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ADDITION OF METHOXIDE TO (DIALLYL ETHER) PLATINUM(II) CHLORIDE. ABSOLUTE CONFIGURATION OF A DIASTEREOISOMERIC PRODUCT, AND STEREOCHEMICAL IMPLICATIONS

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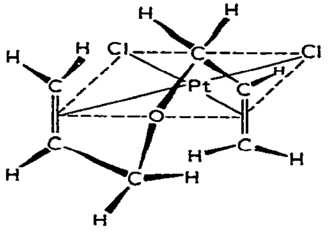
SUMMARY

An attempt has been made to resolve (diallyl ether) platinum(II) chloride. The complex was transformed by methoxide addition to a binuclear product containing carbon–platinum σ bonds. After bridge splitting of the binuclear alkyl derivative with (S)-α-methylbenzylamine, fractional crystallization gave two diastereoisomer complexes. Treatment of these with HCl gave optically inactive (diallyl ether) platinum(II) chloride. The molecular structure of one diastereoisomeric product was established by X-ray analysis.

INTRODUCTION

Investigations[1] have been previously carried out on π-complexes of Pt^{II} and Pd^{II} with dienes (*e.g.*, dicyclopentadiene, cyclooctadiene, vinylcyclohexene, norbornadiene, and 1,5-hexadiene). Those studies were mainly aimed towards elucidation of of the stereochemical features of the addition reactions of alkoxide ions, aliphatic amines, or carbanions to one of the two coordinated double bonds in the π-complex.

A report by Jones[2] prompted us to investigate the addition reaction of a methoxide group to the complex (diallyl ether) platinum(II) chloride. This substrate appears to be particularly interesting, mainly because, according to Jones, the two prochiral faces of the coordinated diene should have the same absolute configuration (structure A), so that only (R,R)- and (S,S)-(diallyl ether) platinum(II) chloride should be present in the synthesized material.



Structure A

Jones' study showed that the exchange of the diene ligand is much slower than the exchange of ethylene in Zeise's anion. It follows that the diene exchange must also be much slower than the exchange of a prochiral α-olefin in Pt^{II}-π-complexes, which are sufficiently stable to be isolated as pure configurational isomers[3].

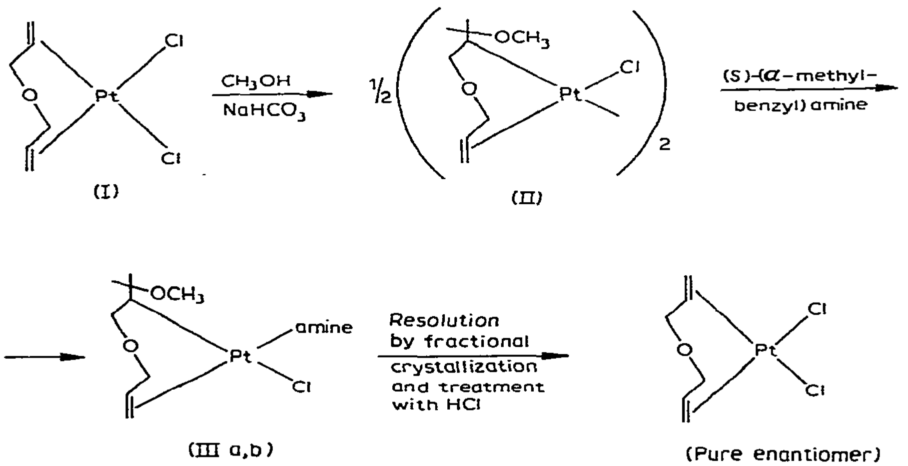
These observations suggest that (diallyl ether) platinum(II) chloride should be resolvable into optical antipodes. The addition of a nucleophile to the diene complex could be a preliminary step towards the resolution, following a previously used procedure[4]. A study of the stereochemistry of the nucleophilic addition to the diallylether complex should also provide more information on the reactivity of open-chain diene π-complexes toward nucleophilic agents: only one such complex has previously been studied from this point of view[5].

