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NORBORNADIENE COMPLEXES OF TRANSITION METALS

II *. STEREOCHEMISTRY OF {2-(α-HYDROXYETHYL)NORBORNADIENE} CYCLOPENTADIENYLRHODIUM COMPLEXES

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Summary

The interaction of $Rh(CO)_2(acac)$ with diastereomeric 2-(α-hydroxyethyl)-norbornadienes affords a racemic mixture of the diastereomeric $Rh\{\eta^4\text{-}C_7H_7CH(OH)Me\}(acac)$ (I), from which the individual isomers Ia and Ib are isolated by fractional crystallization. The *ψ-exo* (IIa) and *ψ-endo* (IIb) carbinols $Rh\{\eta^4\text{-}C_7H_7CH(OH)Me\}(\eta^5\text{-}C_5H_5)$ are derived by substituting the acetylacetonate ligand in Ia and Ib for cyclopentadienyl by the action of TlC_5H_5. Carbinol IIb is also obtained as the only product in the stereoselective reaction of aldehyde $Rh(\eta^4\text{-}C_7H_7CHO)(\eta^5\text{-}C_5H_5)$ with methyllithium. The study of the stereochemistry of the removal of a hydroxy group from carbinols IIa and IIb, to form the cationic *syn* (IVa) and *anti* (IVb) η^3-allylic complexes $[Rh(\eta^5\text{-}C_7H_7\text{-}CHMe)(\eta^5\text{-}C_5H_5)]^+PF_6^-$, respectively, enables one to reliably assign their configuration. An estimation of the preferred conformation of diastereomers IIa and IIb with the aid of IR and ^1H NMR data, as well as of other physical characteristics of the individual carbinols, has been made.

Introduction

In view of the growing interest in cationic complexes generated from transition metal-coordinated norbornadienyl carbinols [2,3], we have previously suggested a convenient method for synthesizing norbornadienecyclopentadienylrhodium derivatives, $Rh(\eta^4\text{-}C_7H_8)(\eta^5\text{-}C_5H_5)$, containing functional groups in the 2-position of the diene ligand [1]. The norbornadiene derivatives substituted in the 2-position are chiral in nature, and the introduction of an additional asym-

* For part 1 see ref. 1.

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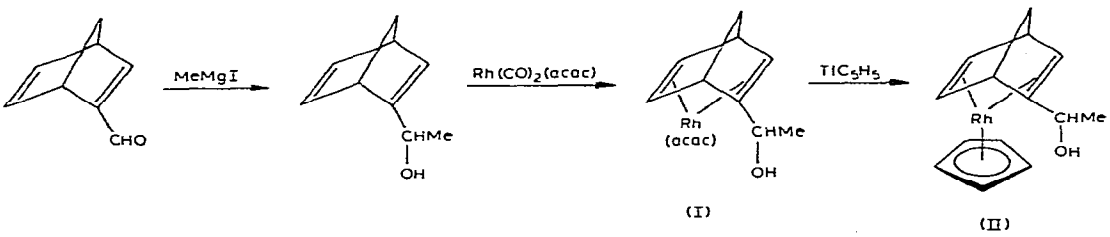
metric center in the substituent allows one to create diastereomeric products, for example, by synthesizing 2-(α-hydroxyethyl)-norbornadienecyclopentadienylrhodium, Rh{η^4-$C_7H_7CH(OH)Me$}(η^5-C_5H_5) (II), according to equation 1.



The synthesis of complex II by the interaction of 2-formylnorbornadienecyclopentadienylrhodium, Rh(η^4-C_7H_7CHO)(η^5-C_5H_5) (III) with methyllithium in ether gives preferential formation (>96%) of only one diastereomer.

This study is devoted to the preparation of individual pairs of diastereomers II, and analysis of their configurations and preferred conformations, based on their spectral data (IR and ^{1}H NMR), as well on their physical and chemical properties.

Results and discussion

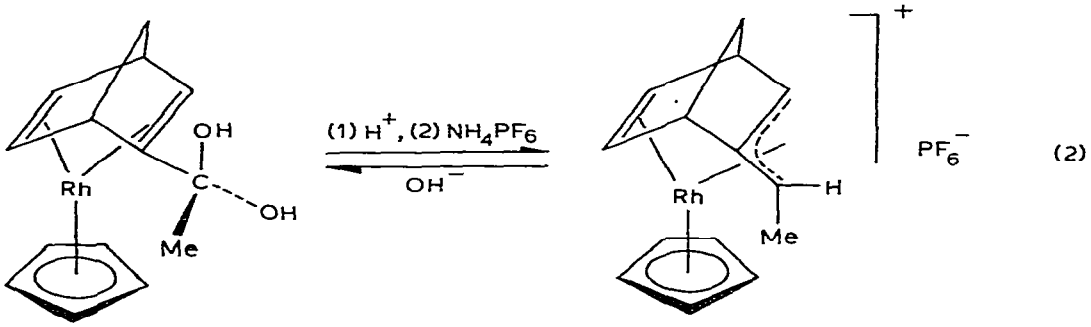
Analysis of ^{1}H NMR spectra on CCl_4 of 2-(α-hydroxyethyl)norbornadiene, obtained by interaction of 2-formylnorbornadiene with methylmagnesium iodide in ether, revealed the presence of two diastereomeric carbinols in approximately equal quantity according to the intensity of the signals of the exocyclic methine protons, with $\Delta\delta$ = 1.22 Hz. This mixture, when treated with $Rh(CO)_2(acac)$, formed the diastereomeric carbinols Rh{η^4-$C_7H_7CH(OH)$-Me}(acac) (I), which fail to separate by TLC on silica gel. However, fractional crystallization enabled us to the separate individual isomers: Ia, m.p. 114—115°C (from n-pentane), and Ib, m.p. 155°C (from acetone).

