sponding Cr complex; a similar question applies to the polymer-stabilized titanium cluster elimination by Cr atoms. Further experiments are being attempted to try to establish these details of the Ti/Cr-DC510 reaction.

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Resolutions Using Metal Complexes. Synthesis, Separation into Diastereoisomers, and Resolution of *o*-Phenylenebis(methylphenylphosphine) Using Palladium Complexes Containing Optically Active Ortho-Metalated Dimethyl(α-methylbenzyl)amines

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Abstract: The new chelating di(tertiary phosphine) *o*-phenylenebis(methylphenylphosphine) has been prepared in 68% yield from *o*-dichlorobenzene by reaction with sodium methylphenylphosphide in tetrahydrofuran solution. The racemic and meso forms of the ligand, (*RR*;*SS*)-diphos and (*RS*)-diphos, respectively, were separated by a combination of direct fractional crystallization of the mixture of diastereoisomers, and by selective precipitation of the sparingly soluble complex [Ni(SCN)((*RS*)-diphos)$_2$]SCN. The diastereoisomeric di(tertiary phosphines) were subsequently identified by analyzing the ^{1}H NMR spectra of their respective substituted 1*H*-1,3-benzodiphospholenium salts. Optimized conditions are described for the large-scale resolution of (*RR*;*SS*)-diphos by a method which involves the separation of internally diastereoisomeric palladium complexes containing the dissymmetric di(tertiary phosphine) and an optically active ortho-metalated dimethyl(α-methylbenzyl)amine. The optically pure enantiomers, $[\alpha]_D \pm 81.5°$ (CH_2Cl_2), are air-stable, crystalline solids, mp 112–113 °C, whose absolute configurations have been determined by X-ray analysis. The optically active di(tertiary phosphines) epimerize rapidly upon heating, although they can be recovered unchanged from concentrated hydrochloric acid solution. Indeed, optically active monoprotonated phosphonium salts can be isolated from these solutions.

Despite the keen interest in the use of soluble rhodium(I) complexes containing optically active di(tertiary phosphines) as catalysts for the asymmetric hydrogenation of prochiral substrate molecules, notably α-amino acid precursors,[1] there is no general and convenient method available, to date, for the resolution of dissymmetric di(tertiary phosphines) containing asymmetric donor atoms. The classical method of fractionally crystallizing diastereoisomeric salts containing an appropriate quaternary derivative of the di(tertiary compound) is fraught with difficulties, among which is the problem of stereospecifically liberating the optically active ditertiary species from the resolved salt. Nevertheless, quaternary *benzyl* salts of bis(methylphenylphosphino)-1,2-ethane[2] and its arsenic analogue[3] have been resolved by this method using D(−)-dibenzoyl hydrogen tartrate as resolving agent and the former has been subsequently reduced by polarographic means to the optically active di(tertiary phosphine), albeit of uncertain optical purity. Another procedure, which obviates the need to resolve a *di*tertiary species, involves the oxidative coupling of α carbanions derived from optically active methyl-substituted mono(tertiary phosphine) oxides. Thus, (+)-(*R*)-ethylmethylphenylphosphine oxide[4] and (+)-*o*-anisylmethylphenylphosphine oxide[5] were dimerized to their respective di(tertiary phosphine) oxides and the latter was subsequently reduced by

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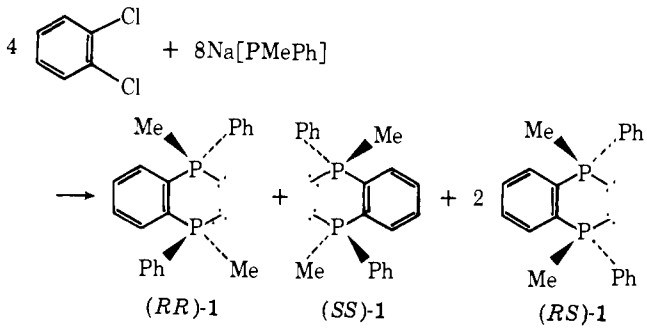
Scheme I



trichlorosilane to the optically active nonmethylated di(tertiary phosphine).

We describe here details of a superior method for the large-scale preparation, separation of internal diastereoisomers, and resolution of the new chelating di(tertiary phosphine) *o*-phenylenebis(methylphenylphosphine). The resolution procedure, which gives *both* enantiomers of the crystalline racemic di(tertiary phosphine) in an optically pure state, relies upon the separation of internally diastereoisomeric palladium complexes containing the di(tertiary phosphine) and orthometalated dimethyl(α-methylbenzyl)amines and follows our earlier work concerning the synthesis[6] and resolution[6,7] of the analogous di(tertiary arsine).

The various stereoisomers of this ligand are powerful probes for investigating the mechanism of inorganic reactions and the stereochemistry of reaction products. Moreover, the stereochemically rigid chelate ring formed by this aromatic derivative simplifies, by comparison with the flexible aliphatic ring formed by other known optically active di(tertiary phosphines), the design of metal complexes of potential interest in connection with the study of reactions leading to asymmetric synthesis.

Results and Discussion

Reaction of *o*-dichlorobenzene with a solution of sodium methylphenylphosphide in tetrahydrofuran affords an equimolar mixture of the diastereoisomeric di(tertiary phosphines) (*RR;SS*)-**1** and (*RS*)-**1** in 68% yield (Scheme I).

The solution of Na[PMePh] in tetrahydrofuran was obtained by sodium metal reduction of PHMePh. The secondary phosphine was prepared in 77% overall yield from triphenylphosphine in a convenient "one-pot" sequence of reactions in liquid ammonia.

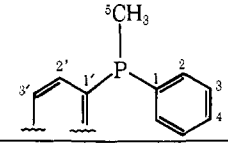
$$PPh_3 \xrightarrow[2.\ t\text{-BuCl}]{1.\ Na/NH_3} Na[PPh_2] \xrightarrow{3.\ MeI} PMePh_2$$

$$\xrightarrow{4.\ Na/NH_3} Na[PMePh] \xrightarrow{5.\ H_2O} PHMePh$$

The mixture of di(tertiary phosphines) distilled as a viscous oil, bp 190–200 °C (0.1 mmHg), which was separated from the volatile side products methyldiphenylphosphine (11%) and 1,2-dimethyl-1,2-diphenyldiphosphine (12%) by fractional distillation.

Separation of Diastereoisomers. Most of the racemic diastereoisomer, (*RR;SS*)-**1**, separated from a hot solution of the original equimolar mixture of racemic and meso di(tertiary phosphines) in methanol upon cooling to room temperature, as colorless prisms, mp 94–95 °C. The fractional crystallization requires care, however, because the meso diastereoisomer, (*RS*)-**1**, tends to cocrystallize. Once the first crop of racemic material has been removed, the remaining mixture of diastereoisomers can then be thermally epimerized to an equimolar mixture of the two by heating the mixture at 200 °C for several minutes at atmospheric pressure, or by distillation at 0.1 mmHg. The fractional crystallization can then be repeated:

Table I. ^{13}C NMR Data for (*RR;SS*)-**1** in $CDCl_3$ (0.5 M)



	o-phenylene			phenyl				methyl
	C(1′)	C(2′)	C(3′)	C(1)	C(2)	C(3)	C(4)	C(5)
δ, ppm[a]	147.6	133.2	130.8	142.8	134.0	130.1	128.9	14.3
"*J*"[b]	18.3	5.5	0	9.2	18.3	5.5	0	9.2

[a] Relative to Me_4Si as internal standard. [b] "*J*" = $|J_{PC} + J_{P'C}|$ (±1 Hz).

$$(RR;SS)\text{-}\mathbf{1} \text{ or } (RS)\text{-}\mathbf{1} \xrightarrow{\Delta} (RR;SS)\text{-}\mathbf{1} + (RS)\text{-}\mathbf{1}$$

In this way, after several cycles of the fractional crystallization-thermal epimerization procedure, 75% of the original di(tertiary phosphine) material had been converted into the resolvable racemic diastereoisomer.

