action.

The quantum yields for CH_2Cl_2 solutions of 0.02 M $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]SbF_6$ ($\phi = 0.084$) increase significantly with the addition of 0.1 M (TBA)Br ($\phi = 0.59$) or (TBA)ClO_4 ($\phi = 0.55$), consistent with the formation of the relatively more reactive $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]Br$ or $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]ClO_4$ ion pairs.

The systematic variation in the quantum yield for dichloromethane solutions with the identity of the anion present and the extent of ion pairing suggest in dichloromethane the paired anion assists in the removal of *p*-xylene *as a nucleophile*, decreasing in the order $CF_3SO_3^- > BF_4^- > Br^- \approx ClO_4^- >> PF_6^- > AsF_6^- \approx SbF_6^-$. The much smaller quantum yield values obtained for PF_6^- and especially AsF_6^- and SbF_6^-, even though these anions exhibit ion pairing to approximately the same extent as BF_4^-, indicate them to be the poorest nucleophiles studied. This result is also consistent with the poor coordinating ability of these anions.[16] The nearly constant quantum yield values obtained for AsF_6^- and SbF_6^- may be due to a substantial fraction of the photochemical reaction proceeding by nucleophilic attack of dichloromethane on the active excited state of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$. Quantum yield determinations in less nucleophilic solvents than CH_2Cl_2 such as SO_2 or SO_2ClF[17] would be needed to discern more accurately the nucleophilicities of CH_2Cl_2, PF_6^-, AsF_6^-, and SbF_6^- and to determine whether a parallel, purely dissociative pathway for arene removal also exists in this system.

Conclusions

The data presented here are consistent with arene removal reactions of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]^+$ that occur predominantly through pathways involving solvent-assisted steps (in polar, nucleophilic solvents) or anion-assisted steps (in nonpolar, weakly nucleophilic solvents). The assistance order determined in this system is $H_2O \approx$ propylene carbonate $\approx CH_3OH \gtrsim CH_3CN > CF_3SO_3^- > BF_4^- > Br^- \approx ClO_4^- >> PF_6^- > CH_2Cl_2 \approx AsF_6^- \approx SbF_6^-$.

The nature of the assistance observed for the arene replacement reaction studied here is consistent with nucleophilic attack of the medium on a LF excited state of Fe. This behavior stands in contrast to the dissociative behavior observed for LF excited states in other low-spin d^6 systems.[5] Without more detailed studies, we can only speculate that the factors that differentiate the photochemical behavior of M(η^6-arene) and analogous $M(CO)_3$ moieties are (1) the availability of alternate (η^4 or η^2) bonding modes in the M–arene system,[18] (2) the higher *total* M–η^6-arene bond energy as compared to the energy of a M–CO bond,[19] and (3) the decrease in the relative labilization gained by populating a M(arene) σ^* level as compared to a $M(CO)_3$ σ^* level.[20] This latter idea is supported by the recent crystal structure report[21] on $[(\eta^5\text{-}C_5H_5)Fe^I(\eta^6\text{-}C_6Et_6)]$ with a $(e_2)^4(a_1)^2(e_1^*)^1$ electronic configuration. The Fe^I–η^6-arene bond in this compound shows considerable thermal stability and is lengthened only 0.03 Å over the distance found for a similar Fe(II) compound.

Acknowledgment. We acknowledge the 3M Co. for the funds used to support this work. The Cary Model 17-D spectrometer was made available by funding received in part from the National Science Foundation (Grant CHE 78-23857).

Registry No. $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}p\text{-xyl})]BF_4$, 74176-24-2; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CN, 75-05-8; $CF_3SO_3^-$, 37181-39-8; BF_4^-, 14874-70-5; Br^-, 24959-67-9; ClO_4^-, 14797-73-0; PF_6^-, 16919-18-9; CH_2Cl_2, 75-09-2; AsF_6^-, 16973-45-8; SbF_6, 17111-95-4; propylene carbonate, 108-32-7.

(16) BF_4^-, ClO_4^-, and PF_6^- have all been found to form complexes with the stability order $BF_4^- \sim ClO_4^- > PF_6^-$: Mayfield, H. G.; Bull, W. E. *J. Chem. Soc. A.* **1971**, 2279. On the basis of the acidities of HMF_6 ($MF_6^- = PF_6^- < AsF_6^- < SbF_6^-$), the opposite order for the "coordination ability" of these anions would be expected: Clifford, A. F.; Beachell, H. C.; Jack, W. M. *J. Inorg. Nucl. Chem.* **1957**, *57*.

(17) (a) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202. (b) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 4752. (c) Popovych, O.; Tomkins, R. P. T. "Nonaqueous Solution Chemistry"; Wiley: New York, 1981; pp 70–72.

(18) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(19) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71. In $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, $\bar{D}(Cr\text{–}CO) \approx 26$ kcal/mol and $\bar{E}(Cr\text{–}\eta^6\text{-}C_6H_6) \approx 43$ kcal/mol.

(20) Geoffrey, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; p 229.

(21) Hamon, J.-R.; Saillard, J.-Y.; Beuze, A. L.; McClinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549.

Contribution from the Research School of Chemistry, The Australian National University, Canberra, ACT 2600, Australia

Enantiomerism in (*R**,*R**)-(±)- and (*R**,*S**)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene: Resolution of Both Diastereoisomers by Metal Complexation

GEOFFREY SALEM and STANLEY BRUCE WILD*

Received March 7, 1983

The resolution of the *R**,*R** and *R**,*S** diastereoisomers of the new asymmetric bidentate 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene has been achieved by the method of metal complexation. Fractional crystallization of internally diastereoisomeric palladium(II) complexes containing the different forms of the bidentate and ortho-metalated (*R*)-dimethyl[1-(1-ethyl)phenyl]amine (*R**,*R** diastereoisomer) or (*R*)-dimethyl[1-(1-ethyl)naphthyl]amine (*R**,*S** diastereoisomer) gives diastereoisomers from which the four enantiomers of the ligand can be individually liberated by stereospecific displacements. This is the first resolution of an asymmetric bidentate containing dissimilar asymmetric donor atoms. The optically pure enantiomers are air-stable crystalline solids with $[\alpha]_D \pm 79°$ (CH_2Cl_2) (*R**,*R**) and $[\alpha]_D \pm 15.5°$ (CH_2Cl_2) (*R**,*S**). Absolute configurations have been assigned by comparison of ^1H NMR spectra of certain internally diastereoisomeric palladium(II) complexes containing a particular enantiomer with similar compounds of known structure. Interconversions between the enantiomers of the *R**,*R** and *R**,*S* forms of the bis(tertiary) species take place under thermal conditions that do not affect the integrity of the asymmetric arsenic centers. Mineral acid catalysis does not epimerize the arsenic centers in these compounds: optically active protonated phosphonium salts are formed.

