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Crystal Structure and Solution Dynamics of an Unusual Complex of Rhodium(I) with the Bridging Schiff-Base Ligand μ-[*N,N'-o*-Phenylenebis(salicylaldiminato)]-bis(η-1,5-cyclooctadiene)dirhodium(I)

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The reaction of di-μ-methoxo-bis(η-1,5-cyclooctadiene)dirhodium(I) with *N,N'-o*-phenylenebis(salicylaldimine) (H_2salophen) leads to a dimeric product with a 2/1 metal to ligand formulation [(Rh(cod))$_2$(salophen)] characterized via an X-ray diffraction study. The title complex crystallizes in the centrosymmetric orthorhombic space group *Pccn* with $Z = 4$. Unit cell parameters are as follows: $a = 12.647$ (2) Å, $b = 15.964$ (2) Å, $c = 14.507$ (3) Å, $V = 2928.9$ Å^3, and $D_{calcd} = 1.67$ g cm^{-3} for 736.5. Diffraction data (Mo Kα radiation) were collected with an automatic Enraf-Nonius CAD-4 diffractometer, and the structure was solved by conventional methods. The resulting discrepancy indices are $R = 0.0382$ and $R_w = 0.0467$ for 1455 independent reflections with $2° \le 2\theta \le 50°$. The salophen ligand takes up a bridging position between two Rh(I) atoms and shows a twisted conformation that is compared to the free molecule H_2salophen. The environment of each metal is quite close to square planar. The ^{13}C variable-temperature NMR shows a fluxional behavior of the cyclooctadiene moiety. The experimental activation energy of the process averaging the environment of the carbon atoms of each double bond is 50 (1) kJ mol^{-1} as found by comparison with simulated spectra.

Introduction

Most of the Schiff-base ligands are synthesized from salicylaldehyde and an amine; in case of a diamine, a potentially tetradentate ligand having ONNO donor atoms is obtained, the best known being salen.[2]

Interest in [M^{II}(salen)] compounds arose mainly from the property of some of them to reversibly bind molecular oxygen. Another related ligand of interest is salophen. These two ligands are capable of serving either as a tetradentate ONNO-type ligand, forming an essentially planar ring, or as a bridging bis-bidentate NO-type ligand for which little is known.

Calligaris and co-workers[3] have shown that salen can bridge two metal centers, acting as a bis-bidentate NO ligand in [Co_2(3-MeOsalen)$_3$]; for [(Rh(cod))$_2$(salen)], a bridged form has also been reported by West and co-workers,[4a] but they did not succeed in synthesizing analogous salophen complexes. They reported[4b,5] other binuclear salophen complexes with 2/1 metal to ligand formulation, but compounds of this kind are very rare. The structure of one of them [(Pd(apo))$_2$(salophen)] has been recently studied[6,7] to prove the bridging configuration of the salophen ligand. We have synthesized complexes of rhodium and iridium with Schiff-base ligands.[8-10] Hereafter, we describe the structure of a 2/1 complex [(Rh(cod))$_2$(salophen)] and its dynamic behavior in solution with also the aim of clearing up the arrangement of the bridging salophen ligand. Since rhodium-103 occurs in 100% natural abundance with spin $I = {}^1/_2$, rhodium–olefin complexes are ideal for such studies.

Table I. Experimental Details of the X-ray Diffraction Study of [((Rh(cod))$_2$(salophen)]

(A) Crystal Parameters[a] at 23 °C

$a = 12.647$ (2) Å	mol formula: $Rh_2C_{36}H_{38}O_2N_2$
$b = 15.964$ (2) Å	mol wt: 736.5
$c = 14.507$ (3) Å	space group: *Pccn*
$V = 2928.9$ Å^3	$Z = 4$
cryst size, mm: 0.23 × 0.16 × 0.09	ρ(calcd) = 1.67 g cm^{-3} ρ(obsd)[b] = 1.66 (3) g cm^{-3}

(B) Experimental Conditions for Data Processing

instrument: Enraf-Nonius CAD-4
radiation: Mo Kα ($\lambda = 0.71069$ Å), graphite monochromated
scan technique: coupled θ(cryst)–2θ(counter)
scan width: variable $\Delta\theta = (0.80 + 0.35 \tan\theta)°$
scan range: $2° \leqslant 2\theta \leqslant 50°$
stds: three reflctns (600), (080), and (008), measured every 100 reflctns, showed no decay
no. of reflctns collected: 2593, yielding 1455 measured above zero and used in the structure refinement
abs: $\mu = 6.8$ cm^{-1}
transmission factors: 0.917–0.948
corn: Lorentz, polarization, anomalous dispersion for Rh[c]

[a] From a least-squares fit to the setting angles of 25 reflections. [b] By flotation in a $ZnBr_2$ aqueous solution. [c] Reference 14.

Experimental Section

All solvents were dried and degassed prior to use under an atmosphere of nitrogen. Reactions were routinely performed under an atmosphere of nitrogen.

Crystal Data. The complex was obtained by reaction between [(Rh(OMe)(cod))$_2$] and the H_2salophen ligand in dichloromethane–pentane solvent as previously described.[8,9] Orange-yellow crystals of [(Rh(cod))$_2$(salophen)] were grown by slow diffusion at

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(1) (a) Laboratorie de Cinétique Chimique. (b) Laboratoire de Chimie Organique Structurale, ERA No. 557. (c) Muséum National d'Histoire Naturelle.

