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ENANTIOMERIC DISCRIMINATION

II *. INCORPORATION OF CHIRAL AMINES IN CHIRAL PLATINUM COMPLEXES. CRYSTAL AND MOLECULAR STRUCTURE OF (CHLORO)(METHYL)((+)-2*S*,3*S*-*O*-ISOPROPYLIDENE-2,3-DIHYDROXY-1,4-BIS(DIPHENYLPHOSPHINO)BUTANE)PLATINUM(II)

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Summary

Diastereomeric platinum complexes of formula [Pt(chelate)CH_3L] ClO_4 have been prepared, where (chelate) is a diphosphine ligand, either 2*S*,3*S*-bis(diphenylphosphino)butane, or (+)-2*S*,3*S*-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane or a chiral aminophosphine, either *S*-*N*,*N*-bis(diphenylphosphino)-1-phenylethylamine or *S*-*N*,*N*-bis(diphenylphosphino)alanine ethyl ester, and L is one of n-butylmethylamine, benzylmethylamine, methylphenylamine, and *R*- and *S*-1-phenylethylamine. Where diastereomers are formed in solution, the relative amounts have been measured by ^{31}P NMR. A single crystal X-ray structure determination of (chloro)(methyl)((+)-2*S*,3*S*-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane)platinum(II) has shown that the compound crystallises in space group $P2_12_12_1$, with cell dimensions *a* 16.282(4), *b* 16.995(4) and *c* 10.973(2) Å. Full-matrix least-squares refinement on *F*, using 2504 observations and 170 variables, converged at *R* = 0.0605. The coordination at the Pt atom is square planar, with Pt—P distances of 2.322(4) and 2.233(4) Å. Pt—Cl and Pt—C were 2.323(5) and 2.17(1) Å respectively. The seven-membered chelate ring adopts a twisted chair conformation. Enantiomeric discrimination in these Pt-amine systems is discussed with reference to the solid state structure of the complex.

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Introduction

In the previous paper of this series [1] we described the stereoselective binding of phosphine ligands in transition metal complexes. A partial resolution of chiral monophosphines was achieved in this way by the use of platinum complexes containing chiral chelate ligands. We describe herein an extension of these studies to diastereomeric platinum complexes containing chiral bidentate ligands and chiral amines. Since the amines, which are chiral at the N atom, are configurationally labile at room temperature, we expected the ratio of diastereomers formed in solution to be strongly dependent upon the nature of the interaction between the amine and the chiral ligand on the Pt atom. To examine the steric constraints imposed upon the amine binding site, we have carried out a single crystal X-ray structure determination of the complex from which the adducts are prepared. The results of these investigations and an evaluation of the factors effecting enantiomeric discrimination in these systems are discussed below.

Experimental

^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer operating at 40.5 Mc s^{-1}, and employing broad band proton decoupler and Fourier transform techniques.

n-Butylmethylamine (NBuMeH) was purchased from Eastman Organic, Inc. Racemic, *R*- and *S*-1-phenylethylamine (pea) were purchased from Norse Laboratories, Inc. Benzylmethylamine, (NBzMeH) and methylphenylamine (NMePhH) were prepared by standard syntheses [2]. $(-)_{589}$-*S*-*N*,*N*-bis(diphenylphosphino)-1-phenylethylamine, *S*-peap, was prepared from *S*-pea, and $(-)_{589}$-*S*-*N*,*N*-bis(diphenylphosphino)alanine ethyl ester, *S*-alap, was synthesised from *S*-alanine [3]. 2*S*,3*S*-Bis(diphenylphosphino)butane (*S*,*S*-chiraphos) was prepared by a minor modification [1] of the published route [4], and (+)-2*S*,3*S*-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((+)-diop) was purchased from the Strem Chemical Co.

Preparations of platinum complexes

The cyclooctadiene complex Pt(COD)CH_3Cl, prepared by the method of Clark et al. [5] was used as the starting material. Since the same route was used, only one example of each type of synthesis is given.

Pt(*S*-alap)CH_3Cl. 1.5 g (4.2 mmol) of Pt(COD)CH_3Cl was dissolved in 25 ml of CH_2Cl_2, 2.06 g (4.2 mmol) of *S*-alap added, and the solution stirred for 1 h. The volume was reduced to 5 ml, diethyl ether added and the solution cooled. 2.75 g (77%) of Pt(*S*-alap)CH_3Cl was filtered off. Anal. Found: C, 49.06; H, 4.21. $C_{30}H_{32}ClNO_2P_2Pt$ calcd.: C, 48.44; H, 4.49%. Satisfactory analyses and spectral characterizations for the other neutral complexes have been previously reported [3].

