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Metal Complexes Containing Diastereoisomers and Enantiomers of *o*-Phenylenebis(methylphenylarsine) and Its Phosphorus Analogue. 2. Stereochemistry and Dynamic Behavior of Square-Planar and Square-Pyramidal Complexes of Bivalent Palladium and Platinum[1]

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The stereochemistry and dynamic behavior of square-planar and square-pyramidal complexes of bivalent palladium and platinum have been investigated by examining the ^{1}H NMR spectra of appropriate derivatives of each metal containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue. Whereas the square-planar bis(bidentate)metal(II) derivatives of both ligands are kinetically stable and retain their structural integrity in solution, the corresponding square-pyramidal chloro cations undergo rapid axial ligand site exchange, redistribution of di(tertiary arsine) ligands in the case of palladium, and intramolecular isomerization of the chelate rings for both metals containing the various stereoisomers of either ligand.

Introduction

In the previous paper we presented the first direct evidence of intermolecular bidentate ligand exchange (redistribution) and intramolecular isomerization of the chelate rings in square-planar and square-pyramidal nickel(II) cations containing di(tertiary arsines) and di(tertiary phosphines).[2] The various dynamic processes occurring within the cations $[Ni(bidentate)_2]^{2+}$ and $[NiX(bidentate)_2]^+$ were reflected in the variable-temperature ^{1}H NMR spectra of solutions of judiciously chosen stereoisomers of the complexes. Hitherto, the only related work concerned the lability of the axial halogeno bond in the square-pyramidal cations $[MX(diars)_2]^+$ [where M = Ni,[3] Pd,[4] or Pt[3] and diars = *o*-phenylenebis(dimethylarsine)] and $[MX(tetars)]^+$ [where M = Ni, Pd, or Pt and tetars = bis[(3-dimethylarsino)propyl)phenylarsino]-1,2-ethane)[5]].

In the present paper we discuss the stereochemistry and dynamic behavior of analogous bivalent palladium and platinum complexes containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine)[6] and its phosphorus analogue.[7]

Results and Discussion

Preparation of the Neutral Square-Planar Complexes $[MCl_2(diars)]$ and $[MCl_2(diphos)]$ (Where M = Pd or Pt). Although the complexes $[PdCl_2(diars)]$ containing the various stereoisomers of *o*-phenylenebis(methylphenylarsine) could be prepared under the usual reaction conditions, the corresponding di(tertiary phosphine) compounds were not as easily obtained. Insoluble pink precipitates of the type $[Pd(diphos)_2][PdCl_4]$ formed instantly upon mixing solutions of the appropriate reagents, but these could not be converted to the desired dichloropalladium(II) species. For example, the Magnus-type salts containing the di(tertiary phosphine) could be recovered unchanged from DMF–10 M HCl mixture after the solution had been boiled for 1 week. Reaction of either $[PdCl_2(MeCN)_2]$ or $[PdCl_2(PhCN)_2]$ with the di(tertiary phosphine) also afforded the intractable bis(bidentate)palladium(II) salts. Indeed, the stability of bis(*o*-phenylenebis(methylphenylphosphine))palladium(II) salts toward redistribution reactions is a feature of their chemistry (vide infra). Accordingly, a satisfactory route to the desired dichloropalladium(II) derivatives of the di(tertiary phosphine) cannot involve coordination of more than one ligand per palladium atom. During the course of our work concerning the resolution of (*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine),[7] it was found that the chloro-bridged palladium(II) dimer derived from dimethyl(α-methylbenzyl)amine readily underwent bridge-splitting reactions with the di(tertiary phosphine) to afford a mixture of internally diastereoisomeric salts. These, upon reaction with aqueous hydrochloric acid, gave high yields of the complex $[PdCl_2((RR,SS)\text{-diphos})]$. We found this indirect method to be excellent for the preparation of all of the different complexes $[PdCl_2(diphos)]$.

In the case of platinum(II), an indirect route was required in order to obtain dichloroplatinum(II) derivatives of the di(tertiary phosphine) *and* di(tertiary arsine) since direct methods again yielded the intractable Magnus-type salts. Here, because ortho-metalated platinum(II) derivatives of tertiary amines were not available in high yields,[8] we opted for the readily prepared dimer di-μ-chloro-bis(2-methoxycyclooct-5-enyl)diplatinum(II)[9] as intermediate. The dimer was cleaved by the appropriate di(tertiary arsine) or di(tertiary phosphine), and the resulting mixture of internally diastereoisomeric salts reacted with aqueous hydrochloric acid. It was not necessary to isolate the intermediate reagents in order to obtain high yields of the desired products. The use of $[PtCl_2(PhCN)_2]$ also afforded the dichloroplatinum(II) complexes, but the yield and quality of the products were inferior to those obtained by the former method.

Optically Active Complexes $[MCl(bidentate)_2]Cl$ and $[M(bidentate)_2](PF_6)_2$ [Where M = Pd or Pt and bidentate = (*RR*)-diars or -diphos or (*SS*)-diars or -diphos]. (a) Palladium(II) Complexes. The neutral complex $[PdCl_2((SS)\text{-diars})]$ reacted with 1 equiv of (*RR*)-diars in 95% ethanol to give a yellow solution from which bright yellow needles of the salt $[PdCl((SS)\text{-diars})_2]Cl\cdot 2H_2O$ crystallized upon dilution with diethyl ether.

$$[PdCl_2((SS)\text{-diars})] + (RR)\text{-diars} \rightleftharpoons [PdCl((SS)\text{-diars})_2]Cl$$

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(1) In this and the preceding paper, the term di(tertiary arsine) is used to represent a bidentate ligand containing two tertiary arsenic groups. The phosphorus analogue is treated similarly.
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Table I. Physical Properties of the Complexes [MX(bidentate)$_2$]X

compd	Λ_M[a] CH_2Cl_2	Λ_M[a] H_2O	δ(EMe)[b] $CDCl_3$	δ(EMe)[b] D_2O
(+)-[PdCl((*SS*)-diars)$_2$]Cl·2H$_2$O	44 (1:1)	172 (2:1)	1.79	1.99
(+)-[PdI((*SS*)-diars)$_2$]I	35 (1:1)		1.89	
meso-[PdCl((*RR*)-diars)((*SS*)-diars)]Cl·2H$_2$O	38 (1:1)	171 (2:1)	2.49 (25%), 1.79 (75%)	2.37
meso-[PdCl((*RR*)-diars)((*SS*)-diars)]Cl·2(ethane-1,2-diol)	35 (1:1)	173 (2:1)	2.49 (25%), 1.79 (75%)	2.37
meso-[PdI((*RR*)-diars)((*SS*)-diars)]I	34 (1:1)		2.61 (20%), 1.88 (80%)	
anti-[PdCl((*RS*)-diars)$_2$]Cl		170 (2:1)		2.66
(+)-[PdCl((*SS*)-diphos)$_2$]Cl·2H$_2$O	42 (1:1)	174 (2:1)	1.73	1.83
rac-[PdCl((*RR,SS*)-diphos)$_2$]Cl·H$_2$O	35 (1:1)	178 (2:1)	1.74	1.83
meso-[PdCl((*RR*)-diphos)((*SS*)-diphos)]Cl	29 (1:1)	186 (2:1)	2.63	2.71
anti-[PdCl((*RS*)-diphos)$_2$]Cl	42 (1:1)	176 (2:1)	2.68 (18%), 1.65 (82%)	2.71 (47%), 1.70 (53%)
(+)-[PtCl((*SS*)-diars)$_2$]Cl·2H$_2$O	43 (1:1)	176 (2:1)	1.84	2.00
rac-[PtCl((*RR,SS*)-diars)$_2$]Cl·4H$_2$O	38 (1:1)	181 (2:1)	1.84	2.00
meso-[PtCl((*RR*)-diars)((*SS*)-diars)]Cl·0.5H$_2$O	33 (1:1)	181 (2:1)	2.63	2.72
anti-[PtCl((*RS*)-diars)$_2$]Cl		173 (2:1)		2.73 (83%), 1.97 (17%)
(+)-[PtCl((*SS*)-diphos)$_2$]Cl·2H$_2$O	45 (1:1)	183 (2:1)	1.83	1.92
rac-[PtCl((*RR,SS*)-diphos)$_2$]Cl·4H$_2$O	40 (1:1)	184 (2:1)	1.83	1.92
meso-[PtCl((*RR*)-diphos)((*SS*-diphos)]Cl·H$_2$O	40 (1:1)	178 (2:1)	2.73	2.75
anti-[PtCl((*RS*)-diphos)$_2$]Cl·2H$_2$O	45 (1:1)	182 (2:1)	2.80 (14%), 1.71 (86%)	2.64 (38%), 1.66 (62%)

[a] Conductance in cm^2 Ω^{-1} mol^{-1} for 10^{-3} M solutions at 293 K. [b] ^{1}H NMR spectra chemical shift values in ppm relative to Me_4Si in $CDCl_3$ and sodium 3-(trimethylsilyl)propanesulfonate in D_2O.

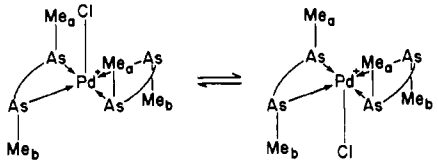

Figure 1. Nonequivalent pairs of methyl groups in the optically active cation [PdCl((*SS*)-diars)$_2$]$^+$.

The product was very soluble in dichloromethane and nitrobenzene and gave in each case a yellow solution which conducted as a uni-univalent electrolyte. However, in aqueous solution the complex was colorless and behaved as a di-univalent electrolyte (Table I). These data were consistent with the presence of a square-planar cation in water and a square-pyramidal complex ion in the less polar solvents, as had previously been noted for similar complexes of *o*-phenylenebis(dimethylarsine).[4]

$$[Pd((SS)\text{-diars})_2]^{2+} + 2Cl^- \rightleftharpoons [PdCl((SS)\text{-diars})_2]Cl$$

The AsMe signal for the complex [PdCl((*SS*)-diars)$_2$]Cl·2H$_2$O in $CDCl_3$ or CH_2Cl_2 appeared as a sharp singlet at δ 1.79 in the room-temperature ^{1}H NMR spectrum.[10] Two AsMe signals would be anticipated for the stereochemically rigid square-pyramidal complex ion provided it were kinetically stable or undergoing relatively slow (with respect to the NMR time scale) site exchange of the axial chloro ligand (Figure 1).

However, as we have shown previously for comparable nickel(II) complexes,[2] the axial chloro ligand in square-pyramidal complex ions of this type undergoes rapid (by comparison with the NMR time scale) site exchange between the alternative axial sites in a bimolecular process involving sterically compatible species. This effect alone is sufficient to account for the single AsMe resonance observed for the optically active complex. However, as shall be evident shortly, there are other factors contributing to averaged observations in square-pyramidal complexes of this type. Bis(di(tertiary arsine)) derivatives of palladium(II) undergo facile intermolecular exchange of bidentate ligands (redistribution) as well as rapid intramolecular isomerization of the chelate rings in the presence of halide ions in solvents promoting five coordination.

(10) NMR spectra of hydrated salts were recorded in the presence of D_2O.

Table II. Physical Properties of the Complexes [M(bidentate)$_2$](PF$_6$)$_2$

compd	Λ_M[a] in Me_2CO	δ(EMe)[b] in Me_2SO-d_6
(+)-[Pd((*SS*)-diars)$_2$](PF$_6$)$_2$	222 (2:1)	1.98
meso-[Pd((*RR*)-diars)((*SS*)-diars)](PF$_6$)$_2$	217 (2:1)	2.49
anti-[Pd((*RS*)-diars)$_2$](PF$_6$)$_2$	206 (2:1)	2.27
(+)-[Pd((*SS*)-diphos)$_2$](PF$_6$)$_2$	222 (2:1)	1.82
rac-[Pd((*RR,SS*)-diphos)$_2$](PF$_6$)$_2$·Me$_2$CO[c]	212 (2:1)	1.79
meso-[Pd((*RR*)-diphos)((*SS*)-diphos)](PF$_6$)$_2$	220 (2:1)	2.52
anti-[Pd((*RS*)-diphos)$_2$](PF$_6$)$_2$	203 (2:1)	1.96
(+)-[Pt((*SS*)-diars)$_2$](PF$_6$)$_2$	222 (2:1)	2.02
rac-[Pt((*RR,SS*)-diars)$_2$](PF$_6$)$_2$	218 (2:1)	2.02
meso-[Pt((*RR*)-diars)((*SS*)-diars)](PF$_6$)$_2$	212 (2:1)	2.64
anti-[Pt((*RS*)-diars)$_2$](PF$_6$)$_2$	212 (2:1)	2.32
(+)-[Pt((*SS*)-diphos)$_2$](PF$_6$)$_2$	227 (2:1)	1.89
rac-[Pt((*RR,SS*)-diphos)$_2$](PF$_6$)$_2$	205 (2:1)	1.89
meso-[Pt((*RR*)-diphos)((*SS*)-diphos)](PF$_6$)$_2$	209 (2:1)	2.74
anti-[Pt((*RS*)-diphos)$_2$](PF$_6$)$_2$	208 (2:1)	1.96

[a] Conductance in cm^2 Ω^{-1} mol^{-1} for 10^{-3} M solutions at 293 K. [b] ^{1}H NMR spectra chemical shift values in ppm relative to Me_4Si in Me_2SO-d_6 solution at 308 K. [c] Observed in ^{1}H NMR spectrum.

