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Asymmetric Synthesis of Bis(tertiary arsines): Highly Stereoselective Alkylations of Diastereomers of a Chiral Phosphine-Stabilized Bis(arsenium triflate)

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The addition of organolithium reagents to an equilibrating mixture of diastereomers of a phosphine-stabilized 1,2-ethanediylbis(phenylarsenium triflate) containing chiral arsenic stereocenters and an enantiomerically pure, atropisomeric tertiary phosphepine derived from lithiated (a*R*)-2,2′-dimethyl-1,1′-binaphthalene generates unequal mixtures of diastereomers and enantiomers of chelating 1,2-ethanediylbis(tertiary arsines), chiral at arsenic, with liberation of the (aR_P)-phosphepine. Thus, the addition of methyllithium in diethyl ether at −95 °C to a dichloromethane solution of the complex (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-[(R_3P)PhAsCH_2CH_2AsPh(PR_3)](OTf)$_2$, where R_3P is (aR_P)-[2-(methoxymethyl)phenyl]phosphepine, generates (R^*_{As},R^*_{As})-(±)-1,2-ethanediylbis(methylphenylarsine) in 78% diastereoselectivity and 95% enantioselectivity in favor of the (R_{As},R_{As}) enantiomer. Under similar conditions, the addition of *n*-butyllithium in hexanes to a solution of the bis(phosphepine-stabilized)-diarsenium triflate at −95 °C gives the corresponding (R^*_{As},R^*_{As})-(±)-1,2-ethanediylbis[(*n*-butyl)phenylarsine) in 77% diastereoselectivity and 93% enantioselectivity in favor of the (R_{As},R_{As}) enantiomer.

Introduction

Chiral tertiary phosphines are of great importance as auxiliaries in homogeneous, metal-catalyzed asymmetric syntheses. Although the pioneering work in the field focused on the use of *P*-chiral mono- and diphosphines,[1,2] the difficulty of synthesizing and resolving tertiary phosphines chiral at phosphorus soon led to investigations of the use of chelating C_2-bis(diphenylphosphines) in which the chirality resided in a spacer group between the two phosphine groups and was transmitted to the coordinated substrate by a dissymmetric edge−face array of two C_2-related pairs of phenyl groups on the phosphorus atoms. Apart from the high enantioselectivities achieved with many of the C_2-bis(diphenylphosphines), the chief advantage of the bis(diphenylphosphines) was their ready preparation from C_2-diols derived from enantiomerically pure compounds in the natural pool.[3] Nevertheless, there are reactions that proceed with greater efficiency when the phosphorus stereocenter is itself chiral.[4] There are also examples of asymmetric syntheses where *As*-chiral tertiary arsines out-perform the phosphorus isosteres.[5] In view of our long-standing interest in the synthesis and resolution of arsines chiral at arsenic,[6] we have now embarked on a program concerned with the asymmetric synthesis of chiral tertiary arsines.[7] Tertiary arsines are less air-sensitive than tertiary phosphines and are frequently easier to synthesize and liberate from metal complexes used for their resolution, which is the current preferred method for the synthesis of *P*- and *As*-chiral phosphines and arsines of high enantiomeric purity.[6]

We recently reported the asymmetric synthesis of (*S*)-(+)-*n*-butylmethylphenylarsine by the addition of *n*-butyllithium at low temperature to a dichloromethane solution of a phosphine-stabilized methylphenylarsenium salt in

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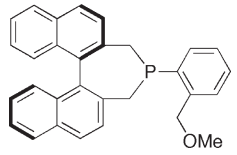
which the phosphine was an enantiomerically pure phosphepine derived from (a*R*)-1,1′-binaphthol, (aR_P)-**1**. Thus, (S_{As})-(*n*-butyl)methylphenylarsine was synthesized in high yield and 85% enantioselectivity (70% enantiomeric excess) by the addition of *n*-butyllithium to a dichloromethane solution of (aR_P,R_{As})/(aR_P,S_{As})-[**1**→AsMePh]PF_6 at −95 °C.[7] Here we report our results concerning the asymmetric synthesis of *As*-chiral 1,2-ethanediylbis(tertiary arsines) by the addition of organolithium reagents to phosphine-stabilized 1,2-ethanediylbis(phenylarsenium triflates).



(aR_P)-**1**

Results and Discussion

General Considerations and Methodology. Phosphine-stabilized arsenium hexafluorophosphates are usually air- and moisture-stable solids that can be prepared in a two-phase system in which a dichloromethane solution of a tertiary phosphine and a secondary iodoarsine is exposed to aqueous ammonium or potassium hexafluorophosphate (eq 1).[8] When the complexes or reactants are moisture sensitive, however, phosphine-stabilized arsenium complexes can be prepared by the addition of trimethylsilyl triflate (eq 2)[9−11] or thallium(I) hexafluorophosphate (eq 3)[12] to a solution of a secondary chloroarsine containing the phosphine.[9] These methods are expedient routes to phosphine-stabilized phosphenium,[13] stibenium,[12,14] and bismuthenium[12] salts, as well as arsine-stabilized arsenium,[9,15] stibenium,[16] and bismuthenium[16] salts.

$$R_3P + IAsR_2 \underset{CH_2Cl_2}{\rightleftharpoons} [R_3P{\rightarrow}AsR_2]I$$

$$\xrightarrow[H_2O]{MPF_6} [R_3P{\rightarrow}AsR_2]PF_6 \quad (1)$$

$$R_3P + ClAsR_2 \xrightarrow[-Me_3SiCl]{Me_3SiOTf} [R_3P{\rightarrow}AsR_2]OTf \quad (2)$$

$$R_3P + ClAsR_2 \xrightarrow[-TlCl]{TlPF_6} [R_3P{\rightarrow}AsR_2]PF_6 \quad (3)$$

Angular, six-electron, arsenium ions of the type $R^1R^2As^+$ are prochiral: addition of a phosphine to the *pro-R* or *pro-S* face of the unsymmetrical arsenium ion will generate a phosphine-stabilized arsenium cation of the type (±)-[$R_3P{\rightarrow}AsR^1R^2]^+$, which has a structure based on the trigonal pyramid in which the arsenic−*carbon* atoms of the R groups of the arsenium ion and the lone pair of electrons occupy the base and the phosphine-*P* atom the apex.[8] The absolute configurations of the enantiomers of the chiral cation can be assigned by viewing the structure down the axis containing the ligand of lowest Cahn−Ingold−Prelog (CIP) priority (the lone pair of electrons, priority 4) and observing the direction of rotation of the remaining ligands of priorities 1 → 3 at the corners of the triangular face at the base of the pyramid.[17] Furthermore, since the phosphorus−arsenic bond in a phosphine-stabilized arsenium complex is labile, the enantiomers of the chiral complex will be in equilibrium through dissociation of the phosphine.[8] For (aR_P,R_{As})/(aR_P,S_{As})-[**1**→AsMePh]PF_6, the slow exchange limit for phosphine exchange is reached at −70 °C, as determined by variable temperature ^{1}H NMR spectroscopy based on the observation of ^{31}P coupling to the arsenic−methyl protons.[7]

