were unsuccessful. Syntheses of new π-accepting ligands which will form Ru(II) complexes that are easier to oxidize but at the same time retain the unusual energy level ordering illustrated in Figure 3 are in progress.

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Registry No. $Ru(azpy)_2(CN)_2$, 80697-52-5; $Ru(azpy)_2(NO_2)_2$, 80697-51-4; $Ru(azpy)_2(btz)^{2+}$, 80697-57-0; $Ru(azpy)_2(bpy)^{2+}$, 80697-55-8; $Ru(azpy)_3^{2+}$, 80697-53-6; $Ru(azpy)_2(en)^{2+}$, 80697-59-2; $Ru(azpy)_2(acac)^+$, 80697-64-9; $Ru(azpy)_2Br_2$, 80735-95-1; $Ru(azpy)_2(N_3)_2$, 80697-61-6; $Ru(azpy)_2Cl_2$, 80735-96-2; $Ru(azpy)_2(tu)_2^{2+}$, 80697-62-7; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3; Fe^{2+}, 15438-31-0; Fe^{3+}, 20074-52-6; Ce^{3+}, 18923-26-7; Ce^{4+}, 16065-90-0.

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Stereochemistry and Dynamic Properties of Square-Planar and Square-Pyramidal Cations of Bivalent Nickel, Palladium, and Platinum Containing the Enantiomers of (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene

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Square-planar and square-pyramidal complexes of bivalent nickel, palladium, and platinum containing the enantiomers of (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas) have been prepared, and their behavior in solution has been investigated by ^1H and ^{31}P NMR spectroscopy. All possible stereoisomers of the different species have been detected and unambiguously identified. The kinetically stable complex (+)-[Ni([*R*-(*R**,*S**)]-phas)$_2$]$(ClO_4)_2$ is stereochemically nonrigid at 304 K in MeCN-d_3. The corresponding five-coordinate chloro species are also nonrigid but exhibit facile redistribution of the bidentates under ambient conditions. In the absence of free ligand the compounds [MCl(phas)$_2$]Cl (where M = Pd and Pt) are kinetically stable with respect to redistribution of the bidentate ligands but undergo intramolecular cis–trans isomerization upon heating. Reaction of (*R**,*R**)-(±)-phas with (±)-[MCl_2((*R**,*R**)-phas)] produces crystalline meso complexes only, although the corresponding racemic complexes are of comparable stability. The square-planar cations are more stable: the complexes [Pt(phas)$_2$]$(PF_6)_2$ do not undergo redistribution of bidentates in the presence of free ligand under ambient conditions.

Introduction

Although numerous unsymmetrically substituted bis(tertiary) ligands containing phosphorus and arsenic are known,[1] the stereochemistry and dynamic properties of their metal chelates have been little explored. Chiral molecules of this type are of considerable interest in connection with the development of inorganic systems for asymmetric synthesis, since they are capable of exercising an electronic, as well as steric, control over the site of attack of a reactant on a coordinated prochiral substrate. The present work is concerned with the behavior of bivalent complexes of nickel, palladium, and platinum containing the enantiomers of the unsymmetrical bidentate (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas). The resolution of both diastereoisomers of this ligand has recently been achieved by the method of metal complexation.[2] The four enantiomers of the ligand are depicted in Figure 1.[3,4] The work is complementary to our earlier studies of tetrahedral gold(I) complexes[5] of this ligand, as well as of the symmetrical donor equivalents 1,2-phenylenebis(methylphenylphopshino)[6] and its arsenic analogue,[7] for which the bivalent nickel,[8] palladium, and platinum[9] chemistry has already been described.

Results and Discussion

Preparations. (a) Nickel(II) Complexes. The square-planar complexes [Ni(phas)$_2$]$(ClO_4)_2$ were obtained in high yield from the reaction of [Ni$(H_2O)_6$]$(ClO_4)_2$ with the appropriate form of the ligand in acetone. The salts are orange diamagnetic solids that conduct as di-univalent electrolytes in acetonitrile solution. The corresponding deep-red to purple compounds [NiCl(phas)$_2$]ClO_4 were derived from the square-planar species by the addition of chloride. Conductivity and spectroscopic data are consistent with the assignment of a five-coordinate square-pyramidal geometry to the cationic chloride adducts. Selected physical and spectroscopic data for the various stereoisomeric forms of the compounds [Ni(phas)$_2$]$(ClO_4)_2$ and [NiCl(phas)$_2$]ClO_4 are presented in Table I.

(b) Palladium(II) and Platinum(II) Complexes. The optically active square-planar complexes [$PdCl_2$L] (where L = [*R*-(*R**,*R**)]-, [*S*-(*R**,*R**)]-, [*R*-(*R**,*S**)]-, or [*S*-(*R**,*S**)]-phas) were obtained as described in the resolution procedure.[2] The corresponding racemic compounds were prepared from the appropriate form of the ligand and [$PdCl_2$(MeCN)$_2$] in boiling acetonitrile. Platinum analogues were produced by hydrochloric acid treatment of the cations resulting from

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Table I. Selected Physical Data for the Complexes $[Ni(phas)_2](ClO_4)_2$ and $[NiCl(phas)_2]ClO_4$

	isomer	propn,[a] %	δ(EMe)[b] PMe	δ(EMe)[b] AsMe	δ(P)	temp, K
(−)-$[Ni(([R\text{-}(R^*,R^*)]\text{-phas})_2](ClO_4)_2$	cis	40	1.71 d	1.86 br s	55.7 s	304
	trans	60	1.71 t	1.61 s	53.0 s	304
(+)-$[Ni([R\text{-}(R^*,S^*)]\text{-phas})_2](ClO_4)_2$	cis	93	1.26 t	1.41 s	56.0 s	258
	trans	7	2.44 t	2.38 s	*c*	258
(±)-$[Ni((R^*,R^*)\text{-phas})_2](ClO_4)_2$ (racemic)	cis	40	1.71 d	1.86 br s	55.7 s	304
	trans	60	1.71 t	1.61 s	53.0 s	304
$[Ni((R^*,R^*)\text{-phas})_2](ClO_4)_2$ (meso)	cis	32	2.46 d	2.35 s	54.2 s	304
	trans	68	2.38 t	2.39 s	51.1 s	304
(±)-$[Ni((R^*,S^*)\text{-phas})_2](ClO_4)_2$ (racemic)	cis	95	1.26 t	1.41 s	56.0 s	258
	trans	5	2.44 t	2.38 s	*c*	258
$[Ni((R^*,S^*)\text{-phas})_2](ClO_4)_2$ (meso)	cis	5	2.39 t	2.42 s	*c*	258
	trans	95	1.49 t	1.16 s	51.9 s	258
(−)-$[NiCl([R\text{-}(R^*,R^*)]\text{-phas})_2]ClO_4$	cis	30	1.23 d, 1.51 d	1.41 s, 1.60 s	46.7, 63.0 AB q	213
	trans	70	1.62 t, 1.81 t	1.08 s, 1.31 s	44.4 s, 58.6 s	213
(+)-$[NiCl([R\text{-}(R^*,S^*)]\text{-phas})_2]ClO_4$	cis	96	1.21 d, 1.33 d	1.31 s, 1.42 s	52.6, 54.9 AB q	213
	trans	4	2.53 t	2.35 s	56.5 s	213
(±)-$[NiCl((R^*,R^*)\text{-phas})_2]ClO_4$ (racemic)	cis	50	1.23 d, 1.51 d	1.41 s, 1.60 s	46.7, 63.0 AB q	293
	trans	50	1.62 t, 1.81 t	1.08 s, 1.31 s	44.4 s, 58.6 s	293
(±)-$[NiCl((R^*,S^*)\text{-phas})_2]ClO_4$ (racemic)	cis	96	1.21 d, 1.33 d	1.31 s, 1.42 s	52.6, 58.1 AB q	213
	trans	4	*d*	*d*	*d*	213
$[NiCl((R^*,S^*)\text{-phas})_2]ClO_4$ (meso)	cis	4	*d*	*d*	*d*	213
	trans	96	1.48 t, 1.58 t	1.04 s, 1.21 s	54.4 s, 55.6 s	213

[a] Relative proportions of isomers at equilibrium. [b] ^1H and ^{31}P NMR spectra of diperchlorates were recorded in MeCN-d_3 with δ quoted relative to Me_4Si and H_3PO_4 (85%), respectively; spectra of monoperchlorates were recorded in CD_2Cl_2 with use of the same standards. [c] Signal to noise ratio poor. [d] See text.

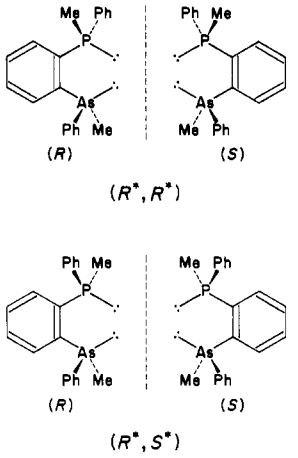

Figure 1. Enantiomerism in (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas).

bridge splitting of bis(μ-chloro)bis(2-methoxycyclooct-5-enyl)diplatinum(II) with the various forms of the ligand.[9]

Bis(bidentate)metal(II) salts were prepared from $[MCl_2L]$ by reaction with an additional 1 equiv of ligand in 95% ethanol:

$$[MCl_2L] + L \rightarrow [ML_2]Cl_2$$

The chloride salts conduct as uni-univalent electrolytes in dichloromethane and methanol solutions, in which they are yellow, and as di-univalent electrolytes in water, where they are almost colorless, consistent with the assignment of a square-pyramidal geometry to the univalent cations in the organic solvents and a square-planar stereochemistry to the dications in water:[9]

$$[ML_2]Cl_2 \rightleftharpoons [MClL_2]Cl$$

The complexes $[ML_2](PF_6)_2$ were isolated from aqueous solutions of the chlorides by treatment with ammonium hexafluorophosphate:

$$[ML_2]Cl_2 + 2NH_4PF_6 \rightarrow [ML_2](PF_6)_2$$

The hexafluorophosphate salts are di-univalent electrolytes in acetone, in which the colorless square-planar dications are present. Selected physical and NMR data for the various forms of the compounds $[ML_2]X_2$ are presented in Table II (X = Cl^-) and Table III (X = PF_6^-).