(2) Abbreviations: salen, *N,N'*-ethylenebis(salicylideniminato); 3-MeOsalen, *N,N'*-ethylenebis(3-methoxysalicylideniminato); apo, acetophenone oxime; cod, 1,5-cyclooctadiene; acac, acetylacetone; biim, 2,2'-biimidazole; S-dbm, thiodibenzoylmethane; *S,S*-chiraphos, (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane; Me, methyl; Ph, phenyl; Me_4Si, tetramethylsilane; salophen, *o*-phenylenebis(salicylaldiminato). According to Dr. K. L. Loening, Chemical Abstracts Service, whom we thank for his assistance, the preferred names would be α,α'-*o*-(phenylenedinitrilo)di-*o*-cresolato or 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis(phenolato).

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(4) (a) Cozens, R. J.; Murray, K. S.; West, B. O. *J. Organomet. Chem.* **1971**, *27*, 399. (b) Murray, K. S.; Reichert, B. E.; West, B. O. *Ibid.* **1973**, *61*, 451.

(5) Murray, K. S.; Reichert, B. E.; West, B. O. *J. Organomet. Chem.* **1973**, *63*, 461.

(6) Fallon, G. D.; Gatehouse, B. M.; Reichert, B. E.; West, B. O. *J. Organomet. Chem.* **1974**, *81*, C28.

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Table II. Final Positional Parameters[a] and Anisotropic Temperature Factors ($\times 10^3$)[b] of the Nonhydrogen Atoms in [(Rh(cod))$_2$(salophen)]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.26947 (7)	0.42902 (5)	0.19674 (6)	29.7 (4)	28.6 (4)	34.2 (4)	1.0 (4)	4.6 (5)	−0.2 (5)
C1	0.2130 (9)	0.4838 (7)	0.3216 (8)	35 (7)	44 (6)	42 (9)	3 (5)	11 (6)	−11 (6)
C2	0.1290 (9)	0.4388 (8)	0.2802 (8)	45 (7)	49 (8)	36 (7)	−1 (6)	13 (6)	−12 (7)
C3	0.0340 (10)	0.4804 (9)	0.2323 (10)	36 (8)	74 (10)	51 (10)	19 (7)	2 (7)	−19 (7)
C4	0.0561 (10)	0.4923 (10)	0.1280 (10)	39 (9)	107 (13)	55 (10)	26 (9)	−7 (7)	2 (9)
C5	0.1762 (11)	0.5041 (8)	0.1053 (9)	69 (10)	61 (7)	39 (9)	40 (8)	16 (7)	23 (7)
C6	0.2461 (14)	0.5548 (6)	0.1499 (9)	81 (10)	19 (5)	67 (9)	5 (7)	12 (9)	−0 (6)
C7	0.2098 (12)	0.6132 (6)	0.2258 (9)	103 (13)	25 (6)	60 (11)	14 (7)	12 (9)	−6 (6)
C8	0.2272 (11)	0.5764 (7)	0.3210 (8)	59 (8)	40 (6)	67 (10)	−8 (8)	4 (7)	−21 (7)
O	0.3769 (6)	0.4214 (5)	0.0929 (5)	40 (5)	39 (5)	36 (4)	−6 (4)	8 (4)	9 (5)
N	0.3301 (6)	0.3184 (6)	0.2520 (6)	25 (6)	34 (5)	26 (5)	−8 (4)	1 (5)	3 (5)
C9	0.4457 (9)	0.3637 (7)	0.0777 (8)	23 (6)	41 (6)	38 (7)	3 (5)	−0 (6)	−10 (6)
C10	0.5041 (10)	0.3713 (8)	−0.0082 (9)	27 (7)	78 (9)	44 (9)	−6 (7)	4 (7)	−8 (7)
C11	0.5793 (10)	0.3070 (8)	−0.0309 (10)	41 (8)	41 (8)	72 (11)	−14 (6)	7 (7)	−4 (7)
C12	0.6021 (9)	0.2420 (11)	0.0332 (10)	24 (8)	62 (9)	86 (12)	−2 (6)	19 (8)	−12 (9)
C13	0.5493 (9)	0.2373 (9)	0.1195 (9)	18 (8)	47 (9)	69 (10)	−3 (5)	15 (7)	−6 (7)
C14	0.4693 (8)	0.2966 (7)	0.1403 (8)	24 (8)	34 (8)	45 (7)	−4 (5)	1 (5)	−1 (6)
C15	0.4131 (8)	0.2796 (7)	0.2236 (7)	23 (8)	37 (6)	39 (7)	−4 (5)	5 (5)	−7 (6)
C16	0.2879 (8)	0.2818 (6)	0.3367 (6)	32 (7)	29 (5)	20 (5)	4 (5)	−4 (5)	−2 (5)
C17	0.3294 (8)	0.3134 (7)	0.4202 (8)	34 (7)	39 (6)	43 (7)	15 (5)	−6 (6)	−4 (6)
C18	0.2903 (10)	0.2816 (7)	0.5068 (7)	57 (10)	52 (8)	32 (6)	25 (6)	−2 (6)	−6 (6)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The temperature factor is of the form $\exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2lha^*c^*U_{13} + 2klb^*c^*U_{23}))$.

