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Resolutions Involving Metal Complexation. Optical Resolution of (±)-Methylphenylphosphine in the Complex [(*S*),(*S*,*S*)]-$(+)_{589}$-[PtCl(PHMePh){1,2-$C_6H_4(PMePh)_2$}]$PF_6 \cdot CH_2Cl_2$

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Abstract: Configurationally homogeneous [(*S*),(*S*,*S*)]-$(+)_{589}$-[PtCl(PHMePh){1,2-C_6H_4 $(PMePh)_2$}]$PF_6 \cdot CH_2Cl_2$ has been isolated and its structure determined by X-ray diffraction.

Compared with the extensive chemistry of chiral tertiary phosphines and their complexes,[1] derivatives of chiral secondary phosphines are few. Nevertheless, investigations conducted hitherto of the reactivity and stereochemical behaviour of various chiral 4-coordinate phosphorus compounds containing P–H bonds have yielded interesting results. Of particular relevance to the present investigation are chiral secondary phosphine–metal complexes ($R_1R_2HP \rightarrow M^+$),[2] – boranes ($R_1R_2HP \rightarrow BH_3$),[3] and – chalcogenides ($R_1R_2HP \rightarrow X$, where X = O, S, or Se).[4] Related systems of importance are the phosphinates [R(RO)HP→O][5] and unsymmetrically substituted phosphonates [$(RO)_2HP \rightarrow O$].[6] Here we report the preparation and crystal structure of the complex [(*S*),(*S*,*S*)]-$(+)_{589}$-[PtCl(PHMePh){1,2-$C_6H_4(PMePh)_2$}]$PF_6 \cdot CH_2Cl_2$, which contains one enantiomer of (±)-methylphenylphosphine.

Optically active (*S*,*S*)-[$PtCl_2${1,2-$C_6H_4(PMePh)_2$}] (**1**)[7] reacts with 1 equiv. of silver nitrate in acetone to give a solution containing [(*S*,*S*),(*S*,*S*)]-[Pt_2Cl_2{1,2-$C_6H_4(PMePh)_2$}$_2$]$(NO_3)_2$ as the predominant species,[8] which, upon treatment with (±)-methylphenylphosphine and ammonium hexafluorophosphate, affords the complex [PtCl(PHMePh){1,2-$C_6H_4(PMePh)_2$}]PF_6 (**2**) as a mixture of the two diastereomers (*R*),(*S*,*S*)-**2** and (*S*),(*S*,*S*)-**2** (Scheme 1). Fractional crystallization of the *ca* 1:3 mixture from dichloromethane–diethyl ether gives the configurationally homogeneous (*S*),(*S*,*S*) diastereomer of **2** as the 1-dichloromethane solvate, *viz.* [(*S*),(*S*,*S*)]-[PtCl(PHMePh){1,2-$C_6H_4(PMePh)_2$}]$PF_6 \cdot CH_2Cl_2$, $[\alpha]_{589}$ +56° (*c* 1, CH_2Cl_2).

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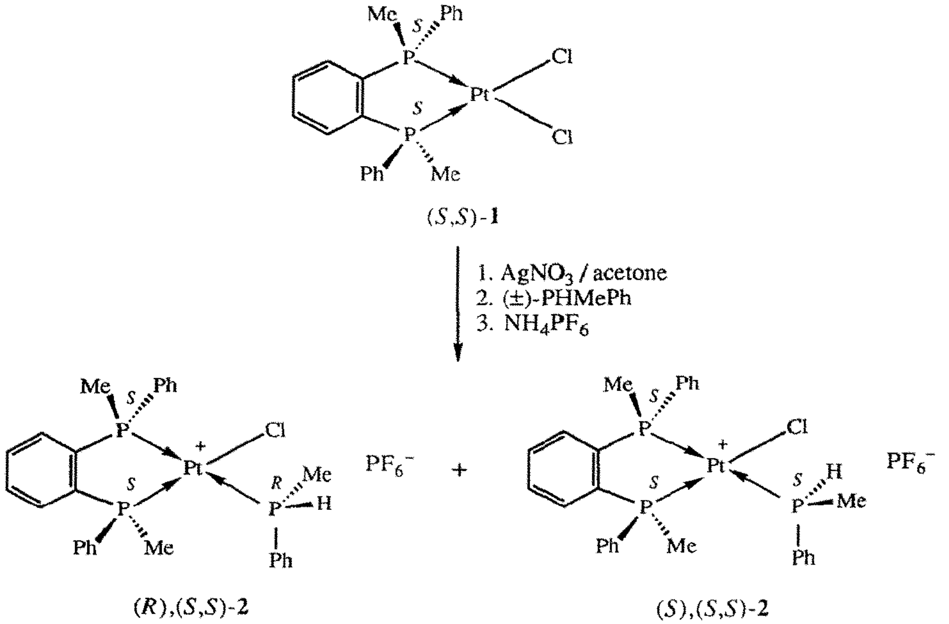
The structure of the cation, as determined by single-crystal X-ray diffraction of (*S*),(*S*,*S*)-**2**·CH_2Cl_2, is given in Figure 1.[9] The geometry around the platinum is square-planar with the angle between the planes defined by P(1), Pt, Cl and P(2), Pt, P(3) being 1.85°. The bonding around the secondary phosphine–*P* stereocentre in the complex cation corresponds closely with that in the complex [(*R**,*R**),(*R**)]-(±)-[(η^5-C_5H_5){1,2-$C_6H_4(PMePh)_2$}Fe(PHMePh)]PF_6·0.5CH_2Cl_2.[2]

