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SYNTHESIS, CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF THE MENTHYLCYCLOPENTADIENYL COMPLEX OF RUTHENIUM (+)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl

EDOARDO CESAROTTI,

Istituto di Chimica Generale ed Inorganica dell'Università e Centro C.N.R., Via Venezian 21, 20133 Milano (Italy)

GIANFRANCO CIANI and ANGELO SIRONI *

Centro di studio per la sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, Reparto Strutture, Via Venezian 21, 20133 Milano (Italy)

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Summary

The diastereoisomeric pair (+)₅₇₈- and (-)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa and IIb) (MCp = (*R*)-(-)-menthylcyclopentadienyl) has been synthesized from (η^5 -MCp)Ru(CO)₂Cl (I) by replacement of one of the two diastereotopic CO groups by P(C₆H₅)₃ in refluxing xylene under nitrogen. Preparative TLC gave the two diastereoisomers optically pure. The structure of diastereomer IIa has been determined by single-crystal X-ray diffraction methods. The compound is orthorhombic, space group *P*2₁2₁2₁ (No. 19) with *a* = 16.667(6), *b* = 22.287(8), *c* = 8.301(3) Å and *Z* = 4. The structure was solved by Patterson and Fourier methods, on the basis of 3046 significant counter reflections, and refined by block-matrix least-squares to a final conventional *R* value of 0.049. The configuration of IIa is *S* (based on Stanley and Baird sequencing rules). The exactly opposite and almost enantiomeric pattern of the CD spectra of IIa and IIb suggests an *R* configuration at ruthenium for complex IIb.

Introduction

A considerable number of cyclopentadienyl complexes of transition metals chiral at the metal center are known. Usually these chiral complexes are prepared as mixtures of diastereoisomers in which a monodentate ligand is responsible for inducing chirality [1,2].

It is known that when η^5 -cyclopentadienyl carbonyl complexes are used as catalysts in hydroformylation or hydrogenation, they do not lose the Cp

ligand except under rather severe experimental conditions [3], and the loss of a monodentate ligand is usually a key step in the reactions. Thus the presence of an appropriate monodentate ligand to induce chirality does not ensure that the metal remains in a chiral environment during a catalytic cycle. This can, however, be accomplished by using a cyclopentadienyl ligand bearing a chiral substituent.

The optically active cyclopentadiene (*R*)-(-)-menthylC₅H₅, subsequently denoted by MCpH, prepared from (+)-neomenthol [4], was used for the synthesis of an optically active organometallic compound of ruthenium. Thus the complex (η^5 -MCp)Ru(CO)₂Cl (I), which contains two diastereotopic CO groups, was treated with P(C₆H₅)₃, so that one of these groups is replaced by the phosphine to form a pair of diastereoisomers, (+)- and (-)-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa and IIb). The mixture of the two diastereoisomers can be quantitatively separated by preparative TLC, and each diastereoisomer is obtained optically pure. The two diastereoisomers are configurationally stable in the solid state as well as in solution, at least until they start to decompose.

In order to elucidate the configuration at the metal center we carried out an X-ray analysis of (+)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa).

Experimental

Synthesis of (+)₅₇₈- and (-)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa, IIb)

100 mg (0.252 mmol) of I are dissolved in 10 ml xylene under nitrogen, and 66 mg (0.252 mmol) P(C₆H₅)₃ are added. The light yellow solution is refluxed and stirred for three hours. The reaction is monitored by IR and stopped when the two ν (CO) bands of I, centered at 2050 and 2000 cm⁻¹, disappear and only one broad band at 1950 cm⁻¹ remains. The solution is evaporated to dryness to leave a microcrystalline yellow mixture of the two diastereoisomers IIa and IIb in an almost quantitative yield. The two diastereoisomers are quantitatively separated by TLC (silica gel; cyclohexane/ethylacetate, 9/1). Analytical data for both diastereoisomers are given in Table 1.

Crystal data

C₃₄N₃₈ClOPRu, mol. wt. 630.2, orthorhombic, *a* = 16.667(6), *b* = 22.287(8), *c* = 8.301(3) Å, *U* = 3083.5 Å³, *D_m* = 1.34(2) (by flotation), *D_c* = 1.36 g cm⁻³ for *Z* = 4, *F*(000) = 1304. Space group *P*2₁2₁2₁ (No. 19) from systematic absences. Mo-*K_α* radiation (λ = 0.7107 Å); μ (Mo-*K_α*) = 6.60 cm⁻¹.