Stereochemistry of the Bis(bidentate)metal Chromophore. (a) Square-Planar Complexes. 1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene (phas) exists in six crystalline forms: the *R**,*R** diastereoisomer and its enantiomers and the *R**,*S** diastereoisomer and its enantiomers (Figure 1). The square-planar bis(bidentate)metal(II) cations that may arise from the various forms of the ligand are shown in Figures 2 and 3. The pure enantiomers of the ligand produce optically active complexes for which cis and trans isomers are possible.[10] The racemic forms of the ligand, however, give rise in each case to a cis–trans pair of achiral internally compensated meso complexes containing ligands of opposite chirality, as well as the racemic forms of the optically active species described above (racemic complexes). Although cis–trans isomerization may occur intramolecularly, racemic–meso interconversion is definitive of intermolecular bidentate ligand exchange and can be observed by NMR spectroscopy in suitably substituted complexes. Furthermore, the signal(s) due to the racemic complex can always be identified if the spectrum of the corresponding optically active complex is available for comparison.

All of the stereoisomers depicted in Figures 2 and 3 are, in principle, identifiable by ^1H or ^{31}P NMR spectroscopy. For complexes containing a pair of cis-PMe groups the ^1H NMR spectra contain doublets ($^2J_{PP'}$ = ca. 0 Hz) or "filled-in" doublets ($0 < {}^2J_{PP'} << |{}^2J_{PH} + {}^4J_{P'H}|$) for the methyl groups,[12] and broadened singlets for the AsMe groups due to coupling with the trans phosphorus atoms ($^4J_{PH}$). In trans complexes the As*Me* groups resonate as sharp singlets and the P*Me* groups as deceptively simple triplets, due to virtual coupling between the trans phosphorus nuclei ($^2J_{PP'} >> |{}^2J_{PH} + {}^4J_{P'H}|$).[13]

(10) The apparent inversion that takes place upon coordination of the asymmetric donor atoms is consistent with the rules of Cahn et al. for absolute configurations.[11]

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Table II. Selected Physical Data for the Complexes $[MCl(phas)_2]Cl$

	isomer	propn,[a] %	δ(EMe)[b] PMe	δ(EMe)[b] AsMe	δ(P)[d]
(+)-[PdCl([*S*-(*R**,*R**)]-phas)$_2$]Cl	cis	50	1.66 d	1.89 br s	51.6 s
	trans	50	2.04 t	1.52 s	50.5 s
(+)-[PdCl([*R*-(*R**,*S**)]-phas)$_2$]Cl	cis	30	1.57 d	1.74 br s	51.5 s
	trans	70	2.72 t	2.61 s	52.8 s
(±)-[PdCl((*R**,*R**)-phas)$_2$]Cl (racemic)	cis	50	1.66 d	1.89 br s	51.6 s
	trans	50	2.04 t	1.52 s	50.5 s
[PdCl((*R**,*R**)-phas)$_2$]Cl (meso)[c]	cis	50	2.42 d	2.61 br s	49.6 s
	trans	50	2.48 t	2.56 s	50.0 s
(±)-[PdCl((*R**,*S**)-phas)$_2$]Cl (racemic)	cis	50	1.56 d	1.73 br s	51.5 s
	trans	50	2.72 t	2.61 s	53.8 s
[PdCl((*R**,*S**)-phas)$_2$]Cl (meso)	cis	50	2.63 d	2.60 br s	54.6 s
	trans	50	1.80 t	1.51 s	48.9 s
(+)-[PtCl([*S*-(*R**,*R**)]-phas)$_2$]Cl·CH_2Cl_2	cis	50	1.74 d	1.95 br s	41.1 s (2798)
	trans	50	2.04 t	1.64 s	40.0 s (2296)
(+)-[PtCl([*R*-(*R**,*S**)]-phas)$_2$]Cl	cis	50	1.71 d	1.86 br s	41.4 s (2767)
	trans	50	2.85 t	2.72 s	41.7 s (2363)
(±)-[PtCl((*R**,*R**)-phas)$_2$]Cl (racemic)	cis	50	1.74 d	1.95 br s	41.1 s (2798)
	trans	50	2.04 t	1.64 s	40.0 s (2296)
[PtCl((*R**,*R**)-phas)$_2$]Cl (meso)	cis	50	2.60 d	2.74 br s	40.2 s (2767)
	trans	50	2.66 t	2.69 s	40.3 s (2268)
(±)-[PtCl((*R**,*S**)-phas)$_2$]Cl (racemic)	cis	50	1.71 d	1.86 br s	41.4 s (2767)
	trans	50	2.85 t	2.72 s	41.7 s (2363)
[PtCl((*R**,*S**)-phas)$_2$]Cl (meso)	cis	50	2.76 d	2.76 br s	41.8 s (2867)
	trans	50	1.93 t	1.64 t	40.2 s (2274)

[a] Relative proportions of isomers at equilibrium. [b] Quoted relative to Me_4Si in MeOH-d_4 at 304 K. [c] ^1H NMR spectrum recorded at 253 K. [d] Quoted relative to H_3PO_4 (85%) in Me_2SO at 304 K with values of $^1J_{PtP}$ in parentheses.

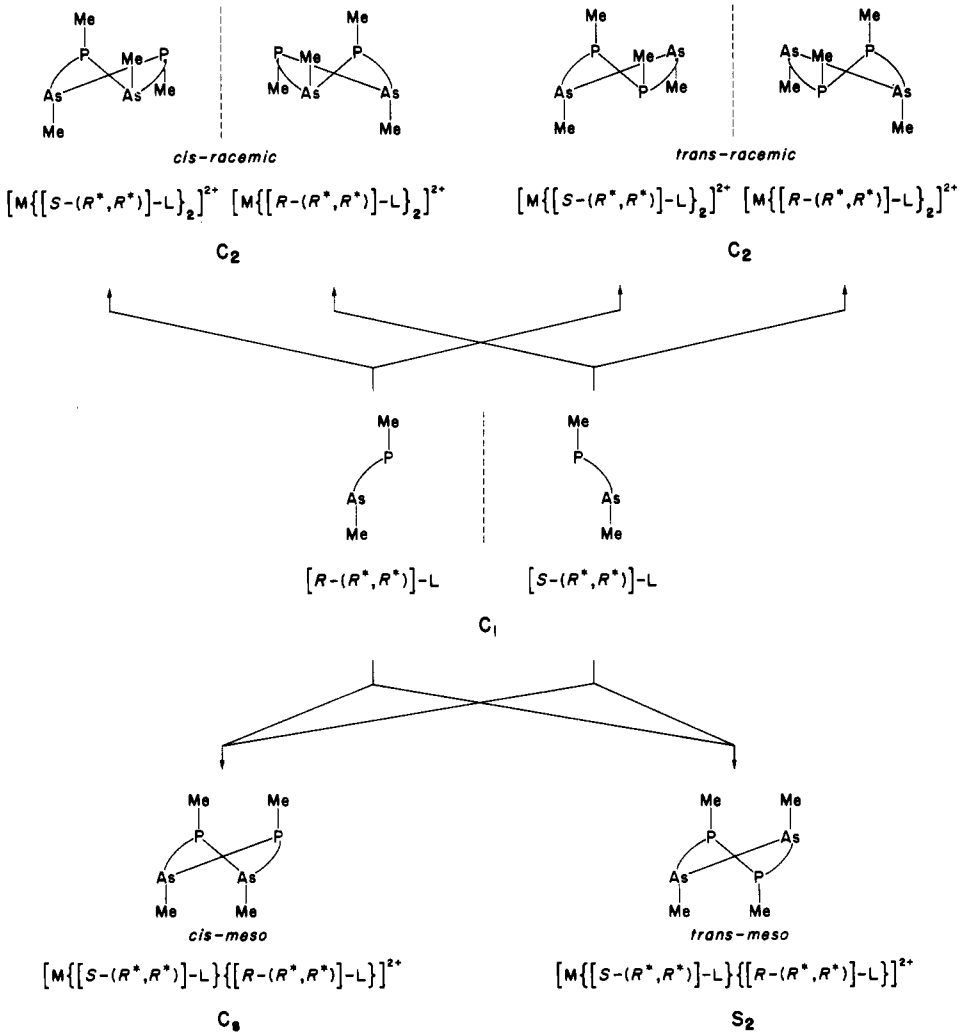

Figure 2. Stereoisomerism in square-planar cations containing the enantiomers of (R^*,R^*)-(±)-phas.

In addition, the value of $^1J_{PtP}$ is diagnostic of geometry in platinum complexes.[14] The magnitude of this coupling constant decreases with increasing trans influence of the ligand trans to the phosphorus atom. In the present system cis iso-

Table III. Selected Physical Data for the Complexes $[M(phas)_2](PF_6)_2$

	isomer	propn,[a] %	δ(EMe)[b] PMe	δ(EMe)[b] AsMe	δ(P)[c]
(+)-[Pd([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$	cis	50	1.69 d	2.14 br s	51.9 s
	trans	50	2.04 t	1.76 s	50.3 s
(+)-[Pd([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$	cis	85	2.01 d	2.30 br s	54.2 s
	trans	15	2.58 t	2.55 s	52.8 s
(±)-[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$ (racemic)	cis	50	1.69 d	2.14 br s	51.9 s
	trans	50	2.04 t	1.76 s	50.3 s
[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$ (meso)	cis	50	2.49 d	2.56 br s	52.1 s
	trans	50	2.49 t	2.53 s	50.3 s
(±)-[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$ (racemic)	cis	90	2.01 d	2.29 br s	54.2 s
	trans	10	2.58 t	2.55 s	52.8 s
[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$ (meso)	cis	10	2.52 d	2.58 br s	50.0 s
	trans	90	2.26 t	2.03 s	52.2 s
(+)-[Pt([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$	cis	50	1.72 d	2.18 br s	44.7 s* (2673)
	trans	50	2.09 t	1.80 s	43.7 s (2214)
(+)-[Pt([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$	cis	85	2.06 d	2.30 br s	46.0 s (2750)
	trans	15	2.70 t	2.66 s	45.7[d]
[Pt((*R**,*R**)-phas)$_2$](PF$_6$)$_2$ (meso)	cis	50	2.61 d	2.68 br s	44.3 s (2703)
	trans	50	2.63 t	2.66 s	43.6 s (2217)
(±)-[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$ (racemic)	cis	75	2.06 d	2.30 br s	46.0 s (2750)
	trans	25	2.70 t	2.66 s	45.7 s (2231)
[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$ (meso)	cis	25	2.80 d	2.70 br s	44.4 s (2735)
	trans	75	2.28 t	2.00 s	45.3 s (2217)

[a] Relative proportions of isomers at equilibrium. [b] Quoted relative to Me_4Si in Me_2SO-d_6 at 304 K. [c] Quoted relative to H_3PO_4 (85%) in Me_2SO at 304 K with values of $^1J_{PtP}$ in parentheses. [d] Resolution inadequate for determination of $^1J_{PtP}$.

