281(9)	−76(6)	3576(3)	1.8(1)
H(3)	188(11)	137(8)	−83(5)	3(2)
H(4,1)	416(13)	−116(9)	−43(5)	4(2)
H(4,2)	230(9)	−135(5)	−85(3)	2(1)
H(4,3)	340(9)	−36(6)	−104(4)	3(1)
H(5,1)	462(12)	334(9)	−75(5)	4(2)
H(5,2)	59(10)	380(7)	6(4)	3(2)
H(5,3)	−95(11)	305(7)	−29(4)	2(2)
H(7)	151(10)	−199(7)	184(4)	2(1)
H(8)	440(9)	−115(6)	207(3)	0(1)
H(10)	251(8)	203(6)	255(3)	1(1)
H(11)	−24(10)	123(6)	225(4)	2(1)
H(12.1)	596(11)	163(8)	288(5)	2(2)
H(12,2)	538(10)	129(7)	213(4)	3(1)
H(12,3)	651(14)	34(9)	268(6)	5(2)

[a] Equivalent isotropic temperature factors are of the form: $B_{\text{iso}}^{\text{eq}} = 1/3\ \Sigma_i \Sigma_j B_{ij} a_i^{\star} a_j^{\star} (\mathbf{a}_i \mathbf{a}_j)$.

group with the vertex in the geminal site of the molecule. It should be emphasized that the conformation of the "carbonyl" fragment in the ring is in good agreement with that of the *p*-benzoquinone cycle in a number of previously studied diene complexes of rhodium with tetramethyl-*p*-benzoquinone (XIXa) [5] and 2,6-di-t-butyl-*p*-benzoquinone (XIXb) [6] ligands. Similar to the above quinoid complexes XIX, the environment of the C(6) atom in the semiquinoid molecule, *exo*-XIV, is not quite planar; the O(3) carbonyl oxygen atom is displaced from the C(6)C(7)C(11) plane towards the metal atom, as shown in Fig. 2. One may assume that this type of geometrical distortions is caused by a tendency to retain the cross-π,π conjugation of the carbonyl group with the diene system of the ring, which would achieve a maximum when the nodal planes of interacting orbitals are parallel. This is indicated

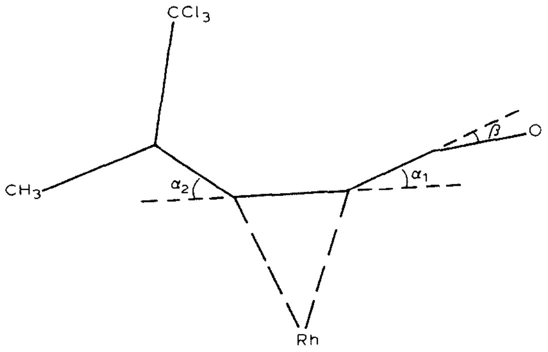

Fig. 2. Conformation of the methyl(trichloromethyl)cyclohexadienone ligand in molecule *exo*-XIV.

by the presence of conjugated carbonyl group absorption bands in the IR spectra of the compounds obtained: 1640 cm^{-1} VIII, 1645 cm^{-1} XII, 1650 cm^{-1} XIV *.

The α_1 and β angles shown in Fig. 2, 21.6(3) and 10.6° respectively, are within the range of values for the corresponding angles (20–25 and 9–11°) in the above-mentioned quinoid complexes, XIX. It is also of interest to note that a similar conformation (angles α and β are equal to 27.5 and 14.4°, respectively)** is characteristic of the acyclic dibenzylideneacetone ligand in complex V [21,22], where, as in the case of cyclohexadienone XIV and quinone XIX complexes, the rhodium(I) atom is η^4-coordinated by two double C=C bonds linked by the carbonyl carbon atom. Taking into account the fact that the *exo*-XIV molecule studied in the present work, without any substituents at the double bonds of the ring, is characterized by the same geometry distortions that were observed in the case of 2,6-disubstituted and 2,3,5,6-tetrasubstituted quinoid systems of the XIXa,b [5,6] type, the present results show that all of the above mentioned peculiarities of molecular geometry are sufficiently general and represent a characteristic structural regularity in a large series of the analogues of cyclohexadienone organorhodium π-complexes.

Comparing, in its turn, XIV with the 2,5-cyclohexadienerhodium complex XVI [8], which has only been structurally studied, it can be stated that, in our case (Fig. 2), the folding of the ring along the C(8) · · · C(10) line, α_2 35.5(3)°, is somewhat smaller than similar angles (42.3° and 44.7°) observed in XVI, which can be caused by the already mentioned steric repulsion between the carbonyl group and the trichloromethyl substituent in the ring of XIV.