Enantiomeric discrimination experiments

Since the same method was used to prepare samples for ^{31}P NMR studies, only one example is described.

[Pt(*S*,*S*-chiraphos)CH_3(NBuMeH)]ClO_4. 109 mg (0.16 mmol) of Pt(*S*,*S*-

chiraphos) CH_3Cl was dissolved in 5 ml of acetone and 10 ml of methylene chloride. 34 mg (0.16 mmol) of $AgClO_4$ was added, the solution stirred for 15 min and centrifuged to remove AgCl. After decantation 14 mg (0.16 mmol) of NBuMeH was added and the solution stirred for 10 min. The solvent was removed, the residue extracted with 2 ml of methylene chloride, and filtered into a tube for ^{31}P NMR studies.

Collection and reduction of X-ray data

Colourless, crystalline blocks of Pt((+)-diop)CH_3Cl were isolated from a CH_2Cl_2 and acetone mixture by addition of diethyl ether during attempts to crystallize the amine adduct, [Pt((+)-diop)CH_3(*S*-pea)]ClO_4. An extensive photographic examination employing Weissenberg and precession techniques showed the crystals were orthorhombic. Systematic absences h odd for $h00$, k odd for $0k0$ and l odd for $00l$ uniquely determined the space group as $P2_12_12_1$, D_2^4, No. 19 [6]. The density, determined by flotation in a mixture of cyclohexane and carbon tetrachloride, suggested four molecules per cell, and no imposed symmetry constraints.

A crystal of approximate dimensions 0.21 × 0.28 × 0.23 mm was chosen and mounted with [$\bar{1}10$] offset approximately 10° from coincidence with the diffractometer ϕ axis. Eight faces were identified as belonging to the forms {110} and {011}. The crystal dimensions were accurately measured on a microscope equipped with a filar micrometer eyepiece. Adequate mosaicity was demonstrated by a number of ω-scans of intense, low-angle reflections [7]; the average width at half-height was 0.13°. Cell constants and an orientation matrix were refined using 24 carefully centered reflections with $25 < 2\theta < 30°$ [8].

Intensity data were recorded on a Picker FACS-1 diffractometer controlled by the Vanderbilt operating system [9]. Crystal and electronic stability was monitored by recording six standard reflections every 250 observations. Over the period of nine days required to record 3029 reflections, a 5 to 10% diminution in intensity occurred. A reexamination of the crystal mosaicity was carried out, but the width at half-height of the ω-scans was unchanged. No correction was made for the change in standard intensities. The data were then corrected for Lorentz, monochromator and polarization effects, and standard deviations assigned as described earlier [10]. A value of 0.03 was chosen for p [11]. All data with $I > 0$ were corrected for absorption effects using the analytical method [12]. For the solution and refinement of the structure, the 2504 unique observations with $I > \sigma(I)$ were used. Details of crystal data and the experimental conditions are given in Table 1.

Structure solution and refinement

A solution was obtained by the heavy atom method and refined by full-matrix least-squares techniques on F. Scattering factors for neutral, non-hydrogen atoms were taken from the International Tables for X-ray Crystallography [6], while those for hydrogen were from Stewart, Davidson and Simpson [13]. Anomalous dispersion corrections were included for the Pt, Cl and P atoms [14]. Two cycles of refinement, varying the positional and isotropic thermal parameters for the 14 non-hydrogen atoms, and treating the four phenyl rings as rigid groups [15], reduced the agreement factors $R_1 = \Sigma||F_o| - |F_c||/$

TABLE 1

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS

Compound	$C_{33}H_{35}ClO_2P_2Pt$	mol. wt. 744.13
Unit cell at 22° C	a 16.282(4) Å c 10.973(2) Å	b 16.995(4) Å V 3036.4 Å^3
Density observed	1.62(1) g cm^{-3}	
calculated	1.622 g cm^{-3} for $Z = 4$	
Space group	$P2_12_12_1$	
Radiation	Mo-K_α, λ 0.71073 Å, graphite monochromator	
Abs. coefficient	μ 46.2 cm^{-1}	
Scan	θ—2θ at 1° min^{-1}	
Range	1.15°, corrected for dispersion	
Backgrounds	10 s stationary crystal, stationary counter at scan limits. 20 s for $2\theta > 35°$.	
Data collected	h, k, l for $0° < 2\theta < 50°$	
Standard reflections	$0\bar{2}0$, 400, 120, 020, 111, 101	

$\Sigma|F_o|$ to 0.0823, and $R_2 = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$ to 0.0904. The function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized, where F_o and F_c are the observed and calculated structure factors, and the weight w is defined as $w = 4F_o^2/\sigma^2(F_o^2)$. Further refinement with anisotropic thermal parameters varied for the non-group atoms, and individual isotropic factors assigned to the group atoms, lowered R_1 to 0.0699 and R_2 to 0.0673. At this stage the 35 hydrogen atoms were located from a difference Fourier synthesis, and their contributions to F_c included, assuming idealized positions, with sp^3 and sp^2 hybridizations, and C—H 0.95A. Two cycles of refinement, with recalculation of hydrogen positions, gave agreement factors $R_1 = 0.0668$ and $R_2 = 0.0630$.