Metal complexation has been shown to be a powerful method for the resolution of chiral ligands.[1] The generality of the approach has been vividly demonstrated by the large-scale resolution of several important types of asymmetric and dis-

0020-1669/83/1322-4049$01.50/0

symmetric chelating agents. Thus, (*R**,*R**)-1,2-phenylenebis(methylphenylphosphine) (diph)[1] and its arsenic analogue (dias),[2] as well as the asymmetric bidentates (±)-methylphenyl(8-quinolyl)phosphine and -arsine,[3] have been resolved by use of easily prepared palladium(II) resolving agents containing optically active ortho-metalated dimethyl[1-(1-ethyl)phenyl]amine or dimethyl[1-(1-ethyl)naphthyl]amine. The ready liberation of the optically pure tertiary phosphines or arsines from the pure internally diastereoisomeric complexes (often with complete recovery of the resolving complex) is a feature of the method. Furthermore, determination of the absolute configuration of an asymmetric phenyl-substituted donor atom is possible by ^{1}H NMR spectroscopy if it is adjacent to an ortho-metalated carbon atom in diastereoisomeric complexes containing an enantiomer of dimethyl[1-(1-ethyl)naphthyl]amine.[3]

In this paper the resolution of the first bidentate containing two dissimilar asymmetric donor atoms is described. The *R**,*R** and *R**,*S**[4] forms of 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas) (Figure 1) have been separated and resolved into their antipodes by the method of metal complexation. The resolution of the *R**,*S** species is significant: it is the first example of a chelating agent of this geometry in optically active form. The use of optically active bidentates containing dissimilar donor atoms has important implications in the area of asymmetric synthesis, since ligands of this type are capable of exercising stereoelectronic control over the reactions of coordinated substrates.

Results and Discussion

Preparation of Ligand and Separation of Diastereoisomers. The ligand was prepared from 1,2-dichlorobenzene in two steps (Scheme I). One equivalent of Na(PMePh) at −78 °C gave

Scheme I

$$1,2\text{-}C_6H_4Cl_2 \xrightarrow{\text{Na(PMePh)}} (\pm)\text{-}1,2\text{-}C_6H_4Cl(PMePh) \xrightarrow{\text{Na(AsMePh)}} (R^*,R^*)\text{-}(\pm)\text{- and } (R^*,S)\text{-}(\pm)\text{-}C_6H_4(AsMePh)(PMePh)$$

the ortho-chloro compound in 76% yield: bp 126–128 °C (0.05 mmHg). Treatment of this substance with a tetrahydrofuran solution of the corresponding arsenide ion at the same temperature produced the bis(tertiary) species, which distilled as a viscous oil: bp 136–140 °C (0.05 mmHg); 87% yield. ^{1}H NMR spectroscopy of the distillate indicated equal quantities of the *R**,*R** (threo) and *R**,*S** (erythro) diastereoisomers (Figure 1). Fractional crystallization of the mixture from hot methanol gave one of these in 60% yield, mp 96–97 °C, although care was required in order to avoid cocrystallization of the other diastereoisomer. The mother liquor was evaporated to dryness, and the residue was reacted with an aqueous solution of nickel(II) chloride in the presence of potassium thiocyanate. A mixture of complexes of the type [Ni(SCN)(phas)$_2$]SCN resulted, from which brown prisms of a sparingly soluble isomer, mp 229–230 °C, were obtained by careful crystallization. Treatment of this compound with an excess of aqueous potassium cyanide produced the second diastereoisomer of the ligand as colorless plates: mp 69–70 °C; 58% yield. The mother liquor remaining after the isolation of the nickel complex was then reacted with an excess of cyanide to liberate the coordinated bis(tertiary) species. One more cycle of the separation procedure led to ca. 90% recovery of the two pure racemic diastereoisomers of **1**.

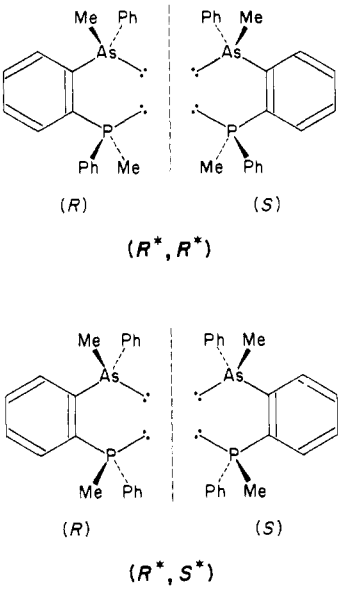


Figure 1. Enantiomerism in 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene (phas).

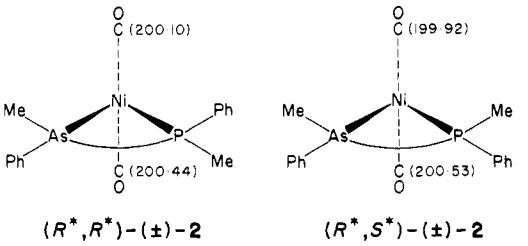


Figure 2. Dicarbonylnickel(0) derivatives of the diastereoisomers of **1**; chemical shifts of the ^{13}C NMR resonances of the carbonyl groups in parentheses (assignment arbitrary). For clarity only *R* configurations of the complexes are shown.

Table I. Some Properties of the Diastereoisomers of **1** and Related Compounds

compd	mp, °C	^{1}H NMR,[a] δ	
		-P*Me*Ph	-As*Me*Ph
(*R**,*R**)-(±)-phas	96–97	1.40 d (*J* = 4 Hz)	1.30 s
(*R**,*R**)-(±)-diph	94–95	1.42 t (*J* = 4 Hz)	
(*R**,*R**)-(±)-dias	88–88.5		1.31 s
(*R**,*S**)-(±)-phas	67–70	1.56 d (*J* = 4 Hz)	1.42 s
(*R**,*S**)-diph	79–80	1.60 t (*J* = 4 Hz)	
(*R**,*S**)-dias	61–62		1.46 s

[a] Chemical shifts relative to Me_4Si in $CDCl_3$.