The more soluble meso phosphine, (*RS*)-**1**, is best obtained via the complex [Ni(SCN){(*RS*)-**1**}$_2$]SCN, which is readily separated from the corresponding complexes formed by (*RR;SS*)-**1**, viz., *meso*-[Ni(SCN){(*RR*)-**1**}{(*SS*)-**1**}]SCN and the enantiomeric complexes [Ni(SCN){(*RR*)-**1**}$_2$]SCN and [Ni(SCN){(*SS*)-**1**}$_2$]SCN. The sparingly soluble complex can be isolated in almost quantitative yield from the reaction of $[Ni(H_2O)_6]Cl_2$ with the mixture of di(tertiary phosphines) in the presence of KSCN. It crystallizes from dichloromethane as the orange-colored solvate [Ni(SCN){(*RS*)-**1**}$_2$]-$SCNCH_2Cl_2$ (**2**). Subsequent treatment of **2** with an excess of KCN affords the pure meso ligand as air-stable, white leaflets, mp 79–89 °C, after recrystallization from methanol.

$$[Ni(SCN)\{(RS)\text{-}\mathbf{1}\}_2]SCN + 4KCN \rightarrow 2(RS)\text{-}\mathbf{1} + K_2[Ni(CN)_4] + 2KSCN$$

The deep red colored filtrate from the original separation of **2**, which contains mainly thiocyanatonickel(II) complexes of (*RR;SS*)-**1**, was also treated with cyanide to displace the coordinated di(tertiary phosphines). Fractional crystallization of these gave (*RR;SS*)-**1** in 57% yield.

Identification of Diastereoisomers. The ^1H and ^{13}C NMR spectra of (*RR;SS*)-**1** and (*RS*)-**1** are deceptively simple, both diastereoisomers showing an apparent 1:2:1 triplet for their P-Me resonances. The triplets in the ^1H NMR spectra may be attributed to a limiting case of an $A_3XX'A_3'$ spin system[8] where, in addition to the expected basic doublet of separation $|J_{PH} + J_{P'H}|$, there is, in the center of the doublet, a single peak arising from several resonances whose chemical shifts coincide because of the relative magnitude of $J_{PP'}$ compared with $|J_{PH} + J_{P'H}|$ ($J_{PP'} \gg |J_{PH} + J_{P'H}|$); these resonances arise from virtual coupling through strong P-P′ and P-H interactions. Deceptively simple ^1H NMR spectra of this type have also been observed for various aliphatic and aromatic linked di(tertiary phosphines).[9] In the case of the square-planar complex [$PdCl_2$]{(*RR*)-**1**}] the coupling constant $J_{PP'}$ is relatively small compared with $|J_{PH} + J_{P'H}|$, and the lines of the subspectrum due to virtual coupling are not resolved from the basic doublet, yet give it a "filled-in" appearance. The virtual coupling is extended to the carbon atoms of the aromatic rings as evidenced by the ^{13}C NMR data presented in Table I, where "*J*" = $|J_{PC} + J_{P'C}|$.

We have unambiguously identified the diastereoisomeric di(tertiary phosphines) by analyzing the ^1H NMR spectra of the 1,3-dimethyl-1,3-diphenyl-1*H*-1,3-benzodiphospholenium hexafluorophosphate salts (*RR;SS*)-**3b** and (*RS*)-**4b**, which

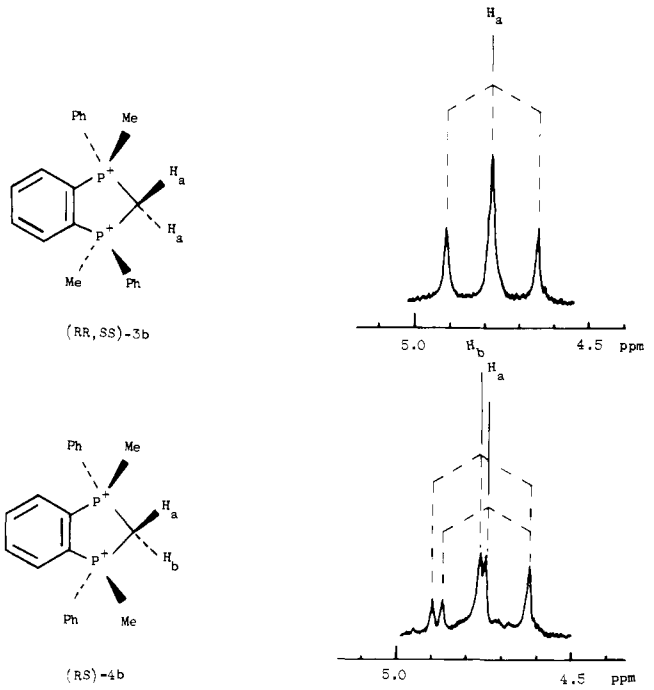


Figure 1. ^{1}H NMR spectra of methylene protons in (*RR;SS*)-**3b** and (*RS*)-**4b** (90 MHz, acetone-d_6).

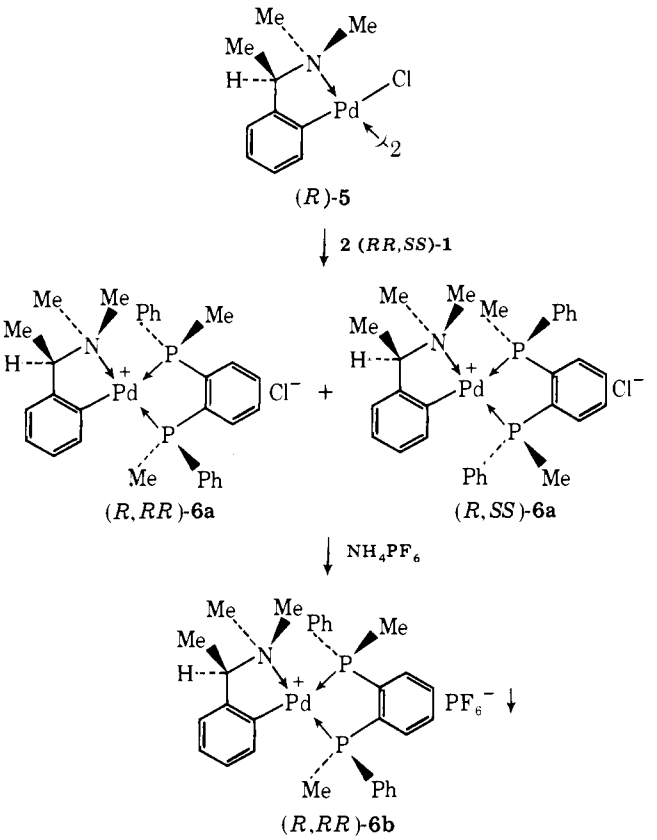
were prepared from (*RR;SS*)-**1** and (*RS*)-**1**, respectively, by reaction with CH_2Br_2, followed by metathesis of the resulting *bromides* with $NH_4[PF_6]$. The ^{1}H NMR spectra of these salts in the methylene region are reproduced in Figure 1. The spectrum of the racemic salt, (*RR;SS*)-**3b** (C_2 symmetry), shows the expected triplet for the equivalent methylene protons ($^2J_{PH}$ = 13.4 Hz). However, the unequal coupling of the ^{31}P nuclei with the nonequivalent methylene protons in the meso salt, (*RS*)-**4b**, gives rise to two sets of triplets ($^2J_{PH}$ = 13.4 and 12.2 Hz) separated by 1.5 Hz. Coupling between H_A and H_B was not observed at 90 MHz.