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF THE TWO DIASTEREOISOMERIC COMPLEXES (η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa, IIb)

	IIa	IIb
IR ν (CO) (s, b) (cm ⁻¹)	1950 ^a	1950 ^a
<i>M⁺</i> (<i>m/e</i>)	630 ^b	630 ^b
Anal. found (calcd.) C	65.62(64.81)	65.84(64.81)
H	5.84(6.04)	6.87(6.04)
α_{578}	(+)	(-)

^a Pentane solution. ^b The highest peak in the multiplet arising from the isotope distribution in Ru and Cl.

Intensity measurements

A crystal of the diastereoisomer IIa of dimensions $0.05 \times 0.05 \times 0.33$ mm was mounted along the c axis on the automatic BASIC diffractometer (see footnote of ref. 5) and 6093 intensities, corresponding to the $\pm h, +k, +l$ (referred to right-handed axes) quarter of the sphere in the 2θ range $6-50^\circ$, were collected using graphite-monochromatized Mo- K_α radiation and the ω -scan technique, with a total scan width of 0.8° and a scan speed of $0.025^\circ/\text{sec}$. The background was measured on both sides of each reflection for half the peak-scanning time. One standard reflection was measured at periodic intervals and no decay was detected. Integrated intensities were reduced to F_0 values by correction for Lorentz and polarization effects; no correction for absorption was applied. 3046 reflections were significantly above background ($\sigma(I)/I < 0.33$), corresponding to two octants (with k or l equal to 0 the $+h$ and $-h$ reflections were averaged) and were used in the structure determination and refinement.

Determination and refinement of the structure

The coordinates of Ru, Cl and P atoms were obtained from an analysis of a three-dimensional Patterson map and, after a preliminary refinement of these parameters a successive difference-Fourier synthesis showed the locations of all the non-hydrogen atoms. Five cycles of least-squares method in the block-diagonal approximation resulted in agreement factors of $R = 0.067$ and $R_w = 0.087$. The atomic parameters at this stage corresponded to an S configuration at the ruthenium atom (*vide infra*). In order to determine the absolute configuration of the molecule the effects of the anomalous dispersion were taken into account and two refinements of the parameters were carried out, both of four cycles, one with $+if''$ for the anomalous scatterer atoms (Ru, Cl, P) and the other one with $-if''$. The results of these refinements were $R^+ = 0.059$, $R_w^+ = 0.066$ and $R^- = 0.061$, $R_w^- = 0.068$. According to the Hamilton R factors significance test [6], that means that the probability that the S form is the correct configuration is well over 99.5%. After the S configuration was assigned, anisotropic thermal factors were assigned to all the atoms except for the phenyl carbon atoms. The phenyl groups of the phosphine ligand were treated as rigid bodies (D_{6h} symmetry, C—C 1.392 Å) with individual atomic temperature factors. The hydrogen atoms were introduced (C—H 1.00 Å), with an isotropic temperature factor of 4.5 \AA^2 , in the computation of the structure factors but not refined. The observation were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$, where A , B and C had values 16.10, -0.40 and 0.0035 , respectively, in the final cycles, and were chosen on the basis of an analysis of $\sum w(F_0 - k|F_c|)^2$. Atomic scattering factors were taken from ref. 7 for all the non-hydrogen atoms and from ref. 8 for hydrogen. The factors for anomalous dispersion for Ru, Cl, P were taken from ref. 9. The final values of the reliability indices were $R = 0.049$ and $R_w = 0.054$. The final difference Fourier map was flat, showing no residual peaks exceeding $0.4 e/\text{\AA}^3$. Attempts were also performed, at this stage, to locate the hydrogen atoms directly; a difference Fourier map computed with the non-hydrogen atoms shows some residual peaks in positions close to computed ones, but attempts to refine them led to oscillation and so we chose to use the ideal hydrogen positions. The results of

(continued on p. 92)

