Journal of Organometallic Chemistry, 358 (1988) 463–494
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Redox-rotational phenomena in organometallic chemistry. Unique features of the crystal structure and stereodynamic behaviour of acetylacetonato- and cyclopentadienyl-rhodium complexes with potentially dipolar two-ring semiquinoid ligands in solution

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(Received May 27th, 1988)

Abstract

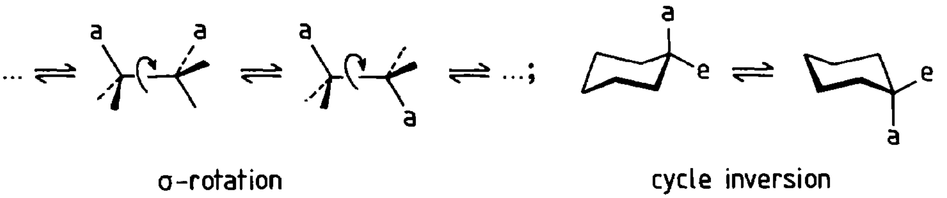
Replacement of the acac group in the 16-electron (metal oxidation state Rh^{I}) (acac)Rh(L) complex **A** (where L is 4-methyl-A-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene) with Cp, under the action of CpTl, gives the 18-electron CpRh(L) complex **B**, in which, according to ^{1}H and ^{13}C NMR spectral data, the η^{4}-diene structure of the ligand L rearranges into the dipolar delocalized form of 1-(4,4-dimethyl-2,6-dioxocyclohexylide)-4-methyl-4-trichloromethylbenzolonium with η^{5}-coordination by the cyclohexadienyl ring to the Rh^{IIII} atom, in a reaction we have termed a ligand redox-exchange. An X-ray diffraction has revealed that the dimedone ring of molecule **B** in the crystal is twisted around the central polarized $C\overset{-}{-}C$ bond by an angle of 28.9°, and ^{1}H and ^{13}C DNMR spectroscopy has shown that the dimedone fragments of the complexes **A** and **B** in solution undergo internal rotation about this band. The effects of solvent on this process, including the enhancing effect by the presence of H^{+}, has been studied. The rotation in the case of complex **B** is faster than that in complex **A** ("redox-rotation"). The kinetic parameters of the stereodynamics of the process (including the accompanying dimedone ring inversion) have been measured (e.g. in acetone-d_6 $\Delta H^{\neq}$ 18.4 kJ/mol, $\Delta S^{\neq}$ -125.8 J mol^{-1} K^{-1}, $\Delta G^{\neq}_{298}$ 56.0 kJ/mol). Treatment of **B** with CF_5COOH gives a stable η^{5}-cyclohexadienyl complex of Rh^{III}, $CpRh(LH)OCOCF_3$, with a protonated oxygen in the CO group of the ligand. A periodic system for virtually all the rotatable β-charged organometallic molecules has been proposed, which includes four structural types (and two classes) of models capable of undergoing either isovalent-odd or anisovalent-even internal rotations, depending on the evenness of the ligand fragment coordinated with the metal.

0022-328X/88/$03.50

Introduction

Since the time that Hassel and Barton discovered the basic principles of conformational analysis [1,2] this field of dynamic stereochemistry has undergone an intensive development in its theoretical concepts and practical applications. In recent years this has revealed the considerable influence exerted by phase states of organic substances on the manifestation of new phenomena and the effects of intramolecular stereochemical dynamics: in normal solutions [3], in host-guest associates [4], in the liquid-crystalline [5] and solid [6] phases, as well as at interfaces [7].

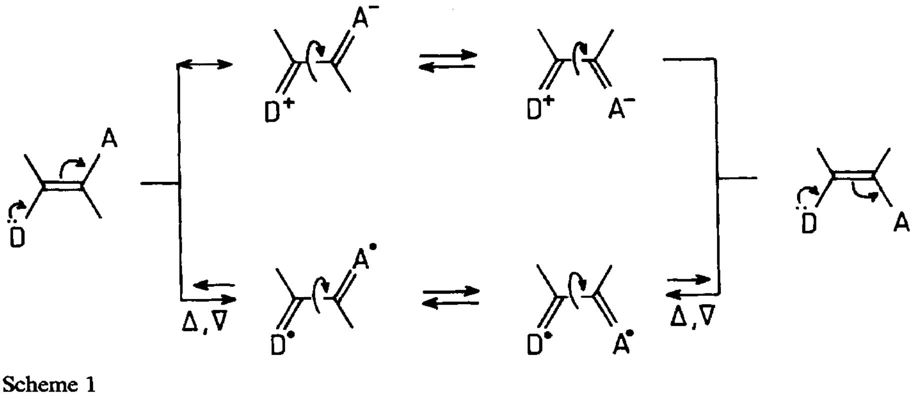
In present-day stereochemical studies in solution extensive use is made of the measurement of ^{1}H and ^{13}C dynamic nuclear magnetic resonance (DNMR) [3]. This technique enables the two principal points of the conformational analysis of saturated organic compounds viz. the free internal rotation around σ-bonds and the inversion of cycles (eq. 1) to be fixed and quantified. The main structural factor causing a decrease in the energy barriers of internal rotation of olefins around the double bond up to now has been the introduction of σ-bonded electron-acceptor and/or electron-donor (of the *p*- and *n*-type) substituents to olefin carbon atom (C(6), C(14)), thus promoting easy diradicalization [8,9] or polarization ("push-pull mechanism") [10–12] in the transition state of the process (Scheme 1).



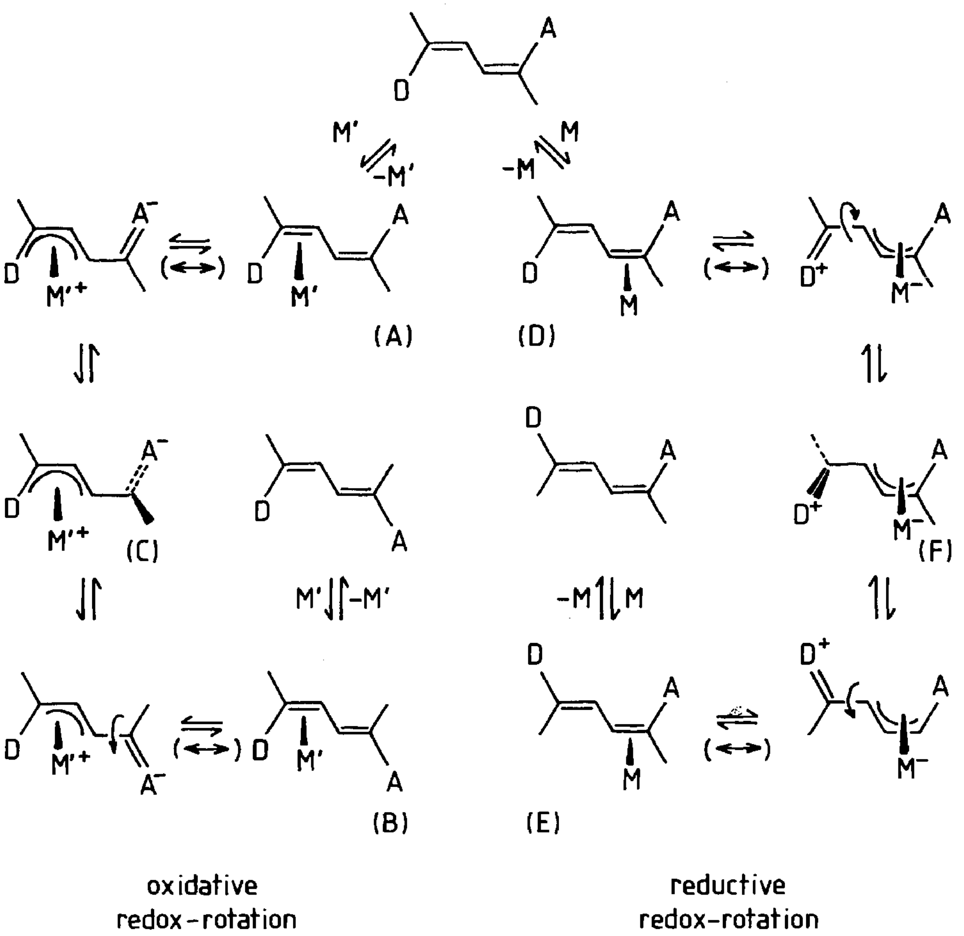
(1)

In view of the diverse, and sometimes even unique, opportunities of chemical and stereochemical design available for organometallic chemistry, it is the organoelement and organometallic systems with their vast variety of possible steric and electronic types of mutual influence by ligand, substituent, and metal that now appear to be the most promising in the search for new manifestations of intramolecular chemical dynamics [13,14].

Here we describe the possibility of finding a purely organometallic means to lowering the level of energy required to cause internal rotation of the olefin around



Scheme 1



Scheme 2

the double bond. This rotation is possible if the molecule is polarized by way of the π-coordination of the transition metal atom to a fragment of a potentially dipolar organic ligand, whose generalized model is shown in Scheme 2 (where D and A are donor and acceptor groups, M, M$'$ are metal equivalents). As compared with the above case of the internal rotation in uncoordinated polarized olefins (Scheme 1), the organometallic internal rotation which we are now considering permits the assumption that there is an important difference [15,16]. It is associated with the possibility of a reversible, and oscillating change (by one or two units), which is generally consistent with conformational geometry, in the valence (oxidation state) * of the coordinated metal atom on going from the initially coplanar (with respect to

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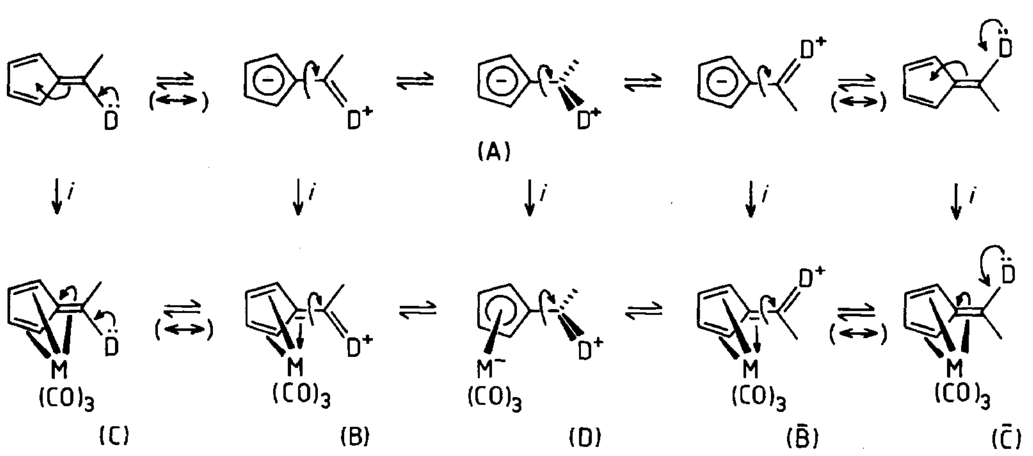
* When the terms "valence" and "change in valance" are used for transition metal complexes, difficulties often arise that are not encountered with the usual inorganic ions (in which, e.g., the oxidant actually detaches 1 or 2 electrons from the metal), since, e.g. in cationic complexes, the electrons are simply redistributed, and the formal electric charge somehow becomes delocalized between the ligand and the metal atom [17,18]. In the context of the present work for definite terminology we associate with the metal the maximal positive oxidation state it acquires in the canonical structure of each complex in terms of the maximum electron transfer from the metal to the ligand.



i : $+M(CO)_3L_3 / -3L$; M = Cr, Mo, W ; $\ddot{D} = \ddot{N}(CH_3)_2$

Scheme 3

the ligand: **A**, **B** and **D**, **E**) to the perpendicular (**C** and **F**) transition conformations of the molecule. Because of this unique feature the phenomenon was regarded as a redox-rotation [15,16] and could be useful as the basis for the design of a great variety of organometallic models, which under the influence of appropriate external physical or internal chemical factors, are able to undergo reversible rearrangement at the structural (geometrical or topological) or the electronic level, and thus can be of considerable theoretical interest and have direct bearing on a number of key problems of present-day organometallic chemistry and stereochemistry.