The phosphine in a phosphine-stabilized arsenium complex of the type (±)-[$R_3P{\rightarrow}AsR^1R^2]^+$ is readily displaced by the *n*-butyl anion in an S_N2-type substitution reaction that results in the synthesis of a chiral tertiary arsine (with displacement of the phosphine) having the configuration at arsenic that corresponds to the configuration of the enantiomer of the substrate phosphine-stabilized arsenium cation.[7] In the reaction of (aR_P,R_{As})/(aR_P,S_{As})-[**1**→AsMePh]PF_6 with *n*-butyllithium, however, the enantioselectivity of the reaction is less than the diastereoselectivity of coordination of the phosphine at the reaction temperature (85% vs 97%, respectively), apparently because of indiscriminate attack of the nucleophile on the more reactive, dissociated methylphenylarsenium ion.[7]

A key element in the diastereofacial discrimination of the prochiral methylphenylarsenium ion by (aR_P)-**1** is the 2-(methoxymethyl)phenyl substituent, the oxygen atom of which interacts with both the arsenic and phosphorus atoms and hinders rotation around the arsenic−phosphorus bond. This anchimeric interaction weakens the arsenic−phosphorus bond by a destabilizing chelate effect, which is indicated by a lengthening of the appropriate bonds in the complexes containing 2-(methoxymethyl)phenyl-substituted phosphines.[7,9] Detailed NMR investigations and density functional theory (DFT) calculations on the diaster-

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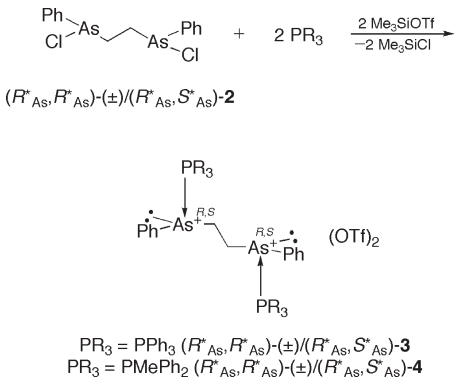
Scheme 1



eomers (aR_P,R_{As})/(aR_P,S_{As})-[**1**→AsMePh]$^+$ indicated a very high propensity of (aR_P)-**1** for coordination to the *pro*-*S* face of the methylphenylarsenium ion.[7]

Model Complexes. (a). Syntheses. The addition of trimethylsilyl triflate to a dichloromethane solution of (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-1,2-ethanediylbis(chlorophenylarsine), (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**2**, containing triphenylphosphine or methyldiphenylphosphine produced the corresponding bis(phosphine-stabilized) diarsenium triflates (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**3** or -**4** after evaporation of the solvent and trimethylsilyl chloride byproduct (Scheme 1). The salts crystallized readily from dichloromethane by the addition of diethyl ether, but were sensitive to hydrolysis, unlike closely related monoarsenium salts.[8]

(b). NMR Spectroscopy. Because of the lability of the As−P bonds in (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**3** and -**4**, the complexes exist in solution as equilibrium mixtures of two diastereomers (Scheme 2). At elevated temperatures, As−P bond dissociation in the complexes is fast on the NMR time-scale and the resonances for the individual diastereomers are not distinguishable, but as the temperature is lowered the averaged resonances broaden and split into the resonances of the individual diastereomers at the slow exchange limit. The ^{31}P{^{1}H} NMR spectra of (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**3** and -**4** in dichloromethane-d_2 at 25 °C consist of sharp singlet peaks at 17.45 and 12.91 ppm, respectively. Triphenylphosphine is a weak ligand for arsenium ions[18] and at −95 °C only minor splitting of the ^{31}P{^{1}H} NMR peak for the diastereomers (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**3** is evident. Alkylphosphines form more stable adducts, however, and the ^{31}P{^{1}H} NMR resonance for (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**4** broadens and coalesces as the temperature is lowered and separates into two peaks of equal intensity with baseline separation at −50 °C that correspond to the individual diastereomers (Figure 1). By substitution of these values into the equation $\Delta G^{\ddagger}_c = 19.14\ T_c\ (10.32 + \log T_c/K_c)$, where T_c is the coalescence temperature and $K_c = 2.22\ \Delta\nu\ s^{-1}$ is the rate of site exchange in hertz at the slow exchange limit,[19] the free energy of activation for phosphine dissociation in (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**4** is calculated to be about 55 kJ mol^{-1}. This value for $\Delta G^{\ddagger}_c$ is similar to the value calculated for phosphine dissociation in (±)-[PhMe$_2$P→AsMePh]OTf in the same solvent, namely, 60 kJ mol^{-1}.[9]

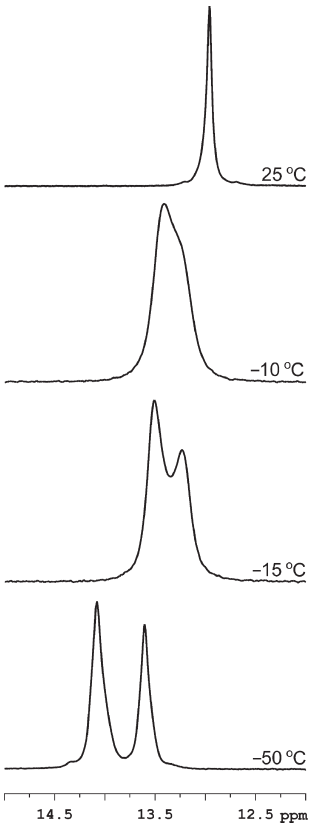
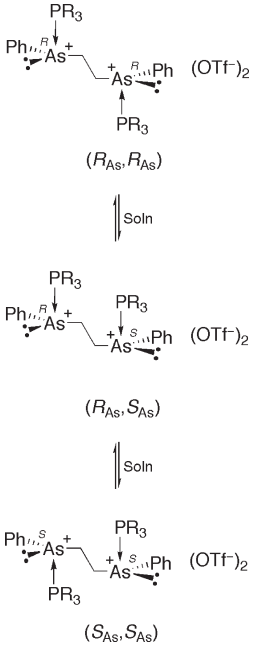


Figure 1. Variable temperature ^{31}P{H} NMR spectra (121.47 MHz) in dichloromethane-d_2 of (R*$_{As}$,R*$_{As}$)-(±)/(R*$_{As}$,S*$_{As}$)-**4**.

Scheme 2



(c). Crystal Structure. The diastereomer (R*$_{As}$,S*$_{As}$)-**4** crystallizes from dichloromethane−diethyl ether by an

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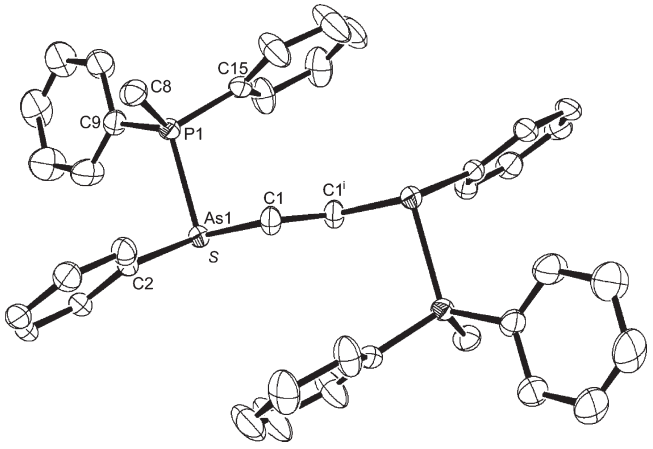