TABLE 2

POSITIONAL AND THERMAL PARAMETERS WITHIN (+)₅78-(η^5 -MCP)Ru(CO)P(C₆H₅)₃Cl^{a,b}

Anisotropic atoms

Atom	x	y	z	b ₁₁	b ₁₂	b ₁₃	b ₂₂	b ₂₃	b ₃₃
Ru	149(1)	2342(1)	1858(1)	26(1)	1(1)	3(1)	12(1)	0(1)	91(1)
Cl	-80(1)	3126(1)	3828(2)	51(1)	1(1)	2(4)	15(1)	-23(2)	162(3)
P	243(1)	1613(1)	3828(2)	28(1)	-1(1)	5(3)	11(1)	-1(2)	100(3)
C	-911(5)	2138(4)	1625(11)	32(3)	3(4)	15(12)	20(2)	-17(9)	85(15)
O	-1567(4)	1997(3)	1411(8)	36(3)	-15(4)	11(10)	45(2)	-24(9)	152(14)
C(1)	1246(5)	2826(4)	976(11)	28(3)	5(4)	-3(13)	17(2)	38(9)	139(16)
C(2)	1398(5)	2217(4)	885(12)	26(3)	6(4)	27(13)	19(2)	43(10)	180(17)
C(3)	832(5)	1956(4)	-169(12)	41(4)	-8(5)	91(13)	16(2)	7(11)	162(17)
C(4)	345(4)	2424(4)	-797(10)	28(3)	8(4)	-4(10)	14(1)	6(8)	118(13)
C(5)	584(5)	2968(3)	-76(11)	22(3)	-4(4)	23(12)	12(1)	4(9)	126(15)
C(6)	255(6)	3591(3)	-417(10)	41(4)	2(5)	-12(14)	15(1)	6(8)	87(12)
C(7)	-667(5)	3585(4)	-539(13)	24(3)	10(4)	-11(14)	17(2)	22(11)	189(19)
C(8)	-1044(7)	4196(5)	-855(14)	57(5)	26(6)	24(17)	23(2)	43(12)	164(20)
C(9)	-1967(6)	4130(6)	-1099(16)	33(4)	48(6)	43(18)	53(4)	94(17)	272(27)
C(10)	-660(7)	4479(5)	-2365(18)	62(5)	8(6)	-16(15)	23(2)	10(11)	120(19)
C(11)	258(6)	4500(4)	-2205(11)	34(3)	4(5)	0(14)	21(2)	50(9)	148(17)
C(12)	615(5)	3867(4)	-2017(12)	37(3)	1(4)	6(14)	16(1)	35(10)	107(15)
C(13)	1551(5)	3871(4)	-2016(18)	30(3)	-9(4)	-7(15)	26(2)	26(12)	121(16)
C(14)	1939(6)	4309(5)	-859(14)	46(4)	-4(6)	-45(17)	29(3)	1(13)	165(21)
C(15)	1833(6)	3998(6)	-3727(14)	45(5)	0(7)	73(17)	39(3)	62(14)	204(22)

Phenyl carbon atoms

Atom	x	y	z	B (Å ²)	Atom	x	y	z	B (Å ²)
CP(11)	159(4)	864(2)	2950(8)	3.2(1)	CP(24)	-1642(3)	1509(3)	7909(7)	5.0(2)
CP(12)	-660(3)	561(2)	3000(7)	3.8(1)	CP(25)	-999(3)	1111(2)	7875(7)	5.2(2)
CP(13)	-045(3)	3(2)	2267(8)	4.7(2)	CP(26)	-428(3)	1153(2)	6661(8)	4.2(2)
CP(14)	9(4)	-252(2)	1483(8)	5.1(2)	CP(31)	1182(3)	1603(3)	4964(8)	2.8(1)
CP(15)	738(3)	50(2)	1433(7)	5.4(2)	CP(32)	1577(4)	1080(2)	5420(8)	4.8(2)
CP(16)	814(3)	609(2)	2166(8)	4.3(2)	CP(33)	2279(3)	1112(2)	6323(8)	6.6(3)
CP(21)	-496(3)	1593(3)	5480(7)	2.8(1)	CP(34)	2587(3)	1669(3)	6771(8)	5.1(2)
CP(22)	-1139(3)	1991(2)	5514(7)	4.0(2)	CP(35)	2192(4)	2192(2)	6315(8)	4.8(2)
CP(23)	-1712(3)	1949(2)	6728(8)	4.7(2)	CP(36)	1490(3)	2159(2)	5412(8)	3.6(2)