Resolution of (*RR;SS*)-1. The reaction leading to the formation of the pair of internal diastereoisomers is summarized in Scheme II. A suspension of the chloro-bridged dimer (*R*)-**5**,[10] derived from (+)-(*R*)-dimethyl(α-methylbenzyl)amine by reaction with lithium tetrachloropalladate(II), was stirred in methanol with 2 equiv of (*RR;SS*)-**1** to produce an almost colorless solution of the internal diastereoisomers (*R,SS*)-**6a** and (*R,RR*)-**6a**. The gradual addition of 1 equiv of $NH_4[PF_6]$ in water to this mixture of complexes selectively precipitated the hexafluorophosphate (*R,RR*)-**6b** in 93% yield, $[\alpha]_D$ −322° (acetone). One recrystallization of this material afforded the optically pure diastereoisomer as large, colorless prisms, $[\alpha]_D$ −328° (acetone). Pure (*R,RR*)-**6b** behaves as a uni-univalent electrolyte in nitrobenzene solution and has a ^{1}H NMR spectrum in acetone-d_6 similar (apart from ^{31}P coupling) to that of the corresponding diastereoisomer containing (−)-(*SS*)-*o*-phenylenebis(methylphenylarsine).[7] The absolute configuration of (−)-(*R,RR*)-**6b** has been confirmed by a single-crystal X-ray analysis.[11]

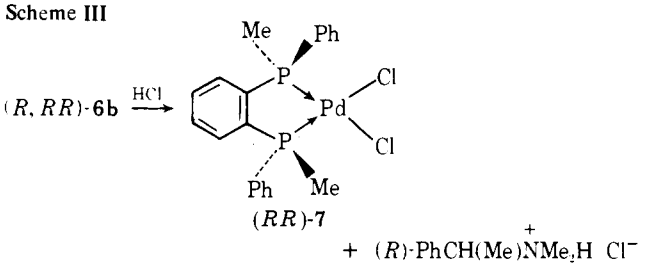
The liberation of the optically active di(tertiary phosphine) from (*R,RR*)-**6b** was performed in two steps. The first involved recovery of the tertiary amine resolving agent, as its hydrochloride, by boiling a suspension of the complex in acetone containing hydrochloric acid (Scheme III).

The complex (*RR*)-**7** precipitated quantitatively during the course of the reaction as pale yellow microcrystals, $[\alpha]_D$ +51° (Me_2SO). The optically pure amine was recovered from the mother liquor after treatment with base. The removal of optically active (*SS*)-**1** from (*RR*)-**7** by cyanide displacement

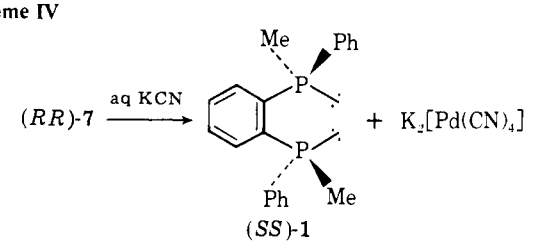
Scheme II



Scheme III



Scheme IV



requires care because the intermediate complex [Pd(CN)$_2$-{(RR)-**1**}] tends to precipitate. If the displacement is carried out in aqueous methanol using a large excess of KCN, however, and the ligand is extracted into petroleum ether as it is liberated, then the complex can be decomposed completely at room temperature (Scheme IV).

The optically pure di(tertiary phosphine) (−)-(*SS*)-**1**, $[\alpha]_D$ −81.5° (CH_2Cl_2), crystallizes from methanol as air-stable, friable rods, mp 112–113 °C (overall yield 85%).

The enantiomer (+)-(*RR*)-**1** was obtained from the more soluble internal diastereoisomer (*R,SS*)-**6a** remaining in the mother liquor after the separation of (*R,RR*)-**6b**. The filtrate was concentrated and boiled with hydrochloric acid to precipitate (*SS*)-**7**. Decomposition of this complex with an excess of KCN as described above gave a partially resolved sample of (*RR*)-**1** which, after recrystallization from methanol, had mp 112–113 °C and $[\alpha]_D$ +81.3° (CH_2Cl_2) (90% yield). The pure internal diastereoisomer (*R,SS*)-**6b**, $[\alpha]_D$ +219°

Table II. ^{1}H NMR Data for Solutions of Di(tertiary phosphines) and Their Benzyl Quaternary Derivatives in Strong Acid Solution

compd	solvent	resonance, δ ppm		
		-PMePh	-$^+$PHMePh	-$^+$PBzMePh
(*RR*;*SS*)-**1**	CF_3CO_2H		2.57, d, J = 14.4 Hz	
(*RS*)-**1**	CF_3CO_2H		2.66, d, J = 14.4 Hz	
(*RS*;*SR*)-**8a**	CF_3CO_2H		2.38, d, J = 14.5 Hz	2.53, d, J = 12.9 Hz
	$CF_3CO_2H + D_2O$	1.52, d, J = 2.0 Hz		2.53, d, J = 13.3 Hz
(*RS*)-**8a**	CF_3CO_2H		2.67, d, J = 13.0 Hz	2.50, d, J = 14.6 Hz
	$(CF_3CO_2H + D_2O$	1.32, d, J = 3.0 Hz		2.44, d, J = 12.8 Hz

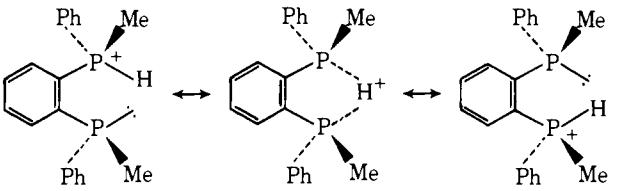
(Me_2CO), was prepared directly from (*R*)-**5** and optically pure (*RR*)-**1** in a separate experiment.

We have repeated the resolution using the equally accessible (*S*)-**5** as resolving agent with the same success.

Quaternization Reactions. Reaction of (*RR*;*SS*)-**1** or (*RS*)-**1** with benzyl bromide or methyl iodide under normal conditions affords mono(quaternary salts) only. Thus, benzyl bromide in stereospecific reactions gives the erythro salt (*RR*;*SS*)-**8a** from (*RS*)-**1**, and the threo salts (*RS*;*SR*)-**8a** and (+)-(*RS*)-**8a** from (*RR*;*SS*)-**1** and (+)-(*RR*)-**1**, respectively. The corresponding hexafluorophosphate salts were prepared from these by metathesis with $NH_4[PF_6]$. Quaternization of either (*RR*;*SS*)-**1** or (*RS*)-**1** with iodomethane affords the same *methiodide*, (*R*;*S*)-**9a**. The ^{1}H NMR spectrum of the hexafluorophosphate of this salt, (*R*;*S*)-**9b**, shows the expected doublet of resonances for the diastereotopic methyl groups of the -$^+$PMe_2Ph moiety. The use of Magic Methyl, $FSO_2(OMe)$, as methylating agent, however, results in the quaternization of both tertiary phosphine groups in (*RR*;*SS*)-**1** and (*RS*)-**1**, yielding, after metathesis with $NH_4[PF_6]$, the symmetrical diphosphonium salt **10**.

