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# PREPARATION AND $^{31}P$ NMR STUDIES OF PLATINUM COMPLEXES OF SOME CHIRAL, BIDENTATE PHOSPHINES

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## Summary

Two chiral diphosphines of formula $RN(P(C_6H_5)_2)_2$, *S*-peap and *S*-alap, have been prepared from *S*-α-phenethylamine and the ethyl ester of *S*-alanine, respectively. Their syntheses, and the preparation of the achiral diphosphine beap, *N,N'*-bis(diphenylphosphino)-*N,N'*-dibenzylethylenediamine, are described. Platinum complexes of these bidentate ligands of formula Pt(chelate)$CH_3Cl$ and [Pt(chelate)$CH_3$(X)]$ClO_4$ (X = acetone; *p*-$YC_5H_4N$, when Y = $CH_3$, $C_2H_5$, CHO, $CO_2CH_3$, H and $N(CH_3)_2$; and a series of monodentate, Group V donor ligands, $P(C_2H_5)_3$, $P(C_3H_7)_3$, $P(C_8H_{17})_3$, $PCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, $P(C_6H_5)_3$, $P(C_6H_{11})(C_6H_5)_2$, $P(C_6H_{11})_2C_6H_5$, $P(C_6H_{11})_3$, $P(C_6H_5)_2N(C_2H_5)_2$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$) have been prepared and their $^1H$ and $^{31}P$ NMR parameters recorded. The cationic pyridine complexes show a correlation of the ρ values of the *para* substituent to some of the $^{31}P$ chemical shifts and coupling constants. The steric and electronic properties of the diphosphine ligands have been investigated by comparing their $^{31}P$ NMR parameters with those of analogous complexes containing (+)-diop and *S,S*-chiraphos.

## Introduction

Wilkinson's original work [1] on the catalytic activity of $Rh(P(C_6H_5)_3)_3Cl$ for hydrogenation reactions has resulted in a great deal of research into the mechanisms of homogeneous catalysis. More recently emphasis has shifted to the development of effective catalysts for asymmetric hydrogenation of prochiral olefins [2—6]. Metal complexes containing chiral, bidentate phosphines, where the chiral centre is on the backbone joining the two phosphorus atoms, have been particularly successful for this purpose [3,5,6]. However, less is

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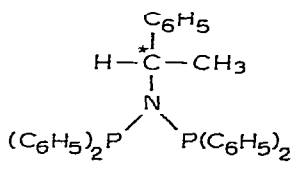
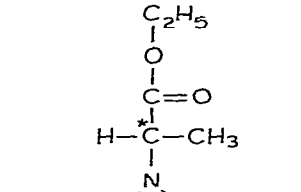
known of the properties of bidentate phosphines which form four-membered rings, or those of phosphine ligands in which the chiral centre is not part of the backbone. Since postulates concerning the nature of the asymmetric interaction between metal complex and the prochiral olefin have been based on the steric properties of these ligands as seen in crystallographic investigations [2,7—9], we decided to synthesize and study some aminophosphine ligands as part of our interest in the uses of chiral phosphines in asymmetric syntheses [7—10]. To this end we have utilized $^{31}P$ NMR to probe both the steric and electronic properties of a number of chiral, bidentate phosphines and their complexes. By a systematic variation of the ligands bound to the metal we have been able to obtain information regarding the nature of the phosphorus—metal interaction, as well as a measure of relative magnitudes of the *cis* and *trans* influences of the ligands. The results of these studies are reported herein, the observed trends are discussed, and the properties of the new bidentate aminophosphine ligands are compared to those of the alkylphosphine chelates.

## Results and discussion

The platinum complexes prepared were of formulae Pt(chelate)$CH_3Cl$ and [Pt(chelate)$CH_3$(X)]$ClO_4$, where (chelate) was either one of two new, chiral, bidentate aminophosphines, $(-)_{589}$-*N*,*N*-bis(diphenylphosphino)-*S*-$\alpha$-phenylethylamine, *S*-peap, **1**, and $(-)_{589}$-*N*,*N*-bis(diphenylphosphino)-*S*-alanine ethyl ester, *S*-alap, **2**, or $(+)_{589}$-2*S*,3*S*-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, (+)-diop, **3**, $(-)_{589}$-2*S*,3*S*-bis(diphenylphosphino)-butane, *S*,*S*-chiraphos, **4**, or $(-)_{589}$-2*S*-bis(diphenylphosphino)propane, *S*-prophos, **5**. Some complexes in which (chelate) was 1,2-bis(diphenylphosphino)ethane, diphos, and *N*,*N*′-bis(diphenylphosphino)-*N*,*N*′-dibenzylethylenediamine, beap, **6**, were also prepared for comparative purposes.



(1)



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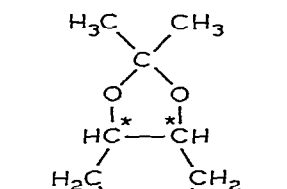

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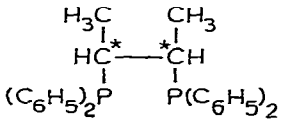

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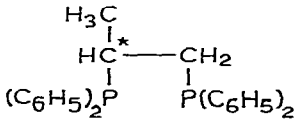

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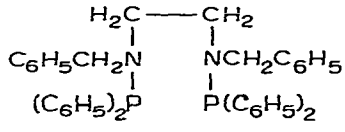


(6)

Chiral bidentate phosphines have until recently presented a synthetic problem [3,6]. The ligands described here (R* is the chiral moiety) are easily

prepared in an optically pure form via reactions 1.

$$R^*—NH_2 + 2\ PPh_2Cl + 2\ NEt_3 \rightarrow R^*—N(PPh_2)_2 + 2\ NEt_3 \cdot HCl$$
$$R^*—NH_3Cl + 2\ PPh_2Cl + 3\ NEt_3 \rightarrow R^*—N(PPh_2)_2 + 3\ NEt_3 \cdot HCl \quad (1)$$

It is known that nucleophilic attack on a phosphorus centre by an amine, with simultaneous loss of HCl, yields the bis(diphenylphosphino)amine [11,12]. HCl is removed by formation of the triethylamine hydrochloride salt. *S*-peap, **1**, and *S*-alap, **2**, were prepared in this fashion, using $(—)_{589}$-*S*-α-phenylethylamine and $(—)_{589}$-*S*-alanine ethyl ester hydrochloride as the respective starting materials. The yields of these bidentate phosphines had the respectable values of 45 and 30 percent, respectively. Application of this route to the symmetric, secondary diamine *N,N'*-dibenzylethylenediamine yielded the achiral bidentate aminophosphine, beap, **6**.

In the preparation of *S,S*-chiraphos, modifications to the reported method [3] increased the yield from 14 to 25 percent, based on the quantity of diol taken. The major factor leading to yield enhancement appears to be the use of the dimesylate of the diol in lieu of the ditosylate. How this affects the mechanism is not clear, though a subtle change in the leaving ability has favoured product formation instead of elimination or other side reactions.