Figure 2. Structure of cation of (R^*_{As},S^*_{As})-**4** (hydrogen atoms omitted for clarity) showing 30% probability ellipsoids. Selected bond lengths (Å) and interbond angles (deg): As1−P1 = 2.3239(12), As1−C1 = 1.986(4), As1−C2 = 1.958(4), P1−C8 = 1.798(5), P1−C9 = 1.794(4), P1−C15 = 1.796(5), C1−C1^i = 1.527(8), P1−As1−C1 = 94.29(15), P1−As1−C2 = 97.22(13), C1−As1−C2 = 100.15(18), As1−P1−C8 = 113.81(17), As1−P1−C9 = 106.45(15), As1−P1−C15 = 109.24(17), C1^i−C1−As1 = 109.6(4).

asymmetric transformation of the second kind[19b] as colorless prisms in the monoclinic space-group $P2_1/c$; the structure of the cation is shown in Figure 2. The crystallographic asymmetric unit consists of half of the bis(phosphine-stabilized) diarsenium dication and one triflate ion related by a crystallographic inversion center; the triflate counterion is disordered. The As−P distance of 2.3239(12) Å in the complex is longer than the sum of the covalent radii for the two main group elements, namely, 2.29 Å,[20] and compares closely with the value of 2.3402(8) Å measured for the corresponding bond in (±)-[$PhMe_2P\rightarrow AsMePh$]OTf.[9] The C1−As1−C2 angles in the cation are 100.15(18)°, and the As−P bonds are almost orthogonal to the plane of the arsenium ion, namely, P1−As1−C1 = 94.29(15)° and P1−As1−C2 = 97.22(13)°.

Enantiomeric Purity and Absolute Configuration. (a). Reference Compounds. The stereoisomeric composition of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-ethanediylbis(methylphenylarsine), (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5**, was determined by the reaction of ligand mixture, which was prepared by a modification of the literature synthesis,[21] with enantiomerically pure (S_P,S_P)-[Pt(diphos)$(OTf)_2$], (S_P,S_P)-**6**;[22] the products of this facile displacement reaction are the diastereomeric salts (S_P,S_P)(R_{As},R_{As})- and (S_P,S_P)(S_{As},S_{As})-**7**, which are derived from (R^*_{As},R^*_{As})-(±)-**5** and have C_2 symmetry, and (S_P,S_P)(R_{As},S_{As})-**7**, which is derived from (R^*_{As},S^*_{As})-**5** and has C_1 symmetry (Scheme 3, R = Me). [Note that coordination of an *As*-chiral arsine to a metal is stereospecific: the apparent inversion of configuration that takes place at arsenic when a chiral arsine coordinates to an element of higher atomic number than 12 is a consequence of the Cahn−Ingold−Prelog (CIP) rules.[17,19b] Upon coordination to the palladium, the lone pair on the free arsine of CIP priority 4 is replaced by a ligand (the metal) of CIP priority 1.] The $^{31}P\{^1H\}$ NMR spectrum of the mixture of C_2 diastereomers of the complex will consist of two singlets (along with the satellites due to the coupling with the ^{195}Pt nuclei of 33.8% abundance[23]); the C_1 diastereomer of the complex exhibits in its $^{31}P\{^1H\}$ NMR spectrum a pair of doublets for the two non-equivalent phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum in dichloromethane-d_2 of the mixture of diastereomers (S_P,S_P)(R_{As},R_{As})/(S_P,S_P)(S_{As},S_{As})/(S_P,S_P)(R_{As},S_{As})-**7**, which were obtained from the reaction of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5** (1/1) with (S_P,S_P)-**6** in dichloromethane, is shown in Figure 3(a). The stereoisomeric composition of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-ethanediylbis[(*n*-butyl)phenylarsine], (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8**, was determined in the same manner; thus, the reaction of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8**, which was prepared by a modification of literature procedures,[24] with (S_P,S_P)-**6** in dichloromethane resulted in the diastereomeric mixture (S_P,S_P)(R_{As},R_{As})/(S_P,S_P)(S_{As},S_{As})/(S_P,S_P)-(R_{As},S_{As})-**9** (Scheme 3, R = *n*-Bu), as indicated in the $^{31}P\{^1H\}$ NMR spectrum of the mixture shown in Figure 4(a).

The diastereomers of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5** were separated by flash column chromatography of the complexes (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-[Pd(**5**)Cl_2], which were prepared by the reaction of the ligand with palladium (II) chloride in methanol containing excess lithium chloride.[25] The complex (R^*_{As},R^*_{As})-(±)-[Pd(**5**)Cl_2] was the first compound to be eluted from the silica column with dichloromethane−tetrahydrofuran (95/5 v/v). The racemic diastereomer of the diarsine, (R^*_{As},R^*_{As})-(±)-**5**, was liberated from (R^*_{As},R^*_{As})-(±)-[Pd(**5**)Cl_2] by treatment with an aqueous sodium cyanide solution and was distilled with retention of configuration at arsenic, bp = 168−170 °C (0.2 mmHg) [Lit.[25] 156−158 °C (0.1 mmHg)].

The chiral ligand (R^*_{As},R^*_{As})-(±)-**5** was resolved by complexation with the enantiomerically pure platinum complex (S_P,S_P)-**6**; the two diastereomers resulting, (S_P,S_P)(R_{As},R_{As})- and (S_P,S_P)(S_{As},S_{As})-**7**, were separated by fractional crystallization from methanol by the addition of diethyl ether. After two recrystallizations of the mixture, the less-soluble diastereomer was obtained as colorless needles that exhibited in chloroform-*d* a single resonance at 39.48 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The identity and absolute configuration of the diastereomer was determined by a single-crystal X-ray structure analysis. The molecular structure of the cation of the complex is shown in Figure 5. The absolute configuration of the arsenic stereocenters in the complex are (R_{As},R_{As}) based on the known absolute configuration of the resolving complex (S_P,S_P)-**6** and refinement of the Flack parameter. Thus, the free diarsine has the (S_{As},S_{As}) configuration.

The diastereomers of the bis[(*n*-butyl)phenylarsine], (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8**, could not be separated by flash chromatography of the complex (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-[Pd(**8**)Cl_2] under conditions similar to those used for the separation of the bis(methylphenylarsine).[26]

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(26) The diastereomers of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8** can be recovered following tedious mechanical separation of the complexes (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-[Pd(**8**)Cl_2].[21]