Protonation Reactions. The di(tertiary phosphines) dissolve in concentrated hydrochloric acid or CF_3CO_2H and can be recovered unchanged from these solutions by the addition of water. Indeed, there was no observable mutarotation of a solution of (*RR*)-**1** in 10 M HCl (161 g L^{-1}) over a 3-week period, the optically pure phosphine being recovered quantitatively upon dilution of the solution with water. The P-Me resonance for both the racemic and meso diastereoisomers occurs as a doublet in CF_3CO_2H which is centered at δ 2.57 ppm for (*RR*;*SS*)-**1** and at δ 2.66 ppm for (*RS*)-**1**, the coupling constants being the same in each case (J_{PH} = 14.4 Hz) (Table II). This value is significantly larger than the corresponding coupling observed in $CDCl_3$ solutions of the di(tertiary phosphines) (ca. 4 Hz). The tertiary -PMePh groups in the mono(quaternary salts)(*RR*;*SS*)-**8a** and (*RS*;*SR*)-**8a** behave similarly when dissolved in CF_3CO_2H, their ^{1}H NMR spectra containing two sets of doublets due to PMe groups in the phosphonium region. We assign one of the doublets in each case to the -$^+$PH*Me*Ph resonance (J_{PH} = 14.5 Hz), $^3J_{HH}$ not being observed because of exchange decoupling. In agreement with this assignment, the phosphonium doublet collapses when the sample is diluted with D_2O and is replaced by a doublet centered at δ 1.52 ppm (J_{PH} = 2 Hz), typical of a tertiary -P*Me*Ph signal. The large difference in the magnitude of J_{PH} observed for free and protonated tertiary P-Me groups is expected.[12] We therefore consider that (*RR*;*SS*)-**1** and (*RS*)-**1** have doubly protonated structures in CF_3CO_2H, although only the monoprotonated salts, (*RR*;*SS*)-**11** and (*RS*)-**11**, could be isolated. The monoprotonated salts are uni-univalent electrolytes in nitrobenzene and can be recrystallized from acetone-diethyl ether mixtures without decomposition. However, in dry CH_2Cl_2 solution the ^{1}H NMR spectra of the salts show a single broad P-Me resonance in each case with a chemical shift value intermediate between that expected for free and protonated tertiary phosphine groups. This observation is consistent with the rapid site exchange of the coordinated proton between the adjacent tertiary phosphine centers as

Scheme V



depicted in Scheme V. Accordingly, as the temperature of a 0.045 M solution of (*RS*)-**11** in dry dichloromethane was lowered, the broad average PMe singlet observed at room temperature further broadened, collapsed at 250 K (T_c), and re-formed two equally intense absorptions at 185 K, viz., δ 2.56 (3 H, d, $^2J_{PH}$ = 14.0 Hz, $^+$PH*Me*Ph) and 1.43 ppm (3 H, br s, PMePh). Pronounced changes were also observed in the aromatic region during the cooling process, and at 185 K a weak, broad set of signals (ca. 0.5 H) appeared at δ 11.4 ppm, which we assign as one-half of the expected $^+$P*H*MePh doublet of quartets. The other half of this doublet of resonances was not observed in a scan of 1770 Hz downfield and we suspect, in view of the large coupling constant expected ($^1J_{PH}$ = 515 ± 10 Hz in $^+$PHMe_3),[12] that the absorption may be concealed beneath the aromatic and solvent signals. The concentration independence of the NMR spectrum also supports the notion of an intramolecular site exchange of the proton, the value of 250 K also being found for T_c in a 0.18 M solution of (*RS*)-**11** in dichloromethane. As expected, the rate constant for this intramolecular proton exchange is significantly higher ($k_c = \pi\Delta\nu/\sqrt{2}$ = 233 s^{-1}) than that of the corresponding intermolecular process for PMe_3 at the same concentration (k_c = 5.2 s^{-1} at 295 K).[12] It is noteworthy that in the crystal structure of (*RS*)-**11** there appears to be a weak interaction between the coordinated proton and the lone pair of electrons associated with the adjacent phosphorus atom.[13]

Oxidation Reactions. The racemic, meso, and optically active isomers of the di(tertiary phosphine) are stereospecifically oxidized to their respective crystalline dioxides by hydrogen peroxide in dichloromethane solution.

We are presently investigating the extensive coordination chemistry of the various stereoisomers of this new di(tertiary phosphine). For example, we have compelling NMR evidence indicating intermolecular chelate ligand exchange and internal isomerism of the chelate rings in square-planar and five-coordinate complexes of Ni(II), Pd(II), and Pt(II) containing this ligand.

Experimental Section

Reactions involving air-sensitive reagents were carried out in an atmosphere of pure nitrogen using the Schlenk technique. Solvents were dried in the usual way and degassed by distillation through a stream of pure nitrogen. The petroleum ether used throughout has bp 60–70 °C. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. The ^{1}H NMR spectra were recorded at 90 MHz using a Bruker HX-90 spectrometer; chemical shift values are quoted relative to Me_4Si except in D_2O, where sodium 3-(trimethylsilyl)propanesulfonate was used as an internal standard. The low-temperature ^{1}H NMR measurements were made using the same instrument, the temperature being measured by a copper-con-

stantan thermocouple located below the sample tube. ^{13}C NMR spectra were obtained under broad band decoupling conditions at 21.115 MHz on a Bruker WP-80 spectrometer. The specific optical rotations were measured using a Perkin-Elmer Model 141 polarimeter in a 1-dm cell thermostated at 20 °C. The molar conductivities were determined by means of a Phillips GM 4249 conductivity bridge at 20 °C.

Methylphenylphosphine. Liquid ammonia (500 ml) was condensed onto a mixture of sodium wire (12 g) and triphenylphosphine (65.5 g). A bright red solution containing $Na[PPh_2]$ formed immediately. The reaction mixture was stirred for 30 min and *t*-BuCl (27 mL) added (to destroy $NaNH_2$) followed by MeI (15 mL) or MeBr until the color of the phosphide ion was discharged. (Methyldiphenylphosphine can be isolated in 96% yield at this stage if desired.) More sodium (12 g) was then added to form a solution of Na[PMePh] which was stirred for 3 h and then hydrolyzed with deoxygenated water (100 mL). The ammonia was allowed to distill off and more water (250 mL) and diethyl ether (300 mL) were added. The organic layer was separated, dried over $MgSO_4$, and distilled to give the pure secondary phosphine, bp 92–95 °C (20 mmHg), 24 g (77%).

***rac*- and *meso*-*o*-Phenylenebis(methylphenylphosphine), (*RR*;*SS*)-1 and (*RS*)-1.** Sodium foil (25 g) was added to a solution of PHMePh (102 g) in tetrahydrofuran (400 mL). The mixture was heated under reflux for 30 min and then cooled and filtered to remove excess sodium. The clear orange-yellow filtrate containing Na[PMePh] was then cooled to −78 °C and treated with a solution of *o*-dichlorobenzene (60.5 g) in tetrahydrofuran (250 mL). The reaction mixture was stirred for 2 h at −78 °C, warmed slowly to room temperature, and finally heated under reflux for 2 h. The solvent was distilled off and diethyl ether (400 mL) and water (500 mL) were added. The organic layer was separated, dried over $MgSO_4$, and distilled at 20 mmHg to remove the solvents, and the pale yellow residue distilled at 0.1 mmHg to give the following compounds: fraction 1, a colorless oil, bp 110–120 °C (18 g, 11%), methyldiphenylphosphine; fraction 2, a colorless oil, bp 140–160 °C (12 g, 12%), which eventually crystallized, mp 78 °C, *1,2-dimethyl-1,2-diphenyldiphosphine;* fraction 3, a viscous oil, bp 190–200 °C (88 g, 68%), the desired product, (*RR*;*SS*)-**1** and (*RS*)-**1**. The ^1H NMR spectrum showed an equimolar mixture of the two diastereoisomers (vide infra). The side products were identified from their ^1H NMR and mass spectra and by comparison with authentic specimens.