By the action of thallous cyclopentedienide on the individual isomers we obtained the diastereomers IIa, m.p. 85—86°C and IIb, m.p. 78°C, respectively. The latter are not equally adsorbed on silica gel, with complex IIb having a large R_f value. The configurations of the isomeric carbinols IIa and IIb were deduced on the basis of their behaviour in acidic media and were supported by the analysis of the preferred conformation of these compounds, obtained with the help of IR and ^{1}H NMR spectroscopy (see below).

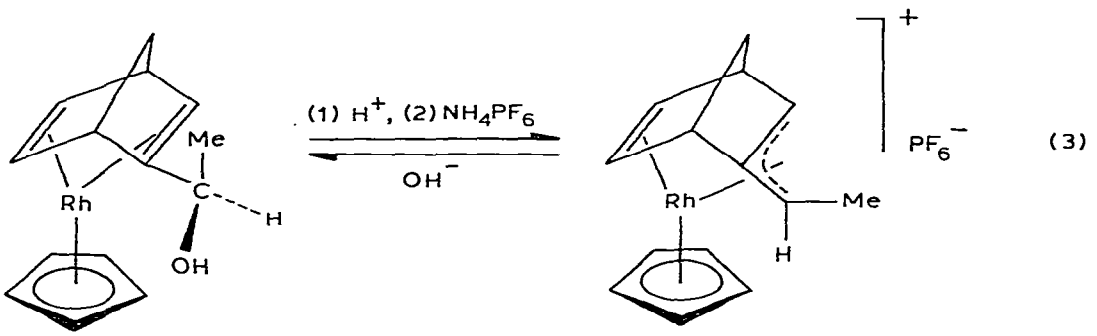
We have shown earlier that cationic organometallic compounds are formed by the action of concentrated H_2SO_4 on {2-(α-hydroxyalkyl)norbornadiene}-cyclopentadienylrhodium and -tricarbonyliron. In these compounds the bicyclic ligand is bonded to the metal atom through η^2-ethylenic and η^3-allylic bonds, the *exo*-carbon atom taking part in the latter bond *. These reactions appear to proceed highly stereoselectively, i.e. depending on the configuration of the

* More details on these and some other cationic rhodium complexes, including a closer analysis of ^{1}H and ^{13}C NMR spectral data and an X ray structure examination of two of them will be discussed in a following paper.

initial complex, carbinols IIa and IIb, cationic complexes IVa and IVb were formed with the methyl group in the *syn* or *anti* position, respectively (eqs. 2 and 3). These compounds were characterized as their stable hexafluorophosphate salts.



(IIa) (IVa) (2)



(IIb) (IVb) (3)

The assignment of configurations to the isomeric complexes IVa and IVb is based on the well-known rule, according to which the substituent protons (hydrogen atom or methyl group) in the *syn* position are less shielded than the protons in the *anti* position in the ^{1}H NMR spectra of η^3-allyl metal complexes [4,5]. Thus, the hydrogen atom of the carbon at the 8 position in complex IVa has a chemical shift of 5.05 ppm, whereas in complex IVb it is 6.80 ppm. As for the methyl groups of these complexes, the relative shielding is opposite, with chemical shifts of 2.31 and 1.60 ppm, respectively.

The stereospecificity of the formation of the isomeric cationic complexes IVa and IVb from the diastereomeric carbinols IIa and IIb is similar to that observed in solvolytic reactions of esters of diastereomeric ferrocene [6] and butadieneiron tricarbonyl carbinols [7] which proceeds through the stage of the formation of the corresponding carbonium ions. It seems reasonable that in generating cationic complexes from IIa and IIb, as in the above-mentioned solvolitic reactions, the leaving group moves in the direction opposite to the metal atom. In such a case the diastereomeric carbinols must have configurations represented by the enantiomers in equation 2 and 3. In accordance with the Cahn-Ingold-Prelog nomenclature [8], the *SS* and *SR* relative stereo-

chemistries should be assigned to the enantiomers represented of complexes IIa and IIb, and *RR* and *RS* stereochemistry to their optical antipodes (relative to the 2- and 8-positioned carbon atoms).

Under alkaline hydrolysis conditions, complexes IVa and IVb are converted back into their carbinol precursors IIa and IIb, which were identified by comparison of their physical constants (m.p., R_f) and ^{1}H NMR spectra. This fact indicates that the attack of hydroxide ion on the η^3-allyl complexes IVa and IVb occurs from the side opposite to the metal, i.e. in the *exo* position. Otherwise, in the case of *endo* attack (most probably occurring with the participation of the rhodium atom), one would expect inversion of configuration and the formation of carbinols IIb and IIa from IVa and IVb, respectively.

The conformational analysis of complexes IIa and IIb is in good agreement with the configurations suggested. The least steric hindrance between the substituent in the diene ligand and the bulky cyclopentadienylrhodium group should arise in the skew conformation, represented in Fig. 1, where the dihedral angle between the substituent in the c position and the double diene bond is approximately 30°.

