77097-21-3; Ni(acacMeDPT), 77097-22-4; Ni(acacPhDPT), 77097-23-5; Cu(acacDPT), 77097-24-6; Cu(acacMeDPT), 77097-25-7; Cu(acacPhDPT), 77097-26-8; Co(benacDPT), 77110-76-0; Co(benacMeDPT), 77097-27-9; Co(benacPhDPT), 77097-28-0; Ni(benacDPT), 77097-29-1; Ni(benacMeDPT), 77097-30-4; Ni(benacPhDPT), 77097-31-5; Cu(benacDPT), 77097-32-6; Cu(benacMeDPT), 77097-33-7; Cu(benacPhDPT), 77097-34-8; Co(*p*-Cl-benacDPT), 77097-35-9; Ni(*p*-Cl-benacDPT), 77097-36-0; Cu(*p*-Cl-benacDPT), 77097-37-1; Co(*p*-Br-benacDPT), 77097-38-2; Ni(*p*-Br-benacDPT), 77097-39-3; Cu(*p*-Br-benacDPT), 77097-40-6; Co(*p*-CH_3benacDPT), 77097-41-7; Ni(*p*-CH_3benacDPT), 77097-42-8; Cu(*p*-CH_3benacDPT), 77097-43-9; Co(*p*-CH_3ObenacDPT), 77097-44-0; Ni(*p*-CH_3ObenacDPT), 77097-45-1; Cu(*p*-CH_3ObenacDPT), 77097-46-2; Hacac, 123-54-6; Hbenac, 93-91-4; DPT, 56-18-8; MeDPT, 105-83-9; PhDPT, 1555-72-2; *p*-chlorobenzoylacetone, 6302-55-2; *p*-bromobenzoylacetone, 4023-81-8; *p*-methylbenzoylacetone, 4023-79-4; *p*-methoxybenzoylacetone, 4023-80-7; $(Et_4N)_2$-$(CoBr_4)$, 2041-04-5; Htfac, 367-57-7.

Supplementary Material Available: A list of elemental chemical analyses for all metal complexes (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

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

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A comparative investigation of the properties of square-planar and square-pyramidal bis(bidentate)nickel(II) complexes containing the internal diastereoisomers and optically active forms of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue has been undertaken. The di(tertiary arsine) yields stable complexes which are labile with respect to bidentate ligand redistribution between different metal centers, but the di(tertiary phosphine) derivatives are inert in this respect. The square-pyramidal chloro complexes of both ligands undergo rapid site exchange of their axial chloro ligands under ambient conditions. Variable-temperature ^1H NMR studies on suitable derivatives indicate that this proceeds by internal isomerization of the chelate rings and by intermolecular exchange of the chloro ligand between sterically compatible complex ions.

Introduction

Although bis(di(tertiary arsine)) and bis(di(tertiary phosphine)) derivatives of group 8 metals are among the most widely studied coordination compounds, there is nevertheless a paucity of information in the literature concerning the dynamic processes of complexes of this type in solution. The extensive and pioneering work of Nyholm and Co-workers[2] led to the view that the stereochemistry of *o*-phenylenebis(dimethylarsine) (diars) derivatives was essentially static. More recent work concerning the coordination chemistry of *o*-phenylenebis(dimethylphosphine) reinforced this impression.[3] Whereas the phenomenon of axial-halogeno lability in the square-pyramidal cations $[MX(diars)_2]^+$ (where M = Ni, Pd, or Pt and X = Cl, Br, I, etc.) was realized at an early stage, following conductimetric and spectrophotometric studies,[4] it is evident that dynamic processes involving the nature of the metal chelate interaction could not be detected by these means. Furthermore, although DNMR spectroscopy could have, in principle, provided an insight into the mechanism of axial-halogeno–metal exchange in these five-coordinate complexes,[5] the inherent difficulty in investigating the phenomena of intramolecular isomerization of chelate rings and intermolecular bidentate ligand exchange (redistribution) in complexes containing symmetrical ligands resides in the centrosymmetry of the square-planar bis(bidentate)metal moiety (vide infra). It will be readily appreciated that a detailed knowledge of the dynamic properties in solution of a particular coordination complex must necessarily precede the rational planning of a successful asymmetric synthesis based upon the stereochemistry of that species.

Accordingly, we present our findings concerning the stereochemistry and dynamic properties of bivalent nickel complexes containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine)[6] and its phosphorus[7] analogue.

Results and Discussion

Stereochemical Considerations. The ditertiary chelating ligands *o*-phenylenebis(methylphenylarsine)[6] and its phosphorus analogue[7] have been separated into dissymmetric racemic (*RR*,*SS*) and internally compensated meso (*RS*) diastereoisomers, and the former subsequently resolved by fractionally crystallizing internally diastereoisomeric palladium(II) complexes containing the chiral ditertiary species and an optically active ortho-metalated dimethyl(α-methylbenzyl)amine.

The various forms of both ligands are air-stable crystalline solids whose identities have been unambiguously established in previous work (Figure 1).[8,9]

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(1) In this and the following paper, the term di(tertiary arsine) is used to represent a bidentate ligand containing two tertiary arsenic groups. The phosphorus analogue is treated similarly.
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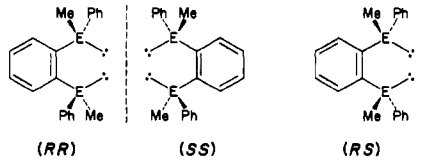

Figure 1. Stereoisomers of o-phenylenebis(methylphenylarsine) (E = As) and its phosphorus analogue (E = P).

The stereoisomers of both ligands react with appropriate nickel(II) salts to give yellow or orange square-planar complexes of the type $[Ni(bidentate)_2](PF_6)_2$ and the more deeply colored square-pyramidal halogeno derivatives $[NiX(bidentate)_2]PF_6$. The stereochemistry of the square-planar cations arising from the different forms of the ligands is summarized in Figure 2. The optically active ligands afford a single optically active product, but the racemic and meso diastereoisomers of the ligands give rise, in principle, to a mixture of optically inactive compounds. Square-planar derivatives of the racemic ligands may be chiral (racemic complex) or achiral (meso complex) depending on whether the bidentate ligands in the complex have the same or different chiralities, respectively. It is noteworthy that the internally diastereoisomeric racemic and meso complexes are not related by an internal axis of rotation. Accordingly, if interconversion between these two stereoisomers of the same complex is observed, redistribution of the bidentate ligands between different metal centers (intermolecular bidentate ligand exchange) must be occurring. The square-planar racemic and meso complexes will each show a single ^1H NMR for the equivalent AsMe or PMe groups, although it may be anticipated that the chemical shift of the signal due to the racemic complex will appear upfield of the corresponding signal due to the meso compound because of the substantially greater shielding of the methyl protons by the phenyl groups in the former structure. It is significant that the AsMe or PMe resonance due to the racemic complex can always be identified if the ^1H NMR spectrum of the corresponding optically active complex is available for comparison.

The meso diastereoisomer of each ligand is achiral, and consequently achiral square-planar complexes are produced. However, these may exist as syn or anti isomers as shown in Figure 2. Again, each geometric isomer will exhibit a single ^1H NMR for the equivalent AsMe or PMe groups present. Unlike the racemic and meso complexes, however, the syn and anti isomers are related by an internal axis of rotation which bisects the five-membered metal–chelate rings. *Consequently, the observation of syn–anti interconverstion implies intramolecular isomerization provided it is certain that intermolecular racemic–meso interconversion does not take place under the same conditions.*

In Figure 3 the stereochemistries of the square-pyramidal halogeno adducts of the respective square-planar cations are summarized. A single product arises from the addition of a fifth ligand to the various square-planar cations, except in the case of the syn isomer where a pair of chemically distinct adducts is possible. A consequence of the addition is the loss of the degeneracy of the methyl group environments in all but the syn case. However, separate resonances due to the pairs of methyl groups exo and endo to the axial ligand are not usually observed in the ^1H NMR spectra of the square-pyramidal cations under ambient conditions, even though the complexes are exceedingly stable.[10] This is because rapid (compared to the NMR time scale) exchange of the halogeno ligand between the alternative axial sites is usually observed in complexes of this type in solution.[5] At lower temperatures the rate of axial site exchange may be reduced sufficiently to observe both pairs of methyl groups, however (vide infra).