To confirm the absolute configuration of the (+)-diop ligand, the model was inverted, the hydrogen atom positions recalculated, and after several cycles of refinement agreement factors $R_1 = 0.0605$ and $R_2 = 0.0424$ were obtained. The inverted model is significantly better than the original, and, moreover, with the S absolute configuration at the two chiral C atoms, has the known absolute configuration of (+)-diop [16]. All further calculations were carried out in this hand.

An inspection of the model at this stage indicated some cause for concern. In particular, the CH_3 carbon atom, C(8), had an unusually low equivalent isotropic thermal parameter of 1.0 Å^2, while that of the Cl atom was unusually high, namely 8.8 Å^2. These values led us to investigate the possibility of disorder of the Cl atom and the methyl group. The two ligands were removed from the model, and structure factors calculated. A difference Fourier synthesis over this region indicated some degree of disorder, as might be expected from the similar Van der Waals radii of the species. Several different models were tried in attempts to account for the disorder. Since we did not expect to be able to refine atoms of fractional multiplicity at each site, we introduced two CH_3Cl fragments as rigid groups, one at the CH_3 site and one at the Cl atom site. A C—Cl distance of 0.22, and a C—H distance of 1.00 Å were assumed. The chosen

TABLE 2

ATOMIC POSITIONAL AND THERMAL PARAMETERS [a,b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	−1046.6(4)	−2060.5(4)	−1924(1)	42.9(3)	42.1(3)	34.7(3)	−0.7(4)	1.6(4)	−3.6(4)
Cl(1)	−1738(4)	−3252(3)	−1766(5)	131(5)	82(4)	120(5)	−36(4)	54(5)	−36(4)
P(1)	−1665(3)	−1708(2)	−97(3)	42(3)	40(2)	36(2)	−4(2)	4(2)	0(2)
P(2)	−376(3)	−940(2)	−2298(3)	48(3)	42(3)	38(3)	2(2)	10(2)	1(2)
O(1)	−1563(6)	1072(6)	−1306(8)	70(8)	37(6)	47(6)	14(6)	15(6)	7(5)
O(2)	−2063(7)	593(6)	503(9)	67(8)	40(6)	52(7)	2(6)	25(6)	8(6)
C(1)	−1006(11)	−66(9)	−2295(11)	62(10)	61(10)	27(8)	−8(11)	0(9)	2(7)
C(2)	−1168(11)	317(8)	−1093(12)	59(12)	43(9)	29(8)	9(10)	4(9)	−3(7)
C(3)	−1803(9)	−64(8)	−239(12)	39(10)	44(10)	31(8)	3(8)	1(8)	−15(8)
C(4)	−1499(9)	−721(8)	575(13)	53(10)	43(10)	40(9)	14(8)	−3(8)	12(8)
C(5)	−1975(11)	1300(10)	−201(15)	63(13)	55(12)	45(11)	15(11)	16(10)	−1(10)
C(6)	−1397(15)	1841(11)	482(16)	178(25)	77(15)	52(11)	−40(15)	16(14)	−6(11)
C(7)	−2765(14)	1632(13)	−536(19)	152(22)	145(20)	79(15)	124(18)	45(16)	43(15)
C(8) [c]	−527(7)	−2630(6)	−3516(9)	13(3)					

[a] Atomic positional parameters are given $\times 10^4$. Thermal parameters are given $\times 10^3$. [b] The form of the thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. $U_{ij} = B_{ij}/2\pi^2 a_i^\star a_j^\star$ (Å^2). Estimated standard deviations are given in parentheses. [c] The thermal parameter of this atom is isotropic and corresponds to $B = 1.0(2)$ Å^2.