Consideration of molecular models reveals that in such an idealized conformation of the dienol complexes there are three sterically different positions which substituents on the carbinol carbon can occupy (Fig. 1):

Position c is severely crowded due to the proximity of the cyclopentadienylrhodium group and the hydrogen atom to the 3-position diene carbon. Position b is less sterically crowded, whereas position a is the least crowded, which to some extent is probably due to some bending of the exocyclic bond in the direction of the metal atom.

Sterically preferred conformations of isomeric carbinols will be those with the largest groups in the relatively uncrowded positions, and the diastereomers are designated *ψ-exo* and *ψ-endo* according to the preferred conformation of the hydroxy group relative to rhodium.

In the *ψ-exo* isomer the hydroxy group is less sterically shielded, and therefore this carbinol, as was already mentioned, is absorbed more readily during chromatography than the *ψ-endo* isomer. IR spectra of solid samples (KBr pellets) reveal a broad absorption band of the hydroxy group centered at 3100 cm^{-1} for isomer IIa, as distinct from a narrow bond at 3515 cm^{-1} for isomer (IIb), which confirms to the ability of carbinol IIa to form an intermolecular hydrogen bond.

However, the most convincing evidence for such a conclusion was from the

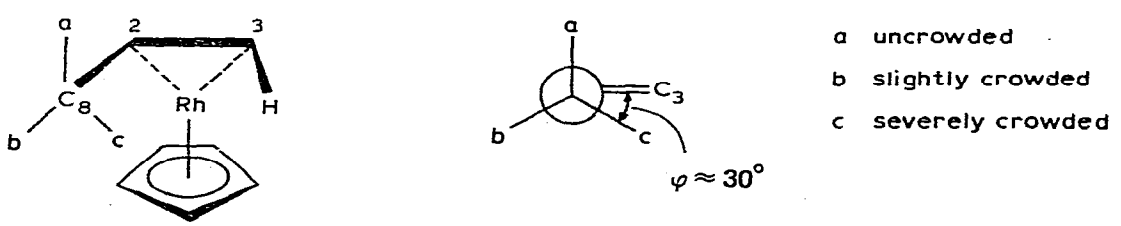
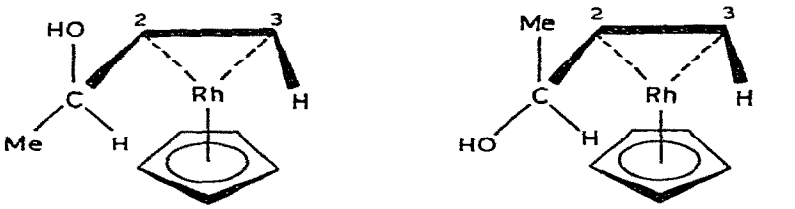


Fig. 1. The skew conformation of the 2-substituted derivative of (norbornadiene)cyclopentadienylrhodium.



(IIa), ψ-exo (IIb), ψ-endo

Fig. 2. Sterically preferred conformations of carbinols IIa and IIb.