Preparation of Complexes. Mixing of a solution of $[Ni(H_2O)_6]Cl_2$ and 2 equiv of the appropriate stereoisomer of the ligand in ethanol gave intensely colored solutions of the square-pyramidal cations $[NiCl(diars)_2]^+$ and $[NiCl(diphos)_2]^+$. The complexes $[NiCl(diars)_2]Cl$ were isolated by the addition of diethyl ether, although satisfactory samples of the corresponding ditertiary phosphine chlorides could not be obtained similarly. However, if NH_4PF_6 was added to either of the reaction mixtures, the highly crystalline salts $[NiCl(diars)_2]PF_6$ or $[NiCl(diphos)_2]PF_6$ precipitated. All of the complexes containing five-coordinate cations behaved as uni-univalent electrolytes in acetonitrile and dichloromethane solution and were intensely colored in these solvents. Details of the physical properties of the complexes are presented in Table I.

The square-planar complexes $[Ni(diars)_2](PF_6)_2$ and $[Ni(diphos)_2](PF_6)_2$ were prepared by reacting the appropriate ligand with nickel(II) acetate in ethanol in the presence of NH_4PF_6.

$$Ni(OAc)_2 + 2((RR)\text{-diars}) + 2NH_4PF_6 \rightarrow [Ni((SS)\text{-diars})_2](PF_6)_2 + 2AcNH_2 + 2H_2O$$

Repeated evaporation of the reaction mixture on the steam bath afforded the products as yellow to orange solids which, in general, crystallized from acetonitrile as brown *solvates*. The solvent molecule was only weakly bound in the adducts, however, since suspension of the salts in acetone, dichloromethane, or ethanol caused an immediate color change and formation of the analytically pure solvent-free complexes. The latter were sparingly soluble in noncoordinating solvents and a pronounced color change from yellow to deep red-brown was observed when they were dissolved in acetonitrile, suggesting coordination of the solvent to the nickel ion. The salts $[Ni(diars)_2](PF_6)_2$ and $[Ni(diphos)_2](PF_6)_2$ behaved as di-univalent electrolytes in acetonitrile solution (Table I), and their electronic spectra in this solvent closely resembled those of the square-pyramidal chloro complexes. The chemical shift values of the AsMe and PMe resonances in the ^1H NMR spectra of the square-planar salts in MeCN-d_3 also correlated closely with the values found for the corresponding square-pyramidal chloro complexes. In dimethyl sulfoxide the complexes $[Ni(diphos)_2](PF_6)_2$ and $[NiCl(diphos)_2]PF_6$ conducted as di-univalent and uni-valent electrolytes, respectively. The corresponding di(tertiary arsine) complexes, however, decomposed in this solvent. The PMe ^1H NMR signal of the cations $[Ni(diphos)_2]^{2+}$ in Me_2SO-d_6 occurred significantly downfield of the corresponding resonances of $[Ni(MeCN)(diphos)_2]^{2+}$ and $[NiCl(diphos)_2]^+$ in MeCN-d_3 solution.

The optically active complex $[Ni((SS)\text{-diphos})_2](PF_6)_2$ was much more soluble in the usual range of solvents than the corresponding racemic material. However, we could not obtain crystalline samples of the optically active di(tertiary phosphine) salts even though they were readily prepared from *anti*-$[Ni((RS)\text{-diars})_2](PF_6)_2 \cdot 0.5MeCN$ in acetonitrile solution. The facile displacement of di(tertiary arsine) ligands by di(tertiary phosphines) is a feature of this system of nickel(II) complexes.

Redistribution of Chelating Di(tertiary arsine) and Di(tertiary phosphine) Ligands in Square-Planar Nickel(II) Complexes. (i) Di(tertiary arsine) Complexes. The optically active ligand (*RR*)-diars reacted with nickel(II) acetate and NH_4PF_6, under the conditions described above, to give $[Ni((SS)\text{-diars})_2](PF_6)_2$ as a yellow powder. This salt dissolved in acetonitrile to form a brown solution from which brown blocks of the hemisolvate $[Ni((SS)\text{-diars})_2](PF_6)_2 \cdot 0.5MeCN$ could be isolated by the addition of methanol. The ^1H NMR

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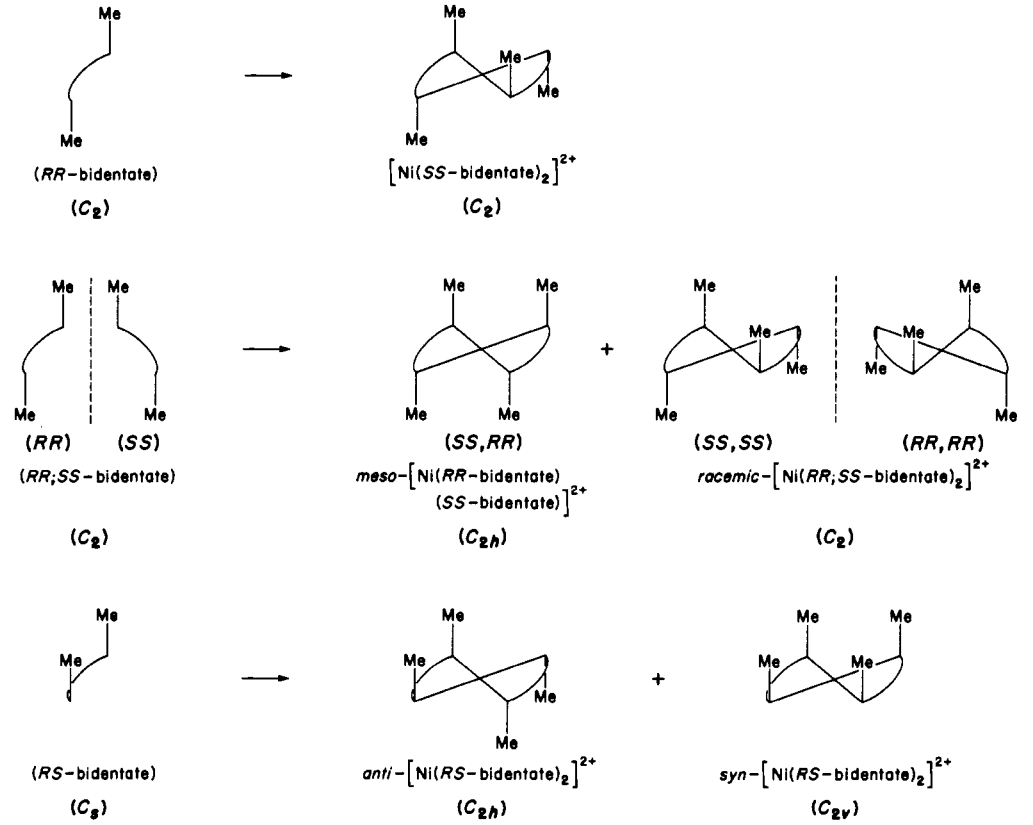

Figure 2. Representation of stereochemistry of the square-planar cations $[Ni(bidentate)_2]^{2+}$.