Platinum complexes of the form $Pt(chelate)CH_3Cl$ were prepared by displacement of 1,5-cyclooctadiene (COD) from $Pt(COD)CH_3Cl$ with the appropriate bidentate phosphine. Subsequent reaction of these platinum halide complexes

$$Pt(COD)CH_3Cl + (P\text{-}P) \rightarrow Pt(chelate)CH_3Cl + COD$$
$$\downarrow \text{AgClO}_4,\ \text{acetone}$$
$$[Pt(chelate)CH_3(X)]ClO_4 \xrightleftharpoons[X]{\text{donor}} [Pt(chelate)CH_3(acetone)]ClO_4 + AgCl \quad (2)$$

with $AgClO_4$ in acetone produced the acetone cation [13] with perchlorate as the non-coordinating anion, and a precipitate of silver chloride. Group V donor molecules readily displace acetone from the cationic complexes since they are better sigma donors (eq. 2). A wide range of possible ligands exists; in the present paper we have restricted our choice to achiral molecules of varying basicity and steric bulk. In this way we have been able to explore one of the important steps in homogeneous catalysis by transition metal complexes of chiral diphosphine ligands, namely the interaction between the coordinatively unsaturated metal complex and an incoming substrate molecule. Thus X was chosen to be one of a series of *para*-substituted pyridines $YC_5H_4N$, where Y is $CH_3$, $C_2H_5$, CHO, $CO_2CH_3$, H and $N(CH_3)_2$; and a number of phosphorus, arsenic and antimony ligands, X = $P(C_6H_5)_3$, $P(C_6H_{11})_3$, $P(C_2H_5)_3$, $P(C_3H_7)_3$, $P(C_8H_{17})_3$, $P(C_6H_5)_2CH_3$, $P(CH_3)_2C_6H_5$, $P(C_6H_{11})_2C_6H_5$, $P(C_6H_5)_2C_6H_{11}$, $P(C_6H_5)_2N(C_2H_5)_2$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$. $^1H$ and $^{31}P$ NMR parameters have been recorded in each case.

### *$^1H$ NMR spectra*

$^1H$ NMR data for the bidentate ligands and their platinum complexes of

TABLE 1

$^1$H NMR DATA FOR LIGANDS AND PT COMPLEXES, Pt($CH_3$)(chelate)Cl

| Species | Chemical shift (ppm) | | | | |
|---|---|---|---|---|---|
| | $C_6H_5$ | CH | $CH_2$ | $CH_3$ | Pt—$CH_3$ |
| *Ligand* | | | | | |
| *S,S*-chiraphos | 7.4(m) | 2.3(m) | | 1.2(d of d) | |
| *S*-alap | 7.6(m) 7.4(m) | 4.1(m) | 4.1(m) | 1.38(d) 1.08(t) | |
| *S*-peap | 7.3(m) | 4.7(m) | | 1.58(d) | |
| (+)-diop | 7.8(m) 7.4(m) | 3.9(m) | 2.4(m) | 1.32(s) | |
| beap | 7—8(br,m) | | 3.1(m) 4.0(br,m) | | |
| *Pt($CH_3$)(chelate)Cl* | | | | | |
| *S,S*-chiraphos | 7.7(m) 7.5(m) | 2.1(m) | | 1.0(m) | 0.36(d of d) |
| *S*-alap | 8.0(m) 7.5(m) | 4.0(m) | 3.43(t) | 0.8(m) | 0.54(d of d) |
| *S*-peap | 7.9(m) 7.5(m) | 4.5(m) | | 1.00(d) | 0.46(d of d) |
| (+)-diop | 7.9(m) 7.4(m) | 3.8(m) | 2.5(m) | 1.18(s) | 0.52(d of d) |
| diphos | 8.0—7.2(br, m) | | | 2.3(m) | 0.68(d of d) |
| beap | 7.8(m) 7.5(m) | | | | |
| | 7.2(m) 6.9(m) | | 3.8(m) 3.2(m) | | 0.42(d of d) |
| *S*-prophos | 7.8(m) 7.5(m) | 2.5(m) | 1.1(m) | 0.95(m) | 0.62(d of d) |
| | | | | | 0.50(d of d) |

formulae Pt(chelate)$CH_3Cl$ are given in Table 1. In the spectrum of *S,S*-chiraphos, coupling between the P atom and the $\beta$ methyl hydrogen atoms is significant (15 Hz), as has been observed before [14]. Although a similar large coupling to the methine protons of *S*-peap and *S*-alap is expected, the multiplicity

TABLE 2

$^1$H NMR DATA FOR COMPLEXES [Pt(chelate)$CH_3$(X)]$ClO_4$

| Compound (chelate) | X | Chemical shifts (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $C_6H_5$ | CH | $CH_2$ | $CH_3''$ | $CH_3'$ | $CH_3$ |
| *S*-alap | $PPh_3$ | 7.4(br,m) | 3.9(m) | 3.4(m) | 0.90(t) | 0.86(d) | 0.65(d |
| | $AsPh_3$ | 7.5(br,m) | 4.0(m) | 3.48(q) | 0.93(t) | 0.90(d) | 0.78(d |
| | $SbPh_3$ | 7.4(br,m) | 3.9(m) | 3.5(q) | 0.88(t) | 0.90(d) | 0.85(m |
| | $C_5H_5N$ | 7.6(br,m) | 3.9(m) | 3.5(q) | 0.92(t) | 0.86(d) | 0.50(d |
| *S*-peap | $PPh_3$ | 7.8—7.0(br,m) | 4.3(m) | | | 0.92(d) | 0.28(d |
| | $AsPh_3$ | 7.3(br,m) | 4.3(m) | | | 0.88(d) | 0.40(d |
| | $SbPh_3$ | 7.2(br,m) | 4.3(m) | | | 0.96(d) | 0.58(d |
| | $C_5H_5N$ | 7.6(br,m), 7.1(m) | 4.5(m) | | | 1.06(d) | 0.22(d |
| (+)-diop | $PPh_3$ | 7.6(m), 7.2(m) | 3.7(m) | 2.8(br,m) | | 1.00(s), 0.94(s) | 0.24(m) |
| | $AsPh_3$ | 7.7(m), 7.3(br,m) | 3.7(m) | 3.1(br,m) | | 1.16(s), 1.12(s) | 0.32(d |
| | $SbPh_3$ | 7.3(br,m) | 3.9(m) | 3.1(br,m) | | 1.10(s), 1.04(s) | 0.48(d |
| | $C_5H_5N$ | 7.7(br,m), 7.2(m) | 4.2(m) | 3.5(br,m) | | 1.30(s), 1.22(s) | 0.50(d |
| *S,S*-chiraphos | $PPh_3$ | 8.0—7.1(br,m) | 2.2(m) | | | 1.1(m) | 0.32(d |
| | $AsPh_3$ | 7.6(m), 7.2(m) | 2.1(m) | | | 0.90(d of d of d) | 0.40(d |
| | $SbPh_3$ | 7.7(m), 7.2(m) | 2.1(m) | | | 1.00(d of d of d) | 0.52(d |
| | $C_5H_5N$ | 7.6(br,m) | 2.1(m) | | | 1.0(m) | 0.20(d |

[a] Not observed. [b] Not measurable due to overlap or broadening. [c] Small degree of overlap. [d] P and P* refer to P
$|J(CH_3'—H)| = 7$

ling constants (Hz)

| I—$CH_3$)\| | \|J(P′—$CH_3$)\| | \|J(P″—$CH_3$)\| | \|J(Pt—$CH_3$)\| | Other |
|---|---|---|---|---|
| | | | | \|J(P—$CH_3$)\| = 15<br>\|J($CH_2$—$CH_3$)\| = 7.5 |
| | 7.5 | 3.5 | 57 | |
| | 8.5 | 3 | 63 | |
| | 8.5 | 3 | 62 | \|J(CH—$CH_3$)\| = 7.5 |
| | 7 | 5 | 54 | |
| | 7 | 4 | 55 | |
| | 7.6 | 4.4 | 55 | |
| | 7.5 | 3.5 | 56 | |
| | 8.0 | 3.5 | 56 | |

of the signal precluded an evaluation of the coupling constant.