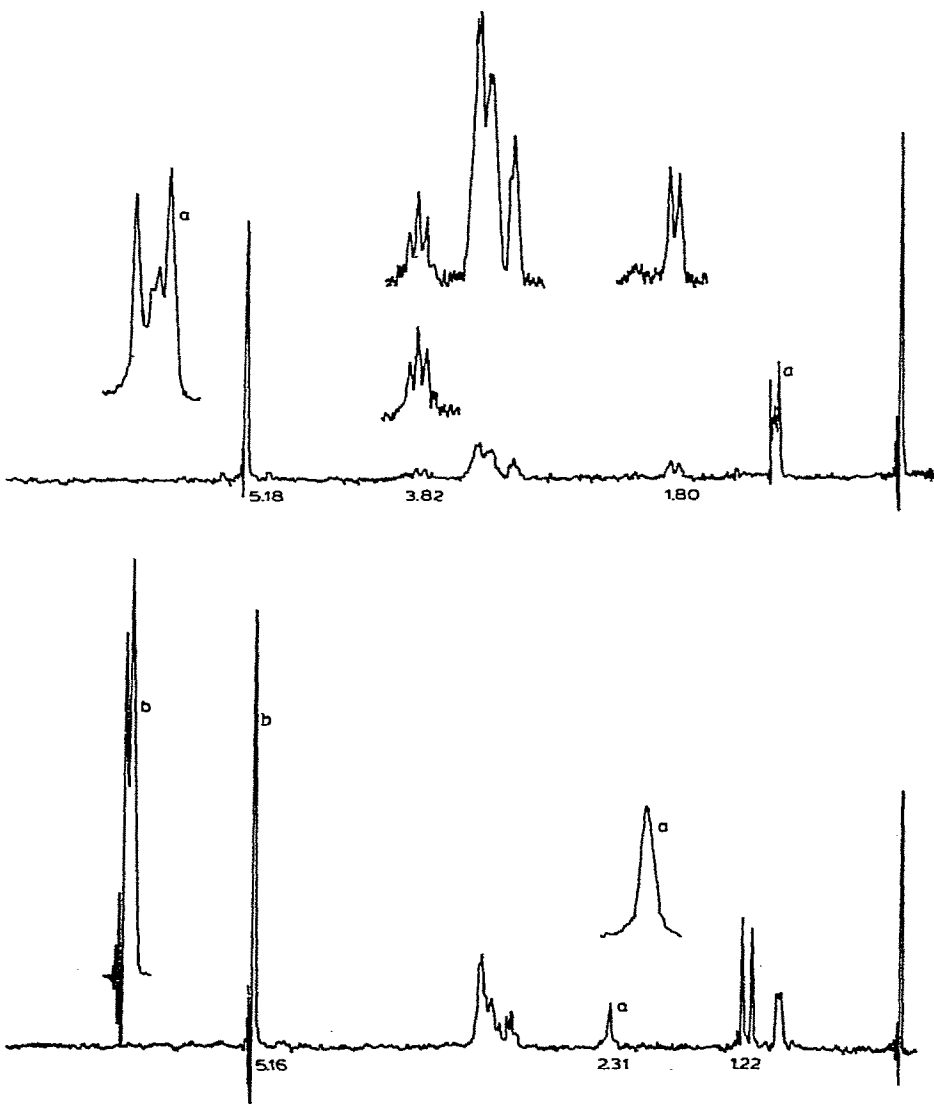


Fig. 3. (a) ^{1}H NMR spectrum of IIa in $CDCl_3$. (b) ^{1}H NMR spectrum of IIb in $CDCl_3$.

investigation of diastereomers IIa and IIb in different solvents by ^1H NMR spectroscopy. The spectrum of complex IIa obtained in $CDCl_3$ (Fig. 3a) reveals a doublet of the methyl group at highest field at δ 1.00 ppm, J (CH_3—H(8)) 6.3 Hz, which, in this case, overlaps H(7_α) and H(7_β) proton signals. The broadened doublet at δ 1.80 ppm, J(OH—H(8)) 5.4 Hz, is assigned by the double resonance technique to the hydroxy group proton. In the range 3.00—3.44 ppm, multiplet diene ligand proton signals are recorded. At δ 3.82 ppm, a poorly resolved quintet with J(H(8)—(OH, CH_3)) 6.0 Hz is recorded, which is also assigned by double resonance to an C(8) atom proton. Finally, at 5.18 ppm, a doublet arises from the five protons of the cyclopentadienyl ring with J(HRh) 0.80 Hz.

In the ^1H NMR spectrum of complex IIb in $CDCl_3$ solution (Fig. 3b) the doublet of the methyl group with J(CH_3—H(8)) 6.3 Hz is at lower field (in

TABLE I

^1H NMR SPECTRA OF THE RHODIUM COMPLEXES [a]