The problem

Depending on whether the transition metal-containing groups M, M′ are electron-accepting or electron-donating, and whether it is coordinated with electron-donor or electron-acceptor fragments of a potentially dipolar π-ligand (Scheme 2), within the framework of the proposed general approach there should be a clear distinction between the "reductive" and the "oxidative" versions of the phenomenon under consideration [15]. Thus, in principle the reductive type of redox-rotation (Scheme 3) can be associated with a known decrease of the energy berrier to internal rotation around the exocyclic polarized bond of 6-dimethylaminofulvene (**A**) as a result of its π-coordination with electron-acceptor $M(CO)_3$ groups (M = Cr, Mo, W) (see [19,20]). In this case the zero-valent metal, bonded to the aromatic-stabilized anionic part of the dipolar (ylide) ligand (**A**), can effectively coordinate the additional pair of electrons appearing in the Cp ring, with a change in its hapticity, and in the limiting case, and even be reduced (cf. X-ray diffraction parameters for the ligand (**A**) and its complex [21,22] (review see ref. 23)), to the oxidation state M^{2-} (**D**, see Scheme 3) * as compared with the unchanged ylene form of the molecule (**C**).

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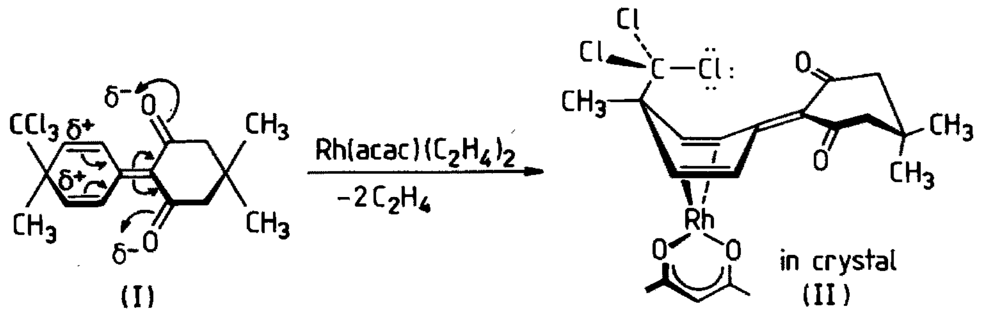
* In agreement with this assumption is the coincidence of the accelerating effect exerted by the above transition metals (Cr > Mo > W [19]) with their ability to undergo reduction in the same series, as well as the possibility of their dialkylaminofulvene complexes to be protonated [20] at the metal atom.



(2)

The oxidative version of the above type of the internal rotation in organometallic molecules agrees in principle with the results of our recent studies [15,16] in which a specially-designed (eq. 2) organometallic complex of a rotationally rigid (at the ^{1}H NMR time scale), cross-conjugated (see [24]), two-ring semiquinoid ligand (I) [25] was used. The electron-donor rhodium(I) acetylacetonate of this complex is coordi-

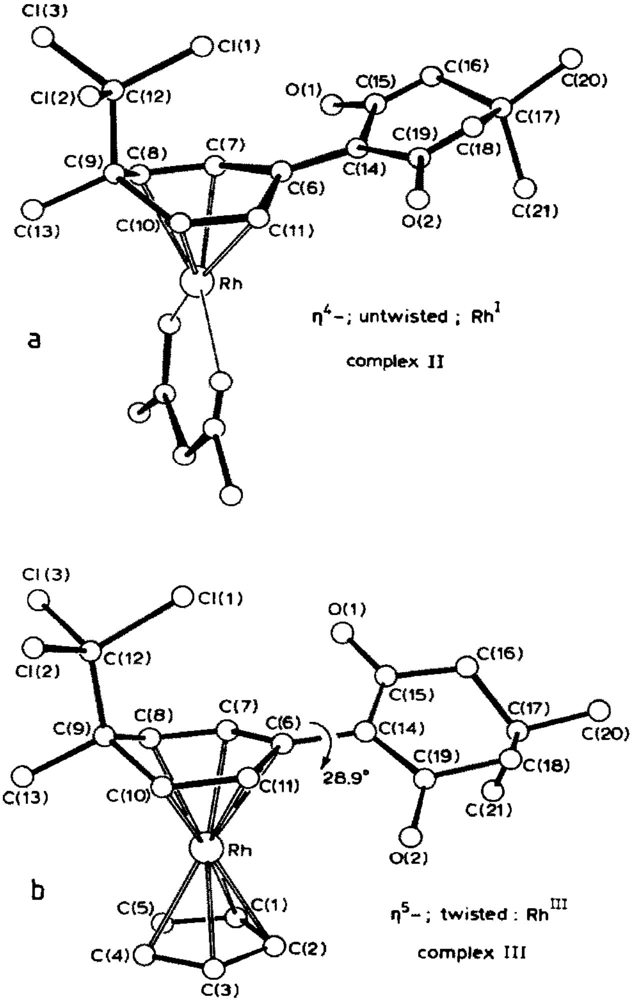
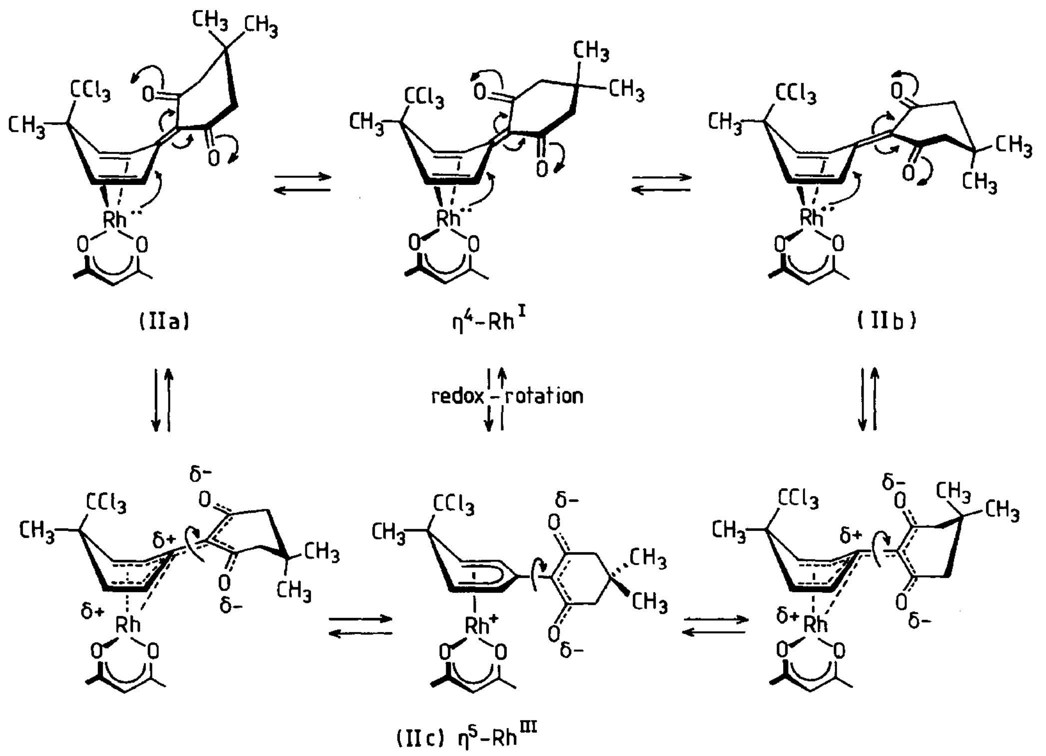


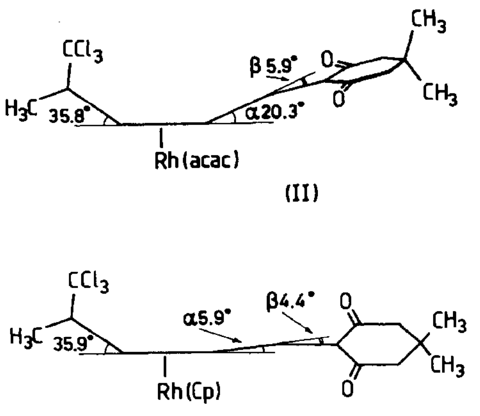
Fig. 1. Comparison of the molecular structures of II and III.



Scheme 4

nated with the potentially cationic fragment of the π-system (II). This complex was found from X-ray diffraction data, to have a normal η^4-diene structure in the crystal (see Fig. 1a), upon dissolution it, undergoes ("phase isomerism" [16]) rapid internal rotation ot its stereoindicatory cyclohexane dione (dimedone) fragment relative to the semiquinoid ring bonded to the metal [15] (Scheme 4).

The fact that this rotation takes place is explicitly indicative of a sharp weakening of the central C(6)=C(14) bond in complex II compared with the free ligand. This weakening is probably caused by a certain loss in overlap of the p_π-orbitals of C(6) and C(14) atoms owing to the geometric effect of C(6) atom pyramidalization (for a discussion of this effect in strained organic molecules see ref. 26), in which the role of the Rh^I atom is not so much to act as a stabilizing electron-donor as to force the molecule mechanically into a conformation that is sterically strained in the region of the C(6)=C(14) bond. However, the β angle in the molecule of II in the crystal (β 5.9°, see Fig. 2) appears to be still insufficiently large to cause the marked weakening of the π-bond in question. This weakening seems to have been caused by the electron-donating capacity of the low-valent Rh^I atom. But in such cases it has to be acknowledged that for the most effective overlapping of the metal *d*-orbitals with the vacant orbital of the C(6) atom, the structure of II should undergo an important change in its geometry in solution, associated with periodic (rotation-wise) and reversible bends of its C(6)C(7)C(11) flap towards the metal atom, which ultimately should lead to the complete rearrangement of the molecule from the η^4-diene into the η^5-cyclohexadienyl structure, in which the most favourable geomet-



(II)

(III)

Fig. 2. The schematic conformational drawings of complexes II and III.

ric conditions are created for the *d*-participation of the metal atom in the stabilization of the positive charge.

The ^{1}H NMR spectra, recorded during a study of the dienone fragment of complex II [15] carried out at low temperature (−70 °C) at which rotation was slowed, did not show any changes, compared with their high-temperature spectra, either in the chemical shifts of the protons H(8), H(10) and H(7), H(11), or in their coupling with the ^{103}Rh nucleus. Thus in each case the ground state of the complex in solution is best described by its usual formula II, and all the other possible geometrical changes are taking place very quickly in the molecule and can only be related to the transition state IIc that arises regularly in the course of rotation. Nevertheless, if one accepts the above theoretical model for the phenomenon observed, it should be assumed that every simple reversible transition between the two extremes, the untwisted conformers (invertomers) (IIa and IIb) of the organometallic complex are at peak potential energy, i.e. the intermediate perpendicular conformation IIc, must also be accompanied reversible changes in the degree of the metal atom oxidation state, viz. its cooperative $Rh^I \rightleftharpoons Rh^{III}$ transitions.

In view of our interest in the problem of the mechanism and the driving force behind redox-stereochemical phenomena under consideration, our objective was to study in greater detail the behaviour of complex II in solutions, to establish the kinetic parameters of its stereodynamics and the influence on these parameters by the nature of the solvent and the addition of protic acids, as well as to compare it under similar conditions (i.e. both in the crystalline phase and in solution) with another example from this series, the trienedione CpRh derivative III, which we synthesized specially for the study.

Results and discussion

1. Cyclopentadienylrhodium complex (III) of 4-methyl-4-trichlormethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene

Starting from the appearance of a positive charge, delocalized by rhodium *d*-orbitals in the region of the metal–ligand band in the transition state of redox-rotation in the 16-electron Rh^I complex II (Scheme 4), which follows from our model

(Scheme 2), the transition to 18-electron complexes of this type could be assumed to promote additional stabilization of this positive charge. To verify this assumption we replaced the 3-electron acac-ligand on the rhodium atom with the 5-electron Cp ligand, using the conventional reagent CpTl [27]. Subsequent study of the complex obtained (III) not only confirmed the above assumption * but also showed, with the help of an X-ray diffraction study, that compound III is altogether different from the initial complex II by virtue of its chemical nature, because even in the crystal it contains a dimedone ring redox-twisted around the C(6)=C(14) bond by 28.9°.

