STRUCTURE DYNAMICS AND ISOMERISM OF BIS[μ-(2-METHYLPHENOLATO)]BIS[(η^2:η^2-CYCLOOCTA-1,5-DIENE)RHODIUM(I)] COMPLEX

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Dinuclear rhodium(I) complex [{Rh^I(cod)}$_2$(μ-OC_6H_4-2-Me)$_2$] (**1**), exhibits the *syn-anti* isomerism consisting in the orientation of methyl groups of the bridge ligands with respect to the plane or distorted plane involving Rh and O atoms. The *syn* isomer predominates in $CDCl_3$ solution (above 90%) at room temperature. EXSY ^{1}H NMR measurements showed that, in $CDCl_3$ solution, complex **1** undergoes at least two independent dynamic processes differing substantially in values of activation parameters: (i) rotation of 2-methylphenyl rings in bridge ligands along the O–C axis, and (ii) formal rotation of cod ligands along the Rh–cod axes, which proves fluxional behavior of cod ligand in Rh^I(cod) complexes.

Keywords: Atom transfer radical polymerization; Dynamic NMR spectroscopy; Hydroformylation; *syn-anti* Isomerism; Polyacetylenes; Rhodium aryloxo complexes; Rhodium diene complexes; Rhodium dinuclear complexes.

Rhodium complexes remain a highly active area of research of academic and industrial interest since they effectively and often stereoselectively catalyze various chemical reactions such as hydroformylation, hydrogenation, hydrosilylation[1] and polymerization of dienes, acetylenes and some other monomers[2]. Rh catalysts show a high activity under mild conditions and high tolerance to functional groups of reactants so they can operate in various reaction media (water, alcohols, hydrocarbons, ionic liquids[3a], etc.). Also, they can be anchored on supports such as mesoporous polybenzimid-

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azole beads[3b], polystyrene matrices[3c] and mesoporous molecular sieves[3d–3f] to form hybrid catalysts that are easy to separate from reaction products.

Recently, we have reported synthesis and catalytic activity of several new dinuclear rhodium complexes in hydroformylation of alkenes[4] ([{Rh(cod)}$_2$-(μ-OC$_6$H$_4$-2-Me)$_2$] (**1**) and [{Rh(nbd)}$_2$(μ-OCOC$_{21}$H$_{43}$)$_2$]), atom transfer radical polymerization of styrene and methyl methacrylate[5] ([{Rh(cod)}$_2$-(μ-OC$_6$H$_4$-4-Me)$_2$] and [{Rh(cod)}$_2$(μ-OCOC$_{21}$H$_{43}$)$_2$]), and polymerization of substituted acetylenes (complex **1**)[6] (cod = cycloocta-1,5-diene and nbd = norborna-1,4-diene bound as η^2:η^2-ligands). In these studies, we observed that NMR spectra of **1** distinctly differ from those of the other Rh^I(cod)-μ-aryloxo complexes, showing two signals of both aliphatic and olefinic protons of cod ligands and other features indicating isomerism of **1**. Therefore, we studied complex **1** more in detail using various NMR techniques to determine and characterize its solution structure and structure dynamics. To verify that the observed phenomena are exclusively due to the presence of CH_3 group in *ortho* position on benzene ring of the bridge ligand we also prepared and studied complex [{Rh(cod)}$_2$(μ-OC$_6$H$_4$-3-Me)$_2$] (**2**), so far not reported in scientific literature. These studies provided us direct evidence on fluxional behavior of cod ligands in **1**, which is of importance for catalytic applications of Rh^I(cod) complexes.

EXPERIMENTAL

Materials

Rhodium(III) chloride trihydrate (Safina, Czech Republic), methanol, ethanol (both Lachema, Czech Republic), deuteriochloroform ($CDCl_3$) and potassium superoxide (both Aldrich) were used as supplied. *o*-Cresol (Lachema) was distilled at reduced pressure and dichloromethane and hexane (both Lachema) were distilled from P_2O_5 and stored under nitrogen atmosphere above molecular sieve. Di(μ-chloro)bis[(η^2:η^2-cycloocta-1,5-diene)rhodium(I)], [{Rh(cod)}$_2$(μ-Cl)$_2$], was prepared from $RhCl_3 \cdot 3H_2O$ and cycloocta-1,5-diene (Aldrich) in ethanol using the well known procedure[7].

