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# NORBORNADIENE COMPLEXES OF TRANSITION METALS

## IV *. CONFORMATIONAL ANALYSIS OF DIASTEREOMERIC {2-(α-HYDROXYETHYL)-NORBORNADIENE} ACETYLACETONATO-RHODIUM COMPLEXES AND MOLECULAR STRUCTURE OF THE HIGH MELTING ISOMER OF [Rh{$\eta^4$-$C_7H_7CH(OH)Me$}(acac)]

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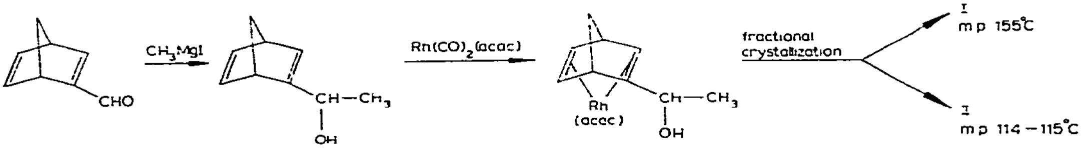
## Summary

Individual diastereomers (I and II) of [Rh{$\eta^4$-$C_7H_7CH(OH)Me$}(acac)] were obtained by fractional crystallization from n-hexane and acetone. According to IR and PMR spectra there is an intramolecular hydrogen bond between the hydroxyl group and the oxygen atom of the acac ligand in both complexes. Analysis of the conformations of I and II was carried out on the basis of molecular models and spectral data. Results of this analysis were confirmed by an X-ray study of isomer I.

## Introduction

Recently, we have reported on the synthesis of a mixture of diastereomeric rhodium complexes [Rh{($\eta^4$-$C_7H_7CH(OH)Me$}(acac)]. By fractional crystallization we succeeded in separating the individual isomers I and II [2].



Carbinols I and II were employed as starting compounds for the synthesis of the diastereomers III and IV of [Rh{$\eta^4$-$C_7H_7CH(OH)Me$}($\eta^5$-$C_5H_5$)] by

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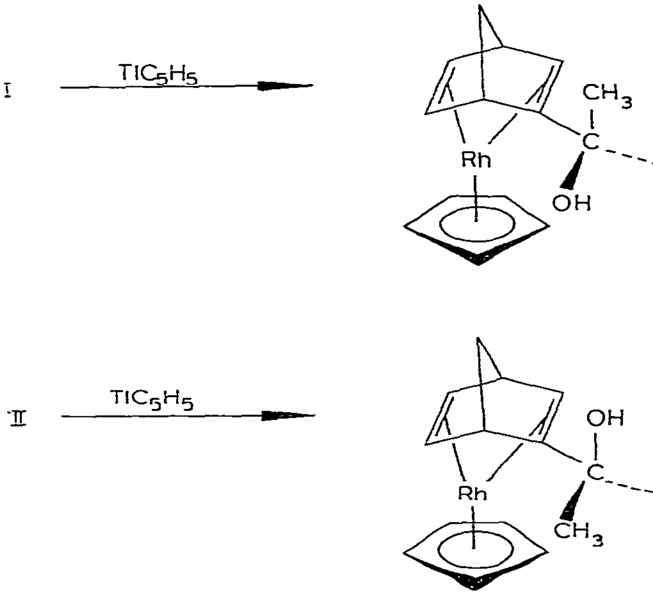
* Part III, see ref. 1.

exchange of the acac ligand for a cyclopentadienyl one, according to the published method [3].



(III), ψ – *endo*

(IV), ψ – *exo*

The relative configuration at the exocyclic carbon atom C(8) in diastereomers III and IV (in the scheme one of the enantiomers of each diastereomer is shown) was assigned on the basis of spectral and, mainly, chemical data [2]. We assigned *SR* and *RS* configurations to the enantiomers of III and *RR* and *SS* configurations to those of IV, relative to the carbon atoms C(2) and C(8).

The formation of only one isomer, III or IV, on substitution of the acac ligand by the cyclopentadienyl one indicates that the reaction is not accompanied by an inversion at the carbon atom C(8) in the coordinated norbornadiene ligand. This conclusion is in full agreement with the results of an X-ray analysis of complex I (see below).

