Stereochemistry and Stability of Free and Coordinated Secondary Phosphines. Crystal and Molecular Structure of [S-[(R*,R*),(R*)]]-(+)$_{589}$-[PtCl{1,2-C$_6$H$_4$(PMePh)$_2$}(PHMePh)]PF$_6$·CH$_2$Cl$_2$[†]

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Optically active (S,S)-[PtCl$_2${1,2-C$_6$H$_4$(PMePh)$_2$}], (S,S)-**1**, reacts with 1 equiv of silver nitrate in acetone to give the corresponding chloro-bridged diplatinum complex, which, when treated with (±)-methylphenylphosphine in the presence of trifluoromethanesulfonic acid, affords, following metathesis of intermediate salts with ammonium hexafluorophosphate, the complex [PtCl{1,2-C$_6$H$_4$(PMePh)$_2$}(PHMePh)]PF$_6$, **2**, as a diastereomeric pair, epimeric at the secondary phosphine-P stereocenter, with (S,S),(S)/(S,S),(R) = 2/1 in dichloromethane-d_2. Recrystallization of this mixture from dichloromethane–diethyl ether gives colorless prisms of (S,S),(S)-[PtCl{1,2-C$_6$H$_4$(PMePh)$_2$}(PHMePh)]PF$_6$·CH$_2$Cl$_2$, (S,S),(S)-**2**·CH$_2$Cl$_2$, having [α]$_{589}$ +56 (c 1, CH$_2$Cl$_2$). The crystal structure of the configurationally homogeneous secondary phosphine complex has been determined. Crystal data for C$_{28}$H$_{31}$Cl$_3$F$_6$P$_4$Pt: triclinic, P1, a = 8.816(1) Å, b = 9.122(1) Å, c = 10.556(1) Å, α = 93.50(1)° β = 97.81(1)°, δ = 94.76(1)° Z = 1, and R = 0.024. Pure (S,S),(S)-**2**·CH$_2$Cl$_2$ is stable in dichloromethane solution, but epimerization at the secondary phosphine-P stereocenter occurs rapidly in the presence of traces of chloride or water to give an equilibrium mixture of the two epimers with (S,S),(S)/(S,S),(R) = 2/1 at 23 °C. All attempts at displacing resolved (±)-PHMePh from (S,S),(S)-**2**·CH$_2$Cl$_2$ were unsuccessful. Indeed, simple secondary phosphines of this type, although possessing a considerable barrier to unimolecular inversion, viz. E$_{inv}$ > 97.5 ± 0.5 kJ mol^{-1}, undergo facile intermolecular proton exchange in the presence of traces of acids or cationic secondary phosphine complexes, for example, (S,S),(S)-**2**·CH$_2$Cl$_2$. Nevertheless, isotopic exchange experiments between (±)-PHMePh and (±)-PDEtPh revealed negligible proton exchange between the phosphines in highly purified acetonitrile containing sodium acetylacetonate as a proton scavenger, thus indicating that the optical resolution of a simple secondary phosphine of the type (±)-PHR^{1}R^2 may be feasible under mildly basic conditions.

Introduction

Since the pioneering work on the resolution of chiral phosphonium salts and phosphine oxides[2] and their subsequent conversion into resolved mono- and bis(tertiary phosphines),[3] a variety of other tertiary phosphines chiral at phosphorus or at neighboring stereogenic centers, axes, or planes have been synthesized.[4] Although optically active four-coordinate adducts of *secondary* phosphines have been described, including sec-

ondary phosphine–metal complexes (R^{1}R^{2}HP→Fe$^+$),[5] −chalcogenides (R^{1}R^{2}HP→X, where X = O, S, or Se),[6] and −boranes (R^{1}R^{2}HP→BH$_3$),[7] as well as certain phosphinates [R(RO)-HP→O][8] and phosphonates [R^{1}O(R^{2}O)HP→O],[9] the displacement of the optically active secondary phosphine from the adducts has not been accomplished. In recent work, however, we described the isolation of a single diastereoisomer of (−)-menthylmesitylphosphine by fractional crystallization of the diastereomeric mixture from acetonitrile in the presence of

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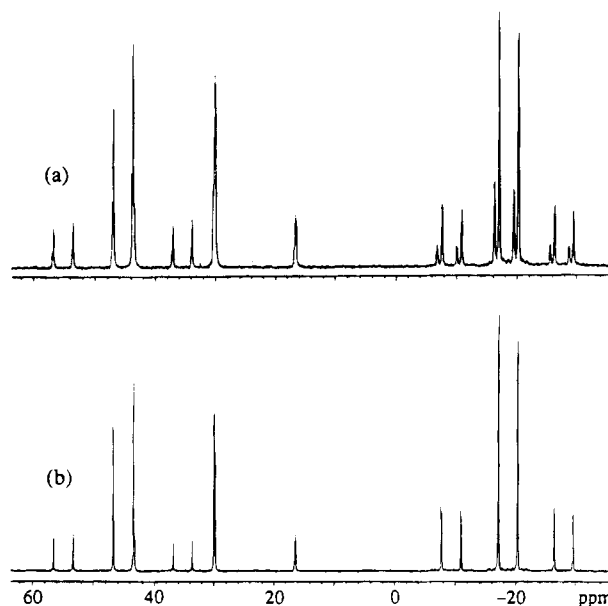
Scheme 1