Identification of Diastereoisomers. A comparison of the physicochemical properties of the pure diastereoisomers of **1** with those of (*R**,*R**)- and (*R**,*S**)-1,2-phenylenebis(methylphenylphosphine)[1] and its arsenic analogue[2] was strongly indicative of the identity of the new compounds. The relative positions of the chemical shifts due to the PMe and AsMe absorptions in the ^{1}H NMR spectra of the various compounds were particularly diagnostic (Table I). The identity of the diastereoisomers was confirmed, however, by analysis of the ^{13}C NMR spectra of the dicarbonylnickel(0) adducts (Figure 2). The shielding of the nonequivalent carbonyl groups by the phenyl groups in complex (*R**,*S**)-(±)-**2** is clearly less symmetrical than it is in diastereoisomer (*R**,*R**)]-(±)-**2**. Thus, the compound exhibiting the larger chemical shift

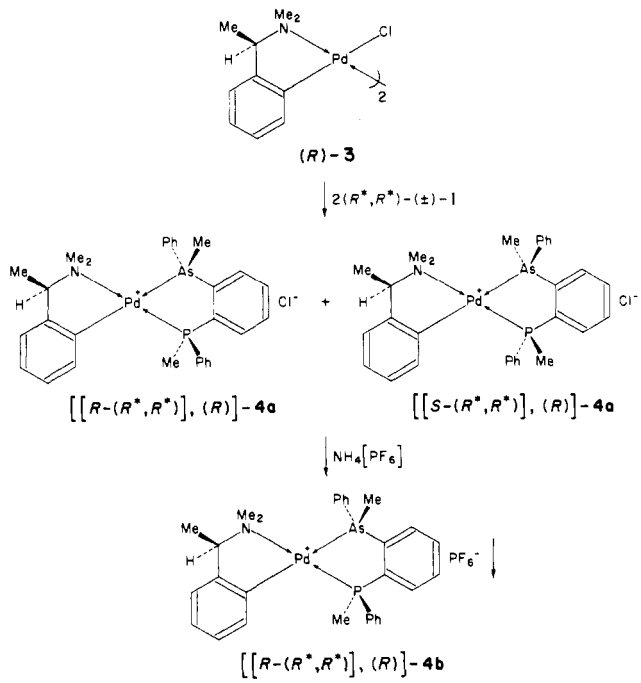
(1) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260 and references therein.
(2) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015–2021.
(3) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007–1014.
(4) The nomenclature used throughout this paper is consistent with that used by the Chemical Abstracts Service.[5] In the present situation [*R*-(*R**,*S**)]-phas denotes *R*-As,*S*-P.
(5) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1–36.

Table II. Specific Rotations and Selected ^{1}H NMR Data for Internally Diastereoisomeric Palladium(II) Complexes Containing (*R*)-Dimethyl[1-(1-ethyl)naphthyl]amine

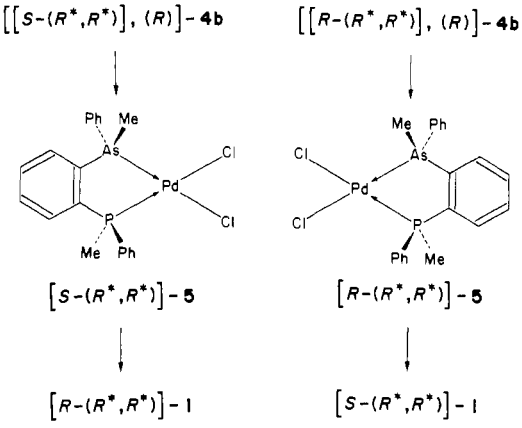
compd	specific rotation $[\alpha]_D$,[a] g/100 mL	concn, g mL^{-1}	δ[d] -As*Me*Ph	-P*Me*Ph	-NMe_2	C(7)H[e]
[[*R*-(*R**,*R**)],(*R*)]-**7b**	−402	0.69[b]	2.36 s	2.44 d (J = 10 Hz)	2.68 br s, 3.16 br d (J = 3 Hz)	
[[*S*-(*R**,*R**)],(*R*)]-**7b**	+246	0.67[c]	2.36 s	2.41 d (J = 10 Hz)	2.86 br s	6.85 d of d
[[*R*-(*R**,*S**)],(*R*)]-**7b**	−143	0.65[c]	2.32 s	2.34 d (J = 10 Hz)	2.74 br s, 3.20 br d (J = 3 Hz)	6.86 d of d
[[*S*-(*R**,*S**)],(*R*)]-**7b**	−26	0.58[c]	2.36 s	2.58 d (J = 10 Hz)	2.88 br s	

[a] Recorded at 21 °C. [b] In Me_2SO. [c] In Me_2CO. [d] Relative to Me_4Si as internal standard (solvent, Me_2SO-d_6). [e] Proton attached to C(7) of naphthalene ring.

Scheme II



Scheme III



difference between the carbonyl resonances most certainly contains the R^*,S^* diastereoisomer of the ligand. The ^{13}C NMR data for the corresponding complexes of 1,2-phenylenebis(methylphenylphosphine) (diph) are the following: (R^*,R^*)-(±)-[$Ni(CO)_2$(diph)], δ 200.6 (t, 2, J_{PC} = 4.8 Hz, 2 CO); (R^*,S^*)-(±)-[$Ni(CO)_2$(diph)], δ 200.4 (t, 1, J_{PC} = 6.5 Hz, CO), 200.8 (t, 1, J_{PC} = 4.0 hz, CO).

Resolution of (R^*,R^*)-(±)-1. A bridge-splitting reaction involving (R^*,R^*)-(±)-**1** and $(-)_{589}$-bis(μ-chloro)bis[(*R*)-2-[1-(dimethylamino)ethyl]phenyl-*C*,*N*]dipalladium(II), (*R*)-**3**, in methanol produced a solution of the pair of internally diastereoisomeric complex chlorides [[*R*-(*R**,*R**)],(*R*)]-**4a** and [[*S*-(*R**,*R**)],(*R*)]-**4a** (Scheme II). The addition of 1 equiv of aqueous NH_4PF_6 to this solution precipitated [[*R*-(*R**,*R**)],(*R*)]-**4b** in 95% yield. Recrystallization from acetone afforded the optically pure diastereoisomer as colorless prisms, $[\alpha]_D$ −300° (acetone). Diastereoisomer [[*S*-(*R**,*R**)],(*R*)]-**4b** was obtained from the mother liquor by adding more NH_4PF_6: it crystallized from methanol as fine white needles, $[\alpha]_D$ +176° (acetone). Both salts behaved as uni-univalent electrolytes in dichloromethane. The ^{1}H NMR spectra of the diastereoisomeric complexes support the structural assignment shown in Scheme II. The strong coupling of the nuclear spin of the phosphorus atom to the nonequivalent NMe groups is diagnostic of a trans arrangement of the phosphorus and nitrogen atoms. Furthermore, the coupling extends to the methine proton α to the aromatic ring ($^4J_{PH}$). No evidence of the alternative pair of diastereoisomeric complexes was found.