Molecular structure of complex III in the crystal. An X-ray study has confirmed the molecular structure of III, which had been suggested on the basis of the NMR data (Fig. 1, Tables 1 and 2). The replacement of the three-electron acac by the five-electron Cp ligand (conversion of the 16e to the 18e complex) gives rise to significant alteration of the geometry of the metal atom coordination which in turn causes important changes in the electronic structure of the central atom. In contrast to the bis-η^2-olefinic, such as η^4-cyclohexadiene-1-one and ligand I Rh(acac)-derivatives studied previously by us [28,15] the present compound should be regarded as an η^5-cyclohexadienyl derivative. Such treatment may be corroborated by a number of geometric parameters, and first of all by a sofa conformation of the 6-membered ring characteristic for a π-cyclohexadienyl ligands. The conformations of the 6-membered rings, coordinated by the Rh atom in II and III are compared in Fig. 2. The dihedral angle α in molecule III is as small as 5.9°, so that the C(6)C(7)C(8)C(10)C(11) atomic group may to a good approximation be regarded as planar (the maximum derivation of the C(6) atom from its mean plane, A, is equal to 0.033(3) Å. All five atoms, C(6), C(7), C(8), C(10), and C(11), are at bonding distances from the Rh atom, the shortest being 2.152(4) Å for C(7) and the longest −2.270(3) Å for C(6). At the same time the C(9) atom is displaced from plane A by 0.597(3) Å, the Rh...C(9) distance is 2.732 Å. Such coordination geometry has been observed in some other π-cyclohexadienyl derivatives, such as the 18e cationic Rh^{III} complex $[Rh(\eta^5\text{-}C_5Me_5Et)\{\eta^5\text{-}C_6H_6P(O)(OMe)_2\}]^+$ [29] which like III has both a cyclopentadienyl and a π-cyclohexadienyl ligand. The Rh–C bond lengths 2.17–2.26 and non-bonded Rh...C distance 2.73 Å [29] are almost exactly the same as those in III. In two of the 16-electron rhodium complexes $((2,6\text{-di-t-Bu-4-MeC}_6H_2O)RhL_2$ $(L_2 = CO$, Ph or COD)) [30] the Rh–C bonds are much longer (2.267–2.479 and 2.259–2.405 Å, respectively), and the non-bonded distances involving the sixth atom of the ring, which does not participate in the π-system, are somewhat shorter (2.665 and 2.586 Å) than in complex III.

On the other hand, some elongation of the Rh–C(6) bond, compared with the other bond lengths in complex III, is not so typical for the π-cyclohexadienyl ligand coordination geometry. Thus, in the simplest cyclohexadienyl complex $(\pi\text{-}C_6H_4)Mn(CO)_3$ [31] the Mn–C distance to the central atom of the π-system is the shortest of all the Mn–C bonds, and in the iron complex $[(\pi\text{-}C_6Me_7)Fe(CO)_3]^+$ $[PF_6]^-$ [32] the corresponding distance is close to the mean value for all the Fe–C lengths involving the atoms of the π-cyclohexadienyl ligand. In all other respects the geometry of the 6-membered cycle in III is characterized by the same principal

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* Internal rotation in III (from ^1H and ^{13}C DNMR data, see text) intensified so sharply that we were unable to slow it down even at temperatures of −90 °C.

Table 1

Atomic coordinates ($\times 10^4$, for Rh $\times 10^5$, for H $\times 10^3$) and temperature factors (isotropic for H, equivalent isotropic for non-H atoms) for compound III

Atom	x	y	z	B_{eq}(Å^2)	Atom	x	y	z	B_{eq}/B_{iso}(Å^2)
Rh	6525(5)	23200(1)	9130(2)	2.914(6)	C(20)	3032(12)	−47(2)	−2252(4)	6.9(2)
Cl(1)	2375(2)	3470(0)	−1411(1)	4.16(3)	C(21)	866(10)	204(2)	−1046(4)	6.2(2)
Cl(2)	−998(2)	4256(1)	−988(1)	5.61(4)	H(1)	323(9)	202(3)	241(4)	7(1)
Cl(3)	3472(2)	4396(1)	−158(1)	5.75(4)	H(2)	35(12)	274(3)	265(5)	10(2)
O(1)	−479(8)	1891(2)	−2107(2)	7.2(1)	H(3)	−330(12)	246(3)	179(5)	10(2)
O(2)	4965(8)	1327(2)	154(4)	10.5(2)	H(4)	−177(11)	140(3)	126(4)	9(2)
C(1)	1889(8)	1975(2)	2201(3)	5.1(1)	H(5)	181(11)	126(3)	156(4)	9(2)
C(2)	236(10)	2371(2)	2313(3)	5.4(1)	H(7)	446(6)	234(2)	35(2)	3.0(7)
C(3)	−1656(9)	2158(3)	1860(4)	6.7(2)	H(8)	377(7)	321(2)	105(3)	4.2(9)
C(4)	−1257(11)	1618(3)	1471(3)	7.4(2)	H(10)	−226(7)	310(2)	1(3)	4.2(9)
C(5)	967(12)	1481(2)	1685(3)	6.6(2)	H(11)	−164(6)	221(1)	−66(2)	2.5(7)
C(6)	1724(6)	2212(1)	−442(2)	2.77(8)	H(131)	−83(8)	403(2)	77(3)	5(1)
C(7)	3296(6)	2525(2)	165(2)	3.03(8)	H(132)	−33(11)	367(3)	140(4)	8(2)
C(8)	2764(6)	3050(2)	594(2)	3.13(9)	H(133)	117(10)	412(3)	118(4)	7(1)
C(9)	886(6)	3452(1)	234(2)	2.86(8)	H(161)	248(14)	113(4)	−272(5)	12(2)
C(10)	−867(6)	2987(1)	−33(2)	2.75(8)	H(162)	30(13)	89(3)	−247(5)	10(2)
C(11)	−465(6)	2455(1)	−477(2)	2.66(8)	H(181)	560(10)	80(3)	−146(4)	7(1)
C(12)	1408(6)	3864(1)	−535(2)	3.18(9)	H(182)	510(10)	47(2)	−78(3)	7(1)
C(13)	191(8)	3852(2)	966(3)	4.6(1)	H(201)	153(13)	−21(3)	−260(5)	10(2)
C(14)	2183(6)	1671(2)	−922(2)	3.11(9)	H(202)	367(9)	−33(2)	−187(4)	7(1)
C(15)	896(8)	1543(2)	−1735(2)	4.3(1)	H(203)	366(9)	4(2)	−268(3)	6(1)
C(16)	1278(11)	963(2)	−2213(3)	5.6(1)	H(211)	35(10)	56(2)	−61(4)	7(1)
C(17)	2371(8)	462(2)	−1662(3)	4.0(1)	H(212)	155(11)	−13(3)	−69(4)	9(2)
C(18)	4341(9)	730(2)	−1141(5)	6.6(2)	H(213)	−44(12)	6(3)	−135(5)	10(2)
C(19)	3868(8)	1268(2)	−586(4)	5.5(1)					

Table 2

Bond lengths *d* (Å) for compound III

Rh–C(1)	2.168(4)	C(4)–C(5)	1.400(9)
Rh–C(2)	2.197(4)	C(6)–C(7)	1.436(5)
Rh–C(3)	2.184(6)	C(6)–C(11)	1.446(5)
Rh–C(4)	2.189(6)	C(6)–C(14)	1.453(5)
Rh–C(5)	2.202(5)	C(7)–C(8)	1.397(5)
Rh–C(6)	2.270(3)	C(8)–C(9)	1.509(5)
Rh–C(7)	2.152(4)	C(9)–C(10)	1.512(5)
Rh–C(8)	2.171(4)	C(9)–C(12)	1.557(5)
Rh–C(10)	2.200(3)	C(9)–C(13)	1.533(5)
Rh–C(11)	2.179(3)	C(10)–C(11)	1.401(5)
Cl(1)–C(12)	1.766(4)	C(14)–C(15)	1.421(5)
Cl(2)–C(12)	1.782(4)	C(14)–C(19)	1.418(6)
Cl(3)–C(12)	1.778(4)	C(15)–C(16)	1.515(6)
O(1)–C(15)	1.232(6)	C(16)–C(17)	1.505(6)
O(2)–C(19)	1.254(8)	C(17)–C(18)	1.490(7)
C(1)–C(2)	1.371(8)	C(17)–C(20)	1.534(7)
C(1)–C(5)	1.428(7)	C(17)–C(21)	1.515(7)
C(2)–C(3)	1.364(8)	C(18)–C(19)	1.516(8)
C(3)–C(4)	1.374(9)		

features as in the Fe and Mn cyclohexadienyl derivatives already mentioned the bond lengths of 1.436(5) Å for C(6)–C(7) and 1.446(5) Å for C(6)–C(11), are elongated compared with 1.397(5) for C(7)–C(8) and 1.401(5) Å for C(10)–C(11); and the endocyclic C(8)C(9)C(10) bond angle is significantly smaller (100.6(3)°). The folding angle of the cyclohexadienyl cycle along the C(8)... C(10) line, of 35.9°, in molecule III is appreciably smaller than those in most of the other cyclohexadienyl complexes, where the corresponding angles are equal to 42.8 [31], 42.9 [29] and 45° [32]. A decrease in this dihedral angle, such as those observed with the conformation of cyclohexadiene ligands in the the Rh(acac)-2,5-cyclohexadiene-1-one complex [28] and in II [15], is caused by the repulsion of one of the chlorine atoms (in this case Cl(1)) of the CCl_3 group by the C(6), C(7), C(8), C(10) and C(11) atoms. The CCl_3 group is in a staggered conformation relative to the C(9)–C(12)

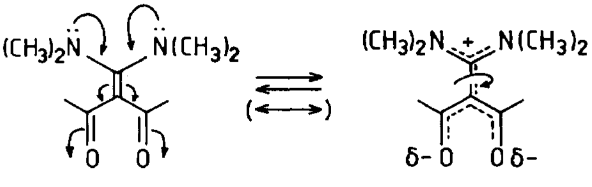
Table 3

Main bond angles (°) for compound III

C(7)C(6)C(11)	113.1(3)	C(6)C(11)C(10)	121.1(3)	C(14)C(15)C(16)	119.5(4)
C(7)C(6)C(14)	124.8(3)	Cl(1)C(12)Cl(2)	106.7(2)	C(15)C(16)C(17)	116.2(4)
C(11)C(6)C(14)	121.8(2)	Cl(1)C(12)Cl(3)	106.4(2)	C(16)C(17)C(18)	106.4(4)
C(6)C(7)C(8)	122.1(3)	Cl(1)C(12)C(9)	114.0(2)	C(16)C(17)C(20)	110.2(4)
C(7)C(8)C(9)	122.3(3)	Cl(2)C(12)Cl(3)	109.1(2)	C(16)C(17)C(21)	111.4(4)
C(8)C(9)C(10)	100.6(3)	Cl(2)C(12)C(9)	110.0(2)	C(18)C(17)C(20)	110.7(4)
C(8)C(9)C(12)	113.8(3)	Cl(3)C(12)C(9)	110.5(2)	C(18)C(17)C(21)	109.6(4)
C(8)C(9)C(13)	110.1(3)	C(6)C(14)C(15)	119.2(3)	C(20)C(17)C(21)	108.5(4)
C(10)C(9)C(12)	113.7(3)	C(6)C(14)C(19)	121.1(4)	C(17)C(18)C(19)	114.6(5)
C(10)C(9)C(13)	109.9(3)	C(15)C(14)C(19)	119.7(4)	O(2)C(19)C(14)	123.3(5)
C(12)C(9)C(13)	108.5(3)	O(1)C(15)C(14)	123.8(4)	O(2)C(19)C(18)	118.2(5)
C(9)C(10)C(11)	123.0(3)	O(1)C(15)C(16)	116.6(4)	C(14)C(19)C(18)	118.4(4)

bond. This steric effect gives rise to C(8)C(9)C(12), C(10)C(9)C(12) and C(9)C(12)Cl(1) angles (Table 3) of 113.8(3), 113.7(3) and 114.0(2)°, respectively, that are larger than the tetrahedral value of 109.5°, and Cl(1)...C(6), Cl(1)...C(7), Cl(1)...C(8), Cl(1)...C(10) and Cl(1)...C(11) distances are still rather short (3.195–3.287 Å) and exclude further bending of the C(8)C(9)C(10) flap away from the Rh atom.