The Pt—$CH_3$ resonance occurs at ca. 0.5 ppm downfield of TMS, and appears as a doublet of doublets when a bidentate phosphine is coordinated to the metal. In these complexes there are two P atoms, one *trans* to the methyl

ling constant (Hz)

| $_3$—P′)\| | \|J($CH_3$—P″)\| | \|J(Pt—$CH_3$)\| | Other [d] |
|---|---|---|---|
| | 6.5 | 64 | \|J($CH_3''$—$CH_2$)\| = 7, \|J($CH_3'$—H)\| = 7, \|J($CH_3$—$P^L$)\| = 6.5 |
| | 5.5 | 63 | \|J($CH_3''$—$CH_2$)\| = 6.5, \|J($CH_3'$—H)\| = 7 |
| | *b* | *a* | \|J($CH_3''$—$CH_2$)\| = 7, \|J($CH_3'$—CH)\| = 7 |
| | 3 | 60 | \|J($CH_3''$—$CH_2$)\| = 7, \|J($CH_3'$—H)\| = 7 |
| | 5.5 | 62 | \|J($CH_3$—$P^L$)\| [d] = 5.5 |
| | 5.5 | 62 | \|J($CH_3'$—H)\| = 7 |
| | 5.5 | *a* | \|J($CH_3'$—H)\| = 7 |
| | 3.0 | 60 | \|J($CH_3'$—H)\| = 7 |
| | *b* | 56 | |
| | 6.0 | 54 | |
| | 5.5 | *a* | |
| | 4.0 | 55 | |
| | 6.0 | 53 | \|J($CH_3$—$P^L$)\| = 6.0 |
| | 5.5 | 58 | \|J($CH_3'$—H)\| = 19, \|J($CH_3'$—P)\| = 13, \|J($CH_3'$—$P^*$)\| = 5 |
| | 5.5 | *a* | \|J($CH_3'$—H)\| = 19, \|J($CH_3'$—P)\| = 13, \|J($CH_3'$—$P^*$)\| = 5 |
| | 3.0 | 56 | |

ligand, P', and one *cis*, P''. In such cases the P'—$CH_3$ coupling is greater than that of P''—$CH_3$, and coupling constant values of ca. 8 and 3 Hz, respectively, were assigned [15].

The $^{195}$Pt satellites flank the main Pt—$CH_3$ resonance. The complexes of the *N,N*-bis(diphenylphosphino)amines show significantly larger Pt—$CH_3$ coupling than the complexes of the other phosphines. This observation is consistent with a poorer donor ability of these phosphines, which results in an increase in the *s* character of the Pt—$CH_3$ bond, and thus a larger $|J(Pt—CH_3)|$ value. This observation is consistent both with the greater electronegativity of the N atom, and the presence of delocalization of the lone pair on the P atom [16].

Data for the complexes in which Cl has been replaced by $PPh_3$, $AsPh_3$, $SbPh_3$ and pyridine are given in Table 2. Phosphorus coupling to the $\beta$ methyl H atoms is again seen in the *S,S*-chiraphos complex (13 Hz), and also to the $\gamma$ protons (5 Hz).

The Pt—$CH_3$ resonance occurs between 0.20 and 0.85 ppm downfield of TMS in these complexes. In general, the position of this resonance shifts downfield as the basicity of the donor decreases. The exception to this trend is the pyridine adduct of the (+)-diop complex. In the $AsPh_3$, $SbPh_3$ and pyridine adducts the methyl resonances appear as a double doublet indicating coupling to the two different phosphorus nuclei, and coupling constant values of approximately 7 and 5 Hz, respectively, were assigned. In the P complexes, additional coupling of the methyl to the third phosphorus atom yields a doublet of triplets. Although the two *cis* phosphorus nuclei are not equivalent, the magnitudes of the coupling constants to the methyl group are equal. Again the aminophosphine complexes show significantly larger Pt—$CH_3$ coupling than the others, while in the case of the $SbPh_3$ adducts, no $^{195}$Pt—$CH_3$ coupling was observed. The signals are broadened by the presence of $^{121}$Sb and $^{123}$Sb, which have nuclear spins of 5/2 and 7/2, and natural abundances of 57 and 43 percent, respectively.

### $^{31}$*P NMR spectra*

Data for the ligands and the Pt complexes containing Cl, acetone and the substituted pyridines are given in Table 3. The absolute values of the coupling constants are listed, as the relative signs were not determined.

The newly prepared bidentate ligands 1 and 2, although chiral, show singlets in the $^1$H-decoupled $^{31}$P NMR spectra, and the diastereotopic inequivalence is not observed. Such splitting is not expected in 3 and 4, whereas there are two doublets in the spectrum of *S*-prophos, with a P—P coupling of 19 Hz, because, in addition to the chiral centre, the two P atoms have different chemical environments. The chemical shifts of the P nuclei in the aminophosphine ligands are well downfield (65—75 ppm) of those of the diarylalkylphosphines. The resonance in beap is ca. 12 ppm downfield of those in *S*-alap and *S*-peap, Table 3, implying a greater deshielding of the P atoms. The observed order of $^{31}$P chemical shifts of the bidentate alkylphosphines is *S,S*-chiraphos > diphos > (+)-diop. The upfield shift of the resonance of (+)-diop is presumably a result of the electron-donating ability of the isopropylidene ring. By a similar argument, one could also have predicted an upfield resonance of *S,S*-chiraphos with respect to diphos, because of the additional electron-releasing methyl substituents on the C atom backbone. Such a rationale, however, is not consis-

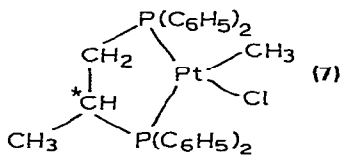
)R LIGANDS AND THEIR Pt COMPLEXES

| Y | Chemical shift (ppm) | | | Coupling constants (Hz) | | | |
|---|---|---|---|---|---|---|---|
| | δ(P) | δ(P′) | δ(P″) | \|J(P′—P″)\| | \|J(Pt—P′)\| | \|J(Pt—P″)\| | J(P—P*) |
| | −11.0 | | | | | | |
| | 52.9 | | | | | | |
| | 51.5 | | | | | | |
| | −25.0 | | | | | | |
| | −14.1 | | | | | | |
| | 63.8 | | | | | | |
| | −1.1, | | | | | | |
| | −23.3 | | | | | | 19 |
| *te)Cl* | | | | | | | |
| | | 45.8 | 41.9 | 11 | 1686 | 4458 | |
| | | 54.9 | 36.8 | 36 | 1400 | 4042 | |
| | | 55.5 | 36.4 | 38 | 1399 | 4014 | |
| | | 7.8 | 4.8 | 13 | 1681 | 4288 | |
| | | 42.2 | 41.2 | — | 1724 | 4262 | |
| | | 81.5 | 63.0 | 16 | 2071 | 4750 | |
| (i) | | 52.3 | 33.1 | 3 | 1734 | 4172 | |
| (ii) | | 32.1 | 46.7 | 5 | 1708 | 4215 | |
| *)ne)(chelate)]ClO$_4$* | | | | | | | |
| | | 52.3 | 33.2 | 10 | 1764 | 4541 | |
| | | 64.9 | 31.3 | 33 | 1450 | 4442 | |
| | | 64.3 | 30.5 | 37 | 1449 | 4401 | |
| | | 15.9 | 0.04 | 13 | 1824 | 4701 | |
| *$_5H_4N$)(chelate)]ClO$_4$* | | | | | | | |
| $NMe_2$ | | 48.6 | 36.0 | 11 | 1664 | 3594 | |
| Me | | 49.4 | 35.4 | 12 | 1671 | 3653 | |
| Et | | 49.6 | 35.3 | 12 | 1669 | 3652 | |
| H | | 49.8 | 35.2 | 12 | 1671 | 3667 | |
| $CO_2Me$ | | 49.9 | 35.1 | 12 | 1676 | 3698 | |
| CHO | | 50.0 | 35.1 | 12 | 1677 | 3701 | |
| $NMe_2$ | | 57.8 | 35.3 | 31 | 1440 | 3498 | |
| Me | | 58.2 | 34.6 | 32 | 1436 | 3581 | |
| Et | | 58.2 | 34.5 | 32 | 1437 | 3574 | |
| H | | 58.5 | 34.4 | 32 | 1436 | 3594 | |
| $CO_2Me$ | | 58.2 | 34.1 | 33 | 1437 | 3626 | |
| CHO | | 58.0 | 33.8 | 33 | 1438 | 3624 | |
| $NMe_2$ | | 57.5 | 34.7 | 33 | 1448 | 3465 | |
| Me | | 57.9 | 34.0 | 34 | 1436 | 3549 | |
| Et | | 58.0 | 34.0 | 34 | 1437 | 3544 | |
| H | | 58.1 | 33.8 | 34 | 1435 | 3565 | |
| $CO_2Me$ | | 57.9 | 33.4 | 35 | 1438 | 3599 | |
| CHO | | 58.1 | 33.5 | 35 | 1436 | 3601 | |
| $NMe_2$ | | 9.6 | 0.7 | 13 | 1681 | 3665 | |
| Me | | 9.6 | 0.5 | 13 | 1705 | 3742 | |
| Et | | 9.7 | 0.5 | 14 | 1707 | 3736 | |
| H | | 9.8 | 0.4 | 14 | 1711 | 3761 | |
| $CO_2Me$ | | 9.9 | 0.4 | 14 | 1723 | 3800 | |
| CHO | | 9.8 | 0.4 | 14 | 1724 | 3803 | |

