effect of inclusion of relativity on the uranium–nitrogen bonding. This is best seen in the overlap population results in Table V. These show a significant increase in the U–N($2p_\pi$) overlap populations and thus an increase in the U–N π bond strength from the nonrelativistic to the relativistic case. Examination of the forms of the appropriate molecular orbitals (Table I) shows that this is associated with an increase in the contribution of the U 6d orbitals and a decrease in the contribution of the U 5f orbitals to the molecular orbitals. Since the 6d orbitals are more diffuse than the 5f orbitals, this results in an increase in the overlap population and bond strength for the bond concerned. The importance of the role of 6d orbitals in the relativistic description of the bonding in actinide compounds has been pointed out previously.[12] It has also been pointed out previously[13] that nonrelativistic LDF (Xα) calculations overemphasize the covalency contributions of actinide 5f orbitals and underestimate those of 6d orbitals as compared to a relativistic calculation. Inspection of Table I confirms these trends for the present system. However, the 6d contribution to the bonding is small in absolute terms and is also significantly smaller than in the $U(BH_4)_4$ complex.[14]

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Conclusions

The calculations carried out to date do not support the assignment of the N $2p_\pi$ transitions in the PE spectrum of $[(Me_3SiN)U(N(SiMe_3)_2)_3]$ (**3**) given previously.[11] These assignments could be understood if the ligand fragments showed little (or equal) interaction with the uranium atom. However, analysis of the results of the calculations reveals that the imide N $2p_\pi$ orbitals are much more involved in the metal–ligand bonding than are the amide N $2p_\pi$ orbitals, and this effect is sufficient to reverse the orders of the N $2p_\pi$ ionization energies in the complex and lead to a new interpretation of the photoelectron spectrum of complex **3**. Similar bonding effects may be expected for other uranium complexes with multiply-bonded ligands.

Acknowledgment. We thank J. C. Green for suggesting this interesting problem and R. A. Andersen for communicating structural data prior to publication. G.A.B. acknowledges the grant of a period of study leave from the University of Auckland and the grant of a research fellowship from the Alexander von Humboldt Foundation. The work of N.R. is supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Rearrangements in Square-Planar and Square-Pyramidal Complexes of Palladium(II) and Platinum(II) Containing the Enantiomers of (±)-Methylphenyl(8-quinolyl)arsine and Its Phosphorus Analogue

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Received July 24, 1991

Square-planar complexes containing (±)-methylphenyl(8-quinolyl)arsine, As*N, or its phosphorus analogue, P*N, of the type $[M(E^*N)_2](PF_6)_2$ and square-pyramidal complexes of the type $[MCl(E^*N)_2]X$ (where M = Pd(II) or Pt(II), E = As or P, and X = Cl or PF_6) have been prepared in enantiomerically and diastereomerically homogeneous forms and their behavior in solution has been investigated by variable-temperature NMR spectroscopy. The square-planar cations, which have the cis coordination geometry, undergo facile intermolecular ligand redistribution (As > P) for both metals (Pd > Pt); the corresponding square-pyramidal cations show, in addition to the above, even more rapid axial chloro site exchange.

Introduction

Asymmetric bidentates of the type A*B are powerful probes of stability and stereochemistry in metal complexes of the type $[M(A^*B)_n]$ (where n = 2 or 3).[1] For the square-planar complexes $[M(A^*B)_2]$ four diastereomers are possible and interconversions between these will be diagnostic of intramolecular rearrangement and intermolecular redistribution.[2] Thus, it is important in designing an A*B bidentate to incorporate within it appropriate substituents for spectroscopic analysis. Accordingly, we synthesized the asymmetric bidentate (±)-methylphenyl(8-quinolyl)arsine, As*N, and the phosphorus congener (±)-methylphenyl(8-quinolyl)phosphine, P*N, and resolved both ligands by the method of metal complexation.[3] With use of the ligands, in optically active and racemic forms, we have now prepared the square-planar complexes $[M(E^*N)_2](PF_6)_2$ (where M = Pd or Pt and E = P or As) and the square-pyramidal derivatives $[MCl(E^*N)_2]X$ (where X = Cl or PF_6) and investigated their behavior in solution by NMR spectroscopic analysis. In earlier work, we had synthesized the SbN ligands dimethyl- and (±)-methylphenyl(8-quinolyl)stibine and isolated the square-planar dichloropalladium(II) and dichloroplatinum(II) derivatives.[4] In other laboratories, the AsN ligands dimethyl- and diphenyl(8-quinolyl)arsine have been synthesized and used to prepare derivatives of palladium(II), platinum(II),[5] ruthenium(II), rhodium(I), and rhodium(III),[6] and the PN ligands bis(dimethylamino)-, diethyl-, dimethyl-, (dimethylamino)methyl-, diphenyl-, and methyl(8-quinolyl)phosphine have been prepared[7] and the coordination compounds of the diphenylphosphino ligand with cobalt(II), copper(II), iron(II), and nickel(II) investigated.[8]

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Table I. Selected Physical Data for the Complexes $[MCl(E^*N)_2]X$

compd	Λ_M[a] CH_2Cl_2	Λ_M[a] H_2O	NMR δ(EMe)[b]	NMR δ(P)[c]	T_c, K	ΔG^{*}[d]
(*S,S*)-*cis*-$[PdCl(As^*N)_2]Cl\cdot CH_2Cl_2$	24	207	1.24 s, 2.50 s		228	44.8
(*S,S*)-*cis*-$[PdCl(As^*N)_2]PF_6$	45		1.10 s, 2.45 s		248	48.5
(*R*,R**)-*cis*-$[PdCl(As^*N)_2]Cl$[e]	21	173	1.24 s, 2.50 s		228	44.8
(*R*,S**)-*cis*-$[PdCl(As^*N)_2]Cl$[e]	21	173	2.16 s, 2.46 s		228	47.3
(*R*,R**)-*cis*-$[PdCl(As^*N)_2]PF_6$[e]	42		1.10 s, 2.45 s		248	48.5
(*R*,S**)-*cis*-$[PdCl(As^*N)_2]PF_6$[e]	42		1.98 s, 2.51 s		248	50.6
(*S,S*)-*cis*-$[PdCl(P^*N)_2]Cl\cdot 2H_2O$	46	176	2.16 d	22.7		
(*R*,R**)-*cis*-$[PdCl(P^*N)_2]Cl$[e]	43	174	2.16 d	22.7		
(*R*,S**)-*cis*-$[PdCl(P^*N)_2]Cl$[e]	43	174	2.39 d	23.7		
(*S,S*)-*cis*-$[PdCl(As^*N)(P^*N)]Cl\cdot CH_2Cl_2$	15	192	1.88 d, 2.30 s			
(*S,S*)-*cis*-$[PtCl(As^*N)_2]Cl\cdot CH_2Cl_2$	40	192	1.88 d, 2.30 s		301	59.8
(*S,S*)-*cis*-$[PtCl(As^*N)_2]PF_6\cdot 0.5Me_2CO$	52		1.00 s, 2.48 s		348	69.0
(*R*,R**)-*cis*-$[PtCl(As^*N)_2]Cl$[e]	40	188	1.25 s, 2.46 s		301	59.8
(*R*,S**)-*cis*-$[PtCl(As^*N)_2]Cl$[e]	40	188	2.17 s, 2.42 s		301	63.2
(*R*,R**)-*cis*-$[PtCl(As^*N)_2]PF_6\cdot Me_2CO$[e]	51		1.00 s, 2.48 s		348[f]	69.0
(*R*,S**)-*cis*-$[PtCl(As^*N)_2]PF_6\cdot Me_2CO$[e]	51		2.00 s, 2.42 s		348[f]	72.4
(*S,S*)-*cis*-$[PtCl(P^*N)_2]Cl\cdot CH_2Cl_2$	40	173	2.22 d	1.2 (3560)		
(*R*,R**)-*cis*-$[PtCl(P^*N)_2]Cl$	41	203	2.22 d	1.2 (3560)		
(*R*,S**)-*cis*-$[PtCl(P^*N)_2]Cl$	36	168	2.52 d	1.9 (3560)		

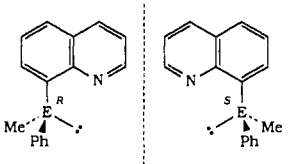
[a] Conductance in $cm^2\ \Omega^{-1}\ mol^{-1}$ for 10^{-3} M solutions at 293 K. [b] ^1H NMR chemical shift values in ppm relative to Me_4Si in dichloromethane-d_2. [c] $^{31}P\{^1H\}$ NMR chemical shifts in ppm relative to external H_3PO_4 (85%) in dichloromethane-d_2 at 304 K. [d] Estimated from coalescence temperature (T_c) with use of the Eyring equation (kJ mol^{-1}).[17] [e] Data for individual diastereomers taken from those for mixtures at equilibrium. [f] Value determined from spectra recorded in nitrobenzene-d_5.