In D_2O, the optically active complex exists as a square-planar dication; the AsMe singlet occurs at δ 1.99, consistent with the higher formal charge on the complex ion in this medium. Accordingly, when NH_4PF_6 was added to an aqueous solution of the salt, [Pd((*SS*)-diars)$_2$](PF$_6$)$_2$ precipitated. The latter behaved as a di-univalent electrolyte in acetone (Table II), and its ^{1}H NMR spectrum in Me_2SO-d_6 exhibited an AsMe singlet at δ 1.98. However, when NaI was added to an aqueous solution of [PdCl((*SS*)-diars)$_2$]Cl·2H$_2$O, the orange complex [PdI((*SS*)-diars)$_2$]I precipitated; this was five-coordinate in dichloromethane and displayed a correspondingly downfield AsMe singlet at δ 1.89 for the square-pyramidal complex ion undergoing rapid axial iodo site exchange (Table I).

The optically active di(tertiary phosphine) (*RR*)-diphos formed a similar series of four- and five-coordinate palladi-

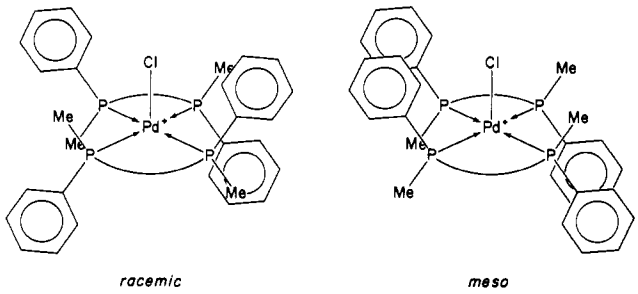

Figure 2. Stereochemistry of the cations *rac*-[PdCl((*RR*,*SS*)-diphos)$_2$]$^+$ and *meso*-[PdCl((*RR*)-diphos)((*SS*)-diphos)]$^+$.

um(II) complexes. The physcial properties of these compounds are also summarized in Tables I and II.

(b) Platinum(II) Complexes. The optically active complex [PtCl((*SS*)-diars)$_2$]Cl·2H$_2$O was prepared from [PtCl$_2$]$_n$ and (*RR*)-diars by heating a mixture of the two in acetonitrile. The crude product was recrystallized from dichloromethane by the addition of wet diethyl ether. However, the corresponding di(tertiary phosphine) compound was better prepared from [PtCl$_2$(PhCN)$_2$]. Both complexes formed insoluble bis(hexafluorophosphate) salts upon metathesis with NH_4PF_6 in boiling water (Tables I and II).

Internal Diastereoisomers *rac*- and *meso*-[MCl(bidentate)$_2$]Cl and -[M(bidentate)$_2$](PF$_6$)$_2$ [Where M = Pd or Pt and bidentate = (*RR*,*SS*)-diars or -diphos]. (a) Palladium(II) Complexes. A suspension of [PdCl$_2$((*RR*,*SS*)-diphos)] in 95% ethanol was reacted with 1 equiv of (*RR*,*SS*)-diphos at room temperature. The initial complex quickly dissolved to give a yellow solution from which a yellow complex analyzing as [PdCl(diphos)$_2$]Cl·2H$_2$O could be precipitated by the addition of diethyl ether. The ^{1}H NMR spectrum of this material in $CDCl_3$ showed two broad (^{31}P coupled) PMe singlets centered at δ 2.63 and 1.74 in the intensity ratio 2:1, respectively. The lower field signal was assigned to the PMe resonance of the racemic cation [PdCl((*RR*,*SS*)-diphos)$_2$]$^+$ on the basis that the optically active cation [PdCl((*SS*)-diphos)$_2$]$^+$ exhibited a resonance in the same position in this solvent (Table I). The PMe resonance at δ 2.63 was therefore attributed to the internally compensated cation *meso*-[PdCl((*RR*)-diphos)((*SS*)-diphos)]$^+$, rapid axial site exchange of the chloro ligand again accounting for the singlet resonance observed in each case.

$$[PdCl_2((RR,SS)\text{-diphos})] + (RR,SS)\text{-diphos} \rightarrow [PdCl((RR,SS)\text{-diphos})_2]Cl + [PdCl((RR)\text{-diphos})((SS)\text{-diphos})]Cl$$

The relative chemical shift values of the PMe resonances of the internally compensated five-coordinate cations were consistent with those found for the corresponding pair of nickel(II) complexes in the same solvent, viz., meso (δ 2.43) and racemic (δ 1.51).[2] The different shielding effects, which presumably account for this large discrepancy in chemical shift values of the diastereoisomeric cations, were apparent in molecular models of the complex cations, diagrams of which are shown in Figure 2.

Clearly the methyl groups in the racemic cation experience a greater shielding by the phenyl groups than those of the corresponding meso cation, which results in a relatively downfield PMe resonance being observed in the latter diastereoisomer.

The racemic and meso complexes derived from the racemic di(tertiary phosphine) were kinetically inert in the absence of added di(tertiary phosphine). Indeed, the initial 2:1 mixture of diastereoisomers could be fractionally crystallized. The ^{1}H NMR spectra of the separated complexes in $CDCl_3$ did not

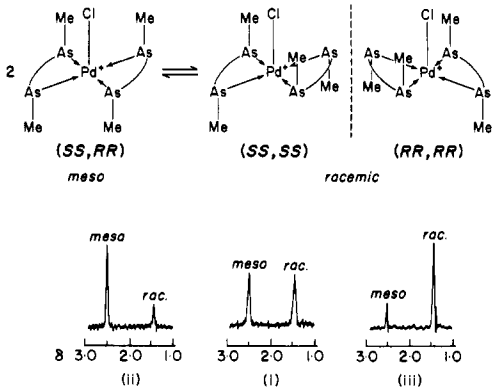

Figure 3. Solvent dependent redistribution of the bidentate ligands in the system *meso*-[PdCl((*RR*)-diars)((*SS*)-diars)]Cl $\rightleftharpoons$ *rac*-[PdCl((*RR*,*SS*)-diars)$_2$]Cl. Spectrum i shows AsMe resonances of the equilibrium mixture of complexes in Me$_2$SO-d_6. Spectra ii and iii are of similar solutions in Me$_2$SO-d_6 diluted with D$_2$O or $CDCl_3$, respectively.

alter over a 1-week period at 25 °C. Heating of a solution of either of the diastereoisomers in D$_2$O at 100 °C for 6 h similarly did not affect their structural integrity. Nevertheless, when a trace of free (*RR*,*SS*)-diphos was added to a solution of either of the pure diastereoisomeric complexes in $CDCl_3$, an equilibrium mixture of the redistribution products (meso:racemic = 1:6) formed within 15 min at 25 °C.

$$2[PdCl((RR)\text{-diphos})((SS)\text{-diphos})]Cl \overset{\text{cat.}}{\rightleftharpoons} [PdCl((RR)\text{-diphos})_2]Cl + [PdCl((SS)\text{-diphos})_2]Cl$$

As expected, both diastereoisomers behaved as uni-univalent electrolytes in CH_2Cl_2 and $PhNO_2$ but as di-univalent electrolytes in water. In D$_2$O the PMe resonances of the cations *rac*-[Pd((*RR*,*SS*)-diphos)$_2$]$^{2+}$ and *meso*-[Pd((*RR*)-diphos)((*SS*-diphos)]$^{2+}$ occurred at δ 1.83 and δ 2.71, respectively, and the corresponding bis(hexafluorophosphate) salts could be precipitated from aqueous solution by the addition of NH_4PF_6 (Table II).

The racemic di(tertiary arsine), (*RR*,*SS*)-diars, reacted under mild conditions with [PdCl$_2$((*RR*,*SS*)-diars)] to give a bright yellow solution from which yellow crystals of the 2:1 derivative deposited upon the addition of diethyl ether. However, during the process of isolation these crystals apparently lost solvent of crystallization, crumbling to a yellow powder which analyzed as [PdCl(diars)$_2$Cl·2H$_2$O. Beautiful long needles of this compound were also obtained from boiling water, but these lost water of crystallization during isolation. The ^{1}H NMR spectrum of the product in $CDCl_3$ indicated the presence of 1:3 mixture of the five-coordinate meso (δ 2.49 AsMe) and racemic (δ 1.79 AsMe) complexes, respectively (Table I). In D$_2$O solution, however, only one AsMe signal at δ 2.37 ppm was observed which was due to the square-planar cation *meso*-[Pd((*RR*)-diars)((*SS*)-diars)]$^{2+}$. Accordingly, when NH_4PF_6 was added to an aqueous solution of the initial complex, only *meso*-[Pd((*RR*)-diars)((*SS*)-diars)](PF$_6$)$_2$ precipated (δ 2.49 AsMe in Me$_2$SO-d_6). In contradistinction to the situation found in $CDCl_3$, the ^{1}H NMR spectrum of the initial *chloro* complex in Me$_2$SO-d_6 showed two AsMe singlets of approximately *equal* intensity due to the two internal diastereoisomers, and the proportion of each could be altered in favor of the meso complex by adding D$_2$O or altered toward the racemic complex by diluting the NMR sample with $CDCl_3$ (Figure 3).

Clearly, the di(tertiary arsine) ligands in the system [PdCl(diars)$_2$]Cl undergo a facile redistribution between different metal centers (intermolecular bidentate ligand exchange) since it is not possible to interconvert the racemic and

meso diastereoisomers of this complex by an internal rearrangement.

$$2[PdCl((RR)\text{-diars})((SS)\text{-diars})]Cl \rightleftharpoons [PdCl((RR)\text{-diars})_2]Cl + [PdCl((SS)\text{-diars})_2]Cl$$

The position of the equilibrium depends markedly upon the nature of the solvent and presumably reflects the different solvation energies of the various four- and five-coordinate cations present and of the chloride ions. Further experiments with *meso*-$[Pd((RR)\text{-diars})((SS)\text{-diars})](PF_6)_2$ provided additional information on this aspect of the problem. The ^1H NMR spectrum of the pure salt (recrystallized from acetone–diethyl ether mixture) exhibited one stable AsMe singlet in Me_2SO-d_6 at δ 2.49. However, when a trace of (*RR*,*SS*)-diars was added to the solution, a new signal at δ 1.98 rapidly appeared. The chemical shift value of the new signal corresponded to the expected value of the racemic cation. At equilibrium the meso:racemic ratio was 3:1.

In a separate ^1H NMR experiment, a catalytic quantity of chloride ions (as LiCl) was added to a solution of *meso*-$[Pd((RR)\text{-diars})((SS)\text{-diars})](PF_6)_2$ in Me_2SO-d_6. Again, a rapid redistribution of bidentate ligands occurred leading to an equilibrium 3:1 mixture of the meso and racemic square-planar complexes, respectively. The gradual addition of more LiCl to this solution further augmented the concentration of the racemic complex at the expense of its meso counterpart. Furthermore, as the addition proceeded, the solution became more yellow and the position of the AsMe signal due to the racemic square-planar cation (δ 1.98) moved steadily toward the value expected for the corresponding five-coordinate species $[PdCl((RR,SS)\text{-diars})_2]^+$, viz., δ 1.79. Thus chloride ions, as well as catalyzing di(tertiary arsine) ligand exchange, also appear to destabilize the meso cation. Dreiding molecular models of the two diastereoisomers indicated that the introduction of a chloro ligand to an axial site of the meso structure interfered with the neighboring pair of phenyl groups which, prior to the irruption of the chloro ligand, had been favorably arranged facing one another. Thus in $CDCl_3$ and CH_2Cl_2 solutions, where five-coordinate chloro species predominate, the racemic diastereoisomer is more stable, but in more polar solvents (D_2O or Me_2SO-d_6) the square-planar meso cation has the greater stability.