The method of liberation of the optically active forms of (R^*,R^*)-**1** is shown in Scheme III. Treatment of [[*R*-(*R**,*R**)],(*R*)]-**4b** or [[*S*-(*R**,*R**)],(*R*)]-**4b** in acetone with concentrated hydrochloric acid removes the optically active amine (as its hydrochloride) and produces the respective dichloropalladium(II) complexes, [*R*-(*R**,*R**)]-**5** and [*S*-(*R**,*R**)]-**5**. Reaction of these with aqueous potassium cyanide solution liberated respectively the bis(tertiary) compounds [*R*-(*R**,*R**)]-**1** and [*S*-(*R**,*R**)]-**1**, which were isolated as colorless air-stable prisms: mp 93–94 °C; $[\alpha]_D$ ±79° (CH_2Cl_2).[6] The stereospecificity of the displacement was confirmed by repreparing complexes [[*R*-(*R**,*R**)],(*R*)]-**4b** and [[*S*-(*R**,*R**)],(*R*)]-**4b** from the respective bis(tertiary) species.

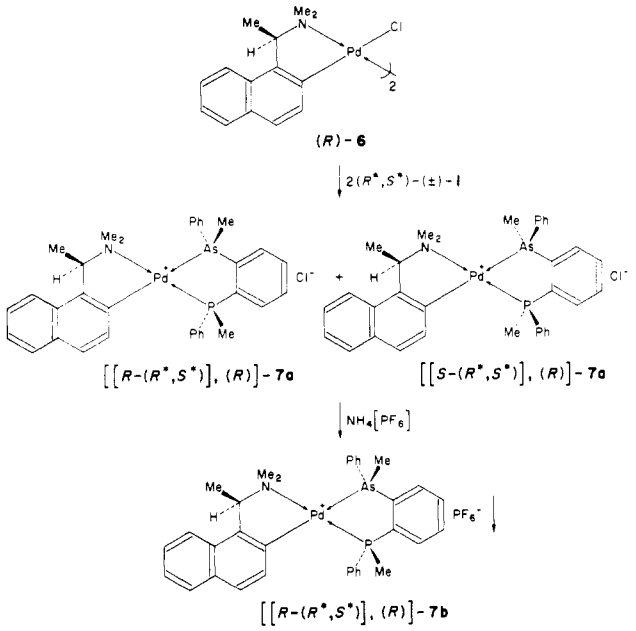
Resolution of (R^*,S^*)-(±)-1. The resolution of (R^*,S^*)-**1** was carried out as shown in Scheme IV. (Use of the resolving agent (*R*)-**3** gave an inseparable mixture of complexes.) A suspension of (*R*)-**6** and (R^*,S^*)-(±)-**1** in methanol reacted to give a pale yellow solution of the salts [[*R*-(*R**,*S**)],(*R*)],(*R*)]-**7a** and [[*S*-(*R**,*S**)],(*R*)]-**7a**. One equivalent of NH_4PF_6 selectively precipitated the complex cation [[*R*-(*R**,*S**)],(*R*)]-**7b**. Recrystallization from acetone brought this compound to purity as colorless prisms, $[\alpha]_D$ −143° (acetone). Excess NH_4PF_6 deposited [[*S*-(*R**,*S**)],(*R*)]-**7b** from the mother liquor, which had $[\alpha]_D$ −26° (acetone) after two recrystallizations from ethyl methyl ketone–diethyl ether mixture. Both complexes behave as uni-univalent electrolytes in dichloromethane and have ^{1}H NMR spectra consistent with the proposed structures (Table II).

Concentrated sulfuric acid removed the ortho-metalated naphthylamine from the internally diastereoisomeric complexes. Thus, [[*R*-(*R**,*S**)],(*R*)]-**7b** was dissolved in the concentrated acid, and the resulting solution was poured onto ice. Addition of lithium chloride produced [*R*-(*R**,*S**)]-**8**, which, after extraction into dichloromethane and recrystallization from a dichloromethane–methanol mixture, had $[\alpha]_D$

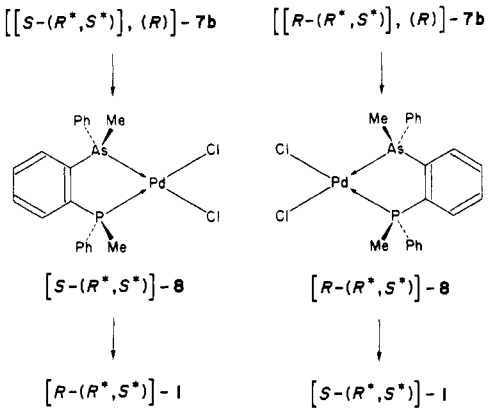
(6) The apparent inversion that takes place upon liberation of the bis(tertiary) ligand is consistent with the specification of Cahn et al. for absolute configurations.[7]

(7) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

Scheme IV



Scheme V



+10.7° (CH_2Cl_2) (Scheme V). Decomposition of [[*S*-(*R**,*S**)],(*R*)]-**7b** afforded [*S*-(*R**,*S**)]-**8** of similar purity. The optically pure tertiary amine was recovered from the initial mother liquor. Reaction of the dichloropalladium(II) complexes with cyanide liberated the optically pure enantiomers of (*R**,*S**)-**1**: mp 67–68 °C; $[\alpha]_D$ ±15.5° (CH_2Cl_2).

Absolute Configurations. Analysis of the ^1H NMR spectra of the internally diastereoisomeric complexes containing ortho-metalated (*R*)-dimethyl[1-(1-ethyl)naphthyl]amine and one or other of the four enantiomers of **1** led to an almost certain assignment of the absolute configurations of the bis(tertiary) species (Table II). The latter pair of complex cations were prepared by the usual bridge-splitting reactions and precipitated by NH_4PF_6. In an earlier investigation of related compounds we found[3] that a substantial upfield shift of the proton on C(7) of the naphthalene ring (to ca. δ 7) occurs when the neighboring coordinated phenyl-substituted phosphorus or arsenic atom has the *S* absolute configuration (Table II). The origin of the shielding effect is evident in the X-ray crystal structure of a complex containing (*R*)-dimethyl[1-(1-ethyl)-naphthyl]amine.[3] A coupling between the proton on C(7) of the naphthalene ring and the adjacent phosphorus atom (J_{PH} = 6 Hz) is also apparent in the complexes showing the upfield shift. In the corresponding complexes containing a phosphorus atom of *R* absolute configuration, this resonance is not discernible within the broad manifold of aromatic resonances.