RESULTS

A. Attempt to resolve the diene complex

The attempt to obtain (diallyl ether) platinum(II) chloride as a pure enantiomer followed the route summarized in Scheme 1:

SCHEME 1



The first step of the reaction is similar to established procedure[6]. The bridge splitting was easily brought about by adding a stoichiometric amount of the amine to a cold chloroform solution of the binuclear complex. The crude product was fractionated by crystallization from acetone and methanol. The less soluble product (IIIa) was recrystallized to constant rotation ($[\alpha]_D^{20}$ −73.6, *c* 1.0, methylene chloride), the yield of crude product being 34%. Another product (IIIb) was obtained in 36% yield, with a rotation $[\alpha]_D^{20}$ of +55.3 (*c* 1.0, methylene chloride). The two products have similar PMR spectra, and the analyses for both agree with the formulation (III). The products must thus be regarded as a diastereoisomeric pair.

It must be noted that the methoxide attack to the diene complex can, in principle, involve either of the two carbon atoms of a coordinated double bond, or both.

Furthermore, the mechanism of this attack can involve *trans* or *cis* addition: actually, in all the known cases, the nucleophile addition to a coordinate diene is stereospecific, and with one exception[7] *trans* addition is involved[1].

In our case, if the nucleophile attacks only the external carbon atom, the product (III) must be composed simply of one diastereoisomeric pair, regardless of the addition mechanism. If, on the contrary, the internal carbon atom is attacked, *cis* addition could generate a diastereoisomeric pair (III) different from that formed by *trans* addition; however, from the results[1] on the stereospecificity of the addition reactions, we can exclude the possibility that both *trans* and *cis* addition occur together and assume the formation of only one diastereoisomeric pair.

Of course, two diastereoisomeric pairs, which are structural isomers, could be formed if both the two unsaturated carbon atoms were attacked, *i.e.* in a non-regiospecific addition. We were not able to isolate products other than those described by crystallization of crude (III): an oily residue, partially decomposed, was obtained as the last fraction.

The two crystalline fractions (IIIa) and (IIIb) were treated with a methanolic solution of HCl to give the starting diene π-complex, which should in the light of the analysis above be recovered as an enantiomer from each diastereoisomer. On dissolution of the diastereoisomer in the acid a white precipitate formed in a few minutes, and this material gave PMR and IR spectra identical to those spectra of the starting diene π-complex. The optical activity of this material was determined both in chloroform and in tetrachloroethane; in the latter, solutions with *c* 1.7 g/100 ml could be obtained, but they showed no optical activity at 589, 578, 546, and 465 nm.

B. Crystal structure of (IIIa)

In view of the above results, it seemed of interest to elucidate the crystal structure of (diallyl ether) platinum(II) chloride, by an X-ray study, but attempts to obtain single crystals of suitable size were unsuccessful. Such crystals of suitable size were however obtained for (IIIa), and an X-ray analysis carried out.

Crystals of (IIIa) belong to the orthorhombic system, space group $P2_12_12_1$, with $a = 15.31(3)$, $b = 10.43(1)$ and $c = 10.56(2)$ Å. 1490 Independent non-zero reflections were collected with an automated diffractometer using Cu-$K\alpha$ radiation. The structure was solved by application of the heavy atom method. The refinement of the atomic parameters was carried out by means of six cycles of 4 × 4 block diagonal least-squares procedures (the last three cycles were performed with anisotropic thermal parameters for the platinum and the chlorine). The imaginary part of the atomic scattering factor of the platinum[8] was introduced (correction made on the $F_{\text{calc.}}$ values) and refinement was continued until the maximum shift in the atomic coordinates and the anisotropic thermal shifts on the average was less than 1/3 of the corresponding standard deviations. The weighting scheme used corresponds to that suggested by Cruickshank[9]. At the end of the refinement the R value $[R = \Sigma||F_o| - |F_c||/\Sigma F_o]$ was 0.071 for the 1490 independent non-zero reflections.