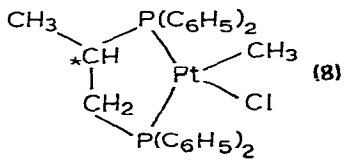
tent with the observed order, since steric, in addition to electronic factors, influence the chemical shift. In the case of *S,S*-chiraphos and diphos, electronic influences are of similar magnitudes, and thus differences in chemical shifts can be rationalized on the basis of the size of the substituents on the P atoms. In *S,S*-chiraphos, the larger substituents cause a greater distortion from $sp^3$ hybridization, and thus a decrease in the *s* character of the lone pair electrons, which produces a downfield resonance. A similar argument has been used to explain orders or chemical shifts for monophosphines when electronic differences between substituents are small [17]. Application of this rationale to the chemical shift values of *S*-prophos allowed us to assign the downfield resonance to the P atom adjacent to the secondary C atom.

The $^1$H-decoupled $^{31}$P NMR spectra of the platinum complexes consist of two doublets. Phosphorus—phosphorus coupling constants varied from not observable to 40 Hz, with the $^{195}$Pt satellites flanking the centre band resonances. In all cases save one, the low-field resonances have $|J(Pt—P)|$ values ranging from 1400 to 2100 Hz, whereas the high field doublet has $|J(Pt—P)|$ values of 3450—4500 Hz. The assignments of the low field signals to P′ and the high field signals to P″ are based on platinum-phosphorus coupling constants [15,17—19].

The assignment of the spectral lines for the *S*-prophos complex presents additional complications. Two possible isomers exist, 7 and 8, corresponding to the two different methyl substituent positions, andas a result four doublets with appropriate satellites are seen in the spectrum. These were divided into pairs of doublets resulting from each of the isomers by comparison of the $|J(P—P)|$ values, where both P are nuclei in the ligand. Signals were assigned to




(7)




(8)

P′ or P″ nuclei based on the $|J(Pt—P)|$ values. On the basis of chemical shift comparisons to Pt(diphos)$CH_3Cl$ and Pt(*S,S*-chiraphos)$CH_3Cl$, resonances (i), Table 3, were assigned to 7, and resonances (ii) to 8. With this assignment, the P atom adjacent to the secondary C atom in *S*-prophos is downfield in both isomers, and thus the steric bulk of the substituents on the P atom has a greater influence on the chemical shift than the difference in the *trans* influence of methyl and chloride. Incidentally this effect gives rise to the only case where a downfield signal corresponds to the P″ atom coordinated to the Pt atom. No attempt was made to separate the two geometric isomers, which were present in solution approximately equal amounts.

The data for the phosphine, arsine and stibine adducts are recorded in Table 4. Computer refinement of these parameters was required as a result of second order effects. Only the absolute values of the coupling constants are given. However, the refinements were achieved using *trans* phosphorus—phosphorus coupling constants of opposite sign to the other coupling constants.

The $^1$H-decoupled $^{31}$P NMR spectra of the platinum monophosphine complexes [Pt(chelate)$CH_3(P^L)$]$ClO_4$ consist of three doublets of doublets. The

arsine and stibine derivatives exhibit two doublets. $|J(P—P)|$ values range from 14 to 429 Hz. $^{195}Pt$ satellites flank the centre band resonances, with $|J(Pt—P)|$ values ranging from 1467 to 3216 Hz.

*Variations in chemical shifts*

On coordination the $^{31}P$ resonances of *S,S*-chiraphos, (+)-diop, *S*-prophos and diphos all shift downfield from the free ligand values. Those of the aminophosphines do not, for that of P′ shifts downfield slightly, and that of P″ upfield. With the exception of the *S*-prophos complex, the P′ nuclei resonate downfield of the P″ nuclei. This may be explained as follows. Firstly, coordination to a metal removes electron density from the P atom. This accounts for the observed downfield shift on coordination of monophosphines [19] and the bidentate alkylphosphines studied here. This effect has only a minimal influence on the $^{31}P$ resonance of the aminophosphines, presumably because they are poorer electron donors as a result of some P—N multiple bond character [16]. The second factor affecting the $^{31}P$ resonances is the *trans* influence of the substituents on the Pt. In these complexes the methyl group has a larger *trans* influence than the chloride, acetone or pyridine ligands, and thus the P atom *trans* to the methyl ligand, P′, resonates downfield of the *cis* P atom, P″.

The competition between the factors affecting the P nuclei is evident in the $^{31}P$ NMR data for the cationic pyridine and acetone complexes. The resonances of the P″ nucleus shift upfield as the donor ability of the pyridine decreases

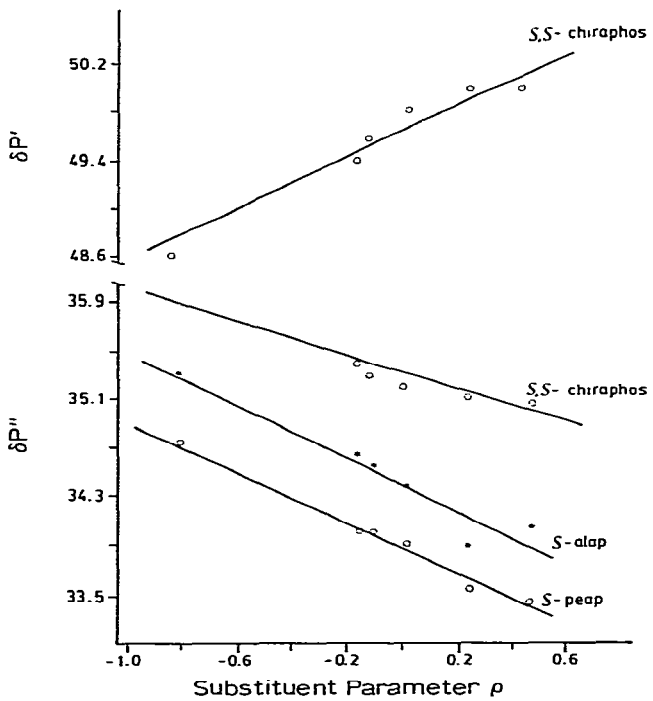



**Fig. 1. Plot of phosphorus chemical shifts versus ρ, the Hammett substituent parameters of the *para*-substituted pyridines.**