TABLE 3

RIGID GROUP PARAMETERS [a]

Group	x_g	y_g	z_g	δ	ϵ	η
Ph(1)	−0.3628(4)	−0.1639(3)	−0.0174(6)	−1.670(7)	−3.106(6)	1.405(6)
Ph(2)	−0.1174(4)	−0.2830(4)	0.2162(6)	0.369(9)	2.259(6)	0.515(10)
Ph(3)	0.1105(4)	−0.0539(4)	−0.0491(6)	1.831(9)	2.489(7)	2.481(8)
Ph(4)	0.0545(6)	−0.0798(4)	−0.4892(8)	1.71(2)	−2.068(9)	2.12(2)

[a] x_g, y_g and z_g are the fractional coordinates of the group origin; δ, ϵ and η (radians) are the group orientation angles, see ref. 15.

orientation of the methyl hydrogens was arbitrary. The two groups were initially positioned so that the Pt—Cl distances were 2.31 Å, and the multiplicities of the groups (n in one site, $1 - n$ in the other) were refined with the appropriate constraints upon the derivatives. An 80/20 disorder ratio was obtained after two cycles of refinement, including recalculated hydrogen atom contributions, with agreement factors $R_1 = 0.0632$ and $R_2 = 0.0445$. This ratio was then fixed, and overall group thermal parameters were varied. No change was seen in the residuals. Six cycles of least-squares refinement followed, with anisotropic thermal parameters assigned to all individual atoms, individual isotropic thermal parameters refined for the carbon atoms of the four phenyl rings, and overall group thermal parameters varied for the two CH_3Cl groups. Convergence was slow, so hydrogen atom positions were recalculated and two further cycles computed, after which R_1 was 0.0623 and R_2 was 0.0431. The maximum shift was still 1.34 σ, so a difference Fourier synthesis was calculated, and showed a peak of 1.4(2) eA^{-3} at the site of the Cl atom with 0.80 multiplicity. We then compared the two models. No significant differences were found in the (+)-diop ligands, while the residual electron density, the agreement factors and the errors on the molecular dimensions were all greater for the disordered model. We therefore concluded that the molecular structure of the complex is well represented by the first model, which behaved much better during the refinement. One final cycle gave convergence at agreement factors $R_1 = 0.0605$ and $R_2 = 0.0424$. No parameter shift in this cycle exceeded 0.009 of a standard deviation. A total difference Fourier synthesis contained no features of chemical significance, the highest peak being of electron density 1.2(2) eA^{-3} associated with the Pt—CH_3 region. The disordered carbon atom, C(8), was assigned an isotropic thermal parameter for the last cycles. The final atomic positional and thermal parameters for the non-group atoms are given in Table 2, the group parameters in Table 3, and derived group atom positional and thermal parameters are listed in Table 4. Hydrogen atom parameters are given in Table 5, while structure amplitudes have been deposited.

Description of the structure

The crystals are built up from discrete neutral molecules, the shortest Pt—Pt distance being approximately 9.24 Å. The shortest intermolecular distance is 2.21 Å between H(2)C(8) and H(1)C(7). Principal intramolecular bond distances

(continued on p. 211)

TABLE 4

DERIVED GROUP ATOM PARAMETERS [a]

Atom	*x*	*y*	*z*	*B* (Å^2)	Atom	*x*	*y*	*z*	*B* (Å^2)
Ph(1)					*Ph(3)*				
C(11)	−2778(4)	−1721(6)	−129(10)	3.3(3)	C(31)	449(5)	−707(6)	−1261(8)	3.6(3)
C(12)	−3241(6)	−1794(6)	931(7)	4.2(4)	C(32)	661(6)	−1232(5)	−340(10)	3.9(4)
C(13)	−4091(6)	−1713(6)	886(8)	4.5(4)	C(33)	1318(7)	−1065(7)	430(9)	6.5(5)
C(14)	−4478(5)	−1558(7)	−220(11)	5.4(4)	C(34)	1762(6)	−372(8)	280(10)	6.6(5)
C(15)	−4015(7)	−1484(6)	−1280(8)	6.4(4)	C(35)	1550(7)	154(6)	−641(11)	5.9(5)
C(16)	−3164(7)	−1566(6)	−1234(7)	4.9(4)	C(36)	893(7)	−14(6)	−1411(8)	4.8(4)
Ph(2)					*Ph(4)*				
C(21)	−1370(5)	−2344(5)	1183(7)	2.5(3)	C(41)	142(8)	−851(7)	−3777(9)	4.2(4)
C(22)	−773(5)	−2113(5)	2016(9)	4.0(3)	C(42)	947(8)	−1115(7)	−3887(12)	7.6(5)
C(23)	−577(5)	−2598(6)	2995(9)	4.7(3)	C(43)	1351(6)	−1062(8)	−5002(16)	9.5(7)
C(24)	−978(7)	−3315(6)	3142(8)	5.7(4)	C(44)	949(10)	−744(8)	−6008(10)	8.0(6)
C(25)	−1575(6)	−3547(5)	2308(10)	5.5(4)	C(45)	143(10)	−480(7)	−5898(10)	8.7(6)
C(26)	−1772(5)	−3061(6)	1329(8)	4.4(4)	C(46)	−261(6)	−534(7)	−4783(13)	6.6(5)

[a] Positional parameters are given $\times 10^4$.