Table II. Selected Physical Data for the Complexes $[M(E^*N)_2](PF_6)_2$

compd	Λ_M[a]	NMR δ(E*Me*)[b]	NMR δ(P)[c]	NMR $^1J_{^{195}Pt-^{31}P}$
(*S,S*)-*cis*-$[Pd(As^*N)_2](PF_6)_2$	182	1.80 s		
(*R*,R**)-*cis*-$[Pd(As^*N)_2](PF_6)_2$[d]	200	1.80 s		
(*R*,S**)-*cis*-$[Pd(As^*N)_2](PF_6)_2$[d]	200	2.46 s		
(*S,S*)-*cis*-$[Pd(P^*N)_2](PF_6)_2$	212	2.05 d		
(*R*,R**)-*cis*-$[Pd(P^*N)_2](PF_6)_2$	192	2.05 d		
(*R*,S**)-*cis*-$[Pd(P^*N)_2](PF_6)_2$	210	2.64 d		
(*S,S*)-*cis*-$[Pt(As^*N)_2](PF_6)_2$	228	1.82 s		
(*R*,R**)-*cis*-$[Pt(As^*N)_2](PF_6)_2$[e]	215	1.82 s		
(*R*,S**)-*cis*-$[Pt(As^*N)_2](PF_6)_2$[e]	215	2.48 s		
(*S,S*-*cis*-$[Pt(P^*N)_2](PF_6)_2$	206	2.10 d	12.1 s	3310
(*R*,R**)-*cis*-$[Pt(P^*N)_2](PF_6)_2$	204	2.10 d	12.1 s	3310
(*R*,S**)-*cis*-$[Pt(P^*N)_2](PF_6)_2$	196	2.76 d	12.3 s	3320

[a] Conductance in $cm^2\ \Omega^{-1}\ mol^{-1}$ for 10^{-3} M solutions in acetone. [b] ^1H NMR chemical shift values in ppm relative to Me_4Si in dimethyl-d_6 sulfoxide. [c] ^{31}P NMR chemical shifts in ppm relative to external H_3PO_4 (85%) in dimethyl-d_6 sulfoxide at 304 K. [d] Equilibrium mixture of diastereomers with *R*,R**:*R*,S** = 1:1. [e] Equilibrium mixture of diastereomers with *R*,R**:*R*,S** = 11:9.

Apart from the present work, however, little stability or stereochemical information was gleaned from these studies.



As*N (E = As)

P*N (E = P)

Results and Discussion

The compounds described in this work are listed in Tables I and II. The solution behavior of complexes has been investigated by conductance measurements and with use of NMR spectroscopy. The various aspects of the work will be introduced in the sections that follow.

(a) Synthesis of Metal Complexes. (i) (±)-$[MCl_2(E^*N)]$. The compound (±)-$[PdCl_2(As^*N)]$ was prepared in optically active or racemic form by treatment of a solution of tetrachloropalladate(II) in methanol with (*R*)-(+)-As*N, (*S*)-(−)-As*N, or (±)-As*N. Enantiomers (*R*)-(+)- and (*S*)-(−)-$[PdCl_2(P^*N)]$ were prepared according to ref 3; (±)-$[PdCl_2(P^*N)]$ was obtained from (±)-P*N and $[PdCl_2(MeCN)_2]$. The various forms of (±)-$[PtCl_2(E^*N)]$ were prepared by adding hydrochloric acid to solutions of bis(μ-chloro)bis(2-methoxycycloocta-5-enyl)diplatinum(II) containing the appropriate ligand.[9]

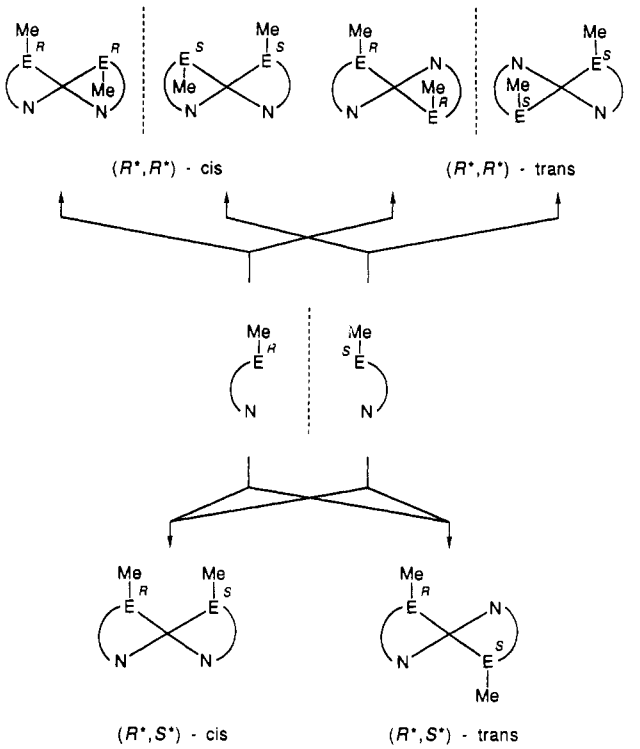


Figure 1. Square-planar diastereomers of the type $[M(E^*N)_2]^{2+}$.

(ii) $[MCl(E^*N)_2]X$ and $[M(E^*N)_2(PF_6)_2]$. The compounds (±)-$[MCl_2(E^*N)]$ react with (±)-E*N in 95% ethanol to give the salts $[MCl(E^*N)_2]Cl$. Conductivity and selected ^1H NMR data for the compounds $[MCl(E^*N)_2]X$ are presented in Table I; similar information for the salts $[M(E^*N)_2](PF_6)_2$ can be found

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in Table II. It will be noticed from Table I that most of the chloro complexes conduct as uni-univalent electrolytes in dichloromethane, but as di-univalent electrolytes in water, due to dissociation of the chloro ligand:

$$[MCl(E^*N)_2]Cl \rightleftharpoons [M(E^*N)_2]Cl_2$$

The salts $[MCl(As^*N)_2]Cl$, which are four-coordinate with one bidentate attached through arsenic only (see below), when treated with ammonium hexafluorophosphate in water, yield $[MCl(As^*N)_2]PF_6$ (Table I); the chloro complexes, when dissolved in acetone and the solution treated with aqueous ammonium hexafluorophosphate, give $[M(As^*N)_2](PF_6)_2$ (Table II). The corresponding P*N complexes, $[MCl(P^*N)_2]Cl$ (both P*N chelating), yield $[(M(P^*N)_2](PF_6)_2$ directly from water with ammonium hexafluorophosphate.

(b) Stereochemical Considerations. (i) Diastereomerism in $[M(E^*N)_2](PF_6)_2$. The ligands (±)-E*N can give rise to four square-planar diastereomers of the type $[M(E^*N)_2](PF_6)_2$, two chiral, (*R**,*R**)-cis and (*R**,*R**)-trans, and two achiral, (*R**,*S**)-cis and (*R**,*S**)-trans (Figure 1). The *R**,*R** and *R**,*S** diastereomers cannot be interconverted by internal rearrangement; thus, *R**,*R** ⇌ *R**,*S** interconversion is diagnostic of intermolecular ligand redistribution. It is noteworthy that the *R**,*R** diastereomer of a complex can be identified in an *R**,*R**/*R**,*S** mixture if the NMR spectrum of one of the enantiomers (*R*,*R* or *S*,*S*) of the complex is available for spectroscopic analysis. As a further aid to diagnosis in the present systems, the P*Me* groups in the P*N complexes will resonate as doublets ($^2J_{PP'} \simeq 0$ Hz) or "filled-in" doublets ($0 < {}^2J_{PP'} \ll |{}^2J_{PH} + {}^4J_{P'H}|$) when the phosphorus atoms are cis to one another[10] and as deceptively simple triplets ($^2J_{PP'} \gg |^2J_{PH} + {}^4J_{P'H}|$) when the phosphorus atoms are trans to one another.[11] (In the cis-phosphine complexes reported here, strong coupling was also observed between the phosphorus of one ligand and the 2-*H* proton of the quinolyl ring of the adjacent ligand ($^4J_{PH}$ = 2–5 Hz).)