The salient features of the geometry of complex III, which become clear when the structures of III and II are compared, are associated not only with the function of the 6-membered cyclic ligand but also with the substantial twisting around the C(6)–C(14) double bond, its considerable elongation, and simultaneous redistributed of bond lengths in the dimedone cycle. Thus, although the C(6) and C(14) atoms in molecule III or II, retain their planar environment (the sums of the bond angles subtended at these atoms are 359.7 for C(6) and 360.0° for C(14), these two planes in III, as distinct from II, do not coincide and so are at a dihedral angle of 29.8° to each other. We described recently the structure of II [15] that the double bond of 1.371 Å linking the cyclohexadiene and the dimedone cycles is noticeably elongated compared with the usual value of 1.337 Å [33]. However, the degree of the elongation of this bond in II is not significant and, as mentioned previously [15], could in principle be caused by conjugation with the neighbouring carbonyl groups of the dimedone ring. The large increase in the C(6)–C(14) bond length in complex III to 1.453(5) Å, which in fact coincides with the length of the standard C(sp^2)–C(sp^2) single bond, 1.460 Å [35], is accompanied by twisting of the olefin fragment plane (see above), the shortening of the C(14)–C(15) and C(14)–C(19) bond lengths to 1.421(5) and 1.418(6) Å respectively, compared with 1.487 Å for the same bonds in II, and the elongation of neighbouring carbonyl bonds to 1.232(6) and 1.254 Å (in II, 1.208 Å) cannot be attributed only to the effects of the usual cross-π,π,π-conjugation, and thus exclude metal participation. In order to understand the unique features of the molecular geometry of III, it is of importance to mention the analogy between III and the well-known conventional polarized olefins (of types IV, V), in which the weakening of the double bond is caused by the "push-pull mechanism" [10–12,35] (see Scheme 1). In these compounds one of the



(IV)

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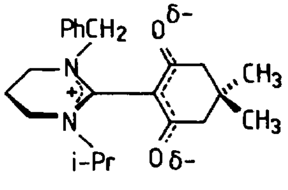

(V)

olefinic atoms is bonded to the strong n-donor, e.g. dialkylamine, and the other to a strong acceptor, group such as carbonyl or thiocarbonyl. Such an environment causes the mesomeric weakening of the C=C double bond, which accounts for its considerable elongation to 1.482(6) Å [10], the shortening of the adjacent C–N and C–C bonds, and the distortion of planarity of the whole system, e.g. in the $(PhCH_2)\overline{NCH_2CH_2N(CH_2Ph)C}{=}\overline{CC(=S)CH_2CMe_2CH_2C}(=S)$ [10] the twist angle about the former double bond is equal to 80.8°. The specificity of III manifested in the role played in our case by the metal-containing electron-donor fragment, in stabilizing the component adjacent to the vacant centre and the partial positive charge arising on it is compensated by the metal atom orbital rearrangement with probable $Rh^{I} \rightleftharpoons Rh^{III}$ change in oxidation state (see Scheme 4).

One of the structural studies carried out [36] revealed there is a distinct correlation between the length of the polarized double bond in such olefins and the height of the energy barrier to rotation around this bond. For instance, $(MeS)_2C{=}C(CN)COC_6H_4Br$ which has a short double bond of 1.369 Å [37], its barrier to rotation is 79.8 kJ/mol, but in $Me\overline{NCH_2CH_2N(Me)C}{=}C(CN)COC_6H_4Br$, in which the double bond is 1.448 Å [36] close to that found by us in III, this barrier is only 39.9 kJ/mol. The fact that there is a relatively long C(6)=C(14) bond in crystalline III * thus confirms the low internal rotation barrier in this molecule, and is thereby also consistent with the results of our DNMR study, described below.

In molecule III in contrast to molecule II, the dimedone cycle is not in a chair but in a somewhat distorted sofa conformation: the C(17) atom is displaced from the planer by 0.05 Å C(14)C(15)C(16)C(18)C(19) atomic group, by 0.633(4) Å. The folding angle along the C(16)...C(18) line is 45.6°. The Rh atom is symmetrically and, moreover, antiprismatically coordinated by the η^5-cyclopentadienyl ligand. The Rh–C distances in III, lie between 2.168 and 2.202 Å, and are close to similar distances in the previously investigated cyclopentadienyl derivatives, e.g. 2.20–2.22 Å in $[CpRh(C_7H_7CH_2)]^+PF_6^-$ [38] and 2.187–2.254 Å in $[\{CpRh(C_7H_6CHOH)\}_2\text{-}OOPF_2]^+PF_6^-$ [39]; the Cp ligand is planar to within 0.014 Å, and forms a dihedral angle of 5.4° with plane A.

A unique structural feature in the chemistry of transition metals has thus been revealed, in which the coordination of the metal with a cross-π,π-conjugated system in the ligand leads to a change not only in the geometry but in the very topology of the ligand. Twisted forms are in fact frequently observed in the chemistry of sterically crowded olefins, because in order to achieve overlap of p_π-orbitals [40,41] overlap, twisting of the double bond takes place. In the case we are studying there is no steric hindrance, thus the reason for the twisting is different and is undoubtedly caused by the direct participation of the metal *d*-orbitals in the flattening of the C(6)C(7)C(11) flap, with significant weakening of the C(6)=C(14) double bond. The twisting is even present in the ground state of the complex. Since the very same structural changes were assumed to be taking place in the transitional internal-rotation state IIc of complex II (Scheme 4), the twisting observed in III is a clear-cut redox, and it can therefore be regarded as an example of an internal redox-rotation transitional state in organometallic molecules.

If, on the other hand, the obtained result is considered from the viewpoint of an interaction between a low-valent CpRh group and an initially planar, but long, electron-acceptor π-system of a poly-unsaturated ligand, it will correspond not to the usual π-coordination (as in the case of (acac)Rh group in the crystal of II [15]), but in fact to the oxidative addition of the metal to the enone system, topologically equivalent to the formation of either 7- (**A**) of 5-membered (**B**), transition states

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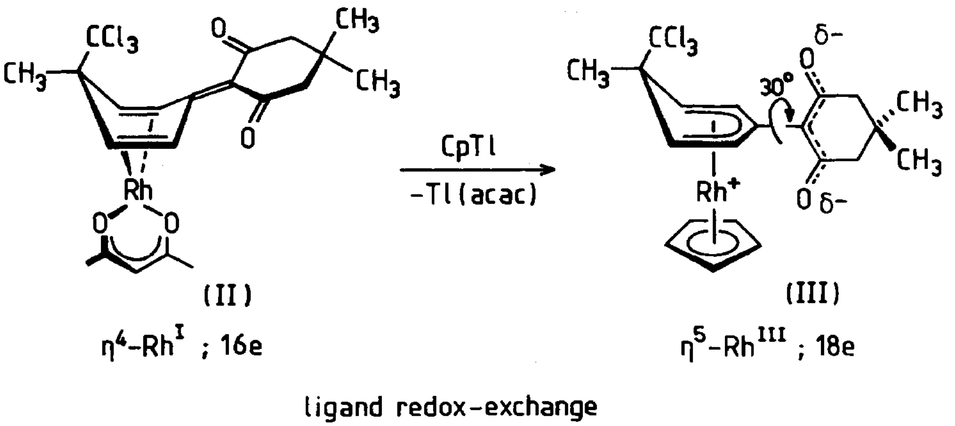
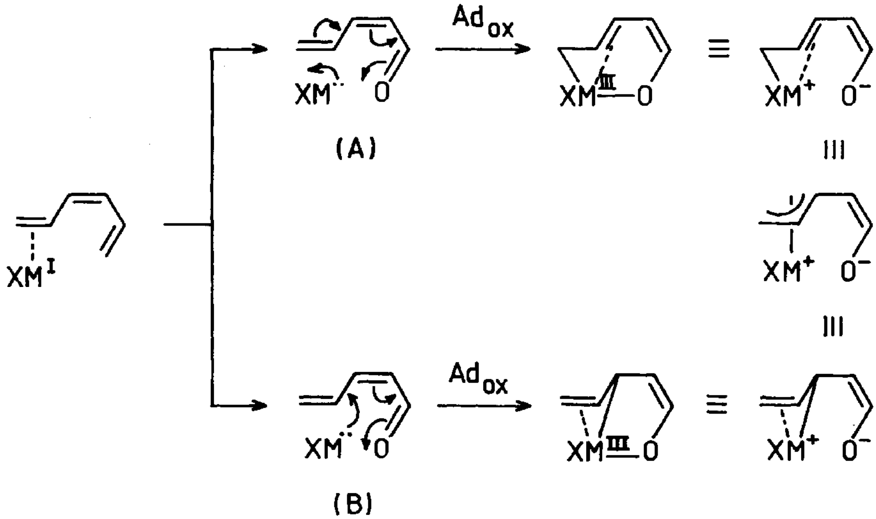
* It should be noted here that in contrast to the C=C bond lengths the degrees of twist in the crystal are determined not only by the barrier to rotation but also by a combination of intramolecular and packing effects. It is not surprising that there is no reliable correlation between the double bond lengths and the twist angles. Thus the double bond length of 1.461 Å [36] in IV, is almost the same as in III and corresponds to the twist angle of 56.9°, which is substantially higher than that in III, whereas the twist angle of 34.8° in $(Me_2N)_2C{=}C(COMe)Ph$, which is close to that found by us in III corresponds to a much shorter bond, of 1.409 Å [36].



Scheme 5

(Scheme 6). From the principles of mathematical chemistry, however, the realization of odd-membered transition states (as opposed to the 4-membered transition states usually encountered in organometallic chemistry [42]), must by accompanied by a change in valence of at least one of the atoms of the molecule undergoing the transition (cf. [43]). To classify this ligand-exchange reaction, leading to the considerably more important haptoelectrono-geometric changes in the molecule on going from its initial to its final state (the changes are much greater than those expected when the acac group is replaced by the Cp group at the Rh atom in the (remote) periphery of an organometallic complex) and so we have designated this type of reaction as a ligand redox-exchange (Scheme 5).

Investigation of the stereochemical non-rigidity of complex III in solution. When the ^1H and ^{13}C NMR spectra of complex III in different solvents were studied, even cooling the solutions to $-70\,°C$ ($CDCl_3$; ^1H, ^{13}C) and to $-90\,°C$ (toluene-d_8; ^1H) caused neither the appearance of the AB system of the $C(16,18)H_2$-group protons nor the splitting of the averaged singlet signal from the two CH_3 groups of the dimedone fragment. In fact the signals showed only a slight broadening which does



Scheme 6

not depend on the nature of the solvent *. Thus, on going from the 16-electron (II) to the 18-electron complex (III) the rate of internal rotation of the molecule around the central C(6)–C(14) bond sharply increases; the extent of this increase was estimated as being more than 10-fold (Table 8). No special differences are expected between the (acac)Rh and the CpRh groups in their acting as purely geometric fixers of the boat-like conformation of the coordinated 1,4-cyclohexadiene rings (as, indicated by the similarity between the structural parameters of the two complexes previously investigated: (acac)Rh(4,4-disubstituted cyclohexadienone) [28] and CpRh(1,4-disubstituted 2,5-cyclohexadiene) [44]), It is clear that any difference observed in the rotational behaviour of the (acac)Rh and the CpRh derivatives of triendione I will be caused not by the geometric (pyramidalization) but by the electronic differences between these two geometallic groups. The rate of rotation increased in complex III, despite an obvious diminishing of the pyramidalization of its C(6) atom (since, in this case the β angle decreases to 4,4°, cf. the conformations of two complexes depicted in Fig. 2) testifies to the fact that, also in the acetylacetonate derivative II rotation of the dimedone fragment of the molecule observed in solution, is a consequence of the electronic participation of the rhodium atom. As a result, we believe that the increase in internal rotation observed in the CpRh complex III can be explained in terms of the greater polarization of its C(6)=C(14) bond with more direct participation of the 18-electron Rh shell, compared with the 16-electron (acac)Rh complex (II), and by the twisting of the "sesquibond" (consistent with X-ray) data which precludes any additional equirements (and probably characteristic for the acac complex II such as the conformation bending of the C(7)C(6)C(11) flap towards the metal atom and the difference between the energy levels of the ground and the transition states ** is lessened.