$(S,S) - 1$

1. AgNO$_3$/Me$_2$CO
2. (±)-PHMePh
3. NH$_4$PF$_6$

$(S,S),(R) - 2$ + $(S,S),(S) - 2$
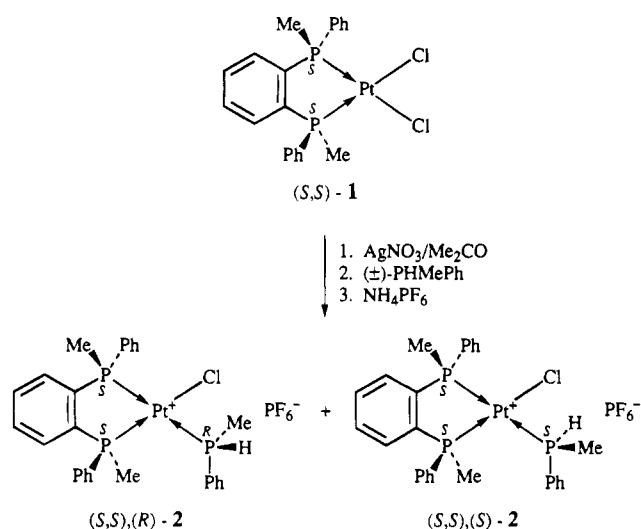
sodium acetylacetonate as a proton scavenger, thereby effecting the first resolution of a free secondary phosphine.[10] Here we describe the reaction between $[S-(R^*,R^*)]-(+)_{589}$ - [PtCl$_2$\{1,2-C$_6$H$_4$(PMePh)$_2$\}], (S,S)-1[11] and the simple secondary phosphine (±)-methylphenylphosphine and the isolation and characterization of $[S-(R^*,R^*),(R^*)]-(+)_{589}$-[PtCl\{1,2-C$_6H_4$(PMePh)$_2$\}(PHMe-Ph)]PF$_6$•CH$_2Cl_2$, $(S,S),(S)$-2•CH$_2$Cl$_2$, and comment upon the stability and potential use of the complex as a source of the enantiomers of (±)-methylphenylphosphine. As part of the work, we have investigated unimolecular inversion and intermolecular H/D exchange between secondary phosphines under acid- and base-catalyzed conditions. A preliminary account of part of the work has been published.[12] The various aspects of the work will be introduced in the sections that follow.

Results and Discussion

(a) Synthesis and Isolation of $(S,S),(S)$-2•CH$_2$Cl$_2$. Optically pure (S,S)-[PtCl$_2$\{1,2-C$_6$H$_4$(PMePh)$_2$\}], (S,S)-1, reacts with 1 equiv of silver nitrate in acetone to give a solution of the chloro-bridged dimer as the predominant species;[13] the solution upon acidification with trifluoromethanesulfonic acid and treatment with (±)-methylphenylphosphine and ammonium hexafluoro-phosphate affords in high yield crystalline [PtCl\{1,2-C$_6$H$_4$-(PMePh)$_2$\}(PHMePh)]PF$_6$, 2, as 2:1 mixture of diastereomers, viz. $(S,S),(S)$- and $(S,S),(R)$-2, which are epimeric at the secondary phosphine-P stereocenter (Scheme 1). The 2:1 mixture arises from equilibration between the diastereomers under the reaction conditions (see below). As a model for the chloro-bridged intermediate, $(S,S),(S,S)$-[Pt$_2$Cl$_2$\{1,2-C$_6$H$_4$-(PMePh)$_2$\}$_2$](AsF$_6$)$_2$, $(S,S),(S,S)$-3, was isolated: in acetone-d_6 the dimer is in equilibrium with a small quantity (ca. 28%) of the acetone-d_6 complex (S,S)-[PtCl\{1,2-C$_6$H$_4$(PMePh)$_2$\}(Me$_2$-CO-d_6)]AsF$_6$ (Scheme 2). The ^{31}P\{^{1}H\} NMR spectrum of the mixture of $(S,S),(S)$- and $(S,S),(R)$-2 in dichloromethane-d_2 at

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Figure 1. (a) ^{31}P\{^{1}H\} NMR spectrum of equilibrium mixture of $(S,S),$-(S)- and $(S,S),(R)$-2 in dichloromethane-d_2 at 23 °C. (b) ^{31}P\{^{1}H\} NMR spectrum of of $(S,S),(S)$-2•CH$_2$Cl$_2$ under similar conditions.

Scheme 2

$(S,S),(S,S) - 3$

Me$_2$CO
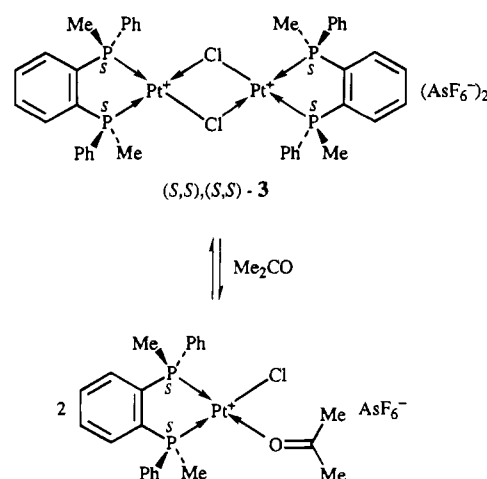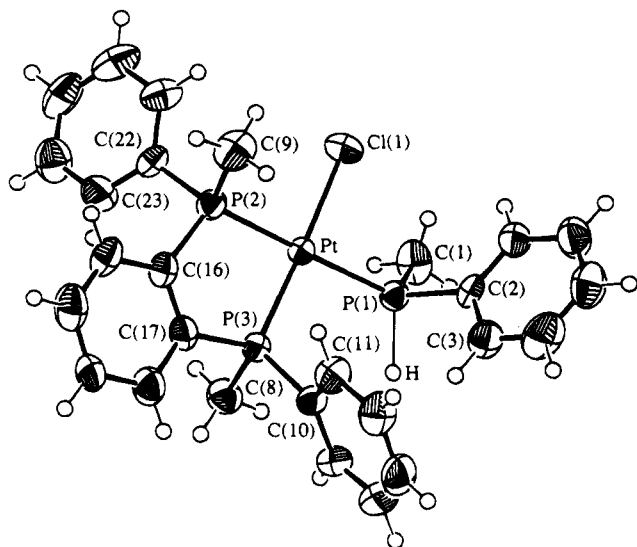