Epimerization Studies. Epimerization of the asymmetric phosphorus centers in the various forms of **1** takes place upon heating. Thus, either [*R*-(*R**,*R*)]- or [*R*-(*R**,*S**)]-**1** is converted into an equimolar mixture of the two species upon heating to 140 °C for ca. 2 h (Figure 3). The mixture can be separated by fractional crystallization. Obviously, similar results are obtained if either [*S*-(*R**,*R**)]- or [*S*-(*R**,*S**)]-**1** is heated. It was not, however, found possible to epimerize the tertiary arsenic centers by mineral acid catalysis (as is usually the case[2]); instead, optically active protonated phosphonium salts are formed, viz. [*R*-(*R**,*R**)]-**9** and [*R*-(*S**,*S**)]-**9**. These salts are completely stable over a wide range of conditions in the presence of halide ions. The already weak basicity of the tertiary arsenic center is apparently eliminated altogether in the phosphonium salts. Details concerning the kinetics of epimerization of the asymmetric phosphorus and arsenic centers in these and related tertiary phosphines and arsines will be reported in a future paper.[8]

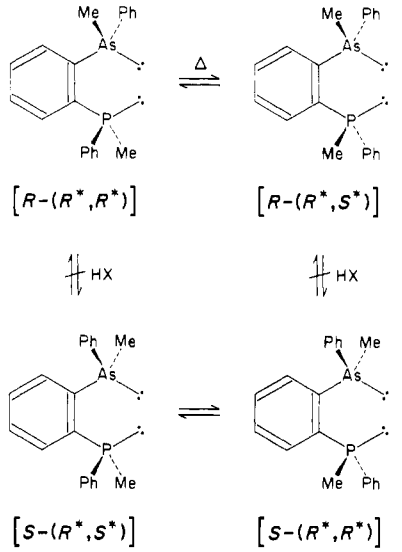


Figure 3. Interconversions between the enantiomers of **1**.

Experimental Section

General Information. Reactions involving air-sensitive compounds were run under a positive pressure of argon. ^1H NMR spectra were recorded on Varian HA-100 (100-MHz) spectrometer. A Bruker CXP-200 instrument operating at 50.3 MHz was used to obtain the ^{13}C NMR spectra. ^1H and ^{13}C NMR chemical shifts are reported as δ values relative to internal Me_4Si. Optical rotations were measured on the specified solutions in a 1-dm cell with a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the school and were found to be satisfactory for all new compounds.

The compounds [*T*-4-(*R**,*R**)]-(±)-[Ni(CO)$_2$(diph)] and [*T*-4-(*R**,*S**)]-(±)-[Ni(CO)$_2$(diph)] were prepared as previously described.[9]

(±)-1-Chloro-2-(methylphenylphosphino)benzene. A solution of Na(PMePh) was prepared from PHMePh (94.5 g) and sodium foil (17.8 g) in tetrahydrofuran (800 mL). The filtered solution was slowly added to 1,2-dichlorobenzene (112 g) in the same solvent (600 mL) at −78 °C. After the phosphide was added, the reaction mixture was warmed to room temperature and stirred overnight. The tetrahydrofuran was removed by distillation. The product was extracted into diethylether (500 mL), water (500 mL) added to dissolve the salt, the organic extract dried ($MgSO_4$), and the product recovered in the usual way. Distillation afforded the compound, as a colorless oil: bp 126–128 °C (0.05 mmHg); 136 g (76%); ^1H NMR ($CDCl_3$) δ 1.50 (d, 3, *J* = 4 Hz, PMe), 6.7–7.6 (m, 9, aromatics).

(*R,*R**)- and (*R**,*S**)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene (1).** A filtered solution of Na(AsMePh), obtained from AsHMePh (96.3 g) and sodium foil (13.5 g) in tetrahydrofuran over 2 h, was added to a well-stirred solution of (±)-1-chloro-2-(methylphenylphosphino)benzene (134.5 g) in tetrahydrofuran (800 mL) at −78 °C. The reaction mixture was then

(8) Harrowfield, J.; Salem, G.; Wild, S. B., to be submitted for publication.
(9) Roberts, N. K.; Wild, S. B. *Inorg. Chem.* **1981**, *20*, 1892–1899.

warmed to room temperature, and stirring was continued for 20 h. The usual workup (diethyl ether, water) produced the crude product, which distilled as a viscous oil: bp 136–140 °C (0.05 mmHg); 182.5 g (87%); ^{1}H NMR ($CDCl_3$) shows an equimolar mixture of the expected diastereoisomers (vide infra).

(R*,R*)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, (R*,R*)-(±)-1. The mixture of diastereoisomers (182.5 g) was dissolved in boiling methanol (2.1 L). Slow cooling of the solution produced large white prisms of a compound subsequently shown to be (R*,R*)-(±)-1: mp 96-97 °C; 55 g; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3, AsMe), 1.40 (d, 3, J = 4 Hz, PMe), 7.2–7.6 (m, 14, aromatic). The mother liquor, which was decanted from the crystals to avoid cocrystallization of the erythro diastereoisomer, was shown by ^{1}H NMR spectroscopy to contain (R*,R*)- and (R*,S*)-1 in the ratio of 1:2.5 (127.5 g).

(R*,S*)-(±)-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, (R*,S*)-(±)-1. This diastereoisomer was separated as its (thiocyanato)nickel(II) complex. A two-phase system involving the mixture of diastereoisomers (127.5 g) in dichloromethane (750 mL) and a solution of nickel(II) chloride (41.4 g) and KSCN (34 g) in water (350 mL) was shaken for ca. 30 min. The organic fraction was separated and dried ($MgSO_4$), and ethanol (700 mL) was added. The solution was then reduced in volume to ca. 600 mL. Cooling caused the sparingly soluble complex [NiSCN[(R*,S*)-1]$_2$]SCN to deposit as deep brown prisms: mp 229–230 °C; 68 g. The complex was dissolved in dichloromethane (800 mL) and treated with potassium cyanide (40 g) in water (120 mL). This liberated the R*,S* ligand, the crude form of which was isolated from the organic layer and purified by extraction into diethyl ether (600 mL) and recrystallization from methanol (800 mL): air-stable white plates; mp 69–70 °C; 53 g. The remainder of the ligand was recovered from the impure mixture of complexes and subjected to another cycle of the separation procedure. This yielded a further 27 g of (R*,R*)-1 and 25 g of (R*,S*)-1. Altogether, ca. 90% of each diastereoisomer was recovered from the original mixture.