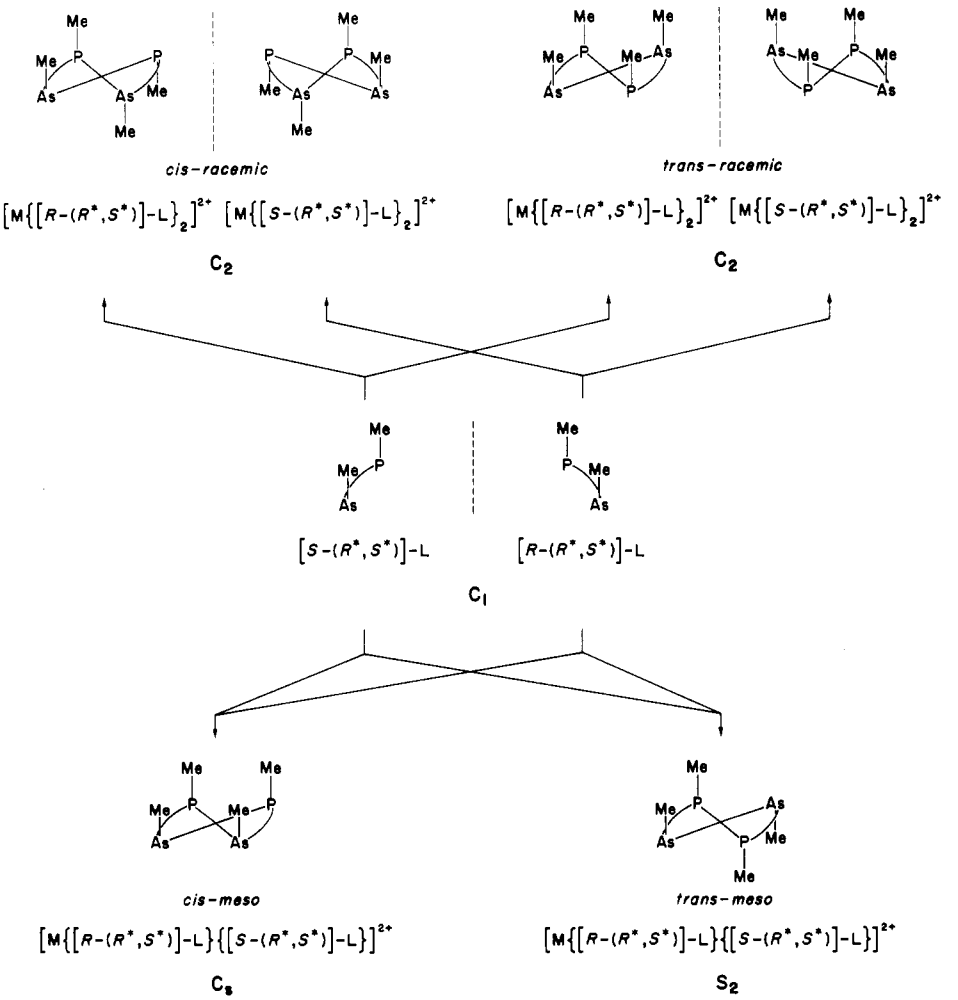

Figure 3. Stereoisomerism in square-planar cations containing the enantiomers of (*R**,*S**)-(±)-phas.

mers give rise to the larger values of $^1J_{PtP}$.

(b) Square-Pyramidal Complexes. The stability of the M–Cl bond varies markedly in cations of the type $[MCl(bidentate)_2]^+$ containing bis(tertiary arsines and phosphines).[8,9] For nick-

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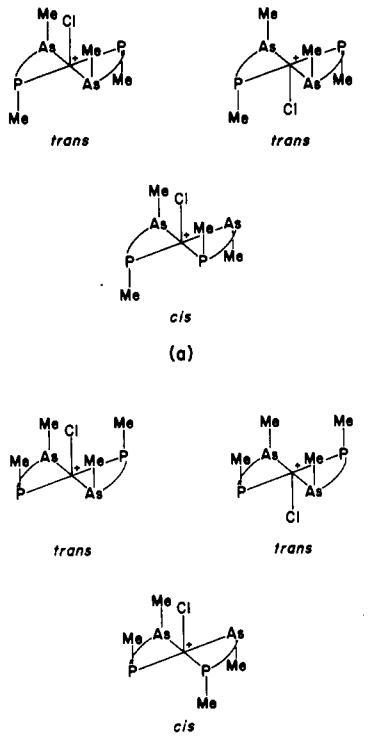

Figure 4. Stereoisomerism in (a) *cis*- and *trans*-[NiCl([*R*-(R^*,R^*)]-phas$_2$]$^+$ and (b) *cis*- and *trans*-[NiCl([*R*-(R^*,S^*)]-phas)$_2$]$^+$.

el(II) the bond is not ionized in polar solvents, although the chlorine atom is labile. In similar palladium and platinum compounds ionization of the bond occurs readily in polar solvents such as water, but not in dichloromethane or methanol:

$$[MCl(bidentate)_2]^+ \rightleftharpoons [M(bidentate)_2]^{2+} + Cl^-$$

Site exchange of the chlorine ligand between the alternative axial positions of the square pyramid is rapid for all three metals. Both intra- and intermolecular factors contribute to the exchange mechanism: the former can be unambiguously detected by variable-temperature NMR spectroscopy in suitably substituted complexes.[8,9] The rates are faster for palladium(II) and platinum(II) than they are for nickel(II). Thus, stereoisomerism arising from the siting of a chlorine atom in one of the alternative axial sites has not been observed by NMR spectroscopy, to date, in square-pyramidal palladium(II) and platinum(II) compounds. The chemical shift values observed for the methyl groups of the optically active cations are thus an average value arising from several species in rapid equilibrium (Figure 4).

Square-Planar and Square-Pyramidal Complexes of Nickel(II). The ^{1}H NMR spectrum of (−)$_{589}$-[Ni([*R*-(R^*,R^*)]-phas)$_2$](ClO$_4$)$_2$ in Me$_2$CO-d_6 exhibited four methyl resonances that were assigned to cis and trans isomers as indicated in Table I (cis:trans = 2:3). The P*Me* resonance of the cis compound appeared as a "filled-in" doublet, as found in numerous other species containing cis-coordinated PMe groups.[12] In MeCN-d_3 the pattern of methyl resonances was similar, but the peaks were shifted upfield. The ^{31}P NMR data for the compound were consistent with the ^{1}H NMR data (Table I). It was not found possible to separate the two isomers by fractional crystallization.

The optically active compound (+)-[Ni([*R*-(R^*,S^*)]-phas)$_2$](ClO$_4$)$_2$ in MeCN-d_3 at 304 K exhibited a broad singlet for the methyl groups, centered at δ 1.35. When the sample was cooled to 258 K, separate resonances appeared in this region of the spectrum: a 1:1:1 P*Me* triplet and an As*Me* singlet (ca. 93%) and, as a minor feature, another 1:2:1 P*Me* triplet and an As*Me* single (Table I). Consideration of steric factors in molecular models of the two possible diastereoisomers led to the assignment of the upfield set of resonances to the cis isomer, where each methyl group is shielded by a phenyl group (Figure 3).

In related complexes of (R^*,S^*)-1,2-phenylenebis(methylphenylarsine) and its phosphorus analogue, no evidence of the isomer containing the syn arrangement of methyl and phenyl groups was found.[8] The overwhelming stability of the diastereoisomer with the anti disposition of similar substituents is also found in the solid state and appears to be an important factor contributing to the ready separation of R^*,R^* and R^*,S^* diastereoisomers of ligands of this type by metal complexation.

The rapid cis–trans isomerization observed at 304 K appears to be an intramolecular process in MeCN-d_3. The coalescence temperature observed was independent of concentration for 0.05 and 0.10 M solutions. Redistribution of the bidentate ligands does not occur under these conditions, although it is facile in the corresponding cations [NiCl(phas)$_2$]$^+$ (see below).

Use of (R^*,R^*)-(±)-phas as ligand produced a separable mixture of racemic and meso complexes. The meso complex precipitated in 48% yield from an acetone solution of [Ni(H$_2$O)$_6$](ClO$_4$)$_2$ upon the addition of the ligand. In MeCN-d_3 solution it consists of a 2:1 mixture of cis and trans isomers (Table I). The corresponding racemic complex crystallized from the mother liquor during concentration and was shown by NMR spectroscopy to be a 2:3 mixture of cis and trans isomers. The ^{1}H and ^{31}P NMR spectra of this compound are of course identical with those of the corresponding optically active complex under the same conditions. Redistribution of the bidentate ligands (between the racemic and meso cations) was not detected in either of the pure complexes over a 7-day period at 304 K in MeCN-d_3.

The ^{1}H NMR spectrum of the complex prepared from (R^*,S^*)-(±)-phas in MeCN-d_3 at 304 K consisted of two broad signals centered at δ 1.22 and 1.53. Upon cooling of the sample to 258 K the broad peaks resolved into eight separate resonances that were assigned as indicated in Table I. The major components in the mixture were the cis-racemic and trans-meso diastereoisomers (ca. 95%). Cis–trans isomerization is therefore facile in both forms (racemic and meso) of the cations [Ni((R^*,S^*)-phas)$_2$]$^{2+}$ at 304 K. The ^{31}P NMR resonances due to the minor diastereoisomers were not detected.