(ii) Diastereomerism in $[MCl(E^*N)_2]X$. Whereas the axial coordination sites of the (*R**,*R**)-cis and (*R**,*S**)-trans diastereomers of square-planar ions of the type $[M(E^*N)_2]^{2+}$ are equivalent (homotopic), the corresponding sites of the (*R**,*R**)-trans and (*R**,*S**)-cis diastereomers are inequivalent (heterotopic). Thus, the addition of chloride to the (*R**,*R**)-trans and (*R**,*S**)-cis forms of $[M(E^*N)_2]^{2+}$ will lead to syn/anti mixtures, as depicted in Figure 2.

(c) Stabilities of Complexes. (i) $[M(E^*N)_2](PF_6)_2$. The ^{1}H NMR spectra of optically active (*S*,*S*)-(+)-$[M(P^*N)_2](PF_6)_2$ (where M = Pd or Pt) in dimethyl-d_6 sulfoxide at 293 K contain doublets for the P*Me* groups, typical of cis coordination geometries. In the $^{31}P\{^1H\}$ NMR spectrum of the platinum complex in the same solvent, the phosphorus nuclei resonate as a singlet at δ 12.1 with platinum-195 satellites ($^1J_{^{195}Pt-^{31}P}$ = 3310 Hz). This value of the platinum–phosphorus coupling constant is typical of phosphorus trans to nitrogen.[12,13] The ^{1}H NMR spectra of the corresponding arsenic complexes under the same conditions contain singlets for the As*Me* groups at ca. δ 1.80. Accordingly, both sets of complexes have been assigned cis stereochemistries. The spectra of the corresponding racemates contain pairs of resonances of approximately equal intensity for the E*Me* groups present (Table II). In each case, the upfield resonance corresponds to the signal of the respective *optical isomer*. Thus, the downfield resonances have been assigned to the (*R**,*S**)-cis isomers in each case.

The pure diastereomer (*R**,*R**)-*cis*-$[Pt(P^*N)_2](PF_6)_2$ can be obtained by either of the following two methods: (a) fractional crystallization of the cis–trans mixture from acetone–propan-2-ol; (b) treatment of an aqueous solution of pure (*R**,*R**)-*cis*-$[PtCl(P^*N)_2]Cl$ (see below) with ammonium hexafluorophosphate. The pure (*R**,*S**)-cis diastereomer was obtained by method a following removal of the (*R**,*R**)-cis isomer. Only the (*R**,*R**)-cis form of the analogous palladium complex could be isolated in a pure state, however.

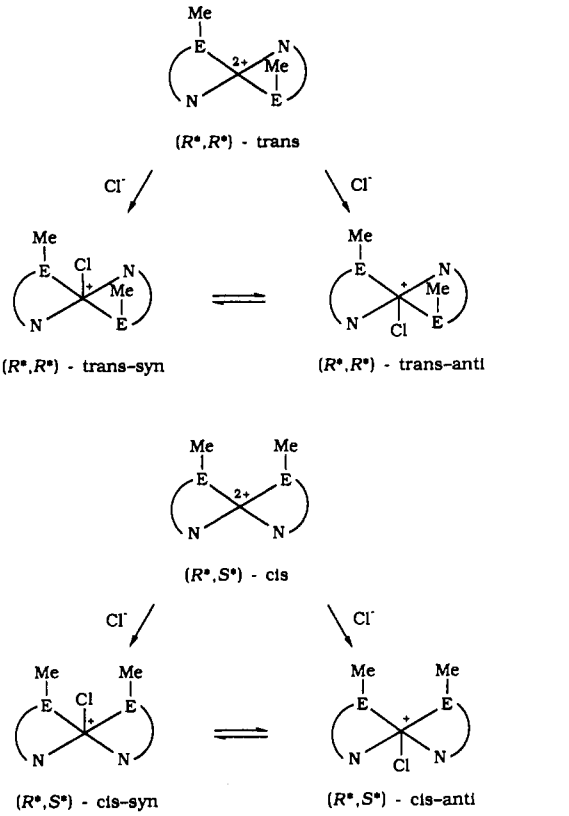

Figure 2. Heterotopic chloride addition to (*R**,*R**)-*trans*- and (*R**,*S**)-*cis*-$[M(E^*N)_2]^{2+}$. One enantiomer only depicted of *R**,*R** diastereomers.

Both sets of complexes undergo ligand redistribution in solution. Thus, (*R**,*R**)-*cis*-$[Pd(P^*N)_2](PF_6)_2$ in dimethyl-d_6 sulfoxide at 298 K rearranges over 7.5 h into an equilibrium mixture of cis diastereomers with (*R**,*R**)-*cis*:(*R**,*S**)-cis = 11:9. In acetonitrile-d_3 at 298 K equilibrium is reached within 18 h with (*R**,*R**)-cis:(*R**,*S**)-cis = 3:2. The platinum complex is considerably more stable: (*R**,*R**)-*cis*-$[Pt(P^*N)_2](PF_6)_2$ in dimethyl sulfoxide at 298 K requires 64 h to reach equilibrium with (*R**,*R**)-cis:(*R**,*S**)-cis = 11:9. In acetonitrile-d_3 at this temperature, no redistribution of bidentates was observed in the platinum complex over 7 days.

The complexes $[M(As^*N)_2](PF_6)_2$ are considerably more labile than the corresponding phosphine complexes. Thus, the mixing together of equimolar solutions of the pure *enantiomers* (*R*,*R*)-*cis*- and (*S*,*S*)-*cis*-$[Pd(As^*N)_2](PF_6)_2$ in acetonitrile-d_3 at 304 K produces an equilibrium 1:1 mixture of the *diastereomers* (*R**,*R**)-*cis*- and (*R**,*S**)-*cis*-$[Pd(As^*N)_2](PF_6)_2$ within the time of mixing of the solutions and recording of the ^{1}H NMR spectrum (ca. 5 min). The corresponding platinum complex appears to be more labile still according to a similar experiment: the resonance for the As*Me* groups after mixing of solutions of the enantiomers consisted of a broad singlet at 304 K, which was resolved into a pair of singlets at 227 K. Platinum-195 coupling to the As*Me* protons in the complex was absent at the fast-exchange limit, and, at the slow-exchange limit, the As*Me* chemical shifts corresponded to the (*R**,*R**)-cis and (*R**,*S**)-cis diastereomers.

(ii) $[MCl(E^*N)_2]X$ (Where X = Cl or PF_6). The ^{1}H NMR spectra of the complexes (*S*,*S*)-*cis*-$[MCl(P^*N)_2]Cl$ in dichloromethane-d_2 at 304 K contain sharp doublets for the P*Me* groups (Table I). Cooling of the solutions to 178 K did not lead to significant changes in the spectra. For the platinum complex the $^1J_{^{195}Pt-^{31}P}$ value of 3560 Hz supported further the assignment of the cis stereochemistry. The observation of a sharp P*Me* doublet for each complex at low temperatures is consistent with facile

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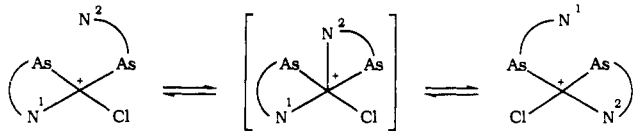

Figure 3. Intramolecular quinoline-*N* exchange in the square-planar cations $[MCl(As^*N\text{-}As)(As^*N\text{-}As,N)]^+$.

intermolecular site exchange of the axial chloro ligands between the (*S*,*S*)-cis-syn and (*S*,*S*)-cis-anti diastereomers (Figure 2) or with stereoselective coordination of chloride.[2]