In the refined model the asymmetric carbon atoms C(2), C(5), C(8) have the (*R*), (*R*), and (*S*) absolute configurations, respectively. The incorrect solution with the amine having the (*R*) configuration [from the preparation of the compound the chiral amine must have the (*S*) configuration] gave a value for the *R* factor of 0.076. Applying the Hamilton test[10] we may reject at a significance level less than 0.005

the hypothesis that the absolute configuration is the one having the (*S*), (*S*), and (*R*) configurations for the three asymmetric centers.

The final atomic coordinates and the thermal factors are reported in Table 1. In Fig. 1 is shown the molecular structure of (IIIa), with some significant bond distances and bond angles of the molecule. The carbon–carbon distances and bond angles in the benzene ring which are not reported have a mean value of 1.36±0.15 Å and 120°±6°, respectively*. Even if the large errors on the light atoms parameters are disappointing, the overall geometry appears to be reliable; as an example the benzene ring is planar and the mean square distance of the six benzene atoms and C(8) from the best plane passing through them is 0.03 Å.

TABLE 1

FINAL ATOMIC PARAMETERS

A. Atomic coordinates and isotropic thermal factors, with their standard deviations[a]

Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B(\sigma)$
Pt	0.5756(1)	0.8610(1)	0.3841(1)	
Cl	0.5160(5)	0.6517(7)	0.4346(7)	
O(1)	0.774(1)	0.983(2)	0.327(2)	0.0(5)
O(2)	0.619(1)	1.258(2)	0.424(2)	6.6(4)
N	0.456(1)	0.910(2)	0.294(2)	4.7(4)
C(1)	0.676(2)	0.833(4)	0.510(3)	7.5(8)
C(2)	0.705(2)	0.775(3)	0.405(3)	6.3(6)
C(3)	0.772(2)	0.848(4)	0.303(4)	8.1(8)
C(4)	0.703(2)	1.043(3)	0.265(3)	5.8(6)
C(5)	0.618(2)	1.042(2)	0.331(3)	4.9(5)
C(6)	0.628(2)	1.125(3)	0.463(2)	4.9(4)
C(7)	0.639(2)	1.351(3)	0.522(3)	6.7(7)
C(8)	0.380(2)	0.927(2)	0.385(3)	5.3(5)
C(9)	0.295(2)	0.941(3)	0.311(3)	5.4(5)
C(10)	0.399(2)	1.031(3)	0.481(3)	5.2(5)
C(11)	0.410(2)	0.997(4)	0.602(4)	8.5(9)
C(12)	0.428(3)	1.109(4)	0.689(4)	8.3(8)
C(13)	0.418(3)	1.227(4)	0.647(4)	8.8(9)
C(14)	0.407(3)	1.256(4)	0.540(4)	8.2(9)
C(15)	0.392(2)	1.152(3)	0.447(3)	6.1(6)

B. Anisotropic thermal factors, with their standard deviations[a]

Temperature factor given in the form:

$$\exp -\tfrac{1}{4}(h^2\cdot a^{*2}\cdot B_{11}+k^2\cdot b^{*2}\cdot B_{22}+l^2\cdot c^{*2}\cdot B_{33}+2\,h\cdot k\,a^*\cdot b^*\cdot B_{12}+2\,h\cdot l\cdot a^*\cdot c^*\cdot B_{13}+2\,k\cdot l\cdot b^*\cdot c^*\cdot B_{23})$$

Atom	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{12}(\sigma)$	$B_{13}(\sigma)$	$B_{23}(\sigma)$
Pt	4.37(3)	4.67(3)	3.23(3)	0.20(4)	−0.22(3)	−0.02(4)
Cl	7.29(35)	4.63(28)	5.36(31)	0.00(28)	−0.59(28)	0.32(26)

[a] Standard deviations are in units of the last significant figure.