[T-4-(R*,R*)]-(±)-Dicarbonyl[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]nickel(0), (R*,R*)-(±)-2. Nickel carbonyl (1 mL) and (R*,R*)-(±)-1 (2 g) were reacted together in diethyl ether (60 mL). After carbon monoxide evolution had ceased, the solvent was removed and the residue was recrystallized from a dichloromethane–methanol mixture to give the pure complex as pale yellow crystals: mp 142–143 °C, 2.4 g (92%); ^{1}H NMR (CD_2Cl_2) δ 1.84 (s, 3, AsMe), 1.95 (d, 3, J = 5 Hz, PMe), 7.2–7.6 (br m, 14, aromatics); ^{13}C NMR (CD_2Cl_2) δ 13.71 (d, 1, J = 7.2 Hz, AsMe), 17.82 (d, 1, J = 19.3 Hz, PMe), 128.8–148.9 (br m, 18, aromatics), 200.10 (d, 1, J = 6.4 Hz, CO), 200.44 (d, 1, J = 8.0 Hz, CO); IR (CH_2Cl_2) 2005 s, 1942 vs cm^{-1} [ν(CO)].

[T-4-(R*,S*)]-(±)-Dicarbonyl[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]nickel(0), (R*,S*)-(±)-2. This compound was prepared in the same way: it formed pale yellow plates: mp 172–173 °C; 90% yield; ^{1}H NMR (CD_2Cl_2) δ 1.84 (s, 3, AsMe), 1.97 (d, 3, J = 5 Hz, PMe), 7.2–7.6 (br m, 14, aromatics); ^{13}C NMR (CD_2Cl_2) δ 13.80 (d, 1, J = 8.0 Hz, AsMe), 17.91 (d, 1, J = 19.3 Hz, PMe), 128.7–149.0 (br m, 18, aromatics), 199.92 (d, 1, J = 7.2 Hz, CO), 200.53 (d, 1, J = 5.6 Hz, CO); IR (CH_2Cl_2) 2005 s, 1942 vs cm^{-1} [ν(CO)].

Resolution of (R*,R*)-(±)-1. Formation and Separation of Internally Diastereoisomeric Complexes. [SP-4-4-1-[R-(R*,R*)],2-(R)]-[2-[1-(Dimethylamino)ethyl]phenyl-C,N][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II) Hexafluorophosphate, [[R-(R*,R*)],(R)]-4b. Stirring of a suspension of (R*,R*)-(±)-1 (10 g) and (R)-3[2] (7.9 g) gave a pale yellow solution of the complex chlorides [[R-(R*,R*)],(R)]-**4a** and [[S-(R*,R*)],(R)]-**4a**. One equivalent of $NH_4(PF_6)$ (2.25 g) in water (10 mL) was then added, followed by a further 100 mL of the same solvent at a slower rate. The white precipitate was collected, washed with water, aqueous methanol, and diethyl ether, and then dried. Recrystallization from acetone (200 mL) gave the pure diastereoisomer: mp 235 °C dec; 9.5 g (90%); $[\alpha]_D$ −300° (c 0.83, Me_2CO); ^{1}H NMR (Me_2SO-d_6) δ 1.35 (d, 3, J = 6 Hz, CMe), 2.32 (s, 3, AsMe), 2.38 (d, 3, J = 10 Hz, PMe), 2.80 (br s, 6, Hz, CMe), 2.32 (s, 3, AsMe), 2.38 (d, 3, J = 10 Hz, PMe), 2.80 (br s, 6, NMe_2), 4.07 (m, 1, CH), 6.7–8.1 (br m, 18, aromatics); conductivity Λ_M = 43.7 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[SP-4-4-1-[S-(R*,R*)],2-(R)][2-[1-(Dimethylamino)ethyl]-phenyl-C,N][1-(methylphenylarsino)-2-(methylphenylphosphino)-benzene-As,P]palladium(II) Hexafluorophosphate, [[S-(R*,R*)],-(R)]-4b. Excess $NH_4(PF_6)$ in water precipitated this diastereoisomer from the mother liquor remaining after the separation of [[R-(R*,R*)],(R)]-**4b**. The white powder crystallized from hot methanol as fine white needles: mp 217 °C dec; 9.0 g (86%); $[\alpha]_D$ + 176° (c 0.50, Me_2CO); ^{1}H NMR (Me_2SO-d_6) δ 1.53 (d, 3, J = 6 Hz, CMe), 2.34 (s, 3, AsMe), 2.42 (d, 3, J = 10Hz, PMe), 2.72 (br s, 3, NMe), 2.83 (br s, 3, NMe), 3.77 (m, 1, CH), 6.6–8.3 (br m, 18, aromatics); conductivity Λ_M = 43.2 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[SP-4-[R-(R*,R*)]]-Dichloro[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II), [R-(R*,R*)]-5. Diastereoisomer [[R-(R*,R*)],(R)]-**4b** (9.5 g) was heated for 20 min in acetone (500 mL) containing hydrochloric acid (10 M, 11 mL). The pale yellow product crystallized upon reduction of the volume to ca. 100 mL and was recrystallized from a dichloromethane–methanol mixture. It formed colorless plates: mp >300 °C; 6.5 g (97%); $[\alpha]_D$ +79.4° (c 0.60, CH_2Cl_2); ^{1}NMR (Me_2SO-d_6) δ 2.39 (s, 3, AsMe), 2.45 (d, 3, J = 10.5 Hz, PMe), 7.4–8.1 (br m, 14, aromatics). The optically active amine was recovered as previously described.[2]

[SP-4-[S-(R*,R*)]]-Dichloro[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II), [S-(R*,R*)]-5. This compound was prepared in the same way as its enantiomer; $[\alpha]_D$ −79.4° (c 0.61, CH_2Cl_2).

[S-(R*,R*)]-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, [S-(R*,R*)]-1. Enantiomer [R-(R*,R*)]-**5** (6.5 g) in dichloromethane (500 mL) was decomposed by KCN (6.2 g) in water (100 mL). The liberated ligand was recovered from the organic layer and recrystallized from methanol. It formed air-stable white prisms: mp 93–94 °C; 4.0 g (91%); $[\alpha]_D$ −79° (c 0.67, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) identical with that of the corresponding racemic material.

