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STUDIES IN ENANTIOMERIC DISCRIMINATION

I. CHIRAL PHOSPHINE COMPLEXES OF PLATINUM

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Summary

Diastereomeric Pt complexes of formula $[Pt(P\text{-}P)CH_3(P^*)]ClO_4$, where P-P is bis(diphenylphosphino)ethane or a chiral bidentate phosphine, one of 2*S*-3*S*-bis(diphenylphosphino)butane, (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, *S*-*N*,*N*-bis(diphenylphosphino)-1-phenylethylamine and *S*-*N*,*N*-bis(diphenylphosphino)alanine ethyl ester, and P* is a chiral monodentate phosphine of formula $PC_6H_5R'R''$, have been prepared. In the presence of an excess of the racemic modification of the monodentate ligand, varying degrees of stereoselective binding to the metal complex containing the chiral chelate ligand were observed. A partial resolution of several chiral monophosphines was thus achieved in situ, monitored by ^{31}P NMR and optical rotary dispersion spectra. The configuration of the preferentially bound enantiomer was investigated using single crystal X-ray techniques, and identified by optical rotary dispersion spectra. The factors affecting the degree and nature of the enantioselectivity are discussed.

Introduction

One of the more recent advances in the field of homogeneous catalysis has been the development of effective catalysts for the asymmetric hydrogenation [1—5] and hydrosilation [6—8] of prochiral substrates. Rh complexes containing chiral bidentate phosphines have been used for this purpose. Although chelates in which the donor atoms are chiral have been used [1], great success has been achieved with bis(diphenylphosphine) chelates in which the chirality

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is incorporated into the backbone of the ligand [3—5]. The nature of the interaction between such chelates and substrate molecules has been of interest to us for some time [9—13]. In this paper we report our investigations of a non-catalytic system in which enantiomeric discrimination occurs in solution. A series of platinum complexes containing several different chiral chelates were allowed to bind chiral monophosphine ligands. Conditions were chosen so as to allow the observation of enantiomeric discrimination by ^{31}P NMR and optical rotatory dispersion (ORD) spectra. Several complexes effected a partial resolution of the chiral monophosphine through preferential coordination of one enantiomer to the metal. The configuration of the monophosphine that is preferentially bound has been determined using ORD spectra. The factors responsible for the observed enantioselectivity are discussed in terms of the ligand geometries.

Experimental section

Manipulations involving the monophosphines were carried out under a blanket of dry N_2 gas. Melting points are reported uncorrected. ORD spectra were recorded with a Jasco optical rotary dispersion recorder, model ORD/UV-5. Combustion analyses were performed by Gygli Microanalysis Laboratories, Toronto, and Guelph Chemical Labs. Guelph, Ontario. A representative sampling of the analytical data is given in Table 1.

Preparations of the phosphine ligands

The chiral chelates, *S-N,N*-bis(diphenylphosphino)-1-phenylethylamine, *S*-peap, *S-N,N*-bis(diphenylphosphino)alanine ethyl ester, *S*-alap, [13] and 2*S*,3*S*-bis(diphenylphosphino)butane, *S,S*-chiraphos, [3] were prepared as previously described. The ligand $(+)_{589}$-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane, (+)diop, was purchased from the Strem Chemical Co. The racemic modifications of the chiral monophosphines were prepared by our published route [12]. The neutral Pt complexes of formula Pt(P-P)-CH_3Cl were prepared from $Pt(C_8H_{12})CH_3Cl$ [14]. The complexes of formula $[Pt(P\text{-}P)CH_3(PPhR'R'')]ClO_4$ were synthesized from the neutral chloro complex by reaction with $AgClO_4$ and the appropriate monodentate phosphine [13].