Crystals of *meso*-$[PdCl((RR)\text{-diars})((SS)\text{-diars})]Cl\cdot 2H_2O$ were unsuitable for an X-ray structural analysis. However, recrystallization of the hydrate from ethane-1,2-diol–ethanol–diethyl ether mixture afforded satisfactory crystals of the solvate *meso*-$[PdCl((RR)\text{-diars})((SS)\text{-diars})]Cl\cdot 2(HOCH_2CH_2OH)$. The molecular structure found in the solid state was that of the meso diastereoisomer in which opposing pairs of phenyl groups were in an eclipsed configuration.[11] Because of the interaction between the phenyl groups and the axial chlorine atoms, the Pd–Cl bonds were bent away from the vertical axis by 14.7°. The solvent molecules occupied voids within the crystal lattice. On the basis of this structure we also assigned the meso formulation to the *dihydrate*. The ethane-1,2-diol *solvate* also underwent redistribution of bidentate ligands upon dissolution in $CDCl_3$, the ^1H NMR spectrum containing two AsMe signals (meso:racemic = 1:3, Table I) as well as signals due to the free glycol.

Metathesis of *meso*-$[PdCl((RR)\text{-diars})((SS)\text{-diars})]Cl\cdot 2H_2O$ with NaI in aqueous solution produced an orange precipitate of the anhydrous iodo complex. An X-ray crystal structure analysis of this complex[11] again confirmed the meso arrangement of di(tertiary arsine) ligands in the solid state. However, in $CDCl_3$ solution *meso*-$[PdI((RR)\text{-diars})((SS)\text{-diars})]I$ rapidly disproportionated into an equilibrium 1:4 = meso:racemic mixture of diastereoisomers (Table I) and a 1:1 mixture in Me_2SO-d_6.

(b) Platinum(II) Complexes. The reaction of $[PtCl_2]_n$ with 2 equiv of either (*RR*,*SS*)-diars or (*RR*,*SS*)-diphos in acetonitrile afforded the corresponding pale yellow bis(bidentate) complexes. The ^1H NMR spectra of these compounds indicated the presence of a 1:3 mixture of diastereoisomers in each case. The mixture of diastereoisomers could be fractionally crystallized for both ligands, in contrast to the behavior of the corresponding palladium(II) complexes where only the di(tertiary phosphine) complexes were kinetically stable. All of the different complexes (Table I) behaved as uni-univalent electrolytes in dichloromethane in which they were yellow and as di-univalent electrolytes in water where the colorless square-planar cation was present. The colorless bis(hexafluorophosphate) salts were precipitated from aqueous solutions of the respective chlorides (Table II).

The ^1H NMR spectra of the diastereoisomeric chloroplatinum(II) complexes of each ligand in $CDCl_3$ and D_2O solutions closely resembled (apart from ^{195}Pt coupling) the spectra of the corresponding palladium derivatives (Table I). Again, rapid site exchange of axial chloro ligand in the five-coordinate structure accounted for singlet AsMe or PMe resonance observed in each case. The pure diastereoisomeric complexes of both ligands were stable in solution. Redistribution of the bidentate ligands was not promoted by chloride ions, as evidenced by the static ^1H NMR spectrum of each complex in $CDCl_3$. Moreover, the ^1H NMR spectrum of a solution of *rac*-$[PtCl((RR,SS)\text{-diars})_2]Cl\cdot 4H_2O$, or its phosphorus analogue, in D_2O did not alter when the solution was heated for 6 h at 100 °C. In the presence of free (*RR*,*SS*)-diars, however, there was a slow redistribution of the bidentate ligands in the case of the di(tertiary arsine) complexes. For example, the ^1H NMR spectrum of a mixture of *meso*-$[PtCl((RR)\text{-diars})((SS)\text{-diars})]Cl\cdot 0.5H_2O$ (0.04 M) and (*RR*,*SS*)-diars (0.01 M) in $CDCl_3$ initially showed only the presence of the square-pyramidal meso cation (δ 2.63 AsMe), but, after several minutes at 37 °C, a peak due to the diastereoisomeric racemic cation (δ 1.85 AsMe) was noticeable. After 65 h at 20 °C, the proportion of diastereoisomers was 1:1, and after ca. 2 weeks the system had reached an equilibrium situation involving a 1:3 mixture of racemic and meso complexes, respectively. The same equilibrium mixture of complexes was obtained beginning with *rac*-$[PtCl((RR,SS)\text{-diars})_2]Cl\cdot 4H_2O$.

The corresponding meso and racemic bis(di(tertiary phosphine)) complexes of platinum(II) were inert with respect to redistribution of bidentate ligands by themselves and in the presence of excess chloride ions *or* free (*RR*,*SS*)-diphos at 20 °C in $CDCl_3$.

Geometric Isomers *syn*- and *anti*-[MCl(bidentate)$_2$]Cl [Where M = Pd or Pt and bidentate = (*RS*)-diars or -diphos]. The reaction of $[PdCl_2((RS)\text{-diphos})]$ with an equimolar quantity of (*RS*)-diphos in 95% ethanol gave a yellow solution from which a yellow gum could be precipitated by the addition of petroleum ether. The ^1H NMR spectrum of this material in $CDCl_3$ displayed two PMe singlets at δ 2.68 and 1.64 in the intensity ratio of 1:4.5, respectively. Recrystallization of the gum from dichloromethane–petroleum ether mixture afforded a yellow crystalline solid. The solid had a ^1H NMR spectrum identical with that of the original gum and analyzed as $[PdCl(diphos)_2]Cl$. For reasons which will become apparent shortly, this compound was formulated *anti*-$[PdCl((RS)\text{-diphos})_2]Cl$. Solutions of the complex in dichloromethane are yellow and the substance conducts therein as a uni-univalent electrolyte (Table I).

The two PMe signals in the ^1H NMR spectrum of a solution of *anti*-$[PdCl((RS)\text{-diphos})_2]Cl$ in $CDCl_3$ have been assigned

(11) Skelton, B.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 1556.

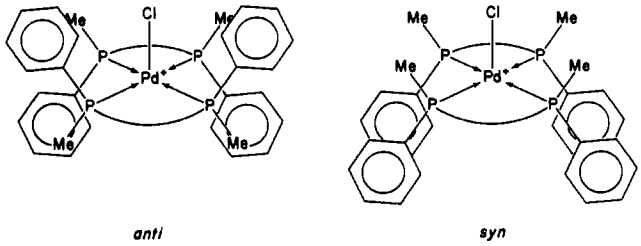

Figure 4. Stereochemistry of the cations *syn*-[PdCl((*RS*)-diphos)$_2$]$^+$ and *anti*-[PdCl((*RS*)-diphos)$_2$]$^+$.

to the syn and anti isomers depicted in Figure 4. Again, one averaged PMe signal was observed for each isomer due to the rapid exchange of the axial chloro ligand. Inspection of molecular models of both isomers revealed that each methyl group in the anti complex was opposite a phenyl group of the neighboring ligand (and hence shielded by it) whereas this interaction was absent in the syn structure. The averaged PMe signal of the anti complex consequently appeared upfield of the corresponding signal for the syn isomer.

The yellow crystalline complex *anti*-[PdCl((*RS*)-diphos)$_2$]Cl dissolved in water to give a colorless solution in which it behaved as a di-univalent electrolyte due to the presence of square-planar *anti*-[Pd((*RS*)-diphos)$_2$]$^{2+}$. In D_2O at 20 °C the chloride exhibited only one PMe signal at δ 1.70. However, upon gentle heating of the D_2O solution, a new PMe signal appeared at δ 2.71 which we have assigned to the isomeric cation *syn*-[Pd((*RS*)-diphos)$_2$]$^{2+}$. Equilibrium within the system was attained within ca. 10 min at 100 °C, the ratio of isomers at that stage being syn:anti = 7:8. The isomerization process *must* be intramolecular in nature since we have shown that interconversion does not take place between the cations *mseo*-[PdCl((*RR*)-diphos)((*SS*)-diphos)]$^+$ and *rac*-[PdCl((*RR*,*SS*)-diphos)$_2$]$^+$ under similar conditions. Interconversion between the latter pair of complexes unambiguously identifies an intermolecular redistribution reaction involving exchange of the bidentate ligands between different metal centers. However, it should be noted that internal isomerization of the bidentate ligands (C_2 rotation about the metal–bidentate bond axis) cannot be detected by ^{1}H NMR spectroscopy in the case of the meso and racemic complexes.

It is significant that syn $\rightleftharpoons$ anti interconversion proceeded at a much faster rate in $CDCl_3$ than in D_2O. This suggests that the active species in the intramolecular isomerization is the five-coordinate cation [PdCl((*RS*)-diphos)$_2$]$^+$. The degree of stereochemical nonrigidity in these cations is evident from the ^{1}H NMR spectra shown in Figure 5.

The room-temperature ^{1}H NMR spectrum of a solution of *anti*-[PdCl((*RS*)-diphos)$_2$]Cl in benzonitrile contained two PMe singlets of approximately equal intensity at δ 2.70 and 1.66 which corresponded to a mixture of the five-coordinate geometric isomers. As the temperature of the sample was raised, the signals broadened, coalesced (T_c = 370 K), and eventually reemerged as a singlet resonance situated midway between the original two. Thus, at temperatures above 370 K, the rate of isomerization between the syn and anti isomers was rapid with respect to the NMR time scale, an averaged PMe signal being recorded for the two interconverting species. Upon cooling of the sample, the averaged signal reverted back to the original pair of resonances, showing that decomposition of the complex had not taken place. Reversibility also implied that Pd–P bonds were not broken during the isomerization since free PMePh moieties would have epimerized at the elevated temperatures involved.[12] If this had happened, the room-temperature NMR spectrum, after heating, would have

(12) Salem, G.; Wild, S. B., unpublished work.

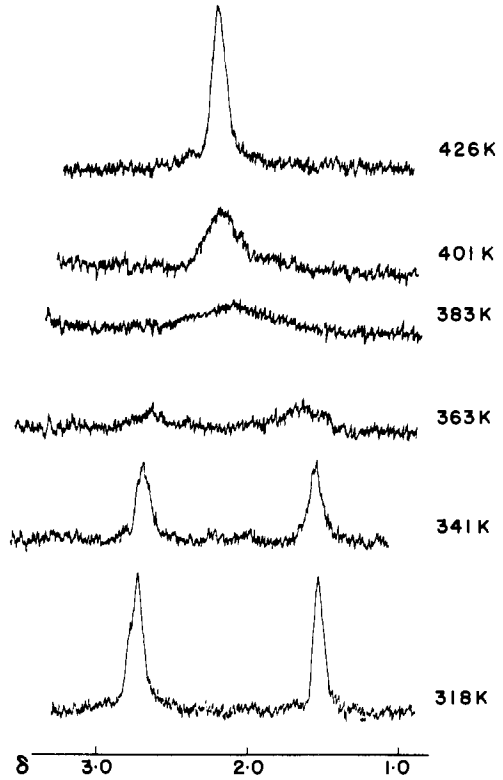

Figure 5. Variable-temperature ^{1}H NMR spectra of an equilibrium mixture of the complexes *syn*- and *anti*-[PdCl((*RS*)-diphos)$_2$]Cl in the PMe region (0.03 M solution of *anti*-[PdCl((*RS*)-diphos)$_2$]Cl in benzonitrile).

contained additional peaks due to the epimeric meso and racemic diastereoisomers.