## Results and discussion

Consideration of molecular models of I and II reveals that, as in the case of the 2-(α-hydroxyethyl)norbornadienecyclopentadienylrhodium complexes, III

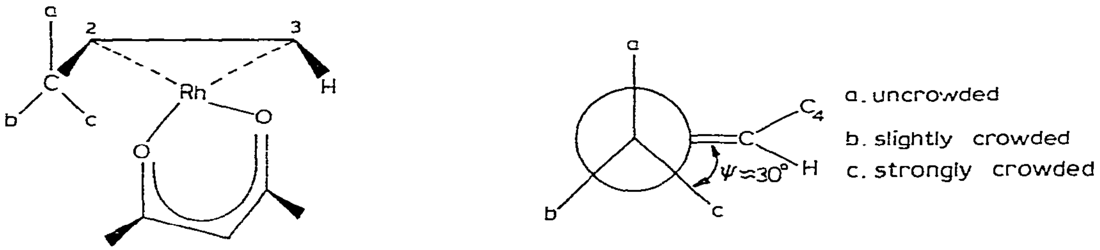


Fig. 1. The preferred skewed conformation of the 2-substituted derivative of norbonadienerhodium acetylacetonate.

and IV, the least steric hindrance between a substituent in the diene ligand and, in this case, the rhodium acetylacetonate group arises in the skewed conformation, with a dihedral angle (see Fig. 1) of ca. 30°.

In such an idealized conformation of the dienol complexes there should be three sterically different positions, a, b and c, which substituents can occupy at the carbinol carbon C(8) (Fig. 1). Therefore, one would expect the same positions of substituents at C(8) as in the cyclopentadienyl derivatives III and IV, i.e. in accordance with their steric requirements.

However, IR data of diastereomers I and II (Table 1) revealed in both complexes the presence of an intramolecular hydrogen bond between the hydroxyl group and the oxygen atom of the acac ligand. Thus, in the IR spectra of isomers I and II in the solid state, absorption bands of the hydroxyl groups appear at 3450 and 3423 $cm^{-1}$, whereas in $CCl_4$ solution these bands are observed at 3460 and 3450 $cm^{-1}$, respectively, i.e. they remain practically identical in both states. Besides, in comparison with IR spectra for $CCl_4$ solutions of the isomeric carbinols III and IV, (see Table 1) the frequencies of the hydroxyl group in complexes I and II are decreased on the average by 80 $cm^{-1}$.

Since position c is situated nearest to the oxygen atom of the acac ligand in the idealized conformation (Fig. 1), one may assume that the hydroxyl group in both diastereomers occupies this position or is near to it. This assumption is an agreement with PMR data on carbinols I and II in various solutions (Table 2). The most informative data (chemical shifts and coupling constants for hydroxyl protons) are presented in a separate column in Table 2.

In the PMR spectrum of complex I in $CCl_4$ the signal of the hydroxyl proton appears as a doublet at $\delta$ 2.62 ppm, with $J$(OH—H(8)) = 10 Hz (the signal assignment is accomplished by the double resonance technique). In complex II this signal appears as a broadened singlet (line width $\leqslant$2 Hz) at $\delta$ = 3.36 ppm.

In acetone-$d_6$ solution a marked downfield shift, $\Delta\delta$ = 0.56 ppm, is observed for complex I whereas for complex II this shift is only 0.15 ppm.

The rather high value of the coupling constant $J$(OH—H(8)) in the case of isomer I, approximately twice as much as the usually observed values (4—5 Hz [4]), can be explained by the *trans*-position of the methyne proton and the proton of the hydroxyl group (relative to the C(8)—O(1) bond), due to the participation of the latter in hydrogen bonding with the oxygen atom of the acac ligand (Fig. 2a). The $J$(OH—H(8)) value for complex II is appreciably lower being

TABLE 1

IR SPECTRA OF CARBINOL COMPLEXES I—IV [a,b]

| Compound | Experimental conditions | Absorption frequency $\nu$(OH) ($cm^{-1}$) |
|---|---|---|
| I | KBr pellets | 3450 |
| II | KBr pellets | 3423 |
| I | $CCl_4$ | 3460 |
| II | $CCl_4$ | 3450 |
| III | $CCl_4$ | 3535 |
| IV | $CCl_4$ | 3500—3600 |

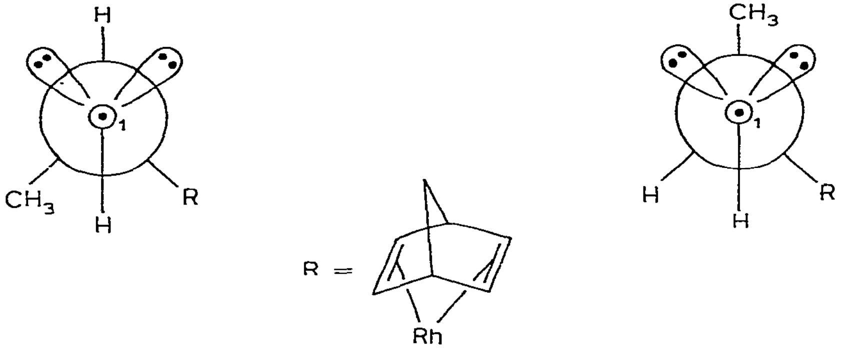
[a] Concentration of solutions of I—IV in $CCl_4$ was 0.05 *M*. [b] Spectra were recorded with an UR-20 spectrometer.