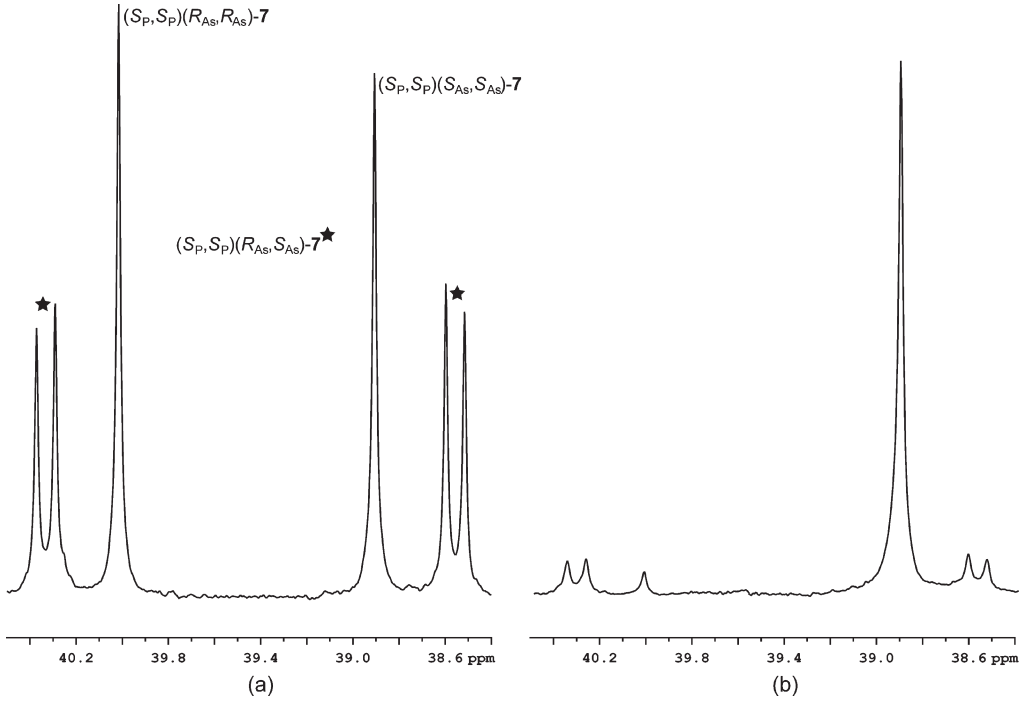
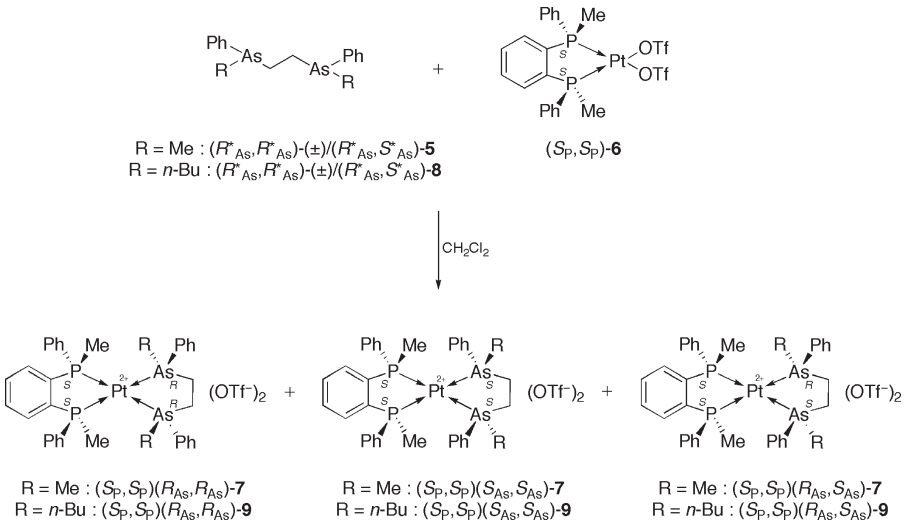


Figure 3. $^{31}P\{^{1}H\}$ NMR spectra (121.47 MHz, 25 °C) spectra in dichloromethane-d_2 of the diastereomers (S_P,S_P)(R_{As},R_{As})/(S_P,S_P)(S_{As},S_{As})/(S_P,S_P)(R_{As},S_{As})-**7** arising from the reaction of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5** with a stoichiometric amount of the reference complex (S_P,S_P)-**6** (a) and the corresponding spectrum resulting from the asymmetric synthesis (b).

Scheme 3



Thus, the configuration of the major stereoisomer of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8** arising from the asymmetric synthesis was assumed to be the same as that observed in the synthesis of the bis(methylphenylarsine) and is in agreement with previous results concerning alkylations of a closely related mono(phosphepine-stabilized) arsenium complex.[7]

Bis(chiral phosphine-stabilized) Diarsenium Complexes. (a). Synthesis. The bis(phosphine-stabilized) diarsenium salt (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** was isolated in 65% yield from the reaction between the phosphepine (aR_P)-**1** (2.1 equiv), (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (1 equiv), and trimethylsilyl triflate (2.1 equiv) in dichloromethane (Scheme 4). The moisture-sensitive salt (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** crystallized from the equilibrating mixture of diastereomers in 65% yield as fine, feather-like clumps of needles from dichloromethane−diethyl ether having mp = 240−242 °C and $[\alpha]_D^{25}$ = +76 (c 1.0, CH_2Cl_2). A number of attempts at growing crystals of the complex suitable for X-ray crystallography were unsuccessful.

(b). NMR Spectra. The $^{31}P\{^{1}H\}$ NMR spectrum of (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})-(aR_P)-**10** in dichloromethane-d_2 at 25 °C contains three overlapping peaks between 39.6 and 40.2 ppm and a singlet at 17.8 ppm that correspond to a mixture of the three diastereomers of the complex (Scheme 5). On cooling the solution, the intensity of the peak in the spectrum at 17.8 ppm decreased and at −25 °C the overlapping peaks at 39.6 and 40.0 ppm had coalesced. At −95 °C, an

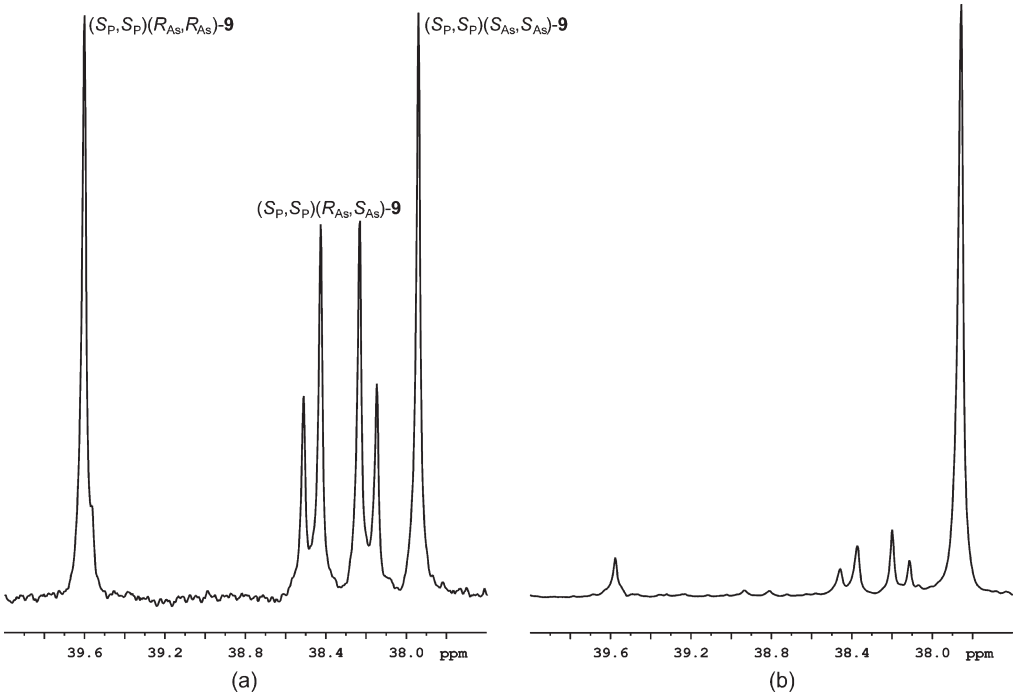


Figure 4. $^{31}P\{^{1}H\}$ NMR spectra (121.47 MHz, 25 °C) spectra in chloroform-*d* showing the three diastereomers of $(S_P,S_P)(R_{As},R_{As})/(S_P,S_P)(S_{As},S_{As})/(S_P,S_P)(R_{As},S_{As})$-**9** arising from the reaction of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8** with a stoichiometric amount of the reference complex (S_P,S_P)-**6** (a) and the corresponding spectrum resulting from asymmetric synthesis (b).