Compound	Chemical shift (multiplicity [b], relative intensity, J [c], assignment)
Ia	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_3COCHCOCH_3); 1.21(m, 2, H(7_α), H(7_β); 1.18(d, 3, J(CH_3—H(8)) = 6.0 Hz, CH_3).
Ib	5.33(s, 1, COCHCO); 4.15(m, 2, H(5,6)); 3.66(m, 4, H(1, 3, 4, 8)); 3.12(d, 1, J(OH—H(8)) = 10 Hz, OH); 1.84(s, 6, CH_3COCHCOCH_3); 1.63(d, 3, J(CH_3—H(8)) = 6.0 Hz, CH_3); 1.25(m, 2, H(7_α), H(7_β).
IIa [d]	5.18(d, 5, J(H—Rh) = 0.8 Hz, C_5H_5); 3.82(qw, br, 1, J(H(8)—(OH, CH_3)) = 6.0 Hz, H(8); 3.33(m, 4, H(1, 4—6)); 3.07(t, br, 1, H(3)); 1.80(d, br, 1, J(OH—H(8)) = 6.0 Hz, OH); 1.00(d, 3, J(CH_3—H(8) = 6.0 Hz, CH_3); 0.92(m, 2, H(7_α), H(7_β).
IIa	5.17(d, 5, J(H—Rh) = 0.82 Hz, C_5H_5); 3.71(qw, br, 1, J(H(8)—(OH, CH_3) = 6.3 Hz, H(8)); 3.38(q, 1, J = 3.5 Hz, H(5)); 3.32(q_d, 1, J_1 = 3.8 Hz, J_2 = 1.2 Hz, H(6)); 3.29(m, 1, H(1)); 3.21(m, 1, H(4)); 3.04(t, br, 1, J = 3.5 Hz. H(3)); 2.93(d, br, 1, J(OH—H(8)) = 5.3 Hz OH); 1.33(d, 3, J(CH_3—H(8)) = 7.2 Hz, CH_3); 1.01(d_t, 1, J(H($7_{\beta(\alpha)}$)—H($7_{\beta(\alpha)}$)) = 9.0 Hz, J(H($7_{\beta(\alpha)}$)—H(1,4) = 1.8 Hz, H($7_{\beta(\alpha)}$)); 0.97(d_t, 1, J(H($7_{\alpha(\beta)}$)—H($7_{\beta(\alpha)}$)) = 9.0 Hz, J(H($7_{\alpha(\beta)}$)—H(1,4) = 1.8 Hz, H($7_{\alpha(\beta)}$)).
IIb	5.16(d, 5, J(H—Rh) = 1.0 Hz, C_5H_5); 3.33(m, 5, H(1,4—6.8); 3.09(t, br, 1, = 3.5 Hz, H(3); 2.31(s, br, 1, OH); 1.22(d, 3, J(CH_3—H(8)) = 7.0 Hz, CH_3); 0.95(m, 2, H(7_α), H(7_β)).
IIb [d]	5.21(d, 5, J(H—Rh) = 0.82 Hz, C_5H_5); 3.49(q, br, 1, J(H(8)—(OH, CH_3)) = 6.3 Hz, H(8)); 3.37(m, 1, J = 3.6 Hz, H(5)); 3.35(m, 1, H(1)); 3.33(m, 1, J = 4.1 Hz, H(6); 3.23(m, 1, H(4); 3.11(t, br, 1, J = 3.6 Hz, H(3); 2.65(d, br, 1, J(OH—H(8)) = 2.7 Hz, OH); 1.15(d, 3, J(CH_3—H(8)) = 7.2 Hz, CH_3); 0.98(d_t, 1, J(H($7_{\beta(\alpha)}$)—H($7_{\alpha(\beta)}$)) = 9.0 Hz; J(H($7_{\beta(\alpha)}$)—H(1,4) = 1.8 Hz, H($7_{\beta(\alpha)}$)); 0.93(d_t, 1, J(H($7_{\alpha(\beta)}$)—H($7_{\beta(\alpha)}$)) = 9.0 Hz, J(H($7_{\alpha(\beta)}$)—H(1,4) = 1.8 Hz, H($7_{\alpha(\beta)}$)).
IVa	5.85(d, 5, J(H—Rh) = 0.8 Hz, C_5H_5); 5.05(q, br, 1, J(H(8)—CH_3) = 6.0 Hz, H(8)); 4.88(m, 1, H(3); 4.44(m, 1, H(6)); 4.2(m, 1, H(5)); 3.72(m, 2, H(1,4)); 2.31(d, 3, J(CH_3—H(8)) = 6.0 Hz, CH_3); 1.85(d, br, 1, J(H($7_{\beta(\alpha)}$)—H($7_{\alpha(\beta)}$)) = 10.0 Hz, H($7_{\beta(\alpha)}$)); 1.59(d_t, 1, J(H($7_{\alpha(\beta)}$)—H($7_{\beta(\alpha)}$)) = 10.0 Hz, J(H($7_{\alpha(\beta)}$)—H(1,4)) = 1.6 Hz, H($7_{\alpha(\beta)}$)).
IVb	6.80(q_d, 1, J(H(8)—CH_3) = 7.0 Hz, J(H(8)—Rh) = 1.5 Hz. H(8)); 5.80(d, 5, J(H—Rh) = 1.0 Hz, C_5H_5); 4.88(m, 1, H(3)); 4.74(q_d, 1, J_1 = 3.0 Hz, J_2 = 1.0 Hz, H(6)); 4.29(m, 1, H(5)); 3.80(m, 1, H(4(1))); 3.28(m, 1, H(1(4))); 1.75(d_t, 1, J(H($7_{\beta(\alpha)}$)—H($7_{\alpha(\beta)}$)) = 10 Hz, J(H($7_{\beta(\alpha)}$)—H(1,4) = 1.2 Hz, H($7_{\beta(\alpha)}$)); 1.60(d, 3, J(CH_3—H(8)) = 7.0 Hz, CH_3); 1.59(d_t, 1, J(H($7_{\alpha(\beta)}$)—H($7_{\beta(\alpha)}$)) = 10 Hz, J(H($7_{\alpha(\beta)}$)—H(1,4) = 1.2 Hz, H($7_{\alpha(\beta)}$)).

[a] Solvent is deuterioacetone unless otherwise indicated. [b] s = singlet, d = doublet, t = triplet, q = quadruplet, q_w = quintet, m = multiplet, t_d = triplet of doublets, d_t = doublet of triplets, q_d = quadruplet of doublets, [c] J is signal split in observed spectra. [d] In deuteriochloroform solvent.