*(Continued on p. 214)*

TABLE 4

$^{31}$P NMR DATA FOR CATIONIC PLATINUM COMPLEXES CONTAINING P, As AND Sb LIGANDS

| (chelate) | X | Chemical shifts (ppm) [a] | | | Coupling constants (Hz) [a] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\delta(P')$ | $\delta(P'')$ | $\delta(P^L)$ | $\lvert J(P''-P')\rvert$ | $\lvert J(P''-P^L)\rvert$ | $\lvert J(P'-P^L)\rvert$ | $\lvert J(Pt-P')\rvert$ | $\lvert J(Pt-P'')\rvert$ | $\lvert J(Pt-P^L)\rvert$ |
| *S,S*-chiraphos | $PPh_3$ | 45.1 | 49.2 | 25.1 | 18 | 375 | 18 | 1785 | 2711 | 2768 |
| | $AsPh_3$ | 45.1 | 47.7 | | 17 | | | 1785 | 3260 | |
| | $SbPh_3$ | 44.9 | 49.4 | | 17 | | | 1770 | 3550 | |
| | $PEt_3$ | 42.7 | 47.3 | 11.9 | 18 | 361 | 19 | 1761 | 2526 | 2640 |
| | $PPhMe_2$ | 43.2 | 47.6 | −8.5 | 17 | 378 | 19 | 1759 | 2577 | 2684 |
| | $PPh_2Me$ | 44.0 | 47.9 | 6.7 | 18 | 377 | 19 | 1751 | 2645 | 2719 |
| | $P(n\text{-}Pr)_3$ | 42.7 | 47.0 | 2.6 | 18 | 361 | 18 | 1756 | 2520 | 2627 |
| | $P(n\text{-octyl})_3$ | 42.8 | 47.6 | 4.2 | 18 | 361 | 19 | 1765 | 2514 | 2630 |
| | $PCy_3$ | 41.4 | 47.6 | 22.6 | 18 | 348 | 18 | 1767 | 2532 | 2641 |
| | $PCy_2Ph$ | 42.2 | 46.4 | 23.8 | 18 | 357 | 18 | 1751 | 2617 | 2692 |
| | $PCyPh_2$ | 42.8 | 48.3 | 23.9 | 18 | 365 | 18 | 1784 | 2652 | 2668 |
| | $PPh_2NEt_2$ | 44.5 | 48.8 | 73.4 | 18 | 391 | 17 | 1780 | 2613 | 3084 |
| *S*-peap | $PPh_3$ | 53.6 | 44.1 | 23.1 | 41 | 407 | 15 | 1522 | 2578 | 2771 |
| | $AsPh_3$ | 53.5 | 41.3 | | 43 | | | 1493 | 3144 | |
| | $SbPh_3$ | 51.6 | 41.6 | | 46 | | | 1468 | 3336 | |
| | $PEt_3$ | 50.7 | 45.6 | 14.5 | 40 | 395 | 15 | 1512 | 2393 | 2660 |
| | $PPhMe_2$ | 50.9 | 45.0 | −9.6 | 40 | 413 | 15 | 1502 | 2452 | 2679 |
| | $PPh_2Me$ | 52.2 | 44.9 | 5.0 | 41 | 411 | 15 | 1508 | 2519 | 2727 |
| | $P(n\text{-}Pr)_3$ | 50.8 | 45.5 | 5.0 | 40 | 395 | 15 | 1511 | 2391 | 2642 |
| | $P(n\text{-octyl})_3$ | 50.5 | 45.5 | 6.3 | 40 | 395 | 14 | 1515 | 2384 | 2649 |
| | $PCy_3$ | 52.3 | 44.6 | 26.8 | 40 | 380 | 15 | 1513 | 2401 | 2649 |
| | $PCy_2Ph$ | 52.7 | 44.5 | 27.3 | 41 | 391 | 14 | 1497 | 2495 | 2703 |
| | $PCyPh_2$ | 52.1 | 44.8 | 25.8 | 41 | 400 | 14 | 1521 | 2532 | 2679 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SbPh_3$ | 52.9 | 42.3 | | 43 | | | 1467 | 3358 | |
| | $PEt_3$ | 52.0 | 46.3 | 14.9 | 36 | 395 | 15 | 1513 | 2408 | 2682 |
| | $PPhMe_2$ | 52.0 | 45.6 | −9.4 | 37 | 414 | 16 | 1504 | 2468 | 2705 |
| | $PPh_2Me$ | 52.2 | 44.4 | 5.0 | 38 | 412 | 15 | 1520 | 2529 | 2757 |
| | $P(n\text{-}Pr)_3$ | 52.0 | 46.3 | 5.4 | 37 | 396 | 15 | 1511 | 2406 | 2664 |
| | $P(n\text{-octyl})_3$ | 51.5 | 46.0 | 6.4 | 36 | 396 | 15 | 1516 | 2399 | 2670 |
| | $PCy_3$ | 54.0 | 45.9 | 27.4 | 36 | 380 | 15 | 1502 | 2426 | 2672 |
| | $PCy_2Ph$ | 53.3 | 45.8 | 27.5 | 38 | 393 | 14 | 1487 | 2519 | 2722 |
| | $PCyPh_2$ | 53.5 | 45.6 | 25.6 | 38 | 401 | 15 | 1518 | 2555 | 2709 |
| | $PPh_2NEt_2$ | 54.9 | 44.9 | 70.9 | 37 | 429 | 16 | 1523 | 2498 | 3109 |
| (+)-diop | $PPh_3$ | 2.8 | 26.4 | 9.9 | 21 | 386 | 21 | 1880 | 2900 | 2808 |
| | $AsPh_3$ | 3.2 | 10.0 | | 20 | | | 1926 | 3401 | |
| | $SbPh_3$ | 0.2 | 12.0 | | 21 | | | 1970 | 3525 | |
| | $PEt_3$[b] | 1.1 | 9.7 | 9.7 | 22 | [c] | 22 | 1910 | 2650 | 2640 |
| | $PPhMe_2$ | 1.3 | 9.2 | −6.2 | 22 | 390 | 23 | 1864 | 2687 | 2772 |
| | $PPh_2Me$ | 1.4 | 9.3 | 7.6 | 21 | [c] | 21 | 1861 | 2741 | 2823 |
| | $P(n\text{-}Pr)_3$ | 1.3 | 9.4 | 1.1 | 22 | 373 | 22 | 1881 | 2604 | 2685 |
| | $P(n\text{-octyl})_3$ | 1.4 | 9.7 | 2.3 | 21 | 372 | 22 | 1887 | 2596 | 2682 |
| | $PCy_3$ | 1.1 | 20.4 | 7.2 | 20 | 361 | 21 | 1856 | 2742 | 2585 |
| | $PCy_2Ph$ | −0.2 | 23.7 | 6.0 | 20 | 367 | 21 | 1821 | 2803 | 2673 |
| | $PCyPh_2$ | 0.8 | 23.4 | 8.3 | 20 | 377 | 21 | 1880 | 2808 | 2738 |
| | $PPh_2NEt_2$ | 2.0 | 8.8 | 73.0 | 21 | 402 | 22 | 1852 | 2705 | 3216 |

[a] In order to account for second order effects, approximate values of the various parameters were taken from the spectra and refined using the computer program LAOCN3. The solution was considered converged when the experimental and calculated resonance positions differed by no greater than 1 Hz. The resulting errors are: chemical shifts, ±0.05 ppm; coupling constants, ±1 Hz. [b] The extreme second order distortion of the spectrum made computer fitting impossible. Since only the observed parameters are reported, the error associated with the values must be larger than that obtained for the refined parameters (i.e. chemical shift error ±0.5 ppm, Pt—P coupling constant error ±10 Hz). [c] The nature of the spectra precluded evaluation of this parameter.