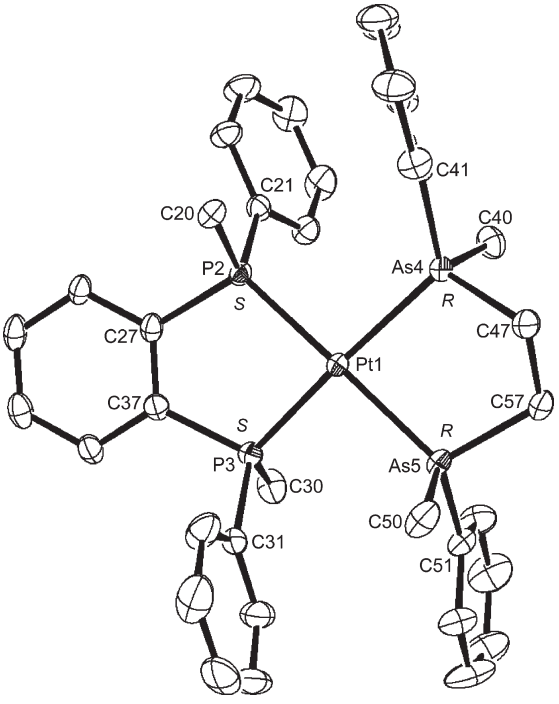
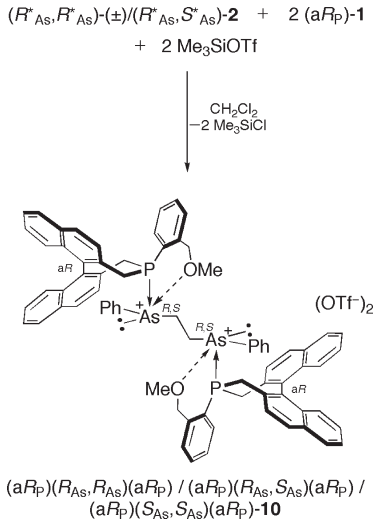


Figure 5. Structure of the cation $(S_P,S_P)(R_{As},R_{As})$-**7** (hydrogen atoms omitted for clarity). Ellipsoids show 30% probability levels. Selected bond lengths (Å) and interbond angles (deg): Pt1−P2 = 2.2704(10), Pt1−P3 = 2.2810(9), Pt1−As4 = 2.4307(4), Pt1−As5 = 2.4139(4), P2−C20 = 1.803(4), P2−C21 = 1.808(4), P2−C27 = 1.820(4), P3−C30 = 1.800(4), P3−C31 = 1.806(4), P3−C37 = 1.931(4), As4−C40 = 1.921(5), As4−C41 = 1.912(4), As4−C47 = 1.963(5), As5−C50 = 1.914(4), As5−C51 = 1.910(4), As5−C57 = 1.963(4), P2−Pt1−P3 = 86.80(4), P2−Pt1−As4 = 95.06(3), P3−Pt1−As5 = 95.34(3), As4−Pt1−As5 = 83.821 (14), P2−Pt1−As5 = 172.65(3), P3−Pt1−As4 = 171.69(3).

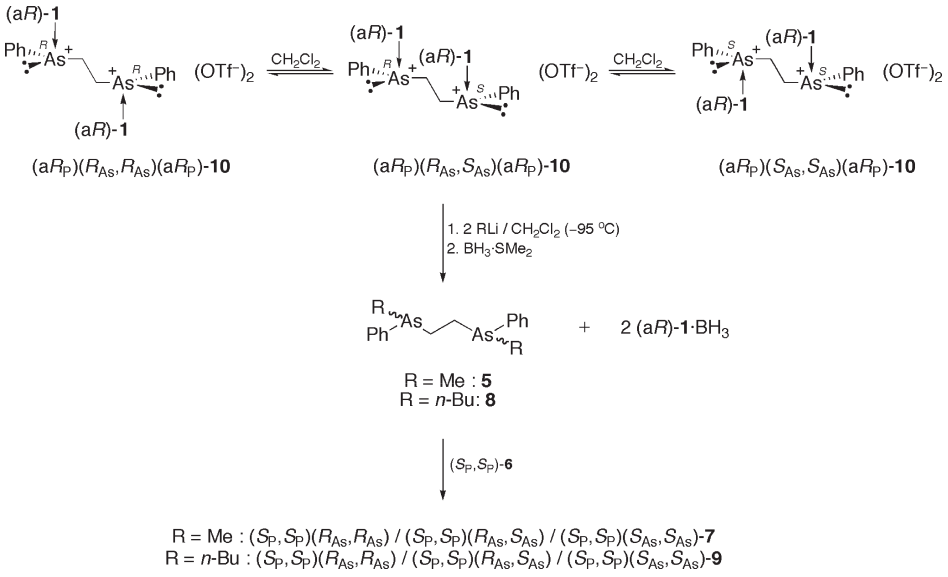
intense peak was observed in the spectrum at 39.23 ppm, which was consistent with the presence of a single C_2 diastereomer in large excess (ca. 90%), together with several smaller peaks corresponding to the two other two diastereomers (Figure 6). Comprehensive NMR spectroscopic investigations and DFT calculations on the complex $(aR_P,R_{As})/(aR_P,S_{As})$-[**1**→AsMePh]$PF_6$, which crystallized by an asymmetric transformation of the second kind as the (aR_P,S_{As}) diastereomer, indicated that the (aR_P)-phosphepine preferentially binds to the *pro-S* face of the methylphenylarsenium ion.[7] On the basis of this observation, it was reasonable to assume that the diastereomer in large excess in the diarsenium system was $(aR_P)(S_{As},S_{As})(aR_P)$-**10**.

Scheme 4



(b). Stereoselective Synthesis of (R_{As},R_{As})-5. A solution of methyllithium (2.2 equiv, 1.6 M in diethyl ether) was added to a solution of $(aR_P)(R_{As},R_{As})(aR_P)/(aR_P)$

Scheme 5



(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** (1 equiv) in dichloromethane at −95 °C. [Dichloromethane does not appreciably react with alkyllithium reagents at temperatures below −74 °C.[27]] After about 5 min, water was added to the reaction mixture, and the cooling bath was removed. The stereoselectivity of the nucleophilic additions at the two prochiral arsenium stereocenters in the complex under these conditions was determined by reaction of the resulting diarsine, (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5**, with the enantiomerically pure platinum complex (S_P,S_P)-**6** (after treatment of the reaction mixture with borane dimethyl sulfide to deactivate the phosphepine coordination to the platinum) (Scheme 5, R = Me). Integration of the peaks in the $^{31}P\{^1H\}$ NMR spectrum of the resulting complex gave the following result for the synthesis: (S_P,S_P)(R_{As},R_{As})-**7**:(S_P,S_P)(R_{As},S_{As})-**7**:(S_P,S_P)(S_{As},S_{As})-**7** = 4:22:74, Figure 3(b). Thus, the stereoselectivity of the synthesis of the diarsine (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5** is 78% (R^*_{As},R^*_{As}) diastereomer and 22% (R^*_{As},S^*_{As}) diastereomer, the former consisting of 95% of the (R_{As},R_{As}) enantiomer.