As expected, a similar situation regarding internal isomerization of the chelate rings prevailed for the corresponding derivatives of platinum(II). Although di(tertiary phosphine) complexes of this metal were known to be exceptionally stable with respect to substitution, it was anticipated that the activation energies for intramolecular processes would be of the same order of magnitude as those found for comparable palladium complexes. The complex *anti*-[PtCl((*RS*)-diphos)$_2$]Cl·2H_2O was isolated in high yield from the reaction between [$PtCl_2$((*RS*)-diphos)] and (*RS*)-diphos in 95% ethanol. A sample of the complex in D_2O (gentle heating was required to effect solution) exhibited only one PMe signal at δ 1.66 due to the divalent cation *anti*-[Pt((*RS*)-diphos)$_2$]$^{2+}$. However, when the solution was heated for ca. 30 min at 100 °C, an equilibrium mixture of the two possible geometric isomers resulted [syn (δ 2.64 PMe):anti (δ 1.66 PMe) = 3:5]. The rate of isomerization was very much faster in solvents favoring five-coordination. For example, a freshly prepared solution of *anti*-[PtCl((*RS*)-diphos)$_2$]Cl·2H_2O in $CDCl_3$ reached equilibrium within 3 min at 25 °C, the ^{1}H NMR spectrum at this stage containing PMe signals at δ 2.80 and 1.71 in the ratio of 1:6 for the cations *syn*- and *anti*-[PtCl((*RS*)-diphos)$_2$]$^+$, respectively.

The corresponding di(tertiary arsine) complexes of palladium(II) and platinum(II) were also isolated. Although the salts *anti*-[MX((*RS*)-diars)$_2$]X (where M = Pd or Pt and X = Cl or I) were not sufficiently soluble (<10^{-4} M) in $CDCl_3$, CH_2Cl_2, Me_2SO-d_6, or $PhNO_2$ for satisfactory ^{1}H NMR spectra to be recorded in these solvents, the chloride salts of both metals were moderately soluble in water, in which they conducted as di-univalent electrolytes, and their ^{1}H NMR spectra in D_2O exhibited AsMe singlets due to both the syn and anti dications (Table I). Thermal equilibration of the anti

Table III. Physical Properties of the Complexes [MCl((*RS*)-bidentate)((*SS*)-bidentate)]Cl

	conductance[a]		^{1}H NMR spectra[b]							
			δ(EMe)							
compd	Λ_M	solvent	Me^3	Me^1	Me^2	Me^4	solvent	T, K	T_c, K	$\Delta G^{\ddagger}$ [c]
[PdCl((*RS*)-diars)((*SS*)-diphos)]Cl	20 (1:1)	CH_2Cl_2	*d*	2.56 s	1.44 s		CH_2Cl_2	308		
			2.83 d	2.56 s	1.44 s	1.60 d	CH_2Cl_2	227	251	11.8
	205 (2:1)	H_2O	2.91 d	2.55 s	1.77 s	1.94 d	D_2O	308		
[PdCl((*RS*)-diphos)((*SS*)-diars)]Cl	21 (1:1)	CH_2Cl_2		2.66 d	1.92 d		CH_2Cl_2	308		
			2.61 d	2.66 d	1.92 d	0.97 s	CH_2Cl_2	215	247	11.5
	207 (2:1)	H_2O	2.63 s	2.71 d	1.97 d	1.16 s	D_2O	308		
[PdCl((*RS*)-diphos)((*SS*)-diphos)]Cl·2H_2O	46 (1:1)	CH_2Cl_2	2.84 d	2.72 d	1.79 d	1.36 d	CH_2Cl_2	308		
	25 (1:1)	$PhNO_2$	3.10 d	2.93 d	2.03 d	1.59 d	$PhNO_2$	308	368	17.4
	180 (2:1)	H_2O	2.63 br s[e]		1.60 br s[e]					
[PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O	46 (1:1)	CH_2Cl_2		2.63 s	1.88 s		CH_2Cl_2	308		
			2.78 s	2.67 s	1.82 s	1.35 s	CH_2Cl_2	243	296	14.0
	178 (2:1)	H_2O	2.58 s	2.55 s	1.74 s	1.57 s	D_2O			
[PtCl((*RS*)-diars)((*SS*)-diphos)]Cl·0.5Me_2CO[f]	38 (1:1)	CH_2Cl_2		2.72 s	1.69 s		CH_2Cl_2	308		
			2.97 d	2.72 s	1.69 s	1.82 d	CH_2Cl_2	228	278	13.2
	205 (2:1)	H_2O	2.98 d	2.79 s	1.83 s	2.13 d	D_2O	308		
[PtCl((*RS*)-diphos)((*SS*)-diars)]Cl·2H_2O	40 (1:1)	CH_2Cl_2		2.84 d	2.13 d		CH_2Cl_2	308		
			2.83 s	2.84 d	2.13 d	1.20 s	CH_2Cl_2	228	266	12.4
	180 (2:1)	H_2O	2.78 s	2.89 d	2.09 d	1.45 s	D_2O			
[PtCl((*RS*)-diphos)((*SS*)-diphos)]Cl·2H_2O	48 (1:1)	CH_2Cl_2	2.98 m	2.82 d	1.86 m	1.46 d	CH_2Cl_2	308		
			3.17 m	2.99 d	2.04 m	1.46 d	PhCN/ Me_2SO-d_6[g]	298	ca. 410[h]	ca. 19.5

[a] Conductance in $cm^2\ \Omega^{-1}\ mol^{-1}$ for 10^{-3} M solutions at 293 K. [b] Chemical shift values for methyl groups in ppm relative to Me_4Si in organic solvents and $Me_3Si(CH_2)_3SO_3Na$ in D_2O (s = singlet, br s = broad singlet, m = multiplet, and d = doublet (J_{PH} = 5.8–11.5 Hz, J_{PtH} observed for platinum complexes)). [c] Estimated from the coalescence temperature (T_c) for Me^3 and Me^4 with use of the Eyring equation as described in text (kcal mol^{-1}). [d] Signal collapsed at 308 K. [e] Broad singlet integrated for 6 H (accidentally coincident resonances). [f] Solvent of crystallization observed in ^{1}H NMR spectrum. [g] PhCN:Me_2SO-d_6 = 10:1. [h] T_c uncertain due to broadness of signal.

Table IV. Physical Properties of the Complexes [M((*RS*)-bidentate)((*SS*)-bidentate)]$(PF_6)_2$

		δ(EMe)[b]			
compd	Λ_M[a]	Me^3	Me^1	Me^2	Me^4
[Pd((*RS*)-diars)((*SS*)-diphos)]$(PF_6)_2$	203 (2:1)	2.82 d	2.62 s	1.68 s	2.20 d
[Pd((*RS*)-diphos)((*SS*)-diars)]$(PF_6)_2$	224 (2:1)	2.61 s	2.78 d	2.06 d	1.66 s
[Pd((*RS*)-diphos)((*SS*)-diphos)]$(PF_6)_2$	215 (2:1)	2.69 s[c]		1.76 s[c]	
[Pt((*RS*)-diars)((*SS*)-diars)]$(PF_6)_2$	202 (2:1)	2.68 s	2.53 s	2.33 s	2.15 s
[Pt((*RS*)-diars)((*SS*)-diphos)]$(PF_6)_2$	210 (2:1)	2.87 d	2.68 s	1.73 s	2.23 d
[Pt((*RS*)-diphos)((*SS*)-diars)]$(PF_6)_2$	212 (2:1)	2.47 s	2.84 d	2.10 d	1.75 s
[Pt((*RS*)-diphos)((*SS*)-diphos)]$(PF_6)_2$	217 (2:1)	2.80 s[c]		1.88 s[c]	

[a] Conductance in $cm^2\ \Omega^{-1}\ mol^{-1}$ for 10^{-3} M solutions at 293 K (solvent, Me_2CO). [b] Chemical shift values in ppm relative to Me_4Si at 308 K [s = singlet, d = doublet ($J_{PH} \approx 11$ Hz)]; solvent was Me_2CO-d_6. [c] Singlets integrate for 6 H (accidentally coincident Me resonances).

isomer of the di(tertiary arsine) complex in D_2O was much more rapid (5 min at 100 °C) than for the corresponding di(tertiary phosphine) compound. The syn:anti ratio for the platinum(II) complex at equilibrium was 5:1, but the palladium analogue isomerized completely to the syn isomer upon dissolution in D_2O. It was not found possible, however, to isolate the syn isomer for either metal, the anti complex crystallizing from solution when attempts were made. It should be noted that the isomerization of *anti*-[PdCl((*RS*)-diars)$_2$]Cl may proceed by an intermolecular route involving redistribution of the bidentate ligands. On the other hand, the cations *anti*-[PtCl((*RS*)-diphos)$_2$]$^+$, *anti*-[PtCl((*RS*)-diars)$_2$]$^+$, and *anti*-[PdCl((*RS*)-diphos)$_2$]$^+$ are inert to disproportionation in the presence of chloride ions, and consequently an intramolecular pathway is required to account for the facile isomerization observed.

All of the spectra displaying syn ⇌ anti interconversion were independent of the concentration of the sample. The dynamic behavior is clearly intramolecular in nature and the various data strongly implicate the mediation of a stereochemically labile five-coordinate cation. We have confirmed this suspicion by analyzing the variable-temperature ^{1}H NMR spectra of a series of kinetically stable palladium(II) and platinum(II) complexes containing a specific arrangement of di(tertiary ligands) (vide infra).

Mixed-Ligand Complexes [MCl((*RS*)-bidentate)((*SS*)-bidentate)]Cl and [M(*RS*)-bidentate)((*SS*)-bidentate)](PF$_6$)$_2$ (Where M = Pd or Pt). The mixed-ligand complexes [MCl((*RS*)-bidentate)((*SS*)-bidentate)]Cl were prepared in a stepwise fashion from the di(tertiary arsine) or di(tertiary phosphine) and [MCl_2(bidentate)]. For the complexes containing a di(tertiary arsine) and a di(tertiary phosphine) ligand, the best results were obtained when the di(tertiary arsine) was reacted with the appropriate complex [MCl_2(diphos)]. The alternative method of synthesis often yielded a mixture of complexes. Although the complexes [PdCl((*RS*)-diphos)-((*SS*)-diars)]Cl and [PdCl((*RS*)-diars)((*SS*)-diphos)]Cl could not be precipitated from dichloromethane without disproportionation, the respective cations were stable in this solvent and their properties consistent with those of other mixed-ligand complexes (Table III).

Metathesis of the mixed-ligand chlorides with NH_4PF_6 in aqueous solution afforded the expected square-planar salts [M((*RS*)-bidentate)((*SS*)-bidentate)](PF$_6$)$_2$ (where M = Pd or Pt). The cations in these salts exhibited four methyl signals in their ^{1}H NMR spectra (Table IV).

The methyl groups were also nonequivalent in the ^{1}H NMR spectra of the corresponding five-coordinate compound [PdCl((*RS*)-diphos)((*SS*)-diphos)]Cl·2H_2O and its platinum analogue in $CDCl_3$ at 25 °C. However, the spectrum of

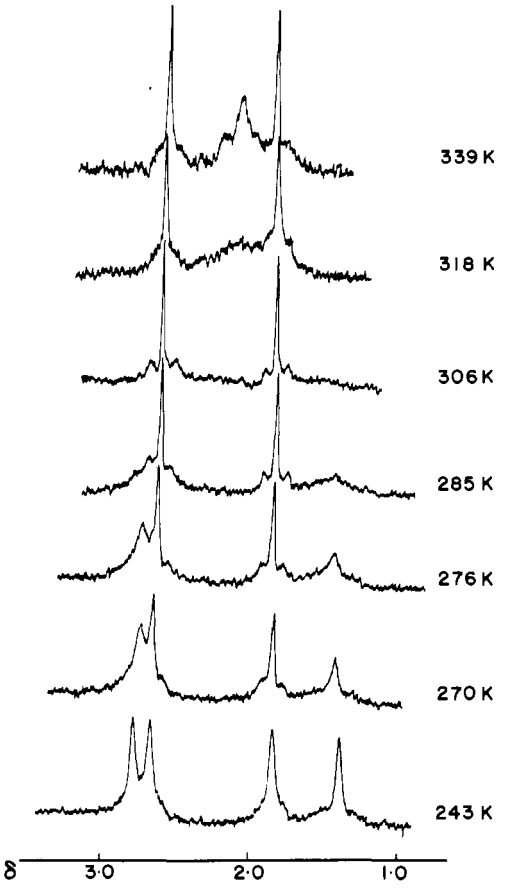

Figure 6. Variable-temperature ^1H NMR spectra of a 0.05 M solution of [PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O in the AsMe region in CH_2Cl_2 (243–306 K) and nitrobenzene (318–339 K).

[PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O under similar conditions consisted of only two sharp AsMe resonances (each integrating as 3 H) superimposed on a broad background signal. The nature of the spectrum, however, was dependent upon the temperature at which it was recorded (Figure 6). When the sample was cooled the NMR spectrum sharpened and at 243 K consisted of the four sharp singlets expected for a static structure. At 339 K in nitrobenzene, however, it was evident that the diffuse background signal had transformed into a relatively sharp singlet resonance.

Since we have shown in separate experiments that five-coordinate cations of the type $[PtCl(diars)_2]^+$ are kinetically stable with respect to bidentate ligand redistribution in the absence of free di(tertiary arsine), the observed temperature dependence of the ^1H NMR spectrum of [PtCl((*RS*)-diars)((*SS*)-diars)]$^+$ is decisive evidence of rapid internal isomerization of the bidentate ligands at the elevated temperatures, as depicted in Figure 7.

The situation is analogous to that found for the corresponding di(tertiary phosphine) derivative of nickel(II),[2] viz., [NiCl((*RS*)-diphos)((*RR,SS*)-diphos)]$^+$. The methyl groups of the meso ligand (Me^1 and Me^2) are diastereotopic by virtue of the chirality of the bidentate (*SS*)-diphos in the stereochemically labile molecule and hence are always magnetically nonequivalent. The corresponding groups of the optically active ligand (Me^3 and Me^4) on the other hand, exchange positions upon rearrangement and consequently appear as a singlet resonance in the ^1H NMR spectrum of the cation at the fast exchange limit (339 K in nitrobenzene). At 243 K a spectrum corresponding to a static (with respect to bidentate ligand rotation) square-pyramidal structure, nevertheless undergoing rapid axial chloro site exchange, was observed. It

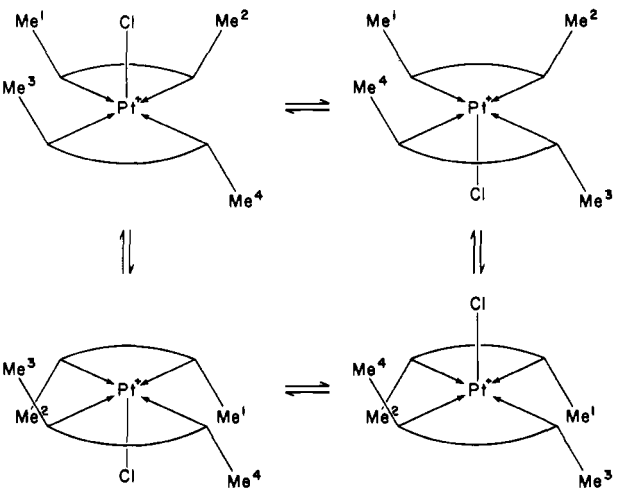

Figure 7. Stereochemical permutations of the chelate rings in the cation [PtCl((*RS*)-diars)((*SS*)-diars)]$^+$.

is noteworthy that rapid internal rearrangement provides an alternative, although higher energy, intramolecular route for axial chloro site exchange. Provided the temperature of the solution did not exceed 345 K, the observed spectral changes were exactly reversed upon cooling.

The profile of the broad AsMe signal due to the methyl groups of (*SS*)-diars in the room-temperature spectrum of [PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O in CH_2Cl_2 provided a sensitive measure of the ease with which rearrangement occurred. An identical methyl signal profile was obtained when an equimolar mixture of [PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O and [Pt((*RS*)-diars)((*SS*)-diars)]$(PF_6)_2$ was dissolved in Me_2SO-d_6 and the ^1H NMR spectrum recorded. Consequently, since the salt in solution in the mixture corresponded to [PtCl((*RS*)-diars)((*SS*)-diars)]PF_6, the rate of intramolecular rearrangement is independent of the nature of the counterion. Furthermore, as expected for an intramolecular process, the rate was independent of the concentration of the sample, the same coalescence temperature (296 K) being observed for 0.05 and 0.19 M solutions of [PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O in CH_2Cl_2. Finally, the instrumentality of the five-coordinate species [PtCl((*RS*)-diars)((*SS*)-diars)]$^+$ in the rearrangement in CH_2Cl_2 and $PhNO_2$ was confirmed by recording the spectrum of the salt in D_2O, where the square-planar complex [Pt((*RS*)-diars)((*SS*)-diars)]$^{2+}$ predominates. Under these conditions the cations exhibited four distinct AsMe resonances as expected for a stereochemically static structure (Table III). We also have evidence that Pt–As bonds are not disrupted during the internal rearrangement. A solution of [PtCl((*RS*)-diars)((*SS*)-diars)]Cl·2H_2O in $CDCl_3$–CF_3CO_2H (1:1) appears to be indefinitely stable. If free tertiary AsMePh moieties were liberated during the rearrangement (which is occurring rapidly under these conditions), we would have anticipated rapid epimerization of these centers in the presence of the ambient H^+ and Cl^- ions.[12] A high degree of stereochemical nonrigidity was also found in other mixed-bidentate complexes of bivalent palladium and platinum. Limiting fast exchange ^1H NMR spectra were obtained for CH_2Cl_2 solutions of [PtCl((*RS*)-diphos)((*SS*)-diars)]Cl·2H_2O and [PdCl((*RS*)-diphos)((*SS*)-diars)]Cl at approximately room temperature. Cooling of the solutions brought about the expected reemergence of the separate AsMe resonances due to the chiral ligand. Complementary results were also obtained for the isosteres [PtCl((*RS*)-diars)((*SS*)-diphos)]Cl·0.5H_2O and [PdCl((*RS*)-diars)((*SS*)-diphos)]Cl. It is noteworthy that ^{195}Pt–^1H coupling was observed for both of the platinum complexes in

CH_2Cl_2. A higher barrier to internal rearrangement was observed for the corresponding complex [PdCl(*RS*)-diphos)(*SS*)-diphos)]Cl·$2H_2O$ and its platinum analogue (Table II). It is apparent that axial chloro site exchange is occurring rapidly at the lower exchange limit to bidentate ligand isomerisation in these complexes.

The approximate free energy barriers to rearrangement for the various five-coordinate mixed-ligand complexes are presented in Table III. These were determined from the DNMR spectra of each complex with use of the expression $\Delta G^{\ddagger} = 0.004573T_c[9.97 + \log (T_c/\Delta\nu)]$ (where T_c is the coalescence temperature of the chiral methyl resonances and $\Delta\nu$ the difference in resonance frequency between them). It is evident from the table that the nature of the donor atoms is an important factor in determining the barrier height. Transition-state geometries appear to be more easily attained when at least one di(tertiary arsine) ligand is present. The lowest energy barriers to rearrangement were found in complexes containing both a di(tertiary arsine) and a di(tertiary phosphine) ligand; this suggests Pt–As bond weakening is further augmented by the trans effect of the phosphorus donor atoms of the other ligand. Significantly, the complex [PdCl((*RS*)-diphos)((*SS*)-diars)]Cl and its isostere [PdCl-((*RS*)-diars)((*SS*)-diphos)]Cl could not be isolated in a crystalline state. This is apparently a manifestation of the particularly weak Pd–As bonds in these complexes.

Steric factors appeared to play only a minor part in determining the barriers to rearrangement in the square-pyramidal complexes: the nature of the metal atom was more important and electronic factors even more so in unsymmetrically substituted complexes. The barrier heights to rearrangement for the trigonal-bipyramidal cations $[M[P(OR)_3]_5]^{2+}$ were found to be relatively insensitive to variation of the central atom although the ordering M = Ni > Pd < Pt was established by Jesson and Meakin.[13] Our ordering, however, for the square-pyramidal species $[MCl(diphos)_2]^+$ is M = Ni < Pd < Pt. A detailed analysis of the DNMR spectra of these and related complexes will appear in a forthcoming article.

Electronic Spectra. Solutions of the five-coordinate complexes [MCl(bidentate)$_2$]Cl (where M = Pd or Pt) containing the various forms of both ligands in nonaqueous ionizing solvents ranged in color from deep yellow (where M = Pd and bidentate = diars) to very pale yellow (where M = Pt and bidentate = diphos). A square-pyramidal stereochemistry was assigned to all of the complex cations in dichloromethane on the basis of their electronic spectra. The spectra were dominated by charge-transfer and intraligand absorptions, and these obscured most of the bands due to d–d transitions. The spectra are typical of other complexes of this type[5,14] (see Experimental Section). Several iodo complexes of the type [PdI(diars)$_2$]I were also prepared. Their electronic spectra in dichloromethane solution exhibited the three bands expected[5] for the square-pyramidal cations $[PdI(diars)_2]^+$ in the d–d region.

In aqueous solution the five-coordinate chloro complexes dissociated to give the divalent cations $[M(bidentate)_2]^{2+}$, which were colorless. The d–d absorption bands of these square-planar dications were completely obscured by intense charge-transfer bands.

Experimental Section

Reactions involving air-sensitive reagents were carried out in a nitrogen atmosphere with use of the Schlenk technique. The diastereoisomers and optically active forms of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue were obtained according to ref 6 and 7, respectively, and the products were characterized with use of the instrumentation described in the preceding article.[2]

Dichloro[(*RR,SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II).[15] Palladous chloride (0.89 g) was dissolved in ethanol (50 mL) containing LiCl (0.4 g) by heating the mixture at 60 °C for 1 h. The resulting reddish brown solution was filtered and reacted with a solution of (*RR,SS*)-diars in diethyl ether (20 mL). A brown precipitate of the "Magnus-type" salts precipitated immediately. This was collected and converted into the desired product by heating in acetonitrile (25 mL) for 15 min. The pure complex was isolated as a yellow microcrystalline powder (2.77g, 97%).

Dichloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II)[15] was prepared similarly.

$(+)_{589}$-Dichloro[(*RR*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) and its enantiomer were prepared as described in ref 6.

Dichloro[(*RR,SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II). A suspension of (*RR,SS*)-diphos (1.5 g) and di-μ-chlorobis[(*R,S*)-dimethyl(α-methylbenzyl)aminato-*2-C,N*]dipalladium(II)[6] (1.4 g) in methanol (40 mL) was stirred for 15 min to give an almost colorless solution of diastereoisomeric salts. The reaction mixture was concentrated to ca. 10 mL, and hydrochloric acid (5 mL, 10 M) was added. The reaction mixture was heated for ca. 30 min on the steam bath whereupon pale yellow microcrystals of the product precipitated; mp >300 °C, 2.3 g (99%). Anal. Calcd for $C_{20}H_{20}Cl_2P_2Pd$: C, 48.1; H, 4.0. Found: C, 48.0; H, 4.0. NMR($CDCl_3$) δ 2.93 (d, 6, J_{PH} = 11.8 Hz, PMe), 7.28–7.80 (m, 14, aromatics).

Dichloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) was prepared in 97% yield from (*RS*)-diphos with use of the same procedure; mp >300 °C. Anal. Calcd for $C_{20}H_{20}Cl_2P_2Pd$: C, 48.1; H, 4.0. Found: C, 47.9; H, 4.1. NMR(CH_2Cl_2) δ 2.44 (d, 6, J_{PH} = 11.8 Hz, PMe), 7.28–7.80 (m, 14, aromatics).

$(+)_{589}$-Dichloro[(*RR*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) and its enantiomer were prepared as described in ref 7.

Dichloro[(*RR,SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II).[15] A suspension of [$PtCl_2$(1,5-C_8H_{12})] (0.23 g) and Na_2CO_3 (0.12 g) was heated in methanol (20 mL) for 15 min. The resulting solution was filtered and reated with (*RR,SS*)-diars (0.66 g) to afford a mixture of internally diastereoisomeric complexes in solution. The addition of hydrochloric acid (5 mL, 10 M) caused the precipitation of the desired product as white microcrystals; mp 298–300 °C, 0.99 g (92%). NMR(CH_2Cl_2) δ 2.17 (s, 6, J_{Pt-H} = 22 Hz, AsMe), 7.23–7.80 (m, 14, aromatics).