The square-planar cations were converted into the corresponding square-pyramidal species by adding chloride to acetone solutions of the former. The chloro species conducted as uni-univalent electrolytes in acetonitrile solution, and their electronic spectra in this solvent were consistent with the square-pyramidal stereochemistry.[8]

The optically active complex (−)-[NiCl([*R*-(R^*,R^*)]-phas)$_2$]ClO$_4$ exhibited two broad singlets at δ 1.45 and 1.67 for the methyl groups (CD$_2$Cl$_2$ at 304 K). At 213 K this region of the spectrum consisted of eight signals, four of which were of twice the intensity of the other four. The more intense set of signals was assiged to the alternative pair of trans isomers, both of which have equivalent pairs of methyl groups at the slow-exchange limit (Figure 4). The spectra were identical for 0.1 and 0.2 M solutions of the complex in this solvent. When a sample of the complex in PhNO$_2$-d_5 was heated to 343 K, the two broad resonances observed at 304 K changed into a singlet (δ 1.55) and triplet (δ 1.64). This spectrum is very similar to that obtained for (+)-[PdCl([*S*-(R^*,R^*)]-phas)$_2$]Cl at elevated temperatures, where it was

(15) The full formula of the meso complexes has been given for clarity in Figures 2 and 3: the systematic formula for these diastereoisomers is [MCl((R^*,R^*)-phas)$_2$]Cl.

considered to represent the fast-exchange limit of cis–trans isomerization. Thus, the complex (−)-[NiCl([*R*-(*R**,*R**)-phas)$_2$]ClO_4 undergoes facile axial chloro site exchange, as well as cis–trans isomerism, over the temperature range 213–343 K. Both processes have an intermolecular component to their mechanism, since bidentate ligand redistribution was observed between racemic and meso complexes (derived from (*R**,*R**)-(±)-phas) under the conditions of the experiment. Variable-temperature ^{31}P NMR spectra were consistent with the ^1H NMR findings. At 205 K separate phosphorus resonances were observed for the alternative axially substituted cis isomers. For the cis isomer, however, the nonequivalent phosphorus atoms gave rise to an AB quartet with chemical shifts of δ 63.0 and 43.7 with a $^2J_{PP'}$ of 56.2 Hz.

The ^1H NMR spectrum of the optically active complex (−)-[NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO_4 at 304 K (in CD_2Cl_2) contained a broad singlet resonance at δ 1.56 due to methyl groups. At 213 K this region of the spectrum consisted of six resonances (T_c = 263 K). The major contribution (ca. 96%) consisted of a pair of P*Me* doublets (δ 1.21 and 1.33) and an associated pair of As*Me* singlets (δ 1.31 and 1.42), which were assigned to the static square-pyramidal cis cation (Figure 4). (The anti disposition of methyl and phenyl groups is the thermodynamically favored arrangment in the corresponding compounds of (*R**,*S**)-1,2-phenylenebis(methylphenylarsine) and its phosphorus analogue.[8]) The minor peaks in the low-temperature ^1H NMR spectrum of [NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO_4 (a triplet at δ 2.53 and a singlet at δ 2.35) have been assigned to one of two possible axially substituted trans diastereoisomers (Figure 4). (A detailed analysis of the ^1H NMR spectrum of the compound (±)-[NiCl((*R**,*R**)-diphos)((*R**,*S**)-diphos)]ClO_4 (where diphos = 1,2-C_6H_4-$(PMePh)_2$) at the slow-exchange limit has revealed that the chlorine ligand is associated only with the side of the square plane containing the methyl groups, as found in the solid state.[16]) Heating of the NMR sample to 343 K led to the appearance of a doublet at δ 1.65 and a singlet at δ 1.70. The variable-temperature spectra in CD_2Cl_2 appear to be independent of concentration (0.05 and 0.10 M solutions). The ^{31}P NMR spectrum of the complex at the slow-exchange limit (213 K) exhibited an AB quartet (δ 58.1 and 52.6; $^2J_{PP'}$ = 54.9 Hz), comprising ca. 96% of the intensity, and a barely discernible singlet at δ 56.5. The quartet was accordingly assigned to the (±)-cis isomer and the singlet to the meso-trans species.

The kinetically stable square-planar diastereoisomer (±)-[Ni((*R**,*R**)-phas)$_2$]$(ClO_4)_2$ and the meso compound [Ni(*R**,*R**)-phas)$_2$]$(ClO_4)_2$[15] were individually treated with sodium chloride in acetone. The meso compound produced an equimolar mixture of both internally diastereoisomeric square-pyramidal cations, viz. (±)-[NiCl((*R**,*R**)-phas)$_2$]$^+$ and [NiCl((*R**,*R**)-phas)$_2$]$^+$. Only the racemic species, however, crystallized from solution as the perchlorate. Accordingly, reaction of the racemic salt (±)-[Ni((*R**,*R**)-phas)$_2$]$(ClO_4)_2$ with chloride produced (±)-[NiCl((*R**,*R**)-phas)$_2$]$^+$ only in solution, as evidenced by ^1H NMR spectroscopy. Clearly intermolecular redistribution of the bidentate ligands is facile in the less stereochemically rigid five-coordinate cations, the racemic cation being favored in solution and in the solid state.

The variable-temperature ^1H and ^{31}P NMR spectra of (±)-[NiCl((*R**,*R**)-phas)$_2$]ClO_4 appear to be indistinguishable from those of the corresponding optically active material over the temperature range 304–213 K for 0.5 and 0.10 M solutions in CD_2Cl_2.

The ^1H NMR spectrum of [NiCl((*R**,*S**)-phas)$_2$]ClO_4 in CD_2Cl_2 at 304 K consisted of two broad singlets (δ 1.29 and 1.55) in the methyl region. Upon cooling of the sample to 213 K these resolved into eight separate signals of equal intensity (T_c = 263 K) (ca. 96% of intensity). The resonances were assigned by comparison with the low-temperature spectrum of (−)-[NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO_4 and are given in Table I. Broad minor peaks in the region δ 2.3–2.7 are presumably due to the presence of small quantities of the corresponding trans-racemic and cis-meso cations. When a sample of the complex in $PhNO_2$-d_5 was heated to 343 K, two new singlets (δ 1.43 and 1.70), a doublet (δ 1.65), and a triplet (δ 1.75) were observed in the ^1H NMR spectrum, in agreement with the finding of rapid cis–trans isomerization in these systems under ambient conditions. The variable-temperature ^{31}P NMR spectra of the five-coordinate complex of (*R**,*S**)-(±)-phas corroborated the ^1H NMR results. At 213 K the spectrum consisted of a pair of AB quartets of equal intensity. These were accordingly assigned to the cis-racemic cation (δ 58.1 and 52.6; $^2J_{PP'}$ = 54.9 Hz) and trans-meso cation (δ 55.6 and 54.4; $^2J_{PP'}$ = 236 Hz). Resonances due to the two other possible diastereoisomers were not found in the spectrum.

Complexes of Palladium(II) and Platinum(II). The ^1H NMR spectra of (+)-[PdCl([*S*-(*R**,*R**)]-phas)$_2$]Cl and its platinum isostere, (+)-[PtCl([*S*-(*R**,*R**)]-phas)$_2$]Cl·CH_2Cl_2, in MeOH-d_4 at 304 K each contain four methyl resonances of equal intensity. The spectra do not change significantly when the samples are cooled to 178 K, thus confirming the already known high rate of axial chloro site exchange in complexes of this type.[9] The methyl signals were assigned to cis and trans isomers as indicated in Table II. The complexes are kinetically stable under ambient conditions in the absence of free ligand: platinum complexes showed satellites due to $^3J_{PtH}$ and $^1J_{PtP}$ in the ^1H and ^{31}P NMR spectra, respectively. Thus, the mixing of equimolar MeOH-d_4 solutions of the optically pure enantiomeric complexes of opposite chirality does not lead to the formation of meso complexes for either metal (even after 7 days at 304 K), although the latter are known to be stable under these conditions (see below). Heating of $PhNO_2$-d_5 solutions of the complexes does result in a coalescence of the methyl peaks in both cases, however. For the palladium compound the peaks coalesced at 318 K and subsequently emerged as a triplet (δ 2.08) for the PMe groups and as a singlet (δ 1.92) for the AsMe groups at 373 K. The platinum complex behaved similarly (T_c = 348 K), but the upper limiting spectrum could not be observed due to decomposition of the sample at the elevated temperatures involved. The values of T_c were identical for 0.10 and 0.20 M solutions of both complexes, and the spectral changes were reversed on cooling. It was not found possible to fractionally crystallize either of the mixtures, presumably due to a similarity in the lattice energies of the cations, which are almost isostructural outside of the first coordination sphere.

Optically active complexes containing the *R**,*S** diastereoisomer of the ligand were also isolated. At 304 K in MeOH-d_4 the compounds (−)-[MCl([*R*-(*R**,*S**)]-phas)$_2$]Cl (where M = Pd or Pt) exhibited four methyl resonances and were each readily shown to be a mixture of cis and trans isomers (Table II). The cis:trans ratio was 1:1 for platinum but was ca. 3:7 for palladium.

The cis–trans mixtures of the chloride salts were converted into the corresponding mixture of hexafluorophosphates by treatment with ammonium hexafluorophosphate in water. The optically active square-planar complexes containing the *R**,*R** diastereoisomer of the ligand consisted of 1:1 mixtures of cis and trans isomers for both metals. The NMR assignments are given in Table III. Heating of either sample to 373 K in $PhNO_2$-d_5 did not cause changes in the ^1H NMR spectra. The complexes (+)-[M([*R*-(*R**,*S**)]-phas)$_2$]$(PF_6)_2$ were isolated as the expected mixtures (cis:trans = ca. 6:1): NMR as-

(16) Wood, D. L.; Wild, S. B., unpublished work.

signments are given in Table III.