TABLE 2

PMR SPECTRA OF DIASTEREOMERS I AND II

| Compound | Solvent[a] | Spectra[b] ($\delta$, ppm, multiplicity[c], relative intensity, $J$ in Hz, assignment) | $\delta$(OH) (ppm) $J(\mathrm{OH}{-}^{8}\mathrm{H})$ (Hz) | $\Delta\delta$(OH) (ppm) relative to $\delta$(OH) for $CCl_4$ solution |
|---|---|---|---|---|
| I | A | 5.16(s,1,COCHCO); 3.90(m,2,H(5,6)); 3.64(m,3,H(3,4(1)8)); 3.44(m,1,H(1(4))); 2.62(d,1,$J$(OH—H(8)) = 10 Hz, OH); 1.87(S,6,$CH_3$-COCHCO$CH_3$); 1.70(d,3,$J$($CH_3$—H(8)) = 6.3 Hz, $CH_3$); 1.22(m,2,H(7)$_{\alpha,\beta}$) | 2.62<br>(10.0) | — |
| I | B | 5.33(s,1,COCHCO); 4.15(m,2,H(5,6)); 3.66(m,4,H(1,3,4,8)); 3.18(d,1,$J$(OH—H(8)) = 10 Hz, OH); 1.84(s,6,$CH_3$COCHCO$CH_3$); 1.63(d,3,$J$($CH_3$—H(8)) = 6.0 Hz, $CH_3$); 1.25(m,2,H(7)$_{\alpha,\beta}$) | 3.18<br>(10.0) | 0.56 |
| II | A | 5.20(s,1,COCHCO); 4.60(q,br,1,$J$(H(8)—$CH_3$ = 6.0 Hz, H(8)); 4.00(m,2,H(5,6)); 3.70(m,2,H(3,4(1))); 3.44(m,1,H(1(4))); 3.36(s,br,1,OH); 1.88(s,6,$CH_3$COCHCO$CH_3$); 1.22(d,3,$J$($CH_3$—H(8)) = 6 Hz, $CH_3$); 1.18(m,2,H(7)$_{\alpha,\beta}$); | 3.36<br>(2) | — |
| II | B | 5.31(s,1,COCHCO); 4.53(q,br,1,$J$(H(8)—$CH_3$) = 6.0 Hz, H(8)); 3.90(m,2,H(5,6)); 3.62(m,2,H(3,4(1))); 3.51(m,2,H(1(4)),OH); 1.84(s,6,$CH_3$COCHCO$CH_3$); 1.21(m,2,H(7)$_{\alpha,\beta}$); 1.18(d,3,$J$($CH_3$—H(8)) = 6.0 Hz, $CH_3$) | 3.51<br>(2) | 0.15 |

[a] A = $CCl_4$; B = $(CD_3)_2CO$. [b] Spectra were recorded with an Perkin-Elmer R-32 spectrometer. [c] s = singlet, d = doublet, q = quartet, m = multiplet.



(2a,I) (acac) (2b,II)

Fig. 2. Preferred conformations of diastereomeric complexes I and II relative to the C(8)—O(1) bond. bond.

$\leq$2 Hz; therefore one could assume that a skewed or similar conformation relative to the C(8)—O(1) bond arises in this diastereomer (Fig. 2b). Thus, according to the idealized conformation assumed by us for these complexes, the preferred conformation of isomer I, relative to the C(2)—C(8) bond, is the one represented in Fig. 3a and the preferred conformation of isomer II is shown in Fig. 3b.

At first glance one would expect an approximately equally strong intramolecular hydrogen bond in diastereomers I and II. However, a more thorough study of their physical properties and physico-chemical characteristics revealed a substantial difference between the diastereomers in this respect.

The melting points of isomers I and II are 155°C and 114—115°C, respectively. At the same time, comparison of the melting points of the isomers in dry and moistened states gave the following results: for II $\Delta T$ was only 16°C, whereas for I this value was approximately twice as large, being 36°C. Usually, this method of comparison allows one to distinguish between intramolecular and intermolecular associations [5,6]. However, in the present case these results can likely be used for a qualitative estimation of the relative strength of the intramolecular hydrogen bond. This allows us to conclude that in the solid state the intramolecular hydrogen bond is stronger in carbinol II than in carbinol I.

(3a, I) (3b, II)

Fig. 3. Preferred conformations of diastereomeric complexes I and II.