23 °C is reproduced in Figure 1a. Fractional crystallization of the mixture from dichloromethane−diethyl ether afforded the configurationally homogeneous $(S,S),(S)$ diastereomer as the 1-dichloromethane solvate in 50% yield as colorless prisms having [α]$_{589}$ +56 (c 1, CH$_2$Cl$_2$). The molecular structure of the diastereomer was confirmed by X-ray crystallography (see below).

(b) Crystal and Molecular Structure of $(S,S),(S)$-2•CH$_2$Cl$_2$. The molecular structure of the cation of $(S,S),(S)$-2•CH$_2$Cl$_2$ is depicted in Figure 2. Crystal data for the complex are given in Table 1. Table 2 gives positional parameters for the compound, employing the atom-labeling scheme given in Figure 2; Table 3 lists most important bond distances and angles. The Pt−P(1) bond of the coordinated secondary phosphine in the complex is significantly longer than the distances Pt−P(2) and Pt−P(3) of the chelated bis(tertiary phosphine), which reflects the weaker coordinating ability of the secondary phosphine. The geometry around the platinum in the complex is close to planarity, with an angle of 1.85° between the planes defined by the atoms P(1), Pt, Cl(1) and P(2), Pt, P(3). The bonding around P(1) is similar to that in $[(R^*,R^*),(R^*)]-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}-Fe(PHMePh)]PF_6$•CH$_2Cl_2$.[5]

Figure 2. ORTEP view of cation of $(S,S),(S)$-2·CH$_2$Cl$_2$ showing the atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels.

Table 1. Crystallographic Data for $(S),(S,S)$-2·CH$_2$Cl$_2$[a]

formula	C$_{28}$H$_{31}$Cl$_3$F$_6$P$_4$Pt
fw	906.88
cryst form	colorless trigonal prisms
cryst system	triclinic
space group	$P1$
a, Å	8.816(1)
b, Å	9.122(1)
c, Å	10.556(1)
α, deg	93.50(1)
β, deg	97.81(1)
γ, deg	97.81(1)
V, Å^3	835.87
Z	1
cryst dimens, mm	0.20 × 0.13 × 0.24
d_{calcd}, g cm^{-3}	1.801
μ(Cu Kα), cm^{-1}	125.3
X-ray radiation (λ, Å)	Cu Kα (1.5418)
T, °C	20(1)
data range, deg in 2θ	4–128
no. of data colld	2785
no. of data refined	2785 [$I > 3\sigma(I)$]
no. of variables	372
R^b	0.024
$R_w{}^c$	0.030
GOF^d	1.52
$F(000)$	442

[a] Estimated standard deviations for the data in this table and elsewhere in this paper refer to the least significant figure and are given in parentheses. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma(wF_o)^2\}^{1/2}$. [d] GOF $= \{\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})\}^{1/2}$.

(c) ^{31}P{^{1}H} NMR Spectra of Diastereomers. The diastereomers of **2** are unambiguously distinguished by their ^{31}P{^{1}H}-NMR spectra in dichloromethane-d_2 (Figure 1). Each diastereomeric cation gives rise to an ABX line pattern with satellites due to ^{31}P$-^{195}$Pt coupling;[13–15] the spectrum of the $(S,S),(S)$ diastereomer is reproduced in Figure 1b. The ^{31}P{^{1}H} NMR spectrum in each case is first-order and spin-simulation results confirmed the assignments for the two complexes; the NMR data are compiled in Table 4. The phosphorus nuclei of the

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters^a (Å) for Non-Hydrogen Atoms in $(S),(S,S)$-2·CH$_2$Cl$_2$