An X-ray crystal structure determination on (*S*,*S*)-$[PdCl(As^*N)_2]Cl$, which can be isolated as red or as yellow crystals, revealed square-planar coordination about palladium, one As*N ligand acting as a unidentate through arsenic and both arsenic atoms cis to one another (Figure 3).[14] The red form of the complex contains a weak $Pd^+\cdots Cl^-$ interaction, which is absent in the yellow form. In solution, however, both forms have identical ^1H NMR spectra. In dichloromethane-d_2 at 298 K, a broad singlet was observed for the As*Me* groups, but when the solution was cooled to 228 K, this signal broadened further, coalesced, and reemerged as a pair of sharp singlets at δ 1.24 and 2.50 with T_c ca. 228 K. The signal to higher field was assigned to the As*Me* group of the fully coordinated As*N ligand on the basis of NMR data for the mixed ligand complex (S_{As},S_P)-*cis*-$[PdCl(As^*N)(P^*N)]Cl$. The low-temperature ^1H NMR spectrum of (*S*,*S*)-*cis*-$[PdCl(As^*N)_2]Cl$ also contains two sets of quinolyl proton resonances; the low-field singlet at δ 10.14 was assigned to 2-*H* of the bidentate As*N and the singlet at δ 9.09 to the unidentate As*N. This proton in free (±)-As*N resonates at δ 8.80 under similar conditions. The variable-temperature ^1H NMR spectra of the complex in dichloromethane-d_2 were independent of concentration (0.10–0.21 M solutions). The solution behavior of the corresponding hexafluorophosphate salt, and the platinum analogues, were similar (Table I). The different values of T_c for the chloride and hexafluorophosphate salts is consistent with the intermolecular exchange process depicted in Figure 3.

The reaction of (±)-$[MCl_2(E^*N)]$ (where M = Pd or Pt) with (±)-E*N in boiling 95% ethanol affords the complexes $[MCl(E^*N)_2]Cl$ as mixtures of cis diastereomers. The platinum salts conducted as uniunivalent electrolytes in dichloromethane, but the palladium–arsenic complexes had conductivity values consistent with considerable dissociation of one of the As*N ligands, according to

$$[PdCl(As^*N)_2]Cl \rightleftharpoons [PdCl_2(As^*N)] + As^*N$$

For palladium complexes containing (±)-P*N, (*R**,*R**)-cis:(*R**,*S**)-cis = 6:4; for platinum, (*R**,*R**)-cis:(*R**,*S**)-cis = 1:1 (Table I). Recrystallization of the platinum mixture from dichloromethane–carbon tetrachloride gave the pure (*R**,*R**)-cis isomer as colorless needles. The (*R**,*S**)-cis isomer could not be obtained pure by fractional crystallization. When dissolved in dichloromethane-d_2 at 298 K, the pure (*R**,*R**)-cis isomer of the platinum complex rearranged with redistribution of ligands into a mixture of the two cis isomers; equilibrium was attained within 24 h with (*R**,*R**)-cis:(*R**,*S**)-cis = 1:1. The palladium complex is more labile still: within 5 mins of mixing equimolar solutions of the *enantiomers* (*R**,*R**)-*cis*- and (*S*,*S*)-*cis*-$[PdCl(P^*N)_2]Cl$ in dichloromethane-d_2 at 298 K, an equilibrium mixture of the two cis *diastereomers* was observed with (*R**,*R**)-cis:(*R**,*S**)-cis = 6:4.

For the racemic complex (*R**,*R**)-*cis*-$[PdCl(As^*N)_2]Cl$, the ^1H NMR spectra in dichloromethane-d_2 at 298 K were dependent upon the concentrations of the samples. Thus, the spectrum of a 0.10 M solution of the racemate contains two broad singlets for the As*Me* groups; the spectrum of a 0.20 M solution contains a singlet resonance for these groups. Moreover, there is a difference in the temperature dependence of the spectra of the chloride and hexafluorophosphate salts under similar conditions. At the slow-exchange limit, the spectrum of the racemic complex contains four As*Me* resonances, two of which correspond to the signals of the pure optical isomer. Thus, as well as rapid intramolecular exchange of free and coordinated nitrogen in these complexes, there is also rapid intermolecular bidentate exchange between (*R**,*R**)-cis and (*R**,*S**)-cis diastereomers. Similar behavior was observed for the platinum analogues.

(14) Skelton, B. W.; White, A. H. Personal communication.

Experimental Section

Proton NMR spectra were recorded at 34 °C on JEOLCO MH 100 or Varian HA 100 spectrometers. Variable-temperature ^1H NMR spectra were obtained with use of Varian HA 100 or Bruker CXP 200 spectrometers. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker FX 60 spectrometer operating at 24.28 MHz. ^1H NMR chemical shifts are reported as δ values relative to internal Me_4Si and $^{31}P\{^1H\}$ NMR chemical shifts are quoted as δ values relative to external H_3PO_4 (85%). Optical rotations were measured at 589 nm (sodium D-line) on the specified solutions in 1-dm cells at 20 °C with use of a Perkin-Elmer Model 241 polarimeter. Molar conductivity measurements were determined on 10^{-3} M solutions at 20 °C in the solvents specified with use of a Wissenschaftlich-Technische Werkstätten (D-8120 Weilheim, Germany) conductivity bridge. Elemental analyses were performed by staff within the Research School of Chemistry.

The ligands (±)-methylphenyl(8-quinolyl)arsine and its phosphorus analogue were prepared and resolved as previously described.[3] The preparation of (*S*)-$[PdCl_2(P^*N)]$ is also described in ref 3.

[*SP*-4-2-(*S*)]-(−)-Dichloro[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) [(*S*)-$[PdCl_2(As^*N)]$]. A suspension of palladium(II) chloride (0.63 g, 3.4 mmol) and lithium chloride (1.4 g, 33 mmol) in methanol (50 mL) was stirred for 1 h to give a red-brown solution of $Li_2[PdCl_4]$. The solution was filtered, and the filtrate was added slowly to a solution of (*R*)-As*N (1.0 g, 3.4 mmol) in dichloromethane (50 mL). When the resulting yellow solution was reduced in volume (to ca. 30 mL), the product separated: orange rosettes; mp 220–221 °C; yield 1.45 g (91%); $[\alpha]_D$ −69.1° (*c* 0.84, CH_2Cl_2). Anal. Calcd for $C_{16}H_{14}NAsCl_2Pd$: C, 40.7; H, 3.0; N, 3.0. Found: C, 40.8; H, 3.1; N, 2.8. ^1H NMR (Me_2SO-d_6): δ 2.43 (s, 3 H, AsMe), 7.46–8.84 (m, 10 H, aromatics), 10.12 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 0.20 cm^2 Ω^{-1} mol^{-1} (CH_2Cl_2). The corresponding racemate was prepared similarly.

[*SP*-4-2]-(±)-Dichloro[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II)–Water [(±)-$[PdCl_2(As^*N)]\cdot H_2O$]: bright orange needles, mp 180 °C; 88% yield. Anal. Calcd for $C_{16}H_{16}NAsCl_2OPd$: C, 39.2; H, 3.3; N, 2.9. Found: C, 39.2; H, 3.0; N, 2.8. ^1H NMR (Me_2SO-d_6): identical to that of the pure enantiomer, except for a resonance at δ 3.36 due to water.

[*SP*-4-3]-(±)-Dichloro[methylphenyl(8-quinolyl)phosphine-*N*,*P*]palladium(II)–1.5-Water [(±)-$[PdCl_2(P^*N)]\cdot 1.5H_2O$]. Freshly prepared $[PdCl_2(NCCH_3)_2]$[15] (2.06 g, 8 mmol) and (±)-P*N (2 g, 8 mmol) were suspended in dichloromethane (50 mL). After being heated for 2 h at 50 °C, the reaction mixture was filtered and methanol (50 mL) was added to the filtrate. The volume of the solution was then reduced to ca. 30 mL, whereupon the product crystallized: yellow prisms; mp 198 °C; yield 3.16 g (87%). Anal. Calcd for $C_{16}H_{17}NCl_2O_{1.5}PPd$: C, 42.2; H, 3.8; N, 3.1. Found: C, 42.2; H, 3.7; N, 3.1. ^1H NMR (Me_2SO-d_6): δ 2.45 (d, 3 H, $^2J_{PH}$ = 13.4 Hz, PMe), 3.36 (s, 3 H, H_2O), 7.40–8.94 (m, 10 H, aromatics), 10.11 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 0.16 cm^2 Ω^{-1} mol^{-1} (CH_2Cl_2).