TABLE 3

ATOMIC COORDINATES (X $10^5$ FOR NON-HYDROGEN ATOMS AND X$10^3$ FOR H ATOMS) AND TEMPERATURE FACTOR PARAMETERS [a] (X$10^2$ FOR NON-HYDROGEN ATOMS AND X10 FOR H ATOMS)

| Atom | $X$ | $Y$ | $Z$ | $B_{11}$ or $B_{\rm iso}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Rh | 20029(4) | 14338(1) | 14109(3) | 86(2) | 92(2) | 117(2) | −2(1) | 3(1) | −10(1) |
| O(1) | −9652(38) | 3963(12) | 23033(35) | 122(11) | 158(14) | 245(12) | −39(9) | 23(8) | −21(10) |
| O(2) | −5461(40) | 14011(8) | 30212(34) | 145(11) | 125(11) | 175(11) | 0(7) | 21(9) | −21(8) |
| O(3) | 31168(35) | 20550(8) | 26483(31) | 161(10) | 109(11) | 179(10) | −11(8) | 5(8) | −24(8) |
| C(1) | 43527(52) | 6925(13) | 351(43) | 93(13) | 141(16) | 148(14) | 30(12) | −7(11) | −3(12) |
| C(2) | 20346(49) | 6902(12) | 6887(41) | 116(13) | 92(14) | 115(13) | 4(11) | −16(10) | −29(11) |
| C(3) | 7999(55) | 9587(13) | −5279(43) | 100(14) | 137(15) | 139(14) | −6(11) | −18(10) | −38(11) |
| C(4) | 23405(55) | 11172(13) | −19282(47) | 150(14) | 151(16) | 114(13) | −10(12) | −27(12) | 12(12) |
| C(5) | 36775(59) | 14966(13) | −8928(48) | 123(14) | 120(16) | 145(15) | −14(11) | 49(12) | 9(11) |
| C(6) | 49296(55) | 12303(13) | 3379(44) | 87(14) | 132(16) | 159(15) | −22(12) | 30(12) | −24(12) |
| C(7) | 38834(58) | 6769(15) | −19283(44) | 160(14) | 164(17) | 138(14) | −19(13) | 19(12) | −18(13) |
| C(8) | 12671(54) | 3261(13) | 19955(45) | 143(14) | 100(16) | 168(15) | 13(11) | 33(11) | 0(12) |
| C(9) | 26263(65) | 3335(17) | 36687(47) | 197(16) | 246(20) | 123(15) | 14(14) | 7(12) | 46(14) |
| C(10) | −8926(52) | 16998(14) | 42570(44) | 136(14) | 197(17) | 122(14) | 71(12) | 14(11) | 26(12) |
| C(11) | 3600(59) | 21006(14) | 47022(47) | 244(16) | 158(17) | 98(15) | 66(13) | 18(12) | −23(12) |
| C(12) | 22663(55) | 22505(13) | 39494(45) | 173(15) | 131(15) | 141(15) | 52(12) | −24(12) | 9(12) |
| C(13) | −28144(65) | 15704(17) | 52921(54) | 175(16) | 283(19) | 196(17) | 0(15) | 54(13) | 19(16) |
| C(14) | 34763(73) | 26759(16) | 47306(61) | 274(19) | 154(19) | 224(18) | −7(14) | −3(15) | −41(15) |

| | | | | |
|---|---|---|---|---|
| H(0) | −110(6) | 63(2) | 264(5) | 10(9) |
| H(1) | 525(5) | 46(1) | 49(4) | 3(6) |
| H(3) | −79(6) | 93(1) | −66(4) | 6(6) |
| H(4) | 174(5) | 121(1) | −293(5) | 4(6) |
| H(5) | 384(5) | 186(1) | −124(4) | 11(7) |
| H(6) | 616(7) | 132(1) | 100(5) | 22(9) |
| H(7,1) | 523(7) | 78(2) | −252(5) | 26(9) |
| H(7,2) | 322(5) | 40(1) | −231(5) | 10(7) |
| H(8) | 132(6) | 1(1) | 149(4) | 8(7) |
| H(9,1) | 422(6) | 29(1) | 351(5) | 16(7) |
| H(9,2) | 216(6) | 8(1) | 444(5) | 16(8) |
| H(9,3) | 248(8) | 66(2) | 418(7) | 43(11) |
| H(11) | −5(6) | 225(1) | 560(5) | 15(8) |
| H(13,1) | −258(7) | 125(2) | 592(6) | 34(10) |
| H(13,2) | −311(6) | 184(2) | 611(6) | 37(11) |
| H(13,3) | −417(10) | 149(2) | 459(8) | 48(13) |
| H(14,1) | 495(9) | 262(2) | 475(6) | 42(11) |
| H(14,2) | 300(8) | 279(2) | 569(8) | 44(12) |
| H(14,3) | 351(9) | 292(2) | 413(8) | 48(14) |

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[a] Anisotropic temperature factor in the form of $T = \exp[-1/4(B_{11}h^2a^{*2} + \cdots + 2B_{23}klb^*c^*)]$.