Separation of Diastereoisomers. *rac*-*o*-Phenylenebis(methylphenylphosphine), (*RR*;*SS*)-1. A mixture of the diastereoisomers (108 g) was dissolved in boiling methanol (990 mL) and the solution allowed to cool slowly overnight. Large, transparent prisms of (*RR*;*SS*)-**1** deposited during this period. The mother liquor was carefully decanted from the crystals [filtration tended to initiate the cocrystallization of (*RS*)-**1**] which were washed with cold methanol (40 mL) and dried in vacuo to yield the pure racemic di(tertiary phosphine), mp 94–95 °C (35 g, 65%). Anal. Calcd for $C_{20}H_{20}P_2$: C, 74.5; H, 6.3. Found: C, 74.3; H, 6.2. ^1H NMR spectrum in $CDCl_3$: δ 1.42 (6 H, t, $^2J + {}^5J$ = 4.0 Hz, P-Me), 7.11–7.48 ppm (14 H, br m, aromatics). The filtrate, after the removal of solvent, consisted of a viscous oil which was shown by ^1H NMR analysis to be a ca. 3:1 mixture of (*RS*)-**1** and (*RR*;*SS*)-**1**, respectively. This material was converted to an equimolar mixture of the two diastereoisomers by heating to 200 °C for 0.25 h, and was then fractionally crystallized from boiling methanol (670 mL) to yield another crop of (*RR*;*SS*)-**1** (19.8 g). Four fractional crystallization–epimerization cycles netted 81 g of (*RR*;*SS*)-**1** (75% of the original mass of di(tertiary phosphine) material).

***meso*-*o*-Phenylenebis(methylphenylphosphine), (*RS*)-1.** A mixture of the diastereoisomers (1:1, 88 g) was dissolved in dichloromethane (300 mL) and a solution of $[Ni(H_2O)_6]Cl_2$ (34 g) in water (50 mL) added. Upon shaking the organic layer rapidly became orange-red. A solution of KSCN (30 g) in water (30 mL) was then added causing a further intensification of the color to deep red. After shaking for several minutes, the organic layer was separated, thoroughly washed with water, dried ($MgSO_4$), and concentrated to ca. 200 mL. Dilution of this solution with petroleum ether (600 mL) precipitated a red gum containing the various thiocyanatonickel(II) complexes of the di(tertiary phosphines). These were collectively dissolved in boiling ethanol (1 L) and the solution cooled to room temperature and then stirred for 12 h. The complex [Ni(SCN){(*RS*)-**1**}$_2$]SCN separated during this period as a yellow powder which was filtered off and washed with ethanol. The powder was purified by Soxhlet extraction into dichloromethane (1.7 L). Concentration of the extract, followed by dilution with diethyl ether, afforded **2**, an orange-colored, crystalline monodichloromethane solvate, mp 255–260 °C dec (56.7 g, 92%). Anal. Calcd for $C_{43}H_{42}Cl_2N_2NiP_4S_2$: C, 61.0; H, 5.0. Found: C, 60.8; H, 4.8. The free meso ligand (*RS*)-**1** was liberated from **2** as follows. A mixture of the complex (18.4 g) and KCN (43 g) was suspended in dichloromethane (20 mL) and water (70 mL), and the mixture stirred until dissolution was complete. Petroleum ether (700 mL) was then slowly added to the mixture. The usual workup of the organic layer left the product as an oil which was once again extracted into boiling petroleum ether, filtered, and freed of solvent. Recrystallizations of this residue from boiling methanol (160 mL) by the careful addition of water (100 mL) gave the pure meso ligand, (*RS*)-**1**, as white leaflets, mp 79–80 °C (13.7 g, 96%). Anal. Calcd for $C_{20}H_{20}P_2$: C, 74.5; H, 6.3. Found: C, 74.1, H, 6.4. ^1H NMR spectrum in $CDCl_3$: δ 1.60 (6 H, t, $^2J + {}^5J$ = 4 Hz, P-Me), 7.08–7.36 ppm (14 H, br m, aromatics).

The original filtrate from the separation of the [Ni(SCN){(*RS*)-**1**}$_2$]SCN was evaporated to dryness and the red gum dissolved in dichloromethane (200 mL) and reacted with KCN (130 g) in water (500 mL). The mixture was stirred rapidly and petroleum ether (400 mL) gradually added. The organic layer became almost colorless and was separated and dried ($MgSO_4$). The solvent was evaporated and the residual oil once again dissolved in hot petroleum ether (400 mL) and filtered. Removal of the solvent from the filtrate left a colorless oil which soon crystallized. Recrystallization of this material from boiling methanol (600 mL) produced colorless prisms of pure (*RR*;*SS*)-**1**, mp 94–95 °C (25 g, 57%).

Identification of Diastereoisomers. Conversion of (*RR*;*SS*)-1 into (*RR*;*SS*)-1,3-Dimethyl-1,3-diphenyl-1*H*-1,3-benzodiphospholenium Bromide Hydrate, (*RR*;*SS*)-3a, and Hexafluorophosphate, (*RR*;*SS*)-3b. A solution of (*RR*;*SS*)-**1** (0.33 g) in dibromomethane (2 mL) was heated on a steam bath for 15 min and then cooled and diluted with petroleum ether (bp 60–70 °C, 30 mL). A gum deposited which was triturated in warm 2-propanol until crystalline, and then filtered off, washed with the same solvent, and dried in vacuo. White microcrystals of the monohydrate (*RR*;*SS*)-**3a** were obtained, mp 197–200 °C (0.5 g, 98%). Anal. Calcd for $C_{21}H_{24}Br_2OP_2$: C, 49.0; H, 4.7. Found: C, 49.0; H, 4.7. ^1H NMR spectrum in D_2O: δ 4.92 (6 H, d, J_{PH} = 14.6 Hz, $^+$PMe), 9.50–10.65 ppm (14 H, m, aromatics); $^+PCH_2P^+$ obscured by $^+$PMe. A solution of (*RR*;*SS*)-**3a** (0.5 g) in water (7 mL) was treated with $NH_4[PF_6]$ (0.4 g) in the same solvent (5 mL). The hexafluorophosphate (*RR*;*SS*)-**3b** precipitated immediately and was recrystallized from acetone–diethyl ether as colorless fronds, mp 248–257 °C dec (0.54 g, 86%). Anal. Calcd for $C_{21}H_{22}F_{12}P_4$: C, 40.3; H, 3.5. Found: C, 40.6; H, 3.5. ^1H NMR spectrum in acetone-d_6: δ 3.12 (6 H, d, J_{PH} = 15.5 Hz, $^+$PMe), 4.78 (2 H, t, J_{PH} = 13.4 Hz, $^+PCH_2P^+$), 7.40–8.83 ppm (14 H, m, aromatics).

(*RS*)-1,3-Dimethyl-1,3-diphenyl-1*H*-1,3-benzodiphospholenium Bromide Hydrate, (*RS*)-4a, and Hexafluorophosphate, (*RS*)-4b. From (*RS*)-**1** (0.65 g) and CH_2Br_2 (4 mL) the dibromide hydrate was obtained as a white powder, mp >280 °C, after the reaction mixture was diluted with petroleum ether (0.82 g, 99%). Anal. Calcd for $C_{21}H_{24}Br_2OP_2$: C, 49.0; H, 4.7. Found: C, 49.0; H, 4.5. ^1H NMR spectrum in D_2O: δ 3.11 (6 H, d, J_{PH} = 14.6 Hz, $^+$PMe), 9.53–10.72 ppm (14 H, m, aromatics); $^+PCH_2P^+$ obscured by $^+PCH_3$. By metathesis with $NH_4[PF_6]$ in water the corresponding hexafluorophosphate (*RS*)-**4b** was obtained as colorless plates from acetone–diethyl ether, mp 253–263 °C dec (92%). Anal. Calcd for $C_{21}H_{22}F_{12}P_4$: C, 40.3; H, 3.5. Found: C, 40.4; H, 3.8. ^1H NMR spectrum in acetone-d_6: δ 3.24 (6 H, d, J_{PH} = 15.2 Hz, $^+$PMe), 4.75 (1 H, t, J_{PH} = 12.2 Hz, $^+PCH_AH_BP^+$), 4.77 (1 H, t, J_{PH} = 13.4 Hz, $^+PCH_ACH_BP^+$), 7.51–8.40 ppm (14 H, m, aromatics).