TABLE 5. DERIVED HYDROGEN ATOM PARAMETERS [a]

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
H1C(1)	−1553	−211	−2653	3.85	H1C(15)	−4281	−1382	−2033	7.05
H2C(1)	−735	332	−2830	3.25	H1C(16)	−2850	−1517	−1959	5.41
H1C(2)	−637	396	−650	4.31	H1C(22)	−499	−1623	1915	4.41
H1C(3)	−2279	−258	−731	4.31	H1C(23)	−168	−2440	3562	5.13
H1C(4)	−899	−642	724	3.96	H1C(24)	−842	−3647	3808	6.25
H2C(4)	−1799	−688	1372	3.96	H1C(25)	−1848	−4037	2407	6.05
H1C(6)	−869	1557	647	8.73	H1C(26)	−2179	−3220	759	4.88
H2C(6)	−1285	2320	−19	8.73	H1C(32)	359	−1706	−240	4.28
H3C(6)	−1655	1999	1274	8.73	H1C(33)	1464	−1425	1054	7.07
H1C(7)	−2992	1928	179	11.07	H1C(34)	2211	−259	803	7.19
H2C(7)	−2688	2001	−1237	11.07	H1C(35)	1853	627	−742	6.43
H3C(7)	−3146	1200	−767	11.07	H1C(36)	747	347	−2037	5.28
H1C(8)	−595	−3213	−3437	1.13	H1C(42)	1218	−1333	−3197	8.47
H2C(8)	−820	−2442	−4262	1.13	H1C(43)	1901	−1244	−5070	10,59
H3C(8)	69	−2497	−3575	1.13	H1C(44)	1228	−709	−6765	8.88
H1C(12)	−2974	−1897	1686	4.55	H1C(45)	−127	−263	−6587	9.53
H1C(13)	−4405	−1761	1612	4.89	H1C(46)	−810	−351	−4713	7.12
H1C(14)	−5058	−1504	−247	5.91					

[a] H1C(1) is hydrogen bonded to C(1) etc. Positional parameters are given ×10^4.

TABLE 6. SELECTED BOND DISTANCES AND ANGLES

Bond	Distance (Å)	Bond	Distance (Å)
Pt—P(1)	2.322(4)	C(1)—C(2)	1.49(2)
Pt—P(2)	2.233(4)	C(2)—C(3)	1.54(2)
Pt—Cl	2.323(5)	C(3)—C(4)	1.51(2)
Pt—C(8)	2.17(1)	C(2)—O(1)	1.45(2)
P(1)—C(4)	1.85(1)	C(3)—O(2)	1.45(1)
P(1)—C(11)	1.81(1)	C(5)—O(1)	1.44(2)
P(1)—C(21)	1.84(1)	C(5)—O(2)	1.44(2)
P(2)—C(1)	1.81(2)	C(5)—C(6)	1.51(2)
P(2)—C(31)	1.81(1)	C(5)—C(7)	1.45(2)
P(2)—C(41)	1.84(1)		

Atoms	Angle (°)	Atoms	Angle (°)
P(1)—Pt—P(2)	98.7(1)	P(2)—C(1)—C(2)	117(1)
P(1)—Pt—Cl	87.2(2)	C(1)—C(2)—C(3)	118(1)
P(2)—Pt—C(8)	92.3(3)	C(1)—C(2)—O(1)	109(1)
Cl—Pt—C(8)	82.0(3)	C(3)—C(2)—O(1)	100(1)
C(4)—P(1)—Pt	120.9(5)	C(2)—C(3)—C(4)	117(1)
C(4)—P(1)—C(11)	99.6(4)	C(2)—C(3)—O(2)	102(1)
C(4)—P(1)—C(21)	101.0(6)	C(4)—C(3)—O(2)	110(1)
C(11)—P(1)—Pt	114.4(3)	C(2)—O(1)—C(5)	108(1)
C(11)—P(1)—C(21)	105.6(4)	C(3)—O(2)—C(5)	108(1)
C(21)—P(1)—Pt	113.3(3)	O(1)—C(5)—O(2)	106(1)
C(1)—P(2)—Pt	115.1(6)	O(1)—C(5)—C(6)	107(1)
C(1)—P(2)—C(31)	103.9(6)	O(1)—C(5)—C(7)	108(1)
C(1)—P(2)—C(41)	101.2(6)	O(2)—C(5)—C(6)	108(1)
C(31)—P(2)—Pt	115.8(4)	O(2)—C(5)—C(7)	112(2)
C(31)—P(2)—C(41)	101.4(5)	C(6)—C(5)—C(7)	116(2)
C(41)—P(2)—Pt	117.2(4)	P(2)—C(31)—C(32)	120.1(7)
P(1)—C(11)—C(12)	121.8(7)	P(2)—C(31)—C(36)	119.9(7)
P(1)—C(11)—C(16)	117.9(7)	P(2)—C(41)—C(42)	118.9(9)
P(1)—C(21)—C(22)	121.2(7)	P(2)—C(41)—C(46)	121.1(9)
P(1)—C(21)—C(26)	118.7(7)		