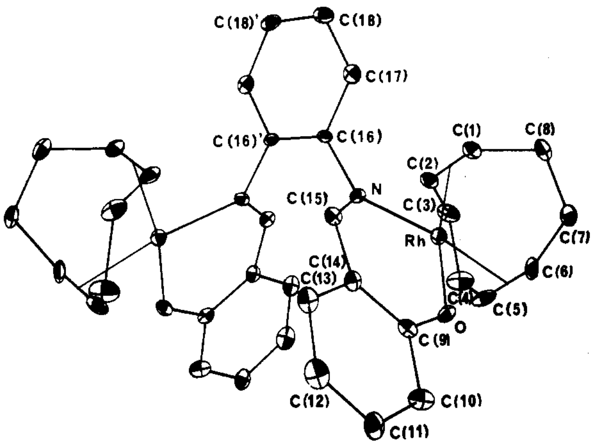

Figure 1. Perspective drawing of [(Rh(cod))$_2$(salophen)]. The vibrational ellipsoids are drawn at the 50% probability level. Half of the molecule is generated through a binary axis located at the midpoints of C(16)–C(16)′ and C(18)–C(18)′. Primed atoms are related to those without primes by the binary axis.

Table III. Interatomic Distances (Å) and Angles (Deg)

Rhodium-Ligand Bond Lengths			
Rh–O	2.032 (7)	Rh–M(1)	2.02 (1)
Rh–N	2.085 (9)	Rh–M(2)	2.03 (1)
Distances within cod Fragment			
C(1)–C(2)	1.42 (2)	C(5)–C(6)	1.36 (2)
C(2)–C(3)	1.54 (2)	C(6)–C(7)	1.51 (2)
C(3)–C(4)	1.55 (2)	C(7)–C(8)	1.52 (2)
C(4)–C(5)	1.57 (2)	C(8)–C(1)	1.49 (1)
Distances in salophen Moiety			
O–C(9)	1.29 (1)	C(14)–C(9)	1.44 (2)
C(9)–C(10)	1.45 (2)	N–C(15)	1.29 (1)
C(10)–C(11)	1.44 (2)	N–C(16)	1.46 (1)
C(11)–C(12)	1.42 (2)	C(16)–C(16)′	1.40 (2)
C(12)–C(13)	1.42 (2)	C(16)–C(17)	1.41 (1)
C(13)–C(14)	1.42 (2)	C(17)–C(18)	1.44 (2)
C(14)–C(15)	1.43 (1)	C(18)–C(18)′	1.43 (2)
Angles about Rhodium Atom			
O–Rh–N	89.3 (3)	O–Rh–M(2)	85.6 (5)
M(1)–M(2)	86.8 (5)	N–Rh–M(1)	98.9 (4)
Angles within the cod Fragment			
C(2)–C(1)–C(8)	126 (1)	C(4)–C(5)–C(6)	127 (1)
C(1)–C(2)–C(3)	124 (1)	C(5)–C(6)–C(7)	121 (1)
C(2)–C(3)–C(4)	110 (1)	C(6)–C(7)–C(8)	112 (1)
C(3)–C(4)–C(5)	113 (1)	C(7)–C(8)–C(1)	112 (1)
Angles in salophen Moiety			
Rh–O–C(9)	128.7 (7)	C(13)–C(14)–C(9)	121 (1)
O–C(9)–C(10)	116 (1)	Rh–N–C(15)	125.8 (7)
O–C(9)–C(14)	124 (1)	C(9)–C(14)–C(15)	125 (1)
C(9)–C(10)–C(11)	118 (1)	C(17)–C(16)–C(16)′	121.0 (7)
C(10)–C(11)–C(12)	120 (1)	N–C(16)–C(16)′	122.8 (5)
C(11)–C(12)–O(13)	121 (1)	N–C(16)–C(17)	116.2 (9)
C(12)–C(13)–C(14)	119 (1)	C(16)–C(17)–C(18)	120 (1)
C(13)–C(14)–C(15)	114 (1)	C(17)–C(18)–C(18)′	119.4 (7)

5 °C of methanol into a concentrated dichloromethane solution. Crystal data are listed in Table IA. Details of our diffractometer and methods of data collection and data reduction have been outlined previously.[11] Specific parameters pertaining to the collection of data are summarized in Table IB.

Structure Solution and Refinement. The position of the rhodium atom was found by solution of the three-dimensional Patterson function.[12] The remaining nonhydrogen atoms were found by combination of difference-Fourier syntheses and full-matrix least-squares refinement techniques. The refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to convergence with $R = 0.0382$ and $R_w = 0.0467$ for 1455 reflections and 190 variables.[13] Values of the atomic scattering factors for all atoms were obtained from the usual source.[14] The error in an observation of unit weight was 0.191 electron. The final difference-Fourier map did not reveal any chemically significant features other than some hydrogen positions that were not included in any calculation. The final atomic coordinates with their estimated standard deviations are given in Table II. Listings of observed and calculated structure factors, most least-squares planes and atomic deviations therefrom, and the derived root-mean-square amplitudes of vibration for all atoms are available.[15]

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(11) Potvin, C.; Manoli, J. M.; Pannetier, G.; Chevalier, R.; Platzer, N. *J. Organomet. Chem.* **1976**, *113*, 273.

(12) All calculations have been performed with the CII IRIS 80 computer of the Atelier d'Informatique. In addition to various local programs, modified versions of the following were employed: Zalkin's FORDAP Fourier summation program; Johnson's ORTEP thermal ellipsoid plotting program; Busing and Levy's ORFFE error function program; Ibers's NUCLS full-matrix program which in its nongroup form closely resembles the Busing and Levy's ORFLS program; D. M. Blow's PLAN (least-squares).