Resolution of (R*,S*)-(±)-1. Formation and Separation of Internally Diastereoisomeric Complexes. [SP-4-4-1-[R-(R*,S*)],2-(R)]-[1-[1-(Dimethylamino)ethyl]naphthyl-C,N][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II) Hexafluorophosphate, [[R-(R*,S*)],(R)]-7b. A mixture of (R)-6[3] (9.3 g) and (R*,S*)-(±)-1 (10 g) was stirred in methanol (120 mL). In a short time the solids had dissolved, giving a solution of the internally diastereoisomeric complex chlorides [[R-(R*,S*)],(R)]-**7a** and [[S-(R*,S*)],(R)]-**7a**. The addition of 1 equiv of NH_4PF_6 (2.22 g) in water (5 mL) followed by another 100 mL of water (slowly) precipitated almost pure [[R-(R*,S*)],(R)]-**7b**. After being washed with water, aqueous methanol, and diethyl ether, this material was recrystallized from acetone as the pure complex: mp 226 °C dec; 10.3 g (92%); $[\alpha]_D$ −143° (c 0.65, Me_2CO); ^{1}H NMR (Me_2SO-d_6) δ 1.91 (d, 3, J = 6 Hz, CMe), 2.32 (s, 3, AsMe), 2.34 (d, 3, J = 10 Hz, PMe), 2.74 (br s, 3, NMe), 3.20 (br d, 3, J = 3 Hz, NMe), 4.72 (m, 1, CH), 6.86 (d of d, 1, J_{HH} = 9 Hz, J_{PH} = 6 Hz, C(7)H), 7.3–8.2 (br m, 19, aromatics); conductivity Λ_M = 43.9 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[SP-4-4-1-[S-(R*,S*)],2-(R)][1-[1-(Dimethylamino)ethyl]-naphthyl-C,N][1-(methylphenylarsino)-2-(methylphenylphosphino)-benzene-As,P]palladium(II) Hexafluorophosphate, [[S-(R*,S*)],-(R)]-7b. After removal of [[R-(R*,S*)],(R)]-**7b**, the original mother liquor was treated with an excess of aqueous NH_4PF_6. The fine precipitate was twice recrystallized from hot ethyl methyl ketone (ca. 40 mL) and was obtained as pale yellow plates: mp 236–7 °C dec; 10.1 g (90%); $[\alpha]_D$ −26° (c 0.58, Me_2CO); ^{1}H NMR (Me_2SO-d_6) δ 1.65 (d, 3, J = 6 Hz, CMe), 2.36 (s, 3, AsMe), 2.58 (d, 3, J = 10 Hz, PMe), 2.88 (br s, 6, NMe_2), 4.65 (m, 1, CH), 7.2–8.1 (br m, 20, aromatics); conductivity Λ_M = 39.4 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[SP-4-[R-(R*,S*)]]-Dichloro[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II), [R-(R*,S*)]-8. Compound [[R-(R*,S*)],(R)]-**7b** (5.2 g) was dissolved in sulfuric acid (18 M, 50 mL) and the solution poured onto ice. Lithium chloride (7.8 g) was then added and the solution extracted with dichloromethane. The extract was dried ($MgSO_4$) and the product obtained by the addition of methanol and slow evaporation of the dichloromethane. It was isolated as pale yellow plates: mp >300 °C; 3.3 g (96%); $[\alpha]_D$ +10.7° (c 1.13, CH_2Cl_2); ^{1}H NMR (Me_2SO-d_6) δ 2.40 (s, 3, AsMe), 2.49 (d, 3, J = 10.5 Hz, PMe), 7.3–8.1 (br m, 14, aromatics).

[SP-4-[S-(R*,S*)]]-Dichloro[1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-As,P]palladium(II), [S-(R*,S*)]-8. As

above, but by use of [[*S*-(*R**,*S**)],(*R*)]-**7b**, this complex was produced in 96% yield as pale yellow plates: mp >300 °C dec; $[\alpha]_D$ −10.7° (*c* 0.51, CH_2Cl_2).

[*S*-(*R,*S**)]-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, [*S*-(*R**,*S**)]-1.** Decomposition of [*R*-(*R**,*S**)]-**8** by the usual method liberated this enantiomer in 90% yield as white plates: mp 67–68 °C (after recrystallization from methanol); $[\alpha]_D$ +15.5° (*c* 0.42, CH_2Cl_2); ^1H NMR ($CDCl_3$) identical with that of the corresponding racemic material.

[*R*-(*R,*S**)]-1-(Methylphenylarsino)-2-(methylphenylphosphino)benzene, [*R*-(*R**,*S**)]-1.** This enantiomer was displaced from [*R*-(*R**,*S**)]-**8** by cyanide in 90% yield. It crystallized as white needles: mp 67–68 °C; $[\alpha]_D$ −15.5° (*c* 0.48, CH_2Cl_2); ^1H NMR ($CDCl_3$) identical with that of the racemic material.

[*SP*-4-4-1-[*R*-(*R,*R**)],2-(*R*)]-[1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) Hexafluorophosphate, [[*R*-(*R**,*R**)],-(*R*)]-7b.** Bridge splitting of (*R*)-**6** by [*R*-(*R**,*R**)]-**1** in methanol, followed by the addition of NH_4PF_6, produced this compound in 90% yield as colorless prisms (from acetone–diethyl ether): mp 251 °C dec; $[\alpha]_D$ −402° (*c* 0.69, Me_2CO); ^1H NMR (Me_2SO-d_6) δ 1.83 (d, 3, *J* = 6 Hz, CMe), 2.36 (s, 3, AsMe), 2.44 (d, 3, *J* = 10 Hz, PMe), 2.68 (br s, 3, NMe), 3.16 (br d, 3, *J* = 3 Hz, NMe), 4.68 (m, 1, CH), 7.1–8.1 (br m, 20, aromatics); conductivity Λ_M = 43.0 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

[*SP*-4-4-1-[*S*-(*R,*R**)],2-(*R*)]-[1-[1-(Dimethylamino)ethyl]naphthyl-*C*,*N*][1-(methylphenylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) Hexafluorophosphate, [[*S*-(*R**,*R**)],-(*R*)]-7b.** As above, but by use of [*S*-(*R**,*R**)]-**1**, this compound was isolated in 92% yield: mp 252–53 °C dec; $[\alpha]_D$ +246° (*c* 0.67, acetone); ^1H NMR (Me_2SO-d_6) δ 1.69 (d, 3, *J* = 6 Hz, CMe), 2.36 (s, 3, AsMe), 2.41 (d, 3, *J* = 10 Hz, PMe), 2.86 (br s, 6, NMe_2), 4.63 (m, 1, CH), 6.85 (d of d, 1, J_{HH} = 9 Hz, J_{PH} = 6 Hz, C(7)H), 7.3–8.4 (br m, 19, aromatics); conductivity Λ_M = 38.8 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in CH_2Cl_2 at 20 °C).

Epimerization Studies. Enantiomer [*R*-(*R**,*R**)]-**1** was heated at 140 °C for 2 h. ^1H NMR spectroscopy indicated a 1:1 mixture of [*R*-(*R**,*R**)]- and [*R*-(*R**,*S**)]-**1**. Recrystallization from hot methanol gave a sample of [*R*-(*R**,*R**)]-**1**, mp 93–94 °C. Enantiomer [*R*-(*R**,*S**)]-**1** was isolated via its (thiocyanato)nickel(II) complex, mp 233–4 °C.