PMR and IR data for these isomer (Tables 1 and 2) are in agreement with this conclusion. Thus, in the PMR spectra signals of the hydroxyl proton (in various solvents), appear of weaker fields for diastereomer II than do those for diastereomer I, whereas the value of the $\Delta\delta$(OH) shift in passing from solution in $CCl_4$ to that in acetone-$d_6$ is substantially less for diastereomer II than for diastereomer I (Table 2).

In the IR spectra of solid and dissolved (in $CCl_4$) isomer II, the absorption bands of the hydroxyl group are observed at lower frequencies than in the IR spectra of isomer I. At the same time, chemical shifts of the hydroxyl protons and the $\nu$(OH) values of both isomers suggest only a rather weak intramolecular hydrogen bond.

The above conclusions on the configuration and the prefered conformation of the diastereomeric carbinols were fully supported by an X-ray study of diastereomer I. Single crystals of complex I were prepared by slow evaporation of a diluted solution in acetone. The crystals are monoclinic, $a = 6.201(2)$, $b = 27.429(7)$, $c = 7.754(2)$ Å, $\beta = 92.33(2)°$. $V = 1317.7(8)$ Å$^3$, $M = 338.24$, $d_{calc.} = 1.705$ g/cm$^3$ for $Z = 4$; space group $P2_1/n$. Unit cell parameters and intensities of 1597 reflections with $I \geqslant 2\sigma$ were measured with a Syntex $P2_1$ automatic diffractometer ($\lambda M_0$-$K_\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta_{max} \leqslant 25°$). Absorption collections were neglected, $\mu(M_0K_\alpha) = 12.6$ cm$^{-1}$.

The structure was solved by the heavy atom technique and refined by the least-squares procedure in a full matrix anisotropic (isotropic for hydrogen atoms, all of which were located in a difference synthesis) approximation; $R = 0.022$, $R_w = 0.035$. Atomic coordinates and temperature factors are given in Table 3, bond angles in Table 4, equations of some planar molecular fragments in Table 5. The molecular geometry with bond lengths is represented in Fig. 4 *. The rhodium atom has the square-planar coordination usual for RhLL'(acac) complexes, formed by the chelating acac ligand and two isolated double bonds of the diene ligand. The dihedral angle RhO(2)O(3)RhQQ' equals 3.1° (Q and Q' are centroids of the C(2)—C(3) and C(5)—C(6) bonds, respectively).

As was expected, the most characteristic feature of the molecule is the intramolecular hydrogen bond O(1)—H···O(2) between the hydroxyl group and one of the oxygen atoms of the acac ligand. This bond is relatively weak since the distances O(1)···O(2) of 2.821(4) Å and H···O(2) of 2.15(4) Å are close to the upper limits of the usually observed values [7]. Nevertheless, this bond still exerts some on the molecule influence, since the C(2)—C(8) bond is bent towards the metal atom so that the carbinol atom C(8) is displaced out of the C(2)—C(3)—C(5)—C(6) plane by 0.346(4) Å. However, the Rh···C(8) distance of 3.108(4) Å is non-bonding, as is observed in the complex $[Rh(\eta^5\text{-}C_7H_7CH_2)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ [1], where the Rh···C(8) distance equals 2.27 Å.

The H(O) and H(8) hydrogen atoms are in *trans*-positions relative to the O(1)—C(8) bond, which is in agreement with the rather large value of $J$(OH—H(8)) = 10 Hz observed in the PMR spectrum of this complex (the torsion angle of H(O)—O(1)—C(8)—H(8) equals —177°). The C(9) methyl group is

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* To avoid overcrowding of the drawing, only the hydrogen atom of the hydroxyl group participating in the intramolecular hydrogen bond is shown.

TABLE 4

BOND ANGLES (DEG.)

| Angle | ω | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| O(2)RhO(3) | 90.27(9) | C(12)O(3)Rh | 125.0(2) | C(3)C(4)C(7) | 100.5(3) |
| RhO(2)C(10) | 125.5(2) | C(2)C(1)C(6) | 99.7(3) | C(5)C(4)C(7) | 102.1(3) |
| O(2)C(10)C(11) | 125.7(3) | C(2)C(1)C(7) | 100.6(3) | C(4)C(5)C(6) | 105.9(3) |
| O(2)C(10)C(13) | 114.0(3) | C(6)C(1)C(7) | 102.2(3) | C(5)C(6)C(1) | 106.0(3) |
| C(11)C(10)C(13) | 120.2(3) | C(1)C(2)C(3) | 105.5(3) | C(1)C(7)C(4) | 94.0(3) |
| C(10)C(11)C(12) | 127.2(3) | C(1)C(2)C(8) | 123.0(3) | O(1)C(8)C(2) | 110.9(3) |
| C(11)C(12)O(3) | 126.1(3) | C(3)C(2)C(8) | 128.3(3) | O(1)C(8)C(9) | 111.3(3) |
| C(11)C(12)C(14) | 118.4(3) | C(2)C(3)C(4) | 106.6(3) | C(2)C(8)C(9) | 112.6(3) |
| O(3)C(12)C(14) | 115.5(3) | C(3)C(4)C(5) | 99.2(3) | C(8)O(1)H(O) | 108(3) |