2. *(Acac)Rh (II) and CpRh (III) complexes of 4-methyl-4-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene: NMR-spectral comparison of η^4- and η^5-coordinated structures*

The results of the preceding section confirm that the organometallic redox conversion of the potentially bipolar two-ring semiquinoid ligand I into the truly bipolar delocalized 4-methyl-4-trichloromethylbenzolonoum 1-(4,4-dimethyl-2,6-dioxocyclohexylide) under the influence of transition-metal π-coordination can take *** place. Thus the question of defining the NMR-spectral criteria for the

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* Because only one type of *hem*-$C(CH_3)_2$ signal, from the dimedone fragment, was observed in the ^1H NMR spectrum of the acac-complex II, recorded under conditions favourable for fast axial-equatorial exchange at room temperature, we thought [15] that there could have been accidental isochrony of these stereo-indicatory groups. This suspicion was however unfounded because the phenomenon also manifested itself in the Cp analogue III in which the Rh-atom substituent is very different by virtue of its magnetic anisotropy.

** It is noteworthy that when the temperature of the solution of complex III in $CDCl_3$ is changed from 0 to -70 ° C the signal from the C(2) atom in the ^{13}C NMR spectrum is shifted by 1.5 ppm to weaker field, and that from the C(5) atom is shifted by 2.3 ppm to stronger field. This is probably due either to purely thermal effects on the chemical shifts or to structural or electronic changes that are caused in the complex by the different temperatures.

*** The cationic fragment of this ylide can be regarded as the arenonium ion of electrophilic aromatic substitution (Wheland's complex [45]) stabilized by the transition metal (cf. [46]). Other examples of arenonium ions stabilized in this way are described elsewhere [47]. Up to now organometallic ylene-ylide transitions have been most comprehensively studied in the series of truly bipolar fulvene ligands (see review [23]), in which the transition-metal atom is coordinated with the anionic fragment of the π-system (cf. [19,20], see Scheme 3).

Table 4

^{1}H NMR spectral data for compounds I, II, III (ppm, in $CDCl_3$, T 295 K)

Compound	H(13)	H(8,10)	H(7,11)	H(16,18)	H(20,21)	CH_{acac}	CH_{3acac}	Cp
I [a]	1.57	7.55	6.72	2.61	1.04 1.09	–	–	–
II	2.65	6.38 [b]	4.10 [c]	2.50	1.08	5.43	2.05	–
III	1.97	7.10 [d]	4.18 [d]	2.31	1.00	–	–	5.66

[a] Atomic numbering is the same as that in Fig. 1. [b] $J(^{103}Rh–C(10)–^1H)$ 0.6 Hz. [c] $J(^{103}Rh–C(11)–^1H)$ 1.2 Hz. [d] $J(^{103}Rh–C(10)–^1H)$ $J(^{103}Rh–C(11)–^1H)$ 1.2 Hz.

structural assignment of the ground state of the above complexes to the η^4- or η^5-coordinated types in solution was raised. It should be noted that in all the ^{1}H and ^{13}C NMR spectral comparisons (in inert and magnetically isotopic $CDCl_3$, Tables 4 and 5) of the free ligand I parameters with those of its organometallic complexes (cf. [15,25]), it is necessary to take into account the inevitable changes in the hybridization of the carbon atom participating directly in the π-coordination with the transition-metal atoms ("coordinative shifts" (cf. ref. 48,49)).

^{1}H NMR spectra. The information gleaned from these spectra was not very useful to solving the problem in hand (Table 4). The $^1H–^{103}Rh$ spin–spin coupling constants and the chemical shifts for the C(7,11)H protons in the non-conjugated positions of the ring turned out to be almost the same for η^4-II and η^5-III coordinated complexes, reflecting the usual displacement compared with ligand I, η^5-III signal to the high field by approximately 3 ppm (see ref. 28). The only spectral indication that there was η^5-coordination was an almost complete absence of a similar high-field coordinative shift for the C(8,10)H proton situated in the conjugated (with C=O groups) positions ions of the ring) in complex III, as compared with the η^4-coordinated complex II (where it amounted to approximately 1 ppm) as well as a slight increase in the $J(^1H–^{103}Rh)$, which can be explained in terms of an increase in the formal positive charge on the C(8,10) atoms in the η^5-coordinated structure III and the strengthened bonding of these atoms with the metal atom.

^{13}C NMR spectra. In accord with the above observation the signals of C(8,10) carbon atoms in complex III undergo, compared with complex II, a noticeable (11.6 ppm) shift down-field (Table 5). However, the parameters that provided the most information on the structure were the ^{13}C chemical shifts (and the $J(^{13}C–^{103}Rh)$ for the carbon atoms in the inter-ring $C(6)\overset{\cdots}{-}C(14)$ "sesquibond". (Because these carbon atoms are not directly coupled with the protons, their exact positions in the spectra of both complexes studied were found, (when recorded with ^{1}H noise decoupling) with chemical shifts of 137 and 109 ppm for II and 121.5 and 107 ppm for III, once use had been made of the double heteronuclear resonance technique. When the spectra of both these complexes are re-recorded without ^{1}H-decoupling the signals at 137 and 107 ppm appear as the expected broadened triplets (with $J(^{13}C–^1H) \approx 4.5$ Hz which correspond to the spin–spin coupling across two chemical bonds). In view of the fact that the selective decoupling in both the spectra at frequencies corresponding to the resonance of the protons at C(7,11) carbon atoms, which led to the disappearance of the coupling $J(^1H–^{13}C)$ for the very same pair of signals, it is

Table 5

^{13}C NMR data for compounds I, II, III (in $CDCl_3$, *T* 295 K)

Parameter	Compound	C(13)	C(12)	C(9)	C(8,10)	C(7,11)	C(6)	C(14)	C(15,19)	C(16,18)	C(20)	C(21)	C(17)	Cp	$C{=}O_{acac}$	CH_{acac}	CH_{3acac}
δ (ppm)	I	23.4	104.5	55.8	142.2	126.6	140.8	131.3	199.8	55.3	28.5 or 28.2	28.2 or 28.5	–	–	–	–	–
δ (ppm)	II	29.98	101.11	54.64	73.63	62.6	137.22	108.87	200.2	53.94	28.25	28.25	–	–	186.56	99.60	26.71
$J(^{13}C–^{103}Rh)$ (Hz)	II	–	–	4.0	7.0	12.0	–	–	–	–	–	–	–	–	–	–	–
δ (ppm)	III	31.09	101.84	52.9	85.22	57.29	107.04	121.51	195.13	53.01	28.65	28.65	30.77	87.30	–	–	–
$J(^{13}C–^{103}Rh)$ (Hz)	III	–	–	–	6.0	9.5	3.0	4.5	–	–	–	–	–	5.5	–	–	–

possible to assign unambiguously those at 137 and 107 ppm to the C(6) atoms and those at 109 and 121.5 ppm to the C(14) atoms in complexes II and III, respectively.

The ^{13}C NMR spectra have thus revealed that inversion takes place in the relative positions of the signals of the C(6) and the C(14) atoms on going from η^4-II to η^5-III, which is manifested in an infinitesmal shift of C(6) signal of only 3 ppm to high field compared with that for complex II. The magnitude of the same shift for complex III is much larger (30 ppm to high field). The larger shift would be an indication a of the high degree of electron-density transferred from the metal to the C(6) atom of the ligand which, in our opinion, is the most important criterion to the η^5-coordinated structure of complex III in solution. This suggestion is confirmed by a pronounced $J(^{13}C-^{103}Rh)$ coupling with the C(6) atom (3 Hz) in complex III. The positions of the C(14) signals in the spectra of complexes II and III are also characterized by an upfield shift compared with the free ligand I, the shift being more pronounced for II, (23 ppm) than for III (10 ppm). The appearance of the coupling $J(^{13}C-^{103}Rh)$ 4.5 Hz, for the C(14) atom in III, in view of the remoteness of this atom from the metal, seems to be caused by its transmission via the C(6)=C(14) bond, and not by direct Rh...C(14) interaction.

The other chemical shifts in the ^{13}C NMR spectra of the two complexes studied show little or no selectivity with respect to η^4- or η^5-type coordination (Table 5). In the ^{13}C NMR spectra of complex II two signals are observed in the region of carbonyl carbon atoms; the first (186 ppm) was assigned by us to the $C{=}O_{acac}$ group (cf. ref. 50), and the second (200 ppm) to the C(15,19)=O groups that correspond to the free-ligand carbonyl groups (199.8 ppm, cf. ref. 51). This indicates a small contribution by their polarization to the shielding of the ground state of the compound in question *. Some displacement of this C(15,19) signal to higher field on going to complex III (by 5 ppm) could indicate that there is an increase in the polarity of the η^5-coordinated structure (cf. an upfield shift of the simplest dimedones C=O groups upon enolization [53]).

To conclude our examination of the unique spectral features of complex II in its ground state we should note that additions of pyridine-d_8, so as to vary the [Py]/[II] ratio, to a solution of II in $CDCl_3$ caused a sharp change in the signal from the residual α-proton of the pyridine ring and in those from the H(8), H(10) and H(7,10) chemical shifts, while the signals from H(16) and H(18) protons were shifted only slightly.

The relationships observed here are unambiguously indicative of the possibility that compound II can form a complex with the pyridine. Thus in such a complex the location of the pyridine molecule (with respect to the Rh atom) on the cyclohexadienyl ring side seems to be more probable than that on the dimedone one. The complexes formed in this case (and those obtained when DMFA was used in place of Py) are unstable in solution and decompose after a few hours to give the free ligand I.

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* Incidentally, the proximity of the chemical shifts of the CCl_3 group ^{13}C nuclei in the 2,5-cyclohexadienones [51], complex II and complex III (see Table 5), in spite of too short a distance (3.05 Å [15]) from Cl(1) atom to the C(6) atom of the exocyclic double bond, measured in the crystal of II and the longer one (3.214(4) Å) in II, indicates that for II in solution there is no appreciable transannular contribution by possible overlapping of the $-\overset{..}{\underset{..}{Cl}}$: atom with the C(6) AO to the kinetics of lowering the barrier to internal rotation around the $C(6)\overset{..}{=}\dot{C}(14)$ bond.

Table 6

The effect of the [Py]/[II] ratio on the chemical shifts of the H(8,10), H(7,11) and α-CH pyridine protons (ppm, $CDCl_3$, T 295 K)

[Py]/[II]	H(8,10)	H(7,11)	α-CH
0	6.38	4.10	–
0.5	6.92	3.71	8.40
2.0	6.92	3.70	8.53
10.0	–	–	8.70
300	7.74	3.99	8.81

Stereochemical non-rigidity of complex II and its activation parameters. To complete this part of our work we studied the nature and the kinetics of the processes of intramolecular stereochemical dynamics that characterize complex II by means of DNMR spectroscopy.

It is noteworthy that the CH_2 fragment is observed in the ^1H NMR spectrum of the free ligand I as an AB-quartet *, and the $C(CH_3)_2$ group as two (but not as four, as would be expected for separate invertomers (IIa and IIb)) singlets; these signals retain their structure both irrespective of an increase or a decrease in temperature [15]. This pattern is in good agreement with fast (on the NMR time scale) dimedone ring inversion in molecule II, an inversion that is known to take place in other derivatives of the dimedone series [51,54,55]. Even slight structural variations in their magnetic environment because of the dissimilar shielding by the spatially remote CCl_3 and CH_3 groups in the cyclohexadiene ring will cause non-equivalence of the $C(16,18)H^AH^B$ and $C(20)H_3$, $C(21)H_3$ fragments within the two stereoindicatory groups. Introduction of the rhodium atom into this ring results in an enhancement of the above structural differences. In spite of this, however, we have found that in the ^1H NMR spectra of complex II in $CDCl_3$ solution the resonance absorption lines of both the stereoindicatory fragments of the molecule, its $C(16,18)H_2$ as well as the $C(17)(CH_3)_2$ groups, are observed under normal conditions (20 °C) as broadened singlets. Their subsequent temperature-induced evaluation was explained in terms of two kinds of intramolecular conformational motions appearing in complex II, (i) the inversion of the C(16)C(17)C(18) flap in the dimedone ring of the molecule and (ii) the rotation of this ring as a whole around the polarized C(6)=C(14) double bond, the weakening of which is due to action by the Rh atom *d*-orbitals (Scheme 4). The stereodynamic behaviour of complex II was also confirmed by using solvents with strongly differing dielectric constants: acetone-d_6 $CDCl_3$, pyridine-d_5, toluene-d_8, methanol-d_4 and DMFA-d_6. This, incidentally, made it possible to determine their influence on the rate at which the

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* The quartet nature of this group in I, which is important for understanding its uniqueness as a stereoindicator and revealed now only as a result of our detailed analysis of the spectra, remains sufficiently disguised because of the low intensity of its external spectral lines ($I/\Delta\sigma_{AB} = 5$), which thus provoked its being described previously [15,25] in the molecule of I ($CDCl_3$, C_6D_6; 20 °C) as a singlet. Of the solvents we have used up to now it is only in toluene that this group for the compound I clearly manifests itself as an AB-quartet ($I/\Delta\sigma_{AB}$ 0.9). In the light of the above it is justified to regard the presence, or the appearance, of an AB-quartet of this group in the spectra of the compounds I and II as an argument in favour of complete inhibition (or, correspondingly, temperature-induced deceleration) of the inversion processes [15] (cf. [54,55]) and of the rotation.