Table I. Physical Properties of the Complexes $[Ni(bidentate)_2](PF_6)_2$ and $[NiCl(bidentate)_2]PF_6$

compd	Λ_M[a] in MeCN	abs spectra[b] λ	abs spectra[b] ϵ_{max}	δ(EMe)[c] MeCN-d_3	δ(EMe)[c] Me_2SO-d_6
(+)-[Ni((*SS*)-diars)$_2$]$(PF_6)_2$·0.6MeCN	272 (2:1)	463	1010[d]	1.51 s	
meso-[Ni((*RR*)-diars)((*SS*)-diars)]$(PF_6)_2$·MeCN	288 (2:1)	463	1010[d]	1.51 s, 2.33 s[f]	
anti-[Ni((*RS*)-diars)$_2$]$(PF_6)_2$·0.5MeCN	296 (2:1)	455	1090[d]	1.55 s	
(+)-[Ni((*SS*)-diphos)$_2$]$(PF_6)_2$	275 (2:1)	405	2270[d]	1.44 br s	1.82 br s
rac-[Ni((*RR,SS*)-diphos)$_2$]$(PF_6)_2$	273 (2:1)	405	2280[d]	1.44 br s	1.82 br s
meso-[Ni((*RR*)-diphos)((*SS*)-diphos)]$(PF_6)_2$	273 (2:1)	399	2130[d]	2.41 br s	2.55 br s
anti-[Ni((*RS*)-diphos)$_2$]$(PF_6)_2$·MeCN	275 (2:1)	395	2230[d]	1.30 br s	1.73 br s

compd	Λ_M MeCN	Λ_M CH_2Cl_2	abs spectra[b] λ	abs spectra[b] ϵ_{max}	^{1}H NMR spectra δ(EMe)[c] in CH_2Cl_2	T_c, K	$\Delta G^{\ddagger}$[h]
(+)-[NiCl((*SS*)-diars)$_2$]Cl	71 (1:1)	49 (1:1)	515	1400[e]	insufficiently soluble		
(+)-[NiCl((*SS*)-diars)$_2$]PF_6	116 (1:1)	41 (1:1)	515	1570[e]	1.51 s (293); 1.55 s, 1.21 s (200)	251	12.5
rac-[NiCl((*RR,SS*)-diars)$_2$]Cl	59 (1:1)	28 (1:1)	515	1260[e]	insufficiently soluble		
rac-[NiCl((*RR,SS*)-diars)$_2$]PF_6	121 (1:1)	48 (1:1)	515	1490[e]	1.50 s (293); 1.49 s, 1.14 s (170)	198	9.75
anti-[NiCl((*RS*)-diars)$_2$]Cl	57 (1:1)	38 (1:1)	502	1430[e]	insufficiently soluble		
anti-[NiCl((*RS*)-diars)$_2$]PF_6	128 (1:1)	48 (1:1)	496	1780[e]	1.50 s (291); 1.28 s, 1.11 s (170)	240	12.3
(+)-[NiCl((*SS*)-diphos)$_2$]PF_6	160 (1:1)	47 (1:1)	440	2000[e]	1.50 br s (293); 1.54 br s, 1.24 br s (213)	290	14.5
rac-[NiCl((*RR,SS*)-diphos)$_2$]PF_6	143 (1:1)	43 (1:1)	440	1740[e]	1.51 br s (293); 1.63 br s, 1.32 br s (170)	190	9.4
meso-[NiCl((*RR*)-diphos)((*SS*)-diphos)]PF_6	120 (1:1)	42 (1:1)	428	1990[e]	2.34 br s (293); 2.58 br s, 2.22 br s (200)	263	13.1
anti-[NiCl((*RS*)-diphos)$_2$]PF_6	133 (1:1)	47 (1:1)	427	2100[e]	1.37 br s (293); 1.23 br s, 1.11 br s (230)	278	14.5
rac-[NiCl((*RS*)-diphos)((*RR,SS*)-diphos)]PF_6	133 (1:1)	50 (1:1)	423	1590[e]	2.38 br s, 1.4 br s (300); 2.52 d, 2.38 d, 1.4 d, 1.04 d (216)[g]	305	14.4
(−)-[NiCl((*RS*)-diphos)((*RR*)-diphos)]PF_6·CH_2Cl_2	132 (1:1)	50 (1:1)	423	1590[e]	as above	305	14.4

[a] Conductance in $cm^2\ \Omega^{-1}\ mol^{-1}$ for 10^{-3} M solutions at 293 K. [b] Bands due to d–d transitions for 10^{-3} M solutions in MeCN (*d*) and CH_2Cl_2 (*e*). [c] ^{1}H NMR spectra chemical shift values in ppm relative to Me_4Si for 0.05 M solutions at the temperature indicated in parenthesis. [d] In MeCN. [e] In CH_2Cl_2. [f] An equilibrium mixture of racemic and meso complexes. [g] $^2J_{PH} = 10$ Hz. [h] $\Delta G^{\ddagger}$ (kcal mol^{-1}) = $0.004573T_c[9.97 + \log(T_c/\Delta\nu)]$ where T_c is the coalescence temperature and $\Delta\nu = |\nu(EMe_A) - \nu(EMe_B)|$ at the slow exchange limit.

spectrum of the recrystallized material in MeCN-d_3 showed the presence of free MeCN, and the AsMe resonance occurred as a sharp singlet at δ 1.51. Cooling of the NMR sample to 170 K did not result in broadening of the sharp AsMe signal. This behavior is consistent with the rapid site exchange of an axially coordinated solvent molecule in solution,[11] two reso-

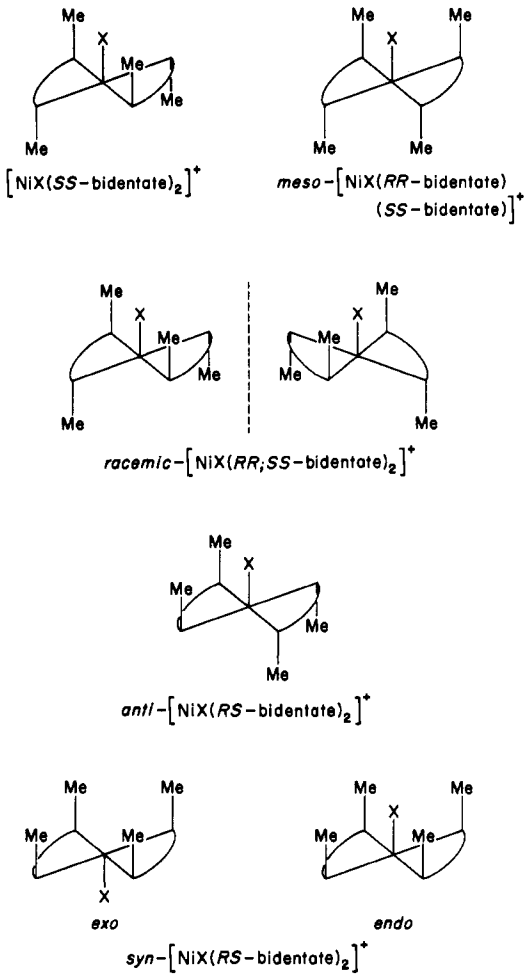

Figure 3. Representation of stereochemistry of the square-pyramidal cations $[NiX(bidentate)_2]^+$.

nances being expected for the cation $[Ni(MeCN\text{-}d_3)((SS)\text{-diars})_2]^{2+}$ at its lower exchange limit (vide supra). The other square-planar complexes behaved similarly in this respect.