All other bond lengths of XIV are unexceptional. Thus, the Rh–O distances of 2.011(4) and 2.014(4) Å correspond to the lower boundary of the 2.02–2.09 Å range of values typical for Rh^I acetylacetonate complexes (see, e.g., [32–34,38]). Only in one case, viz. in acetylacetonate(duroquinone)rhodium XIXb [6], the Rh–O bonds, shorter than in XIV, 1.97 and 1.98 Å, were found. It is natural to assume that a decisive role in the shortening or the lengthening of Rh–O(acac) bonds is played by the nature of the *trans*-ligand. Therefore, one can suppose that somewhat shorter

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* These absorption bands, as is usually the case, are shifted by 20–30 cm^{-1} into a low-frequency region (cf. [2–4,21]) as compared with the corresponding non-coordinated ligands.

** These values of angles have been calculated by us using the coordinates from [22].

Rh–O distances in Rh^I complexes with *p*-benzoquinone XIX and cyclohexadienone XIV ligands in comparison with the complexes containing olefin ligands with isolated double bonds [32–34], are caused by the influence of the carbonyl groups of dienone ligands whose electron–acceptor properties can enhance the back donation from the metal to the ligand and lead to the shortening of Rh–O bonds.

It is important to note that while the (trichloromethyl)methylcyclohexadienone ligand in XIV has an almost ideal mirror symmetry the Rh(acac) group turns out to be somewhat shifted in respect to the symmetry plane of the cyclohexadienone ligand passing through the C(6)C(9)C(13) atoms (the rhodium atom is displaced from this plane by 0.0663(4) Å), which results in shorter Rh–C(7) and Rh–C(8) distances of 2.123(6) and 2.117(6) Å respectively as compared with the Rh–C(10) and Rh–C(11) distances of 2.158(6) and 2.140(6) Å *.

The asymmetrical position of the Rh(acac) group is caused by specific features of the molecular packing in the crystal of XIV. Thus, the C(2) and C(5) atoms of the acac ligand, as distinct from C(1) and C(4), take part in a number of short contacts with the CCl_3 groups of neighbouring molecules (C(2) $\cdots$ Cl(1) $(1-x, 1/2+y, 1/2-z)$ 3.406(7) Å, C(5) $\cdots$ Cl(1) $(1-x, 1/2+y, 1/2-z)$ 3.650(7) Å, C(5) $\cdots$ Cl(2) $(-x, 1/2+y, 1/2-z)$ 3.742(7) Å, C(5) $\cdots$ Cl(3) $(x, 1/2-y, -1/2+z)$ 3.783(7) Å). It is the repulsion from these CCl_3 groups that seems to result not only in the above-mentioned displacement of the Rh(acac) group relative to the ligand mirror plane but also in a substantial, 0.151(8) Å, displacement of the C(5) atom from the planar within 0.03 Å atomic group O(1)C(1)C(3)C(2)O(2) of the acac ligand (the displacement of the C(4) atom from this plane only amounts to 0.009(8) Å).

Experimental

^1H NMR spectra were recorded on a Bruker WP-200Sy instrument (200 MHz) in C_6D_6 and $CDCl_3$ solutions. Chemical shifts were measured relative to the signals of residual C_6D_5H and $CHCl_3$ admixtures in the solvents (δ 7.25 and 7.27 ppm, respectively). Mass spectra were measured on an MS-30 instrument at ionizing potential 70 eV. IR spectra (KBr pellets) were recorded on a UR-20 instrument. Starting dienones VI [39], IX [40], X [41] and XIII [42] were obtained according to procedures described in the literature. $Rh(acac)(C_2H_4)_2$ (VII) was obtained by the method described in [11] and $Rh(acac)(CO)_2$ was prepared as in [28].

X-ray structural study

Single crystals of *exo*-XIV suitable for an X-ray study were obtained by slow crystallization (3 d) from a saturated benzene solution at room temperature. The crystals are monoclinic, a 7.673(3), b 10.794(4), c 18.38(1) Å, β 100.89(4)°, V 1495(1) $Å^3$, $M = 427.4$, d(calcd.) 1.889 g cm^{-3}, $Z = 4$, space group $P2_1/c$. Unit cell parameters and the intensities of 2420 reflections with $F^2 > 4\sigma$ were measured with a four-circle automatic diffractometer Syntex $P2_1$ (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $\theta \leqslant 26°$), absorption correction (μ(Mo-K_α) 16.5 cm^{-1}) was not applied.