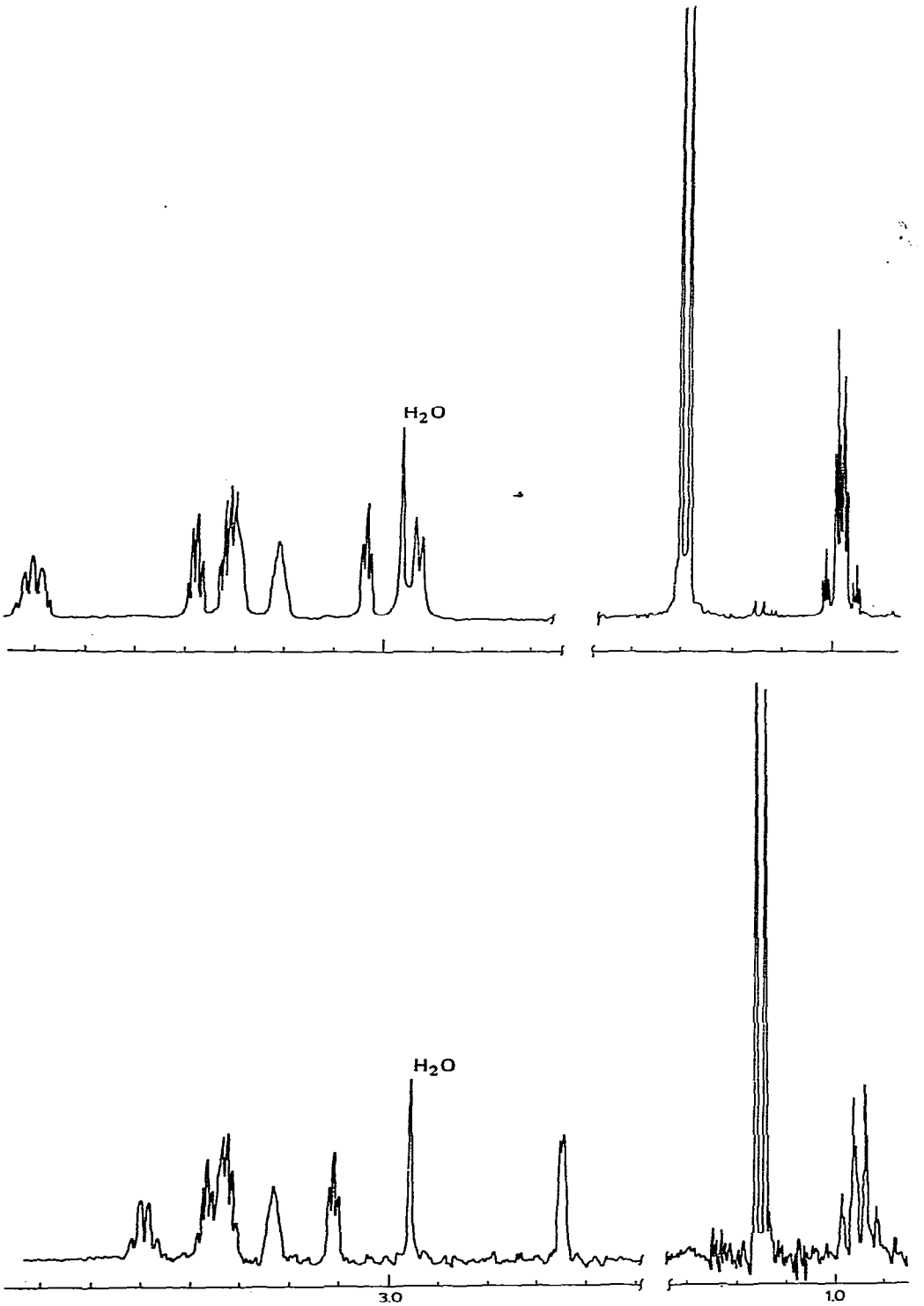


Fig. 4. (a) ^1H NMR spectrum in IIa in acetone-d_6. (b) ^1H NMR spectrum of IIb in acetone-d_6 (C_5H_5 signals are omitted).

comparison with IIa), δ = 1.22 ppm; a broadened hydroxy proton singlet is present at 2.31 ppm. The signal of the diene ligand protons and that of the methine proton are in the range 3.00—3.38 ppm. The chemical shifts of the rest of the signals differ slightly from those indicated above for complex IIa (see Table 1).

Replacing deuterochloroform by deuteroacetone as solvent in the case of IIa and IIb (Fig. 4a, b) leads to a variation, most pronounced in the signals of the exocyclic part of the molecule *. The most remarkable is the significant downfield shift of the signal of the hydroxy group in the case of IIa ($\Delta\delta$ = 1.13 ppm), whereas the value $\Delta\delta$ for (IIb) is only 0.34 ppm. As for the coupling constant values, they remain practically invariable for the hydroxy and methine proton signals in the case of IIa, whereas in the case of IIb, the replacement of the solvent, on the contrary leads to a splitting of the hydroxy proton signal into a doublet, with J(OH—H(8)) 2.6 Hz and to a downfield shift of the broadened methine proton signal, δ = 3.49 ppm.

Such variations in the chemical shift of the hydroxy proton when going from inert (CCl_4, $CHCl_3$) to sufficiently donor, polar solvents (acetone, DMSO) are characteristic of hydroxy-containing compounds capable of forming intermolecular hydrogen bonds [9]; whereby the observed value of the downfield signal of the hydroxy group in IIa (δ = 1.13 ppm) in comparison with that of IIb (δ = 0.34 ppm) indicates a stronger tendency of *ψ-exo* carbinol toward forming intermolecular hydrogen bonds (in this case with a molecule of the donor solvent). Besides, analysis of the coupling constant J(OH—H(8)) shows that in isomer IIa, the rotation around the C—O bond is a free one (J(OH—H(8)) 5.4 Hz)*, whereas in isomer IIb (J(OH—H(8)) 2.6 Hz) one conformation of the hydroxy proton is realized preferentially in respect to this bond, with a nearly *cis* position of the interacting nuclei (Fig. 5). These data, together with IR characteristics and R_f values of isomers IIa and IIb, as was noted above, are in full agreement with the preferred conformations suggested for them (see Fig. 2).

As was noted above, the interaction of complex III with methyllithium, in contrast to the reaction of the uncoordinated ligand with methylmagnesium iodide, proceeds highly stereoselectively with a preferential formation of the *ψ-endo* isomer IIb. It is reasonable to assume that the introduction of a bulky cyclopentadienylrhodium group into the molecule brings about the difference in the stereochemical result of these reactions.