The racemic di(tertiary arsine) (*RR,SS*)-diars also reacted with nickel(II) acetate in the presence of NH_4PF_6 to give a yellow powder which, after recrystallization from an acetonitrile–diethyl ether mixture, analyzed as $[Ni(diars)_2](PF_6)_2 \cdot CH_3CN$. However, in this case the ^1H NMR spectra of the original and recrystallized sample were different. The original material exhibited two AsMe resonances at δ 2.33 and 1.51 in MeCN-d_3 with the intensity ratio of 3:1, respectively, but within ca. 15 min the ratio of intensities was 1:4, and the spectrum stable (Figure 4). Since the corresponding optically active complex gave rise to an AsMe singlet at δ 1.51 in the same solvent, the resonance in this position in the spectrum of the initial product derived from the racemic di(tertiary arsine) must be due to the racemic cation $[Ni(MeCN\text{-}d_3)((RR,SS)\text{-diars})_2]^{2+}$. The signal at δ 2.33 could then by confidently assigned to the corresponding meso cation $[Ni(MeCN\text{-}d_3)((RR)\text{-diars})((SS)\text{-diars})]^{2+}$. The recrystallized product, however, initially showed a single sharp ^1H NMR signal at δ 2.33 in MeCN-d_3, but the spectrum changed rapidly and, after ca. 15 min, had reached an equilibrium condition in which the proportions of meso:racemic species were again 1:4, respectively. The same equilibrium mixture of complexes

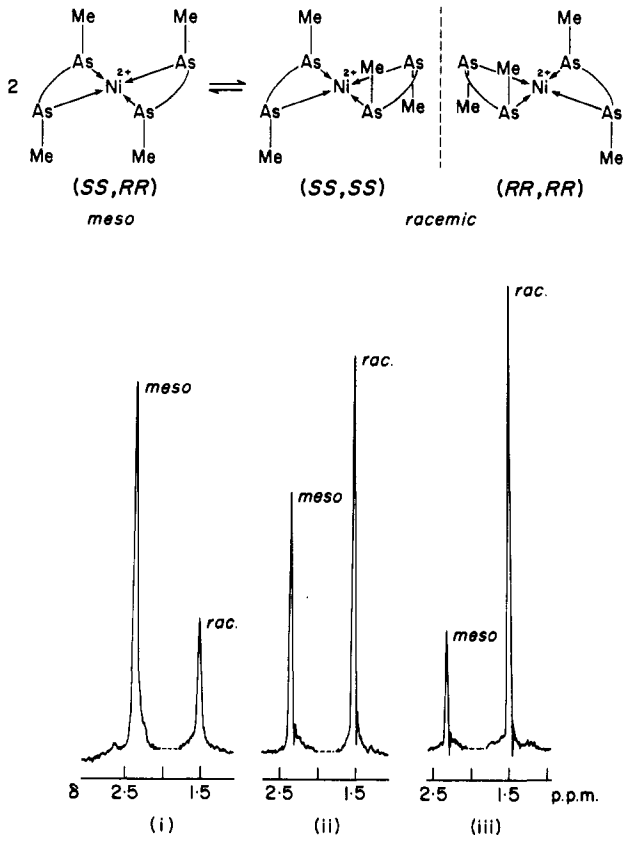

Figure 4. ^1H NMR spectra of *meso*-$[Ni((RR)\text{-diars})((SS)\text{-diars})](PF_6)_2 \cdot MeCN$ in MeCN-d_3 at 0 °C in the AsMe region: spectrum (i) recorded after 3 min, (ii) after 9 min, and (iii) after 15 min (equilibrium mixture of complexes).

resulted if equimolar MeCN-d_3 solutions of the enantiomorphic complexes $[Ni((RR)\text{-diars})_2](PF_6)_2 \cdot 0.5MeCN$ and $[Ni((SS)\text{-diars})_2](PF_6)_2 \cdot 0.5MeCN$ were mixed. Evidently, although the racemic cation is the thermodynamically favored species in solution, the meso cation forms the more stable crystal lattice. The process must involve an intermolecular exchange of the bidentate ligands (redistribution) since the two diastereoisomeric complexes are not related by an internal axis of rotation. Presumably a bidentate ligand is initially displaced by solvent molecules and then rapidly reassociated with a similar metal center, since the overall system of complexes is stable.

The meso di(tertiary arsine) (*RS*)-diars yielded brown blocks of the geometric isomer *anti*-$[Ni((RS)\text{-diars})_2](PF_6)_2 \cdot 0.5MeCN$ following the usual method of preparation and recrystallization of the crude product from acetonitrile. The ^1H NMR spectrum of this complex was time independent and contained a single sharp AsMe resonance at δ 1.55. The spectrum did not alter upon cooling to 170 K. We have assigned the anti configuration to this complex in solution on the basis of a comparison of the chemical shift value of the AsMe resonance with that found in the kinetically stable complex *anti-trans*-$[RuCl_2((RS)\text{-diars})_2]$, which we have unambiguously characterized in separate work.[12] Large chemical shift differences for the AsMe resonances are found in syn and anti isomers of this kind due to a pronounced shielding of the methyl protons by the phenyl groups in the latter structure (vide supra). A comparison of molecular models of both isomers indicates substantially less steric congestion in the anti structure. Presumably this steric factor contributes significantly to the overwhelming thermodynamic

(11) If the complex existed as predominantly $[Ni(MeCN\text{-}d_3)_2\ (SS\text{-diars})_2]^{2+}$ in MeCN-d_3, a singlet AsMe resonance would also be expected in the NMR spectrum. However, we consider rapid axial site exchange of the MeCN-d_3 in $[Ni(MeCN\text{-}d_3)(SS\text{-diars})_2]^{2+}$ more likely because of the similarity of spectroscopic data for this species and $[NiCl(SS\text{-diars})_2]^+$.

(12) Grocott, S. C.; Wild, S. B., unpublished work.

stability of the complex ion *anti*-[Ni(MeCN-d_3)((*RS*)-diars)$_2$]$^{2+}$ in solution.

(ii) Di(tertiary phosphine) Complexes. The bis(tertiary phosphine) complexes [Ni(diphos)$_2$](PF$_6$)$_2$ (Table I) were also prepared in high yield by the usual method. The initial product derived from (*RR*,*SS*)-diphos dissolved in MeCN-d_3 to give a brown solution which showed two singlet PMe absorptions (broadened by ^{31}P coupling) centered at δ 2.41 and 1.44 in the intensity ratio of 2:3, respectively. The optically active complex [Ni((*SS*)-diphos)$_2$](PF$_6$)$_2$ exhibited a broad PMe singlet at δ 1.44. The initial product derived from the racemic ligand therefore consisted of a 2:3 mixture of racemic and meso internal diastereoisomers. The ^{1}H NMR spectrum of the mixture of complexes in MeCN-d_3 was static, and indeed the two diastereoisomers could be fractionally crystallized. The meso complex was only sparingly soluble in hot methanol whereas the racemic material dissolved readily. The marked stability of the di(tertiary phosphine) complexes toward redistribution of the bidentate ligands was in direct contrast to the behavior of the corresponding di(tertiary arsine) compounds, where exchange reactions of this type were facile. Indeed, the ^{1}H NMR spectra of the separate racemic and meso di(tertiary phosphine) complexes did not alter over a 1-week period in MeCN-d_3 solution, even in the presence of free di(tertiary phosphine) ligand.

The meso di(tertiary phosphine) (*RS*)-diphos yielded the single product *anti*-[Ni((*RS*)-diphos)$_2$](PF$_6$)$_2$ under the usual reaction conditions and was isolated as an acetonitrile solvate. The PMe resonance of the pure complex occurred as a broad singlet at δ 1.30 in MeCN-d_3 which did not broaden further upon cooling to 170 K. The chemical shift value may be compared with that of δ 1.55 found for the corresponding di(tertiary arsine) compound in the same solvent. Because of the pronounced stability of di(tertiary phosphine) complexes of this type toward bidentate ligand redistribution reactions, the anti isomer appears to have been formed stereospecifically in this reaction. Alternatively, a facile intramolecular pathway for syn–anti isomerization may have existed in which the equilibrium concentration of the syn isomer was undetectably small, the anti isomer crystallizing preferentially because of its higher lattice energy.

Axial Chloro Site Exchange in Square-Pyramidal Nickel(II) Complexes. The various internal diastereoisomers of the type [NiCl(diars)$_2$]PF$_6$ and [NiCl(diphos)$_2$]PF$_6$ behaved as uniunivalent electrolytes in acetonitrile and dichloromethane solutions (Table I) and their electronic absorption spectra were typical of other square-pyramidal complexes of this type. The spectra accurately obeyed Beer's law over the concentration range 10^{-2}–10^{-4} M in dichloromethane, which indicated that the five-coordinate species were stable but not necessarily inert under these conditions. However, the ^{1}H NMR spectra of 5 × 10^{-2} M solutions of all of the five-coordinate chloro complexes in dichloromethane were markedly temperature dependent. The spectra of the optically active di(tertiary arsine and -phosphine) complexes are typical, and the methyl absorptions for each at different temperatures are reproduced in Figure 5. At 300 K both compounds show a singlet resonance for the AsMe and PMe groups. This peak broadened and eventually transformed into two equally intense signals as the temperature was lowered. Futhermore the spectra were concentration dependent, the coalescence temperature being lower for more concentrated solutions of the same complex.