	x/a	y/b	z/c	U_{eq}
Pt	$^1/_2$	$^1/_2$	$^1/_2$	0.03337(8)
P(1)	0.4973(4)	0.4828(4)	0.2790(4)	0.038(1)
P(2)	0.5074(5)	0.5259(4)	0.7178(4)	0.041(1)
P(3)	0.6015(4)	0.2869(3)	0.5285(3)	0.0345(7)
Cl(1)	0.3966(6)	0.7276(4)	0.4826(5)	0.065(1)
C(1)	0.3184(9)	0.521(1)	0.1858(9)	0.059(3)
C(2)	0.6464(8)	0.6007(8)	0.2253(6)	0.039(2)
C(3)	0.791(1)	0.553(1)	0.2211(9)	0.055(3)
C(4)	0.902(2)	0.640(3)	0.179(2)	0.079(6)
C(5)	0.876(1)	0.779(1)	0.140(1)	0.073(4)
C(6)	0.734(1)	0.828(1)	0.143(1)	0.065(3)
C(7)	0.6184(9)	0.7401(9)	0.1869(8)	0.050(2)
C(8)	0.4778(9)	0.1238(9)	0.4680(8)	0.052(2)
C(9)	0.615(1)	0.693(1)	0.7919(9)	0.065(3)
C(10)	0.7815(7)	0.2761(7)	0.4656(6)	0.039(2)
C(11)	0.9012(9)	0.3807(9)	0.5176(8)	0.052(2)
C(12)	1.0434(9)	0.380(1)	0.470(1)	0.062(3)
C(13)	1.060(1)	0.276(1)	0.375(1)	0.066(3)
C(14)	0.941(1)	0.175(1)	0.323(1)	0.067(3)
C(15)	0.799(1)	0.1746(9)	0.3695(8)	0.052(2)
C(16)	0.6059(8)	0.3720(9)	0.7841(7)	0.044(2)
C(17)	0.6485(8)	0.2680(8)	0.7002(7)	0.042(2)
C(18)	0.725(1)	0.1504(9)	0.7467(6)	0.056(3)
C(19)	0.753(1)	0.1366(9)	0.8799(7)	0.055(3)
C(20)	0.711(1)	0.244(1)	0.9628(6)	0.070(3)
C(21)	0.634(1)	0.3591(9)	0.9158(7)	0.057(3)
C(22)	0.3225(8)	0.5160(8)	0.7756(6)	0.043(2)
C(23)	0.253(1)	0.382(1)	0.799(1)	0.056(3)
C(24)	0.109(2)	0.373(2)	0.841(2)	0.068(5)
C(25)	0.041(1)	0.500(1)	0.861(1)	0.073(4)
C(26)	0.111(1)	0.636(1)	0.839(1)	0.078(4)
C(27)	0.252(1)	0.645(1)	0.795(1)	0.061(3)
P(4)	0.2930(3)	0.0346(2)	0.0672(2)	0.0575(7)
F(1A)^b	0.258(3)	−0.105(3)	0.146(2)	0.104(4)^c
F(1B)^b	0.290(2)	−0.135(2)	0.056(2)	0.104(4)^c
F(2)	0.4621(8)	0.0575(9)	0.1460(7)	0.089(3)
F(3A)^b	0.236(2)	0.118(2)	0.182(2)	0.109(3)^c
F(3B)^b	0.224(2)	0.008(2)	0.201(2)	0.109(3)^c
F(4A)^b	0.337(2)	0.195(2)	0.018(2)	0.110(3)^c
F(4B)^b	0.263(2)	0.199(2)	0.105(2)	0.110(3)^c
F(5)	0.1274(9)	0.012(1)	−0.0088(9)	0.117(3)
F(6A)^b	0.375(2)	−0.041(2)	−0.041(2)	0.116(4)^c
F(6B)^b	0.340(2)	0.070(2)	−0.063(2)	0.116(4)^c
C(28)	1.031(2)	0.860(2)	0.522(1)	0.091(5)
Cl(2)	0.8364(4)	0.8046(4)	0.5231(4)	0.095(1)
Cl(3)	1.1058(5)	0.9908(5)	0.6424(4)	0.111(1)

^{a} $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$. ^{b} Occupancy 0.5. ^{c} Isotropic U with constraint $U[F(nA)] = U[F(nB)]$.

Table 3. Selected Bond Distances and Angles for $(S),(S,S)$-2·CH$_2$Cl$_2$

Distances (Å)			
Pt−P(1)	2.325(4)	Pt−P(2)	2.288(4)
Pt−P(3)	2.226(3)	Pt−Cl(1)	2.343(4)
P(1)−C(1)	1.813(9)	P(1)−C(2)	1.803(8)
P(2)−C(9)	1.80(1)	P(2)−C(22)	1.814(9)
P(2)−C(16)	1.836(9)	C(16)−C(17)	1.37(1)
P(3)−C(8)	1.800(8)	P(3)−C(10)	1.810(8)
P(3)−C(17)	1.826(8)		

Angles (deg)			
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(1)	88.7(2)
P(3)−Pt−Cl(1)	176.7(1)	P(2)−Pt−Cl(1)	89.9(2)
Pt−P(2)−C(16)	107.1(3)	Pt−P(3)−C(17)	108.8(3)
Pt−P(2)−C(9)	113.8(4)	Pt−P(2)−C(22)	115.9(3)
Pt−P(3)−C(8)	115.6(3)	Pt−P(3)−C(17)	108.8(3)
P(2)−C(16)−C(17)	118.1(5)	C(16)−C(17)−P(3)	118.6(6)

bis(tertiary phosphine) give rise to the AB part of the spectrum, and the secondary phosphine gives rise to the X part. The secondary phosphine-P nucleus of each diastereomer resonates

Table 4. $^{31}P\{^1H\}$ NMR Data for $(S),(S,S)$-2 and $(R),(S,S)$-2[a]

	$\delta(P_A)$, $\delta(P_B)$, $\delta(P_C)$	$\|^2J(P_AP_B)\|$, $\|^2J(P_AP_C)\|$, $\|^2J(P_BP_C)\|$	$\|^1J(PtP_A)\|$, $\|^1J(PtP_B)\|$, $\|^1J(PtP_C)\|$
$(S,S),(S)$-2	47.1, 31.9, −16.7	6.1, 390.6, 15.3	2393, 3279, 2268
$(S,S),(R)$-2	47.3, 32.2, −15.9	6.1, 393.0, 17.5	2396, 3290, 2275