Scheme 1



The diastereomers (*R*),(*S*,*S*)-**2** and (*S*),(*S*,*S*)-**2** are readily distinguished by their $^{31}P\{^1H\}$ NMR spectra in dichloromethane-d_2. Each diastereomer gives rise to an ABX line pattern with satellites due to ^{31}P–^{195}Pt coupling.[10] The chemical shifts and coupling constants for the two isomers are within the normal ranges.[11] Pure (*S*),(*S*,*S*)-**2** is configurationally stable in dichloromethane-d_2 for at least 24 h at 20 °C. Interconversion between the diastereomers is catalyzed, however, by traces of chloride or water. The mechanism of the interconversion is believed to involve reversible displacement of the secondary phosphine, which racemizes under the experimental conditions in the free state.

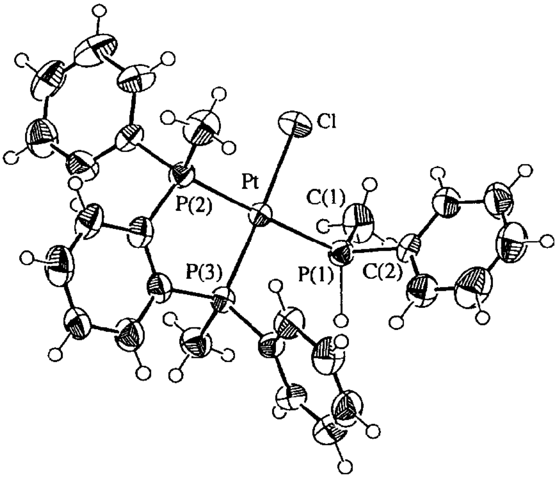


Figure 1. ORTEP plot of the cation of (*S*),(*S*,*S*)-2·CH_2Cl_2. Selected interatomic distances and angles are as follows: Pt-P(1) 2.325(4), Pt-P(2) 2.288(4), Pt-P(3) 2.226(3), Pt-Cl 2.343(4), P(1)-C(1) 1.813(9), P(1)-C(2) 1.803(8) Å; P(1)-Pt-P(2) 177.8(1), P(1)-Pt-P(3) 94.4(1), P(2)-Pt-P(3) 86.9(1), P(1)-Pt-Cl 88.7(2), P(3)-Pt-Cl 176.7(1), P(2)-Pt-Cl 89.9(2)°.

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9. Crystal data: (*S*,*S*),(*S*)-**2**, $C_{28}H_{31}Cl_3F_6P_4Pt$, M = 906.88, triclinic; space group $P1$, a = 8.816(1), b = 9.122(1), c = 10.556(1) Å, α = 93.50(1), β = 97.81(1), γ = 94.76(1)°, U = 835.87 Å^3, Z = 1, D_c = 1.801 g cm^{-3}, $F(000)$ = 442, μ (Cu K_α) = 125.3 cm^{-3}. All of the 2785 data collected (Philips PW 1100/20 diffractometer, 20 °C) were considered observed [$I > 3\sigma(I)$]. After the data were corrected for absorption, the structure was solved by Patterson synthesis, ΔF synthesis, and full-matrix least-squares refinement to give values for R and R_w of 0.024 and 0.030, respectively. Full details of the crystal structure have been deposited at the Cambridge Data Centre.
10. $^{31}P\{^1H\}$ NMR data (121.42 MHz, CD_2Cl_2, 20 °C) of (*S*,*S*),(*S*)-**2** [(*S*,*S*),(*R*)-**2**]: $\delta(P_A)$ 47.1 [47.3], $\delta(P_B)$ 31.9 [32.2], $\delta(P_C)$ −16.7 [−15.9] ppm: $|^2J(P_AP_B)|$ 6.1 [6.1], $|^2J(P_AP_C)|$ 390.6 [393], $|^2J(P_BP_C)|$ 15.3 [17.5], $|^1J(PtP_A)|$ 2393 [2396], $|^1J(PtP_B)|$ 3279 [3290], $|^1J(PtP_C)|$ 2268 [2275] Hz.
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