This behavior is consistent with the concept of rapid site exchange of the axial chloro ligand from one side of the square plane to the other, via an intermolecular mechanism, and has been observed previously by Bosnich et al. in studies of related complexes of nickel(II) containing the tetra(tertiary arsine) bis[(3-(dimethylarsino)propyl)phenylarsino]-1,2-ethane (tetars).[5] For the complexes [NiX(tetars)]ClO$_4$ (where X = Br or I) in dichloromethane-d_2, it was found that the axial site exchange process occurred much faster in the optically active complexes than in the corresponding racemic material at the same concentration. This subtle difference in behavior of the optically active and racemic forms of the same complex, combined with the observation of concentration dependence of the NMR spectra, strongly suggested the involvement of energetically distinct diastereoisomeric transition states in the axial ligand site exchange process. Molecular models of the interacting cations in the [NiX(tetars)]ClO$_4$ system were consistent with this notion. The pairing of two square-pyramidal complex ions of the same chirality (via a μ-chloro bridge) resulted in a sterically more favorable dimer than the similar pairing of two enantiomorphic complex ions (meso dimer), in agreement with the faster rate of halogeno site exchange observed for the optically active complex. We find, however, that the racemic complex [NiCl((*RR*,*SS*)-diars)$_2$]-PF$_6$, and its phosphorus analogue, exchange *very much* faster than the corresponding optically active complexes in MeCN-d_3 at the same concentration. This property is reflected in the relative coalescence temperatures of the two forms of the same complex (Table I). The ^{1}H NMR spectra are also concentration dependent in this case, implying the existence of an intermolecular site exchange mechanism. We have rationalized this behavior in terms of the steric factors operating within the different diastereoisomeric dimer exchange intermediates. At the likely exchange distances involved, phenyl–phenyl group interactions appear to govern whether a dimer intermediate is eclipsed or staggered with respect to the alignment of the *o*-phenylene rings. Thus, the eclipsed structure (Figure 6a) is sterically less congested for interacting complex ions of the same chirality than the staggered structure (Figure 6b), which is more suitable when a meso intermediate is possible. Given this basic orientation discrimination of the *o*-phenylene rings on the basis of the minimization of phenyl–phenyl group interactions, the next most important repulsive effect in the dimer appears to involve phenyl–methyl group interactions. There are four of these in each of the dimers, but the degree of interaction is decidely less in the case of the meso dimer. Thus, the racemic square-pyramidal

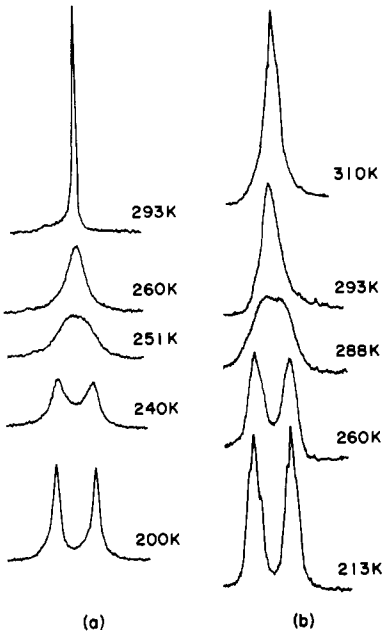

Figure 5. Variable-temperature ^{1}H NMR spectra of 0.05 M solutions of (+)-[NiCl((*SS*)-diars)$_2$]PF$_6$ (a) and (+)-[NiCl((*SS*)-diphos)$_2$]PF$_6$ (b) in CH_2Cl_2 in the methyl region.

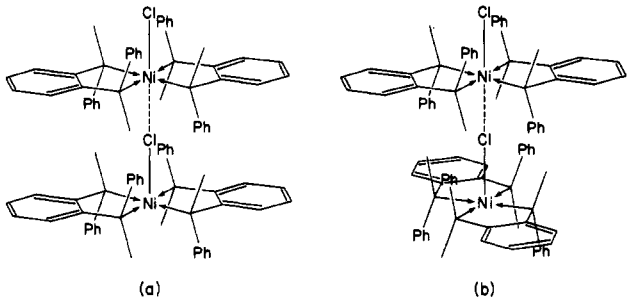

Figure 6. Diastereoisomeric dimer intermediates for axial chloro site exchange involving an eclipsed (chiral dimer) (a) and staggered (meso dimer) (b) arrangement of *o*-phenylene rings.

complexes have a choice of exchange pathways, one of which involves a meso dimer as intermediate. This appears to be a more favorable route on steric grounds and is consistent with the lower coalescence temperatures observed for the racemic forms of the complexes.

The ^{1}H NMR spectra of the complexes *anti*-[NiCl((*RS*)-diars)$_2$]PF_6 and *anti*-[NiCl((*RS*)-diphos)$_2$]PF_6 were also temperature and concentration dependent in dichloromethane solution. The singlet resonance observed for the Me groups in each complex at room temperature broadened upon cooling and split into two equally intense singlets at 240 and 278 K for the di(tertiary arsine) and di(tertiary phosphine) complexes, respectively. Furthermore, a mixture of *anti*-[NiCl((*RS*)-diphos)$_2$]PF_6 or *meso*-[NiCl((*RR*)-diphos)-((*SS*)-diphos)]PF_6 with either of the corresponding optically active or racemic di(tertiary phosphine) complexes showed the separate PMe signals of the individual rapidly exchanging square-pyramidal species at room temperature. This observation emphasized the importance of steric compatibility of interacting species during the axial chloro ligand site exchange and confirmed the structural integrity of the basic di(tertiary phosphine)nickel(II) unit in each complex during the process. However, we have shown that internal isomerization of the chelate rings provides an alternative mechanism of axial chloro site exchange in related complexes, which is of comparable energy.

Intramolecular Isomerization of Chelate Rings in Square-Pyramidal Nickel(II) Complexes. In order to unambiguously identify this process in solution, it was necessary to prepare the mixed ligand complex *rac*-[NiCl((*RS*)-diphos)((*RR*,*SS*)-diphos)]PF_6. This was obtained in high yield according to the sequence of reactions

$$[Ni(CO)_4] + (RR,SS)\text{-diphos} \xrightarrow[-2CO]{}$$

$$[Ni(CO)_2((RR,SS)\text{-diphos})] \xrightarrow[-2CO,\ -SO_2]{SO_2Cl_2}$$

$$[NiCl_2((RR,SS)\text{-diphos})] \xrightarrow{(RS)\text{-diphos}}$$

$$[NiCl((RS)\text{-diphos})((RR,SS)\text{-diphos})]Cl \xrightarrow[-NH_4Cl]{NH_4PF_6}$$

$$[NiCl((RS)\text{-diphos})((RR,SS)\text{-diphos})]PF_6$$

The variable-temperature ^{1}H NMR spectra of the complex are reproduced in Figure 7. At the slow exchange limit (216 K in CH_2Cl_2), the NMR spectrum consisted of four distinct doublets (J = 10 Hz) in the PMe region, consistent with a static square-pyramidal structure.