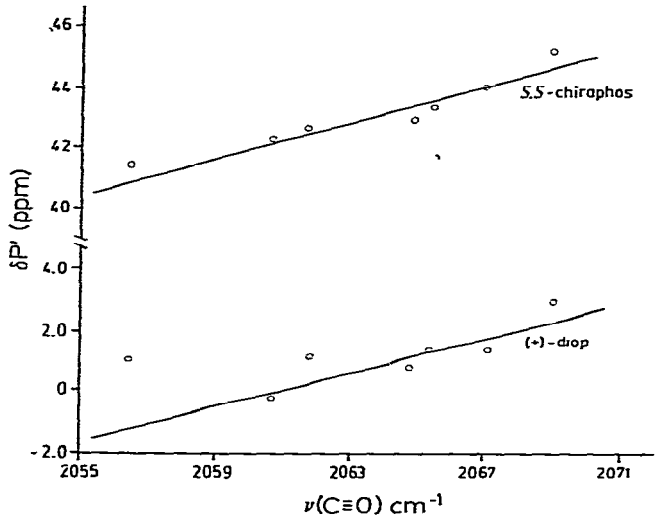



Fig. 2. A plot of $\delta(P')$ values versus the $\nu(C{\equiv}O)$ values measured in $Ni(CO)_3X$ complexes for the *S,S*-chiraphos and (+)-diop series.

(increasing $\rho$ values) in the *S,S*-chiraphos, *S*-alap and *S*-peap series. On the other hand, the chemical shift of the P′ nucleus in the *S,S*-chiraphos series increases as the $\rho$ values increase (see Fig. 1). In an analogous Pd diphosphine series [20], the opposite trend was observed for the P″ nucleus. The order seen here is probably due to an increase in Pt—P bond *s* character as the Pt—Py bond decreases in strength. In cases where competing effects are of comparable magnitude, no trends in the chemical shift values were observed and thus these data are not presented in the figures. Examples are the $\delta(P')$ values for *S*-alap and *S*-peap, and the P′ and P″ values for the (+)-diop series, Table 3.

For the phosphine, arsine and stibine complexes, Table 4, the $\delta(P')$ values tend to decrease as the basicity of the ligand decreases. Tolman used $\nu(C{\equiv}O)$ values to measure the electronic properties of such ligands in $Ni(CO)_3X$ complexes [21], and a plot of $\delta(P')$ values for the *S,S*-chiraphos and (+)-diop complexes shows a generally monotonic relationship between these parameters, Fig. 2. The chemical shifts of the P″ nuclei appear to depend on both the electronic and steric properties of the ligand X, since no direct correlation is observed with either parameter independently. However, a tendency for $\delta(P'')$ to be large in the (+)-diop complexes when X is of large steric bulk is noticeable. A plot showing the relationship between the chemical shifts of the P nuclei of the monodentate ligands and the chemical shifts of the free phosphines is presented in Fig. 3. Since we have shown a qualitative relationship between the chemical shift of a phosphine with the cone angles of the substituents [10], this plot implies a similar relationship between the $\delta(P^L)$ values and the size of the ligands.

*Variations in coupling constants*

P—P coupling constants varied over a wide range, with larger values observed

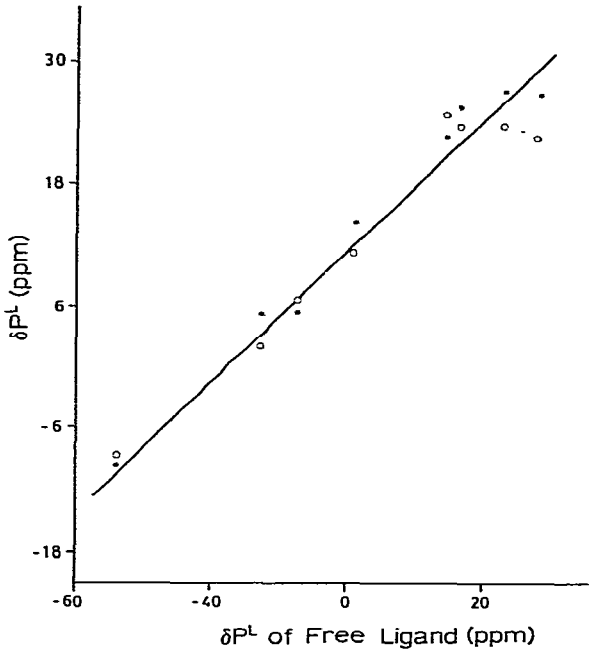



Fig. 3. A plot of the chemical shift of $P^L$ versus the chemical shift of the free ligand $P^L$. * - point corresponding to the aminophosphine series. o - points corresponding to the *S,S*-chiraphos series.

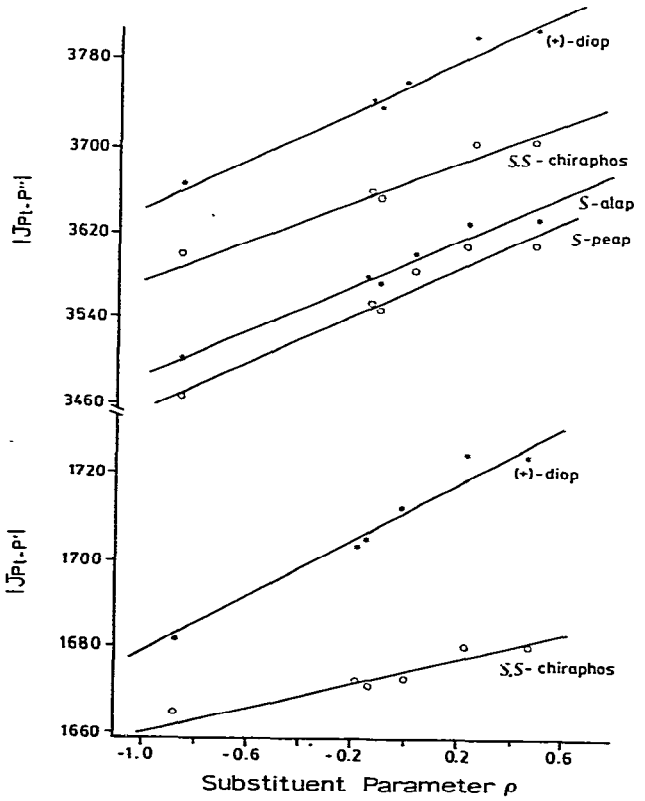



Fig. 4. Plot of the phosphorus—platinum coupling constants versus the Hammett substituent parameters of the *para*-substituted pyridines.

for the *S*-alap and *S*-peap complexes. This may be attributed to the greater proximity of the P atoms in the four-membered chelate ring. Also, $|J(P'—P'')|$ values were greater than $|J(P'—P^L)|$ values, as might be expected. $|J(P''—P^L)|$ values ranged from 350 to 430 Hz, with the larger couplings measured in complexes containing ligands of smaller steric bulk, ie. $PCy_3 < PCy_2Ph < PCyPh_2 < PPh_3$. If, however, we consider two phosphines of similar steric bulk, for example $PPh_3$ and $PEt_3$, we observe that the more basic donor yields a lower $|J(P''—P^L)|$ value. Clearly, this is consistent with the weakening of the P''—Pt bond as result of the increase in *trans* influence of $P^L$.

Platinum—phosphorus coupling constants are also affected by the *trans* ligands. The $|J(Pt—P')|$ values are significantly lower than the other Pt—P couplings due to the large *trans* influence of the methyl group. $|J(Pt—P'')|$ values increase linearly with a decrease in pyridine donor ability, Fig. 4, and a similar trend was found for the $|J(Pt—P')|$ values in the *S*,*S*-chiraphos and (+)-diop complexes. In the phosphine, arsine and stibine complexes, the $|J(Pt—P'')|$ values are affected by the steric and electronic properties of $P^L$ in a fashion similar to that already described for $|J(P''—P^L)|$. $|J(Pt—P')|$ and $|J(Pt—P^L)|$ values appear to be a complicated function of the properties of X as no trends emerge in the data.

In subsequent papers in this series we shall describe the use of chiral monophosphines of formula PRR'R'', and chiral amines, of formula NHRR', as the group V donor ligands.