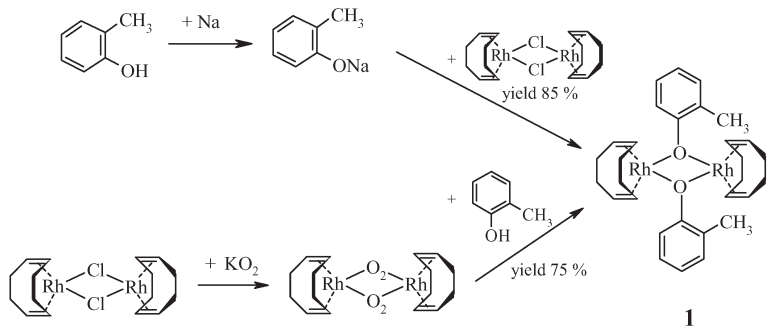
Measurements

NMR spectra were recorded on a Varian ^{UNITY}INOVA 400 instrument (400 MHz) in $CDCl_3$. For ^{1}H NMR spectra, tetramethylsilane (TMS) was used as internal standard, chemical shifts (δ-scale, ppm) and coupling constants (*J*, Hz) were obtained by the first-order analysis. ^{13}C NMR chemical shifts were referenced to the solvent signal (δ 77.00). COSY ^{1}H NMR experiments were recorded in the absolute-value mode using the standard two-pulse sequence. To evaluate spatial contacts, NOESY ^{1}H NMR experiments were performed in the phase-sensitive mode with standard three-pulse sequence (mixing time 0.3 s) and exchange spectroscopy ^{1}H NMR experiments (EXSY) with mixing times from 0.03 to 0.3 s. HSQC and HMBC measurements were performed as gradient experiments. All 2-D experiments were re-

corded with spectral windows 5000 Hz for proton and 25 000 Hz for carbon. Rate constants of intramolecular dynamic processes, k, were calculated from the EXSY exchange cross-peaks in the standard way[8] according to equation $k = 1/[t_M(I_d/I_c + 1)]$, where t_M is mixing time, I_d diagonal-peak integral, and I_c cross-peak integral. Activation enthalpy, $\Delta H^{\#}$, and activation entropy, $\Delta S^{\#}$, of the processes were obtained from coefficients of semilogarithmic plots ln (k/T) vs $1/T$ (where k is the rate constant and T thermodynamic temperature) according to the well-known Eyring equation. Infrared spectra (ν, cm^{-1}) were recorded on a Nicolet Magna 760 FTIR instrument with Inspector IR Microscope using both non-diluted and KBr-diluted samples and the diffuse reflectance technique (128 or more scans at resolution 4 cm^{-1}).

Bis[μ-(2-methylphenolato)]bis[(η^2:η^2-cycloocta-1,5-diene)rhodium] (**1**)

Complex **1** was prepared by two methods (Scheme 1): (i) the ultrasound-assisted procedure described in detail in ref.[5] and (ii) the procedure derived from that one currently used in the synthesis of [{Rh(cod)}$_2$(μ-OCH$_3$)$_2$] (ref.[9]). The ultrasound-assisted procedure (i) is easier to perform; it uses cheaper activating reagent (metallic sodium instead of potassium superoxide) and provides a bit higher yield of the desired product compared with the procedure (ii) in which [{Rh(cod)}$_2$(μ-Cl)$_2$] is first transformed into the μ-dioxo(1–) complex. Nevertheless, the quality of recrystallized product does not depend on the procedure used. Procedure (ii): A solution of [{Rh(cod)}$_2$(μ-Cl)$_2$] (100 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) was slowly added (within 15 min) to a suspension of finely powdered potassium superoxide (100 mg, 1.41 mmol) in CH_2Cl_2 (5 ml) under argon. The reaction mixture was allowed to react at laboratory temperature for 3 h under stirring. During the first hour, the color of the mixture changed from orange to dark green and back to orange. After 3 h, the unreacted KO_2 and formed KCl were filtered off using the standard Schlenk technique and a solution of *o*-cresol (71 mg, 0.6 mmol) in CH_2Cl_2 (1 ml) was added to the orange filtrate. Then the mixture was concentrated to a quarter of its volume, cold hexane (15 ml) was slowly added and the product was allowed to crystallize at 0 °C overnight. The formed yellow solid (yield 75%) was filtered off, washed with cold hexane and dried in vacuum. Crude **1** prepared by both procedures were recrystallized using the CH_2Cl_2/hexane system.