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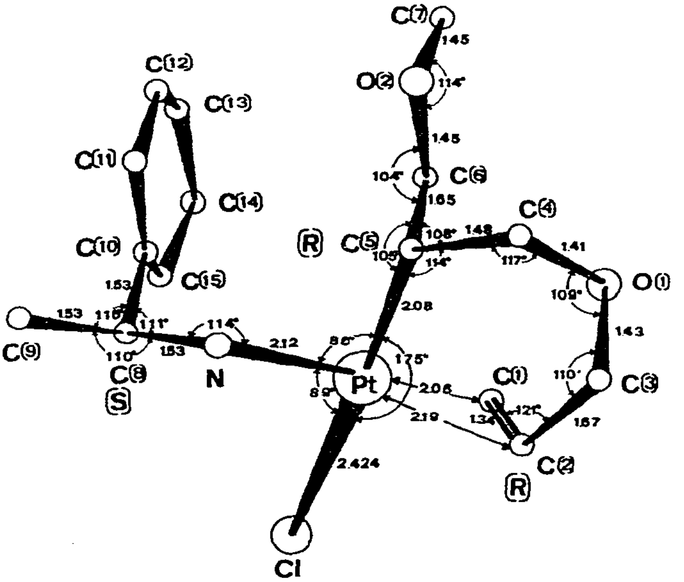
* In the present study the deviation associated with any average value indicates the range of the individual values.

The complex shows the usual, almost undistorted square-planar coordination of the ligands around the platinum atom, with the chlorine atom in the *cis*-position with respect to the nitrogen; the centre of the coordinated double bond and the σ-bonded carbon atom C(5) occupy the other two sites of coordination. Furthermore, the chlorine atom is in a *trans*-position with respect to the σ-bonded C(5) carbon atom. The large trans-effect of the σ-bond is reflected in the large Pt–Cl bond distance (2.424±0.007 Å), as shown by comparison with Pt–Cl bond distances recently reported[11].

The conformation of the ring (Fig. 2) is described by a sequence of internal rotation angles as listed in Table 2 and represented in Fig. 2. The residue C(2)–C(3)–O–C(4)–C(5) shows a pseudo mirror plane passing through the oxygen atom, as indicated by the opposite values of the internal rotation angles around the C(3)–O and the C(4)–O bonds.



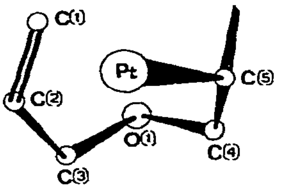


Fig. 1. Molecular model of the complex (IIIa); some of the bond distances and bond angles are shown. The absolute configurations of the asymmetric centers are indicated.

Fig. 2. Projection of a portion of the molecule of complex (IIIa) as seen along the axis passing through the Pt atom and perpendicular to the axis C(5)-center of the double bond.

TABLE 2

SOME INTERNAL ROTATION ANGLES (*trans*-CONFORMATION = 180°) OF THE COMPLEX (IIIa)