(13) The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma(F_o^2)$; the unweighted and weighted residuals are defined as follows: $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(14) Cromer, O. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.A and 2.3.1.

Variable-Temperature NMR Spectra. ^{13}C NMR spectra were recorded on a JEOL-PS 100 in the Groupe de Mesures Physiques de Paris Centre and on a Bruker-WP 80 in the Muséum National d'Histoire Naturelle, the observation frequency being respectively 25.15 and 20.1 MHz. The temperature of the variable-temperature unit was regulated with an accuracy of ±1 K.

The compound was dissolved in $CDCl_3$ (25.15 MHz) or C_6D_5Cl (20.1 MHz); the solutions were carefully degassed by freeze–pump–thaw cycles, and the tubes were sealed. Me_4Si was used as internal standard. Calculated spectra were obtained with the DNMR3 program.[12,17,18]

Results and Discussion

Description of the Crystal Structure. The molecular geometry of the dinuclear complex is shown in Figure 1. The asymmetric unit consists of half of [(Rh(cod))$_2$(salophen)]. Thus half of the dinuclear complex which is identified by primed atom labels is generated through a binary axis, located at the midpoints of C(16)–C(16)′ and C(18)–C(18)′ bonds. The interatomic distances and the bonds are listed in Table III.

The coordination geometry about each rhodium atom is a distorted square plane. A mean plane consisting of Rh,N,O,M(1),M(2)[19] revealed deviations of −0.127 to 0.118 Å from that plane. The M(1)–Rh–M(2) angle of 86.8° containing the olefin bonds of cyclooctadiene deviates from square geometry. This value is fairly close to that recently reported[20–22] (85.2–88.4°) in rhodium complexes of this diene. The "bite" angle O–Rh–N (89.3(3)°) is consistent with square-planar coordination and is in agreement with similar angles found in related complexes containing the salicylaldiminato group and presenting an approximately square-planar configuration at the central atom. Other angles of the square plane, M(1)–Rh–N = 98.9° and M(2)–Rh–O = 85.6°, merely reflect the distortion due to steric interactions between the cod and salophen ligands.

The Rh–C(olefinic carbon) bond lengths are equivalent and lie within the range 2.13 (1)–2.15 (1) Å. Both smaller and greater metal–olefin distances have been reported for related Rh(I) complexes. The Rh double-bond distances in [(Rh(cod))$_2$(biim)][22] (2.098 (6)–2.126 (6) Å), in [Rh(cod)(acac)][21] (2.092 (8)–2.115 (7) Å), and in [Rh(cod)(*S,S*-chiraphos)]$^{+}$[20] (2.238 (6)–2.247 (5) Å) show that the nature of the other ligand has an appreciable effect on the strength of the Rh–olefin bond. Our values compare well with other determinations, but the esd is too large to draw any conclusion about the possible trans influence of the opposite ligand. The cyclooctadiene ligand has a skewed conformation as observed in the free molecule[23] and when coordinated to other metals. The coordinated double bonds C(1)–C(2) and C(5)–C(6) have lengths of 1.42 (2) and 1.36 (2) Å compared to an uncoordinated olefinic distance of 1.34 Å.[23] This lengthening is expected to arise according to the Dewar–Chatt–Duncanson[24–26] model for olefin bonding. Carbon–carbon single-bond distances range from 1.49 (1) to 1.57 (2) Å, results typical for 1,5-cyclooctadiene bonded to an heavy metal. The C(1)–C(2) and C(5)–C(6) double bonds of cod are oriented approximately normal to the Rh,M(1),M(2) plane, with each bond twisted slightly in the same direction by 4.7 and 6.1°, respectively, as often observed for coordinated double bonds.

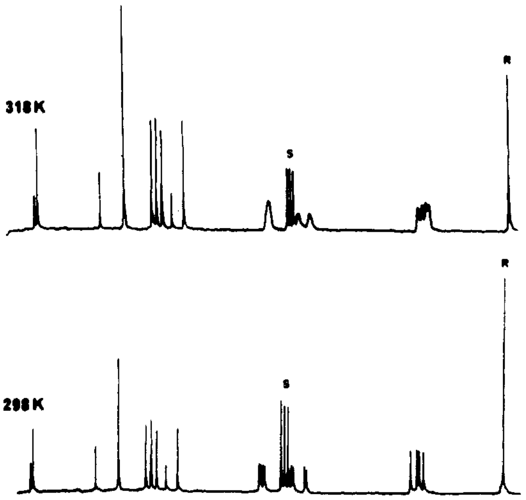

Figure 2. ^{13}C NMR spectra at 25.15 MHz in $CDCl_3$ at 298 and 318 K: R, reference Me_4Si; S, solvent peaks.

The Rh–N bond length is 2.085 (9) Å while the Rh–O bond distance is 2.032 (7) Å; this latter distance is typical of this bond as reported for [Rh(cod)(acac)][21] (2.054 (5)–2.066 (5) Å), for which the trans ligand is the same diene and the bite angle O–Rh–O is close to 90°.