SCHEME 1
Synthesis paths used for a preparation of **1**

Bis[μ-(3-methylphenolato)]bis[(η^2:η^2-cycloocta-1,5-diene)rhodium] (**2**)

Complex **2** was prepared using the ultrasound-assisted procedure described in detail in ref.[5] for the preparation of **1**. The yield of crude product was 98%; it dropped to 83% upon recrystallization from a CH_2Cl_2/hexane mixture. FT-IR (KBr-diluted sample): 2988 (w), 2941 (m), 2913 (w), 2880 (m), 2834 (m), 1591 (s), 1574 (s), 1479 (vs), 1428 (m), 1376 (w), 1326 (w), 1269 (vs), 1212 (vw), 1149 (s), 1081 (w), 999 (m) (cod), 962 (m) (cod), 934 (s), 891 (m), 869 (w), 832 (w), 790 (s), 780 (s), 744 (m), 703 (m), 622 (m), 591 (m), 581 (m), 492 (s), 445 (s). For $C_{30}H_{38}O_2Rh_2$ (636.4) calculated: 56.62% C, 6.02% H; found: 56.12% C, 6.03% H. For NMR data see Table I.

RESULTS AND DISCUSSION

*Structure of Species **1***

Although the prepared μ-aryloxo complexes were recrystallized several times, the obtained needle crystals were either too small for X-ray diffraction measurements or they were druses. Therefore, the molecule-structure information on the prepared complexes was obtained from NMR spectra (Table I). As can be seen, the spectra of *m*-cresolato complex **2** contain signals of aromatic bridge ligands and one signal for each kind of protons and carbons of cod ligands (olefinic protons, H_{ol}, equatorial, H_{eq}, and axial, H_{ax}, alifatic protons, olefinic carbons, C_{ol}, and alifatic carbons, C_{alif}). These spectral features prove a uniform way of binding of the diene as well as bridge aryloxo ligands, which is consistent with the planarity of the complex $(Rh–O)_2$ ring that has been established for analogous complex [{Rh(cod)}$_2$-(μ-OMe)$_2$] (ref.[9b]). It is worth to mention that the complex [{Rh(cod)}$_2$-(μ-OC_6H_4-4-Me)$_2$] (**3**) carrying methyl groups in *para* positions has NMR spectra[4] qualitatively equal to those of **2**. On the contrary, each kind of atoms in cod ligands is represented by two signals of equal intensity in NMR spectra of **1**. Thus, it is clear that the observed doubling of NMR signals of cod atoms in **1** is caused by the presence of methyl groups in the *ortho* positions on benzene ring of the bridge ligand in **1**. In addition, these methyl groups show two ^{1}H NMR signals of the intensity ratio ca. 10:1 (at 25 °C), which indicates the presence of two kinds of complexes **1**: (i) major species further denoted as **1a** (δ_{Me} 3.10 ppm at 25 °C) and (ii) minor species **1b** (δ_{Me} 3.16 ppm at 25 °C). Signals attributable to aromatic ligands of species **1b** are visible in NOESY ^{1}H NMR spectra of **1** (see Table I).

Hereafter, protons of the same kind subject to weaker shielding are denoted by the subscript –w while those subject to stronger shielding by the subscript –s. Thus, a set of $H_{–w}$ protons ($H_{ol–w}$, $H_{eq–w}$ and $H_{ax–w}$) and a set of

TABLE I

Temperature dependence of ^{1}H and ^{13}C NMR signals (δ in ppm, *J* in Hz; $CDCl_3$) as obtained from one-dimensional as well as COSY, NOESY and EXSY ^{1}H NMR measurements for **1a** and **1b**, and ^{1}H and ^{13}C NMR signals of **2** measured at 25 °C