## Experimental

The preparations of the bidentate phosphines were carried out under an atmosphere of dry, oxygen-free nitrogen, though such precautions were not necessary for the preparation of the platinum complexes. The $^{31}P$ NMR spectra were recorded from ether solutions of the isolated phosphines, acetone solutions of the cationic platinum acetone complexes, and methylene chloride solutions of all the other platinum complexes. 10 mm sample tubes were employed. $(CH_3O)_3PO$ was used as an external reference. Chemical shifts downfield of the reference are reported with a positive sign. The spectra were recorded on a Varian Associates XL100 instrument operating at 40.5 MHz $s^{-1}$, with broadband proton decoupling and employing Fourier transform techniques. The second order effects observed in all the ABX centre-band spectra were accounted for by computer refinement of all the spectral parameters using the program LAOCN-III. In addition, the platinum coupling constants seen in the satellite spectra were also corrected in this fashion. Proton NMR spectra were recorded on both XL100 and T60 spectrometers. Infrared spectra were measured on a Perkin-Elmer 621 infrared spectrometer. Optical rotations were determined using a Jasco optical rotatory dispersion recorder, model ORD/UV-5. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Analyses were performed by the Gygli Microanalysis Lab., Toronto, Ontario, and these quantities are given in Tables 5 and 6.

$(-)_{589}$-2*R*,3*R*-Butanediol was purchased from Burdick and Jackson Laboratories, Inc. $(-)_{589}$-*S*-α-Phenylethylamine, *S*-alanine, chlorodiphenylphosphine, $PPh_3$ and $PEt_3$ were purchased from Aldrich Chemical Company. $SbPh_3$ was

TABLE 5

PHYSICAL AND ANALYTICAL DATA

| Compound | M.p. (°C) | Analysis (%) | | | |
|---|---|---|---|---|---|
| | | Calcd. | | Found | |
| | | C | H | C | H |
| (—)-[$(CH_3)CH(OSO_2CH_3)]_2$ | 115—117 | 29.26 | 5.73 | 29.14 | 5.74 |
| *S,S*-chiraphos | 101—103 | 78.86 | 6.62 | 78.57 | 6.52 |
| *S*-alap | 97—100 | 71.74 | 6.02 | 71.79 | 5.97 |
| *S*-peap | 97—100 | 78.51 | 5.97 | 78.95 | 5.84 |
| beap | 124—127 | 78.93 | 6.29 | 78.52 | 6.12 |
| *Pt(chelate)$CH_3Cl$ complexes* | | | | | |
| *S,S*-chiraphos | 242—247(d) | 51.83 | 4.65 | 51.81 | 4.84 |
| *S*-alap | 185—191(d) | 48.44 | 4.49 | 49.06 | 4.21 |
| *S*-peap | 227—233(d) | 53.92 | 4.39 | 53.88 | 4.46 |
| (+)-diop | 200—205(d) | 51.65 | 4.74 | 51.57 | 4.66 |
| diphos | 250—255(d) | 50.36 | 4.23 | 50.47 | 4.27 |
| beap | 215—220(d) | 57.65 | 4.84 | 57.31 | 4.97 |
| *S*-prophos | 235—239(d) | 51.11 | 4.44 | 51.32 | 4.63 |
| *[Pt(chelate)$CH_3(YC_5H_4N)]ClO_4$ · solvent complexes* | | | | | |
| (chelate) Y solvent | | | | | |
| (+)-diop $NMe_2$ — | 195—200(d) | 50.35 | 4.88 | 50.46 | 5.01 |
| (+)-diop $CO_2Me$ — | 200—206(d) | 49.50 | 4.58 | 49.51 | 4.41 |
| *S,S*-chiraphos $CO_2Me$ — | 205—210(d) | 49.52 | 4.39 | 49.53 | 4.56 |
| *S,S*-chiraphos $NMe_2$ — | 215—220(d) | 50.38 | 4.82 | 50.32 | 4.95 |
| *S*-alap H — | 182—185(d) | 47.37 | 4.33 | 47.20 | 4.55 |
| *S*-alap $NMe_2$ $CH_2Cl_2$ | 102—107 | 44.97 | 4.28 | 44.58 | 4.32 |
| *S*-peap $CH_3$ $CH_2Cl_2$ | 117—122 | 49.17 | 4.23 | 48.45 | 4.76 |

obtained from Alfa Inorganic Inc., and (+)-diop, diphos and $PCy_3 \cdot CS_2$ were supplied by Strem Chemical Company. Several of the monodentate ligands including $PPh_2NEt_2$, $PPh_2Cy$, $PPhCy_2$, $PPhMe_2$, $PPh_2Me$ and $AsPh_3$ were prepared by conventional methods. P(n—Pr)$_3$ and P(n-octyl)$_3$ were purchased from the Pressure Chemical Company, while a sample of *S*-prophos was kindly supplied by Dr. B. Bosnich of the University of Toronto.

*Preparation of $(-)_{589}$-2S,3S-bis(diphenylphosphino)butane, S,S-chiraphos, 4*

The chiral starting material was the dimesylate of $(-)_{589}$-2*R*,3*R*-butanediol. This was prepared by the approach of Crossland and Servis [22]. 19.28 g of the diol was dissolved in 450 ml of dichloromethane and 90 ml of triethylamine was added. To this 54 ml of methanesulfonyl chloride was added dropwise with cooling in an ice bath. The mixture was stirred for four hours, and the solution then extracted successively with 250 ml each of water, 10% HCl solution, saturated bicarbonate solution and saturated brine solution. The dichloromethane layer was dried over magnesium sulfate, filtered, the solvent removed by rotary evaporation and the oil crystallized by addition of ether. The white solid was isolated by filtration and washed with tetrahydrofuran. $^1$H NMR, IR and mass spectra verified the formulation as the dimesylate of 2,3-butanediol.

190 g of triphenylphosphine was then dissolved in 600 ml of dried tetra-

TABLE 6

PHYSICAL AND ANALYTICAL DATA FOR [Pt(chelate)$CH_3$(X)]$ClO_4$ · solvent

| (chelate) | X | Solvent | M.p. (°C) | Analysis (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Calcd. | | Found | |
| | | | | C | H | C | H |
| *S*-alap | $PPh_3$ | | 214—219(d) | 54.00 | 4.53 | 53.71 | 4.68 |
| | $AsPh_3$ | | 203—208(d) | 51.82 | 4.35 | 51.70 | 4.49 |
| | $PCy_2Ph$ | | 187—191(d) | 53.39 | 5.62 | 53.50 | 5.55 |
| | $PPh_2NEt_2$ | | 178—180(d) | 51.95 | 5.04 | 51.72 | 5.25 |
| | $PEt_3$ | $CH_2Cl_2$ | 152—158 | 43.85 | 5.01 | 43.63 | 5.21 |
| | $PPh_2Me$ | $CH_2Cl_2$ | 150—160 | 48.35 | 4.44 | 48.01 | 4.62 |
| | $PCy_3$ | $CH_2Cl_2$ | 135—140 | 50.20 | 5.88 | 50.40 | 5.72 |
| | $PPr_3$ | $CH_2Cl_2$ | 145—150 | 45.56 | 5.39 | 45.21 | 5.82 |
| | $PPhMe_2$ | $CH_2Cl_2$ | 115—120 | 45.36 | 4.51 | 45.57 | 4.52 |
| | $SbPh_3$ | | 172—175(d) | 49.69 | 4.17 | 49.41 | 4.36 |
| *S*-peap | $PPh_3$ | | 200—206(d) | 57.71 | 4.46 | 57.63 | 4.68 |
| | $AsPh_3$ | | 200—206(d) | 55.42 | 4.29 | 55.74 | 4.33 |
| | $PCy_2Ph$ | | 212—216(d) | 57.06 | 5.54 | 57.08 | 5.62 |
| | $PCy_3$ | | 220—225(d) | 56.74 | 6.07 | 56.55 | 6.38 |
| | $SbPh_3$ | | 160—164(d) | 53.17 | 4.11 | 52.78 | 4.25 |
| | $PPh_2Cy$ | $CH_2Cl_2$ | 118—125 | 53.92 | 5.31 | 53.75 | 5.46 |
| | $PPh_2Me$ | 1.5 $CH_2Cl_2$ | 95—100 | 48.00 | 4.36 | 48.01 | 4.82 |
| (+)-diop | $PEt_3$ | | 219—224(d) | 49.28 | 5.44 | 49.26 | 5.25 |
| | $SbPh_3$ | | 198—203(d) | 51.72 | 4.34 | 51.52 | 4.32 |
| | $AsPh_3$ | | 210—215(d) | 53.89 | 4.52 | 53.69 | 4.53 |
| | $PPh_2Me$ | | 190—195(d) | 53.60 | 4.80 | 53.48 | 4.92 |
| | $PPr_3$ | | 205—210(d) | 50.86 | 5.83 | 50.18 | 5.99 |
| *S-S*-chiraphos | $PPh_3$ | | 239—241(d) | 56.55 | 4.64 | 56.29 | 4.42 |
| | $PPh_2Me$ | | 170—175(d) | 53.88 | 4.74 | 53.68 | 4.61 |
| | $PCy_2Ph$ | | 237—239(d) | 55.87 | 5.79 | 55.74 | 5.91 |
| | $SbPh_3$ | | 205—210(d) | 51.83 | 4.26 | 51.62 | 4.38 |