[*SP*-4-2-(*S*)]-(+)-Dichloro[methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II)–Dichloromethane [(*S*)-$[PtCl_2(As^*N)]\cdot CH_2Cl_2$]. A well-ground mixture of anhydrous sodium carbonate (0.33 g, 3.1 mmol) and dichloro(cycloocta-1,5-diene)platinum(II)[16] (0.63 g, 1.7 mmol) was suspended in methanol (70 mL), and the mixture was heated under reflux for 5 min. The resulting pale yellow solution was filtered, and (*R*)-As*N (0.5 g, 1.7 mmol) was added to the filtrate. When the ligand had completely dissolved, hydrochloric acid (16 mL, 10 M) was added and the volume of the solution was reduced to ca. 35 mL. The microcrystalline pale yellow powder that separated was collected and recrystallised from dichloromethane–methanol to give the pure compound: yellow prisms; mp 162–163 °C; yield 0.96 g (88%); $[\alpha]_D$ +17.8° (*c* 0.67, CH_2Cl_2). Anal. Calcd for $C_{17}H_{16}NAsCl_4Pt$: C, 31.6; H, 2.5; N, 2.2. Found: C, 31.5; H, 2.4; N, 1.9. ^1H NMR (Me_2SO-d_6): δ 2.33 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe), 5.74 (s, 2 H, CH_2Cl_2), 7.45–8.93 (m, 10 H, aromatics), 10.54 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 8.4 cm^2 Ω^{-1} mol^{-1} (CH_2Cl_2).

(15) Hartley, F. R.; Murray, S. G.; McAuliffe, C. A. *Inorg. Chem.* **1979**, *18*, 1394.
(16) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496.
(17) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411.

The following compounds were prepared similarly.

[*SP*-4-2]-(±)-Dichloro[methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) [(±)-[PtCl$_2$(As*N)]]: yellow plates; mp 154–155 °C; 90% yield. Anal. Calcd for $C_{16}H_{14}NAsCl_2Pt$: C, 34.2; H, 2.5; N, 2.5. Found: C, 34.1; H, 2.5; N, 2.5. ^{1}H NMR (Me$_2$SO-d_6): identical to that of pure enantiomer.

[*SP*-4-3-(*S*)]-(+)-Dichloro[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II)–Dichloromethane [(*S*)-[PtCl$_2$(P*N)]·CH$_2$Cl$_2$]: yellow prisms; mp 182–183 °C; 85% yield; $[\alpha]_D$ +16.9° (*c* 0.76, CH$_2$Cl$_2$). Anal. Calcd for $C_{17}H_{16}NCl_4PPt$: C, 33.9; H, 2.7; N, 2.3. Found: C, 33.8; H, 2.6; N, 2.5. ^{1}H NMR (Me$_2$SO-d_6): δ 2.45 (d, 3 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PH}$ = 13.4 Hz, PMe), 5.74 (s, 2 H, CH$_2$Cl$_2$), 7.40–9.01 (m, 10 H, aromatics), 10.51 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 8.1 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$).

[*SP*-4-3]-(±)-Dichloro[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II)–0.5-Water [(±)-[PtCl$_2$(P*N)]·0.5H$_2$O]: yellow plates; mp 169–170 °C; 90% yield. Anal. Calcd for $C_{16}H_{15}NCl_2O_{0.5}PPt$: C, 36.5; H, 2.9; N, 2.7. Found: C, 36.6; H, 2.6; N, 2.4. ^{1}H NMR (Me$_2$SO-d_6): identical to that of pure enantiomer.

[*SP*-4-3-[(*S*),(*S*)]]-(+)-Chloro[methylphenyl(8-quinolyl)arsine-*As*]-[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Chloride–Dichloromethane [(*S*,*S*)-*cis*-[PdCl(As*N)$_2$]Cl·CH$_2$Cl$_2$] (Yellow Form). The complex (*S*)-[PdCl$_2$(As*N)] (0.40 g, 0.85 mmol), when combined with (*R*)-As*N (0.25 g, 0.85 mmol), dissolved in ethanol (50 mL) to give a deep yellow solution. After filtration, the solvent was removed from the filtrate; recrystallization of the residue that remained from dichloromethane (15 mL) by the addition of diethyl ether afforded the pure product as pale yellow prisms: mp 129–130 °C; 0.66 g (91%); $[\alpha]_D$ +149° (*c* 0.78, CH$_2$Cl$_2$). Anal. Calcd for $C_{33}H_{30}N_2As_2Cl_4Pd$: C, 46.5; H, 3.6; N, 3.3. Found: C, 46.4; H, 3.5; N, 3.1. ^{1}H NMR (CD$_2$Cl$_2$ at 178 K): δ 1.24 (s, 3 H, AsMe-*As*,*N*), 2.50 (s, 3 H, AsMe-*As*), 5.33 (s, 2, CH$_2$Cl$_2$), 7.02–8.55 (m, 20 H, aromatics), 8.85 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-*H*-*As*), 10.14 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*,*N*). Λ_M = 24 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 207 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

(*S*,*S*)-[PdCl(As*N)$_2$]Cl·0.5CH$_2$Cl$_2$ (Red Form). When the *yellow* form of the complex was left in contact with the mother liquor for ca. 12 h, a small quantity of *red* crystals formed. A quantitative yield of the red form of the compound was obtained by dissolving the yellow form in dichloromethane (10 mL), seeding the solution with a crystal of the red form, and then adding diethyl ether to give deep red prisms of the 0.5 dichloromethane solvate, mp 195–196 °C. Anal. Calcd for $C_{32.5}H_{29}N_2As_2Cl_3Pd$: C, 48.2; H, 3.6; N, 3.5. Found: C, 48.1; H, 3.6; N, 3.2. Solution properties were identical to those of yellow form (apart from the decreased intensity of dichloromethane-*H* peak).

The following compounds were prepared similarly.