and angles are presented in Table 6. An illustration of the chelate backbone and the Pt atom coordination geometry is presented in Fig. 1, while a stereoview of the molecule is given in Fig. 2. Atoms are drawn as 50% probability thermal ellipsoids.

The coordination of the Pt atom is essentially square-planar, formed by two P atoms, the Cl atom, and the methyl group, C(8). Discussion of the dimensions is somewhat limited by the disorder observed, but the two Pt—P distances are significantly different, $\Delta/\sigma = 15.7$. The longer bond is *trans* to the 0.8 multiplicity methyl group, a result consistent with *trans* influence arguments. The P—Pt—P angle is 98.7(1)°, considerably larger than the value of 83.82(6)° observed in the *S,S*-chiraphos complex [17], but consistent with values quoted in reports of (—)-diop complexes of Fe, Pd, Pt and Ni which have recently appeared [18—20]. Dimensions within the diop ligand agree well with those already determined.

The absolute configurations of the two chiral carbon atoms in (+)-diop have been confirmed by this analysis as *S*. The seven-membered chelate ring adopts a 'twist-chair' conformation, Fig. 1. C(4) is very nearly in the plane formed by the Pt and two P atoms, while atoms C(1), C(2) and C(3) are displaced from

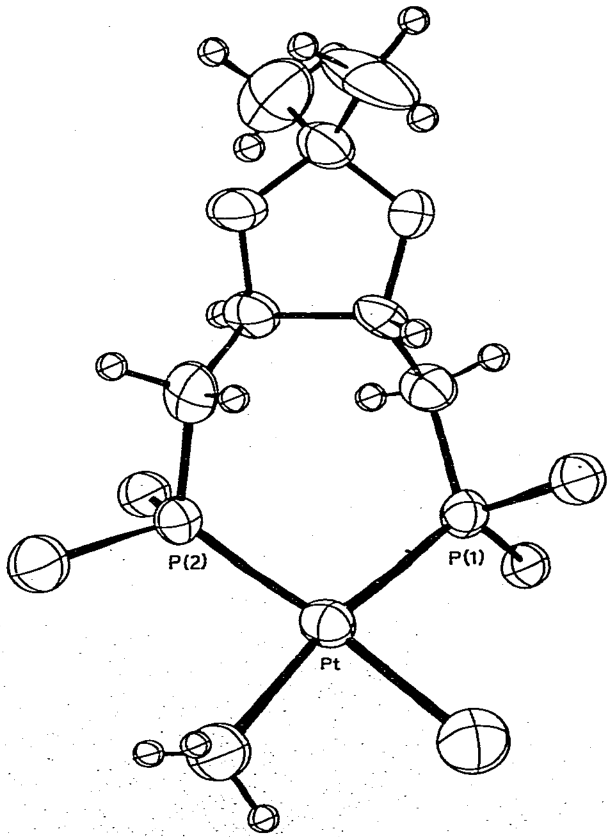

Fig. 1. The chelate backbone and the inner coordination sphere of the Pt atom. The thermal parameter of C(8) has been set to 5.0 Å^2.

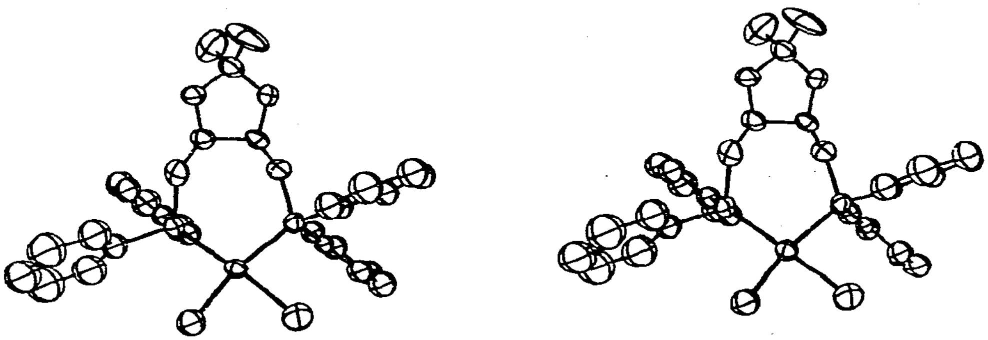

Fig. 2. A stereoview of the molecule.

this plane by 1.33(2), 1.10(2) and 1.22(2) Å, respectively.