hydrofuran, 10 g of freshly cut lithium added, and the solution stirred for three hours. To the deep red-orange solution was added 78.4 ml of freshly distilled t-butylchloride in a dropwise fashion. The solution was stirred for 45 minutes. 43.2 g of the mesylate of $(-)_{589}$-2*R*,3*R*-butanediol was added over the next hour, with cooling of the solution to —4°C. The solution was stirred at room temperature for one and a half hours. 500 ml of water purged with nitrogen was added slowly. The major portion of the tetrahydrofuran was distilled off under reduced pressure, and the remaining liquid was extracted with two 250 ml portions of ether. The ether layers were combined and dried over magnesium sulfate. The solution was filtered into a hot solution of 51 g of $Ni(NO_3)_2 \cdot 6\ H_2O$ in 400 ml of ethanol. To this solution was added 71 g of sodium thiocyanate in 350 ml of ethanol. 86.4 g of a moss-green nickel complex was collected and washed with ethanol and ether.

This complex was suspended in 850 ml of ethanol. 40 g of sodium cyanide in 400 ml of water was added quickly to this suspension. This mixture was stirred for one hour and 200 ml of water added. After stirring for 12 hours, this solution was extracted with several portions of ether totalling 700 ml. The ether was back extracted with two 400 ml portions of water and then with two

200 ml portions of brine. The ether layer was dried over magnesium sulfate for one hour. The solvent was removed by rotary evaporation, and the white solid recrystallized from ethanol. 21 g of product was obtained (yield 25% from the mesylate) $[\alpha]_D^{25} = -266°$.

*Preparation of N,N-bis(diphenylphosphino)-S-alanine ethyl ester, S-alap, 2*

10 g of *S*-alanine was suspended in 100 ml of absolute ethanol. This solution was refluxed and HCl gas was bubbled through it for 30 minutes. Refluxing was continued for another 30 minutes, and then the solvent was removed and the remaining colourless oil kept under vacuum for 24 hours to remove traces of solvent. This product, the ethyl ester of alanine hydrochloride, was not crystallized. The oil was dissolved in 200 ml of toluene, and 60 ml of triethylamine added. 30 ml of chlorodiphenylphosphine was added in a dropwise fashion with stirring. The solution was stirred overnight, filtered to remove triethylamine hydrochoride, and the solvent removed. Addition of diethyl ether and charcoal was followed by solution filtration and solvent removal. The resulting oil solidified on stirring in 95% ethanol. 16 g of product was obtained (yield 30%) $[\alpha]_D^{25} = -75°$.

*Preparation of N,N-bis(diphenylphosphino)-S-α-phenethylamine, S-peap, 1*

15 ml of $(-)_{589}$-*S*-α-phenethylamine was added to a mixture of 150 ml of chloroform and 32.9 ml of triethylamine. To this solution 42.2 ml of chlorodiphenylphosphine was added in a dropwise fashion. The solution was stirred for 24 hours, the solution filtered, and the solvent removed. Ether was added and the solution was refiltered. The solvent was removed and the resulting oil solidified from methanol. 27 g of product was obtained (yield 45%) $[\alpha]_D^{25} = -120°$.

*Preparation of N,N'-bis(diphenylphosphino)-N,N'-dibenzylethylenediamine, beap, 6*

5.5 g of *N,N'*-dibenzylethylenediamine was dissolved in benzene and 4.5 g (6.2 ml) of triethylamine was added. 10 g (8.1 ml) of chlorodiphenylphosphine was added dropwise and the resulting mixture was stirred overnight at room temperature. The solution was filtered to remove the triethylamine hydrochloride. The solvent was removed, ether was added and the solution filtered once again, removing the last trace of the amine salt. The ether was removed by rotary evaporation and the yellow oil solidified on stirring in methanol. 4.7 g of product was filtered off (yield 32%).

*Preparation of Pt(chelate)$CH_3Cl$ and [Pt(chelate)$CH_3$(X)]$ClO_4$ complexes*

A similar procedure was used to prepare these cationic and neutral complexes, so only a representative preparation is given for each class.

*Preparation of Pt(S-alap)$CH_3Cl$*

1.5 g of Pt(COD)$CH_3$Cl [13] was dissolved in 25 ml of dichloromethane, 2.06 g of *S*-alap was added, and the solution stirred for one hour. The volume was reduced to 5 ml, ether was added and the solution cooled. 2.75 g of white powder was filtered off (yield 77%).

*Preparation of [Pt(S,S-chiraphos)$CH_3(PPh_3)$]$ClO_4$*

109 mg of Pt(*S,S*-chiraphos)$CH_3Cl$ was dissolved in 5 ml of acetone and 10 ml of dichloromethane. 34 mg of $AgClO_4$ was added and the solution stirred for 15 minutes. The solution was centrifuged to remove the AgCl which precipitated. After decantation 42 mg of triphenylphosphine was added and the solution stirred for 10 minutes. The solvent was removed, the residue taken up in 2 ml of dichloromethane and filtered into a 10 mm $^{31}P$ NMR tube. Where solid samples were isolated, ether addition to the dichloromethane solution caused crystallization.

*Preparation of [Pt(S,S,-chiraphos)$CH_3(C_5H_5N)$]$ClO_4$*

109 mg of Pt(*S,S*-chiraphos)$CH_3Cl$ was dissolved in 5 ml of acetone and 10 ml of dichloromethane. 34 mg of $AgClO_4$ was added, and the solution stirred for 15 minutes. The solution was centrifuged to remove the AgCl. After decantation 25 $\mu$l of pyridine was added, and the solution again stirred for 10 minutes. The solvent was removed, the residue taken up in 2 ml of dichloromethane and filtered into a 10 mm $^{31}P$ NMR tube. Where samples were isolated, ether was added to the dichloromethane solution until crystallization occurred.

The cationic complexes [Pt(chelate)$CH_3$(acetone)]$ClO_4$ were prepared in an analogous manner, and the $^{31}P$ NMR spectra were recorded in acetone.

Satisfactory analytical data for the new bidentate phosphines, their chloromethylplatinum complexes and a representative sampling of the cationic pyridine complexes were obtained, Table 5. Elemental analyses for a number of the cationic phosphine, arsine and stibine complexes are given in Table 6. In addition, the $^{31}P$, $^1H$ NMR and IR spectra of these platinum complexes and all phosphines were consistent with their formulations.

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