[*SP*-4-3-(*R,*R**),(*R**,*S**)]-Chloro[methylphenyl(8-quinolyl)arsine-*As*][methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Chloride [(*R**,*R**),(*R**,*S**)-*cis*-[PdCl(As*N)$_2$]Cl]**: orange crystals; mp 204–205 °C; 90% yield. Anal. Calcd for $C_{32}H_{28}N_2As_2Cl_2Pd$: C, 50.1; H, 3.7; N, 3.6. Found: C, 49.7; H, 3.6; N, 3.3. ^{1}H NMR (CD$_2$Cl$_2$ at 178 K): δ 1.24 (s, 1.5 H, AsMe-*As*,*N*-(R*,R*)), 2.16 (s, 1.5 H, AsMe-*As*,*N*-(*R**,*S**)), 2.46 (s, 1.5 H, AsMe-*As*-(*R**,*S**)), 2.50 (s, 1.5 H, AsMe-*As*-(*R**,*R**)), 6.70–10.26 (m, 22 H, aromatics). Λ_M = 21 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 173 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-5-1-5-[(*S*),(*S*)]]-(+)-Chlorobis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]palladium(II) Chloride–2-Water [(*S*,*S*)-*cis*-[PdCl(P*N)$_2$]-Cl·2H$_2$O]: fine yellow needles, mp 195–196 °C; 88% yield; $[\alpha]_D$ +347° (*c* 0.57, CH$_2$Cl$_2$). Anal. Calcd for $C_{32}H_{32}N_2Cl_2O_2P_2Pd$: C, 53.7; H, 4.5; N, 3.9. Found: C, 53.9; H, 4.3; N, 3.9. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.16 (d, 6 H, $^2J_{PH}$ = 10 Hz, PMe), 1.26 (s, 4 H, H$_2$O), 7.30–8.60 (m, 20 H, aromatics), 9.47 (m, 2 H, 2-H). ^{31}P NMR (CH$_2$Cl$_2$): δ 22.7 (s, 2 P). Λ_M = 46 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 176 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-5-1-5-(*R,*R**),(*R**,*S**)]-Chlorobis[methylphenyl(8-quinolyl)-phosphine-*N*,*P*]palladium(II) Chloride [(*R**,*R**),(*R**,*S**)-*cis*-[PdCl-(P*N)$_2$]Cl]**: bright yellow prisms; mp 255–257 °C; 92% yield. Anal. Calcd for $C_{32}H_{28}N_2Cl_2P_2Pd$: C, 56.5; H, 4.2; N, 4.1. Found: C, 56.3; H, 4.2; N, 4.1. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.16 (d, 3 H, $^2J_{PH}$ = 10 Hz, PMe-(*R**,*R**)), 2.39 (d, 3 H, $^2J_{PH}$ = 10 Hz, PMe-(*R**,*S**)), 7.16–8.60 (m, 20 H, aromatics), 9.47 (m, 2 H, 2-H). ^{31}P NMR (CH$_2$Cl$_2$): δ 22.7 (s, 1 P, (*R**,*R**)), 23.7 (s, 1 P, (*R**,*S**)). Λ_M = 43 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 174 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-5-2-5-(*S*,*S*)]-Chloro[methylphenyl(8-quinolyl)arsine-*As*,*N*][methylphenyl(8-quinolyl)phosphine-*P*,*N*]palladium(II) Chloride–Dichloromethane [(*S*,*S*)-[PdCl(As*N)(P*N)]Cl·CH$_2$Cl$_2$]. (*S*)-[PdCl$_2$(P*N)] (0.4 g) and (*R*)-As*N (0.28 g) dissolved in ethanol (50 mL) to give a deep yellow solution from which the mixed-bidentate complex was isolated and recrystallized from dichlormethane–diethyl ether to give pale yellow prisms of the dichloromethane solvate: mp 88–89 °C; yield 0.79 g, 81%; $[\alpha]_D$ +83° (*c* 0.60, CH$_2$Cl$_2$). Anal. Calcd for $C_{33}H_{30}AsCl_4PPd$: C, 49.0; H, 3.7; N, 3.5. Found: C, 49.0; H, 3.9; N, 3.4. ^{1}H NMR (CD$_2$Cl$_2$ at 248 K): δ 1.88 (d, 3 H, $^2J_{PH}$ = 12 Hz, PMe), 2.30 (s, 3 H, AsMe), 5.37 (s, 2 H, CH$_2$Cl$_2$), 7.28–7.88 (m, 20 H, aromatics), 9.06 (d of d, 1 H, $^3J_{AB}$ = 5 Hz, $^4J_{AC}$ = 2 Hz, H$_A$), 10.03 (d of d, 1 H, $^3J_{AB}$ = 5 Hz, $^4J_{AC}$ = 2 Hz, H$_A$). Λ_M = 15 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 192 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-4-3-(*S*),(*S*)]-Chloro[methylphenyl(8-quinolyl)arsine-*As*][methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Chloride–Dichloromethane [(*S*,*S*)-*cis*-[PtCl(As*N)$_2$]Cl·CH$_2$Cl$_2$]: colorless prisms; mp 157–158 °C; 91% yield; $[\alpha]_D$ + 160° (*c* 0.78, CH$_2$Cl$_2$). Anal. Calcd for $C_{33}H_{30}NAs_2Cl_4Pt$: C, 42.1; H, 3.2; N, 3.0. Found: C, 42.0; H, 3.2; N, 2.90. ^{1}H NMR (CD$_2$Cl$_2$ at 248 K): δ 1.25 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*), 2.46 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*), 5.33 (s, 2 H, CH$_2$Cl$_2$), 6.95–8.93 (m, 20 H, aromatics), 9.03 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*), 10.46 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*,*N*). Λ_M = 40 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 174 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-4-3-(*R,*R**),(*R**,*S**)]-(±)-Chloro[methylphenyl(8-quinolyl)arsine-*As*][methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Chloride [(*R**,*R**),(*R**,*S**)-*cis*-[PtCl(As*N)$_2$]Cl]**: pale yellow crystals; mp 223–224 °C; 95% yield. Anal. Calcd for $C_{32}H_{28}N_2As_2Cl_2Pt$: C, 44.9; H, 3.3; N, 3.3. Found: C, 44.7; H, 3.2; N, 3.3. ^{1}H NMR (CD$_2$Cl$_2$ at 248 K): δ 1.25 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*-(*R**,*R**)), 2.17 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*-(*R**,*S**)), 2.42 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*-(*R**,*S**)), 2.46 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*-(*R**,*R**)), 6.95–10.52 (m, 22 H, aromatics). Λ_M = 40 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 188 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-5-1-5-(*S*),(*S*)]-(+)-Chlorobis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II) Chloride–Dichloromethane [(*S*,*S*)-*cis*-[PtCl-(P*N)$_2$]Cl·CH$_2$Cl$_2$]: colorless prisms; mp 226–227 °C; 91% yield; $[\alpha]_D$ +180° (*c* 0.59, CH$_2$Cl$_2$). Anal. Calcd for $C_{33}H_{30}N_2Cl_4P_2Pt$: C, 46.4; H, 3.5; N, 3.3. Found: C, 46.4; H, 3.5; N, 3.7. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.22 (d, 6 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PtH}$ = 10 Hz, PMe), 5.34 (s, 2 H, CH$_2$Cl$_2$), 7.30–8.57 (m, 20 H, aromatics), 9.64 (m, 2 H, 2-H). ^{31}P NMR (CH$_2$Cl$_2$): δ 1.2 (s, 2 P, $^1J_{PtH}$ = 3560 Hz). Λ_M = 40 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 173 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-5-1-5-(*R,*R**),(*R**,*S**)]-(±)-Chlorobis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II) Chloride [(*R**,*R**),(*R**,*S**)-*cis*-[PtCl(P*N)$_2$]Cl]**: colorless prisms; mp 289–290 °C; 92% yield. Anal. Calcd for $C_{32}H_{28}N_2Cl_2P_2Pt$: C, 50.0; H, 3.7; N, 3.6. Found: C, 49.9; H, 3.6; N, 3.6. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.22 (d, 3 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PH}$ = 10 Hz, PMe-(*R**,*R**)), 2.52 (d, 3 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PH}$ = 10 Hz, PMe-(*R**,*S**)), 7.10–9.64 (m, 22 H, aromatics). ^{31}P NMR (CH$_2$Cl$_2$): δ 1.2 (s, 1 P, $^1J_{PtP}$ = 3560 Hz, (*R**,*R**)), 1.9 (s, 1 P, $^1J_{PtP}$ = 3560 Hz, (*R**,*S**)). Λ_M = 36 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 168 cm^2 Ω^{-1} mol^{-1} (H$_2$O). Recrystallization of the mixture from dichloromethane by the careful addition of carbon tetrachloride gave the pure *R**,*R** diastereomer: colorless needles; mp 286–287 °C; 96% yield. Anal. Calcd for $C_{32}H_{28}N_2Cl_2P_2Pt$: C, 50.0; H, 3.7; N, 3.6. Found: C, 49.7; H, 3.6; N, 3.5. ^{1}H and ^{31}P NMR (CD$_2$Cl$_2$): identical to (*S*,*S*)-*cis*-[PtCl(P*N)$_2$]Cl. Λ_M = 41 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 203 cm^2 Ω^{-1} mol^{-1} (H$_2$O).

[*SP*-4-3-(*S*),(*S*)]-(+)-Chloro[methylphenyl(8-quinolyl)arsine-*As*]-[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Hexafluorophosphate [(*S*,*S*)-*cis*-[PdCl(As*N)$_2$]PF$_6$]. A hot solution of (*S*,*S*)-*cis*-[PdCl-(As*N)$_2$]Cl·CH$_2$Cl$_2$ (0.30 g, 0.37 mmol) in water (15 mL) was treated with an excess of NH$_4$[PF$_6$] (0.12 g) in water (5 mL). The pale yellow precipitate was collected and redissolved in dichloromethane (30 mL). The solution was dried (MgSO$_4$), filtered, and the solvent was removed under reduced pressure. Recrystallization of the residue from methanol by the addition of diethyl ether afforded the pure product: lemon-colored prisms; mp 164–165 °C; 0.28 g (92%); $[\alpha]_D$ +315° (*c* 0.67, CH$_2$Cl$_2$). Anal. Calcd for $C_{32}H_{28}N_2As_2ClF_6PPd$: C, 43.8; H, 3.2; N, 3.2; Cl, 4.0. Found: C, 44.1; H, 3.5; N, 3.1; Cl, 4.0. ^{1}H NMR (CD$_2$Cl$_2$ at 178 K): δ 1.10 (s, 3 H, AsMe-*As*,*N*), 2.45 (s, 3 H, AsMe-*As*), 6.94–8.73 (m, 20 H, aromatics), 9.10 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*), 10.17 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-*H*-*As*,*N*). Λ_M = 45 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 129 cm^2 Ω^{-1} mol^{-1} (Me$_2$CO).