Atom	Complex **1**				Complex **2**
	–25 °C	0 °C	25 °C	50 °C	25 °C
			1a		
H_{ar3}	7.13	7.11	7.09 d (*J* = 7.2)	7.07	–
H_{ar5}	6.93	6.91	6.89 dt (J_1 = 7.5, J_2 = not determ.)	6.88	6.95 t (*J* = 7.63)
H_{ar4}	6.71	6.69	6.67 dt (J_1 = 7.3, J_2 = 1.2)	6.65	6.62–6.74 m (H_{arom-2}+H_{arom-4})
H_{ar6}	6.61	6.60	6.59 d (*J* = 7.6)	6.60	6.53 d (*J* = 7.2)
CH_3	3.15	3.12	3.10	3.09	2.25
H_{ol-w}	3.28	3.29	3.29	3.30	3.18 br s
H_{ol-s}	2.51	2.52	2.54	2.56	
H_{eq-w}	2.40	2.40	2.40	2.39	2.30 m
H_{eq-s}	2.18	2.18	2.18	2.18	
H_{ax-w}	1.36	1.36	1.36	1.36	1.35 m
H_{ax-s}	1.30	1.30	1.31	1.32	
C_{ar1}	158.63	158.86	159.04	159.28	160.72
C_{ar3}	130.28	130.29	130.32	130.36	138.06
C_{ar5}	129.45	129.50	129.53	129.57	127.92
C_{ar2}	125.88	125.91	125.93	125.94	120.80
C_{ar4}	121.31	121.41	121.52	121.68	119.61
C_{ar6}	119.83	119.86	119.89	119.92	123.23
C_{ol}	74.71 d (*J* = 15.4)	74.71 d (*J* = 15.3)	74.78 d (*J* = 14.7)	74.53 br	74.62 d (*J* = 15.2)
C_{ol}	74.51 d (*J* = 14.8)	74.45 d (*J* = 14.7)	74.42 d (*J* = 14.5)		
C_{alif}	30.05	30.11	30.17 br	30.22 br	30.05
C_{alif}	30.01	30.08			
CH_3	18.88	18.72	18.59	18.46	21.39
			1b		
H_{ar3}	7.13	7.11	7.10	–	
H_{ar5}	6.95	6.92	6.90	–	
H_{ar4}	6.72	6.70	6.68	–	
H_{ar6}	6.69	6.68	6.67	6.67	
CH_3	3.19	3.18	3.16	3.15	

H_{-s} protons (H_{ol-s}, H_{eq-s} and H_{ax-s}) are present in ^1H NMR spectrum of **1**. The observed chemical-shift differences, $\Delta\delta_{w-s}$, of corresponding H_{-w} and H_{-s} protons of the same kind are (at 25 °C): 0.75 ppm for H_{ol}, 0.22 ppm for H_{eq} and 0.07 ppm for H_{ax}. Differences $\Delta\delta_{w-s}$ observed for carbon signals are: 0.36 ppm for C_{ol} at 25 °C, and 0.03 and 0.04 ppm for C_{alif} at 0 and –25 °C, respectively.

The following discussion concerns to the major complex **1a**, spectral features of which are well seen in the NMR spectra of **1**. The observations described above can be explained at least in three ways: (i) complex **1a** is approximately equimolar (1:1) mixture of two species differing in the way of binding of cod ligands only, (ii) there is only one kind of species **1a**, in which two cod ligands are bound non-equivalently, and (iii) there is only one kind of species **1a**, in which cod ligands are bound in the same way but both non-symmetrically. To find which of the above-suggested hypotheses are appropriate we measured COSY, NOESY and EXSY ^1H NMR spectra of **1** at temperatures from –25 to 50 °C. COSY ^1H NMR spectra of **1** (Fig. 1) clearly show the connectivity between H_{ol-w} and H_{ol-s} and proves that both these protons belong to the same double bond. This observation conclusively rules out hypotheses (i) and (ii), according to which the H_{ol} belonging to the same cod double bond should be shielded equally. Also the fact