TABLE 1

PHYSICAL AND ANALYTICAL DATA

Compound	M.p. (°C)	Analysis (%)			
		Calcd.		Found	
		C	H	C	H
[Pt(diphos)Me(PPhMeBz)]PF_6	214—218(d)	50.91	4.34	50.45	4.01
[Pt(diphos)Me(PPhMeBz)]ClO_4	195—197(d)	53.40	4.59	53.45	4.71
[Pt(diphos)Me(PPhMeEt)]ClO_4	180—190(d)	50.27	4.69	49.58	4.72
[Pt(diphos)Me(PPhMePr)]$ClO_4 \cdot CH_2Cl_2$	85—90	47.59	4.62	47.32	4.85
[Pt(*S,S*-chiraphos)Me(PPhCyEt)]ClO_4	250—255(d)	54.10	5.48	53.60	5.66
[Pt(*S,S*-chiraphos)Me(PPhMeBz)]$ClO_4 \cdot CH_2Cl_2$	135—140	51.05	4.67	51.41	4.81
[Pt(*S*-peap)Me(PPhCyEt)]ClO_4	175—180	55.38	5.24	55.80	5.60
[Pt(*S*-peap)Me(PPhCyPr)]ClO_4	146—150	55.79	5.36	55.20	5.62

TABLE 2

CRYSTALLOGRAPHIC DATA

	[Pt(*S*-peap)CH_3-(PPhCyEt)]ClO_4 · 1/2 CH_2Cl_2	[Pt(*S,S*-chiraphos)CH_3-(PPhMeBz)]ClO_4 · CH_2Cl_2
Formula	$C_{47.5}H_{58}Cl_2NO_4P_3Pt$, F.W. = 1060.9	$C_{44}H_{48}Cl_3O_4P_3Pt$, F.W. = 1035.2
Space group	Monoclinic, $P2$	Monoclinic, $P2_1$
Cell constants	a = 18.42(5) Å, b = 20.02(5) Å c = 12.86(5) Å, β = 96.92(5) ° V = 4706 Å^3	a = 16.89(5) Å, b = 23.22(5) Å c = 11.14(5) Å, β = 92.75(5) ° V = 4367 Å^3
Density (measured in)	1.50(1) gcm^{-3}(CCl_4, cyclohexane)	1.58(1) gcm^{-3} (CCl_4, hexanes)
Density (calculated)	1.50 gcm^{-3}	1.58 gcm^{-3}
Z	4	4

X-ray photographic studies

Crystals of [Pt(*S,S*-chiraphos)CH_3(PPhMeBz)]ClO_4 · CH_2Cl_2 and [Pt(*S*-peap)-Me(PPhCyEt)]ClO_4 · 1/2 CH_2Cl_2 were recrystallized from a methylene chloride/diethyl ether mixture. Weissenberg and precession photographs employing Cu radiation indicated monoclinic symmetry for each salt. The densities were determined by the flotation method.

The systematic absences observed allowed an unambiguous assignment of the space groups for the *S,S*-chiraphos and *S*-peap complexes as $P2_1$ and $P2$ [15], respectively. The cell parameters and other data are listed in Table 2. In each case the data are consistent with two formula units per asymmetric unit.

Determination of configuration of excess phosphine

Pt(*S,S*-chiraphos)CH_3Cl (354 mg) and $AgPF_6$ (132 mg) in CH_2Cl_2 (20 ml) were stirred for 0.5 h, and then centrifuged to remove precipitated AgCl. PPhCyEt (235 mg) was added to the decanted supernatant liquid, and the mixture stirred for 10 minutes. The solvent was removed, and the excess phosphine extracted into ether. The solid Pt complex was filtered off, and the ether extracts concentrated to 2.00 ml. The ORD spectra of this solution had $[\alpha]_D^{25} = -5.1°$ (c = 5, l = 0.1).

^{31}P NMR spectra

Spectra were recorded on a Varian XL-100 spectrometer operating at 40.5 MHz s^{-1}, employing a broad-band proton decoupler, and Fourier transform techniques. In all cases the proposed formulations were confirmed.

Results

^{31}P NMR spectral data are given in Table 3. The cations containing the achiral chelate ligand diphos exist as enantiomers, since the P atom of the monophosphine is the only chiral centre. The ^{31}P NMR spectra of these compounds show the expected ABX centre-band signal, with the appropriate satellites. The assignment of the spectral lines to the respective P nuclei were based on the |J(P—P)| and |J(Pt—P)| values [16].