The following compounds were prepared similarly.

(±)-[*SP*-4-3-(*R,*R**),(*R**,*S**)]-(±)-Chloro[methylphenyl(8-quinolyl)arsine-*As*][methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Hexafluorophosphate [(*R**,*R**),(*R**,*S**)-*cis*-[PdCl(As*N)$_2$]PF$_6$]**: yellow prisms; mp 175–176 °C; 91% yield. Anal. Calcd for $C_{32}H_{28}N_2As_2ClF_6PPd$: C, 43.8; H, 3.2; N, 3.2; Cl, 4.0. Found: C, 44.0; H, 3.6; N, 2.8; Cl, 4.0. ^{1}H NMR (CD$_2$Cl$_2$ at 178 K): δ 1.10 (s, 1.5 H, AsMe-*As*,*N*-(*R**,*R**)), 1.98 (s, 1.5 H, AsMe-*As*,*N*-(*R**,*S**)), 2.45 (s, 1.5 H, AsMe-*As*-(*R**,*S**)), 2.51 (s, 1.5 H, AsMe-*As*-(*R**,*R**)), 6.58–10.29 (m, 22 H, aromatics). Λ_M = 42 cm^2 Ω^{-1} mol^{-1} (CH$_2$Cl$_2$). Λ_M = 135 cm^2 Ω^{-1} mol^{-1} (Me$_2$CO).

[*SP*-4-3-(*S*),(*S*)]-(+)-Chloro[methylphenyl(8-quinolyl)arsine-*As*]-[methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Hexafluoro-

phosphate–0.5-Acetone [(*S*,*S*)-*cis*-[PtCl(As*N)$_2$]PF$_6$·0.5Me$_2$CO]: yellow prisms; mp 172–173 °C; 91% yield; $[\alpha]_D$ +183° (*c* 0.55, CH_2Cl_2). Anal. Calcd for $C_{33.5}H_{31}N_2As_2ClF_6O_{0.5}PPt$: C, 40.4; H, 3.1; N, 2.8; Cl, 3.6. Found: C, 40.4; H, 3.3; N, 2.4; Cl, 3.7. ^{1}H NMR (CD_2Cl_2 at 248 K): δ 1.00 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*), 2.10 (s, 3 H, Me_2CO), 2.48 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*), 6.78–8.76 (m, 20 H, aromatics), 9.06 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*), 10.47 (d of d, 1 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H-*As*,*N*). Λ_M = 52 cm^2 Ω^{-1} mol^{-1} (CH_2Cl_2). Λ_M = 130 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-3-(*R,*R**),(*R**,*S**)]-(±)-Chloro[methylphenyl(8-quinolyl)arsine-*As*][methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Hexafluorophosphate–Acetone [(*R**,*R**),(*R**,*S**)-*cis*-[PtCl(As*N)$_2$]PF$_6$·Me$_2$CO]**: yellow prisms; mp 171–172 °C; 92% yield. Anal. Calcd for $C_{35}H_{34}N_2As_2ClF_6OPPt$: C, 41.0; H, 3.4; N, 2.7; Cl, 3.5. Found: C, 40.9; H, 3.3; N, 2.4; Cl, 3.6. ^{1}H NMR (CD_2Cl_2 at 248 K): δ 1.00 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*-(*R**,*R**)), 2.00 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*,*N*-(*R**,*S**)), 2.42 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*-(*R**,*S**)), 2.48 (s, 1.5 H, $^3J_{PtH}$ = 22 Hz, AsMe-*As*-(*R**,*R**)), 2.10 (s, 6 H, Me_2CO), 6.70–10.58 (m, 22 H, aromatics). Λ_M = 51 cm^2 Ω^{-1} mol^{-1} (CH_2Cl_2). Λ_M = 128 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-4-(*S*),(*S*)]-(+)-Bis[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Hexafluorophosphate [(*S*,*S*)-*cis*-[Pd(As*N)$_2$](PF$_6$)$_2$]. (*S*,*S*)-*cis*-[PdCl(As*N)$_2$]PF$_6$ (0.25 g, 0.28 mmol) was dissolved in acetone (30 mL), and the solution was treated with an excess of NH_4PF_6 (0.20 g, 1.2 mmol) in water (5 mL). More water (50 mL) was then added to the solution and the resulting white precipitate was filtered off. Recrystallization of the precipitate from acetone–diethyl ether gave the pure product: colorless needles; mp 245–246 °C; 0.26 g (92%); $[\alpha]_D$ +256° (*c* 0.64, Me_2CO). Anal. Calcd for $C_{32}H_{28}N_2As_2F_{12}P_2Pd$: C, 39.0; H, 2.9; N, 2.8. Found: C, 39.0; H, 2.8; N, 2.6. ^{1}H NMR (CH_3CN-d_3): δ 1.80 (s, 6 H, AsMe), 7.50–8.93 (m, 20 H, aromatics), 9.17 (d of d, 2 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 182 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

The following compounds were prepared similarly.

[*SP*-4-4-(*R,*R**),(*R**,*S**)]-(±)-Bis[methylphenyl(8-quinolyl)arsine-*As*,*N*]palladium(II) Hexafluorophosphate [(*R**,*R**),(*R**,*S**)-*cis*-[Pd(As*N)$_2$](PF$_6$)$_2$]**: colorless needles; mp 256–257 °C; 92% yield. Anal. Calcd for $C_{32}H_{28}N_2As_2F_{12}P_2Pd$: C, 39.0; H, 2.9; N, 2.8. Found: C, 39.0; H, 2.8; N, 2.9. ^{1}H NMR (CH_3CN-d_3): δ 1.80. (s, 3 H, AsMe-(*R**,*R**)), 2.46 (s, 3 H, AsMe-(*R**,*S**)), 7.10–9.19 (m, 22 H, aromatics). Λ_M = 200 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-4-(*S*),(*S*)]-(+)-Bis[methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Hexafluorophosphate [(*S*,*S*)-*cis*-[Pt(As*N)$_2$](PF$_6$)$_2$]: colorless needles; mp 281–282 °C; 92% yield; $[\alpha]_D$ +302° (*c* 0.61, Me_2CO). Anal. Calcd for $C_{32}H_{28}N_2As_2F_{12}P_2Pt$: C, 35.7; H, 2.6; N, 2.6. Found: C, 35.4; H, 2.5; N, 2.5. ^{1}H NMR (CH_3CN-d_3 at 227 K): δ 1.82 (s, 6 H, $^3J_{PtH}$ = 22 Hz, AsMe), 7.60–9.04 (m, 20 H, aromatics), 9.20 (d of d, 2 H, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 2 Hz, 2-H). Λ_M = 228 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-4-(*R,*R**),(*R**,*S**)]-(±)-Bis[methylphenyl(8-quinolyl)arsine-*As*,*N*]platinum(II) Hexafluorophosphate ((*R**,*R**),(*R**,*S**)-*cis*-[Pt(As*N)$_2$](PF$_6$)$_2$]**: colorless needles; mp 209–210 °C; 90% yield. Anal. Calcd for $C_{32}H_{28}N_2As_2F_{12}P_2Pt$: C, 35.7; H, 2.6; N, 2.6. Found: C, 35.8; H, 2.8; N, 2.4. ^{1}H NMR (CH_3CN-d_3): δ 1.82 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-(*R**,*R**)), 2.48 (s, 3 H, $^3J_{PtH}$ = 22 Hz, AsMe-(*R**,*S**)), 7.20–9.18 (m, 22 H, aromatics). Λ_M = 215 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-4-(*S*),(*S*)]-(+)-Bis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]palladium(II) Hexafluorophosphate [(*S*,*S*)-*cis*-[Pd(P*N)$_2$](PF$_6$)$_2$]. (*S*,*S*)-*cis*-[PtCl(P*N)$_2$Cl·2H$_2$O (0.20 g, 0.28 mmol) was dissolved in hot water (10 mL) and the solution was treated with NH_4PF_6 (0.20 g, 1.2 mmol) in water (5 mL). The colorless precipitate that formed was collected and recrystallised from acetone–diethyl ether to afford the product: colorless needles; mp 210–211 °C; 0.24 g (91%); $[\alpha]_D$ +386° (*c* 0.49, Me_2CO). Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pd$: C, 42.8; H, 3.1; N, 3.1. Found: C, 42.6; H, 3.1; N, 3.0. ^{1}H NMR (Me_2SO-d_6): δ 2.05 (d, 6 H, $^2J_{PH}$ = 10 Hz, PMe), 7.46–9.08 (m, 20 H, aromatics), 9.30 (m, 2 H, 2-H). Λ_M = 212 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

The following compounds were prepared similarly.