Resolution of (*RR*;*SS*)-1. (−)-Di-μ-chloro-bis[(*R*)-dimethyl(α-methylbenzyl)aminato-2-*C*,*N*]dipalladium(II), (*R*)-5, was prepared in 94% yield as described previously[7] as a yellow powder, mp 195–200 °C dec, $[\alpha]_D$ +50.1° (*c* 0.65, CH_2Cl_2).

Formation and Separation of Internal Diastereoisomers. (−)-[(*R*)-dimethyl(α-methylbenzyl)aminato-2-*C*,*N*][(*RR*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Hexafluorophosphate, (*R*,*RR*)-6b. A suspension of (*R*)-**5** (11.6 g, 20 mmol) and (*RR*;*SS*)-**1** (12.9 g, 40 mmol) in methanol (240 mL) was stirred to give a clear, almost colorless, solution of the internally diastereoisomeric chlorides (*R*,*RR*)-**6a** and (*R*,*SS*)-**6a**. The solution was filtered and $NH_4[PF_6]$ (3.3 g, 20 mmol) in water (25 mL) gradually added to the filtrate. More water (25 mL) was added and the white slurry stirred for 4 h. The precipitate was then collected, washed with 50% aqueous meth-

anol (120 mL) and diethyl ether, and dried to give almost pure (*R,RR*)-**6b** as a white powder, $[\alpha]_D$ −322° (*c* 1.1, Me_2CO) (13 g, 93%). Recrystallization from boiling acetone (400 mL) by the careful addition of diethyl ether (300 mL) afforded the optically pure product as colorless prisms, mp 220–223 °C dec, 12.7 g (91%), $[\alpha]_D$ −328° (*c* 0.63, Me_2CO). Anal. Calcd for $C_{30}H_{34}F_6NP_3Pd$: C, 49.9; H, 4.8; N, 1.9. Found: C, 49.9; H, 4.7; N, 1.8. ^1H NMR spectrum in acetone-d_6: δ 1.62 (3 H, d, *J* = 6.7 Hz, CH*Me*), 2.48 (3 H, d, *J* = 8 Hz, PMe), 2.58 (3 H, d, *J* = 11 Hz, PMe), 2.7–2.8 (6 H, m, NMe_2), 4.11 (1 H, q, *J* = 6.7 Hz, C*H*Me), 6.7–8.3 ppm (18 H, br m, aromatics). Conductivity: Λ_M = 25.3 Ω^{-1} cm^2 mol^{-1} (1.2×10^{-3} M in $PhNO_2$ at 20 °C).

Dichloro[(*RR*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II), (*RR*)-7. A suspension of (*R,RR*)-**6b** (12.7 g) in acetone (130 mL) containing hydrochloric acid (10 M, 15 mL) was heated under reflux for 15 min. A quantitative yield of the complex (*RR*)-**7** precipitated during this period as pale yellow microcrystals (after concentration and dilution with water), mp >300 °C (8.7 g, 99%), $[\alpha]_D$ +51° (*c* 0.68, Me_2SO). Anal. Calcd for $C_{20}H_{20}Cl_2P_2Pd$: C, 48.1; H, 4.0. Found: C, 48.4; H, 4.1. ^1H NMR spectrum in CH_2Cl_2: δ 2.37 (6 H, d, *J* = 11.7 Hz, PMe), 7.13–7.74 ppm (14 H, br m, aromatics). The optically pure resolving agent (+)-(*R*)-dimethyl(α-methylbenzyl)-amine was recovered from the filtrate after base hydrolysis of the hydrochloride.

(−)-(*SS*)-*o*-Phenylenebis(methylphenylphosphine), (*SS*)-1. The complex (*RR*)-**7** (8.7 g) was suspended in deoxygenated methanol (440 mL) and petroleum ether (850 mL) and KCN (44 g) were added. The mixture was thoroughly shaken, water (115 mL) was added, and the two layers were separated. The yellow aqueous layer was further diluted with water (350 mL) and once again extracted with petroleum ether (720 mL). The petroleum ether extracts were combined, washed with water, and then dried over $MgSO_4$. Removal of the solvent in vacuo gave the white, crystalline di(tertiary phosphine) (5.5 g, 99%) which, after one recrystallization from methanol (370 mL), formed large, friable rods, mp 112–113 °C, $[\alpha]_D$ −81.5° (*c* 0.98, CH_2Cl_2), 5 g (90%). Anal. Calcd for $C_{20}H_{20}P_2$: C, 74.5; H, 6.3. Found: C, 74.5; H, 6.4. ^1H NMR spectrum in $CDCl_3$: δ 1.48 (6 H, t, $^2J + {}^5J$ = 4 Hz, PMe), 7.10–7.44 ppm (14 H, br m, aromatics).

(+)-(*RR*)-*o*-Phenylenebis(methylphenylphosphine), (*RR*)-1. The filtrate from the isolation of (*R,RR*)-**6b** was concentrated and heated under reflux with hydrochloric acid (10 M, 15 mL). The complex (−)-dichloro[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II), (*SS*)-**7**, separated as a fine, yellow powder, $[\alpha]_D$ −47° (*c* 0.54, Me_2SO). Treatment of this complex with KCN as described above liberated (*RR*)-**1** (6.8 g, 99%), which after recrystallization from boiling methanol (460 mL) formed large rods, mp 112–113 °C, $[\alpha]_D$ + 81.3° (*c* 0.88, CH_2Cl_2), 5.8 g (90%). The ^1H NMR spectrum was identical with that of its enantiomer (*SS*)-**1**.

(+)-[(*R*)-Dimethyl(α-methylbenzyl)aminato-2-*C,N*][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Hexafluorophosphate (*R,SS*)-6b. A suspension of (*R*)-**5** (0.15 g) and (*RR*)-**1** (0.16 g) was stirred in methanol (5 mL) until a colorless solution resulted. The addition of $NH_4[PF_6]$ (0.1 g) in water (2 mL) caused the gradual precipitation of the product as colorless rosettes, mp 158–164 °C, $[\alpha]_D$ +219° (*c* 1.17, Me_2CO), 0.3 g (87%). Anal. Calcd for $C_{30}H_{34}F_6NP_3Pd$: C, 49.9; H, 4.8; N, 1.9. Found: C, 49.6; H, 4.5; N, 1.8. ^1H NMR spectrum in $CDCl_3$: δ 1.48 (3 H, d, *J* = 6.5 Hz, CH*Me*), 2.23 (3 H, d, *J* = 7.2 Hz, PMe), 2.33 (3 H, d, *J* = 11 Hz, PMe), 2.42 (3 H, br s, NMe), 2.81 (3 H, br s, NMe), 3.56 (1 H, q, *J* = 6.5 Hz, C*H*Me), 6.67–8.13 ppm (18 H, m, aromatics). An identical procedure using (*S*)-**5** and (*SS*)-**1** gave (*S,RR*)-**6b**, $[\alpha]_D$ −218° (*c* 1.1, Me_2CO).