A main feature of the structure is the bridging salophen molecule. Usually salophen acts as a tetradentate ONNO ligand with the four donor atoms around the central metal atom. The ligand in the tetracoordinate complex is very nearly planar as described by X-ray structural determinations.[7,27,28] In the binuclear Rh(I) complex, the salophen has an extremely warped conformation and therefore allows two Rh(I) atoms to coordinate to the bis-bidentate NO ligand, each Rh(I) being also bound to one cod chelate ring. The resulting arrangement leads to a Rh–Rh separation of 5.737 (1) Å, thus excluding any metal–metal bonding interaction. This intramolecular distance is considerably greater than that of the Pd atoms (3.696 (4) Å) in [(Pd(apo))$_2$(salophen)].[7] Bridging by the salophen ligand is achieved by twisting the salicylaldiminato residue (N,O,C(15),C(9)–C(14)) out of the plane of the phenylene bridge about the N–C(16) bond, the two salicylaldiminato moieties being inclined at 85° respectively to the plane of the phenylene bridge. This distortion is about twice that observed in the palladium complex.[7]

The major structural changes occurring within the ligand framework following ONNO-type complexation were first mentioned by Nardin and co-workers.[27] From geometrical data, these authors established the molecule H$_2$salophen to have an enolamine form in the solid state. Moreover, the geometry of the whole molecule is not planar; salicylidenamine residue is removed from the plane of all the other atoms of the molecule by rotation around the bond equivalent to N–C(16), the mean planes of the two fragments making an angle of 56.8°. Upon coordination the extent of delocalization in the salicylaldiminato moiety approaches that observed with the tetradentate ONNO ligand driving to complexes of formula [M^{II}(salophen)].[7,27,28]

Dynamic Behavior in Solution. The NMR spectrum observed at 25.15 MHz (Figure 2) at 298 K is in accord with

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(15) See paragraph at end of paper regarding supplementary material.
(16) Kleier, D. A.; Binsch, G., DNMR3 program.
(17) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1978**, *32*, 145.
(18) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411.
(19) M(1) is the midpoint of C(1)–C(2); M(2) is the midpoint of C(5)–C(6).
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(25) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.
(26) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
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(28) Cassoux, P.; Gleizes, A. *Inorg. Chem.* **1980**, *19*, 665.

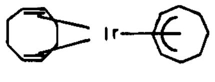
the crystalline structure, and it may be safely concluded that this is, indeed, the instantaneous structure of the molecule in solution. The proposed assignment has been previously given.[8] The olefinic carbon atoms of the cod moiety (C(1)–C(2)–C(5)–C(6)) give four doublets due to coupling with the rhodium atom. The ^{103}Rh–^{13}C(olefin) spin–spin coupling constants (trans-O atoms ca. 12.5 Hz and trans N atoms ca. 14.5 Hz) are in agreement with those found in the literature.[29–31]

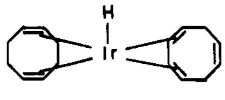
In the ^{13}C variable-temperature NMR, fluxional character was shown to be present in the cyclootadiene moiety (Figure 2); but at the same time no fluxional character was apparently present in the Schiff-base ligand. We thus have one type of fluxional behavior which averages the environment of the carbon atoms of each double bond.

Owing to the low boiling point of $CDCl_3$, we were unable in a first series of experiments to go beyond the coalescence of one group of doublets. To obtain more data, we undertook a new series of experiments, working at a lower frequency (20.13 MHz) and using a solvent with a higher boiling point: C_6D_5Cl.[32] The corresponding spectra are presented in Figure 3. Several features of these spectra are noteworthy: (i) the Schiff-base part of the spectra does not change significantly in contrast to findings in the corresponding cyclooctadiene system; (ii) the changes in the cyclooctadiene system are reversible; (iii) the high-temperature spectra indicate equivalence of both carbon atoms of the double bonds; (iv) retention of the ^{103}Rh–^{13}C coupling in the high-temperature-limit spectra demonstrated that the exchange process is *intramolecular.*

This last point is also established in another experiment in which temperature-dependent behavior is unaltered on the addition of free cod, the signals of the cod being also unperturbed. *The observed signals depend, therefore, on an intramolecular exchange process involving the cod ligand.*

As far as we know, intramolecular arrangements of diolefins in complexes are very rare. A rotation of cod around the metal–ligand axis is proposed by Muller and co-workers[33] in





An intramolecular exchange process was also encountered in $[(Li(THF)_2)_2Ni(cod)_2]$ by Jonas and Krüger,[34] but it involves the breaking of one metal–olefin bond. With rhodium complexes, Heitner and Lippard[35,36] postulate the nucleophilic attack of a solvent molecule on [Rh(diene)(S-dbm)] to form a five-coordinate intermediate which undergoes one or more polytopal rearrangements. This tends to cause the *four carbon atoms to become equivalent.*

This cannot prevail in our case because in the high-temperature-limiting spectra, the signals corresponding to the double bonds *did not show any tendency to merge.*

In order to bring more light on this phenomena, we attempted a simulation of the spectra using the program DNMR3.[16–18] The NMR data were analyzed on the basis of a "jump" model and therefore only give information concerning the permutation which relates the initial labeled nuclear configuration to the configuration after rearrangement (see the labeling scheme Figure 1). No direct mechanistic information is obtained to indicate the actual physical path involved. The possible permutations which convert the initial labeled configuration into all other possible labeled configurations form the group S_4 of order 4! = 24. According to King,[37] the symmetry permutations can be divided into five groups (Table IV). The symmetry of the system is too low to afford any simplification. Some of the 24 permutations are impossible from a chemical point of view because they break bonds in the cod moiety. Using a simulation with DNMR3 program, we concluded that the only possible permutational mechanism is (C(5)C(6))(C(1)C(2)).