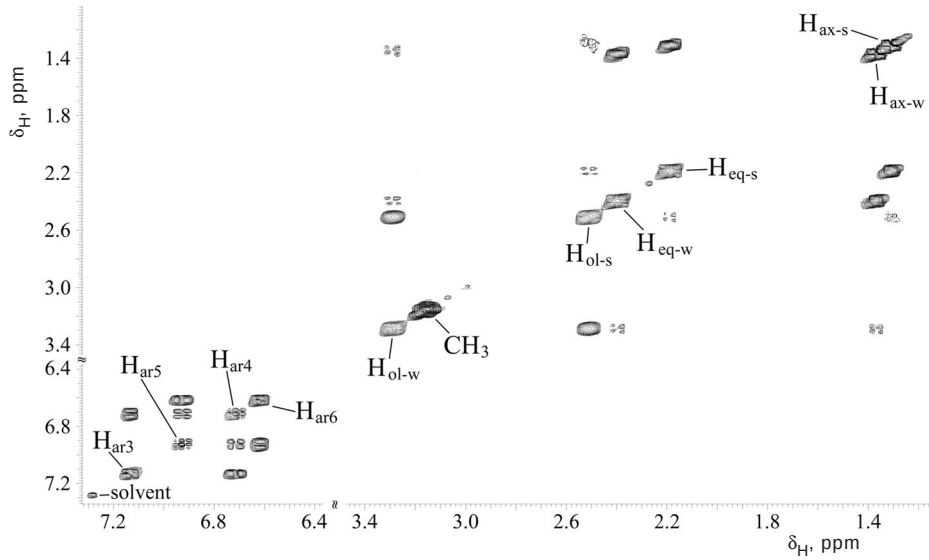
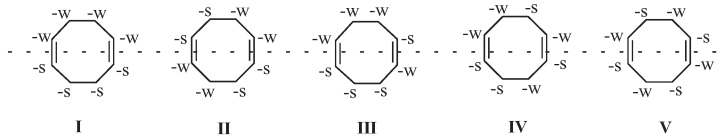


FIG. 1
COSY ^1H NMR spectrum of **1** measured in $CDCl_3$ at –25 °C

that signals of aromatic proton of **1a** are not split correspondingly supports the last conclusion. The observed $\Delta\delta_{w-s}$ values, particularly that found for C_{ol}, are rather high and it is not probable that such difference in binding of cod ligands would not affect aromatic bridged ligands.

Having established that each cod double bond comprises both H_{ol-w} and H_{ol-s} atoms, one can draw several shielding schemes for cod ligands in species **1a** (Scheme 2). A selection of plausible shielding schemes can be made on the basis of connectivity of both olefinic and aliphatic protons that is observed in COSY ^{1}H NMR spectrum of **1**. This spectrum shows connectivity between olefinic and aliphatic protons of the same relative shielding (–w or –s) only. Intensive cross-peaks are present: H_{ol-w}–H_{eq-w}, H_{ol-s}–H_{eq-s}, H_{eq-w}–H_{ax-w} and H_{eq-s}–H_{ax-s} as well as low-intensity cross-peaks: H_{ol-w}–H_{ax-w} and H_{ol-s}–H_{ax-s} in the COSY ^{1}H NMR spectra of **1** but not a cross-peak of protons of different relative shielding: H_{ol-w}–H_{eq-s}, H_{ol-s}–H_{eq-w}, H_{ol-w}–H_{ax-s}, H_{ol-s}–H_{ax-w}, H_{eq-w}–H_{ax-s} and H_{eq-s}–H_{ax-w}. Also NOESY ^{1}H NMR spectra of **1** show spatial contacts between protons of equal relative shielding only, except for the above-discussed interactions H_{ol-s}–H_{ol-w}. These observations are consistent with the shielding scheme **I** only (see Scheme 2), in which the plane passing through centers of cod double bonds perpendicularly to the bonds divides the cod ligand into two parts with different shielding.

Configuration of methyl groups in major species **1a** has been identified on the basis of NOESY ^{1}H NMR spectra. The presence of spatial contacts between aromatic H^6 and H_{ol-w} and contacts between H_{CH3} and H_{ol-s} together with the absence of the contacts H^6–H_{ol-s} and H_{CH3}–H_{ol-w} prove that both CH_3 groups occur at more strongly shielded part while H^6 protons at less strongly shielded part of cod ligands. Thus, it can be concluded that the methyl groups of the *o*-cresolato bridge ligands occur on the same side of the plane (or distorted plane) passing through Rh and O atoms, i.e., that they have the *syn* conformation in species **1a** and that double bonds of coordinated cod ligands are approximately perpendicular to the plane of the $(Rh–O)_2$ ring. The observed non-symmetric shielding of cod ligands can be due to both the shielding effect of aromatic groups acting on one side only



SCHEME 2
Possible shielding schemes of cod units with non-symmetrically shielded double bonds

and a slope and/or small shift of cod ligands to the opposite side of the $(Rh–O)_2$ plane caused by a joint steric effect of methyl groups (Scheme 3). Accordingly, compound **1b** can be characterized as the *anti* isomer complementary to the *syn* compound **1a**.