The structure was solved by the heavy-atom method and refined by the least

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* This difference does not, however, affect the lengths of coordinated double bonds of the ring.

squares technique. Non-hydrogen atoms were refined in the anisotropic approximation; H atoms located in the difference Fourier synthesis were included in the refinement with isotropic temperature factors. All calculations were performed with an Eclipse S/200 computer using the INEXTL programmes [43]. The final discrepancy factors are $R = 0.034$, and $R_w = 0.048$. Atomic coordinates and temperature factors are listed in Table 4.

Preparation of XI, XII, XIII and XIV

Solutions of mixtures of VII 0.08–0.4 mmol (20–100 mg) with equimolar quantities of the corresponding dienones in 5 ml benzene were stirred at room temperature for 1 h under an argon stream. After the reaction was complete (TLC control on Silufol UV-254 plates), followed by distilling off the solvent, the products were isolated with a quantitative yield as air stable yellow-orange crystals and purified for elemental analysis by recrystallization from pentane (−70°C) XII or reprecipitation with pentane from benzene solutions of VIII, XI, XIV.

η^4-(4,4-Dimethylcyclohexadiene-2,5-one-1)rhodium-2,4,-O,O′-pentanedionate (VIII). R_f (ether) 0.3. T(decomp.) 152°C. Mass spectrum: M^+ 324 (M(calcd.) 324). IR spectrum: 1640 cm^{-1} (C=O). Found: C, 48.27; H, 5.40. $C_{13}H_{17}O_3Rh$ calcd.: C, 48.15; H, 5.25%.

(η^4-4-Methyl-4-n-butylcyclohexadiene-2,5-one-1)rhodium-2,4-O,O′-pentanedionate (mixture of exo-XI and endo-XI stereoisomers in the ratio of 1/1). R_f (ether) 0.3 and 0.2. T(decomp.) 167°C. Mass spectrum: M^+ 366 (M(calcd.) 366).

The substance obtained was enriched with less soluble *exo*-isomer to the ratio of 15/1 (NMR) by recrystallization from pentane (20°C). R_f (ether) 0.3.

(η^4-4-Methyl-4-dichloromethylcyclohexadiene-2,5-one-1)rhodium-2,4-O,O′-pentanedionate (mixture of exo- and endo-XII stereoisomers in the ratio of 1/1). R_f (ether) 0.35 and 0.25. Mass spectrum: M^+ 392 (M(calcd.) 392).

The less soluble *exo*-XII stereoisomer was isolated from the mixture obtained by recrystallization from hexane (20°C). T(decomp) 176°C. R_f (ether) 0.35. IR spectrum: 1645 cm^{-1} (C=O). Found: C, 40.08; H, 3.50; Cl, 18.05. $C_{13}H_{15}Cl_2O_3Rh$ calcd.: C, 39.70; H, 3.81; Cl, 18.06%.

(η^4-4-Methyl-4-trichloromethylcyclohexadiene-2,5-one-1)rhodium-2,4-O,O′-pentanedionate (exo-isomer XIV). R_f (ether) 0.4. M.p. 192°C (with decomp.). Mass spectrum: M^+ 426 (M(calcd.) 426). IR spectrum: 1650 cm^{-1} (C=O). Found: C, 36.35; H, 3.13; Cl, 25.06. $C_{13}H_{14}Cl_3O_3Rh$ calcd.: C, 36.49; H, 3.27; Cl, 24.91%.

Reversible interaction of complex XII with ethylene

A solution of a 20 mg *exo*- and *endo*-XII mixture in 5 ml of benzene was heated to boiling and cooled to 0°C in an ethylene atmosphere. 5 min later dienone X (R_f (ether) 0.6) and complex VII (R_f (ether) 0.8) were found in the reaction mixture by means of TLC. X and VII disappeared gradually from the reaction mixture which was controlled by chromatography while stirring under argon current to remove gaseous ethylene* and the complex, XII, was isolated.

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* When conducted in closed ampoules of an NMR spectrometer the reaction proceeds much slower, which can be explained by the fact that ethylene in this case is not removed from the reaction medium. This observation is in agreement with the reversible (in principle) nature of ligand exchange reaction.

Reaction of dienone X with Rh(acac)(CO)$_2$

A solution of 8 mg X and 13.5 mg Rh (acac)(CO)$_2$ mixture in 5 ml of benzene was boiled for 5 h. The reaction mixture was evaporated to dryness, the residue washed with pentane, dissolved in benzene, filtered off from the black precipitate formed (possibly, metallic rhodium), and the solvent was distilled off. The yield of the *exo-* and *endo-*XII mixture is 3.5 mg (20%).

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