The data do not lend themselves to accurate calculations, but the best fit is presented in Figure 3. It is not possible to obtain accurate calculation of absolute activation energies for this exchange process. However, data presented in the form of an Arrhenius plot in Figure 4 lead to the rate expression rate $(k) = 10^{9.5}e^{-50\times10^3/RT}$. With the best fit deduced from the olefinic carbon signals, we obtain a good agreement between the observed and the calculated spectra for the CH_2 carbon atoms (Figure 3). This supports our results even if there is probably an important experimental error arising from the

Table IV. Permutation Analysis of $[(Rh(cod))_2(salophen)]$[a] (Permutational Group S_4, No Symmetry Constraint)

equiv basic permutational set	permutation[b]		desig
I: $1x_1^4$	(1)(2)(5)(6)		identity
II: $8x_1x_3$	(1)(265)	(1)(256)	not possible, destroy the cod moiety
	(2)(561)	(2)(651)	
	(5)(621)	(5)(612)	
	(6)(125)	(6)(152)	
III: $6x_1^2x_2$	(1)(2)(56)	(1)(5)(26)	
	(1)(6)(25)	(2)(5)(16)	
	(2)(6)(15)	(5)(6)(12)	
IV: $6x_4$	(5261)	(6521)	
	(2651)	(1562)	
	(5612)	(1625)	
V: $3x_2^2$	(21)(65)		up–down twist
	(51)(62)		half-turn
	(61)(52)		O/N exchange

[a] Only cod olefinic carbon atoms are considered. [b] Numbers refer to the labeling of the molecule (see Figure 1).

Table V. Rotational Barriers in Some Diene Complexes of Rhodium or Iridium

compd	geometry[a]	solvent	ΔG^*, kJ mol^{-1}	ref
$[Ir(Me)(cod)(PMe_2Ph)_2]$	TBP	C_6H_5Cl	68.1	38
$[IrH(cod)(PMe_2Ph)_2]$	TBP	CH_2Cl_2	55.6	38
$[Ir(Me)(cod)(PMePh_2)_2]$	TBP	CH_2Cl_2	70.6	38
$[IrH(cod)(PMePh_2)_2]$	TBP	CH_2Cl_2	58.9	38
$[Ir(Me)(cod)(PPh_3)_2]$	TBP	CH_2Cl_2	58.5	38
$[IrH(cod)(PPh_3)_2]$	TBP	C_6H_5Cl	74.0	38
$[IrH(cod)(PEtPh_2)_2]$	TBP	CH_2Cl_2	73.6	38
$[IrH(cod)(PiPrPh_2)_2]$	TBP	CH_2Cl_2	86.1	38
$[IrH(cod)(PCyPh_2)_2]$	TBP	CH_2Cl_2	84	38
[Ir(Me)(cod)(diphos)]	TBP	CH_2Cl_2	37.6	38
[Ir(Me)(cod)(dppp)]	TBP	CH_2Cl_2	56.0	38
[Ir(Me)(cod)(dppb)]	TBP	CH_2Cl_2	69.0	38
[Ir(Me)(cod)(1,2-bis-(dimethylarsino)benzene)]	TBP	CH_2Cl_2	49.7	38
$[Ir(Me)(cod)(AsMe_2Ph)_2]$	TBP	CH_2Cl_2	64.8	38
[Rh(nbd)(Sdbm)]	SQ	NO_2Ph	87.9	36
[Rh(nbd)(Sdbm)]	SQ	o-$C_6H_4Cl_2$	74.1	36
[Rh(cod)(Sdbm)]	SQ	o-$C_6H_4Cl_2$	46.5	36
[Rh(nbd)(Sdbm)]	SQ	o-$C_6H_4Cl_2$	77.8	35
[Rh(nbd)(Sdbm)]	SQ	NO_2Ph	82.4	35

[a] TBP = trigonal bipyramidal; SQ = square planar.