Hydrogen atoms

Atom	x	y	z	Atom	x	y	z
H(1)	1546	3120	1660	H(14)3	1767	4727	-1131
H(2)	1835	1999	1468	H(15)1	2433	4003	-3756
H(3)	784	1520	-428	H(15)2	1623	4397	-4084
H(4)	-91	2377	-1610	H(15)3	1629	3678	-4463
H(6)	409	3859	499	HP(12)	-1039	745	3564
H(7)1	-821	3310	-1439	HP(13)	-1169	-214	2303
H(7)2	-886	3427	498	HP(14)	-44	-653	956
H(8)	-942	4463	91	HP(15)	1209	-132	870
H(9)1	-2207	4534	-1305	HP(16)	1338	827	2130
H(9)2	-2211	3952	-108	HP(22)	-1189	2308	4666
H(9)3	-2072	3861	-2040	HP(23)	-2173	2236	6753
H(10)1	-869	4897	-2600	HP(24)	-2053	1479	8782
H(10)2	-806	4235	-3331	HP(25)	-948	795	8724
H(11)1	490	4692	-3191	HP(26)	35	867	6637
H(11)2	403	4745	-1236	HP(32)	1357	681	5099
H(12)	429	3618	-2945	HP(33)	2563	737	6651
HP(13)	1737	3459	-1720	HP(34)	3092	1693	7420
H(14)1	2536	4278	-947	HP(35)	2413	2592	6637
H(14)2	1771	4211	266	HP(36)	1207	2536	5085

^a All parameters $\times 10^4$, except for the isotropic B factors. ^b The b_{ij} values are the coefficients of $\exp -(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hkb_{12} + hlb_{13} + hlb_{23})$.

the refinement are shown in Table 2. The final list of observed and calculated structure factor moduli can be obtained from the authors.

All the computations were carried out on an UNIVAC 1100/80 computer with local programs.

Results and discussion

The crystal structure consists of discrete molecules packed with normal Van der Waals contacts. A view of the particular enantiomer is shown in Fig. 1. Relevant bond parameters are reported in Table 3.

The coordination around the ruthenium atom, shown in Fig. 2, may be regarded as close to octahedral, as suggested by the values of the angles between monodentate ligands, with the Cp moiety occupying three *fac* coordination sites.

The Ru—C(Cp) (mean 2.237 Å), the C(Cp)—C(Cp) (mean 1.414 Å) and the Ru—C(CO) bond distances are comparable with those previously reported [10]. The Ru—P bond length of 2.310(2) Å is in the lower range of the Ru^{II}—phosphine distances in the literature [11]. The Ru—Cl bond distance can be regarded as normal, and is intermediate between the values of 2.454(3) and 2.415(2) Å found in RuCl₂(CO)(C₂H₄)(PMe₂Ph)₂ [12].

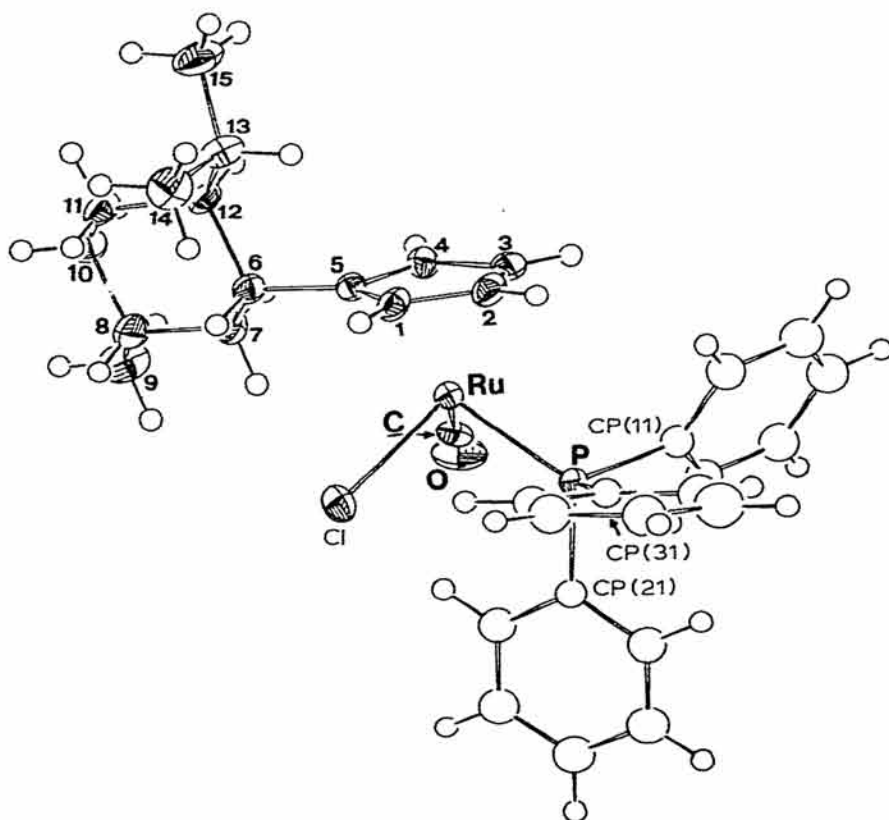


Fig. 1. A view of the (+)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl complex IIa. The carbon atoms of the MCp moiety are indicated by their number sequence.