Enantiomer [*S*-(*R**,*S**)]-**1** was similarly converted into a 1:1 mixture of itself and [*S*-(*R**,*R**)]-**1** as evidenced by ^1H NMR spectroscopy and isolation of the components.

Protonation Reactions. [*R*-(*R,*R**)]-Methyl[2-(methylphenylarsino)phenyl]phenylphosphonium Tetrafluoroborate, [*R*-(*R**,*R**)]-9.** A solution of [*R*-(*R**,*R**)]-**1** (0.5 g) in dichloromethane (50 mL) was treated with aqueous HBF_4 (40% w/w, 5 mL). The mixture was shaken for 5 min and the organic layer separated, washed with water, and dried ($MgSO_4$). The product was isolated from the organic phase. Recrystallization from a dichloromethane–diethyl ether mixture gave white needles: mp 163–164 °C; 0.54 g (87%); $[\alpha]_D$ +99.8° (*c* 0.46, CH_2Cl_2); ^1H NMR at −90 °C (CD_2Cl_2) δ 1.03 (s, 3, AsMe), 2.62 (br d, 3, PMe), 7.10–8.20 (br m, 14, aromatics), 8.45 (br d, 1, *J* = 530 Hz, PH) (PH not observed at 34 °C).

[*R*-(*R,*S**)]-Methyl[2-(methylphenylarsino)phenyl]phenylphosphonium Tetrafluoroborate, [*R*-(*R**,*S**)]-9.** This salt was prepared from [*R*-(*R**,*S**)]-**1** in 90% yield by the method described above. It was isolated as white needles: mp 132–133 °C; $[\alpha]_D$ +37.9° (*c* 0.42, CH_2Cl_2); ^1H NMR at −90 °C (CD_2Cl_2) δ 1.42 (s, 3, AsMe), 2.59 (br d, 3, PMe), 6.85–8.36 (br m, 14, aromatics), 8.62 (br d, 1, *J* = 527 Hz, PH)(PH not observed at 34 °C).

No evidence of epimerization of the tertiary arsenic centers in either of the phosphonium salts was found upon heating to 80 °C in 1,2-dichlorobenzene in the presence of HBr.

Registry No. (*R**,*R**)-(±)-**1**, 87711-52-2; (*R**,*S**)-(±)-**1**, 87711-53-3; [*S*-(*R**,*R**)]-**1**, 87760-08-5; [*R*-(*R**,*R**)]-**1**, 87760-09-6; [*S*-(*R**,*S**)]-**1**, 87760-10-9; [*R*-(*R**,*S**)]-**1**, 87760-11-0; (*R**,*R**)-(±)-**2**, 87711-57-7; (*R**,*S**)-(±)-**2**, 87760-14-3; (*R*)-**3**, 73089-54-0; [[*R*-(*R**,*R**)],(*R*)]-**4a**, 87728-20-9; [[*S*-(*R**,*R**)],(*R*)]-**4a**, 87760-27-8; [[*R*-(*R**,*R**)],(*R*)]-**4b**, 87711-59-9; [[*S*-(*R**,*R**)],(*R*)]-**4b**, 87760-16-5; [*R*-(*R**,*R**)]-**5**, 87711-60-2; [*S*-(*R**,*R**)]-**5**, 87760-17-6; (*R*)-**6**, 80145-77-3; [[*R*-(*R**,*S**)],(*R*)]-**7a**, 87760-28-9; [[*S*-(*R**,*S**)],(*R*)]-**7a**, 87760-75-6; [[*R*-(*R**,*S**)],(*R*)]-**7b**, 87711-62-4; [[*S*-(*R**,*S**)],(*R*)]-**7b**, 87760-19-8; [[*R*-(*R**,*R**)],(*R*)]-**7b**, 87760-23-4; [[*S*-(*R**,*R**)],(*R*)]-**7b**, 87760-25-6; [*R*-(*R**,*S**)]-**8**, 87760-20-1; [*S*-(*R**,*S**)]-**8**, 87760-21-2; [*R*-(*R**,*R**)]-**9**, 87760-12-1; [*R*-(*R**,*S**)]-**9**, 87760-13-2; [NiSCN-[(*R**,*S**)-**1**]$_2$]SCN, 87711-56-6; (*R**,*R**)-(±)-[Ni(CO)$_2$(diph)], 87760-26-7; (*R**,*S**)-(±)-[Ni(CO)$_2$(diph)], 77029-28-8; (*R**,*R**)-(±)-dias, 55289-90-2; (*R**,*S**)-diph, 72091-02-2; (*R**,*S**)-dias, 55289-91-3; PHMePh, 6372-48-1; AsHMePh, 53979-86-5; (±)-1-chloro-2-(acetylphenylphosphino)benzene, 87711-54-4; 1,2-dichlorobenzene, 95-50-1.

Contribution from the Research School of Chemistry,
The Australian National University, Canberra, ACT 2600, Australia

Stereochemistry and Dynamic Properties of Tetrahedral Gold(I) Complexes Containing Chiral Phosphorus and Arsenic Bidentates

JUDITH A. L. PALMER and STANLEY BRUCE WILD*

Received March 7, 1983

Bis(bidentate)gold(I) complexes containing the diastereoisomers and enantiomers of the ligands 1,2-phenylenebis(methylphenylphosphine) and its arsenic analogue and of 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene have been prepared and their stereochemistry and dynamic properties investigated by ^1H NMR spectroscopy. Rapid redistribution of the bidentates occurs in the complexes of the bis(tertiary arsine) and in those of the mixed-donor ligand, but in complexes of the bis(tertiary phosphine) redistribution is slow enough to allow separation of racemic and meso complexes by fractional crystallization. Furthermore, variable-temperature ^1H NMR studies of complexes of the type (±)-[Au((*R**,*S**)-bidentate)$_2$]PF_6 indicate facile epimerization of the tetrahedral gold center.

Introduction

Whereas a considerable expansion in the study of gold chemistry has taken place in recent years, notably concerning aspects of organometallic and of cluster compounds,[1] very little additional work on classical bis(bidentate)gold(I) systems has been reported since the pioneering studies of Nyholm[2] and of Mann.[3,4] This earlier work did not concern itself with the dynamics of the tetrahedral cations in solution, although the

(1) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 728.

(2) Harris, C. M.; Nyholm, R. S. *J. Chem. Soc.* **1957**, 63.
(3) Cochran, W.; Hart, F. A.; Mann, F. G. *J. Chem. Soc.* **1957**, 2816. Hart, F. A.; Mann, F. G. *Ibid.* **1957**, 2828.
(4) Davis, M.; Mann, F. G. *J. Chem. Soc.* **1964**, 3791.

0020-1669/83/1322-4054$01.50/0