As the temperature of the NMR sample was raised, the signals bradened and those due to the racemic ligand eventually coalesced (T_c ca. 305 K) and reemerged as a relatively sharp singlet at 365 K (in MeCN-d_3). The spectra were concentration independent, and the observed changes were exactly reversed upon cooling of the sample. The dynamic behavior is clearly intramolecular in nature and is in agreement with

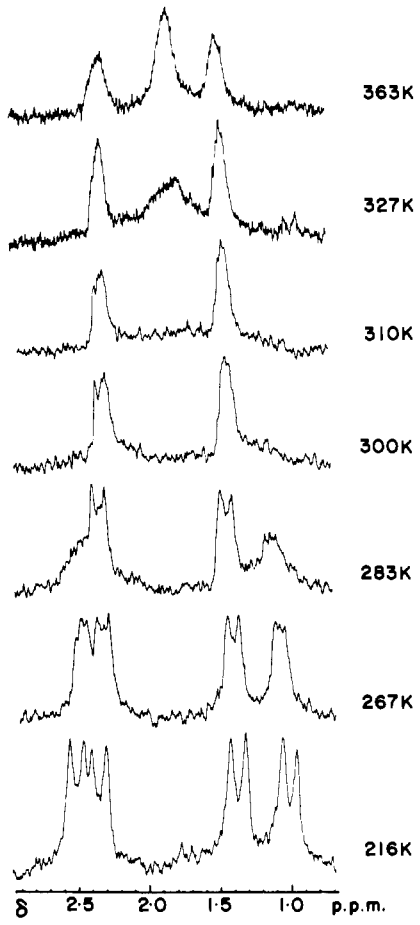

Figure 7. Variable-temperature ^{1}H NMR spectra of a 0.05 M solution of [NiCl((*RS*)-diphos)((*RR*,*SS*)-diphos)]PF_6 in the PMe region in CH_2Cl_2 (216–310 K) and in MeCN-d_3 (327–363 K).

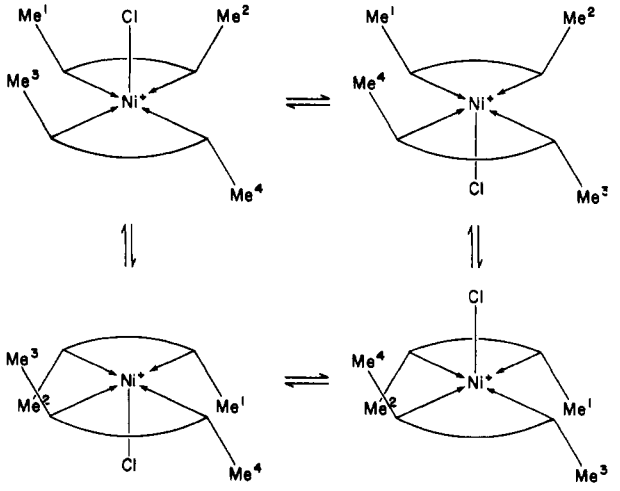

Figure 8. Stereochemical permutations of the chelate rings in the cation [NiCl((*RS*)-diphos)((*RR*,*SS*)-diphos)]$^+$.

our earlier observations concerning the kinetic stability of di(tertiary phosphine) complexes of this type. The stereochemical permutations for the chelate rings in the square-pyramidal cation are summarized in Figure 8.

It is clear from Figure 8 that the methyl groups of the meso ligand (Me^1 and Me^2) are diastereotopic in the stereochemically labile molecule due to the chirality of the racemic ligand. On the other hand, the methyl groups of the racemic ligand (Me^3 and Me^4) exchange positions during the rearrangement process. Accordingly, at the fast-exchange limit one averaged

PMe resonance (integrating as 6 H) is observed for the methyl groups of the racemic ligand, whereas the methyl groups of the meso ligand give rise to two separate signals. It is noteworthy that this internal rearrangement provides an alternative route to axial ligand site exchange. At ambient temperatures the spectrum represents an intermediate situation between the fast- and slow-exchange limits where the intramolecular process is proceeding at a rate comparable with the methyl proton relaxation rates.

The internal rearrangement of this mixed di(tertiary phosphine) complex is a degenerate transformation where interchange of the donor atoms results in a molecule which is indistinguishable from the original one. The free energy barrier to rearrangement in the cation may therefore be estimated from the coalescence temperature (T_c) of the chiral methyl resonances by use of the expression $\Delta G_\ddagger = 0.004573T_c[9.97 + \log (T_c/\Delta\nu)]$ which is derived from the Eyring equation by substitution of $\pi\Delta\nu/2^{1/2}$ for the rate constant at the coalescence temperature (T_c). An approximate value of 14.4 kcal mol^{-1} was obtained for the free energy of activation for the intramolecular rearrangement of the chelate rings in the square-pyramidal cation [NiCl((*RS*)-diphos)((*RR*,*SS*)-diphos)]$^+$ with use of this method. The spectra of the corresponding optically active complex are identical. The observation of four rather than eight methyl resonances in the low-temperature spectra of both complexes signifies unusually rapid intermolecular axial chloro site exchange in this system ($\Delta G^\ddagger < 10$ k cal mol^{-1}) or stereospecific formation of one of the two alternative square-pyramidal cations. A detailed analysis of the variable-temperature NMR spectra of these and related complexes will appear in a forthcoming article.

Experimental Section

Reactions involving air-sensitive reagents were performed in a nitrogen atmosphere with use of the Schlenk technique. Solvents were purified and degassed by distillation through a stream of pure nitrogen. The ^{1}H NMR spectra were recorded at 90 MHz by use of a Bruker HX-90 spectrometer; chemical shift values are quoted relative to Me_4Si at 308 K unless otherwise stated. The variable-temperature ^{1}H NMR spectra were recorded on the same instrument with use of Wilmad 507 PP sample tubes, temperatures being measured with a copper-constantan thermocouple located just below the sample tube and calibrated with use of a similar thermocouple held coaxially within the spinning sample tube. The specific optical rotations were measured with use of a Perkin-Elmer 141 polarimeter in a 1-dm cell thermostated at 20 °C. The electronic spectra of the complexes were obtained by means of Beckman ACTA M-Series UV/visible spectrophotometer. Molar conductivities were determined by using a Philips GM 4249 conductivity bridge in cells calibrated at 20 °C.

The diastereoisomers and optically active forms of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue were obtained according to ref 6 and 7, respectively.

***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylarsine)][(*SS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Hexafluorophosphate Acetonitrile Solvate.** A suspension of (*RR*,*SS*)-diars (2.2 g), Ni(CH_3CO_2)$_2$·4H_2O (0.65 g), and NH_4PF_6 (1.7 g) was heated under reflux with stirring for 15 min. The reaction mixture was evaporated, and the resulting purple residue heated in vacuo (100 °C (20 mmHg)). More ethanol (50 mL) was added to the residue and the process repeated until the purple color had disappeared, leaving a yellow precipitate consisting of a mixture of the desired diastereoisomeric hexafluorophosphate salts. The crude solid was washed with water, dried, and crystallized from acetonitrile solution by the addition of diethyl ether. Brown flakes of the pure meso complex crystallized as an acetonitrile monosolvate, mp 265–280 °C dec, 2.8 g (92%). Anal. Calcd for $C_{42}H_{43}As_4F_{12}NNiP_2$: C, 41.5; H, 3.6. Found: C, 41.5; H, 3.6. NMR (MeCN-d_3) (an equilibrium mixture of racemic and meso complexes) δ 1.51 (s, 80%, *rac*-AsMe), 2.33 (s, 20%, *meso*-AsMe), 7.02–7.85 (m, 28, aromatics).

$(+)_{586}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Hexafluorophosphate Acetonitrile Hemisolvate. The procedure was as above but with the use of (*RR*)-diars (0.62 g) as the ligand. Several evaporation cycles afforded an orange precipitate of [Ni((*SS*)-diars)$_2$](PF_6)$_2$ (0.7 g, 81%). The crude complex was dissolved in acetonitrile (5 mL), the solution filtered, and the filtrate diluted with methanol (30 mL). Slow evaporation of this mixture at 20 mmHg gave brown blocks of the pure enantiomer: mp 222–226 °C dec, 0.43 g (47%); $[\alpha]_D$ +220° (*c* 0.24, CH_2Cl_2). Anal. Calcd for $C_{41}H_{41.5}As_4F_{12}N_{0.5}NiP_2$: C, 41.4; H, 3.5. Found: C, 41.4; H, 3.6. NMR (MeCN-d_3) δ 1.51 (s, 12, AsMe), 7.33–7.88 (m, 28, aromatics).