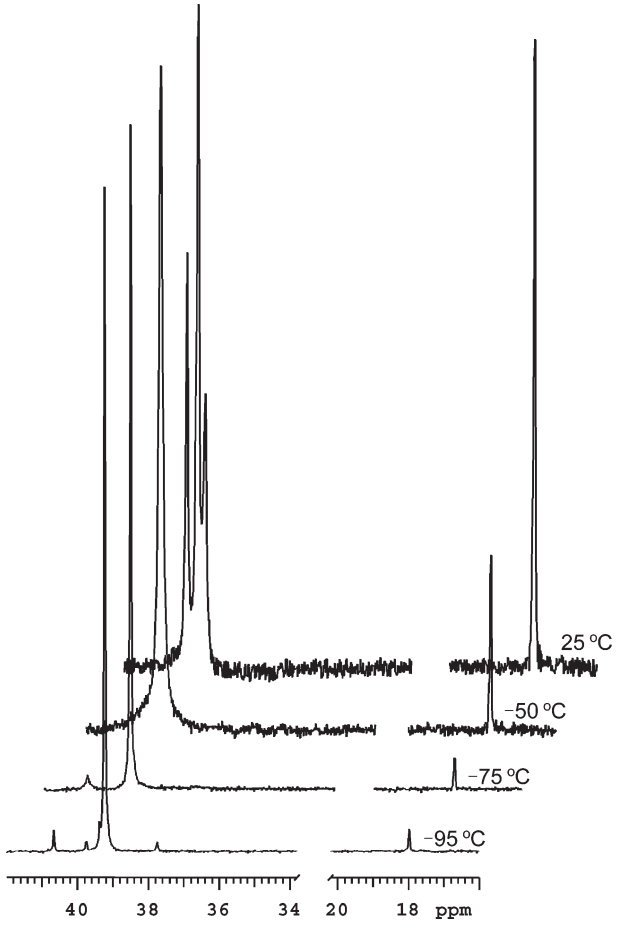


Figure 6. Variable temperature $^{31}P\{H\}$ NMR spectra (121.47 MHz) in dichloromethane-d_2 of (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)-(R_{As},S_{As})(aR_P)-**10**.

(c). Stereoselective Synthesis of (R_{As},R_{As})-8. By the procedure described above for the synthesis of the 1,2-ethanediylbis(methylphenylarsine), the bis[(*n*-butyl)phenylarsine] (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8** was synthesized by the addition of *n*-butyllithium (2.2 equiv, 1.5 M in hexanes) to a dichloromethane solution of (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** at −95 °C (Scheme 5, R = *n*-Bu). After workup and complexation with (S_P,S_P)-**6**, the $^{31}P\{^1H\}$ NMR spectrum shown in Figure 4(b) was obtained; integration of the resonances gave (S_P,S_P)(R_{As},R_{As})-**9**:(S_P,S_P)(R_{As},S_{As})-**9**:(S_P,S_P)(S_{As},S_{As})-**9** = 5:23:72. Thus, the diastereoselectivity of the *n*-butyllithium addition to the (aR_P)-phosphepine-stabilized bis(arsenium triflate) (**10**) leading to (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**8** is 77% in favor of the (R^*_{As},R^*_{As}) diastereomer, which, in turn, is enriched to the extent of 93% in the (R_{As},R_{As}) enantiomer. [The enantioselectivity of the synthesis of (S_{As})-As(*n*-Bu)MePh was 85% by a similar route.[7] The opposite configuration at arsenic obtained for the asymmetric synthesis of (S_{As})-As(*n*-Bu)MePh to the (R_{As},R_{As})-diarsines is due to a reversal of the CIP priority of the nucleophile when proceeding from the

(27) Köbrich, G.; Merkle, H. R. *Chem. Ber.* **1966**, *99*, 1782–1792.

monoarsine to the diarsine, rather than an inversion of configuration.]

Conclusion

The first bis(phosphine-stabilized) diarsenium salts have been synthesized by the addition of trimethylsilyl triflate to anhydrous solutions of the appropriate tertiary phosphine and (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-ethanediylbis(chlorophenylarsine) in dichloromethane. The addition of methyl- and *n*-butyllithium reagents to solutions of a bis[(aR_P)-phosphepine-stabilized] 1,2-ethanediylbis(phenylarsenium triflate) at −95 °C in dichloromethane results in stereoselective syntheses of the corresponding 1,2-ethanediylbis(tertiary arsines): the methyllithium addition gave (R^*_{As},R^*_{As})-(±)-1,2-ethanediylbis(methylphenylarsine) with 78% diastereoselectivity and 95% enantioselectivity in favor of the (R_{As},R_{As}) enantiomer; the addition of *n*-butyllithium to the diarsenium salt under similar conditions gave (R^*_{As},R^*_{As})-(±)-1,2-ethanediylbis[(*n*-butyl)phenylarsine] with 77% diastereoselectivity and 93% enantioselectivity for the same enantiomer.

Experimental Section

General Methods. Manipulations involving air-sensitive compounds were performed under dinitrogen with use of Schlenk techniques. Solvents were dried over appropriate drying agents and distilled before use.[28] Reaction temperatures of −95 °C were achieved with an ethanol−liquid nitrogen slush bath. NMR spectra were recorded at 25 °C, unless otherwise stated, on Varian Inova 300 and 500 spectrometers: for ^{1}H spectra, chemical shifts are reported in ppm and referenced to the residual solvent peaks; for ^{31}P{^{1}H} spectra, chemical shifts are quoted relative to external 85% aq. H_3PO_4 with positive shifts lying downfield of the standard. Optical rotations were measured on the specified solutions with a Perkin−Elmer Model 241 spectropolarimeter. Specific rotations are within ± 0.05 deg cm^2 g^{-1}. (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2**,[24] $MePh_2P$,[29] (aR_P)-**1**,[7] and (S_P,S_P)-**6**[22] were prepared by the literature methods. Elemental analyses were performed by staff within the Research School of Chemistry.

General Procedure for Preparation of 1,2-Ethanediylbis[(phosphine)phenylarsenium Triflates]. The tertiary phosphine (2.0−2.1 equiv) was added to a solution of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (1.0 equiv) in dichloromethane containing Me_3SiOTf (2.0−2.1 equiv). After about 0.5 h, the solvent and Me_3SiCl were removed in vacuo. The residues were dissolved in small quantities of dichloromethane, and the crude products were precipitated by the addition of diethyl ether to separate them from the excess phosphine. The crude product in each case was dried and crystallized from dichloromethane−diethyl ether.

(R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-Ethanediylbis[(triphenylphosphine-*P*)phenylarsenium Triflate], (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-3. (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (1.0 g, 2.5 mmol), PPh_3 (1.4 g, 5.2 mmol), Me_3SiOTf (1.2 g, 1.0 mL, 5.2 mmol). Colorless prisms: 2.05 g (71%); mp = 157−159 °C. Anal. Calcd $C_{52}H_{44}As_2F_6O_6P_2S_2$: C, 54.08; H, 3.84. Found: C, 53.89; H, 3.91. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, br, 4H, AsCH_2), 6.22−7.73 (m, 40H, Ar*H*). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 17.45 (s).