C(1)–C(2)–C(3)–O(1)	−15°
C(2)–C(3)–O(1)–C(4)	−84°
C(3)–O(1)–C(4)–C(5)	84°
O(1)–C(4)–C(5)–Pt	−54°

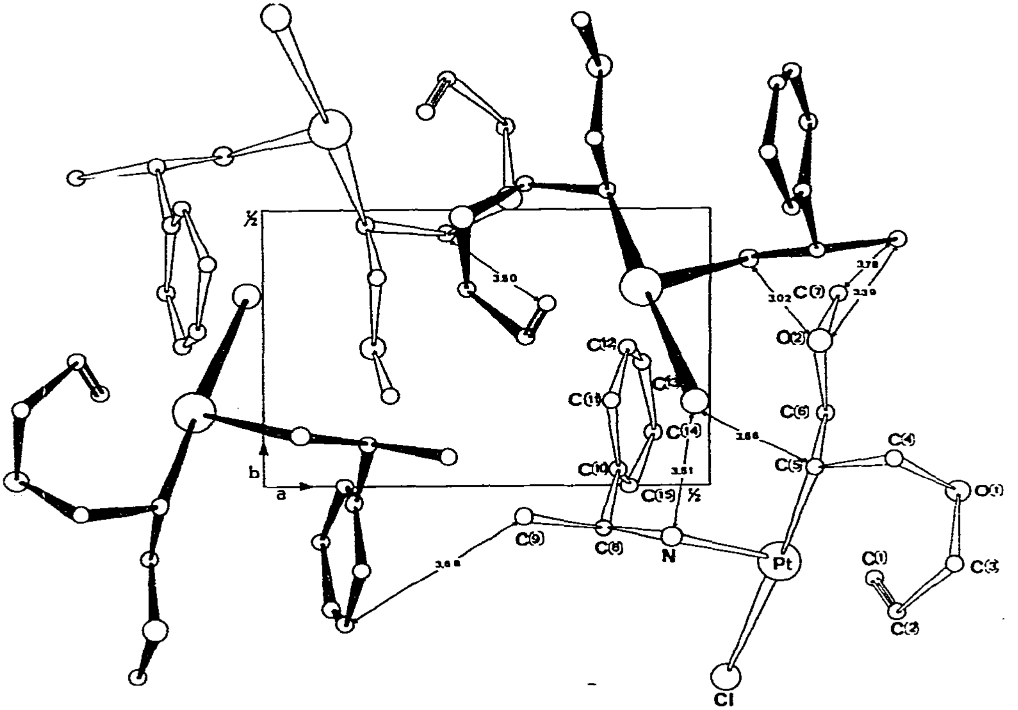


Fig. 3. Mode of packing along the *c* axis for complex (IIIa). Some of the shortest intermolecular distances are reported.

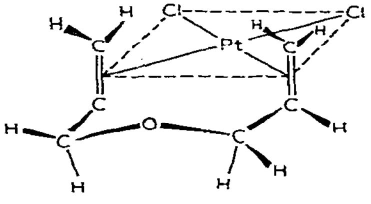
In Fig. 3 the mode of packing along the *c* axis is reported with the shortest intermolecular distances. The contact O(2)–N of 3.02 Å seems to indicate the presence of a hydrogen bond between molecules related by a screw axis.

DISCUSSION

Two features of the structure of (IIIa) are noteworthy. First, the addition of the methoxide group has occurred at the external carbon atom of the double bond. Second, the resulting absolute configuration of the carbon atom C(5), which is σ-bonded to the metal, and that of the prochiral π-coordinated double bond are both *R*.

On the basis of the structure A assigned[2] by Jones to (diallyl ether) platinum(II) chloride, the crystal structure of (IIIa) can be accounted for only by assuming that an inversion of configuration occurs during the addition or subsequently. In fact, from an (*R,R*)- unit the addition would give an (*S*)-σ-, (*R*)-π- (III) species, as the addition involves the external carbon atom, while an (*R*)-σ-, (*S*)-π- (III) species would be formed from an (*S,S*)- unit. To get the (*R*)-σ-, (*R*)-π-configuration, which had been found in (IIIa), one or other chiral center would have to change its absolute configuration: the inversion of the double bond configuration after the attack, to give an (*S,S*)-unit, would seem the more likely process. Furthermore, to explain the lack of optical activity in the diene complex obtained from (IIIa), two alternative suggestions can be made. It could be assumed that the diene complex (IIIa) no longer has the molecular structure of the starting π-complex, but this hypothesis must be rejected in the light of the PMR spectra. Alternatively, a racemization process leading to an (*R,R*) and (*S,S*) equimolecular mixture might occur during the elimination of the methoxide group or subsequently.

A simpler explanation can be given for our result if the molecular structure of (diallyl ether) platinum(II) is different from that proposed by Jones. In fact, if the diene π-complex has a molecular structure with a mirror plane (structure B) the crystal structure of (IIIa) would be a direct consequence of the methoxide attack to a diene π-complex unit of (*R,S*) or (*S,R*) configuration. On the other hand no optical activity would be expected from the (*R,S*)- diene π-complex restored through methoxide elimination.



Structure B

This latter hypothesis appears more convincing, since Jones' arguments in favour of structure A, based on the values of spin–spin coupling constants, are open to criticism. First, one would expect the whole aliphatic moiety to be very flexible, especially since it contains an oxygen atom. Thus it is not justifiable to consider only one conformation in calculating the probable values of the coupling constants; instead it is necessary to average the dihedral angles among those of all conformations of comparable internal energy. Secondly, it must be stressed that the Karplus equation $J_{vic}=A+B\cdot\cos\varphi+C\cdot\cos 2\varphi$ is applicable only when all the carbon atoms are tetrahedral and even in such a case the values of the constants A, B, C cannot be taken as 4.0, −0.5 and 4.5 Hz (*i.e.* those originally proposed by Karplus) but rather 7, −1, and 5 Hz, respectively, as shown by many measurements of coupling constants in compounds of known geometry[12].