(−)-Bis[(*RR*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Hexafluorophosphate Acetonitrile Hemisolvate. This complex was prepared by using (*SS*)-diars and was recrystallized in the same way as its enantiomer forming brown prisms: mp 220–226 °C dec (55%), $[\alpha]_D$ − 225° (*c* 0.31, CH_2Cl_2). NMR (MeCN-d_3) identical with that of its enantiomer.

***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Hexafluorophosphate Acetonitrile Hemisolvate.** Under similar conditions (*RS*)-diars (2.2 g) afforded crude [Ni((*RS*)-diars)$_2$](PF_6)$_2$ as a yellow powder. Recrystallization from acetonitrile-diethyl ether mixture yielded brown crystals of the pure anti isomer; mp 270–280 °C dec, 2.1 g (67%). Anal. Calcd for $C_{41}H_{41.5}As_4F_{12}N_{0.5}NiP_2$: C, 41.4, H, 3.5. Found: C, 41.3; H, 3.7. NMR (MeCN-d_3) δ 1.55 (s, 12, AsMe), 7.14–7.88 (m, 28, aromatics).

***meso*-[(*RR*)-*o*-Phenylenebis(methylphenylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate and *rac*-Bis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate.** The reaction between (*RR*,*SS*)-diphos (0.33 g), Ni(CH_3CO_2)$_2$·4H_2O (0.13 g), and NH_4PF_6 (0.17 g) under the usual conditions afforded a mixture of diastereoisomeric hexafluorophosphate salts as a yellow solid. The mixture was extracted with boiling methanol (80 mL) for 15 min and the insoluble residue separately recrystallized from acetonitrile–diethyl ether. The brick-red crystals which initially deposited lost solvent of crystallization (probably CH_3CN) during filtration, affording the pure meso complex as a yellow powder; mp >280 °C, 0.17 g (35%). Anal. Calcd for $C_{40}H_{40}F_{12}NiP_6$: C, 48.4; H, 4.1. Found: C, 48.6; H, 4.0. NMR(MeCN-d_3) δ 2.41 (br s, 12, PMe), 7.0–7.73 (m, 28, aromatics); (Me_2SO-d_6) δ 2.55 (br s, 12, PMe), 7.15–7.85 (m, 28, aromatics).

The yellow methanol extract from the original mixture was concentrated to ca. 10 mL and upon cooling deposited yellow needles of the racemic complex; mp 265–285 °C, 0.2 g (40%). Anal. Calcd for $C_{40}H_{40}F_{12}NiP_6$: C, 48,4; H, 4.1. Found; C, 48.5; H, 4.0. NMR(MeCN-d_3) δ 1.44 (br s, 12, PMe), 7.27–7.91 (m, 28, aromatics); (Me_2SO-d_6) δ 1.82 (br s, 12, PMe), 7.20–7.91 (m, 28, aromatics).

$(+)_{589}$-Bis[(*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate. A solution of (*RR*)-diphos (0.3 g) in diethyl ether (5 mL) was added dropwise to a well-stirred solution of *anti*-[Ni((*RS*)-diars)$_2$](PF_6)$_2$·0.5CH_3CN, (0.55 g) in acetonitrile (20 mL). The resulting brown solution, after filtration and dilution with diethyl ether (100 mL), afforded the product as a yellow gum. The gum could not be crystallized and was washed several times with diethyl ether and dried in vacuo (0.39 g, 84%); $[\alpha]_D$ +230° (*c* 0.22, CH_2Cl_2). NMR(MeCN-d_3) δ 1.43 (br s, 12, PMe), 7.25–7.90 (m, 28, aromatics); (Me_2SO-d_6) δ 1.82 (br s, 12, PMe), 7.22–7.91 (m, 28, aromatics).

***anti*-Bis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate Acetonitrile Solvate.** This was prepared in the same way as its arsenic analogue from (*RS*)-diphos (0.32 g). Recrystallization of the crude product from acetonitrile–diethyl ether gave the pure geometric isomer as a yellow microcrystalline solid; mp 280 °C, 0.49 g (95%). Anal. Calcd for $C_{42}H_{43}F_{12}NNiP_6$: C, 48.8; H, 4.2. Found: C, 48.7; H, 4.0. NMR(MeCN-d_3) δ 1.30 (br s, 12, PMe), 7.06–7.96 (m, 28, aromatics); (Me_2SO-d_6) 1.73 (br s, 12, PMe), 7.01–7.81 (m, 28, aromatics).

***rac*-Chlorobis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Chloride.** A solution of (*RR*,*SS*)-diars (4.1 g) in ethanol (40 mL) was added to a hot solution of [Ni(H_2O)$_6$]Cl_2 (1.2 g) in ethanol (40 mL). The resulting deep purple solution was concentrated and then gradually diluted with petroleum ether (20 mL) to give purple flakes of the product; mp 234–239 °C, 4.7 g (98%). Anal. Calcd for $C_{40}H_{40}As_4Cl_2Ni$: C, 50.6; H, 4.2. Found: C, 50.8; H, 4.7. [NMR—insufficiently soluble.]

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Chloride. A similar reaction with use of the optically active ligand (*RR*)-diars (0.5 g) gave the optically pure complex which crystallized from ethanol upon dilution with diethyl ether as bright green needles; mp 234–242 °C, 0.45 g (78%), $[\alpha]_D$ +355° (*c* 0.23,

CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_4Cl_2Ni$: C, 50.6; H, 4.2. Found: C, 50.2; H, 4.2. [NMR—insufficiently soluble.]

***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Chloride.** This compound was prepared as described in ref 6.

***rac*-Chlorobis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylarsine)]-nickel(II) Hexafluorophosphate.** A solution of NH_4PF_6 (0.3 g) in water (3 mL) was added rapidly to a well-stirred solution of the corresponding chloride (0.6 g) in ethanol (25 mL), and the mixture was quickly diluted with water (150 mL). The purple precipitate was collected, washed with water, and dried. Recrystallization from acetone by the addition of diethyl ether gave the product as purple flakes; mp 212–215 °C, 0.66 g (99%). Anal. Calcd for $C_{40}H_{40}As_4ClF_6NiP$: C, 45.3; H, 3.8. Found: C, 44.8; H 4.0. NMR(CH_2Cl_2 at 293 K) δ 1.50 (s, 12, As Me), 7.15–7.75 (m, 28, aromatics).

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphenylarsine]nickel(II) Hexafluorophosphate. This compound was prepared from the corresponding chloride (1.28 g) in the same manner as its racemic analogue. Recrystallization from acetone–diethyl ether yielded the pure enantiomer as purple needles; mp 260–265 °C, 1.2 g (85%), $[\alpha]_D$ +220° (*c* 0.16, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}As_4ClF_6NiP$: C, 45.3; H, 3.8. Found: C, 45.4; H, 3.8. NMR(CH_2Cl_2 at 298 K) δ 1.51 (s, 12, AsMe), 7.15–7.75 (m, 28, aromatics).

***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylarsine)]nickel(II) Hexafluorophosphate.** A solution of the anti chloride (1.0 g) in ethanol (50 mL) was treated with concentrated aqueous NH_4PF_6 (0.5 g) and the mixture stirred and then diluted with water (250 mL). The preciptate was dried and recrystallized from acetone–diethyl ether to give fine reddish purple needles of the pure hexafluorophosphate; mp 250–255 °C, 0.96 g (85%). Anal. Calcd for $C_{40}H_{40}As_4ClF_6NiP$: C, 45.3; H, 3.8. Found: C, 45.3; H, 3.8. NMR(CH_2Cl_2 at 291 K) δ 1.37 (s, 12, AsMe), 6.99–7.88 (m, 28, aromatics).

***meso*-Chloro[(*RR*)-*o*-phenylenebis(methylphosphine)][(*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate.** A suspension of the *meso*-bis-hexafluorophosphate) (0.3 g) and LiCl (0.02 g) in acetone (15 mL) was stirred until the reagents dissolved to give an orange solution. Dilution of the reaction mixture with diethyl ether precipitated the product as orange crystals. These were collected, washed well with water, dried, and recrystallized from acetone–diethyl ether. The pure compound formed orange rosettes; mp 230–232 °C, 0.25 g (93%). Anal. Calcd for $C_{40}H_{40}ClF_6NiP_5$: C, 54.4; H, 4.6. Found: C, 54.5; H, 4.7. NMR(CH_2Cl_2 at 298 K) δ 2.34 (br s, 12, PMe), 6.82–7.83 (m, 28, aromatics).