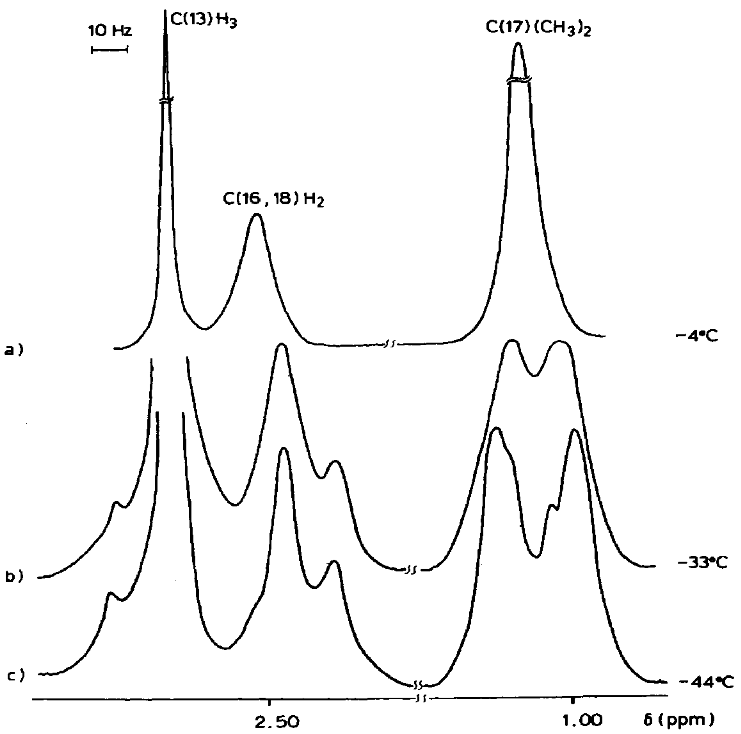

Fig. 3. Variable temperature ^1H NMR signals of the stereoindicatory $C(16,18)H_2$ and $C(17)(CH_3)_2$ groups of complex II (acetone-d_6).

process takes place. The effects of change of temperature (in acetone-d_6) are shown in Fig. 3. The results are consistent with those described previously [15], in the spectrum of complex II in $CDCl_2$ at −4°C. Singlets of the CH_2 and CH_3 groups were also observed (Fig. 3a). This alone permits the assertion that the appearance in the molecule under consideration of an additional (cf. ligand I) process which averages the magnetic environment of the protons in these stereoindicatory groups, an event that can only be effected by the internal rotation of the dimedone ring around the C(6)=C(14) bond. A decreased rate of this process as the temperature is lowered to −33°C results in the expected AB-quartet ($\Delta\delta_{AB}$ 0.23 ppm, J 15 Hz) and the two singlets characterizing the CH_2 and the $C(CH_3)_2$ group, appearing in the spectra (Fig. 3b). A further decrease in temperature reveals 4 singlets of the axial and equatorial *exo-* and *endo-*CH_3 groups with pairwise unequal intensities (Fig. 3c). This unambiguously corresponds to the slowing of dimedone cycle inversion and the observation of a pair of organometallic invertomers (IIa and IIb) in an unequal distribution seems to be caused by structural differences between the Rh and the CCl_3 bearing the "upper" and the "lower" halfspaces of the dimedone ring *. As to the nature of the temperature-induced evaluation of signals from

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* This result is of interest from the viewpoint of organometallic stereochemistry, as it indicates that the introduction of the metal atom in the peripheral position of our two-ring molecule increases the energy barrier of its dimedone fragment inversion, compared with the purely organic dimedone derivatives, for which a similar slowing down to inversion had been previously observed only at temperatures below of −120°C [54]. For organic examples with sufficiently high barriers of inversion, such as in methylene-bis-dimedone series, see ref. 55.

complex II, the spectra of II recorded in different solvents, such as DMFA, and $CDCl_3$ with the addition of C_5D_5N showed it to be similar to that of chloroform and acetone for both the stereoindicators, whereas in toluene the differences in the chemical shifts of the CH_3 group at low temperatures (down to −90 °C) were so small that they could only be fixed by the use of spectral line mathematical narrowing. In methanol the process was so rapid that only the broadening of the singlet resonance signals was observed for both the stereoindicators. The dynamic behaviour of complex II was also confirmed by DNMR and ^{13}C NMR spectroscopy. Thus as opposed to the free ligand I, whose $C(17)(CH_3)_2$ fragment in $CDCl_3$ at 20 °C manifests itself as two narrow singlet signals. In the ^{13}C NMR spectrum of complex II this fragment appears as the only strongly broadened singlet signal, which transforms at 20 °C into two (also strongly broadened) singlets, once the temperature drops to below −18 °C. However, for the problem in hand this method appears to be less convenient than ^1H DNMR, because cooling down to −66 °C caused no further splitting of the above signals in the ^{13}C spectrum, a fact which seems to be associated with the very small difference in the chemical shifts of the invertomers IIa and IIb *.

During the course of solving the problem that of determining the energy parameters concerning the stereochemical non-rigidity of complex II we encountered a number of difficulties associated both with the complexity of a dynamic process (a combination (cf. ref. 56) of rotation and inversion, with the latter, in its turn, able to proceed by several different mechanisms [57]) **. In addition there was the problem of choosing the most convenient (depending on the solvent) $C(16,18)H_2$ or $C(17)(CH_3)_2$ stereoindicatory fragments of the molecule and hence the assignment of the signals of $exo_{\text{a or e}}$ and $endo_{\text{a or e}}$ substituents to them. Since in the ^1H NMR spectra the differences in the chemical shift of the above four CH_3 groups and of the two CH^AH^B spin systems (usually observed here not as separate signals, but as a unified AB-quarter (Fig. 3c)) for the two invertomers in question (IIa and IIb) were too small to measure the energy barrier separately for the inversion and the rotation processes on an instrument with an operating frequency of 200 MHz. Thus to carry out the subsequent complete line shape analysis on the temperature-dependent spectra of complex II in different solvents we had to use the two-sided exchange approximation with computer program realized along existing lines [58,59]. In this analysis we determined the lifetimes (τ) of the corresponding stereoisomers, from which, by use of the Arrhenius and Eyring equations, we then obtained the kinetic parameters of the stereodynamic processes, outlined in Tables 7 and 8. It is noteworthy that in spite of the approximations good agreement is observed between the τ values derived from the line-shape analysis for the stereoindicatory signals of the CH_2 and of the CH_3 groups in the ^1H DNMR spectra and between the results from the ^{13}C DNMR spectra (for the $C(17)(CH_3)_2$ stereoindica-

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* It is noteworthy that the chemical shifts of the investigated stereoisomers show dependence not only on temperature but also on their concentration. Thus, a two-fold increase in the concentration of complex II, as compared with the concentration previously used by us [15], in $CDCl_3$ at −68 °C the quaternary nature in the ^1H NMR spectrum practically does not change for the $C(16,18)H_2$ fragment of the molecule, but becomes much less-pronounced than in [15] for its $C(17)(CH_3)_2$ fragment.

** Thus, for all the conformations depicted in Scheme 4 those with twisted dimedone ring (as a whole) may in principle not be excluded.

Table 7

The effect of various solvents on the kinetics of the stereodynamic process in compound II (^1H DNMR)

No.	Solvent	ϵ	τ [a] (s)	(T K)	E_{act} (kJ/mole)	log A	$H^{\neq}$ (kJ/mole)	$S^{\neq}$ (J mole^{-1} K^{-1})	$G^{\neq}_{298}$ (kJ/mole)
1	Toluene-d_8	2.38	0.153	(233)	21.7±1.3	5.8±1.1	19.2±1.3	−141.7±5.0	61.4
			0.0476	(253)					
2	$CDCl_2$	4.70	0.026	(223)	19.2±0.4	6.0±0.4	16.7±0.4	−136.7±3.3	57.3
			0.0074	(254)					
3	(NMR ^{13}C-{^1H})		(0.035)	(224)	(19.2±1.3)	(5.7±1.0)	(17.1±1.3)	(−141.7±4.2)	(59.3)
4	$CDCl_3$ + Py-d_5 [b]	4.70	0.0267	(223)	23.4±0.4	7.1±0.5	21.3±4.2	−115.4±2.1	55.7
	[II]^3/[Py] 2/1		0.0081	(243)					
5	$CDCl_3$ + Py-d_5	4.70	0.0262	9223)	23.4±0.4	7.1±0.5	21.7±4.2	−115.4±2.1	56.0
	[II^3]/[Py] 1/2		0.0092	(243)					
6	$CDCl_3$ + D-Py	4.70	0.0342	(223)	22.6±2.1	6.8±2.1	20.5±2.1	−121.0±8.8	56.4
	[II^3]/[Oy] 1/10		0.0064	(243)					
7	Acetone-d_6	20.7	0.064	(219)	22.6±0.4	6.6±0.4	18.4±0.4	−125.8±2.1	56.0
			0.038	(229)					
			0.0086	(259)					
8	Methanol-d_3	32.6	0.005	(223)	10.0±0.4	4.7±0.5	7.9±0.4	−160.5±2.1	55.7
			0.0024	(253)					
			0.00112	(273)					
9	DMFA-d_6	36.7	0.0120	(227)	26.7±3.3	9.1±3.0	24.7±3.3	−100.3±12.5	54.3
			0.0062	(257)					
			0.00166	(277)					

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[a] For entries 1, 3, 4, 5, 6 τ values determined by using the C(17)$(CH_3)_2$-stereoindicator, for entries 2, 7,8, and 9 determined by averaging of τ values for the C(16,18)H_2 and C(17)$(CH_3)_2$ stereoindicatory groups. [b] Py = pyridine.

Table 8

An NMR study of the stereodynamic process for compounds

Compound	$\Delta G^{\neq}$ (kJ/mole)	τ (s)	T (K)	Solvent	Remarks
I	> 73.6	0.129	323	toluene-d_8	Calculated according to the Gutovsky–Holm equation
II	64.8	0.00458	323	toluene-d_8	Calculated from the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values
	61.0	0.001	323	$CDCl_3$	
	45.9	0.042	213		
III	< 41.7	0.004	213	$CDCl_3$	Calculated by the line shape analysis using the $\Delta\delta_0$ for compound II

tor, see Table 7). In addition a very good correlation coefficient ($r = 0.998$) for the temperature dependence of the stereodynamic process in Arrhenius coordinates (Fig. 4) was obtained.

The kinetics of the stereodynamics for all the investigated solvents are listed in Table 7.

From Table 7 it follows that in all the solvents the observed organometallic stereodynamic process is characterized by usually small (compared with the other numerous known organic compounds able to undergo internal rotation viz., polarized ethylenes, [3,10,11]) activation enthalpies (between 7.9 and 24.7 kJ/mol) and in contrast, by a high entropic term (between -100 and -160 J mol^{-1} K^{-1}). Thus in the organometallic mode of rotation, the energy is used for steric rearrangement of the transition state, whose structure must thereby differ considerably from that of the ground state molecule. The obtained kinetic data obtained thus may be considered as evidence in favour of our suggested mechanism and is thus the driving force behind the redox internal rotations, which require significant geometrical (and, moreover, topological) changes in the initial molecules along the reaction time scale.