(Continued on p. 227)

TABLE 3

^{31}P NMR DATA FOR THE CATIONIC Pt COMPLEXES, [Pt(P—P)CH$_3$(P*)]X

Compound ligand, P*	Shifts (ppm) [a]			Coupling constants (Hz) [a]							Diastereomeric ratio [c]
	δ(P′)	δ(P″)	δ(P*)	|J(P″—P′)|	|J(P″—P*)|	|J(P″—P*)|	|J(Pt—P′)|	|J(Pt—P″)|	|J(Pt—P*)|	Other	
[Pt(diphos)Me(P*)]ClO$_4$											
PPhMeEt	51.9	46.4	0.4	6	379	18	1770	2624	2674		
PPhMePr	51.7	46.3	−2.5	5	378	18	1768	2620	2670		
PPhMeBz	52.1	46.8	−0.6	6	380	18	1782	2654	2717		
PPhMeCy	52.0	46.0	2.9	6	374	18	1778	2618	2662		
PPhCyEt	51.0	45.5	18.5	5	368	15	1766	2644	2700		
PPhCyPr	50.5	45.8	15.3	5	368	16	1753	2632	2682		
[Pt(diphos)Me(P*)]PF$_6$											
PPhMeBz	52.0	46.7	−0.7	6	382	18	1720	2650	2624	δ(PF$_6$) = −20.0 |J(P—F)| = 716	
[Pt(S,S-chiraphos)Me(P*)]ClO$_4$											
PPhMeEt	43.6, 43.2	47.8, 47.7	1.8, 1.1	19	372	18	1751	2587	2672		*d*
PPhMePr	43.6, 43.3	47.7, 47.6	−1.0, −2.0	19	372	18	1750	2587	2686		*d*
PPhMeBz	43.9, 42.5	47.7, 47.4	−1.1, −1.4	17	375	19	1730	2615	2710		50 : 50
PPhMeCy	43.0, 41.5	46.9, 46.9	5.1, 2.4	17	390	17	1765	2576	2659		50 : 50
PPhCyEt	43.9, 42.8	46.5, 46.4	17.8, 19.8	17	360	18	1739	2603	2695		67 : 33
PPhCyPr	44.5, 43.3	46.9, 46.8	17.2, 14.5	18	362	18	1735	2604	2693		60 : 40

[Pt(S-peap)Me(P)]ClO$_4$*										
PPhMeEt	50.5	45.0	1.2, 1.0	37	403	16	1520	2430	2662	*d*
PPhMePr	50.4	44.3	−2.0, −2.4	37	404	15	1514	2418	2648	*d*
PPhMeBz	50.4, 50.2	44.4, 44.3	−0.2, −0.4	40	409	15	1512	2487	2735	*d*
PPhMeCy	51.0, 50.9	45.7	6.2, 5.0	40	400	16	1514	2458	2668	50 : 50
PPhCyEt	51.7	45.3	20.8	39	395	14	1508	2460	2680	*e*
PPhCyPr	51.4	45.2	18.0	36	396	15	1510	2460	2665	*e*
[Pt(S-alap)Me(P)]ClO$_4$*										
PPhMeEt	50.8	44.7	0.0	36	406	16	1508	2471	2686	*e*
PPhMePr	50.7	44.8	−3.1	36	407	16	1506	2473	2687	*e*
PPhMeBz	50.7, 50.3	44.7, 44.5	−0.4, −0.5	37	410	16	1512	2504	2757	*d*
PPhMeCy	51.4	44.5	4.5	35	401	16	1502	2473	2675	*e*
PPhCyEt	52.0, 51.8	45.9, 45.5	19.9, 19.8	37	397	16	1500	2480	2722	50 : 50
PPhCyPr	51.3, 51.2	44.8, 44.4	17.0, 17.1	36	397	16	1505	2479	2707	50 : 50
[Pt((+)-diop)Me(P)]ClO$_4$*										
PPhMeEt [f]	*D* = 0.4	*D* = 0.1	*D* = 1.2	23	377	21	1869	2751	2752	*d*
PPhMePr [f]	*D* = 0.6	*D* = 0	*D* = 1.1	23	371	21	1867	2756	2698	*d*
PPhMeBz [f]	*D* = 1.5	*D* = 0.1	*D* = 2.7	22	383	22	1896	2777	2726	50 : 50
PPhMeCy [f]	*D* = 0.4	*D* = 0.8	*D* = 1.4	23	383	21	1891	2721	2687	*b*
PPhCyEt [f]	*D* = 0.2	*D* = 0.5	*D* = 1.0	22	383	21	1867	2760	2679	*d*
PPhCyPr [f]	*D* = 0	*D* = 0.4	*D* = 0.6	22	372	21	1872	2766	2714	*d*