(R^*_{As},S^*_{As})-1,2-Ethanediylbis[(methyldiphenylphosphine-*P*)-phenylarsenium Triflate], (R^*_{As},S^*_{As})-4. (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (0.79 g, 2.0 mmol), $PMePh_2$ (0.8 g, 4.1 mmol), Me_3SiOTf (0.9 g, 0.8 mL, 4.1 mmol). Colorless prisms: 1.58 g (77%); mp = 136−138 °C. Anal. Calcd for $C_{42}H_{40}As_2F_6O_6P_2S_2$: C, 48.94; H, 3.91. Found: C, 49.21; H, 3.98. ^{1}H NMR ($CDCl_3$): δ 2.33 (d, $^2J_{HP}$ = 13.2 Hz, 6H, PCH_3), 2.47 (s, br, 4H, AsCH_2), 7.15−7.68 (m, 30H, Ar*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.91 (s).

(aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-1,2-Ethanediylbis{[(4-(2-methoxymethyl)phenyl)-4,5-dihydro-3*H*-dinaphtho(2,1-*c*;1′,2′-*e*)phosphepine-*P*]phenylarsenium triflate}, (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-10. (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (0.2 g, 0.6 mmol), (aR_P)-**1** (0.6 g, 1.2 mmol), Me_3SiOTf (0.3 g, 0.2 mL, 1.2 mmol). Colorless needles: 0.57 g (65%); mp = 240−242 °C, $[\alpha]_D^{25}$ = +76 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{76}H_{64}As_2F_6O_8P_2S_2$: C, 61.05; H, 4.31. Found: C, 60.84; H, 4.47. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.53−2.38, 3.36−4.44 (m, 22H, aliphatic H), 6.94−8.54 (m, 42H, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 500 MHz): δ 17.76 (s), 39.68 (s), 39.8 (s), 40.20 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, −95 °C, 500 MHz): 17.97 (s), 37.74 (s), 39.23 (s), 39.74 (s), 40.66 (s), (see Figure 6).

(R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-1,2-Ethanediylbis(methylphenylarsine), (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-5. This compound was prepared by a modification of the literature method.[21] Methyllithium (63 mL, 1.6 M in diethyl ether) was slowly added to a solution of (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**2** (16.17 g, 40.0 mmol) in dry THF (300 mL) at 0 °C. The reaction mixture was stirred for 30 min, and then the unreacted methyllithium was quenched with water (50 mL); the volatiles were removed and replaced with dichloromethane (250 mL) and water (200 mL) was added. The organic phase was separated, the aqueous phase was extracted with dichloromethane (2 × 50 mL), and the combined organic fractions were dried ($MgSO_4$) and filtered. The solvent was removed from the filtrate to leave a cloudy oil that was purified by distillation. Yield: 12.81 g (88%); bp = 158−164 °C (0.5 mmHg) [Lit.[21] 140−155 °C (0.05 mmHg)]. Anal. Calcd for $C_{16}H_{20}As_2$: C, 53.06; H, 5.57. Found: C, 52.87; H, 5.65. ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 6H, AsCH_3), 1.69−1.85 (m, 4H, AsCH_2), 7.33−7.47 (m, 10H, Ar*H*).

[*SP*-4-(R^*_{As},R^*_{As})]-(±)-Dichloro[1,2-ethanediylbis(methylphenylarsine)]palladium(II), [*SP*-4-(R^*_{As},R^*_{As})]-(±)-[Pd(5)Cl$_2$]. This compound was prepared by the published procedure.[25] Palladium(II) chloride (6.14 g, 34.6 mmol), lithium chloride (8.00 g, 188.7 mmol), (R^*_{As},R^*_{As})-(±)/(R^*_{As},S^*_{As})-**5** (12.57 g, 34.7 mmol). Yellow solid: 16.36 g (88%). ^{1}H NMR ($CDCl_3$): 1.76 (dd, $^2J_{HH}$ = 21.6 Hz, $^3J_{HH}$ = 13.8 Hz, 2H, (R^*_{As},R^*_{As})-C*H*HC*H*H), 2.02 (s, 6H, AsCH_3), 2.08 (s, 6H, AsCH_3), 2.24−2.34 (m, 2H, (R^*_{As},S^*_{As})-C*H*HC*H*H), 2.38−2.48 (m, 2H, (R^*_{As},S^*_{As})-CH*H*CH*H*), 2.75 (dd, $^2J_{HH}$ = 21.6 Hz, $^3J_{HH}$ = 13.8 Hz, 2H, (R^*_{As},R^*_{As})-CH*H*CH*H*), 7.36−7.87 (m, 20H, Ar*H*). The complex was dissolved in the minimum quantity of dichloromethane and loaded onto a silica column made up with dichloromethane; the first band was eluted with dichloromethane/THF (95/5 v/v) and contained the (R^*_{As},R^*_{As})-(±) diastereomer of the complex. Yellow microcrystals: 6.49 g (79%); mp = 285−287 °C (dec). [Lit.[25] 287−288 °C (dec)]. ^{1}H NMR ($CDCl_3$): 1.76 (dd, 2H, $^2J_{HH}$ = 21.6 Hz, $^3J_{HH}$ = 13.8 Hz, C*H*HC*H*H), 2.02 (s, 6H, AsCH_3), 2.75 (dd, 2H, $^2J_{HH}$ = 21.6 Hz, $^3J_{HH}$ = 13.8 Hz, CH*H*CH*H*), 7.45−7.87 (m, 10 H, Ar*H*).

(R^*_{As},R^*_{As})-(±)-1,2-Ethanediylbis(methylphenylarsine), (R^*_{As},R^*_{As})-(±)-5. This compound was prepared by a published procedure.[25] Sodium cyanide (3.50 g, 71 mmol), (R^*_{As},R^*_{As})-(±)-[$PdCl_2$(**5**)] (6.46 g, 11.9 mmol). Colorless oil: 3.50 g (80%); bp=168−170 °C (0.2 mmHg) [Lit.[25] 156−158 °C (0.1 mmHg)]. ^{1}H NMR ($CDCl_3$): 1.16 (s, 6H, AsCH_3), 1.72 (dd, 2H, $^2J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 5.1 Hz, C*H*HC*H*H), 1.73 (dd, 2H $^2J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 5.1 Hz, CH*H*CH*H*), 7.26−7.44 (m, 10H, Ar*H*).

[*SP*-4-(S_P,S_P)(R_{As},R_{As})]-[1,2-Ethanediylbis(methylphenylarsine)][1,2-phenylenebis(methylphenylphosphine)]platinum(II) Triflate, [*SP*-4-(S_P,S_P)(R_{As},R_{As})]-7. A solution of (R^*_{As},R^*_{As})-

(28) Armarego, W. F. L.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth−Heinemann: Amsterdam, 2003.
(29) Bianco, V. D.; Doronzo, S. *Inorg. Synth.* **1976**, *16*, 155–163.

(±)-**5** (0.48 g, 1.32 mmol) in dichloromethane was added to a solution of the complex (S_P,S_P)-**6** (1.03 g, 1.26 mmol) in the same solvent (10 mL). After 1 h, the volume of resulting solution was reduced by half, and diethyl ether (20 mL) was added. The mixture was stirred for 0.5 h, and the colorless product was filtered off and recrystallized from methanol by the addition of diethyl ether. After two recrystallizations, configurationally pure (S_P,S_P)(R_{As},R_{As})-**7** was obtained as colorless needles: mp = >350 °C; $[\alpha]_D^{25}$ = +199 (*c* 1.0, CH_2Cl_2). Anal. Calcd. for $C_{38}H_{40}As_2F_6O_6P_2PtS_2$: C, 38.75; H, 3.42. Found: C, 38.75; H, 3.64. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.52 (d, 6H, $^4J_{HP(trans)}$ = 1.8 Hz, $^3J_{HPt}$ = 16.2 Hz, AsCH_3), 1.89 (d, 6H, $^2J_{HP}$ = 11.1 Hz, $^3J_{HPt}$ = 33.9 Hz, 6 H, PCH_3), 2.22−2.35 (m, 2H, C*H*HC*H*H), 2.46−2.61 (m, 2H, CH*H*CH*H*), 7.41−7.71 (m, 24H, Ar*H*). ^{31}P{^{1}H} NMR (121.47 MHz, CD_2Cl_2) δ 39.48 (s, $^1J_{PtP}$ = 2700 Hz).