The rotation process in complex II, however, has not been studied in great detail at molecular level. The small difference between the τ values (Table 7) determined for $CDCl_3$ solutions by ^1H DNMR spectroscopy (concentration 2×10^{-2} mol/l)

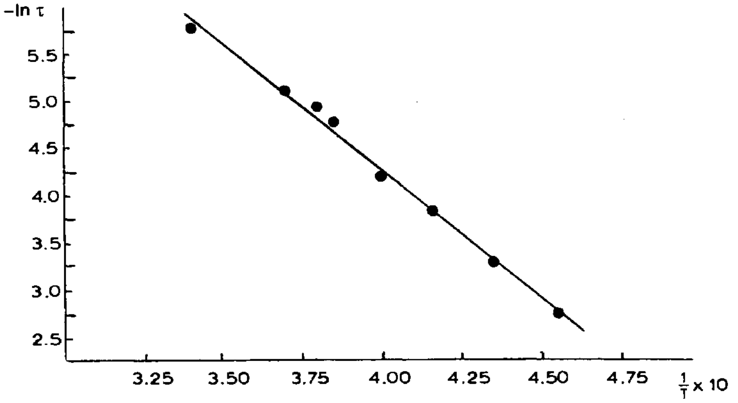


Fig. 4. Arrhenius plot for complex II (acetone-d_6).

and by the ^{13}C DNMR (concentration 8×10^{-2} mol/l) shows that there parameters do not depend on c_0, which testifies to an intramolecular process.

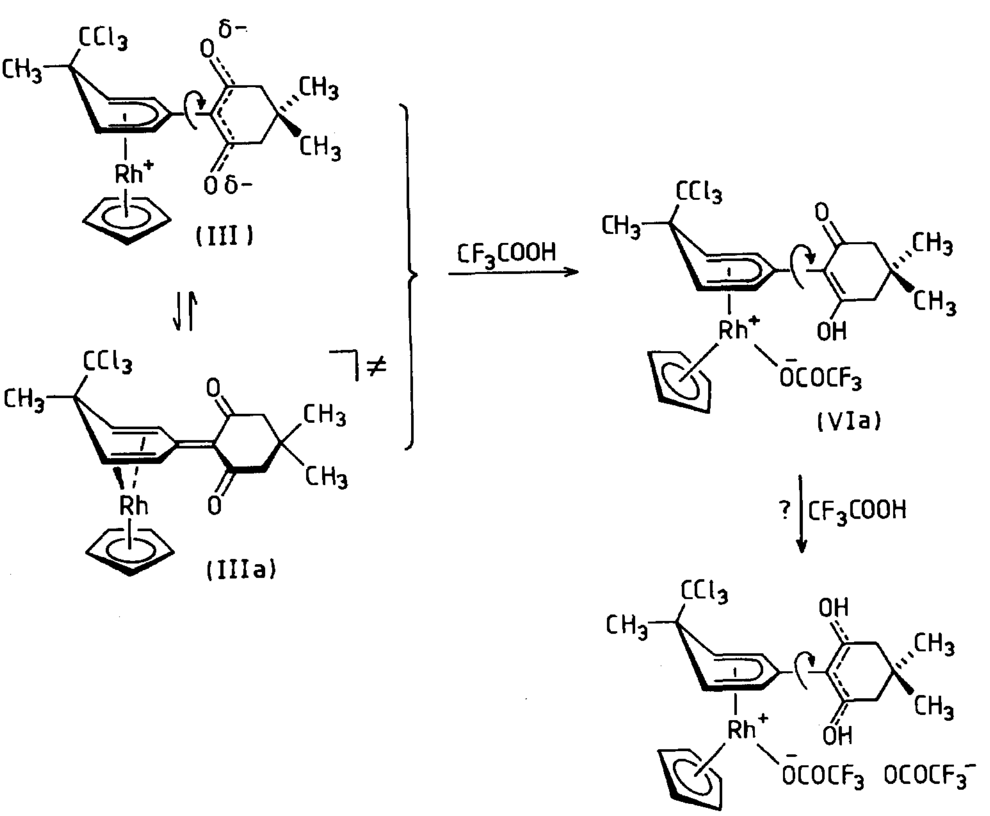
Influence of the solvent on the stereochemical non-rigidity of complex II. From the literature, in which the thermal mechanism of rotation around double bonds in polarized ethylenes [3,10,11] is described, it follows that the kinetic parameters of this rotation strongly depend on the dielectric constant of the solvent, owing to solvation of the polar transition state. In our case, however, for aprotic electron-donor solvents (including the additions of pyridine (in $CDCl_3$ solution) able, to undergo a specific solvation interaction with complex III, the internal rotation values of E_{act}, $\Delta H^{\neq}$ remained constant with increasing polarity of the medium (Table 7). This indicates that the formal positive charge of the polar system that arises out of the short-lived transition state of the rotation process (IIc, see Scheme 4) is not localized to its specific atoms, but is markedly redistributed between the metal and the ligand which in turn may then undergo a transition from the 4-electron to the 5-electron form. Furthermore, the data of Table 7 show the stereodynamic process to be noticeably accelerated by the polar protic solvent CH_3OH, for which the activation energy is the lowest of all those observed by us (E_{act} 10 kJ/mol). This implies that the formal negative charge of the transition-state system delocalized between its two C=O groups (IIc) still is sufficiently accessible to allow its stabilization by proton transfer from the CH_3OH molecule to the dimedone ring oxygen atom, thereby confirming the possible polar nature of this system, assumed in our redox-rotation concept.

The appearance of a negative charge on the carbonyl group oxygen atom, a prerequisite within the framework of our rotation model, implies that any form of its extinction (e.g. by the attack with an appropriate electrophile) would accelerate the process. In order to throw some light on this we carried out some protonation studies.

3. Protonation of the CpRh complex III of 4-methyl-4trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene

Up to now our work has been directed at designing model systems to study the energetics of the successive intermediate conformations in internal rotation processes in a series of two-ring semiquinoid rhodium complexes by means of stepwise reductions in their internal energy. Thus, the possible η^5-coordinated planar transition state of the redox-rotation of complex IIc (metal oxidation state Rh^{III}) is still rich in energy, because this molecule in its ground state has the η^4-diene structure IIa,b (Scheme 4). On going to the Cp derivative III (whose metal oxidation state Rh^{III}) an energy inversion takes place: The ground state of the complex is now η^5-coordinated (in this sense it can be regarded as a redox-rotational transition state of the 16-electron complex (IIc) stabilized by the 18-electron shell of the metal), and its η^4-diene structure (IIIa), if it occurs here at all, is probably an unfavourable transition state. Following on from this we thought it was worth trying to reduce still further the internal energy of the η^5-cyclohexadienyl structure of the molecules II, III, e.g. by prohibiting altogether their existence in diene form.

To prevent the occurrence of the diene form the complexes can be protonated with acids (Scheme 7). It has been shown that upon protonation with CF_3COOH, the 16-electron complex II gradually decomposes in solution, to give eventually signals of a free ligand in the ^{1}H NMR spectra. An excess of acid increases the rate



Scheme 7

of decomposition. In contrast, the 18-electron complex IV formed by protonation of compound III was extremely stable, which can be attributed to coordination saturation of its metal centre *. The reaction is best described as a formal 1,7- or 1,5-addition of the X–Y reagents to the M^+–C–C=C–C=C–O^- of M^+–C–C=C–O^- conjugated systems, respectively, which is probably characteristic for the compounds of this type. The excess of CF_3COOH makes it difficult to say at present whether we are dealing with a mono- (IVa) or di-protonated (IVb) particle **. However, examples of the formation of delocalized 1,3-dioxyallylcarbocations are known in the chemistry of the simplest simedone derivatives [62]. Along with the far from simple dependence of the chemical shifts and the spin–spin coupling constants on the nature of the acidoligand X in a series of even the simplest rhodium allyl derivatives (which can exist as ionic $CpRh(All)^+ X^-$ or as covalent CpRh(All)X [63], this complicates the interpretation of the spectral parameters of the protonated complex. Nevertheless the changes that take place in the ^{13}C NMR spectra on going

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* Cf. other stable η^5-cyclohexadienyl complexes of Rh^{III} [46,47] and examples of diene-dienyl rearrangements, induced by electrophilic attack [60,61].

** Up to now we have shown experimentally that with the addition of more than 2 equivalents of the acid the chemical shifts of C(8,10) and C(16,18) atoms, sensitive to protonation, in ^{13}C NMR spectra of the protonated complex IV at 273 K remain practically constant. It should be noted at the same time that when the spectra of complex III were taken in both pure CF_3COOH and its mixtures with H_2SO_4 or FSO_3H (from 20 to $-30\,°C$) no signals were detected in the region of hydride protons absorption, which makes it possible to discard here the possibility of protonation on the metal atom.

Table 9

Effect of the addition of CF_3COOH on the $^{1}H,^{13}C$ NMR spectral data for III in $CDCl_3$ (ppm, T 295 K)

[CF_3COOH] [III]	C(15,19)	C(14)	C(6)	C(12)	C(8,10) H(8,10)	C(7,11) H(7,11)	C(16,18) H(16,18)	Cp H(Cp)
O	195.13	121.51	107.04	101.84	85.22 7.10	57.39 4.18	53.01 2.31	87.30 5.66
7	190.5	10.547 (or 105.27)	103.04 [a]	105.27 (or 105.47)	93.70 [b] 6.38	60.06 [c] 4.39	46.05 2.54	89.22 [d] 5.88

[a] 'J(Rh–C) 5 Hz. [b] J(Rh–C) 6 Hz. [c] J(Rh–C) 8 Hz. [d] J(Rh–C) 6 Hz.

from III to IV (see Table 9), the C(15,19) and C(6) are shifted to high field (by 5 and 4 ppm, respectively) with a simultaneous down-field shift of the C(8,10), C(7,11) and Cp-ring signals (by 8.48, 2.67 and 1.92 ppm, respectively), are consistent with the presence of an η^5-coordinated cyclohexadienyl ring in the protonated complex IV. The spin coupling of the Rh atom C(7,11) and C(14) carbons is weakened in this case ($J(^{13}C-^{103}Rh)$ decreases by 1.5 and to 0 Hz) and with the C(6) atoms and the Cp ring the coupling intensifies (J increases by 2 and 1.5 Hz, respectively).

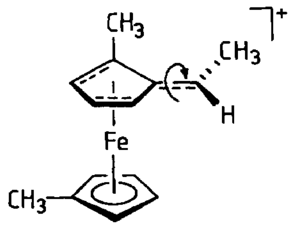
It is not to be excluded that such significant spectral changes indicate that the initial unprotonated complex does not have a purely dipolar structure like III but is more likely to be a set of various configurations one of which is the type IIIa diene form in solution, so that its positive charges on the C(8,10) and C(6) atoms can undergo concurrent stabilization under the influence of (i) the electron pairs on the oxygen of the polarized carbonyl group and (ii) the metal atom. After the oxygen is protonated the degree of Rh atom participation must increase; however, the Rh^+ interaction with the CF_3COO^- counterion should be superimposed on this effect, which then results in the formation of a polar $\overset{(+)}{\mathrm{Rh}}-\overset{(-)}{\mathrm{O}}\mathrm{COCF_3}$ polar bond. Moreover, it is noteworthy that the localization of some positive charge on the Rh atom in the protonated complex agrees with the shifts of the H and C signals of Cp-ring down field (by 0.2 and 1.92 ppm, respectively), which was observed in the ^{1}H and ^{13}C NMR spectra after addition of the acid.

As was mentioned above, in all the investigated solvents, with or without addition of acid, the signals of the protons in the C(16,18)H and $C(17)(CH_3)_2$ groups manifest themselves as singlets (Table 9), indicating that there is almost unhindered rotation of the dimedone ring around the C(6)–C(14) bond in complex IV. It is very important to note here that the free ligand I itself cannot be protonated by the action of CF_3COOH under similar conditions, as was indicated by the insignificant changes in the ^{1}H NMR spectra in $CDCl_3$ when additions of 1 and 2 equivalents of the acid were added. Also important is the fact that in the presence of the acid the protons of the two stereoindicatory CH_3 groups still continue show two normal singlets (at 300 K). Thus, the stereoisomeric transitions of the uncoordinated ligand I, if still taking place, are off the NMR time scale. In our opinion, this once again confirms the specific mechanism rotationalized here and elsewhere [15,16], of the rotation in complexes II and III around the C(6)$\overset{\cdot\cdot}{=}$C(14) bond, and includes the direct participation of the metal atom orbitals in the stabilization of the transition (in II) and the ground (in III) states of the conformational rearrangement described *.