[c] The values reported are those observed, as no correction for 2nd order effects could be made. Chemical shifts are in ppm downfield of $(CH_3O)_3PO$. Where two values are given, they correspond to the two diastereomers. [b] The nature of the spectrum precluded evaluation of this information. [c] These diastereomeric ratios were recorded in the presence of excess phosphine at −40°C. [d] Exchange broadening precluded evaluation of diastereomeric ratio. [e] No differences in chemical shifts were observed, thus the diastereomeric ratio could not be evaluated. [f] The (+)-diop complexes were extremely distorted as a result of second order effects. The signals were all in the range of −3 to +5 ppm. Overlap with the reference precluded its use, thus only the differences (*D*) in chemical shifts are presented. The data were obtained from the Pt satellites. (Note: *D* is given in ppm).

The cations containing a chiral chelate ligand exist as diastereomers. As the diphosphines used were optically pure, only two stereoisomers are possible, and two overlapping ABX patterns are seen. Pairs of signals and their ^{195}Pt satellites could be assigned to the three types of P nuclei. However, assignment of a specific set of resonances to each of the diastereomers was not possible, as no measurable difference in the coupling constants was observed. Consequently second order effects could not be taken into account. In the (+)-diop complexes, small chemical shift differences resulted in grossly distorted spectra. In addition, the proximity of these lines to the reference compound resonance caused us to report only the observed difference in chemical shift for each pair of P resonances.

The magnitude of the difference in chemical shifts for the diastereomers reflects the nature of the chiral environment. In the *S*-alap and *S*-peap complexes, the differences are small when observed at all. The aminophosphine ligands contain chiral centres removed from the chelate ring, and thus only a small diastereomeric interaction results. *S,S*-chiraphos contains chiral centres in the ring which cause the chelate to adopt a preferred conformation [3,9]. In this way the chiral environment is extended towards the *cis* coordination site, and thus larger differences in chemical shifts are seen.

Chiral monophosphines are known to be conformationally rigid at ambient temperatures [17]. In order to investigate the possibility of preferential binding of one enantiomer of monophosphines to the chiral Pt complexes, we recorded the ^{31}P NMR spectra of these complexes in the presence of 2—5 equivalents of the racemic modification of various chiral monophosphines. Although these spectra were recorded at −40°C, exchange broadening precluded the observation of the diastereomeric ratios in several cases. Exchange was observed in all cases for PPhMePr and PPhEtPr, which are the least basic of the chiral monophosphines employed [18]. The larger, more basic phosphines, PPhCyEt and PPhCyPr exchange only in the (+)-diop complexes. (+)-diop, which forms a seven-membered ring, probably has a greater steric interaction with the *cis* coordination site. This is supported by crystallographic data for three of the four chelates employed [9,10,19]. The greater interaction between the monophosphine and (+)-diop presumably weakens the P binding in the *cis* coordination site, thus facilitating exchange. The higher-field P^* values observed are consistent with weaker Pt—P^* bonds. It should be noted that, even though the observation of enantiomeric discrimination was precluded by exchange, it is still possible that the process occurs on a shorter time scale.

When exchange was slow the diastereomeric ratio could be determined (Table 3). It is clear that the inability of *S*-alap and *S*-peap complexes to discriminate between the monophosphine enantiomers arises from the lack of a chiral environment for the incoming ligand. The four-membered ring is essentially planar [19], and thus no mechanism for the extension of the chiral environment exists.

In the *S,S*-chiraphos complexes no enantiomeric discrimination was observed for PPhMeBz or PPhMeCy, while it did occur for PPhCyEt and PPhCyPr (Fig. 1). This suggests that the interaction between the chiral cation and the substrate molecule is extremely sensitive to small changes in the steric nature of the monophosphine, as might be expected for a "lock and key" model for the discriminatory process.