[a] 121.42 MHz, in CD_2Cl_2 at 23 °C. Chemical shifts in ppm relative to external H_3PO_4 with downfield shifts as positive. Coupling constants in Hz. P_A, P_B, and P_C represent the phosphine groups of the chelating diphos and the PHMePh ligand, respectively. P_A and P_C are *trans* to each other.

well upfield of the tertiary phosphine-*P* nuclei of the bis(tertiary phosphine); moreover, the latter nucleus in each case has an additional downfield shift due to its incorporation into a five-membered chelate ring.[16] Each phosphorus atom of each diastereomer of **2** resonates as a doublet of doublets with platinum satellites. The coupling constants ^{31}P–^{31}P and ^{31}P–^{195}Pt for the diastereomers are typical for such complexes, viz. $^2J(PP) < 20$ Hz (P cis to P), $^2J(PP) > 350$ Hz (P trans to P), $^1J(PPt) < 2500$ Hz (P trans to P), and $^1J(PPt) > 3000$ Hz (P trans to Cl).

Pure $(S,S),(S)$-2·CH_2Cl_2 in dichloromethane-d_2 at ca. 20 °C retains its configurational integrity for at least 24 h. In the presence of traces of chloride or water, however, an equilibrium is rapidly established between the $(S,S),(S)$ and $(S,S),(R)$ forms of the complex (first-order asymmetric transformation).[17] The epimerization at the secondary phosphine-*P* stereocenter of $(S,S),(S)$-2 is believed to occur via chloride- or water-induced reversible displacement of the weakly coordinated resolved secondary phosphine. Under the experimental conditions prevailing the free secondary phosphine will racemize (see below) with re-coordination to the metal giving both diastereomers. At equilibrium in dichloromethane-d_2 at 23 °C, $(S,S),$-(S)-2/$(S,S),(R)$-2 = 2/1. The addition of a drop of [Et_4N]Cl in dichloromethane-d_2 (10^{-4} M) to a solution of $(S,S),(S)$-2·CH_2Cl_2 in the same solvent causes substantial line-broadening in the $^{31}P\{^1H\}$ NMR spectrum. Moreover, the signals due to P_A of the bis(tertiary phosphine) trans to PHMePh are shifted slightly downfield in the presence of chloride, whereas the signals due to P_B of the bis(tertiary phosphine) trans to Cl remain unaffected. It is noteworthy that similar behavior is observed in [$PtCl(Ph_2PCH_2PPh_2)(PMePh_2)$]Cl.[15b]

(d) Racemization of Free Secondary Phosphines. Intramolecular inversion barriers for pyramidal trivalent phosphorus compounds are affected by steric effects, effects of conjugation, effects of angular restraint, and effects of substitution at phosphorus.[18] Steric effects are relatively small, but conjugative effects or substitution by electronegative groups at phosphorus can be large. For example, the barriers to inversion of the

(a)

(b)
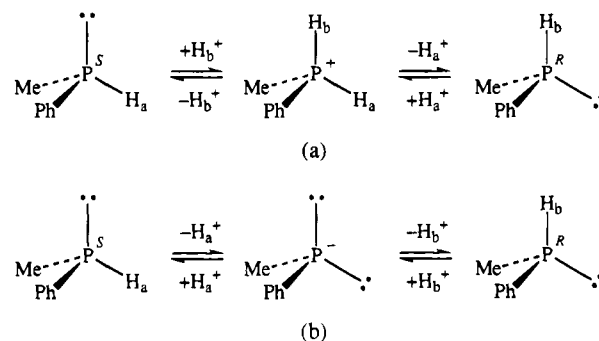
Figure 3. Acid- (a) and base- (b) catalyzed racemization of (±)-methylphenylphosphine.

tertiary phosphines (±)-PMePhR (where R = *n*-Pr, allyl, or *tert*-butyl) fall within the narrow range of values 134−138 kJ mol^{-1}, whereas for (±)-PPh(*iso*-Pr)R (where R = $COCH_3$ or $SiMe_3$) the inversion barrier in each case is 79.5 kJ mol^{-1}. It is not always straightforward, however, to differentiate true first-order pyramidal inversion in a trivalent phosphine from transformations involving dissociation−combination, bimolecular exchange, and other chemical mechanisms. Secondary phosphines fall within the more difficult category because protonation at phosphorus by an adventitious proton source or deprotonation by traces of base symmetrizes the phosphorus stereocenter (see below). To our knowledge, empirical data for first-order inversion in a simple non-cyclic secondary phosphine have not been reported hitherto, although configurational stability at phosphorus has been established by NMR spectroscopy for (±)-PHEtPh in the range 20−60 °C.[19]

(e) Unimolecular Inversion in Secondary Phosphines. The ^1H NMR spectrum in the nonaromatic region of (±)-PHPh-(*iso*-Pr) in *o*-xylene-d_{10} at 23 °C can be interpreted in terms of an A_3B_3CMX spin system because the chemical shift difference between the methyl and methine protons is sufficiently large to permit a first-order analysis. The full spectrum consists of two multiplets in the range 6.99−7.36 ppm (aromatic protons), a doublet ($J_{MX} = 203.7$ Hz) of doublets ($J_{CM} = 6.0$ Hz) centered at 3.89 ppm (PH), a multiplet between 1.77 and 1.95 ppm (C*H*Me$_2$), and two overlapping doublets of doublets at 0.99 ppm ($J_{BX} = 12.6$ Hz, $J_{BC} = 7.2$ Hz) and 0.95 ppm ($J_{AX} = 15.0$ Hz, $J_{AC} = 6.9$ Hz) (CH*Me*$_2$). The 8-line isopropyl-*methyl* multiplet is implicit of chiratopic phosphorus. The spectrum at 140 °C in the same solvent is broadened, but collapse of the isopropyl-*methyl* resonances (which would be indicative of unimolecular inversion at phosphorus) is clearly not evident. If 140 °C is taken as the lower limit for the coalescence that would result from faster inversion, it can be calculated from the NMR data that the lower limit for the rate constant for intramolecular inversion at phosphorus at this temperature is 6.6 s^{-1}. If Eyring's equation is applied, the minimum value for the free energy of activation for inversion at phosphorus in (±)-PHPh-(*iso*-Pr) is 97.5 ± 0.5 kJ mol^{-1} at 140 °C.