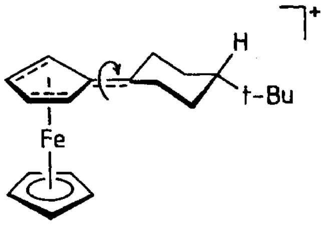
Concluding remarks

We have thus examined some new opportunities afforded by the use of transition metal complexes with *para*-semiquinoid ligands to model some exciting dynamic processes in organometallic stereochemistry. However, there is one additional reason for the interest in the complexes described above viz., they can also serve as specific model systems for investigating the nature of the organometallic β-effect which is a generalization for the different forms of metal atom (or a metal–carbon bond) participation possible in the electronic stabilization, at the β-site of the unsaturated ligand, of the adjacent carbocationic center of the different metal-containing carbocations (see refs. 67–70 and the review in ref. 49).

As we have seen here, a characteristic feature of β-participation in all the organometallic cationic complexes IIc, III, and IV was the possibility of the metal atom being oxidized intramolecularly by the neighbouring carbocation center of the π-ligand, with a change in formal oxidation state of the metal by two units. On the



(VII)



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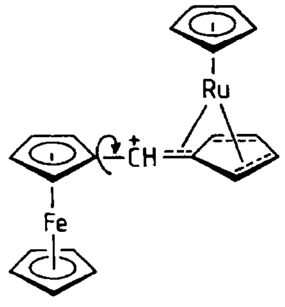

(IX)

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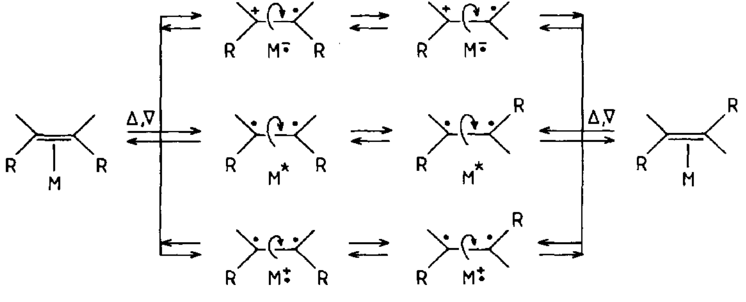
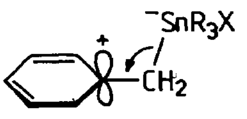
* The proposed concept of redox rotation (a change in oxidation state of the coordinated metal adjoining the multiple bond, undergoing the change in its configuration takes place with each internal rotation) must be distinguished from the widely known examples of the rotation of oxidized or reduced (among other causes, by the action of metals [41,64–66]) forms of strained olefins, which, although seeming to be initiated by the primary redox process, is later able to proceed independently and irreversibly without the requirement of concomitant synchronous changes in the valence of the counter ion metal:





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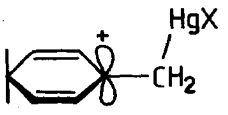

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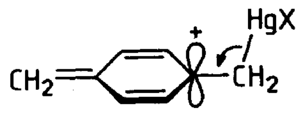

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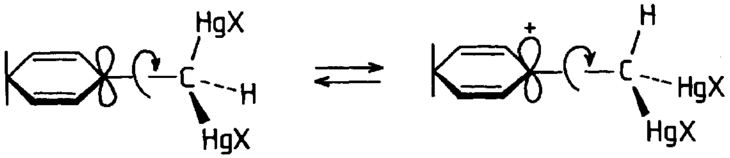


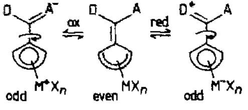
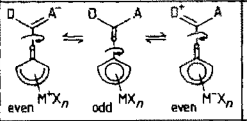
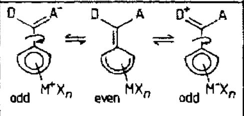
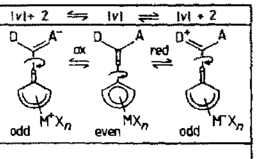
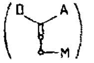
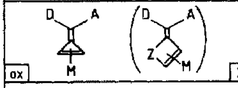
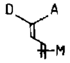
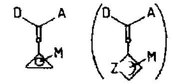
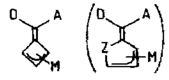
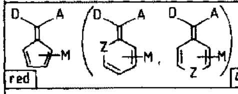
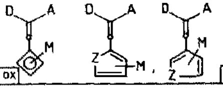
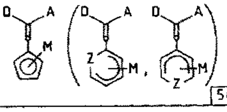
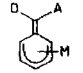
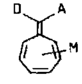
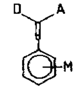
(XIII)

other hand numerous examples are known of almost freely rotatable transition metal (e.g. (VI–VIII) [69,70]) or non-transition metal organometallic cations [67] (including those described by us previously in connection with the β-effect present in various semiquinoid and quinoid ligands (IX–XII) [71]), in which β-stabilization of the neighbouring positive charge need not to be accompanied by changes in addition state of the metal atom. Hence, the question arises of what the structural requirements would be for a model organometallic system for the β-effect to manifest itself either in the former, redox, or in the latter, non-redox versions.

We believe that the main difference between these two types of organometallic β-effect models is whether the number of one-electron-bearing nuclei, in the β-charged π-system of the ligand coordinated with the metal, is odd or even. Note that this principle was used previously [17] to interpret the multiplicity of reactions possible when transition-metal cationic complexes were treated with nucleophiles). The possibility thus emerges of designing two principal, structural types of β-effect models, with *endo-* or *exo*-cyclic disposition of the resulting ionic center in the molecule to present four possible kinds of flexible β-effect organometallic models for stereodynamic processes. They are grouped in Table 10 according to the principles previously verified by us [72] for designing other periodic systems of compounds and reactions. It is noteworthy that is in good agreement with the systems of classification of odd and even (non-alternant and alternant) π-systems proposed by Dewar [73] (cf. also King's ligand tree [74]).

In order to describe adequately the difference between the two classes of organometallic stereodynamic processes we prefer to return to the concept of valence (further denoted as v), though with two important amendments. Firstly, under this structural-electronic parameter we mean the number of σ-bonds that a given molecular system could have, if all of its formal electric charges were saturated by a real or virtual recombination between any of the charged centers in the molecule: either M^+ and A^-, or M^- and D^+ (for completeness, another possible case, that of π-ligand diradicalization: $M^\cdot$ and $A^\cdot$ or $D^\cdot$ though not shown in Table 1a should also be mentioned). And secondly, we have dealt only with the absolute value of the valence parameter $|v|$ for generalizing the differences between the formally "oxidative" and "reductive" types of possible intramolecular stereodynamic processes.

Table 10
A periodic system for virtually rotatable organometallic complexes with potentially dipolar organic ligands

$\lvert v\rvert + 2 \leftrightharpoons \lvert v\rvert \rightleftharpoons \lvert v\rvert + 2$	$\lvert v\rvert + 1 \leftrightharpoons \lvert v\rvert + 1 \rightleftharpoons \lvert v\rvert + 1$	$\lvert v\rvert + 1 \leftrightharpoons \lvert v\rvert + 1 \rightleftharpoons \lvert v\rvert + 1$	$\lvert v\rvert + 2 \leftrightharpoons \lvert v\rvert \rightleftharpoons \lvert v\rvert + 2$
			
—	 1e		—
ox  2e	—	—	 2e
—	 3e	 3e	—
red  4e	—	—	ox  4e
—	 5e	 5e	—
ox  6e	—	—	ox red  6e
even non-alternant π-systems	odd non-alternant π-systems	odd alternant π-systems	even alternant π-systems
"even" anisovalent rotations	"odd" isovalent rotations		"even" anisovalent rotations

This approach was especially appropriate to the case of dipolar organometallic rotatable models for which "oxidation state" (usual in modern organometallic chemistry) of the organic ligand is no less important than that of the metal. The four kinds of structural models given in Table 10 could thus be sorted into two classes, in each class the rotation may be realized either with conservation of $\lvert v \rvert$ (which we have termed "iso-valent" rotation), or with an increase of $\lvert v \rvert$ by two units (dubbed "aniso-valent" rotation). The most probable, in our opinion, charge-inducing subtypes of aniso-valent rotations (ox or red) in which oxidation or reduction of the metal is to be expected are to be found in the lower left hand corner of Table 10.

The variety of organometallic models, represented in Table 10, is extremely wide (see, e.g. ref. 75–77). It is interesting to note that the very character of different possible combinations of the two prominent features of the discussed π-systems (i.e. their being odd or even and whether they are alternant of non-alternant) can determine here the nature of the changes in the σ- and π-bonding in the course of their "switching around" their pivoting bonds. Thus, if both of the mentioned features are "alike" (i.e. the system is either odd and non-alternant, or even and alternant), the rotation must be accompanied by a strengthening of the *exo*-π-bonds. If the features are "not alike" (odd and alternant, or even and non-alternant) then the rotation is bypassed with a weakening of the π-bond in the *exo*-moiety of the molecule.

We are well aware of the fact that the proposed organometallic β-effect rotatable models is more qualitative when quantitative, since it accounts neither for the orbital energy characteristics of the types of ligands and metals studied, nor the aromaticity or antiaromaticity (including the orbital-symmetry requirements in general) of the structures included in it. The possibility of intramolecular one-electron contributions to both the ionic and the radical organometallic β-effect is also excluded, opening up the possibility of a change in the metal atom oxidation state for its models (ref. see 78). Nevertheless, we present here heuristic systematics, bearing in mind that, though subsequent experiments or quantum-chemical calculations could provide specific physical definitions the systematics itself, even in its hypothetical form, can be useful for a molecular stereodesign of new models in the pertinent areas of dynamic organometallic stereochemistry.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 200 SY (200 MHz) instrument with TMS was as an internal standard. To interpret the ^{13}C spectra the noise ^{1}H-decoupling, ^{1}H-decoupling with elimination of the Overhauser effect and long delays between actuating pulses, as well as selective irradiation at the ^{1}H frequency were used.

The initial compounds were prepared by published procedures: I [25], II [15], and CpTl [27].

η^5-Cyclopentadienylrhodium-η^5-(4-methyl-4-exo-trichloromethylbenzolonium)-1-(4,4-dimethyl-2,6-dioxocyclohexylide) (III)

A mixture of 77 mg (0.14 mmol) of complex II and 63 mg (0.23 mmol) of CpTl in 8 ml of benzene was boiled for 25 min under argon, cooled and then evaporated to dryness. The solid residue was extracted with $CHCl_3$ (3 × 10 ml), combined extracts were evaporated to 10 ml and then boiled for 30 min in a stream of air. The mixture was filtered to remove the white precipitate. The filtrate was reduced to 2 ml and kept in a hexane vapour in a closed desiccator for 24 h. The crystals that separated were filtered off, dissolved in 2 ml of $CHCl_3$, then the solution was thoroughly filtered and again kept in a hexane vapour for 40 h. The precipitated yellow-orange crystals were filtered off, washed in 10 ml of cold hexane and dried in vacuo over $CaCl_2$ and paraffin for 12 h. Yield 50 mg (70%). T_{decomp} 130–175 °C.

X-Ray diffraction study of complex III

The single crystal of complex III was prepared by a slow (50 h) crystallization from a saturated solution in a $CHCl_3$/hexane mixture under the atmosphere of hexane vapour in a closed desiccator.

The crystals of III are monoclinic; at +20 °C, a 6.151(1), b 22.201(5), c 15.343(4) Å, 97.12(2)°, V 2079.0(9) Å, $D_{calc.}$ 1.65 g cm^{-3}, space group $P2_1/n$; $Z = 4$. Unit cell parameters and intensities of 3199 unique reflections with $F^2 \geqslant 4\sigma$ were measured with a four-circle automatic diffractometer Syntex $P2_1$ (20 °C, Mo-K_α radiation, graphite monochromator, $\theta \leqslant 28°$).

The structure was solved by heavy-atom techniques. The Rh atom coordinates were determined from a Patterson synthesis, and all other non-hydrogen atoms were located in the subsequent electron density synthesis. The structure was refined by full-matrix least squares, first isotropically and then anisotropically. All hydrogen atoms were located directly in the difference Fourier synthesis and included in the final isotropic refinement. The final R factor is 0.033, weighted R_w factor is 0.037. The atomic coordinates and temperatures factors are listed in Table 1, the bond lengths and angles are given in Table 2 and 3, respectively. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [79].

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