EXPERIMENTAL

Some of the elemental analyses were performed by A. Bernhardt, Mikroanalitische Laboratorium of the Max Planck Institute, Mülheim, and others in this laboratory. Molecular weights were determined in chloroform using a Hitachi–Perkin–Elmer, Model 115 apparatus.

All melting points are uncorrected. Infrared spectra were recorded in Nujol on a Beckman Model IR-9 spectrometer and PMR spectra on a Varian HA-100-15 operating at 29°, using TMS as an internal reference. All the optical activity measurements were taken with an automatic Perkin–Elmer 141 polarimeter.

Materials

All solvents and reagents were of reagent grade purity. (*S*)-(α-methylbenzyl)-amine had $[\alpha]_D^{20}$ −39.5 (neat).

(Diallyl ether) platinum(II) chloride was prepared by a previously described procedure[13]. The sparingly soluble complex was crystallized from chloroform, the use of large amounts of the solvent being avoided by extracting the crude material in a Soxhlet-type extractor under about 500 mm. (Found: Pt, 53.3; C, 19.6; H, 2.91. $C_6H_{10}Cl_2OPt$ calcd.: Pt, 53.6; C, 19.8; H, 2.97%.)

Preparation of complex (II)

To a stirred suspension of 5 g (0.0137 mol) of (diallyl ether) platinum(II) chloride, in 150 ml of boiling methanol, 1 g of $NaHCO_3$ was added in small portions. The total time for the addition was about 10 min. The mixture was cooled to room temperature, and a solid residue was filtered off. Removal of the solvent *in vacuo* from the pale yellow solution gave a viscous oil. This material was mixed with chloroform (40 ml) and a small amount of undissolved (diallyl ether) platinum(II) chloride was removed by filtration. The crude product obtained by removing the chloroform *in vacuo* was used without further purification in the preparation of complex (III). Complex (II) can be recrystallized in a 72% yield from a chloroform/pentane mixture. (Found: Pt, 53.7; C, 23.8; H, 3.67. $C_{14}H_{26}Cl_2O_4Pt_2$ calcd.: Pt, 54.2; C, 23.4; H, 3.64%.)

Preparation of complex (III)

To an ice-cold stirred solution of 6.0 g (0.0834 mol) of complex (II) in 50 ml of chloroform, a solution of 2.02 g (0.167 mol) of (*S*)-(α-methylbenzyl)amine in 20 ml of the same solvent was added dropwise. Removal of the solvent *in vacuo* gave an oily residue, which was throughly washed with petroleum ether.

Fractional crystallization of complex (III)

The crude product (III) (5 g, 0.0104 mol) was dissolved in 40 ml of acetone. After a few minutes at room temperature a white precipitate (1.45 g) was formed, and this was isolated by filtration after 6 h. This first crop had $[\alpha]_D^{20}$ −68.0 (*c* 1.0, methylene chloride). To the solution 10 ml of pentane were added, and after 24 h at 0°, another crop was obtained (0.5 g, $[\alpha]_D^{20}$ −63.2). The solvent was removed *in vacuo* from the mother liquor, and to the oily residue 20 ml of methanol were added. After 6 h a third fraction ($[\alpha]_D^{20}$ +39.6, 1.27 g) was collected. Another fraction ($[\alpha]_D^{20}$ +40.6, 0.83 g) was obtained when the mother liquor was diluted with pentane and set aside for 24 h at 0°. Only oils were obtained when attempts were made to obtain other fractions from this or other solvents.