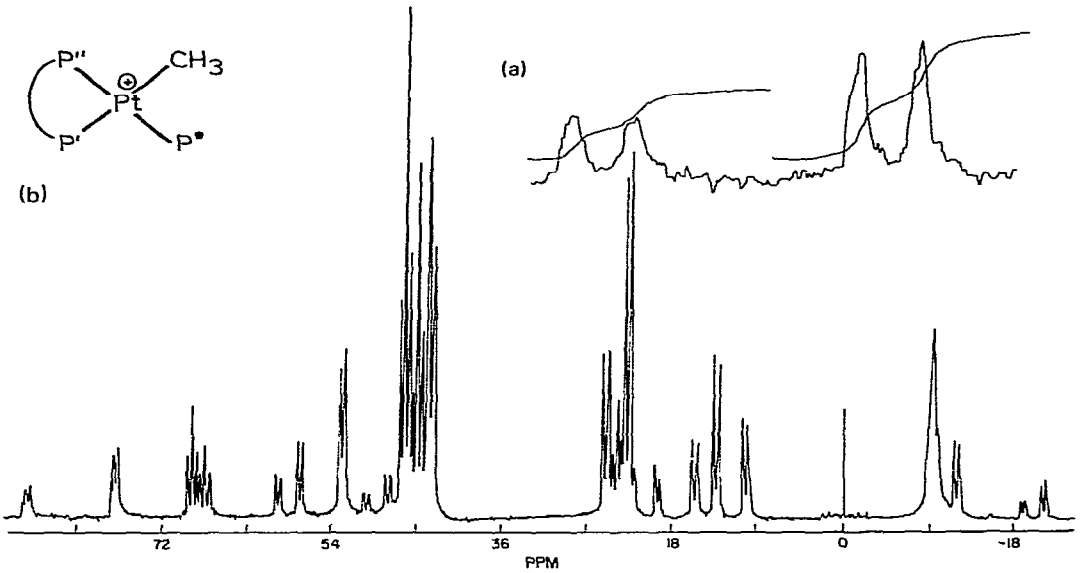

Fig. 1. ^{31}P NMR Spectrum of [Pt(*S,S*-chiraphos)Me(PPhCyEt)]ClO_4 in the presence of excess phosphine. (a) Integration of satellites, (b) Labelling of P atoms.

In those cases where discrimination is observed, we tried repeatedly to carry out a fractional crystallization of the mixtures. With two exceptions, all attempts gave oils. Crystals were obtained of the PPhMeBz adduct of the *S,S*-chiraphos cation, and of the PPhCyEt complex with the *S*-peap cation, and single crystal X-ray investigations were started. In each case there were two formula units per equivalent position. There are two ways in which this could occur. Either the diastereomeric cations crystallized in pairs, with one of each in the asymmetric unit, or each crystal contains only one diastereomer, a spontaneous resolution has occurred, and diastereomeric crystal forms exist. In view of the fact that ^{31}P NMR spectra of selected samples of crystals of each compound showed a 50 : 50 ratio of the two diastereomers, it seems more probable that the former explanation is correct. Accordingly, the crystallographic investigations were not continued as no information regarding the hand of the preferentially bound ligands could be derived from these studies. Instead, we examined the appropriate molecular models. By constructing the *S,S*-chiraphos ligand in the conformation found in the crystal structure of [Rh(*S,S*-chiraphos)(C_7H_8)]ClO_4 [9], we were able to predict that the *R* configuration of the monophosphine will preferentially bind, as fewer repulsive steric interactions occur. We attempted to confirm this result by recording ORD spectra. A solution of [Pt(*S,S*-chiraphos)CH_3(PPhCyEt)]PF_6 was prepared in the presence of an extra equivalent of PPhCyEt. This solution was then extracted with ether. The ORD spectrum of the excess phosphine in the ether extracts showed the presence of an excess of (—)-PPhCyEt. Thus the (+) isomer is preferentially bound to the cation. On the basis of the known absolute configuration of similar phosphines, (+)-PPhCyEt [17] is predicted to have the *R* configuration. This result is consistent with the prediction made from molecular models, and demonstrates the ability of the *S,S*-chiraphos complex

to effect a partial resolution of PPhCyEt in situ. From such considerations we have been able to predict the configuration of the enantiomer bonded. Though these results are encouraging in one sense, the sensitivity to small changes in steric shape and size does not augur well for the design of general prupose catalysts. Instead, a careful tailoring of chiral ligand and substrate molecule would seem to be required.

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