The phenyl rings on the P atoms are positioned unsymmetrically about the P—Pt—P plane. On one P atom the rings are clearly disposed in equatorial and axial positions relative to the coordination plane, while the rings on the other P atom are located in such a way that they bracket the P—Pt—P plane equally, Fig. 3. The phenyl ring arrangement is in direct contrast to the orientation of the rings seen in the *S,S*-chiraphos structure [17] in which a C_2 axis approximately related the rings on one P atom to those on the other. The ring orientation we observed is also different from that observed for the Rh^I-diop complex [21], where again an approximate C_2 symmetry was seen.

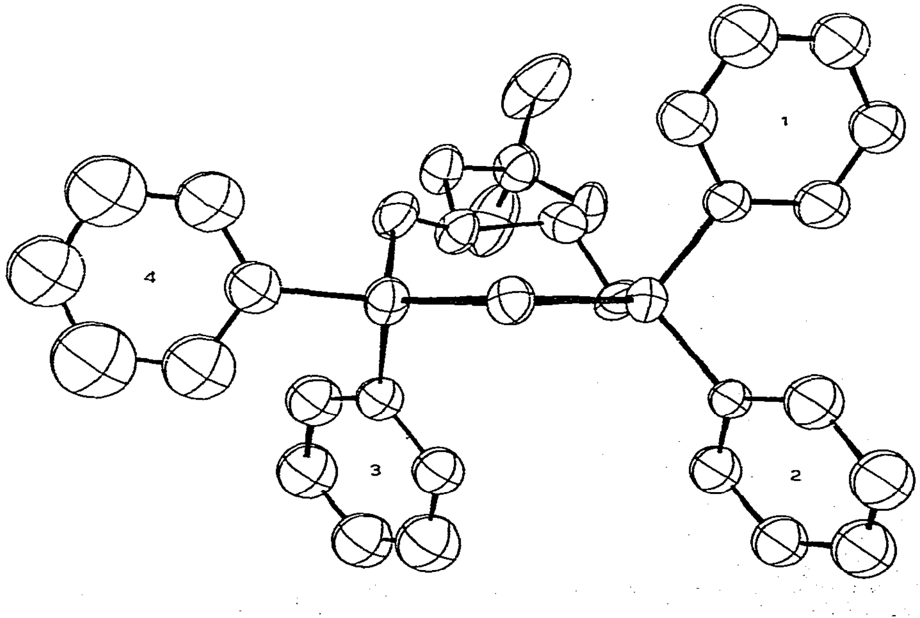

Fig. 3. A view of the Pt((+)-diop) fragment showing the arrangement of the phenyl rings.

Results and discussion

Complexes of formula [Pt(chelate)CH_3(acetone)]ClO_4, prepared by addition of $AgClO_4$ to Pt(chelate)CH_3Cl, react with chiral amines to give diastereomeric adducts when (chelate) is a chiral ligand. By employing optically pure diphosphine chelates, the number of diastereomers was limited to two. The extent of stereospecific binding of the amines to the chiral platinum complex was monitored by ^{31}P NMR. The spectra observed for these complexes consist of two AB patterns, one for each diastereomer, each with ^{195}Pt satellites [22]. Resonances were assigned to the different P atoms, P' *trans* to the methyl group, and P'', *cis* to the methyl group, Table 7, using arguments analogous to those presented in earlier work [1,3].

As was observed in the case of the chiral monophosphine adducts [1], the aminophosphine ligands *S*-peap and *S*-alap showed no ability to effect stereospecific binding of one enantiomer of the chiral amines. This inability has been attributed to the symmetrical dispositions of the phenyl rings [1,23]. In contrast, the amine complexes of *S*,*S*-chiraphos and (+)-diop were formed in diastereomeric ratios ranging from 51/49 to 70/30. Of the two ligands, the *S*,*S*-chiraphos complexes consistently gave the higher selectivity, Table 7, probably as a result of the rigid chelate backbone conformation and the dissymmetric phenyl ring arrangement [17].