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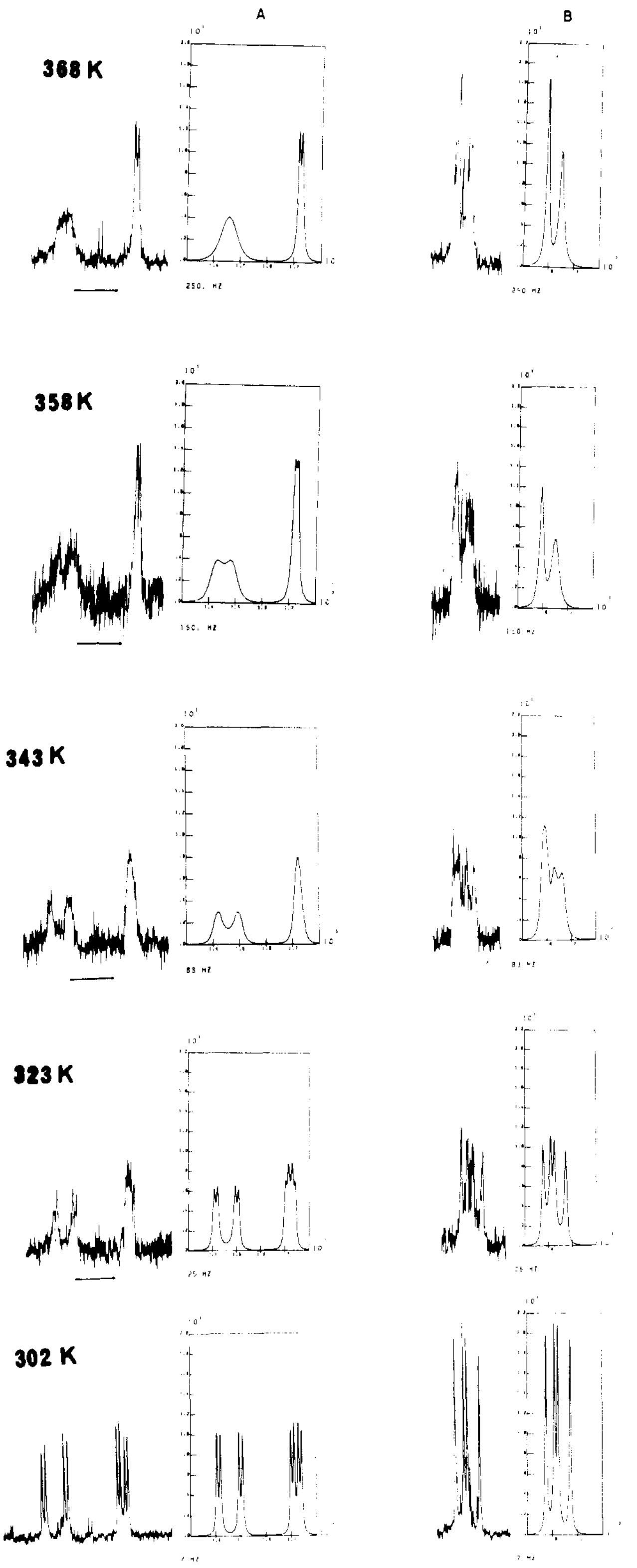

Figure 3. Variable-temperature NMR spectra and simulated spectra obtained with DNMR3 program (at 20.1 MHz in C_6D_5Cl): A, olefinic carbon atoms signals; B, signals of the CH_2 carbon atoms.

limited range over which the measurements were made (302–368 K). The experimental activation energy is 50 (1) kJ mol^{-1}. It is well within the range of the rotational barrier observed for a number of fluxional process in neutral metal–olefin complexes (Table V). However, our data were difficult to interpret. No direct mechanistic information is obtained to indicate the actual physical path involved in part because the line shape contains no mechanistic information since the spectral changes are too simple.

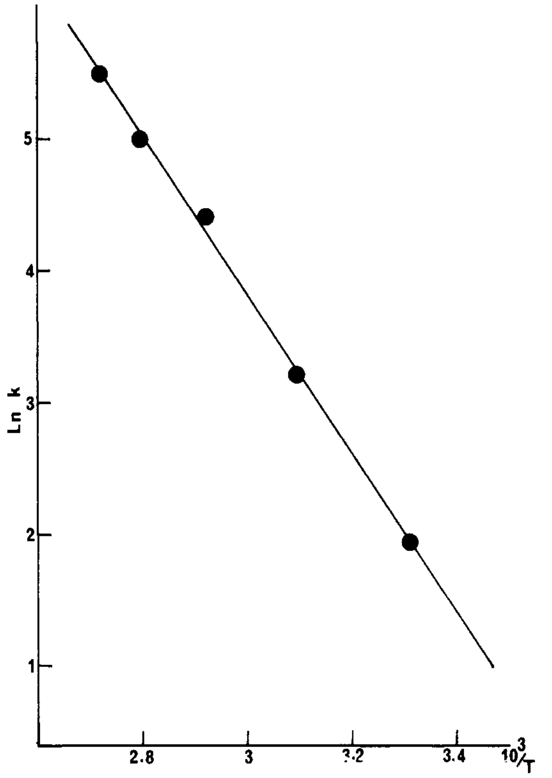

Figure 4. Arrhenius plot relating the rate constants of the fluxional process in Hz to the inverse of the absolute temperature.

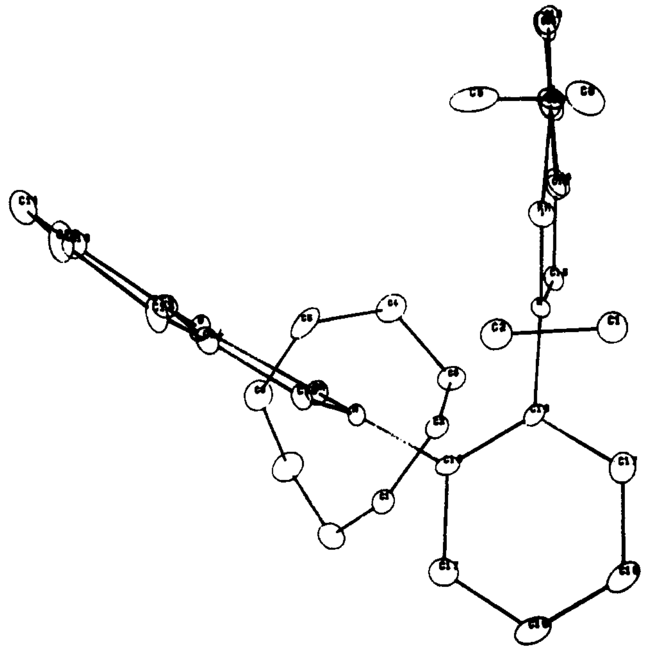

Figure 5. Perspective representation of the molecule viewed from inside the cod "tub". For clarity CH_2 groups of cod are omitted.