Quaternization Reactions. *threo*-(*R;S*)-Benzyl(methyl)[(*S;R*)-(methylphenylphosphino)phenyl]phenylphosphonium Bromide, (*RS;SR*)-8a, and Hexafluorophosphate, (*RS;SR*)-8b. Benzyl bromide (0.5 mL) was reacted with a solution of (*RR;SS*)-**1** (1.2 g) in benzene (10 mL) for 8 h at room temperature. The crystalline precipitate of (*RS;SR*)-**8a** was filtered off, washed with benzene and petroleum ether, and dried to give white microcrystals, mp 180–184 °C (1.7 g, 94%). Anal. Calcd for $C_{27}H_{27}BrP_2$: C, 65.7; H, 5.5. Found: C, 65.4; H, 5.6. ^1H NMR spectrum in $CDCl_3$: δ 1.29 (3 H, d, J_{PH} = 3.7 Hz, PMe), 2.80 (3 H, d, J_{PH} = 13.3 Hz, $^+$PMe), 4.93, 5.43 (2 H, ABX, $^2J_{AB}$ = 15, $^2J_{PH}$ = 14 Hz, $^+PCH_2Ph$), 6.83–8.30 ppm (19 H, br m, aromatics). The bromide (1.2 g) was dissolved in methanol (5 mL) and a solution of $NH_4[PF_6]$ (0.5 g) in water (1 mL) gradually added. The fine, white precipitate of the hexafluorophosphate (*RS;SR*)-**8b** was collected, washed with water, and recrystallized from dichloromethane–diethyl ether as white needles, mp 213–214 °C (1.3 g, 94%). Anal. Calcd for $C_{27}H_{27}F_6P_3$: C, 58.1; H, 4.9. Found: C, 57.8; H, 4.6. ^1H NMR spectrum in acetone-d_6: δ 1.40 (3 H, d, $^2J_{PH}$ = 3.5 Hz, PMe), 2.73 (3 H, d, $^2J_{PH}$ = 13.2 Hz, $^+$PMe), 4.84 (1 H, d, $^2J_{PH}$ = 15.3 Hz, $^+PCH_AH_BPh$), 4.88 (1 H, $^2J_{PH}$ = 15.3 Hz, PCH_AH_BPh), 6.96–8.38 ppm (19 H, m, aromatics).

(+)-(*SR*)-8a and (+)-(*SR*)-8b. Reaction of (+)-(*RR*)-**1** (0.4 g) in benzyl bromide (2 mL) for several minutes followed by dilution with petroleum ether (40 mL) gave (*SR*)-**8a** as a crystalline hemihydrate, mp 188–189 °C (0.51 g, 93%), $[\alpha]_D$ +115° (*c* 0.82, CH_2Cl_2). Anal. Calcd for $C_{27}H_{28}BrO_{0.5}P_2$: C, 64.6; H, 5.6. Found: C, 64.7; H, 5.7. ^1H NMR spectrum in $CDCl_3$: δ 1.28 (3 H, d, $^2J_{PH}$ = 3.7 Hz, PMe), 2.78 (3 H, d, $^2J_{PH}$ = 13.3 Hz, $^+$PMe), 5.03, 5.39 (2 H, ABX, $^2J_{AB}$ = 16, $^2J_{PH}$ = 14 Hz, PCH_2Ph), 6.84–8.30 ppm (19 H, m, aromatics). Metathesis of (*SR*)-**8a** with $NH_4[PF_6]$ in aqueous methanol subsequently gave (*SR*)-**8b** which, after recrystallization from acetone–diethyl ether under nitrogen, formed colorless cubes, mp 154–155 °C (64% yield), $[\alpha]_D$ +101° (*c* 1.01, Me_2CO). ^1H NMR spectrum in acetone-d_6: δ 1.39 (3 H, d, $^2J_{PH}$ = 3.6 Hz, PMe), 2.70 (3H, d, $^2J_{PH}$ = 13.3 Hz, $^+$PMe), 4.80 (1 H, d, $^2J_{PH}$ = 15.3 Hz, $^+PCH_AH_BPh$), 4.84 (1 H, d, $^2J_{PH}$ = 15.3 Hz, $^+PCH_AH_BPh$), 6.93–8.34 ppm (19 H, m, aromatics).

***erythro*-(*R;S*)-Benzyl(methyl)[(*R;S*)-(methylphenylphosphino)phenyl]phenylphosphonium Bromide 2-Propanol Solvate, (*RR;SS*)-8a, and Hexafluorophosphate Dichloromethane Hemisolvate, (*RR;SS*)-8b.** Benzyl bromide (0.5 mL) was reacted with a suspension of (*RS*)-**1** (1.2 g) in 2-propanol (10 mL) at room temperature for 8 h. Colorless cubes of the bromide propan-2-ol solvate crystallized from the reaction mixture during this period which were collected, washed with solvent, and dried, mp 112–113 °C (1.6 g, 87%). Anal. Calcd for $C_{30}H_{35}BrOP_2$: C, 65.1; H, 6.4. Found: C, 65.0; H, 6.5. ^1H NMR spectrum in $CDCl_3$: δ 1.18 (6 H, d, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.23 (3 H, d, $^2J_{PH}$ = 3.2 Hz, PMe), 2.80 (3 H, d, $^2J_{PH}$ = 13.3 Hz, $^+$PMe), 4.03 (1 H, septet, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$), 4.94, 5.43 (2 H, ABX, $^2J_{AB}$ = 14, $^2J_{PH}$ = 14 Hz, $^+PCH_2Ph$), 6.83–8.39 (19 H, br m, aromatics). Metathesis of (*RR;SS*)-**8a** with $NH_4[PF_6]$ in aqueous methanol produced the hexafluorophosphate, which crystallized from dichloromethane–diethyl ether mixture as the dichloromethane hemisolvate (*RR;SS*)-**8b**, mp 166–167 °C (1.27 g, 94%). Anal. Calcd for $C_{27.5}H_{28}ClF_6P$: C, 55.0; H, 4.7. Found: C, 55.1; H, 4.8. ^1H NMR spectrum in acetone-d_6: δ 1.35 (3 H, d, $^2J_{PH}$ = 3.3 Hz, PMe), 2.73 (3 H, d, $^2J_{PH}$ = 13.3 Hz, $^+$PMe), 4.78 (1 H, d, $^2J_{PH}$ = 15.3 Hz, PCH_AH_BPh), 4.84 (1 H, d, $^2J_{PH}$ = 15.3 Hz, $^+PCH_AH_BPh$), 6.95–8.33 ppm (19 H, br m, aromatics).

Dimethyl[(*R;S*)-2(methylphenylphosphino)phenyl]phenylphosphonium Iodide, (*R;S*)-9a, and Hexafluorophosphate, (*R;S*)-9b. A suspension of either (*RR;SS*)-**1** or (*RS*)-**1** (0.7 g in 2-propanol (7 mL) was treated with an excess of iodomethane (1 mL) and the reaction mixture set aside for 48 h. The iodide separated as pale yellow crystals, mp 158–159 °C, which were filtered off, washed with 2-propanol, and dried in vacuo (93 g, 92%). Anal. Calcd for $C_{21}H_{23}IP_2$: C, 54.3; H, 5.0. Found: C, 54.5; H, 5.1. ^1H NMR spectrum in $CDCl_3$: δ 1.29 (3 H, d, $^2J_{PH}$ = 3.5 Hz, PMe), 3.02 (6 H, d, $^2J_{PH}$ = 13.3 Hz, $^+PMe_2$), 6.85–8.41 ppm (14 H, br m, aromatics). By metathesis of (*R;S*)-**9a** in methanol with $NH_4[PF_6]$ in water and recrystallization of the precipitate from acetone–diethyl ether was obtained the hexafluorophosphate (*R;S*)-**9b**, mp 183–184 °C (89% yield). Anal. Calcd for $C_{21}H_{23}F_6P$: C, 52.3; H, 4.8. Found: C, 52.5; H, 4.7. ^1H NMR spectrum in acetone-d_6: δ 1.36 (3 H, d, $^2J_{PH}$ = 3.3 Hz, PMe), 2.87 (3 H, d, $^2J_{PH}$ = 13.5 Hz, $^+$PMe), 2.90 (3 H, d, $^2J_{PH}$ = 13.5 Hz, $^+$PMe), 7.00–8.34 ppm (14 H, br m, aromatics).