The following compounds were prepared similarly. **Dichloro-[(*RS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II):**[15] pale yellow needles, mp >300 °C; 90% yield; NMR(CH_2Cl_2) δ 2.24 (s, 6, J_{Pt-H} = 22 Hz, AsMe), 7.14–7.88 (m, 14, aromatics). **$(+)_{589}$- and $(-)_{589}$-Dichloro[(*RR*)- and (*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II):** pale yellow microcrystals; mp >300 °C; $[\alpha]_D$ +30° and −30°, respectively (*c* 1.2, CH_2Cl_2). Anal. Found: C, 35.5; H, 2.9 (*RR* complex). NMR(CH_2Cl_2) identical with racemic material. **Dichloro[(*RR,SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II):** white microcrystals; mp >300 °C; 87% yield. Anal. Calcd for $C_{20}H_{20}Cl_2P_2Pd$: C, 40.8; H, 3.4. Found: C, 40.8; H, 3.4. NMR(CH_2Cl_2) δ 2.40 (d, 6, J_{PH} = 11.8 Hz, J_{PtH} = 36.4 Hz, PMe), 7.18–8.15 (m, 14, aromatics). **Dichloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II):** white needles; mp >300 °C; 87% yield. Anal. Found: C, 40.8; H, 3.5. NMR(CH_2Cl_2) δ 2.24 (d, 6, J_{PH} = 11.8 Hz, J_{Pt-H} = 36.4 Hz, PMe), 6.88–7.85 (m, 14, aromatics).

$(+)_{589}$- and $(-)_{589}$-Dichloro[(*RR*)- and (*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II): white needles; mp >300 °C; 87% yield; $[\alpha]_D$ +27° and −27°, respectively (*c* 1.0, CH_2Cl_2). Anal found: C, 40.7; H, 3.6 (*SS* complex). NMR(CH_2Cl_2) identical with racemic material.

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) Chloride Dihydrate. A mixture of [$PdCl_2$((*SS*)-diars)] (0.59 g) and (*RR*)-diars (0.41 g) in ethanol (10 mL, 95%) was heated until the solids had dissolved. The bright yellow solution was filtered and the filtrate diluted with diethyl ether (ca. 80 mL) to afford deep yellow needles of the pure complex; mp 185–186 °C, 0.92 g (92%), $[\alpha]_D$ +377° (*c* 1.1, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}As_4Cl_2O_2Pd$: C, 46.5;

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H, 4.3. Found: C, 46.5; H, 4.3. NMR($CDCl_3$) δ 1.79 (s, 12, AsMe), 7.43–7.72 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) 425 (ϵ 310), 325 sh, 287 (27 000), 227 nm (63 000).

The following compounds were prepared similarly. **meso-Chloro[(*RR*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) chloride dihydrate:** yellow powder from ethanol–diethyl ether; mp 250–251 °C; 96% yield. Anal. Calcd for $C_{40}H_{44}As_4Cl_2O_2Pd$: C, 46.5; H, 4.3. Found: C, 46.2; H, 4.1. NMR($CDCl_3$) δ 1.79 (s, 9, AsMe, *rac* diastereoisomer), 2.49 (s, 3, AsMe, *meso* diastereoisomer), 7.08–7.72 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) as above. (The corresponding **ethane-1,2-diol disolvate** was obtained by recrystallizing the **chloride** from an ethanol–ethane-1,2-diol mixture by the addition of diethyl ether): mp 233–244 °C. Anal. Calcd for $C_{44}H_{52}As_4Cl_2O_4Pd$: C, 47.1; H, 4.7. Found: C, 47.2; H, 4.7. NMR($CDCl_3$) δ 1.79 (s, 9, AsMe, *rac* diastereoisomer), 2.49 (s, 3, AsMe, *meso* diastereoisomer), 3.62 (br s, 8, CH_2), 4.02 (br s, 4, OH), 7.04–8.02 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above.) ***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) chloride:** yellow powder from ethanol–diethyl ether; mp >280 °C; 98% yield. Anal. Calcd for $C_{40}H_{40}As_4Cl_2Pd$: C, 48.2; H, 4.1. Found: C, 48.3; H, 4.5. NMR(D_2O) δ 2.66 (s, 12, AsMe, syn isomer, see text), 6.88–8.01 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above. **$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) chloride dihydrate:** pale yellow microcrystals from acetone–diethyl ether; mp 240–251 °C; 98% yield; $[\alpha]_D$ +463° (*c* 0.9, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pd$: C, 56.0; H, 5.2. Found: C, 55.4, H, 5.4. NMR($CDCl_3$) δ 1.73 (br s, 12, PMe), 7.23–7.88 (m, 28, aromatics). λ_{max}(CH_2Cl_2) 390 (ϵ 530), 290 (30 000), 228 nm (55 000).

***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) chloride:** pale yellow needles from dichloromethane–hexane; mp >280 °C; 92% yield. Anal. Calcd for $C_{40}H_{40}Cl_2P_4Pd$: C, 58.4; H, 4.9. Found: C, 58.4; H, 4.8. NMR($CDCl_3$) δ 1.64 (br s, 9.8, PMe, anti isomer), 2.68 (br s, 2.2, PMe, syn isomer), 6.87–7.74 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above.

***meso*-Chloro[(*RR*)-*o*-phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Chloride Dihydrate and *rac*-Chlorobis[(*RR,SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) chloride Hydrate.** A suspension of (*RR,SS*)-diphos (0.64 g) and [$PdCl_2$((*RR,SS*)-diphos)] (1.0 g) was stirred in ethanol (20 mL, 95%) until a clear yellow solution resulted. The addition of hexane (200 mL) to this solution caused the precipitation of a yellow gum which was shown by NMR($CDCl_3$) to be a 2:1 mixture of the meso and racemic complexes, respectively. Trituration of this gum in dichloromethane (15 mL) yielded the crystalline meso diastereoisomer which recrystallized from ethanol–diethyl ether as pale yellow cubes of the dihydrate; mp 220–230 °C, 0.73 g (70%). Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pd$: C, 56.0; H, 5.2. Found: C, 55.8; H, 5.2. NMR($CDCl_3$) δ 2.63 (br s, 12, PMe), 6.94–7.71 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) as above. Evaporation of the dichloromethane extract followed by recrystallization of the residue from a small quantity of boiling water gave the racemic diastereoisomer as a pale yellow prismatic hydrate; mp 238–246 °C, 0.31 g (50%). Anal. Calcd for $C_{40}H_{42}Cl_2OP_4Pd$: C, 54.8; H, 4.8. Found: C, 54.2; H, 4.9. NMR($CDCl_3$) δ 1.74 (br s, 12, PMe), 7.30–7.75 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) as above.

$(+)_{589}$-Iodobis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) Iodide. Sodium iodide (0.4 g) was added to a solution of the corresponding chloride (0.52 g) in hot water. The orange precipitate was separated and recrystallized from dichloromethane–diethyl ether, forming fine orange needles; mp 168–171 °C, 0.4 g (68%), $[\alpha]_D$ +281° (*c* 0.4, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_4I_2Pd$: C, 40.7; H, 3.4. Found: C, 40.8; H, 3.7. NMR($CDCl_3$) δ 1.89 (s, 12, AsMe), 7.45–7.76 (m, 28, aromatics). λ_{max}(CH_2Cl_2) ~500 (ϵ 820), 425 (2300), 374 (2100), 304 (30 000), 227 nm (69 000).

***meso*-Iodo[(*RR*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) iodide** was prepared similarly; mp 231–232 °C (95%). Anal. Calcd for $C_{40}H_{40}As_4I_2Pd$: C, 40.7; H, 3.4. Found: C, 40.4; H, 3.5. NMR($CDCl_3$) δ 1.88 (s, 9.6, AsMe, *rac* diastereoisomer), 2.61 (s, 2.4, AsMe, *meso* diastereoisomer), 7.10–7.72 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above.

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) Chloride Dihydrate. Platinous chloride (0.26 g) and (*RR*)-diars (0.82 g) in acetonitrile (50 mL) were heated under reflux for 3.5 h, giving a yellow solution of the complex. The solvent was removed and the residue extracted with dichloromethane (10 mL); the extract was filtered and carefully diluted with diethyl ether to afford the product as pale yellow crystals; mp 228–230 °C, 1.1 g (98%), $[\alpha]_D$ +320° (*c* 1.1, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}As_4Cl_2O_2Pt$: C, 42.8; H, 4.0. Found: C, 42.6; H, 3.8. NMR($CDCl_3$) δ 1.85 (s, 12, J_{Pt-H} 16.5 Hz, AsMe), 7.38–7.83 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) 365 (ϵ 510), 304 (13 000), 227 nm (60 000).

The following compounds were prepared similarly. ***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) chloride:** white needles from methanol–diethyl ether; mp >280 °C; 88% yield. Anal. Calcd for $C_{40}H_{40}As_4Cl_2Pt$: C, 44.2; H, 3.7. Found: C, 44.0; H, 3.8. NMR(D_2O) δ 1.97 (s, 2, J_{Pt-H} = 16 Hz, AsMe, anti isomer), 2.73 (s, 10, J_{Pt-H} = 16 Hz, AsMe, syn isomer), 7.05–8.18 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above. ***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) chloride dihydrate:** white needles from methanol–diethyl ether; mp >280 °C; 96% yield. Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pt$: C, 50.8; H, 4.7. Found: C, 50.4; H, 4.5. NMR($CDCl_3$) δ 1.71 (br s, 10, J_{Pt-H} = 27.2 Hz, PMe, anti isomer), 2.80 (br s, 2, J_{Pt-H} = 20 Hz, PMe, syn isomer), 7.22–8.10 (m, 28, aromatics). λ_{max}(CH_2Cl_2) as above.

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) Chloride Dihydrate. The addition of (*RR*)-diphos (0.21 g) to a well-stirred suspension of [$PtCl_2$($PhCN)_2$] (0.16 g) in methanol (15 mL) resulted in a clear yellow solution which was filtered and evaporated to dryness. The residue crystallized upon trituration in acetone. Diethyl ether was then added to the mixture and the product isolated as off-white needles; mp >280 °C, 0.29 g (93%), $[\alpha]_D$ +383° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pt$: C, 50.8; H, 4.7. Found: C, 50.7; H, 4.5. NMR($CDCl_3$) δ 1.83 (br s, 12, J_{Pt-H} = 28 Hz, PMe), 7.18–7.93 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) 309 (ϵ 9500), 227 nm (55 000).

***meso*-Chloro[(*RR*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) Chloride Hemihydrate and *rac*-Chlorobis[(*RR,SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) Chloride Tetrahydrate.** A mixture of platinous chloride (0.27 g) and (*RR,SS*)-diars (0.83 g) in acetonitrile was heated under reflux for 24 h. The solvent was removed and the residue extracted into boiling dichloromethane (60 mL). Evaporation of the dichloromethane extract left a yellow gum which was stirred in a mixture of CCl_4 and $CHCl_3$ (1:1, 20 mL). The meso diastereoisomer crystallized and after recrystallization from ethanol–diethyl ether formed white needles; mp 283–285 °C, 0.19 g (70%). Anal. Calcd for $C_{40}H_{41}As_4Cl_2O_{0.5}Pt$: C, 43.9; H, 3.8. Found, C, 43.7; H, 3.7. NMR($CDCl_3$) δ 2.63 (s, 12, J_{Pt-H} = 21.3 Hz, AsMe), 7.05–7.73 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) 365 (ϵ 510), 304 (31 000), 227 nm (60 000). The filtrate from the original separation was evaporated to dryness and the residue recrystallized from boiling water; pale yellow needles of the racemic diastereoisomer separated as the tetrahydrate; mp 198–205 °C; 0.51 g (58%). Anal. Calcd for $C_{40}H_{48}As_4Cl_2O_4Pt$: C, 41.5; H, 4.2. Found: C, 41.5; H, 3.7. NMR($CDCl_3$) δ 1.84 (s, 12, J_{Pt-H} = 17 Hz, AsMe), 7.40–7.77 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) as above.

***meso*-Chloro[(*RR*)-*o*-phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) Chloride Hydrate and *rac*-Chlorobis[(*RR,SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) Chloride Tetrahydrate.** A suspension of platinous chloride (0.27 g) and (*RR,SS*)-diphos (0.65 g) was heated under reflux for 4h. The solvent was removed and the residue stirred in dichloromethane (20 mL). The white solid which did not dissolve was filtered off and recrystallized from hot methanol by the addition of diethyl ether to yield the meso diastereoisomer as white microcrystals; mp >280 °C, 0.28 g (30%). Anal. Calcd for $C_{40}H_{42}Cl_2OP_4Pt$: C, 51.7; H, 4.6. Found: C, 51.7; H, 4.6. NMR($CDCl_3$) δ 2.73 (br s, 12, J_{Pt-H} = 29 Hz, PMe), 7.10–7.83 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) 309 (ϵ 9500), 227 nm (55 000). The addition of diethyl ether to the original mother liquor produced the corresponding racemic diastereoisomer as pale yellow prisms; mp 243–253 °C, 0.48 g (49%). Anal. Calcd for $C_{40}H_{48}Cl_2O_4P_4Pt$: C, 48.9; H, 4.9. Found: C, 48.7; H, 4.6. NMR($CDCl_3$) δ 1.84 (br s, 12, J_{Pt-H} = 28 Hz, PMe), 7.27–7.83 (m, 28, aromatics) (D_2O exchanged). λ_{max}(CH_2Cl_2) as above.