Reaction of (±)-[MCl_2((R^*,R^*)-phas)] with (R^*,R^*)-(±)-phas produces optically inactive complexes of the type [MCl((R^*,R^*)-phas)$_2$]Cl as shown in Figure 2. Use of (R^*,R^*)-(±)-phas permits formation of the achiral meso complexes [MCl((R^*,R^*)-phas)$_2$]Cl,[15] as well as the chiral racemic complexes (±)-[MCl((R^*,R^*)-phas)$_2$Cl. The platinum product exhibited four methyl resonances at 304 K. The spectrum of the palladium complex at this temperature, however, consisted of a broad singlet in the methyl region, although cooling of the sample to 253 K led to four methyl signals of equal intensity. Interestingly, none of the resonances in either system corresponded with those found in the spectra of the corresponding optically active compounds. The spectra did not change over a 7-day period in MeOH-d_4 at 304 K. The addition of a trace of (R^*,R^*)-(±)-phas to either sample, however, led to redistribution of the bidentates and the appearance of four new methyl peaks in both cases. The new signals corresponded exactly with those of the corresponding optically active species: all eight resonances had the same intensity (assignments given in Table II). The redistribution appeared to be instantaneous for palladium but took ca. 6 h for platinum. The reaction of (R^*,R^*)-(±)-phas with (±)-[MCl_2((R^*,R^*)-phas)] is therefore stereospecific for both metals, giving the meso complexes *cis*- and *trans*-[MCl-(R^*,R^*)-phas)$_2$]Cl in equal proportions. The addition of diethyl ether to either of the solutions at equilibrium led to the crystallization of meso complexes only. It may be noted that use of the dissymmetric bis(tertiary arsine) (R^*,R^*)-(±)-1,2-phenylenebis(methylphenylarsine) in a similar reaction of palladium also gave only the meso derivative in the solid state.[9] Steric factors therefore appear to be predominant in determining the lattice structure, as well as the kinetic product, in reactions of this form of the ligand with palladium(II).

Stereospecificity was not found in the reaction of (R^*,R^*)-(±)-phas with (±)-[MCl_2((R^*,S^*)-phas)]. For both metals eight methyl resonances and four phosphorus resonances of equal intensity were observed for the complexes [MCl((R^*,S^*)-phas)$_2$]Cl in MeOH-d_4 at 304 K. Assignments were made by the usual comparison of data for the corresponding optically actrive compounds (identification of racemic and meso complexes), and cis and trans isomers of each complex were subsequently identified by analysis of the values of J_{PtP} and the multiplicity of the PMe resonances (Table II).

Treatment of aqueous solutions of the equimolar mixture of *cis-meso*- and *trans-meso*-[M((R^*,R^*)-phas)$_2$]Cl_2 with NH_4PF_6 precipitated the corresponding mixture of colorless bis(hexafluorophosphates). The NMR assignments are given in Table III. Added (R^*,R^*)-(±)-phas did not cause redistribution of the bidentates in the platinum complexes, but a slow redistribution of bidentates was observed under similar conditions in the corresponding palladium system, where an equilibrium 1:1 mixture of racemic and meso complexes was established within 14 days in Me_2SO-d_6 at 304 K.

Ammonium hexafluorophosphate precipitation of the cations from an aqueous solution of [M((R^*,S^*)-phas)$_2$]Cl_2 gave the expected mixture of four possible diastereoisomeric products (Table III). The major component of the mixture in both cases was an equimolar mixture of the cis- and trans-racemic complexes (ca. 90% for Pd(II) and ca. 75% for Pt(II)), and the minor components were equimolar mixtures of the corresponding cis and trans-meso complexes.

Experimental Section

Proton NMR spectra were recorded at 304 K on a Varian HA 100 spectrometer (100 MHz); ^{31}P NMR spectra were obtained with use of a Bruker 3220 spectrometer (24.28 MHz). ^1H NMR chemical shifts are reported as δ values relative to internal Me_4Si, and ^{31}P NMR chemical shifts are quoted as δ values relative to external 85% H_3PO_4: PMe resonances appear as deceptively simple doublets with "filled-in" appearance or 1:2:1 triplets with $J_{PH} = |^2J_{PH} + {}^4J_{P'H}|$ = ca. 10 Hz. In platinum complexes these signals are flanked by pairs of satellites due to $^1J_{^{195}PtH}$. Optical rotations were measured at 589 nm on the specified solutions in a 1-dm cell at 294 K with a Perkin-Elmer Model 241 polarimeter. Conductivity measurements were made on 10^{-3} M solutions in the solvents indicated at 295 K. Elemental analyses were performed by staff within the Research School of Chemistry.

(R^*,R^*)-(±)- and (R^*,S^*))-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene was prepared and resolved as previously described.[2] The following optically active compounds were obtained as described in ref 2: (−)-[$PdCl_2$([R-(R^*,R^*)]-phas)], (+)-[$PdCl_2$-([S-[R^*,R^*)]-phas)], (+)-[$PdCl_2$([R-(R^*,S^*)]-phas)], and (−)-[$PdCl_2$([S-(R^*,S^*)]-phas)].

(−)-[Ni([R-(R^*,R^*)]-phas)$_2$](ClO_4)$_2$. Nickel(II) perchlorate hexahydrate (0.25 g) and [S-(R^*,R^*)]-phas[10] (0.5 g) were stirred together in acetone (50 mL) until complete dissolution of the ligand occurred. The solution was then filtered, and the filtrate was concentrated to ca. 10 mL whereupon the product crystallized as orange prisms: mp 297–298 °C; 0.64 g (94%); $[\alpha]_D$ −252° (c 0.09, MeCN). Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_8P_2$: C, 48.5; H, 4.1; Cl, 7.2. Found: C, 48.6; H, 4.1; Cl, 7.1. ^1H NMR (Me_2CO-d_6): δ 1.61 (s, 3.6, AsMe), 1.71 (d, 2.4, J_{PH} = 10 Hz, PMe), 1.68 (br s, 2.4, AsMe), 1.96 (t, 3.6, $^2J_{PH}$ = 10 Hz, PMe), 7.4–7.8 (m, 28, aromatics). ^1H NMR (MeCN-d_3): δ 1.34 (s, 3.6, AsMe), 1.42 (d, 2.4, $^2J_{PH}$ = 10 Hz, PMe), 1.61 (br s, 2.4, AsMe), 1.73 (t, 3.6, J_{PH} = 10 Hz, PMe), 7.3–7.9 (m, 28, aromatics). ^{31}P NMR (Me_2CO): δ 49.2 (s, 0.8), 53.0 (s, 1.2). ^{31}P NMR (MeCN): 53.0 (s, 0.8), 55.7 (s, 1.2). Λ_M = 269 Ω^{-1} cm^2 mol^{-1} (MeCN).

The following compounds were obtained similarly.

(+)-[Ni([R-(R^*,S^*)]-phas)$_2$](ClO_4)$_2$: orange needles from acetonitrile–diethyl ether mixture; mp 298–299°C; 90% yield; $[\alpha]_D$ +68.3° (c 0.10, MeCN). Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_8P_2$: C, 48.5; H, 4.1; Cl, 7.2. Found: C, 48.5; H, 4.0; Cl, 7.1. ^1H NMR (MeCN-d_3 at 258 K): δ 1.26 (t, 5.58, J_{PH} = 10 Hz, PMe), 1.41 (s, 5.58, AsMe), 2.38 (s, 0.42, AsMe), 2.44 (t, 0.42, J_{PH} = 10 Hz, PMe), 7.2–7.8 (m, 2, aromatics). ^{31}P NMR (MeCN at 258 K): δ 56.0 (s). Λ_M = 272 Ω^{-1} cm^2 mol^{-1} (MeCN).

(±)-[Ni((R^*,S^*)-phas)$_2$](ClO_4)$_2$: orange needles, mp 321–322°C; 91% yield. Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_8P_2$: C, 48.5; H, 4.1; Cl, 7.2. Found: C, 48.6; H, 4.2; Cl, 7.1. ^1H NMR (MeCN-d_3 at 258 K): δ 1.16 (s, 2.85, AsMe), 1.26 (t, 2.85, J_{PH} = 10 Hz, PMe), 1.41 (s, 2.85, AsMe), 1.49 (t, 2.85, J_{PH} = 10 Hz, PMe), 2.38 (s, 0.15, AsMe), 2.39 (t, 0.15, J_{PH} = 10 Hz, PMe), 2.42 (s, 0.15, AsMe), 2.44 (t, 0.15, $^2J_{PH}$ + $^4J_{P'H}$ = 10 Hz, PMe), 7.4–7.8 (m, 28, aromatics). ^{31}P NMR (MeCN at 258 K): δ 51.9 (s, 1), 56 (s, 1). Λ_M = 269 Ω^{-1} cm^2 mol^{-1} (MeCN).

[Ni((R^*,R^*)-phas)$_2$](ClO_4)$_2$ (Meso Complex) and (±)-[Ni-((R^*,R^*)-phas)$_2$](ClO_4)$_2$ (Racemic Complex). Nickel(II) perchlorate hexahydrate (1.0 g) and (R^*,R^*)-(±)-phas (2.0 g) were stirred together in acetone (200 mL) for 5 min, during which time the meso complex separated as a yellow precipitate. Recrystallization of this material from an acetonitrile–diethyl ether mixture afforded the meso complex as orange needles in 48% yield (1.3 g): mp 301–302 °C. Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_8P_2$: C, 48.5; H, 4.1; Cl, 7.2. Found: C, 49.0; H, 4.2; Cl, 7.1. ^1H NMR (MeCN-d_3): δ 2.35 (s, 1.92, AsMe), 2.38 (t, 4.08, J_{PH} = 20 Hz, PMe), 2.39 (s, 4.08, AsMe), 2.46 (d, 1.92, J_{PH} = 10 Hz, PMe), 6.9–7.8 (m, 28, aromatics). ^{31}P NMR (MeCN): δ 51.1 (s, 0.64), 54.2 (s, 1.36). Λ_M = 276 Ω^{-1} cm^2 mol^{-1} (MeCN). The corresponding racemic complex was obtained by concentration of the mother liquor (to ca. 50 mL): orange prisms; mp 277–278°C; yield 1.2 g (44%). Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_8P_2$: C, 48.5; H, 4.1; Cl, 7.2. Found: C, 48.7; H, 4.4; Cl, 7.3. ^1H and ^{31}P NMR (MeCN-d_3): identical with that of the optically active complex. Λ_M = 271 Ω^{-1} cm^2 mol^{-1} (MeCN).