If we suppose an observer seeing the molecule from inside the "tub" of one cod ligand, the molecule seems very asymmetric and it is difficult to imagine the two carbon atoms of a double bond being equivalent (Figure 5). To explain our experimental findings we can only think that the dissymmetry of the carbons C(1), C(2), C(5), and C(6) is due to steric interactions with the nearest neighbors. It is well-known that in this kind of molecule the double bonds make an angle with the mean plane of the molecule. In the solid state we find 4.7 and 6.1° for this angle (vide supra). We can imagine that variations of this angle, in solution, at high temperature were sufficiently rapid as to make the two carbon atoms of each double bond equivalent. To support this hypothesis of "vicinal differentiation", we can note again[9] that with related complexes where the Schiff base is derived from ortho- or meta-substituted anilines, the dissymmetry introduced by the meta substituent is ineffective in differentiating the carbon atoms of the nearest double bond on the scale of ^{13}C NMR spectroscopy.

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Registry No. $(Rh(cod))_2$(salophen), 68858-45-7; $(Rh(OMe)(cod))_2$, 12148-72-0.

Supplementary Material Available: Listings of root-mean-square amplitudes of vibration, least-squares planes and atomic deviations therefrom, and structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis and Structure of *trans*-$[O_2(en)_2Tc^V]^+$

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The octahedral complex ion *trans*-$[O_2(en)_2Tc]^+$ has been prepared by a facile and general synthetic technique and has been characterized by NMR and electronic absorption spectroscopy. Rapid hydrolysis of the ion occurs in acid media to yield free ethylenediamine. The iodide salt of the complex crystallizes in the triclinic space group $P\bar{1}$. Crystal data: $a = 5.767$ (4) Å, $b = 8.759$ (7) Å, $c = 10.929$ (7) Å, $\alpha = 84.13$ (5)°, $\beta = 92.18$ (6)°, $\gamma = 97.63$ (5)°, $Z = 2$, $V = 544.1$ (6) Å^3, $R = 9.4\%$. The chloride salt forms crystals belonging to the monoclinic space group $P2_1/c$. Crystal data: $a = 5.637$ (1) Å, $b = 11.177$ (2) Å, $c = 16.112$ (3) Å, $\beta = 101.11$ (1)°, $Z = 4$, $V = 996.1$ (3) Å^3, $R = 4.1\%$. The average Tc=O distance is 1.75 Å, the average Tc—N distance is 2.15 Å, and the average N—Tc—N interior angle is 80°. The complex exhibits the $\delta\lambda$ geometry with respect to the ethylenediamine conformation in the iodide salt, while in the chloride salt both the $\delta\delta$ and $\lambda\lambda$ configurations are observed.

The radiophysical properties of ^{99m}Tc are very nearly optimal for imaging various organs and locating anatomical or physiological abnormalities.[1–5] However, owing to the variability of reaction conditions employed in the clinical setting, mixtures of technetium complexes often result. A complicating factor is the short half-life (6 h) of the isotope, which limits the scope of purification procedures that are practical prior to injection. Consequently, there can be substantial variation in the quality of the diagnostic procedure. A major goal in the application of technetium chemistry is to develop a spectrum of synthetic methods that allows for the rapid and reproducible preparation of easily purified organ-specific complexes.

Of special interest are imaging agents that would show a high degree of selectivity for hypoxic or anoxic areas, which occur in tumors or infarcts.[6,7] Since such areas have lower ambient electrochemical potentials relative to the surrounding normal tissue, technetium complexes may be preferentially reduced and undergo substitution reactions which would cause them to localize in these environments. The lower pH of tumor tissue should favor pH-dependent metal ion reduction and may induce the hydrolysis of acid-labile complexes to also cause them to concentrate in the neoplasm.[8] Selective fixation by either method would provide a means for diagnosing and locating the diseased areas for treatment. One way of accomplishing this would be to utilize oxotechnetium complexes that substitute their oxygen ligands on reduction. Analogous chemistry is well-known for the adjacent element, molybdenum, which catalytically undergoes redox-induced substitution of coordinated oxygen in enzymatic systems.[9] The nitrogen ligands of these complexes are acid labile so that they might also selectively concentrate in tumors by the hydrolytic mechanism.

Several research groups have now shown that Tc(V) has a high affinity for O^{2-} and that the technetyl ion often adopts a square-pyramidal structure with chloride, sulfur, or sulfur and oxygen ligands occupying the basal plane.[2,10,11] Early work by Polish[12] and Russian[13] workers suggested that Tc(V), when coordinated with nitrogen ligands, tended to form octahedral complexes with the oxygens trans to each other. In this communication we report a facile synthetic method for the synthesis of *trans*-$[O_2(en)_2Tc]^+$ and the structure of this complex as both the chloride and iodide salts.

Experimental Section

Synthesis. Approximately 150 mg of the starting material, $(n\text{-}Bu_4N)TcOCl_4$ (n-Bu = n-butyl), which was prepared by the method of Trop,[11] was dissolved in a minimum of tetrahydrofuran. Ethylenediamine (5–7 drops) was then added until the green color of the technetium starting material disappeared. When the solution was allowed to stand, a brownish orange to pink aggregate formed, which was removed by filtration and washed with THF. The residue was dissolved in a minimum of water and charged onto a Sephadex CM C-25 chromatographic column. The column was eluted with water

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