$(+)_{589}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) Hexafluorophosphate. A solution of the optically active chloride (0.52 g) in boiling water (200 mL) was treated with NH_4PF_6 (0.3 g) in water (10 mL). A white precipitate of the product formed immediately, and this was filtered off, washed with water, dried, and

recrystallized from hot methanol. The product formed colorless plates; mp >280 °C, 0.44 g (71%), $[\alpha]_D$ +273° (*c* 1.2, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_4F_{12}P_2Pd$: C, 39.5; H, 3.3. Found: C, 40.1; H, 3.4. NMR(Me_2SO-d_6) δ 1.98 (s, 12, AsMe), 7.50–7.97 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 305 (ε 30 000), 250 (26 500), 225 (56 500), 208 nm (89 000).

The following compounds were prepared similarly. ***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) hexafluorophosphate:** colorless cubes from acetone–diethyl ether; mp >280 °C; 93% yield. Anal. Calcd for $C_{40}H_{40}As_4F_{12}P_2Pd$: C, 39.5; H, 3.3. Found: C, 39.7; H, 3.3. NMR(Me_2SO-d_6) δ 2.49 (s, 12, AsMe), 7.06–7.95 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. ***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]palladium(II) hexafluorophosphate:** white microcrystals from dimethyl sulfoxide–methanol; mp >280 °C (85%). Anal. Found: C, 39.7; H, 3.4. NMR (Me_2SO-d_6) δ 2.27 (s, 12, AsMe), 7.17–8.37 (m, 28, aromatics). **$(+)_{589}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate:** white needles from acetone–diethyl ether; mp >280 °C; 83% yield; $[\alpha]_D$ +340° (*c* 1.0, Me_2CO). Anal. Calcd for $C_{40}H_{40}F_{12}P_6Pd$: C, 46.2; H, 3.9. Found: C, 46.0; H, 4.0. NMR(Me_2SO-d_6) δ 1.82 (br s, 12, PMe), 7.48–7.94 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 278 (ε 29 000), 240 (49 000), 207 nm (90 000). ***rac*-Bis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate acetone solvate:** white needles from acetone–diethyl ether; mp >280 °C; 90% yield. Anal. Calcd for $C_{43}H_{46}F_{12}OP_6Pd$: C, 47.0; H, 4.2. Found: C, 46.8; H, 4.2. NMR(Me_2SO-d_6) δ 1.79 (br s, 12, PMe), 2.08 (s, 6, Me_2CO), 7.22–7.94 (28 H, m, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. ***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate:** colorless cubes from acetone–methanol; mp >280 °C; 79% yield. Anal. Found: C, 46.0; H, 3.8. NMR(Me_2SO-d_6) δ 2.52 (br s, 12, PMe), 6.90–7.94 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. ***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate:** white microcrystals from dimethyl sulfoxide–methanol; mp >280 °C; 83% yield. Anal. Found: C, 45.9; H, 3.8. NMR(Me_2SO-d_6) δ 1.96 (br s, 12, PMe), 7.06–8.17 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. **$(+)_{589}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) hexafluorophosphate:** white microcrystals from acetone–diethyl ether, mp >280 °C; $[\alpha]_D$ +211° (*c* 1.3, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_4F_{12}P_2Pt$: C, 36.8; H, 3.1. Found: C, 36.9; H, 3.1. NMR(Me_2SO-d_6) δ 2.02 (s, 12, J_{Pt-H} = 16.5 Hz, AsMe), 7.55–8.17 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 251 (ε 41 000), 225 (57 000) 207 (78 000). ***rac*-Bis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) hexafluorophosphate:** white crystals from acetone–diethyl ether; mp >280 °C; yield. Anal. Found: C, 36.8; H, 3.1. NMR(Me_2SO-d_6) δ 2.02 (s, 12, J_{Pt-H} = 16.5 Hz, AsMe), 7.22–7.16 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. ***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) hexafluorophosphate:** colorless cubes from hot acetone; mp >280 °C; 78% yield. Anal. Found: C, 36.8; H, 3.1. NMR(Me_2SO-d_6) δ 2.64 (s, 12, J_{Pt-H} = 16.0 Hz, AsMe), 7.04–8.10 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. ***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) hexafluorophosphate:** white microcrystals; mp >280 °C; 83% yield. Anal. Found: C, 36.7; H, 3.1. NMR(Me_2SO-d_6) δ 2.32 (s, 12, J_{Pt-H} = 15 Hz, AsMe), 7.47–8.47 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. **$(+)_{585}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** colorless flakes from acetone–diethyl ether; mp >280 °C; 99% yield; $[\alpha]_D$ +253° (*c* 1.2, Me_2SO). Anal. Calcd for $C_{40}H_{40}F_{12}P_6Pt$: C, 42.5; H, 3.6. Found: C, 42.4; H, 3.3. NMR(Me_2SO-d_6) δ 1.89 (br s, 12, J_{Pt-H} = 28.3 Hz, PMe), 7.47–8.0 (m, 28, aromatics). ***rac*-Bis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate acetone solvate:** white needles from acetone–diethyl ether; mp >280 °C; 95% yield. Anal. Calcd for $C_{43}H_{46}F_{12}OP_6Pt$: C, 43.5; H, 4.0. Found: C, 43.5; H, 4.0. NMR(Me_2SO-d_6) δ 1.89 (br s, 12, J_{Pt-H} = 28.5 Hz, PMe), 2.08 (s, 6, Me_2CO), 7.60–8.03 (m, 28, aromatics). ***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** colorless cubes from acetone–methanol; mp >280 °C; 89% yield. Anal. Found: C, 46.1; H, 3.8. NMR(Me_2SO-d_6) δ 2.74 (br s, 12, J_{Pt-H} = 28 Hz, PMe), 7.03–7.98 (m, 28, aromatics). ***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** white microcrystals from dimethyl sulfoxide–methanol; mp >280 °C; 66% yield. Anal. Found: C, 42.3; H, 3.5. NMR(Me_2SO-d_6) δ 1.96 (br s, 12, J_{Pt-H} = 28 Hz, PMe), 7.17–8.10 (m, 28, aromatics).

$(+)_{589}$-Chloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Chloride. A suspension of [$PdCl_2$((*SS*)-diphos)] (0.12 g) in dichloromethane (15 mL) was treated with a solution of (*RS*)-diars (0.1 g) in the same solvent (5 mL). The bright orange solution was filtered and evaporated to dryness to leave an orange gum (0.22 g) which could not be crystallized; $[\alpha]_D$ +165° (*c* 1.1, CH_2Cl_2). NMR(CH_2Cl_2 at 227 K) δ 1.44 (s, 3, AsMe), 1.60 (d, 3, $J_{P-H} \approx 11$ Hz, PMe), 2.56 (s, 3, AsMe), 2.83 (d, 3, J_{P-H} = 11.5 Hz, PMe), 6.71–7.96 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 400 (ε 630), 300 (15 000), 250 nm (50 000).

The following compounds were prepared similarly. (Note: In complexes containing both a di(tertiary arsine) and a di(tertiary phosphine), the free di(tertiary arsine) was reacted with the appropriate coordinated di(tertiary phosphine) precursor.) **$(+)_{589}$-Chloro[(*SS*)-*o*-phenylenebis(methylphenylarsine)][(*RS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) chloride:** an orange gum; $[\alpha]_D$ +140° (*c* 1.1, CH_2Cl_2); NMR(CH_2Cl_2 at 215 K) δ 0.97 (s, 3, AsMe), 1.92 (d, 3, J_{P-H} = 12 Hz, PMe), 2.61 (s, 3, AsMe), 2.66 (d, 3, J_{P-H} = 11.5 Hz, PMe), 6.56–7.96 (m, 28, aromatics); $\lambda_{max}(CH_2Cl_2)$ as above. **$(+)_{589}$-Chloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) chloride dihydrate.** pale yellow microcrystals from ethanol–diethyl ether; mp 278–285 °C; 90% yield; $[\alpha]_D$ +233° (*c* 0.9, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pd$: C, 56.0; H, 5.2. Found: C, 56.2; H, 4.9. NMR($CDCl_3$) δ 1.36 (d, 3, J_{P-H} = 7.8 Hz, PMe), 1.79 (d, 3, J_{P-H} = 6.8 Hz, PMe), 2.72 (d, 3, J_{P-H} = 7.8 Hz, PMe), 2.84 (d, 3, J_{P-H} = 5.8 Hz, PMe), 6.93–8.09 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 390 (ε 530), 290 (30 000), 228 nm (55 000). **$(+)_{589}$-Chloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) chloride dihydrate:** pale yellow needles from ethanol–diethyl ether; mp 245–275 °C; 94% yield; $[\alpha]_D$ +172° (*c* 1.1, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}As_4Cl_2O_2Pt$: C, 42.8; H, 4.0. Found: C, 43.2; H, 3.7. NMR(CH_2Cl_2 at 243 K) δ 1.35 (s, 3, $J_{Pt-H} \approx 15$ Hz, AsMe), 1.82 (s, 3, $J_{Pt-H} \approx 15$ Hz, AsMe), 2.67 (s, 3, $J_{Pt-H} \approx 15$ Hz, AsMe), 2.78 (s, 3, $J_{Pt-H} \approx 15$ Hz, AsMe), 6.54–7.97 (m, 28, aromatics) (D_2O exchanged). λ_{max} (CH_2Cl_2) 365 (ε 510), 304 (13 000), 227 nm (60 000). **$(+)_{589}$-Chloro[(*RS*)-*o*-phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) chloride acetone hemisolvate**: pale yellow needles from acetone–hexane; mp 273–300 °C; 99% yield; $[\alpha]_D$ +196° (*c* 0.98, CH_2Cl_2). Anal. Calcd for $C_{41.5}H_{43}As_2Cl_2O_{0.5}P_2Pt$: C, 48.5; H, 4.2. Found: C, 48.3; H, 4.0. NMR(CH_2Cl_2 at 228 K) δ 1.69 (s, 3, $J_{Pt-H} \approx 11$ Hz, AsMe), 1.82 (d, 3, J_{P-H} = 11 Hz, $J_{Pt-H} \approx 45$ Hz, PMe), 2.72 (s, 3, $J_{Pt-H} \approx 11$ Hz, AsMe), 2.97 (d, 3, J_{P-H} = 11 Hz, $J_{Pt-H} \approx 45$ Hz, PMe), 2.1 (s, 3, Me_2CO), 6.90–7.95 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ 305 (ε 8800), 227 nm (55 000). **$(+)_{589}$-Chloro[(*SS*)-*o*-phenylenebis(methylphenylarsine)][(*RS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) chloride dihydrate:** pale yellow needles from ethanol–hexane; mp 241 °C; 94% yield; $[\alpha]_D$ +154° (*c* 1.3, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}As_2Cl_2O_2P_2Pt$: C, 46.4; H, 4.3. Found: C, 46.5; H, 4.1. NMR(CH_2Cl_2 at 228 K) δ 1.20 (s, 3, $J_{Pt-H} \approx 16$ Hz, PMe), 2.13 (d, 3, J_{P-H} = 11.5 Hz, $J_{Pt-H} \approx 21$ Hz, PMe), 2.83 (s, 3, J_{Pt-H} obscured, AsMe), 2.84 (d, 3, J_{P-H} = 11.5 Hz, $J_{Pt-H} \approx 21$ Hz, PMe), 6.84–7.88 (m, 28, aromatics). $\lambda_{max}(CH_2Cl_2)$ as above. **$(+)_{589}$-Chloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) chloride dihydrate:** rosettes of white needles from ethanol–diethyl ether; mp >280 °C; 95% yield; $[\alpha]_D$ +211° (*c* 1.1, CH_2Cl_2). Anal. Calcd for $C_{40}H_{44}Cl_2O_2P_4Pt$: C, 50.8; H, 4.7. Found: C, 50.5; H, 4.6. NMR($CDCl_3$) δ 1.46 (d, 3, J_{P-H} = 7.8 Hz, J_{Pt-H} = 35.5 Hz, PMe), 1.86 (m, 3, PMe), 2.82 (d, 3, J_{P-H} = 7.8 Hz, J_{Pt-H} = 20.6 Hz, PMe), 2.98 (m, 3, PMe), 7.00–8.14 (m, 28, aromatics) (D_2O exchanged). $\lambda_{max}(CH_2Cl_2)$ 309 (ε 9500), 227 nm (55 000).