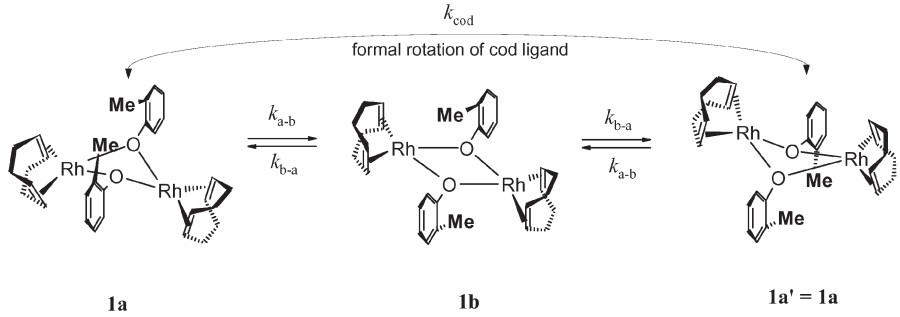
*Dynamic Processes Involving Species **1** in $CDCl_3$ Solution*

A decrease in resolution and ultimate merging of signals of $H_{ax–s}$, $H_{ax–w}$ and H_{CH3} protons is observed in ^1H NMR spectrum of **1** if temperature increases from –25 to 50 °C (Table I). These features prove the presence of dynamic processes running in species **1**. EXSY ^1H NMR spectra of **1** have shown exchange cross-peaks of two kinds:

a) exchange cross-peaks between signals of aromatic protons H_{ar6} in **1a** and **1b** (6.59 vs 6.67 ppm, at 25 °C, see Table I).

b) exchange cross-peaks between signals of $H_{–s}$ and $H_{–w}$ cod protons of the same kind (H_{ol}: 3.29 vs 2.54 ppm; H_{ax}: 1.37 vs 1.30 ppm; and H_{eq}: 2.40 vs 2.18 ppm, at 25 °C), i.e., exchanges between non-equivalent (more and less shielded) parts of cod units.

There is no doubt that the exchange cross-peaks between signals of aromatic protons H_{ar6} should be ascribed to the rotation of bridge-ligand 2-methylphenyl group along the C–O axis. For this rotation, we were only able to determine the rate constants of the conversion of **1a** to **1b**, k_{a-b}, but not that of the reverse process (k_{b-a}), because the diagonal signal of **1b** is always overlapped with signals of two other aromatic protons (Table II). Nevertheless, values of k_{b-a} should be about ten times as high as those of k_{a-b} since equilibrium concentration of **1a** is about ten times as high as that of **1b**. As to the observed exchange between olefinic cod protons, it can be



SCHEME 3
Dynamic processes involving species **1** in $CDCl_3$ solution

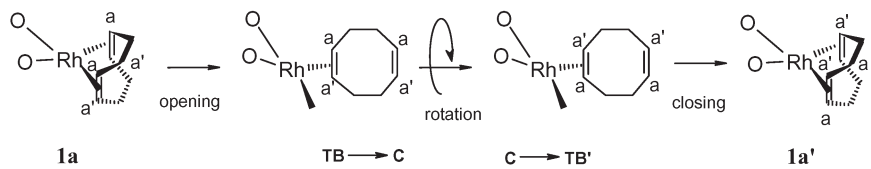
explained as a result of the rotation of both 2-methylphenyl groups about the C–O axes or it can be ascribed to an independent process such as the rotation of the cod ligand about the Rh–cod axis or a more complex process resulting in a formal rotation of cod about the Rh–cod axis. Detailed evaluation of EXSY ^{1}H NMR spectra of **1** gave the average rate constants, k_{cod}, from which corresponding activation parameters of the dynamic process lying behind the observed exchanges were determined (Table II).