(−)-[NiCl([R-(R^*,R^*)]-phas)$_2$]ClO_4. A mixture of (−)-[Ni([R-(R^*,R^*)]-phas)$_2$](ClO_4)$_2$ (0.4 g) and lithium chloride (0.2 g) was stirred in acetone (50 mL) for several minutes. The deep red solution was evaporated to dryness, and the residue was dissolved in methanol and the solution treated with lithium perchlorate (0.2 g) in the same solvent (5 mL). The product crystallized as purple needles from the concentrated solution: mp 292–293°C; yield 0.32 g (86%); $[\alpha]_D$ −404° (c 4.3 × 10^{-2}, MeCN). Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_4P_2$: C, 51.9; H, 4.4; Cl, 7.7. Found: C, 51.6; H, 4.3; Cl, 7.5. ^1H NMR (CD_2Cl_2 at 213 K): δ 1.08 (s, 2 , AsMe), 1.23 (d, 1 , J_{PH} = 10 Hz, PMe), 1.31 (s, 2, AsMe), 1.41 (s, 1, AsMe), 1.51 (d, 1, J_{PH} = 10 Hz,

PMe), 1.60 (s, 1 , AsMe), 1.62 (t, 2, J_{PH} = 10 Hz, PMe), 1.81 (t, 2, J_{PH} = 10 Hz, PMe), 7.0–7.9 (m, 28, aromatics). ^{31}P NMR (CH_2Cl_2 at 205 K): δ 44.4 (s, 0.7), 46.7, 63.0 (AB q, 0.6, $^2J_{PP'}$ = 56.2 Hz), 58.6 (s, 0.7). Λ_M = 116 Ω^{-1} cm^2 mol^{-1} (MeCN).

The following compounds were prepared similarly. **(+)-[NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO$_4$**: deep red needles; mp 205–206°C; 92% yield; $[\alpha]_D$ +65.9° (*c* 4.1 × 10^{-2}, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_4P_2$: C, 51.9; H, 4.4; Cl, 7.7. Found: C, 51.7; H, 4.4; Cl, 7.8. ^{1}H NMR (CD_2Cl_2 at 213 K): δ 1.21 (d, 2.88, J_{PH} = 10 Hz, PMe), 1.31 (s, 2.88, AsMe), 1.33 (d, 2.88, J_{PH} = 10 Hz, PMe), 1.42 (s, 2.88, AsMe), 2.35 (s, 0.24, AsMe), 2.53 (t, 0.24, J_{PH} = 10 Hz, PMe), 6.8–8.6 (m, 28, aromatics). ^{31}P NMR (CH_2Cl_2 at 213 K): δ 52.6, 58.1 (AB q, 0.96, $^2J_{PP'}$ = 54.9 Hz), 56.5 (s, 0.04). Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (MeCN). **(±)-[NiCl((*R**,*R**)-phas)$_2$]ClO$_4$**: obtained from the corresponding meso or racemic complex as purple needles; mp 216–217 °C; 92% yield. Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_4P_2$: C, 51.9; H, 4.4; Cl, 7.7. Found: C, 51.7; H, 4.7; Cl, 7.7. ^{1}H NMR (CD_2Cl_2 at 213 K) and ^{31}P NMR (CD_2Cl_2 at 205 K): identical with that of corresponding optically active material. Λ_M = 122 Ω^{-1} cm^2 mol^{-1} (MeCN). **(±)-[NiCl((*R**,*S**)-phas)$_2$]ClO$_4$**: purple needles; mp 280–281 °C; 92% yield. Anal. Calcd for $C_{40}H_{40}As_2Cl_2NiO_4P_2$: C, 51.9; H, 4.4; Cl, 7.7. Found: C, 51.7; H, 4.6; Cl, 7.6. ^{1}H NMR (CD_2Cl_2 at 213 K): δ 1.04 (s, 1.5, AsMe), 1.21 (d, 1.5, J_{PH} = 10 Hz, PMe), 1.21 (s, 1.5, AsMe), 1.31 (s, 1.5, AsMe), 1.33 (d, 1.5, J_{PH} = 10 Hz, PMe), 1.42 (s, 1.5, AsMe), 1.48 (t, 1.5, J_{PH} = 10 Hz, PMe), 1.58 (t, 1.5, J_{PH} = 10 Hz, PMe), 6.8–8.6 (m, 28, aromatics). ^{31}P NMR (CH_2Cl_2 at 213 K): δ 52.6, 58.1 (AB q, 1, $^2J_{PP'}$ = 54.9 Hz), 54.4, 55.6 (AB q, 1, $^2J_{PP'}$ = 236 Hz). Λ_M = 118 Ω^{-1} cm^2 mol^{-1} (MeCN).

(±)-[PdCl$_2$((*R,*R**)-phas)]**. A suspension of freshly prepared [$PdCl_2$(MeCN)$_2$] (0.71 g) and (*R**,*R**)-(±)-phas (1 g) in acetonitrile (200 mL) was heated under reflux for 5 h. The resulting yellowish orange solution was filtered and then diluted with an equal volume of methanol. Reduction of the volume of this solution to ca. two-thirds of the original afforded yellow plates of the pure product: mp >300 °C; yield 1.36 g, 92%. Anal. Calcd for $C_{20}H_{20}AsCl_2PPd$: C, 44.2; H, 3.7; Cl, 13.0. Found: C, 44.3; H, 3.7; Cl, 13.1. ^{1}H NMR (Me_2SO-d_6): δ 2.39 (s, 3, AsMe), 2.45 (d, 3, J_{PH} = 10.5 Hz, PMe, 7.4–8.1 (m, 14, aromatics). Λ_M = 0.40 Ω^{-1} cm^2 mol^{-1} (CH_2Cl_2).

(±)-[PdCl$_2$((*R,*S**)-phas)]** was prepared from (*R**,*S**)-(±)-phas by use of the same procedure: yellow microcrystals; mp >300 °C; 91% yield. Anal. Calcd for $C_{20}H_{20}AsCl_2PPd$: C, 44.2; H, 3.7; Cl, 13.0. Found: C, 44.4; H, 3.7; Cl, 13.2. ^{1}H NMR (Me_2SO-d_6): δ 2.40 (s, 3, AsMe), 2.49 (d, 3, J_{PH} = 10.5 Hz, PMe), 7.1–8.1 (m, 14, aromatics). Λ_M = 0.68 Ω^{-1} mol^{-1} cm^2 (CH_2Cl_2).

(±)-[PtCl$_2$((*R,*R**)-phas)]**. A mixture of dichloro(cycloocta-1,5-diene)platinum(II) (1.02 g) and finely ground anhydrous Na_2CO_3 (0.60 g) in methanol (120 mL) was heated under reflux for 5 min. The resulting yellow solution was filtered, and (*R**,*R**)-(±)-phas (1.0 g) was added to the filtrate. When the ligand had completely dissolved, hydrochloric acid (30 mL, 10 M) was added to the reaction mixture and the volume of the mixture reduced by half. The white precipitate was collected and recrystallized from a dichloromethane–methanol mixture to produce the pure compound as white needles: mp >300°C; yield 1.6 g (93%). Anal. Calcd for $C_{20}H_{20}AsCl_2PPt$: C, 38.0; H, 3.2; Cl, 11.2. Found: C, 38.2; H, 3.2; Cl, 11.3. ^{1}H NMR (Me_2SO-d_6): δ 2.37 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.45 (d, 3, J_{PH} = 10.5 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.2–8.2 (m, 14, aromatics). Λ_M = 0.45 Ω^{-1} mol^{-1} cm^2 (in CH_2Cl_2).

The following compounds were prepared similarly. **(−)-[PtCl$_2$([*R*-(*R**,*R**)]-phas)] and (+)-[PtCl$_2$([*S*-(*R**,*R**)]-phas)]**: white plates, mp >300 °C, 92% yield; $[\alpha]_D$ −25.7 and +25.5°, respectively (*c* 0.40, CH_2Cl_2). ^{1}H NMR (Me_2SO-d_6): identical with that of racemic material. **(±)-[PtCl$_2$((*R**,*S**)-phas)]**: white needles; mp >300°C; 90% yield. ^{1}H NMR (Me_2SO-d_6): δ 2.33 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.45 (*d*, 3, J_{PH} = 10.5 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.1–8.1 (m, 14, aromatics). Λ_M = 0.38 Ω^{-1} mol^{-1} cm^2 (CH_2Cl_2). **(+)-[PtCl$_2$([*R*-(*R**,*S**)]-phas)] and (−)-[PtCl$_2$([*S*-(*R**,*S**)]-phas)]**: white needles; mp >300 °C; 91% yield; $[\alpha]_D$ +10.6 and −10.4°, respectively (*c* 0.42, CH_2Cl_2). ^{1}H NMR (Me_2SO-d_6): identical with that of racemic material.

(+)-[PdCl([*S*-(*R,*R**)]-phas)$_2$]Cl**. A mixture of (−)-[$PdCl_2$-([*S*-(*R**,*R**)]-phas)] (0.74 g) and [*R*-(*R**,*R**)]-(+)-phas (0.5 g) in ethanol (100 mL) was stirred until complete solution had resulted. The reaction mixture was then filtered and evaporated to dryness. Recrystallization of the residue yielded yellow prisms of the desired product: mp 230–231 °C; yield 1.17 g (94%); $[\alpha]_D$ +440° (*c* 0.52, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pd$: C, 52.8; H, 4.4; Cl, 7.8. Found: C, 52.5; H, 4.1; Cl, 7.5. ^{1}H NMR (MeOH-d_4): δ 1.52 (s, 3, AsMe), 1.66 (d, 3, J_{PH} = 10 Hz, PMe), 1.89 (br s, 3, AsMe), 2.04 (t, 3, J_{PH} = 10 Hz, PMe), 7.3–7.9 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 50.5 (s, 1), 51.6 (s, 1). Λ_M = 47 (CH_2Cl_2), 85 (MeOH), 197 (H_2O) Ω^{-1} cm^2 mol^{-1}.