TABLE 3

BOND DISTANCES AND ANGLES WITHIN (+)₅₇₈-(η^5 -MCp)Ru(CO)(PC₆H₅)₃Cl

Distances (Å)		Angle (°) ^a	
Ru—Cl	2.425(2)	Cl—Ru—Cp*	119.2(3)
Ru—P	2.310(2)	P—Ru—Cp*	126.7(3)
Ru—C	1.838(9)	C—Ru—Cp*	125.7(3)
Ru—C(1)	2.245(9)	Cl—Ru—P	92.3(1)
Ru—C(2)	2.250(9)	Cl—Ru—C	95.8(3)
Ru—C(3)	2.207(10)	P—Ru—C	87.9(3)
Ru—C(4)	2.236(9)	Ru—C—O	177.0(8)
Ru—C(5)	2.249(9)	Ru—P—CP(11)	110.8(2)
C—O	1.149(11)	Ru—P—CP(21)	119.8(2)
P—CP(11)	1.826(6)	Ru—P—CP(31)	115.6(2)
P—CP(21)	1.845(6)	CP(11)—P—CP(21)	102.9(3)
P—CP(31)	1.827(6)	CP(11)—P—CP(31)	105.1(3)
C(1)—C(2)	1.382(13)	CP(21)—P—CP(31)	100.9(2)
C(1)—C(5)	1.442(13)	C(1)—C(2)—C(3)	108.4(8)
C(2)—C(3)	1.413(14)	C(2)—C(3)—C(4)	107.8(8)
C(3)—C(4)	1.422(13)	C(3)—C(4)—C(5)	108.3(8)
C(4)—C(5)	1.410(12)	C(4)—C(5)—C(1)	106.5(7)
C(5)—C(6)	1.519(12)	C(5)—C(1)—C(2)	108.9(8)
C(6)—C(7)	1.542(14)	C(1)—C(5)—C(6)	126.2(8)
C(6)—C(12)	1.582(13)	C(4)—C(5)—C(6)	127.2(8)
C(7)—C(8)	1.523(15)	C(5)—C(6)—C(7)	111.3(7)
C(8)—C(9)	1.558(16)	C(5)—C(6)—C(12)	112.1(7)
C(8)—C(10)	1.542(16)	C(6)—C(7)—C(8)	114.5(8)
C(10)—C(11)	1.540(16)	C(7)—C(8)—C(9)	110.2(9)
C(11)—C(12)	1.538(12)	C(7)—C(8)—C(10)	109.6(9)
C(12)—C(13)	1.561(12)	C(9)—C(8)—C(10)	110.0(10)
C(13)—C(14)	1.513(16)	C(8)—C(10)—C(11)	110.8(9)
C(13)—C(15)	1.522(16)	C(10)—C(11)—C(12)	111.4(8)
		C(11)—C(12)—C(13)	112.4(8)
		C(11)—C(12)—C(6)	107.2(7)
		C(12)—C(13)—C(14)	115.5(9)
		C(12)—C(13)—C(15)	108.0(8)
		C(14)—C(13)—C(15)	109.9(9)

^a Cp* indicates the C(1)—C(5) ring centroid.

The cyclopentadienyl ring is essentially planar (the maximum out-of-plane displacement is of 0.016 Å for C(3)) but C(3) (the carbon atom nearly *trans* to Cl, C(3)—Ru—Cl 151.3(3)°) is slightly closer to the Ru atom than the others.

The menthyl moiety is bound to C(5) (which is staggered with respect to the CO and Cl ligands, see Fig. 2) and shows usual C—C bond distances (mean value 1.540 Å). The three chiral centers C(6), C(8) and C(12) have *R*, *R* and *S* configurations, respectively, as previously reported [13].

CD and UV spectra of (+)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIa) and (–)₅₇₈-(η^5 -MCp)Ru(CO)P(C₆H₅)₃Cl (IIb) are given in Fig. 3. There is evidently good agreement between CD and UV maxima. Moreover the two CD spectra of IIa and IIb are almost enantiomeric, in spite of the diastereoisomeric relationship between the two complexes.