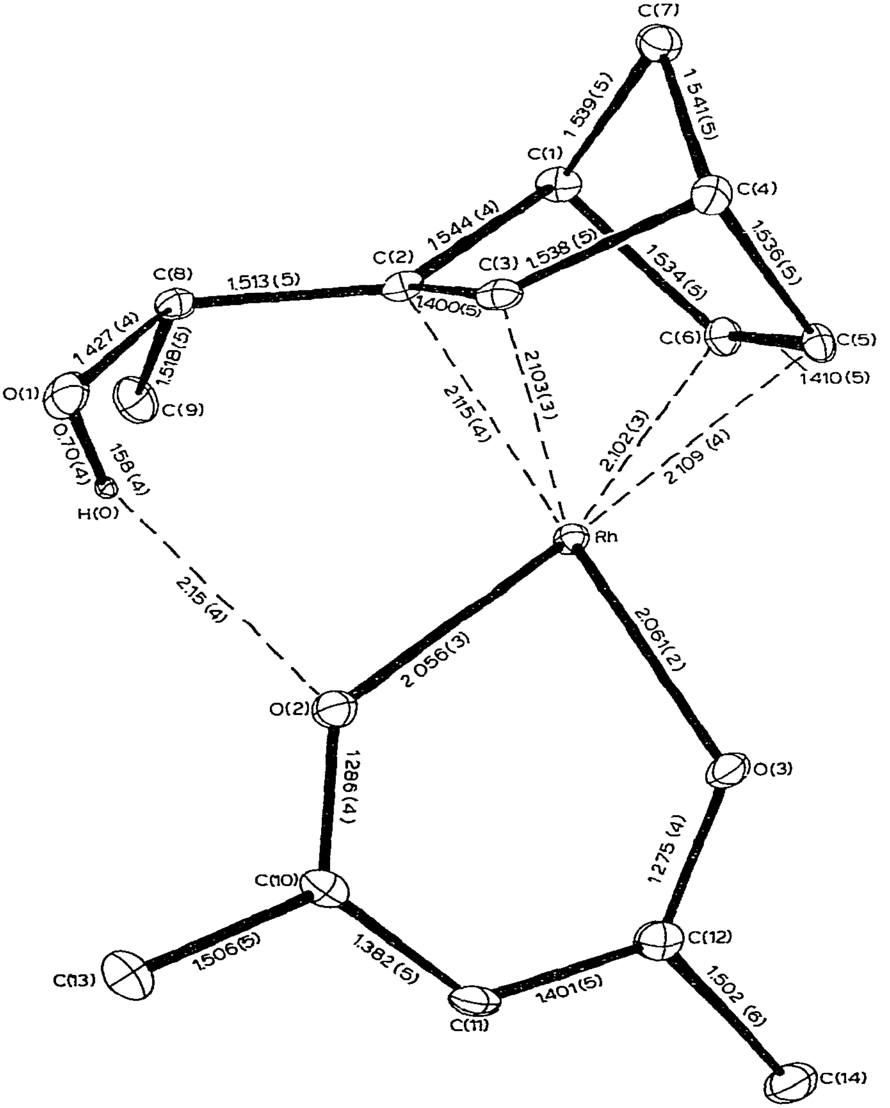

Fig. 4. The structure of isomer I with interatomic distances.