The following compounds were prepared similarly in high yield. **(+)-[PdCl([*R*-(*R**,*S**)]-phas)$_2$]Cl**: yellow needles from a dichloromethane–diethyl ether mixture; mp 271–272 °C; 92% yield; $[\alpha]_D$ +41.4 (*c* 0.40, MeOH). Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pd$: C, 52.8; H, 4.4; Cl, 7.8. Found: C, 52.5; H, 4.4; Cl, 7.8. ^{1}H NMR (MeOH-d_4): δ 1.57 (d, 2, J_{PH} = 10 Hz, PMe), 1.74 (br s, 2, AsMe), 2.61 (s, 4, AsMe), 2.72 (t, 4, J_{PH} = 10 Hz, PMe), 7.0–7.9 (br m, 28, aromatics). ^{31}P NMR (MeOH): δ 51.5 (s, 0.7), 53.8 (s, 1.3). Λ_M = 49 (CH_2Cl_2), 95 (MeOH), 223 (H_2O) Ω^{-1} cm^2 mol^{-1}. Λ_M = 46 (CH_2Cl_2), 79 (MeOH), 202 (H_2O) Ω^{-1} cm^2 mol^{-1}. **[PdCl((*R**,*R**)-phas)$_2$]Cl** (from (±)-[$PdCl_2$((*R**,*R**)-phas)] and (*R**,*R**)-(±)-phas): yellow needles; mp 247–248 °C. Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pd$: C, 52.8; H, 4.4; Cl, 7.8. Found: C, 52.9; H, 4.4; Cl, 7.6. ^{1}H NMR (MeOH-d_4 at 253 K): δ 2.42 (d, 3, J_{PH} = 10 Hz, PMe), 2.48 (t, 3, J_{PH} = 10 Hz, PMe), 2.56 (s, 3, AsMe), 2.61 (br s, 3, AsMe), 7.0–7.9 (m, 28, aromatics). ^{31}P NMR (MeOH at 253 K): δ 49.6 (s, 1), 50.0 (s, 1). Λ_M = 47 (CH_2Cl_2), 91 (MeOH), 207 (H_2O) Ω^{-1} cm^2 mol^{-1}. **[PdCl((*R**,*S**)-phas)$_2$]Cl**: yellow microcrystals; mp 282–283 °C. Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pd$: C, 52.8; H, 4.4; Cl, 7.8. Found: C, 52.6; H, 4.4; Cl, 7.7. ^{1}H NMR (MeOH-d_4): δ 1.51 (s, 1.5, AsMe), 1.56 (d, 1.5, J_{PH} = 10 Hz, PMe), 1.73 (br s, 1.5, AsMe), 1.80 (t, 1.5, J_{PH} = 10 Hz, PMe), 2.60 (s, 1.5, AsMe), 2.63 (br s, 1, AsMe), 2.63 (d, 1.5, J_{PH} = 10 Hz, PMe), 2.71 (t, 1.5, J_{PH} = 10 Hz, PMe), 7.0–7.9 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 48.9 (s, 0.5), 51.5 (s, 0.5), 54.6 (s, 0.5). Λ_M = 46 (CH_2Cl_2), 84 (MeOH), 190 (H_2O) Ω^{-1} cm^2 mol^{-1}. **(+)-[PtCl([*S*-(*R**,*R**)]-phas)$_2$]Cl·CH$_2$Cl$_2$**: colorless needles; mp 232–233 °C; $[\alpha]_D$ +352° (*c* 0.55, CH_2Cl_2). Anal. Calcd for $C_{41}H_{42}As_2Cl_4P_2Pt$: C, 45.5; H, 3.9; Cl, 13.1. Found: C, 45.3; H, 3.6; Cl, 13.2. ^{1}H NMR (MeOH-d_4): δ 1.64 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 1.74 (d, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 1.95 (br s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.04 (t, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 5.3 (s, 2, CH_2Cl_2), 7.3–7.9 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 40.0 (s, 1, $^1J_{PtP}$ = 2296 Hz), 41.1 (s, 1, $^1J_{PtP}$ = 2798 Hz). Λ_M = 42 (CH_2Cl_2), 97 (MeOH), 210 (H_2O) Ω^{-1} cm^2 mol^{-1}. **(+)-[PtCl([*R*-(*R**,*S**)]-phas)$_2$]Cl**: colorless needles; mp 309–310 °C; $[\alpha]_D$ +22.3° (*c* 0.32, MeOH). Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pt$: C, 48.1; H, 4.0; Cl, 7.1. Found: C, 48.0; H, 4.1; Cl, 7.3. ^{1}H NMR (MeOH-d_4): δ 1.71 (d, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 1.86 (br s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.72 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.85 (t, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.0–7.9 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 41.4 (s, 1, $^1J_{PtP}$ = 2767 Hz), 41.7 (s, 1, $^1J_{PtP}$ = 2363 Hz). Λ_M = 48 (CH_2Cl_2), 97 (MeOH), 206 (H_2O) Ω^{-1} cm^2 mol^{-1}. **[PtCl((*R**,*R**)-phas)$_2$]Cl**: colorless needles; mp 285–286 °C. Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pt$: C, 48.1; H, 4.0; Cl, 7.1. Found: C, 47.8; H, 4.1; Cl, 7.3. ^{1}H NMR (MeOH-d_4): δ 2.60 (d, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.66 (t, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz), 2.69 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 7.0–8.0 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 40.2 (s, 1, $^1J_{PtP}$ = 2767 Hz), 40.3 (s, 1, $^1J_{PtP}$ = 2268 Hz). Λ_M = 47 (CH_2Cl_2), 101 (MeOH), 223 (H_2O) Ω^{-1} cm^2 mol^{-1}. **[PtCl((*R**,*S*)-phas)$_2$]Cl**: colorless microcrystals; mp 316–317 °C. Anal. Calcd for $C_{40}H_{40}As_2Cl_2P_2Pt$: C, 48.1; H, 4.0; Cl, 7.0. Found: C, 48.0; H, 4.0; Cl, 7.4. ^{1}H NMR (MeOH-d_4): δ 1.64 (s, 1.5, $^3J_{PtH}$ = 22 Hz, AsMe), 1.71 (d, 1.5, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 1.86 (br s, 1.5, $^3J_{PtH}$ = 22 Hz, AsMe), 1.93 (t, 1.5, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.72 (s, 1.5, $^3J_{PtH}$ = 22 Hz, AsMe), 2.76 (br s, 1.5, $^3J_{PtH}$ = 22 Hz, AsMe), 2.76 (d, 1.5, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.85 (t, 1.5, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.0–8.0 (m, 28, aromatics). ^{31}P NMR (MeOH): δ 41.4 (s, 0.5, $^1J_{PtP}$ = 2767 Hz), 41.7 (s, 0.5, $^1J_{PtP}$ = 2363 Hz), 40.2 (s, 0.5, $^1J_{PtP}$ = 2274 Hz), 41.8 (s, 0.5, $^1J_{PtP}$ = 2867 Hz). Λ_M = 49 (CH_2Cl_2), 95 (MeOH), 223 (H_2O) Ω^{-1} cm^2 mol^{-1}.

(+)-[Pd([*S*-(*R,*R**)]-phas)$_2$](PF$_6$)$_2$**. The complex (+)-[PdCl-([*S*-(*R**,*R**)-phas)$_2$]Cl (0.5 g) was dissolved in hot water (25 mL), and the solution was treated with NH_4PF_6 (0.5 g) in water (5 mL). The white precipitate that formed was collected and recrystallized from an acetone–diethyl ether mixture, producing colorless needles of the desired salt: mp 310–311 °C; yield 0.95 g (90%); $[\alpha]_D$ +304° (*c* 0.56, acetone). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.7; H, 3.7. ^{1}H NMR (Me_2SO-d_6): δ 1.69 (d, 3,

J_{PH} = 10 Hz, PMe), 1.76 (s, 3, AsMe), 2.04 (t, 3, J_{PH} = 10 Hz, PMe), 2.14 (br s, 3, AsMe), 7.5–8.1 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 50.3 (s, 1), 51.9 (s, 1). Λ_M = 220 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

The following compounds were prepared similarly. **(+)-[Pd([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$**: colorless needles; mp 315–316°C; $[\alpha]_D$ +51.1° (*c* 0.4, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.8; H, 3.7. ^{1}H NMR (Me_2SO-d_6): δ 2.01 (d, 5.1, J_{PH} = 10 Hz, PMe), 2.30 (br s, 5.1, AsMe), 2.55 (s, 0.9, AsMe), 2.58 (t, 0.9, $^2J_{PH}$ = 10 Hz, PMe), 7.1–8.3 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 52.8 (s, 0.3), 54.2 (s, 1.7). Λ_M: insufficiently soluble in Me_2CO. **[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$**: fine white needles; mp 303–304 °C. Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.8; H, 3.7. ^{1}H NMR (Me_2SO-d_6): δ 2.49 (d, 3, J_{PH} = 10 Hz, PMe), 2.49 (t, 3, J_{Ph} = 10 Hz, PMe), 2.53 (s, 3, AsMe), 2.56 (br s, 3, AsMe), 7.1–8.0 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 50.3 (s, 1), 52.1 (s, 1). Λ_M = 215 Ω^{-1} cm^2 mol^{-1} (Me_2CO). **[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$**: colorless needles; mp 328–329 °C. Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pd$: C, 42.6; H, 3.6. Found: C, 42.9; H, 3.6. ^{1}H NMR (Me_2SO-d_6): δ 2.01 (d, 2.7, J_{PH} = 10 Hz, PMe), 2.03 (s, 2.7, AsMe), 2.26 (t, 2.7, J_{PH} = 10 Hz, PMe), 2.29 (br s, 2.7, AsMe), 2.52 (d, 0.3, $^2J_{PH}$ = 10 Hz, PMe), 2.55 (s, 0.3, AsMe), 2.58 (br s, 0.3, AsMe), 2.58 (t, 0.3, J_{PH} = 10 Hz, PMe), 7.1–8.3 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 50.0 (s, 0.1), 52.2 (s, 0.9), 52.8 (s, 0.1), 54.2 (s, 0.9). Λ_M: insufficiently soluble in Me_2CO. **(+)-[Pt([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$**: white needles; mp 318–319 °C; $[\alpha]_D$ +222° (*c* 0.43, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5; H, 3.3. Found: C, 39.6; H, 3.4. ^{1}H NMR (Me_2SO-d_6): δ 1.72 (d, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 1.80 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.09 (t, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.18 (br s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 7.5–8.2 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 43.7 (s, 1, $^1J_{PtP}$ = 2214 Hz), 44.7 (s, 1, $^1J_{PtP}$ = 2673 Hz). Λ_M = 216 Ω^{-1} cm^2 mol^{-1} (Me_2CO). **(+)-[Pt([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$**: colorless needles; mp 322–333 °C; $[\alpha]_D$ +30.8 (*c* 0.39, Me_2CO). Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5; H, 3.3. Found: C, 39.5; H, 3.4. ^{1}H NMR (Me_2SO-d_6): δ 2.06 (d, 5.1, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.30 (br s, 5.1, $^3J_{PtH}$ = 22 Hz, AsMe), 2.66 (s, 0.9, $^3J_{PtH}$ = 22 Hz, AsMe), 2.70 (t, 0.9, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.1–8.3 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 45.7 (s, 1.7, $^1J_{PtP}$ = 2750 Hz), 46.0 (s, 0.3). Λ_M: insufficiently soluble in Me_2CO. **[Pt((*R**,*R**)-phas)$_2$](PF$_6$)$_2$**: fine white needles; mp 352–356 °C. Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5, H, 3.3. Found: C, 39.8; H, 3.4. ^{1}H NMR (Me_2SO-d_6): δ 2.61 (d, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.63 (t, 3, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.66 (s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 2.68 (br s, 3, $^3J_{PtH}$ = 22 Hz, AsMe), 7.0–8.1 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 43.6 (s, 1, $^1J_{PtP}$ = 2217 Hz), 44.3 (s, 1, $^1J_{PtP}$ = 2703 Hz). Λ_M: insufficiently soluble in Me_2CO. **[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$**: colorless needles; mp 354–355 °C. Anal. Calcd for $C_{40}H_{40}As_2F_{12}P_4Pt$: C, 39.5; H, 3.3. Found: C, 39.6; H, 3.4. ^{1}H NMR (Me_2SO-d_6): δ 2.00 (s, 2.25, $^3J_{PtH}$ = 22 Hz, AsMe), 2.06 (d, 2.25, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.28 (t, 2.25, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.30 (br s, 2.25, $^3J_{PtH}$ = 22 Hz, AsMe), 2.66 (s, 0.75, $^3J_{PtH}$ = 22 Hz, AsMe), 2.70 (br s, 0.75, $^3J_{PtH}$ = 22 Hz, AsMe), 2.70 (t, 0.75, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 2.80 (d, 0.75, J_{PH} = 10 Hz, $^3J_{PtH}$ = 40 Hz, PMe), 7.0–8.3 (m, 28, aromatics). ^{31}P NMR (Me_2SO): δ 44.4 (s, 0.25, $^1J_{PtP}$ = 2735 Hz), 45.3 (s, 0.75, $^1J_{PtP}$ = 2217 Hz), 45.7 (s, 0.25, $^1J_{PtP}$ = 2735 Hz), 46.0 (s, 0.75, $^1J_{PtP}$ = 2750 Hz). Λ_M: insufficiently soluble in Me_2CO.