$(+)_{589}$-[(*RS*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) Hexafluorophosphate. A solution of the corresponding chloro complex (0.25 g) in water (100 mL) was treated with an excess of NH_4PF_6 (0.1 g) in water. The white precipitate was filtered off, dried, and recrystallized twice from acetone (5 mL) by the addition of methanol (5 mL) followed by diethyl ether (30 mL). The product formed white rosettes; mp, 283–293 °C, 83% yield, $[\alpha]_D$ +170° (*c* 0.7, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.4; H, 3.8. NMR(Me_2SO-d_6) δ 1.68 (s, 3, AsMe), 2.20 (d, 3, J_{P-H} = 11.7 Hz,

PMe), 2.62 (s, 3, AsMe), 2.82 (d, 3, J_{P-H} = 11.8 Hz, PMe), 7.08–8.05 (m, 28, aromatics).

The following compounds were prepared similarly. **$(+)_{589}$-[(*SS*)-*o*-Phenylenebis(methylphenylarsine)][(*RS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate:** white needles; mp 287–289 °C; 64% yield; $[\alpha]_D$ +140° (*c* 1.1, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.7; H, 3.6. NMR(Me_2SO-d_6) δ 1.66 (s, 3, AsMe), 2.06 (d, 3, J_{P-H} = 11 Hz, PMe), 2.61 (s, 3, AsMe), 2.78 (d, 3, J_{P-H} = 11 Hz, PMe), 7.02–8.00 (m, 28, aromatics). **$(+)_{589}$-[(*RS*)-*o*-Phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]palladium(II) hexafluorophosphate:** white microcrystals; mp >300 °C; 94% yield; $[\alpha]_D$ +154° (*c* 1.0, Me_2CO). Anal. Calcd for $C_{40}H_{40}F_{12}P_6Pd$: C, 46.2; H, 3.9. Found: C, 46.2; H, 4.1. NMR(Me_2SO-d_6) δ 1.76 (br s, 6, PMe), 2.69 (br s, 6, PMe), 7.13–7.96 (m, 28, aromatics). **$(+)_{589}$-(*RS*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]platinum(II) hexafluorophosphate:** fine white needles, mp >300 °C; 92% yield; $[\alpha]_D$ +102° (*c* 1.2, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_4F_{12}P_2Pt$: C, 36.8; H, 3.1. Found: C, 36.7; H, 3.2. NMR(Me_2SO-d_6) δ 2.15 (s, 3, AsMe), 2.33 (s, 3, AsMe), 2.53 (s, 3, AsMe), 2.68 (s, 3, AsMe), 7.03–8.44 (m, 28, aromatics). **$(+)_{589}$-[(*RS*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** white needles; mp 303–305 °C; 83% yield; $[\alpha]_D$ +130° (*c* 1.2, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5; H, 3.3. Found: C, 39.3; H, 3.1. NMR(Me_2CO-d_6) δ 1.73 (s, 3, J_{Pt-H} = 15.6 Hz, AsMe), 2.23 (d, 3, J_{P-H} = 11 Hz, J_{Pt-H} = 28 Hz, PMe), 2.68 (s, 3, J_{Pt-H} = 15 Hz, AsMe), 2.87 (d, 3, J_{P-H} = 11 Hz, J_{Pt-H} = 28 Hz, PMe), 6.86–8.06 (m, 28, aromatics). **$(+)_{589}$-[(*SS*)-*o*-Phenylenebis(methylphenylarsine)][(*RS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** white needles; mp 292–295 °C; 64% yield; $[\alpha]_D$ +100° (*c* 1.2, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5; H, 3.3. Found: C, 39.4; H, 3.4. NMR(Me_2CO-d_6) δ 1.75 (s, 3, AsMe), 2.10 (d, 3, J_{P-H} = 11 Hz, J_{Pt-H} = 28 Hz, PMe), 2.47 (s, 3, AsMe), 2.84 (d, 3, J_{P-H} = 11 Hz, J_{Pt-H} = 28 Hz, PMe), 6.89–8.03 (m, 28, aromatics). **$(+)_{589}$-[(*RS*)-*o*-Phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]platinum(II) hexafluorophosphate:** colorless needles; mp >300 °C; 91% yield; $[\alpha]_D$ +130° (*c* 1.1, Me_2CO). Anal. Calcd for $C_{40}H_{40}F_{12}P_6Pt$: C, 42.2; H, 3.5. Found: C, 42.2; H, 3.4. NMR(Me_2CO-d_6) δ 1.88 (br s, 6, J_{Pt-H} = 28 Hz, PMe), 2.80 (br s, 6, J_{Pt-H} = 28 Hz, PMe), 6.85–8.08 (m, 28, aromatics).

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Registry No. (+)-[PdCl((*SS*)-diars)$_2$]Cl, 77029-34-6; (+)-[PdI((*SS*)-diars)$_2$]I, 77029-35-7; *meso*-[PdCl((*RR*)-diars)((*SS*)-diars)]Cl, 77059-70-2; *meso*-[PdI((*RR*)-diars)((*SS*)-diars)]I, 77059-71-3; *anti*-[PdCl((*RS*)-diars)$_2$]Cl, 77059-72-4; (+)-[PdCl((*SS*)-diphos)$_2$]Cl, 77029-36-8; *rac*-[PdCl((*RR*,*SS*)-diphos)$_2$]Cl, 77059-73-5; *meso*-[PdCl((*RR*)-diphos)((*SS*)-diphos)]Cl, 77059-74-6; *anti*-[PdCl((*RS*)-diphos)$_2$]Cl, 77059-75-7; (+)-[PtCl((*SS*)-diars)$_2$]Cl, 77029-37-9; *rac*-[PtCl((*RR*,*SS*)-diars)$_2$]Cl, 77059-76-8; *meso*-[PtCl((*RR*)-diars)((*SS*)-diars)]Cl, 77059-77-9; *anti*-[PtCl((*RS*)-diars)$_2$]Cl, 77059-78-0; (+)-[PtCl((*SS*)-diphos)$_2$]Cl, 77029-38-0; *rac*-[PtCl((*RR*,*SS*)-diphos)$_2$]Cl, 77059-79-1; *meso*-[PtCl((*RR*)-diphos)((*SS*)-diphos)]Cl, 77059-80-4; *anti*-[PtCl((*RS*)-diphos)$_2$]Cl, 77059-81-5; (+)-[Pd((*SS*)-diars)$_2$]$(PF_6)_2$, 77059-83-7; *meso*-[Pd((*RR*)-diars)((*SS*)-diars)]$(PF_6)_2$, 77029-40-4; *anti*-[Pd((*RS*)-diars)$_2$]$(PF_6)_2$, 77059-85-9; (+)-[Pd((*SS*)-diphos)$_2$]$(PF_6)_2$, 77029-42-6; *rac*-[Pd((*RR*,*SS*)-diphos)$_2$]$(PF_6)_2$, 77059-87-1; *meso*-[Pd((*RR*)-diphos)((*SS*)-diphos)]$(PF_6)_2$, 77059-89-3; *anti*-[Pd((*RS*)-diphos)$_2$]$(PF_6)_2$, 77059-91-7; (+)-[Pt((*SS*)-diars)$_2$]$(PF_6)_2$, 77096-18-5; *rac*-[Pt((*RR*,*SS*)-diars)$_2$]$(PF_6)_2$, 77029-44-8; *meso*-[Pt((*RR*)-diars)((*SS*)-diars)]$(PF_6)_2$, 77059-93-9; *anti*-[Pt((*RS*)-diars)$_2$]$(PF_6)_2$, 77059-95-1; (+)-[Pt((*SS*)-diphos)$_2$]$(PF_6)_2$, 77029-46-0; *rac*-[Pt((*RR*,*SS*)-diphos)$_2$]$(PF_6)_2$, 77059-97-3; *meso*-[Pt((*RR*)-diphos)((*SS*)-diphos)]$(PF_6)_2$, 77059-99-5; *anti*-[Pt((*RS*)-diphos)$_2$]$(PF_6)_2$, 77060-01-6; (+)-[PdCl((*RS*)-diars)((*SS*)-diphos)]Cl, 77096-19-6; (+)-[PdCl((*RS*)-diphos)((*SS*)-diars)]Cl, 77029-47-1; (+)-[PdCl((*RS*)-diphos)((*SS*)-diphos)]Cl, 77096-20-9; (+)-[PtCl((*RS*)-diars)((*SS*)-diars)]Cl, 77096-21-0; (+)-[PtCl((*RS*)-diars)((*SS*)-diphos)]Cl, 77060-02-7; (+)-[PtCl((*RS*)-diphos)((*SS*)-diars)]Cl, 77096-22-1; (+)-[PtCl((*RS*)-diphos)((*SS*)-diphos)]Cl, 77096-23-2; (+)-[Pd((*RS*)-diars)((*SS*)-diphos)]$(PF_6)_2$, 77096-25-4; (+)-[Pd((*RS*)-diphos)((*SS*)-diars)]$(PF_6)_2$, 77029-49-3; (+)-[Pd((*RS*)-diphos)((*SS*)-diphos)]$(PF_6)_2$, 77096-27-6; (+)-[Pt((*RS*)-diars)((*SS*)-diars)]$(PR_6)_2$, 77096-29-8; (+)-[Pt((*RS*)-diars)((*SS*)-diphos)]$(PF_6)_2$, 77096-31-2; (+)-[Pt((*RS*)-diphos)((*SS*)-diars)]$(PF_6)_2$, 77029-51-7; (+)-[Pt((*RS*)-diphos)((*SS*)-diphos)]$(PF_6)_2$, 77096-33-4; *rac*-[PdCl((*RR*,*SS*)-diars)$_2$]$^+$, 77170-90-2; *rac*-[PdI((*RR*,*SS*)-diars)$_2$]$^+$, 77060-03-8; *rac*-[Pd(*RS*,*SS*)-diars)$_2$]$^{2+}$, 77060-04-9; *syn*-[PdCl((*RS*)-diphos)$_2$]$^+$, 77060-05-0; *syn*-[PtCl((*RS*)-diphos)$_2$]$^+$, 77060-06-1; *syn*-[Pd((*RS*)-diars)$_2$]$^{2+}$, 77060-07-2; *syn*-[Pd((*RS*)-diphos)$_2$]$^{2+}$, 77060-08-3; *syn*-[Pt((*RS*)-diars)$_2$]$^{2+}$, 77060-09-4; *syn*-[Pt((*RS*)-diphos)$_2$]$^{2+}$, 77060-10-7; (−)-$PdCl_2$((*SS*)-diars), 73089-27-7; (+)-$PdCl_2$((*RR*)-diars), 73089-28-8; (−)-$PdCl_2$((*SS*)-diphos), 72098-71-6; (−)-$PtCl_2$((*SS*)-diars), 77060-11-8; (+)-$PtCl_2$((*RR*)-diars), 77060-12-9; (+)-$PtCl_2$((*RR*)-diphos), 77029-52-8; (−)-$PtCl_2$((*SS*)-diphos), 77060-13-0; $PdCl_2$((*RR*,*SS*)-diphos), 77060-14-1; $PdCl_2$((*RS*)-diphos), 77060-15-2; $PtCl_2$((*RR*,*SS*)-diars), 57385-75-8; $PtCl_2$((*RS*)-diars), 57427-43-7; $PtCl_2$((*RR*,*SS*)-diphos), 77060-16-3; $PtCl_2$((*RS*)-diphos), 77060-17-4; $PdCl_2$((*RR*,*SS*)-diars), 57385-76-9; $PdCl_2$((*RS*)-diars), 77060-18-5; di-μ-chloro-bis[(*R*,*S*)-dimethyl(α-methylbenzyl)aminato-2-*C*,*N*]dipalladium(II), 51371-44-9; $PtCl_2$(1,5-C_8H_{12}), 12080-32-9; $PtCl_2(PhCN)_2$, 14873-63-3; (+)-$PdCl_2$((*RR*)-diphos), 72150-64-2.