Taking the η^5 -cyclopentadienyl ring as one ligand, the configuration at the metal atom in the complex IIa can be assigned according to the *R*, *S* system [14] as extended to organometallic complexes [15]. The priority sequence of

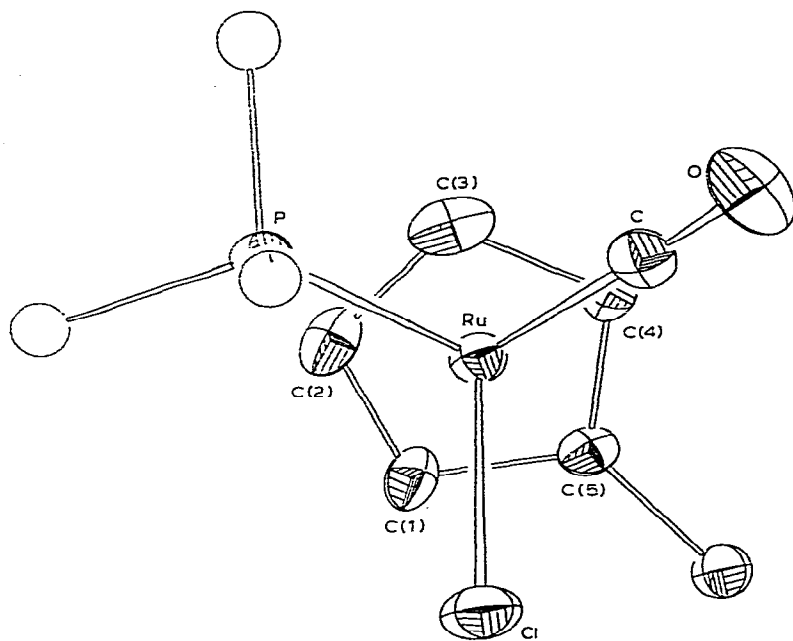


Fig. 2. The coordination around the ruthenium atom.

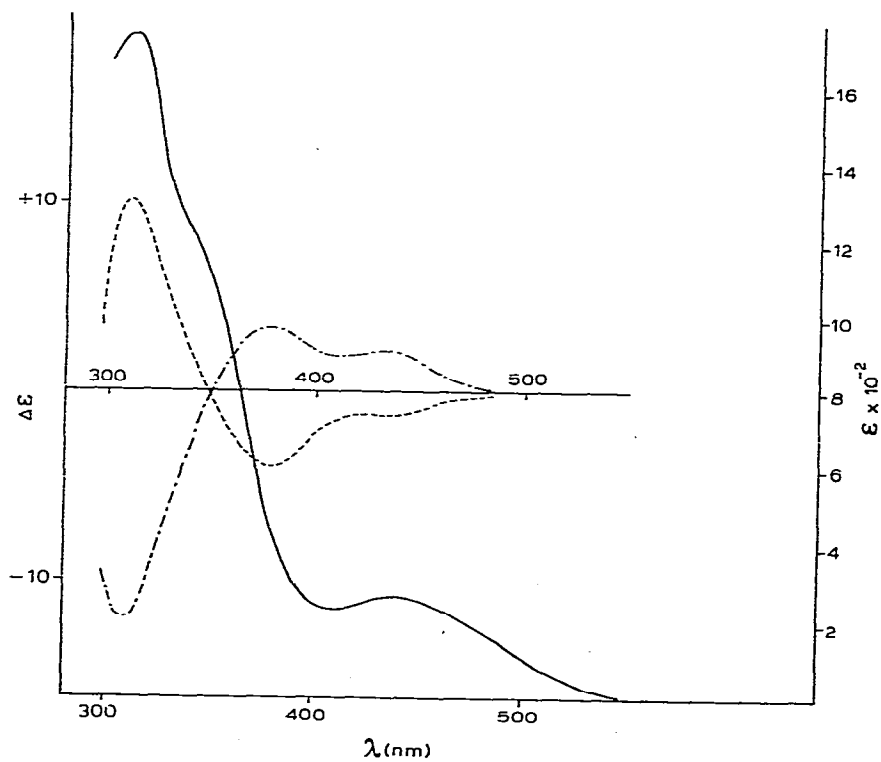


Fig. 3. UV spectrum (—) and CD spectra of (*S*)-(+)-578-IIa (· · · ·) and (*R*)-(-)-578-IIb (---) in chloroform.

the ligands is $\eta^5\text{-MCp} > \text{Cl} > \text{P}(\text{C}_6\text{H}_5)_3 > \text{CO}$, and the configuration at the ruthenium atom is thus *S*. The opposite and almost enantiomeric pattern of the CD spectra of complex IIb indicates that the configuration at the ruthenium atom is *R*.

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