TABLE 5

PLANAR MOLECULAR FRAGMENTS

*a) Atomic deviations Δ(Å) from mean planes*

| | | Δ/σ | | | Δ/σ |
|---|---|---|---|---|---|
| *Plane (1)* | | | *Plane (4)* | | |
| O(2) | −0.003 | 1.12 | C(1) | 0.001 | 0.28 |
| O(3) | 0.005 | 2.20 | C(6) | −0.002 | 0.45 |
| C(10) | 0.001 | 0.24 | C(5) | 0.002 | 0.45 |
| C(11) | 0.014 | 3.76 | C(4) | −0.001 | 0.27 |
| C(12) | −0.020 | 5.63 | C(7)[a] | 0.817 | 230.90 |
| C(13)[a] | −0.061 | 13.96 | | | |
| C(14)[a] | −0.112 | 24.47 | *Plane (5)* | | |
| Rh[a] | −0.028 | 118.44 | Rh | 0.000 | 0.00 |
| | | | C(2) | 0.000 | 0.00 |
| *Plane (2)* | | | C(3) | 0.000 | 0.00 |
| C(2) | 0.002 | 0.51 | | | |
| C(3) | −0.002 | 0.56 | *Plane (6)* | | |
| C(5) | 0.002 | 0.60 | Rh | 0.000 | 0.00 |
| C(6) | −0.002 | 0.57 | C(5) | 0.000 | 0.00 |
| C(1)[a] | 0.897 | 261.05 | C(6) | 0.000 | 0.00 |
| C(4)[a] | 0.901 | 252.33 | | | |
| C(8)[a] | −0.346 | 98.09 | *Plane (7)* | | |
| | | | C(2) | 0.000 | 0.03 |
| *Plane (3)* | | | C(3) | −0.000 | 0.04 |
| C(1) | −0.003 | 0.89 | C(8) | −0.000 | 0.02 |
| C(2) | 0.004 | 1.37 | H(3) | 0.008 | 0.24 |
| C(3) | −0.005 | 1.49 | | | |
| C(4) | 0.003 | 0.96 | *Plane (8)* | | |
| C(7)[a] | 0.849 | 218.44 | C(5) | 0.000 | 0.14 |
| | | | C(6) | −0.000 | 0.15 |
| | | | H(5) | −0.024 | 0.72 |
| | | | H(6) | 0.042 | 0.97 |

*b) Coefficients of equations of mean square-root planes* $Ax + By + Cz - D = 0$

| Plane | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| 1 | −0.5267 | 0.5739 | −0.6270 | 0.9692 |
| 2 | 0.3635 | −0.5795 | −0.7295 | −1.0372 |
| 3 | −0.1786 | −0.8416 | −0.5097 | −2.0912 |
| 4 | 0.7574 | −0.0773 | −0.6484 | 1.8780 |
| 5 | 0.8382 | 0.1604 | −0.5213 | 1.0648 |
| 6 | −0.4073 | −0.8494 | −0.3356 | −4.1949 |
| 7 | 0.1181 | −0.7363 | −0.6662 | −1.6031 |
| 8 | 0.6390 | −0.2857 | −0.7142 | 0.7960 |

*c) Selected dihedral angles* (deg.)

| | | | |
|---|---|---|---|
| (1)—(2) | 86.2 | (3)—(4) | 105.1 |
| (2)—(3) | 37.4 | (5)—(7) | 109.2 |
| (2)—(4) | 37.5 | (6)—(8) | 102.8 |

[a] Atoms not included in calculation of plane equations.

directed towards the rhodium atom (*endo*-orientation) and the distances of Rh···O(1) of 3.474(3) Å and Rh···C(9) of 3.502(4) Å are of about the same length.

Probably due to the proximity of the C(9) and C(1) atoms (the corresponding distance equals 3.209(5) Å), the intramolecular hydrogen bond remains

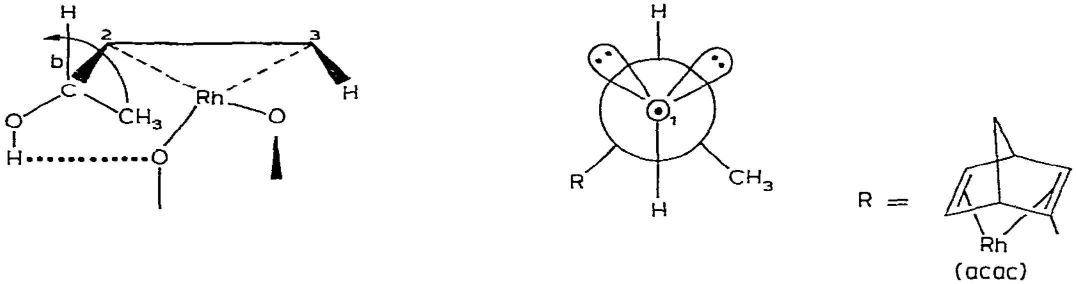

Fig. 5. Another possible conformation of diastereomer II with an intramolecular hydrogen bond.

rather weak and, as a consequence, complex I reveals a certain deviation from the idealized skewed conformation ($\psi \approx 30°$, Fig. 1) of the substituents at the *exo*-carbon relative to the diene double bond and as a result the O(1)—C(8)—C(2)—C(3) torsion angle is only 20°.