The IR spectra obtained from a solution of aldehyde III in CH_2Cl_2 revealed one ν(CO) bond at 1680 cm^{-1}, which is consistent with one preferred conformer present in the solution. In the case of *exo* attack on the carbonyl group of complex III by a nucleophile, the formation of diastereomer IIb is only possible when the aldehyde group relative to the double diene bond has the preferred *s-trans* conformation (eq. 4). An alternative explanation for the

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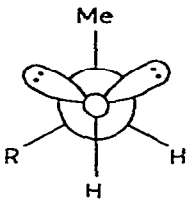
* ^{1}H NMR spectra of IIa and IIb in acetone-d_6 were recorded with a Bruker WH-360 spectrometer. This allowed making the corresponding assignment of the signals of the diene part of the molecule after analyzing the signal patterns and their variation in the chemical shifts from *ψ-endo* to *ψ-exo* carbinols. Here, "*J*" in Table 1 signifies the signal split in the observed spectra.

* The usual value J(OH—H) = 4—5 Hz [10].

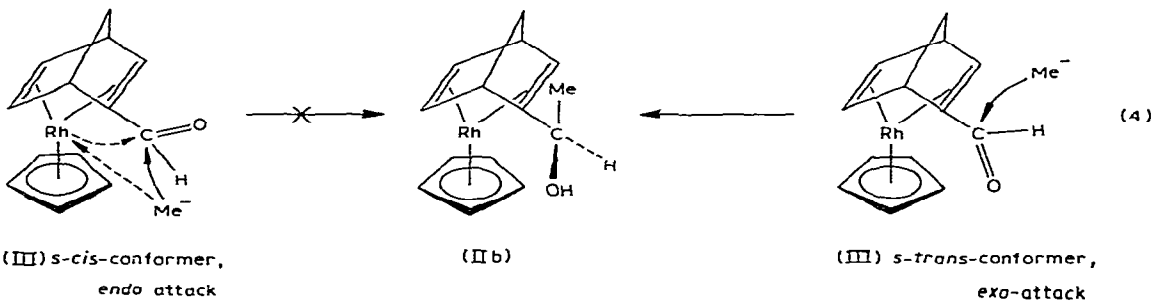


$R = Rh(\eta^4\text{-}C_7H_7)\ (\eta^5\text{-}C_5H_5)$

Fig. 5. The probably most preferred conformation of ψ-*endo* isomer IIb (relative to the C—O bond).

formation of IIb by means of *endo* attack on the aldehyde group of the complex (for example with the initial participation of rhodium atom) seems rather improbable, both because of steric reasons and in the light of *exo* attack on the cationic complexes IVa and IVb by the hydroxide ion, as well mentioned above.

Therefore, of the two possible directions, *endo* or *exo* attack, of the methyllithium on the aldehyde group of complex III, we prefer the latter, with realization of a *s-trans* conformation of the diene ligand in the initial complex.



(4)

(III) s-*cis*-conformer, *endo* attack (IIb) (III) s-*trans*-conformer, *exo*-attack

Interestingly, Clinton and Lillya [11] in analysing the conformation of the (dienone)tricarbonyliron complexes came to the conclusion that the *s-cis* conformation of the diene ligand is energetically more favourable. The saturated aldehydes and ketones normally exist in eclipsed conformations [12], and in our case the carbonyl group occupies such a conformation relative to the saturated C(1)—C(2) bond, whereas in the (dienone)tricarbonyliron complexes, the ketone group prefers occupying a position eclipsed relative to the coordinated double bond possessing a partially saturated character, than relative to the a hydrogen—carbon bond.

Experimental

^{1}H NMR spectra were recorded with a Perkin-Elmer R-32 spectrometer (90 MHz) and a Bruker WH-360 spectrometer (360 MHz), using TMS as an internal standard. IR spectra were taken with UR-20 spectrometer. The course of the reactions in the synthesis of the rhodium complexes was monitored using TLC on Silufol plates; an n-hexane-ether mixture (1 : 1) was used as the eluent.

{2-(α-hydroxyethyl)norbornadiene}acetylacetonatorhodium (diastereomers Ia and Ib)

A mixture of 0.68 g (0.5 mmol) of freshly distilled 2-(α-hydroxyethyl)nor-

bornadiene [13] and 1.03 g (0.4 mmol) of $Rh(CO)_2(acac)$ [14] in 30 ml dry benzene is refluxed in an inert gas atmosphere for 4—5 hours. After the reaction is complete (TLC), the solvent is evaporated in vacuum to one-third of the volume, 15—20 ml n-hexane is added and re-evaporated, the residue is dissolved in a minimum amount of hot n-hexane, filtered and allowed to stand for 12—15 hours at —78°C; the precipitated crystals are filtered, dried in vacuum, yielding 1.23 g (0.36 mmol, 91%) of a mixture of isomers Ia and Ib. A specimen of 0.5 g (0.148 mmol) mixture of diastereomers obtained by this procedure is recrystallized from 10—12 ml acetone, the precipitated crystals are separated from the mother solution by decantation, which is then evaporated in vacuum and the residue is again recrystallized from acetone. Two portions of the substance are combined, and recrystallization is repeated, a pure isomer (Ib) is obtained in the form of yellow needles, 0.2 g (0.059 mmol, 40%), m.p. 155°C (decomp); IR, ν(OH) 3450 cm^{-1} (KBr); (Found: C, 49.83; H, 5.60; Rh, 30.47. $C_{14}H_{19}O_3Rh$ Calculated: C, 49.70; H, 5.62; Rh, 30.47%). The remaining mother solution after a second crystallization is evaporated to dryness and residue recrystallized, first from n-hexane at —78°C, and then twice from n-pentane at —5 to 0°C, yielding 0.148 g (0.44 mmol, 29.7%) of yellow rhombic crystals of pure isomer Ia, m.p. 114—115°C (Found: C, 49.77; H, 5.65; Rh, 30.48. $C_{14}H_{19}O_3Rh$ calculated: C, 49.70; H, 5.62; Rh, 30.47%). IR ν(OH) 3423 cm^{-1} (KBr)).