Registry No. *cis*-(−)-[Ni([*R*-(*R**,*R**)]-phas)$_2$](ClO$_4$)$_2$, 90969-98-5; *trans*-(−)-[Ni([*R*-(*R**,*R**)]-phas)$_2$](ClO$_4$)$_2$, 91048-31-6; *cis*-(+)-[Ni([*R*-(*R**,*S**)]-phas)$_2$](ClO$_4$)$_2$, 91108-35-9; *trans*-(+)-[Ni([*R*-(*R**,*S**)]-phas)$_2$](ClO$_4$)$_2$, 91048-33-8; *cis*-(±)-[Ni((*R**,*R**)-phas)$_2$](ClO$_4$)$_2$, 91048-35-0; *trans*-(±)-[Ni((*R**,*R**)-phas)$_2$](ClO$_4$)$_2$, 91048-37-2; *cis*-[Ni((*R**,*R**)-phas)$_2$](ClO$_4$)$_2$, 91048-39-4; *trans*-[Ni((*R**,*R**)-phas)$_2$](ClO$_4$)$_2$, 91048-41-8; *cis*-(±)-[Ni((*R**,*S**)-phas)$_2$](ClO$_4$)$_2$, 91048-43-0; *trans*-(±)-[Ni((*R**,*S**)-phas)$_2$](ClO$_4$)$_2$, 91048-45-2; *cis*-[Ni((*R**,*S**)-phas)$_2$](ClO$_4$)$_2$, 91048-47-4; *trans*-[Ni((*R**,*S**)-phas)$_2$](ClO$_4$)$_2$, 91048-49-6; *cis*-(−)-[NiCl([*R*-(*R**,*R**)]-phas)$_2$]ClO$_4$, 90970-00-6; *trans*-(−)-[NiCl[*R*-(*R**,*R**)]-phas)$_2$]ClO$_4$, 91048-51-0; *cis*-(+)-[NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO$_4$, 91048-53-2; *trans*-(+)-[NiCl([*R*-(*R**,*S**)]-phas)$_2$]ClO$_4$, 91048-55-4; *cis*-(±)-[NiCl((*R**,*R**)-phas)$_2$]ClO$_4$, 91048-57-6; *trans*-(±)-[NiCl-((*R**,*R**)-phas)$_2$]ClO$_4$, 91048-59-8; *cis*-(±)-[NiCl((*R**,*S**)-phas)$_2$]ClO$_4$, 91048-61-2; *trans*-(±)-[NiCl((*R**,*S**)-phas)$_2$]ClO$_4$, 91048-63-4; *cis*-[NiCl((*R**,*S**)-phas)$_2$]ClO$_4$, 91048-65-6; *trans*-[NiCl((*R**,*S**)-phas)$_2$]ClO$_4$, 91048-67-8; *cis*-(+)-[PdCl([*S*-(*R**,*R**)]-phas)$_2$]Cl, 90970-01-7; *trans*-(+)-[PdCl([*S*-(*R**,*R**)]-phas)$_2$]Cl, 91048-68-9; *cis*-(+)-[PdCl([*R*-(*R**,*S**)]-phas)$_2$]Cl, 91048-69-0; *trans*-(+)-[PdCl([*R*-(*R**,*S**)]-phas)$_2$]Cl, 91048-70-3; *cis*-(±)-[PdCl((*R**,*R**)-phas)$_2$]Cl, 91048-71-4; *trans*-(±)-[PdCl((*R**,*R**)-phas)$_2$]Cl, 91048-72-5; *cis*-[PdCl((*R**,*R**)-phas)$_2$]Cl, 91048-73-6; *trans*-[PdCl((*R**,*R**)-phas)$_2$]Cl, 91048-74-7; *cis*-(±)-[PdCl((*R**,*S**)-phas)$_2$]Cl, 91048-75-8; *trans*-(±)-[PdCl((*R**,*S**)-phas)$_2$]Cl, 91048-76-9; *cis*-[PdCl((*R**,*S**)-phas)$_2$]Cl, 91048-77-0; *trans*-[PdCl((*R**,*S**)-phas)$_2$]Cl, 91048-78-1; *cis*-(+)-[PtCl([*S*-(*R**,*R**)]-phas)$_2$]Cl, 90970-02-8; *trans*-(+)-[PtCl([*S*-(*R**,*R**)]-phas)$_2$]Cl, 91048-79-2; *cis*-(+)-[PtCl([*R*-(*R**,*S**)]-phas)$_2$]Cl, 91048-80-5; *trans*-(+)-[PtCl([*R*-(*R**,*S**)]-phas)$_2$]Cl, 91048-81-6; *cis*-(±)-[PtCl((*R**,*R**)-phas)$_2$]Cl, 91048-82-7; *trans*-(±)-[PtCl((*R**,*R**)-phas)$_2$]Cl, 91048-83-8; *cis*-[PtCl((*R**,*R**)-phas)$_2$]Cl, 91048-84-9; *trans*-[PtCl((*R**,*R**)-phas)$_2$]Cl, 91048-85-0; *cis*-(±)-[PtCl((*R**,*S**)-phas)$_2$]Cl, 91048-86-1; *trans*-(±)-[PtCl((*R**,*S**)-phas)$_2$]Cl, 91048-87-2; *cis*-[PtCl((*R**,*S**)-phas)$_2$]Cl, 91048-88-3; *trans*-[PtCl-((*R**,*S**)-phas)$_2$]Cl, 91048-89-4; *cis*-(+)-[Pd([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$, 90970-04-0; *trans*-(+)-[Pd([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$, 91048-91-8; *cis*-(+)-[Pd([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$, 91048-93-0; *trans*-(+)-[Pd([*R*-(*R**,*S**)]-phas)$_2$](PF$_6$)$_2$, 91048-95-2; *cis*-(±)-[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91048-97-4; *trans*-(±)-[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91048-99-6; *cis*-[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91049-01-3; *trans*-[Pd((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91049-05-7; *cis*-(±)-[Pd-((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-03-5; *trans*-(±)-[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-07-9; *cis*-[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-09-1; *trans*-[Pd((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-11-5; *cis*-(+)-[Pt([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$, 90970-06-2; *trans*-(+)-[Pt([*S*-(*R**,*R**)]-phas)$_2$](PF$_6$)$_2$, 91049-13-7; *cis*-(+)-[Pt([*R*-(*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-15-9; *trans*-(+)-[Pt([*R*-(*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-17-1; *cis*-[Pt((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91049-19-3; *trans*-[Pt((*R**,*R**)-phas)$_2$](PF$_6$)$_2$, 91049-21-7; *cis*-(±)-[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-23-9; *trans*-(±)-[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-25-1; *cis*-[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-27-3; *trans*-[Pt((*R**,*S**)-phas)$_2$](PF$_6$)$_2$, 91049-29-5; (±)-[PdCl$_2$((*R**,*R**)-phas)], 91049-35-3; (±)-[PdCl$_2$((*R**,*S**)-phas)], 91049-36-4; (−)-[PdCl$_2$([*S*-(*R**,*R**)]-phas)], 87711-60-2; (±)-[PtCl$_2$((*R**,*R**)-phas)], 90970-07-3; (−)-[PtCl$_2$([*R*-(*R**,*R**)]-phas)], 91049-30-8; (+)-[PtCl$_2$([*S*-(*R**,*R**)]-phas)], 91049-31-9; (±)-[PtCl$_2$((*R**,*S**)-phas)], 91049-32-0; (+)-[PtCl$_2$([*R*-(*R**,*S**)]-phas)], 91049-33-1; (−)-[PtCl$_2$([*S*-(*R**,*S**)]-phas)], 91049-34-2; $PdCl_2(MeCN)_2$, 14592-56-4; dichloro(cyclo-octa-1,5-diene)platinum(II), 12080-32-9.