(f) Bimolecular H/D Exchange in Secondary Phosphines. Acid-catalyzed racemization of a chiral secondary phosphine involves the formation of an achiral phosphonium salt as indicated in Figure 3a. The P−H protons of the catalytic quantity of the phosphonium ion are enantiotopic and therefore will be removed at identical rates during subsequent proton

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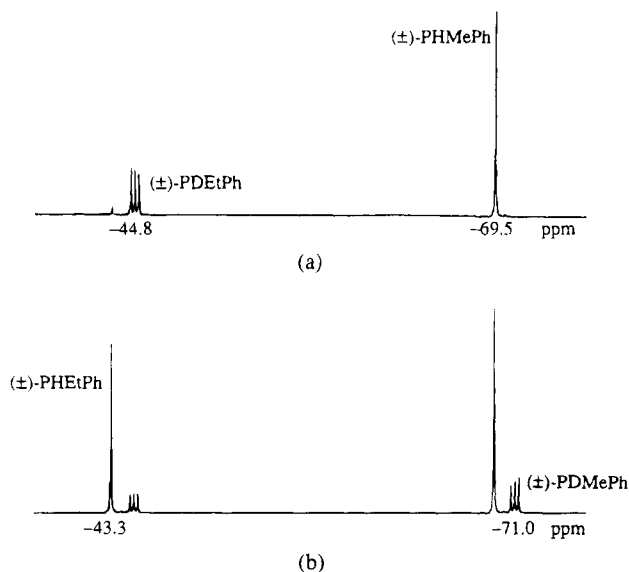
Figure 4. $^{31}P\{^1H\}$ NMR spectrum of an equimolar mixture of ($\pm$)-PHMePh and ($\pm$)-PDEtPh in acetonitrile-d_3 after 5 min (a) and after 12 h (b).

transfer (to free phosphine) to give ultimately equal amounts of the two enantiomers of the secondary phosphine. Adventitious proton sources will thus lead to racemization of optically active secondary phosphines chiral at phosphorus.

In order to establish an approximate time scale for bimolecular proton exchange in a typical secondary phosphine, we have investigated H/D exchange between ($\pm$)-PHMePh and ($\pm$)-PDEtPh at 23 °C in various solvents under acid-free and weakly acidic conditions. H/D exchange between these phosphines will lead to two new phosphines, according to the following equation:

$$(\pm)\text{-PHMePh} + (\pm)\text{-PDEtPh} \rightleftharpoons$$
$$(\pm)\text{-PDMePh} + (\pm)\text{-PHEtPh}$$
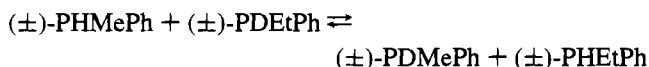
In Figure 4a the $^{31}P\{^1H\}$ NMR spectrum of an approximately equimolar mixture of ($\pm$)-PHMePh and ($\pm$)-PDEtPh in acetonitrile-d_3 at 23 °C is reproduced; Figure 4b shows the spectrum of the same solution after 12 h. A similar situation prevails when the phosphines are dissolved in benzene, diethyl ether, or *n*-hexane. In the presence of a trace of sodium acetylacetonate, however, mixtures of ($\pm$)-PHMePh and ($\pm$)-PDEtPh in pure acetonitrile showed no detectable H/D exchange after 3 days. Thus, sodium acetylacetonate is an effective proton scavenger in acetonitrile but is not sufficiently basic to deprotonate secondary phosphines of this type, which would lead to racemization of phosphines by the base-catalyzed mechanism (Figure 3b).

(g) Attempted Displacement of (*R*)-PHMePh from (*S,S*),-(*S*)-2•CH₂Cl₂. The secondary phosphine in (*S,S*),(*S*)-2•CH₂Cl₂ is readily displaced by 1 equiv of (*S,S*)-1,2-C₆H₄(PMePh)₂ in tetrahydrofuran, giving as the byproduct the sparingly soluble meso complex (*R,R*),(*S,S*)-[Pt{1,2-C₆H₄(PMePh)₂}₂]Cl(PF₆). Despite scrupulous attention to procedures and conditions, however, the secondary phosphine liberated in this reaction was optically inactive. Displacements with cyanide also led to inactive product. It was subsequently discovered that H/D exchange between ($\pm$)-PHMePh and ($\pm$)-PDEtPh was catalyzed by traces of (*S,S*),(*S*)-2•CH₂Cl₂, a weak acid. Moreover, chloride produced in the displacement of the secondary phosphine from **2** by the chelating bis(tertiary phosphine) or cyanide is also capable of catalyzing intermolecular proton exchange between secondary phosphines. Thus, the complex (*S,S*),(*S*)-2•CH₂Cl₂

appears to be an intrinsically unsuitable precursor of resolved methylphenylphosphine.