[*SP*-4-4-(*R,*R**),(*R**,*S**)]-(±)-Bis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]palladium(II) Hexafluorophosphate [(*R**,*R**),(*R**,*S**)-*cis*-[Pd(P*N)$_2$](PF$_6$)$_2$]**: colorless needles; mp 215–216 °C; 90% yield. Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pd$: C, 42.8; H, 3.1; N, 3.1. Found: C, 42.4; H, 3.4; N, 3.1. ^{1}H NMR (Me_2SO-d_6): δ 2.05 (d, 3 H, $^3J_{PH}$ = 10 Hz, PMe-(*R**,*R**)), 2.64 (d, 3 H, $^2J_{PH}$ = 10 Hz, PMe-(*R**,*S**)), 7.00–9.30 (m, 22 H, aromatics). Λ_M = 192 cm^2 Ω^{-1} mol^{-1} (Me_2CO). Recrystallization of the mixture from hot acetone afforded the pure *R**,*R** diastereomer as colorless needles: mp 222–223 °C; 90% yield. Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pd$: C, 42.8; H, 3.1; N, 3.1. Found: C, 42.5; H, 3.0; N, 3.0. ^{1}H NMR (Me_2SO-d_6): identical with that of pure enantiomer. Λ_M = 210 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*SP*-4-4-(*S*),(*S*)]-(+)-Bis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II) Hexafluorophosphate [(*S*,*S*)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$]: colorless needles; mp 209–210 °C; 92% yield; $[\alpha]_D$ +291° (*c* 0.45, Me_2SO). Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pt$: C, 38.9; H, 2.9; N, 2.8. Found: C, 38.9; H, 2.8; N, 2.8. ^{1}H NMR (Me_2SO-d_6): δ 2.10 (d, 6 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PH}$ = 10 Hz, PMe), 7.50–9.18 (m, 20 H, aromatics), 9.40 (m, 2 H, 2-H). ^{31}P NMR (Me_2SO): δ 12.1 (s, 2 P, $^1J_{PtP}$ = 3310 Hz). Λ_M = 206 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

[*S*,*P*-4-4-(*R,*R**)]-(±)-Bis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II) Hexafluorophosphate [(*R**,*R**)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$]**: colorless needles; mp 219–220 °C; 91% yield. Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pt$: C, 38.9; H, 2.9; N, 2.8. Found: C, 38.8; H, 2.7; N, 2.8. ^{1}H and ^{31}P NMR (Me_2SO-d_6): identical to that recorded for pure enantiomer. Λ_M = 204 cm^2 Ω^{-1} mol^{-1} (Me_2CO). This compound was obtained also in 43% yield by the fractional crystallisation of the 1:1 diastereomeric mixture.

[*SP*-4-4-(*R,*S**)]-Bis[methylphenyl(8-quinolyl)phosphine-*N*,*P*]platinum(II) Hexafluorophosphate [(*R**,*S**)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$]**. This compound was obtained from the mother liquor above, after removal of the *R**,*R** diastereomer. Thus, the mother liquor was evaporated to dryness and the residue was recrystallized from dichloromethane–diethyl ether; the pure *R**,*S** diastereomer crystallized as colorless needles; mp 221–222 °C; 39% yield. Anal. Calcd for $C_{32}H_{28}N_2F_{12}P_4Pt$: C, 38.9; H, 2.9; N, 2.8. Found: C, 38.8; H, 2.8; N, 2.8. ^{1}H NMR (Me_2SO-d_6): δ 2.76 (d, 6 H, $^3J_{PtH}$ = 40 Hz, $^2J_{PH}$ = 10 Hz, PMe), 7.00–9.18 (m, 20 H, aromatics), 9.18 (m, 2 H, 2-H). ^{31}P{^{1}H} NMR (Me_2SO): δ 12.3 (s, 2 P, $^1J_{PtP}$ = 3320 Hz). Λ_M = 196 cm^2 Ω^{-1} mol^{-1} (Me_2CO).

Registry No. (*S*)-PdCl$_2$(As*N), 138180-68-4; (±)-PdCl$_2$(As*N), 138256-20-9; (±)-PdCl$_2$(P*N), 138256-21-0; (*S*)-PtCl$_2$(As*N), 138180-69-5; (±)-PtCl$_2$(As*N), 138256-22-1; (*S*)-PtCl$_2$(P*N), 138180-70-8; (±)-PtCl$_2$(P*N), 138256-23-2; (*S*,*S*)-*cis*-[PdCl(As*N)$_2$]Cl, 138180-71-9; *cis*-[PdCl(As*N)$_2$]Cl, 138256-24-3; (*S*,*S*)-*cis*-[PdCl(P*N)$_2$]Cl, 138180-72-0; (*S*,*S*)-[PdCl(As*N)(P*N)]Cl, 138207-63-3; *cis*-[PtCl(As*N)$_2$]Cl, 138180-73-1; (*S*,*S*)-*cis*-[PtCl(P*N)$_2$]Cl, 138180-74-2; (*S*,*S*)-*cis*-[PtCl(As*N)$_2$]PF$_6$, 138180-76-4; *cis*-[PdCl(As*N)$_2$]PF$_6$, 138256-26-5; (*S*,*S*)-*cis*-[PtCl(As*N)$_2$]PF$_6$, 138256-28-7; *cis*-[PtCl(As*N)$_2$]PF$_6$, 138180-78-6; (*S*,*S*)-*cis*-[Pd(As*N)$_2$](PF$_6$)$_2$, 138180-80-0; *cis*-[Pd(As*N)$_2$](PF$_6$)$_2$, 138256-30-1; (*R**,*S**)-*cis*-[Pd(As*N)$_2$](PF$_6$)$_2$, 138256-42-5; (*S*,*S*)-*cis*-[Pt(As*N)$_2$](PF$_6$)$_2$, 138180-82-2; *cis*-[Pt(As*N)$_2$](PF$_6$)$_2$, 138256-32-3; (*R**,*S**)-*cis*-[Pt(As*N)$_2$](PF$_6$)$_2$, 138256-44-7; (*S*,*S*)-*cis*-[Pd(P*N)$_2$](PF$_6$)$_2$, 138180-84-4; *cis*-[Pd(P*N)$_2$](PF$_6$)$_2$, 138256-34-5; (*R**,*S**)-*cis*-[Pd(P*N)$_2$](PF$_6$)$_2$, 138256-46-9; (*S*,*S*)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$, 138180-86-6; *cis*-[Pt(P*N)$_2$](PF$_6$)$_2$, 138256-36-7; (*R**,*S**)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$, 138256-38-9; (*R**,*S**)-*cis*-[PdCl(P*N)$_2$]Cl, 138256-39-0; PdCl$_2$(NCCH$_3$)$_2$, 14592-56-4; dichloro(cycloocta-1,5-dienyl)platinum(II), 12080-32-9; (*S*,*S*)-*cis*-[PtCl(As*N)$_2$]Cl, 138256-47-0; (*R**,*S**)-*cis*-[PtCl(P*N)$_2$]Cl, 138256-40-3.