{2-(α-hydroxyethyl)norbornadiene}cyclopentadienylrhodium (ψ-exo isomer IIa)

A mixture of 0.25 g (0.074 mmol) of complex Ia and 0.23 g (0.086 mmol) of freshly prepared TlC_5H_5 [15] in 4 ml of methylene chloride (distilled under argon) was refluxed in an inert gas atmosphere for 8 h. When cooled to room temperature, the suspension is thoroughly filtered, evaporated and the residue is extracted with ether (3 × 30 ml); the extracts are combined and the solvent is removed in vacuum *. The residue is recrystallized from n-hexane at dry ice temperature, yielding 0.18 g (0.059 mmol, 80%) of isomer IIa in the form yellow-golden whisker crystals, m.p. 85—86°C (Found: C, 55.16; H, 5.60; Rh, 33.97. $C_{14}H_{17}ORh$ calculated: C, 55.26; H, 5.59; Rh, 33.88%). IR ν(OH) 3100 cm^{-1} (br) (KBr); 3512s, 3570w (sh), 3622w cm^{-1} (CCl_4).

{2-(α-hydroxyethyl)norbornadiene}cyclopentadienylrhodium (ψ-endo isomer IIb)

Similarly, a mixture 0.15 g (0.044 mmol) of complex Ib and 0.137 g (0.051 mmol) of TlC_5H_5 yields 0.13 g (0.043 mmol, 96%) isomer IIb, yellow plates m.p. 78°C (n-hexane). (Found: C, 55.21; H, 5.52; Rh, 33.93. $C_{14}H_{17}ORh$ calculated: C, 55.26; H, 5.59; Rh, 33.88%). IR ν(OH) 3515 cm^{-1} (KBr); 3535 cm^{-1} (CCl_4).

Synthesis of syn- and anti-allyl complexes IVa and IVb

3—4 drops of H_2SO_4 are added to a solution of 0.2 g (0.065 mmol) of IIb in

* The procedure must be repeated once or twice in order to provide a more thorough separation of the solution containing the substance from thallous salts.

15 ml of abs. ether in inert gas atmosphere, while stirring and are then stirred for a further 15—20 min, the solvent is decanted from a dark-yellow oil which washed with abs. ether (2 × 10 ml) and dissolved in 2 ml of distilled water. A solution of 0.12 g (0.074 mmol) of NH_4PF_6 in 0.5 ml water ia added dropwise to the resulting bright-yellow solution during mixing. The precipitated amorphous yellow residue is filtered, washed with water on a filter and dried in air, then dissolved in a minimum amount of CH_2Cl_2 (1—2 ml) and re-precipitated from 150 ml of ether, yielding 0.26 g (0.06 mmol, 92%) of *anti*-allyl complex IVb in the form of an amorphous yellow powder which can be transformed into regular crystals by slow recrystallization from alcohol (Found: C, 38.75; H, 3.74; F, 25.78 $C_{14}H_{16}F_6PRh$ calculated: C, 38.89; H, 3.70; F, 26.38%).

Similarly, a mixture of 0.096 g (0.031 mmol) of complex IIa and 0.06 g (0.037 mmol) of NH_4PF_6 yields 0.125 g (0.029 mmol, 93%) of *syn*-allyl complex IVa (Found: C, 38.80; H, 3.65; Rh, 23.92. $C_{14}H_{16}F_6PRh$ calculated: C, 38.89; H, 3.70; Rh, 23.86%).

Hydrolysis of complexes IVa and IVb

1.2 ml of 5 *N* NaOH is added dropwise to 0.26 g (0.06 mmol) of complex IVb in 30 ml of water at 50°C while mixing; the resulting suspension is cooled to room temperature and extracted with ether (2 × 40 ml). The ether extracts are combined, washed with water, dried over anhydrous Na_2SO_4 and the solvent is removed in vacuum; the residue is crystallized from n-hexane at —78°C, yielding 0.16 g (0.052 mmol, 88%) of a product which reveals identical properties (m.p., IR, ^1H NMR, R_f) with complex IIb as described above.

Similarly, a mixture of 0.2 g (0.046 mmol) of complex IVa and 1 ml of 5 *N* NaOH yields 0.12 g (0.039 mmol, 85%) of complex IIa, having identical properties as described above for this compound.

Interaction of (2-formylnorbornadiene)cyclopentadienylrhodium with methyllithium

MeLi solution in ether (0.2 mmol, 3.5 ml, 0.6 *N*) is added dropwise to 0.3 g (0.104 mmol) of complex III [3] in 40 ml of abs. ether while stirring in an inert gas atmosphere at —20°C. The mixture is stirred for 1 hour at —20°C, then at 5°C water (15 ml) is added, the ether layer is separated and the water layer is extracted with ether (2 × 20 ml); the extracts are combined, dried over Na_2SO_4 and evaporated. The residue is crystallized from n-hexane at —78°C, yielding 0.29 g (0.095 mmol, 94%) IIb (Found: C, 55.26; H, 5.76; Rh, 33.93. $C_{14}H_{17}ORh$ calculated: C, 55.25; H, 5.59; Rh, 33.88%).

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