***o*-Phenylenebis(dimethylphenylphosphonium) Hexafluorophosphate, 10.** A solution of (*RR;SS*)-**1** (0.32 g) in dichloromethane (10 ml) was added dropwise to a solution of $FSO_2(OMe)$ (0.4 mL) in the same solvent (20 mL). The reaction mixture was stirred for 3 h and then diluted with diethyl ether (50 mL). The mother liquor was decanted and the gum dissolved in methanol (10 mL) and treated with $NH_4[PF_6]$ (0.5 g) in water. The resulting crystalline precipitate was filtered off, washed with cold acetone (3 ml), and recrystallized from Me_2SO by the addition of methanol to give colorless microcrystals of **10**, mp >280 °C, 0.19 g (30%). Anal. Calcd for $C_{22}H_{26}F_{12}P_4$: C, 41.2; H, 4.1. Found: C, 41.7; H, 4.2. ^1H NMR spectrum in Me_2SO-d_6: δ 2.44 (12 H, d, J_{PH} = 14.1 Hz, $^+PMe_2$), 7.33–8.72 ppm (14 H, m, aromatics).

Protonation Reactions. *threo*-(*R;S*)-Methyl[(*R;S*)-2-(methylphen-

y|phosphino)phenyl]phosphonium Tetrafluoroborate (*RR;SS*)-11. A solution of (*RR;SS*-**1**) (0.32 g) in dichloromethane (30 mL) was shaken with aqueous HBF_4 (43% w/w, 1 mL). The organic layer was separated and dried over $MgSO_4$. Filtration, followed by removal of the solvent and recrystallization of the residue from acetone by the addition of dry diethyl ether, afforded the product as colorless rosettes, mp 115–130 °C (0.35 g, 85%). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.2, H, 5.3. ^1H NMR spectrum in CD_2Cl_2: δ 1.97 (6 H, br s, PMe), 7.01–8.09 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 23\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.3×10^{-3} M in $PhNO_2$ at 20 °C).

(−)-*threo*-(*SS*)-11 was prepared as above, but using (*SS*)-**1**, as needles from acetone–diethyl ether, mp 144–146 °C, $[\alpha]_D$ −106° (*c* 0.98, CH_2Cl_2) (78% yield). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.3; H, 5.2. ^1H NMR spectrum in CD_2Cl_2: δ 1.96 (6 H, br s, PMe), 7.05–8.16 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 24\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.1×10^{-3} M in $PhNO_2$ at 20 °C).

***erythro*-(*R;S*)-Methyl[(*S;R*)-2-(methylphenylphosphino)phenyl]-phenylphosphonium Tetrafluoroborate, (*RS;SR*)-11,** was prepared in the same way from (*RS*)-**1** as colorless cubes, mp 123–125 °C (90% yield). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.6; H, 5.1. ^1H NMR spectrum in CD_2Cl_2: δ 2.11 (6 H, br s, PMe), 7.08–8.0 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 26\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in $PhNO_2$ at 20 °C).

Dioxides of (*RR;SS*)-1 and (*RS*)-1. (*RR;SS*)-*o*-Phenylenebis-(methylphenylphosphine oxide), (*RR;SS*)-12. A solution of (*RR;SS*)-**1** (0.32 g) in dichloromethane (30 mL) was cooled to 0 °C, treated with aqueous H_2O_2 (30% w/w, 1 mL), and then stirred for 0.25 h. The reaction mixture was dried over $MgSO_4$ and then filtered and the solvent evaporated. The colorless gum crystallized from ethyl acetate (5 mL), after the addition of petroleum ether, as colorless needles, mp 189 °C (0.32 g, 90%). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.7. Found: C, 67.8; H, 5.8. ^1H NMR spectrum in $CDCl_3$: δ 2.28 (6 H, d, $^2J_{PH} + {}^5J_{PH}$ = 14 Hz, PMe), 7.06–8.16 ppm (14 H, br m, aromatics).

(+)-(*RR*)-**12** was obtained from (−)-(*SS*)-**1** under similar conditions. It crystallized with difficulty from ethyl acetate in 82% yield as colorless rosettes, mp 197–198 °C, $[\alpha]_D$ +103° (*c* 1.17, CH_2Cl_2). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.8. Found: C, 66.8; H, 5.6. ^1H NMR spectrum in $CDCl_3$: δ 2.31 (6 H, d, $^2J_{PH} = {}^5J_{PH}$ = 13.6 Hz, PMe), 7.06–8.10 ppm (14 H, br m, aromatics).

(*RS*)-*o*-Phenylenebis(methylphenylphosphine oxide), (*RS*)-13, was obtained under similar conditions from (*RS*)-**1** as white microcrystals from *n*-butyl acetate, mp 213–215 °C (77%). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.7. Found: C, 67.5; H, 5.7. ^1H NMR spectrum in $CDCl_3$: δ 1.90 (6 H, d, $^2J_{PH} + {}^5J_{PH}$ = 14.3 Hz, PMe), 7.37–8.17 ppm (14 H, br m, aromatics).

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Model Compounds for the Interaction of Silver(I) with Polyuridine. Crystal Structure of a 1:1 Silver Complex with 1-Methylthymine

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Abstract: The neutralization of uridine in the presence of various quantities of Ag^+ ions has been followed pHmetrically and the data have been interpreted in terms of complexes with 2:1 and 2:2 metal–ligand ratios. The corresponding equilibrium constants have been refined by least squares. Crystals of the 1:1 silver complex with 1-methylthymine (HMT) are monoclinic, space group $C2/c$, with $a = 11.270$ Å, $b = 13.239$ Å, $c = 9.647$ Å, and $\beta = 100.11°$. The structure was refined on 1004 independent nonzero reflections to an *R* factor of 0.028. One-half of the silver atoms have a linear coordination and bind strongly to N(3) atoms of two deprotonated ligands (Ag–N(3) = 2.081 Å). The resulting planar $Ag(MT)_2^-$ units are connected by the remaining silver atoms, which are tetrahedrally surrounded with oxygen atoms from two $Ag(MT)_2^-$ units. Binding to O(2) is much weaker (Ag–O(2) = 2.512 Å) than with O(4) (Ag–O(4) = 2.333 Å). Those results are discussed in connection with silver binding to poly(U).

It is well established that Ag(I) binds strongly to nucleic acids and polynucleotides.[1] However, there are disagreements in the literature concerning poly(U). Recently, Arya and Yang[2] reported that the UV, ORD, and CD spectra are not affected by silver at neutral pH. On the basis of potentiometric data, UV spectra, and hydrodynamic measurements, Daune, Dekker, and Schachman[3] proposed nonspecific silver binding. On the other hand, UV spectra and pHmetric data obtained by Eichhorn et al.[4] have shown that silver reacts with uracil residues of poly(U) for pH >6. Jensen[5] has identified two types of Ag–poly(U) complexes. The metal first reacts with two uracil residues displacing two protons. In a second step, further fixation of Ag(I) leads to a 1:1 stoichiometry without proton exchange. These reactions are simultaneous for pH ≤7, but resolved at pH 8. Similar conclusions have been reached recently by Klotz and Daune,[6] who also noted that nonspecific binding takes place as well at lower pH and lower silver-to-base ratios.

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