***rac*-Chlorobis[(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate.** This compund was prepared in a similar manner to the corresponding meso diastereoisomer and was obtained as large red prisms; mp 225–270 °C (99%). Anal. Calcd for $C_{40}H_{40}ClF_6NiP_5$: C, 54.4; H, 4.6. Found: C, 53.7; H, 4.4. NMR(CH_2Cl_2 at 293 K) δ 1.51 (br s, 12, PMe), 6.98–7.78 (m, 28, aromatics).

$(+)_{589}$-Chlorobis[(*SS*)-*o*-phenylenebis(methylphosphine)]nickel(II) Hexafluorophosphate. Solid (*RR*)-diphos (0.59 g) was added to a warm solution of $[Ni(H_2O)_6]Cl_2$ (0.23 g) in ethanol (7 mL). The resulting red solution, which contained [NiCl((*SS*)-diphos)$_2$]Cl, was cooled and treated with a solution of NH_4PF_6 (0.2 g) in water (1 mL). The mixture upon further dilution with water (30 mL) gave the product as a red precipitate which was collected, washed well with water, and dried. Recrystallization from dichloromethane–diethyl ether afforded orange rosettes of the pure enantiomer; mp 280 °C, 0.72 g (88%), $[\alpha]$ +430° (*c* 0.21, CH_2Cl_2). Anal. Calcd for $C_{40}H_{40}ClF_6NiP_5$: C, 54.4; H, 4.6. Found C, 54.5; H, 4.5. NMR(CH_2Cl_2 at 293 K) δ 1.50 (br s, 12, PMe), 6.97–7.73 (m, 28, aromatics).

***anti*-Chlorobis[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]-nickel(II) Hexafluorophosphate.** This was prepared as above, but with use of (*RS*)-diphos (0.32 g). Recrystallization of the crude product from acetone–diethyl ether yielded fine orange needles of the desired product; mp 265–278 °C, 0.41 g (93%). Anal. Calcd for $C_{40}H_{40}ClF_6NiP_5$: C, 54.4; H, 4.6. Found: C, 54.5; H, 4.5. NMR(CH_2Cl_2 at 293 K) δ 1.37 (br s, 12, PMe), 6.99–7.88 (m, 28, aromatics).

Dicarbonyl[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(0). Nickel carbonyl (2.5 mL) was added to a solution of (*RS*)-diphos (5.0 g) in dichloromethane (10 mL) and diethyl ether (100 mL). The reaction mixture turned yellow, and carbon monoxide was evolved. After 1 h, the solvent was removed and the pale yellow residue redissolved in dichloromethane (50 mL); the solution was filtered and methanol (40 mL) added. Concentration of this solution yielded the desired product as pale yellow crystals; mp 163–166 °C, 6.0 g (89%). Anal. Calcd for $C_{22}H_{20}NiO_2P_2$: C, 60.5% H, 4.6. Found: C, 60.4; H, 4.6. NMR($CDCl_3$) δ 1.98 (br s, 6, PMe), 7.48 (br s, 14, aromatics). IR (CH_2Cl_2) 2002 s, 1945 vs [ν(CO)].

***rac*-Chloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)][(*RR*,*SS*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate.** The dicarbonyl (0.5 g) was dissolved in dichloromethane (10 mL) and the solution treated with SO_2Cl_2 (0.155 g, 1 equiv) in dichloromethane (5 mL) at 0 °C under a N_2 atmosphere. At the beginning of the addition, the reaction mixture was red but became deep green toward completion, CO and SO_2 being evolved. After 20 min, (*RR*,*SS*)-diphos (0.365 g) was added whereupon the solution instantly turned burgundy red. The solvent was removed and the residue redissolved in absolute ethanol (20 mL). The addition of NH_4PF_6 (1 g) in water (2 mL) to the clear alcohol solution precipated crude product, which was thoroughly washed and dried (1.05 g). Recrystallization from dichloromethane (30 mL) by the addition of diethyl ether (20 mL) afforded the pure product as deep orange needles; mp 288–289 °C, 0.95 g (94%). Anal. Calcd for $C_{40}H_{40}ClF_6NiP_5$: C, 54.4; H, 4.6. Found: C, 54.1; H, 4.7. NMR(CH_2Cl_2 at 216 K) δ 1.06 (d, 3, J = 9 Hz, PMe), 1.30 (d, 3, J = 9 Hz, PMe), 2.39 (d, 3, J = 9 Hz, PMe), 2.53 (d, 3, J = 10 Hz, PMe), 7.07–7.67 (m, 28 aromatics).

(−)-Chloro[(*RS*)-*o*-phenylenebis(methylphenylphosphine)]-[(*RR*)-*o*-phenylenebis(methylphenylphosphine)]nickel(II) Hexafluorophosphate Dichloromethane Solvate. This was prepared in the same way as the racemic complex but with use of (*SS*)diphos; deep orange needles, mp 250–251 °C, 93% yield, $[\alpha]_D$ −197° (*c* 0.19, CH_2Cl_2). Anal. Calcd for $C_{41}H_{42}Cl_3F_6NiP_5$: C, 50.9; H, 4.4. Found: C, 51.2; H, 4.5. NMR(CH_2Cl_2) identical with the racemic material.

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Registry No. (+)-[Ni((*SS*)-diars)$_2$]$(PF_6)_2$, 77096-12-9; *meso*-[Ni((*RR*)-diars)((*SS*)-diars)]$(PF_6)_2$, 77029-23-3; *anti*-[Ni((*RS*)-diars)$_2$]$(PF_6)_2$, 77059-49-5; (+)-[Ni((*SS*)-diphos)$_2$]$(PF_6)_2$, 77029-25-5; *rac*-[Ni((*RR*,*SS*)-diphos)$_2$]$(PF_6)_2$, 77059-51-9; *meso*-[Ni((*RR*)-diphos)((*SS*)-diphos)]$(PF_6)_2$, 77059-53-1; *anti*-[Ni((*RS*)-diphos)$_2$]-$(PF_6)_2$, 77059-55-3; (+)-[NiCl((*SS*)-diars)$_2$]Cl, 77096-35-6; (+)-[NiCl((*SS*)-diars)$_2$]PF_6, 77096-37-8; *rac*-[NiCl((*RR*,*SS*)-diars)$_2$]Cl, 77059-56-4; *rac*-[NiCl((*RR*,*SS*)-diars)$_2$]PF_6, 77096-14-1; *anti*-[NiCl((*RS*)-diars)$_2$]Cl, 77059-57-5; *anti*-[NiCl((*RS*)-diars)$_2$]PF_6, 77059-59-7; (+)-[NiCl((*SS*)-diphos)$_2$]PF_6, 77029-27-7; *rac*-[NiCl-((*RR*,*SS*)-diphos)$_2$]PF_6, 77059-61-1; *meso*-[NiCl((*RR*)-diphos)-((*SS*)-diphos)]PF_6, 77059-63-3; *anti*-[NiCl((*RS*)-diphos)$_2$]PF_6, 77059-65-5; *rac*-[NiCl((*RS*)-diphos)((*RR*,*SS*)-diphos)]PF_6, 77059-67-7; (−)-[NiCl((*RS*)-diphos)((*RR*)-diphos)]PF_6, 77059-69-9; (−)-[Ni((*RR*)-diars)$_2$]$(PF_6)_2$, 77096-16-3; $Ni(CO)_2$((*RS*)-diphos), 77029-28-8; [Ni(MeCN-d_3)((*RR*,*SS*)-diars)$_2$]$^{2+}$, 77029-29-9; $Ni(CO)_4$, 13463-39-3; $[Ni(H_2O)_6]Cl_2$, 14322-49-7.