Discrimination studies were also carried out with 1-phenylethylamine, pea, where the chiral atom is not nitrogen, but instead one of the substituent atoms. In the presence of two equivalents of racemic pea we were unable to observe the presence of diastereomers, except in the case of the (+)-diop complex. It appears that the greater distance between the chiral centres of the molecule reduces the inequivalence of the chemical shift of the P atoms. In the case of the (+)-diop complex, we were able to show that the *R*-pea isomer is preferentially bound to the Pt atom, giving a diastereomeric ratio of 60/40. This was achieved by recording the ^{31}P NMR spectra of the *R*- and *S*-pea complexes independently.

Although the configuration of the amine in the more abundant diastereomer has been determined for pea, it is not known for the amines with chiral nitrogen atoms. We made many attempts to crystallize the amine adducts, with a view to determining their structures by X-ray diffraction techniques. These efforts, carried out under varying conditions, were uniformly unsuccessful, though crystals of suitable quality for X-ray analysis were obtained of the starting material, Pt((+)-diop)CH_3Cl. In our earlier studies of the chiral monophosphine complexes [1], we employed molecular models of the *S*,*S*-chiraphos complex [17] to predict the configuration of the preferentially bonded enantiomer. A similar procedure for the amine complexes suggested that the less sterically hindered complex is formed when the amine bound to the Pt atom has the *R* configuration. Though purely qualitative, these suggestions must serve in the absence of more definitive studies.

Our failure to crystallize any amine adduct caused us to take the same approach to the (+)-diop complexes. Here we were fortunate in having crystals of the starting material, and a three dimensional X-ray structure analysis was carried out to determine the dispositions of the phenyl rings. Our study shows

TABLE 7

^{31}P NMR DATA FOR DIASTEREOMERIC Pt-amine COMPLEXES

[Pt(chelate)CH$_3$(L)]ClO$_4$		Chemical shifts (ppm) [a]		Coupling constants (Hz) [a]			Diastereomeric ratio [c]
(chelate)	(L)	δP′	δP″	|J(P″–P′)|	|J(Pt–P′)|	|J(Pt–P″)|	
(+)-diop	NPhMeH	12.6, 12.0	3.8, 3.5	13	1763	3897	50/50
	NBzMeH	11.4, 10.4	–1.8	13	1758	3680	45/55(u)
	NBuMeH	11.8, 11.4	2.5, 1.5	13	1744	3681	45/55(d)
	(+)-pea	9.3	1.9	14	1753	3813	40/60(d) [c]
	(–)-pea	8.6	2.2	14	1751	3798	
(–)-chiraphos	NPhMeH	46.6, 45.9	36.2, 35.0	11	1836, 1868	3700	36/64(u)
	NBzMeH	45.8, 45.3	34.9, 34.8	12	1800, 1780	3537	30/70(u)
	NBuMeH	47.3, 45.6	34.9, 34.0	12	1835, 1823	3565, 3539	43/57(u)
	(±)-pea	45.3	35.1	12	1735	3660	— [b]
(–)-peap	NBuMeH	59.0, 58.6	34.7, 34.4	33	1504	3442	50/50
(–)-alap	NBzMeH	59.3, 59.1	36.3, 35.7	30	1504	3413	50/50

[a] Chemical shifts are downfield from (CH$_3$O)$_3$PO. When two values are given they refer to the two diastereomers. One value is given when no difference was observed. These spectra were recorded at –60°C. [b] This parameter could not be determined. [c] The letter in brackets refers to the more abundant diastereomer; u = isomer with upfield P′ signal, d = isomer with downfield P′ signal. For the (+)-diop-pea complexes, the diastereomeric ratio refers to the ratio observed in the presence of excess (±)-pea. The more abundant diastereomer in this case contains (+)-*R*-pea. P′ is the P atom trans to the CH$_3$ group, P″ that *cis* to the CH$_3$ group.

that the seven-membered chelate ring of the (+)-diop ligand adopted a twist-chair conformation, in contrast to the boat conformation observed in Pt((+)-diop)Cl_2 [18]. These results support the proposition that the ring is conformationally labile, and able to adopt several different energy minima in the solid state, each of which presumably has a different phenyl ring disposition. Similar results have been found in solution [24]. Thus to employ the solid state results to discuss the interaction of the chiral amine with the Pt atom, one must consider several possible conformations of the (+)-diop ligand. If the observed phenyl ring disposition is taken, a tentative prediction is that the *R* enantiomer will be bound preferentially, but little confidence can be placed in this. It is perhaps more interesting to note that, whereas the chiraphos ligand is relatively rigid [17], the diop ligand is much more flexible [24], yet both effect enantiomeric discrimination in these Pt-amine systems to similar extents.

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