Conclusion. Simple enantiomeric secondary phosphines of the type ($\pm$)-PHR¹R² are stable to inversion and intermolecular proton exchange under acid-free conditions. Moreover, the secondary phosphines can be readily resolved in diastereomeric platinum(II) complexes from which they can be displaced under mild conditions. Cationic secondary phosphine complexes of the type employed in this work, however, are sufficiently acidic to cause racemization of resolved secondary phosphines following displacement from the metal.

Experimental Section

Manipulations involving air-sensitive compounds were performed under an argon atmosphere with use of the Schlenk technique. Diethyl ether and dichloromethane were freshly distilled from sodium benzophenone ketyl and calcium hydride, respectively, and stored under argon. Commercial acetonitrile was purified according to the following steps: (i) heating under reflux for 1 h over anhydrous aluminium chloride (15 g L⁻¹) followed by rapid distillation; (ii) heating under reflux over alkaline permanganate (10 g L⁻¹ of KMnO₄ and 10 g L⁻¹ of Li₂CO₃) followed by rapid distillation; (iii) heating under reflux for 1 h over potassium bisulphate (15 g L⁻¹) followed by rapid distillation; (iv) stirring over calcium hydride (2 g L⁻¹) for 12 h followed by heating under reflux for 1 h and then distillation through a column packed with glass helices.[20] The middle fraction of the final distillate (ca. 80%) was collected and stored under argon. Sodium acetylacetonate was prepared and isolated according to the procedure described in ref 21 and recrystallized from purified acetonitrile. ($\pm$)-Methylphenylphosphine and ($\pm$)-ethylphenylphosphine were prepared according to the method in ref 22 given for the methyl compound.

^{31}P and ^1H NMR spectra were recorded in the solvents specified at 23 °C on a Varian 300S spectrometer operating at 121.42 and 299.94 MHz, respectively. Spin-simulation experiments were performed with use of associated software based on the program LAME. Optical rotations were measured in a Perkin-Elmer Model 241 polarimeter in a 1-dm cell at 23 °C. Elemental analyses were carried out by staff within the Research School of Chemistry.

[*SP*-4-2-[*S*-(*R*,R**),(*R**)]-(+)₅₈₉-Chloro(methylphenylphosphine)-[1,2-phenylenebis(methylphenylphosphine)]platinum(II) Hexafluorophosphate−1-Dichloromethane ((*S,S*),(*S*)-2•CH₂Cl₂). A solution of silver nitrate (1.58 g, 9.30 mmol) in water (5 mL) was added to a suspension of (*S,S*)-[PtCl₂{1,2-C₆H₄(PMePh)₂}][10] (5.47 g, 9.30 mmol) in acetone (500 mL). The mixture was stirred for 1 h in the absence of light, whence the silver chloride precipitate was filtered off and washed with hot acetone (50 mL). The combined colorless filtrates were then treated consecutively with the following reagents: (i) trifluoromethanesulfonic acid (1 mL); (ii) ammonium hexafluorophosphate (3.0 g, 18.40 mmol) in water (5 mL); (iii) ($\pm$)-methylphenylphosphine (1.154 g, 9.30 mmol). The solvent was removed from the reaction mixture, the residue was dissolved in dichloromethane (300 mL), and water (150 mL) was added. The organic layer was separated, dried over MgSO₄, and reduced to ca. 50 mL. The concentrate was added slowly to vigorously stirred diethyl ether (1 L). The colorless precipitate, which consisted of an almost pure 2:1 mixture of (*S,S*),-(*S*)- and (*S,S*),(*R*)-**2**, was filtered off, washed with diethyl ether, and dried in vacuo: yield 6.38 g (84%). The mixture of diastereomers of **2** was dissolved in dichloromethane (100 mL), and diethyl ether (45 mL) was added to the solution. Large colorless prisms of the pure (*S,S*),(*S*) diastereomer separated from the dichloromethane−diethyl ether solution over ca. 12 h. Additional product was obtained by adding 20 mL of diethyl ether in 5 mL portions to the filtrate. After each addition of ether, the solution was stirred and set aside for ca. 12 h. The combined product was collected and washed with dichloromethane−diethyl ether (100:65, v/v) and dried: yield 2.8 g (50%); mp 84 °C (decomp); [α]₅₈₉ +56 (*c* 1, CH₂Cl₂). Anal. Calcd for C₂₈H₃₁Cl₃F₆P₄-Pt: C, 37.1; H, 3.5; F, 12.6. Found: C, 37.7; H, 3.5; F, 12.9. ^1H NMR (CD₂Cl₂): δ 1.70−2.65 (m, 9 H, CH₃), 5.32 (s, 2 H, CH₂Cl₂),

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5.38 (d of m, $^1J_{HP}$ = 388 Hz, 1 H, PH), 7.08−7.80 (m, 19 H, aromatics); ^{31}P NMR; see Table 4.