(*R$_{As}$,*R**$_{As}$)-(±)/(*R**$_{As}$,*S**$_{As}$)-1,2-Ethanediylbis(*n*-butylphenylarsine), (*R**$_{As}$,*R**$_{As}$)-(±)/(*R**$_{As}$,*S**$_{As}$)-8.** This compound was prepared by a modification of the literature method.[24] A solution of *n*-butyllithium (47.3 mL, 2.5 M) was added to a solution of (*R**$_{As}$,*R**$_{As}$)-(±)/(*R**$_{As}$,*S**$_{As}$)-**2** (18.00 g, 45.0 mmol) in THF (400 mL) at 0 °C. The reaction mixture was stirred for 30 min and then the excess *n*-BuLi was quenched with water (50 mL). The solvent was evaporated from the mixture and replaced with dichloromethane (250 mL) and water (200 mL). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The combined organic fraction was dried ($MgSO_4$), filtered, and the solvent evaporated to leave the crude product that was purified by distillation. Colorless oil: 17.54 g (87%); bp = 178−181 °C (0.05 mmHg) [Lit.[24] 184−188 °C (0.06 mmHg)]. Anal. Calcd for $C_{22}H_{32}As_2$: C, 59.20; H, 7.23. Found: C, 59.26; H, 7.06. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 6H, $^3J_{HH}$ = 6.9 Hz, As$(CH_2)_3CH_3$), 1.27−1.44 (m, 8H, As$CH_2(CH_2)_2$), 1.61−1.81 (m, 8H, AsCH_2), 7.29−7.43 (m, 10H, Ar*H*).

Asymmetric Syntheses. General. A solution of the appropriate alkyllithium reagent was added to a solution of (aR_P)(R_{As},R_{As})-(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** in CH_2Cl_2 (2 mL) at −95 °C. After stirring for about 5 min, the reaction mixture in each case was quenched with water (100 μL), and the cooling bath removed. When the reaction mixture had reached room temperature, it was dried ($MgSO_4$), filtered, and an excess of $Me_2S\cdot BH_3$ was added to complex the displaced phosphine. After a further 10 min, the solution was evaporated to dryness and heated under vacuum to remove the excess $Me_2S\cdot BH_3$. The residue was dissolved in dichloromethane (2 mL), and a solution of (S_P,S_P)-**6** in the same solvent (2 mL) was added. After 10 min, the solvent was removed from the solution, and the stereoselectivities of the resulting 1,2-ethanediylbis(tertiary arsines) were determined by recording the ^{31}P{^{1}H} NMR spectra of the appropriate platinum complexes, as described below.

Stereoselective Synthesis of (*R$_{As}$,*R**$_{As}$)-(±)/(*R**$_{As}$,*S**$_{As}$)-5.** Methyllithium (1.6 M in diethyl ether, 20 μL), (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** (0.0229 g, 15.3 μmol), (S_P,S_P)-**6** (0.0087 g, 10.7 μmol). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.46 MHz): δ 38.58 (d, $^3J_{PP}$ = 11.05 Hz, 11%, (S_P,S_P)(R_{As},S_{As})-**7**), 38.91 (s, 74%, (S_P,S_P)(S_{As},S_{As})-**7**), 40.03 (s, 4%, (S_P,S_P)(R_{As},R_{As})-**7**), 40.32 (d, $^3J_{PP}$ = 11.05 Hz, 11%, (S_P,S_P)(R_{As},S_{As})-**7**), 43.83 (br s, (aR_P)-**1**·BH_3).

Stereoselective Synthesis of (*R$_{As}$,*R**$_{As}$)-(±)/(*R**$_{As}$,*S**$_{As}$)-8.** *n*-Butyllithium (1.5 M in hexanes, 20 μL), (aR_P)(R_{As},R_{As})(aR_P)/(aR_P)(S_{As},S_{As})(aR_P)/(aR_P)(R_{As},S_{As})(aR_P)-**10** (0.01915 g, 12.8 μmol), (S_P,S_P)-**6** (0.0087 g, 10.4 μmol). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.46 MHz): δ 37.86 (s, 72%, (S_P,S_P)(S_{As},S_{As})-**9**), 38.16 (d, $^3J_{PP}$ = 10.90 Hz, 11.5%, (S_P,S_P)(R_{As},S_{As})-**9**), 38.42 (d, $^3J_{PP}$ = 10.90 Hz, 11.5%, (S_P,S_P)(R_{As},S_{As})-**9**), 39.58 (s, 5%, (S_P,S_P)(R_{As},R_{As})-**9**), 42.70 (br s, (aR_P)-**1**·BH_3).

X-ray Crystallography. X-ray diffraction data were collected at 200 K on a Nonius Kappa CCD diffractometer. Data were processed with the Denzo/Scalepack software[30] with absorption corrections[31] being applied. The structures were solved by direct methods with the program SIR92.[32] Non-hydrogen atoms within the cation were refined anisotropically and hydrogen atoms were placed at idealized positions. Full-matrix least-squares refinement on *F* was performed with the CRYSTALS program.[33] The absolute configuration of the complex [*SP*-4−2-(S_P,S_P)(R_{As},R_{As})]-**7** was determined by refinement of a Flack parameter, final value −0.024(4), and was consistent with the known configuration of the phosphorus stereocenters in the platinum complex (S_P,S_P)-**6**.

Crystal data for (*R**$_{As}$,*S**$_{As}$)-**4**, *M* = 1030.69, monoclinic, space group $P2_1/c$, *a* = 11.5468(2), *b* = 11.2427(2) *c* = 17.0825(3) Å, β = 95.6724(12)°, *V* = 2206.74(7) Å^3, *Z* = 2, *D* = 1.438 g cm^{-3}, μ(Mo Kα) = 1.752 mm^{-1}, *T* = 200 K, colorless prism, crystal size 0.35 × 0.20 × 0.19 mm, 45490 reflections measured, 5057 unique reflections (R_{int} = 0.037), 2863 independent observed reflections ($I > 3.00u(I)$), 326 parameters, *F* refinement, *R* = 0.0373, *wR* = 0.0427.

Crystal data for [*SP*-4-(S_P,S_P)(R_{As},R_{As})]-**7**, *M* = 1171.71, orthorhombic, space group $P2_12_12_1$, *a* = 13.9541(2), *b* = 16.5910(1) *c* = 18.8238(2) Å, *V* = 4357.94(8) Å^3, *Z* = 4, *D* = 1.795 g cm^{-3}, μ(Mo Kα) = 0.71073 mm^{-1}, *T* = 200 K, colorless plate, crystal size 0.52 × 0.36 × 0.22 mm, 61481 reflections measured, 10011 unique reflections (R_{int} = 0.065), 8962 independent observed reflections ($I > 2.00u(I)$), 583 parameters, F^2 refinement, *R* = 0.0241, *wR* = 0.0524.

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Supporting Information Available: Additional crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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