As can be seen from Table II, the ratio of rate constants $k_{a\text{-}b}/k_{cod}$ is ca. 3 at –25 °C but it drops to ca. 0.3 at +25 °C, which is owing to rather high difference in values of activation parameters of these two intramolecular motions. This proves that these two motions are not synchronized. In other words, two consecutive rotations of 2-methylphenyl groups cannot explain the kinetics of the process lying behind the observed EXSY ^{1}H NMR cross-peaks between H_{-w} and H_{-s} cod protons of **1**. As a result, the motion lying behind the observed exchanges between H_{-w} and H_{-s} protons should be assigned as a formal rotation of the cod ligand about Rh–cod axis. Simple rotation of a doubly (η^2:η^2) coordinated cod ligand is improbable (see, e.g., ref.[10]). Therefore, we propose that this process proceeds as a series of at least five partial steps depicted in Scheme 4. In the first step, one of the Rh–cod bonds dissociates ("opening") and an intermediate with only η^2-coordi-

TABLE II
Rate constants and activation enthalpy $\Delta H^{\#}$ and entropy $\Delta S^{\#}$ of dynamic processes in **1**

Rate constant	–25 °C[a]	0 °C[a]	25 °C[b]	50 °C[b]	60 °C	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J mol^{-1} K^{-1}
k_{cod}, s^{-1} [c]	0.022	0.57	4.4	13	53[d]	57	–44
$k_{a\text{-}b}$, s^{-1} [c]	0.065	0.33	1.2	–	–	34	–130

Mixing times: [a] 0.3 s; [b] 0.03 s; [c] determined from the EXSY ^{1}H NMR cross-peaks of H_{ol-w} and H_{ol-s} ; H_{ol-s}; [d] determined from the coalescence point of the H_{ax-s} and H_{ax-w} signals.



SCHEME 4
Suggested mechanism of the rotation of cod ligand in **1**

nated cyclooctadiene ligand in the twisted-boat (**TB**) conformation[11] is formed. The η^2-coordinated ligand then undergoes a change into the chair (C) conformation, rotation about Rh–η^2-bond and a change into the inverse twisted-boat conformation, **TB′**, in which the temporarily free double bond coordinates back ("closing") to the vacant site of Rh atom.

As to the determined values of the activation quantities, they do not contradict to the proposed mechanism. The value $\Delta H^{\#}$ about 60 kJ mol^{-1} correspond to the dissociation of one π-bond accompanied with a simultaneous relaxation of the strained (η^2:η^2-binding) to the less strained (η^2-binding) **TB** conformation of cod ligand. Rather low value of $\Delta S^{\#}$ corresponds to low changes in the skeleton structure of **1** during the formal rotation of cod. On the other hand, relatively low value of $\Delta H^{\#}$ and rather high negative value of $\Delta S^{\#}$ can be expected for the rotation of μ-arene group (process **1a** → **1b**) because this process provides species **1b** of increased symmetry.

It can be concluded that complex **1** exhibits the *syn-anti* isomerism due to the orientation of methyl groups of the *o*-cresolato bridge ligands with respect to the plane or distorted plane involving Rh and O atoms. This is caused by close proximity of cod ligands and *ortho*-methyl groups of the bridge ligands bringing about repulsive interactions of cod and *ortho*-methyl groups. Complexes **2** and **3** do not exhibit such isomerism because *meta*-methyl or *para*-methyl groups of their bridge ligands cannot sterically interact with the cod ligands. The *syn* isomer **1a** unambiguously predominates in $CDCl_3$ solution of **1**; however, the equilibrium amount (up to 10%) of the *anti* isomer **1b** is also present in the solution. Both these species undergo at least two dynamic processes: (i) hindered rotation of benzene rings in the bridge ligands about the C–O axis; (ii) rotation of the cod ligand about the formal cod–Rh axis, which most probably proceeds in a complicated way including cleavage of one of its coordinated π-bonds and inversion of the conformation of temporarily only η^2-coordinated cod molecule. Non-symmetry of molecule **1** allowed us to obtain a direct evidence of fluxional behavior of cod ligand, which is tentatively supposed as a reason for currently observed lowered stability of polymerization species derived from Rh^I(cod) complexes compared to the species derived from Rh^I(nbd) complexes[2,12].

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