The two fractions, having $[\alpha]_D^{20}$ −68.0 and −63.2, respectively, were recrystallized from acetone, until the optical specific activity of the complex, (IIIa), was not changed by successive crystallizations. (IIIa), 1.69 g, 34% yield, had m.p. 130–132° (dec.) $[\alpha]_D^{20}$ −73.6 (*c* 1.0, methylene chloride). (Found: Pt, 40.5; C, 37.3; H, 5.13; N, 3.03. Mol.wt. (chloroform), 470. $C_{15}H_{24}ClNO_2Pt$ calcd.: Pt, 40.5; C, 37.4; H, 5.03; N, 2.91%. Mol.wt., 480.9.)

The two fractions having positive optical activity were recrystallized only once from acetone/pentane. The specific optical activity of the product [(IIIb), 1.81 g, 36% yield, m.p. 120–122 (dec.)] was $[\alpha]_D^{20}$ +55.3 (*c* 1.0, methylene chloride). No further recrystallization was attempted with this more soluble material. (Found: Pt, 41.2; C, 37.0; H, 4.9; N, 2.7; Mol.wt. (chloroform), 465. $C_{15}H_{24}ClNO_2Pt$ calcd.: Pt, 40.5; C, 37.4; H, 5.03; N, 2.91%. Mol.wt., 480.9.)

The PMR spectrum of (IIIa) showed a doublet at δ 1.73 (3H; C–CH$_3$), a singlet at 3.28 (3H; O–CH$_3$) a complex multiplet between 5.0 and 2.7 (10H unresolved), and a singlet at 7.40 ppm (5H; C_6H_5). The PMR spectrum of the diastereoisomer (IIIb) shows a close resemblance to that previously reported for (IIIa). A difference, however, exists in the pattern of the multiplet ranging from δ 5.0 to 2.7 ppm, as one would expect from the protons directly involved in the asymmetric centers.

Preparation of the diene complex from (IIIa)

The complex (IIIa) (0.480 g, 0.001 mol) was dissolved in the minimum amount of a mixture of methanol and methylene chloride (2/1). Dry hydrogen chloride was bubbled through the solution. After a few minutes a white precipitate began to form. The bubbling was continued for about 10 min, the precipitate was collected by filtration, washed with methanol and dried *in vacuo*. This material showed IR, PMR spectra, and chemical analyses similar to the ones of the starting π-complex (I). No optical activity was detectable in chloroform or 1,1,2,2-tetrachloroethane solutions of the π-complex obtained from (IIIa), at 25°. These measurements were carried out in polarimetric tubes of 1 dm length and the concentration of the solutions was respectively 0.6 g/100 ml (chloroform) and 1.7 g/100 ml (1,1,2,2-tetrachloroethane).

X-ray data collection

From preliminary Weissenberg photographs, crystals of (IIIa), obtained by slow evaporation of a xylene solution (m.p. 130–132° dec.), were found to belong to the orthorhombic $P2_12_12_1$ space group (systematic $h00$, $0k0$, and $00l$ absences with h, k, and l odd, respectively). A crystal of approximately cylindrical shape ($r = 0.010$ cm, $l = 0.020$ cm) was centered on a Siemens automated diffractometer equipped with a PDP-8/I digital computer.

The determination of the lattice constants was carried out by a least-squares treatment of the 2θ, χ and φ setting angles of twelve reflections with $2\theta > 80°$ (Cu-$K\alpha$, $\bar{\lambda} = 1.54178$ Å), using a program prepared by Busing and Levy[14]. The resulting parameters are: $a = 15.31 \pm 0.03$, $b = 10.43 \pm 0.01$, $c = 10.56 \pm 0.02$ Å.

The experimental density ($d_{\text{exp}} = 1.88$ g/cm^3 by flotation) agreed with the calculated density assuming four units $PtCl(C_7H_{13}O_2)(C_8H_{11}N)$ per unit cell ($d_{\text{calc}} = 1.89$ g/cm^3).

A total of 1732 integrated intensities were collected by a θ–2θ scan mode with Ni-filtered Cu-$K\alpha$ radiation ($\bar{\lambda} = 1.54178$ Å) in the range of 0–130° of 2θ, using the five value measurements technique; the intensities of the reflections have been corrected for the absorption in the cylindrical approximation ($\mu R = 1.17$).

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