[SP-4-[S-(R*,R*)]]-(+)$_{589}$-[Bis(μ-chloro)bis{1,2-phenylenebis-(methyl-phenylphosphine)}diplatinum(II)] Hexafluoroarsenate ((S,S),-(S,S)-3). A solution of silver hexafluoroarsenate (1.51 g, 5.10 mmol) in dichloromethane (50 mL) was added with stirring to a solution of (S,S)-[PtCl$_2$\{1,2-C$_6$H$_4$(PMePh)$_2$\}]^{10} (3.00 g, 5.10 mmol) in the same solvent (350 mL). After 15 min the mixture was filtered through Celite and the solvent was removed in vacuo. The residue was dissolved in the minimum quantity of dichloromethane and was added dropwise with stirring to diethyl ether. The precipitate was washed with diethyl ether and dried in vacuo, giving a colorless powder of the pure product, mp 205 °C. Anal. Calcd for C$_{40}$H$_{40}$As$_2$Cl$_2$F$_{12}$P$_4$Pt$_2$: C, 32.4; H, 2.7; Cl, 4.8; F, 15.4. Found: C, 32.8; H, 2.8; Cl, 5.5; F, 15.2. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.23 (d, $^2J_{HP}$ = 18.60 Hz, 12 H, CH$_3$), 7.45−7.95 (m, 28 H, aromatics); ^{31}P\{^{1}H\} NMR (CD$_2$Cl$_2$) δ 34.64 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 5675 Hz).

(±)-Phenylisopropylphosphine. A solution of (±)-PClPh(i-Pr) (4.4 g, 23.6 mmol) in diethyl ether (50 mL) was added dropwise to a stirred suspension of LiAlH$_4$ (1.1 g, 28.9 mmol) in the same solvent (50 mL) at 0 °C over a 0.5 h period. After the mixture was stirred for a further 5 h, cautious hydrolysis at 0 °C with water (50 mL) and 0.1 M hydrochloric acid (25 mL) afforded two layers. Separation of the ether layer, drying over MgSO$_4$, filtration, and removal of the solvent afforded a colorless liquid, which after fractional destillation afforded the pure product as a colorless air-sensitive liquid: yield 2.0 g (56%), bp 70−71 °C (13 mmHg). Anal. Calcd for C$_9$H$_{13}$P: C, 71.0; H, 8.6. Found: C, 70.5; H, 8.3. ^{31}P\{^{1}H\} NMR (C$_6$D$_6$): δ −25.21 (s).

(±)-Ethylphenylphosphine-d_1. A solution of (±)-ethylphenylphosphine^{22} (4.47 g, 29.4 mmol) in diethyl ether (30 mL) at 0 °C was treated with a solution of n-butyl lithium (1.6 M n-hexane solution, 20 mL, 33 mmol). After 5 min, deoxygenated deuterium oxide (99.75% isotopic purity) was added to the cooled solution until it was decolorized. The reaction mixture was then filtered through a glass frit and the filtrate collected. The mixture was evaporated to dryness, and benzene (5 mL) was added to the residue, which was subsequently distilled off at atmospheric pressure to remove D$_2$O as the azeotrope. The pure product was isolated as a colorless oil by careful fractional distillation: yield 3.2 g (71%). ^{31}P NMR (CD$_3$CN): δ −44.74 (t, $^1J_{PD}$ = 33.5 Hz). (Note: traces of (±)-PHEtPh were observed in product dried over MgSO$_4$.)

Crystal Strucure Analysis. Crystal data for (S,S),(S)-2·CH$_2$Cl$_2$ are given in Table 1. Two data sets were collected on the same crystal using $\theta-2\theta$ scans of width (1.1 + 0.142 tan θ)° in θ. Set A comprised reflections ±h,±k,±l (−10 ≤ h ≤ 10, −10 ≤ k ≤ 10, −12 ≤ l ≤ 12) collected at a rate of 6° min^{-1} in θ with background counts of 3 s on each side of every scan; set B comprised reflections +h,±k,±l (0 ≤ h ≤ 10, −10 ≤ k ≤ 10, −12 ≤ l ≤ 12) collected at a rate of 1° min^{-1} in θ with background counts of 20 s on each side of every scan. Both

data sets were refined to completeness, but only the results of the more slowly collected set B are quoted here, set A being used for the absolute configuration determination. Three check reflections measured every 120 min showed a 3% decrease in intensity during collection of set B; decomposition corrections were accordingly applied to the data.^{23} Data were corrected for absorption (transmission range 0.390−0.231). The structure was solved by Patterson synthesis, ΔF synthesis, and full-matrix least-squares refinement. Four of the fluorine atoms were modeled over two sites of half-occupancy. Non-hydrogen atoms of full occupancy were refined with anisotropic replacement factors. Hydrogen atoms attached to tetrahedral or trigonal carbon were placed at calculated positions (r_{C-H} = 0.95 Å, with methyl hydrogen atoms staggered with respect to adjacent groups) and not refined. H(4), which is bonded to P(4), was refined positionally. An extinction parameter was also applied (final value: g = 0.33 (2) × 10^4). Examination of bond distances and angles at this stage showed some anomalous values in the region C(33)−C(36); Waser-type restraints were imposed on distances and angles about these atoms.^{24} Refinement was continued until shift/error ratios were <0.08. Refinement of a Flack absolute configuration parameter with data set A yielded final x_{abs} = −0.008-(6), indicating correct assignment of the absolute configuration.

Least-squares refinement was performed by full-matrix methods with minimization of the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F) + (0.0004)F^2]^{-1}$. The maximum and minimum heights in the final difference map were 1.50 and −1.30 e Å^{-3}, respectively, all major features being near the platinum atom. Data reduction and refinement computations were performed with XTAL3.0;^{25} atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 26. Final parameters for the non-hydrogen atoms are given in in Table 2; selected interatomic distances and angles are given in Table 3.

Supplementary Material Available: For (S,S),(S)-2·CH$_2$Cl$_2$, text describing X-ray procedures, tables of bond distances and angles, thermal parameters for non-hydrogen atoms, calculated hydrogen atom parameters, least-squares planes, and selected torsion angles, and an ORTEP plot (18 pages). Ordering information is given on any current masthead page.

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