It is noteworthy that on passing to the diastereomer II, two sterically unfavourable short contact C(9)···C(1) ($\sim$3.1 Å) and C(9)···C(3) (3.4 Å) appear in its conformation (shown in Fig. 3b) with the same O(1)—C(8)—C(2)—C(3) torsion angle of 20°, the contact between the Me group and the C(1) carbon atom being $\sim$0.2 Å shorter. Taking into account this difference, one may assume that the O(1)—C(8)—C(2)—C(3) torsion angle is somewhat larger in the crystal of complex II, which leads to a decrease in the O(1)···O(2) distance and, as a result, to an increase in the strength of the intramolecular hydrogen bond in this complex. Such a supposition is in good agreement with the above-mentioned spectral and physico-chemical properties of this isomer.

In another possible conformation of isomer II, in the idealized initial state (skewed conformation, $\psi \approx 30°$, Fig. 5) the O(1)···O(2) distance ($\sim$3.3 Å) obviously exceeds the upper limit for the formation of the intramolecular hydrogen bond.

However, rotation of the substituent around the C(2)—C(8) bond (in the direction indicated by an arrow in the figure) by 20—40° leads, from this point of view, to a satisfactory result. At the same time such a rotation is extremely unfavourable due to the resulting short contacts between the methyl group and the C(3) atom (the contact C(9)···C(3) equals $\sim$2.8 and $\sim$2.9 Å at 20 and 40° rotations, respectively). Besides, the relative positions of the methyne proton and the proton of the hydroxyl group which is closest to transoidal do not correspond in this case to the observed small value of $J$(OH—H(8)) $\leqslant$2 Hz. Taking into account this fact and the existence of the intramolecular hydrogen bond, the only conformation possible for isomer II in the solid state is the one shown in Fig. 3b with a C(1)—C(8)—C(2)—C(3) torsion angle of 30—35°.

In other respects the molecule of complex I does not differ significantly from other acetylacetonatorhodium complexes studied by X-ray diffraction. The 6-membered metallocycle is almost planar and oriented approximately perpendicular to the planes of the $\pi$-coordinated double bonds C(2)=C(3) and C(5)=C(6) (Table 5). In a similar complex $Rh(C_2H_4)_2$(acac) [9] a mutually perpendicular orientation of the ethylenic bonds and the chelate cycle was also found (dihedral angle 87.4°). The Rh—O bond lengths and the geometrical parameters of the acac ligand are quite common and comparable with the corresponding values in the complexes $Rh(C_2H_4)_2(acac)$, $Rh(C_2H_4)(C_2F_2)(acac)$ [9], $Rh(CO)_2(acac)$ [10] and $Rh(CO)(acac)PPh_3$ [11].

The ethylenic fragments of the norbornadiene skeleton are linked to the rhodium atom symmetrically and the mean Rh—C distance of 2.107(4) Å is very close to those found, for example, in $Rh(C_2H_4)_2(acac)$ (2.13 Å) and $Rh(C_8H_{12})(C_5H_4COOCH_3)$ (2.115 Å) [12], whilst the double bond lengths (mean value of 1.405(5) Å) are, as usual, greater than the standard value of 1.337 Å.

## References

1 A.A. Koridze, I.T. Chizhevsky, P.V. Petrovski, E.I. Fedin, N.E. Kolobova, L.A. Vinogradova, L.A. Leites, V.G. Andrianov and Yu.T. Struchkov, J. Organometal. Chem., 206 (1981) 373.

2 I.T. Chizhevsky, A.A. Koridze, V.I. Bakhmuttov and N.E. Kolobova, J. Organometal. Chem., 206 (1981) 361.

3 I.T. Chizhevsky, A.A. Koridze, V.I. Bakhmutov, N.E. Kolobova, Izv. Akad. Nauk SSSR, Ser. Khim., in press.

4 I.C. Davis and K.K. Deb, Adv. Magn. Res., 4 (1970) 201.

5 G.C. Pimentel and A.L. McClellan, The Hydrogen Bond, Freeman, San Francisco, 1960.

6 H.O. Chaplin and L. Hunter, J. Chem. Soc., (1938) 375.

7 W.C. Hamilton and J.A. Ibers, Hydrogen Bonding in Solids, Pergamon Press, New York, 1968.

8 J.A. Evans and D.K. Russell, Chem. Commun. (1971) 197.

9 F. Hug and A.C. Skapski, J. Cryst. Mol. Struct., 4 (1974) 411.

10 J.G. Leipold, S.S. Basson, L.D.C. Bok and T.I.A. Gerber, Inorg. Chim. Acta, 26 (1978) L35.

11 M. Arthurs, S.M. Nelson and M.G.B. Drew, J. Chem. Soc. Dalton Trans., (1977) 779.

12 S.D. Ittel and J.A. Ibers, Adv. Organometal. Chem., 14 (1976) 33.