most important, from the standpoint of this study, is the result that optical anisotropies measured by light scattering can be related directly to the bond polarizabilities and geometries of molecules. It follows that the light scattering technique can be used either to determine the geometries of molecules possessing well-characterized bonds or the electronic structure of bonds of molecules of known geometry.

Given the direct correlation between Kerr constant-based molecular optical anisotropies and those obtained from light scattering studies in solution, it will prove possible to investigate structurally, in detail, molecules as small as dichlorodimethylsilane. On the other hand much larger molecules can be studied as well. In theory, molecules of dimension up to $^1/_{20}$th of the wavelength of the incident light can be treated. Of course, it is expected that the technique will be most powerful for small molecules, since the optical anisotropy will vary more strongly for such systems as molecular geometry or electronic structure varies. It is anticipated that the light scattering technique will prove especially effective in the study of molecules undergoing rapid exchange processes in solution, that is, molecules usually inaccessible to either nmr or esr methods.

In summary, it has been demonstrated that by using a photometer equipped with a 6328-Å CW laser source the intensity of horizontally polarized Rayleigh-scattered light from solution can be measured precisely. Furthermore, using the equations derived by Bothorel it has proved possible to show that optical anisotropies of solute molecules measured from light scattering are very close in value to those derived from Kerr constants. In addition, it has been noted that a Δ-function model can be used to calculate bond polarizabilities, the resultant molecular polarizability tensors, and optical anisotropies for candidate structures. Since the optical anisotropy can vary substantially from one molecular geometry to another, unambiguous structural assignments can be made even though bond polarizabilities may not be known precisely.

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Resolution and Separation of the Stereoisomers of Tertiary Arsines by Means of Their Metal Complexes

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Abstract: The two optical isomers of methylethylphenylarsine (MeEtPhAs) have been separated by fractional crystallization of the internal diastereoisomeric complex [PtCl(±)-MeEtPhAs(−)-stien]Cl (where (−)-stein = (−)-stilbenediamine). Methods are described for obtaining the two antipodes of the arsine from its complexes in high yield and high optical purity. The two dichloropalladium complexes containing the racemic and *meso* isomers of the ditertiary arsine, ethylene-1,2-bis(methylphenylarsine), have been chromatographically separated on silica gel. After decomposition of the complexes the two isomers can be distilled without interconversion. The structures of the two forms have been established by resolution of the dibenzyldiarsonium salt of the racemic compound. Certain physical data of the arsines and their complexes are recorded and discussed.

Simple dissymmetric tertiary arsines and phosphines are optically stable at room temperature. Hitherto these molecules have been obtained optically active either by electrolytic reduction[2] or, in appropriate cases, by nucleophilic displacement[3] reactions of the resolved quaternary salts.[4] In many cases these methods lead to some racemization of the phosphines or arsines, and in general are long and involved. In view of this, and because these optically active molecules play an important role in the elucidation of reaction mechanisms[5] and also because they may prove useful in the synthesis of asymmetric hydrogenation catalysts,[6,7] it seemed important to develop a simple and direct method for their resolution. Recently,[8] it was shown that methyl-*t*-butylphenylphosphine could be resolved through its platinum(II) complex; and although the free optically active phosphine was removed from the metal in solution, it was not isolated. Methods are reported here which are believed to be of considerable generality for the resolution of and the separation of the geometrical isomers of tertiary arsines. These methods, in essence, involve the formation of the metal complexes

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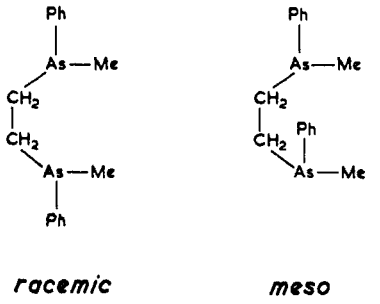

Figure 1.

which may be separated by chromatography for geometrical isomers or, when internal diastereoisomers are formed within the coordination sphere, the arsine may be resolved by fractional crystallization. The two arsines which have been chosen are (±)-methylethylphenylarsine (MeEtPhAs) and the ditertiary arsine, ethylene-1,2-bis(methylphenylarsine) (Dias). The latter arsine can exist in either the racemic or the *meso* form (Figure 1).

Resolution of (±)-Methylethylphenylarsine

rac-Methylethylphenylarsine reacts with an aqueous solution of potassium chloroplatinite(II) to give an essentially quantitative yield of *cis*-[$(MeEtPhAs)_2PtCl_2$]. The *cis* geometry has been assigned on the basis of the pale lemon, almost white, color of the complex; it is now established that complexes of the type *cis*-[L_2PtCl_2] (where L is a tertiary arsine or phosphine) are very pale lemon colored, whereas the *trans*-[L_2PtCl_2] complexes are bright yellow.[9] The *cis*-[$(MeEtPhAs)_2PtCl_2$] complex, which probably consists of a mixture of racemic and *meso* forms, reacts with platinous chloride in naphthalene to give a quantitative yield of the bright orange colored dimeric species *trans*-bis(methylethylphenylarsine)dichloro-μ,μ'-dichloro-diplatinum(II), (*trans*-[(MeEtPhAs)ClPtCl$_2$PtCl(AsPhEtMe)]). The *trans* formulation is also based on analogy with similar complexes and, as in the monomeric *cis*-bisarsine complex, the bridged complex probably exists as a mixture of racemic and *meso* complexes. This complication is eliminated, however, in the next step, when the dimer is treated in cold benzene with (−)-stilbenediamine ((−)-stien), and a quantitative yield of the white colored complex, chloro(±)-methylethylphenylarsine(−)-stilbenediamineplatinum(II) chloride, [PtCl(±)-MeEPhAs(−)-stien]Cl, is obtained.

The complex [PtCl(±)-MeEtPhAs(−)-stien]Cl consists of two physically distinct species, namely, the [(+)-arsine(−)-stien] complex and the [(−)-arsine(−)-stien] complex. We have found that the (+)(−) complex is more soluble (~10 g/l.) in chloroform at room temperature by a factor of 10 than the (−)(−) complex (~1 g/l.), and it is on this basis that the two internal diastereoisomers have been separated. Subsequent recrystallizations gave the two pure isomers having specific rotations of $[\alpha]^{20}D$ −130.1° (methanol) for the [PtCl(−)-MeEtPhAs(−)-stien]Cl complex and $[\alpha]^{20}D$ −64.03° (methanol) for the [PtCl(+)-MeEtPhAs(−)-stien]Cl complex. An identical procedure may be performed using (+)-stilbenediamine, and equal and opposite rotations were obtained for the corresponding salts.

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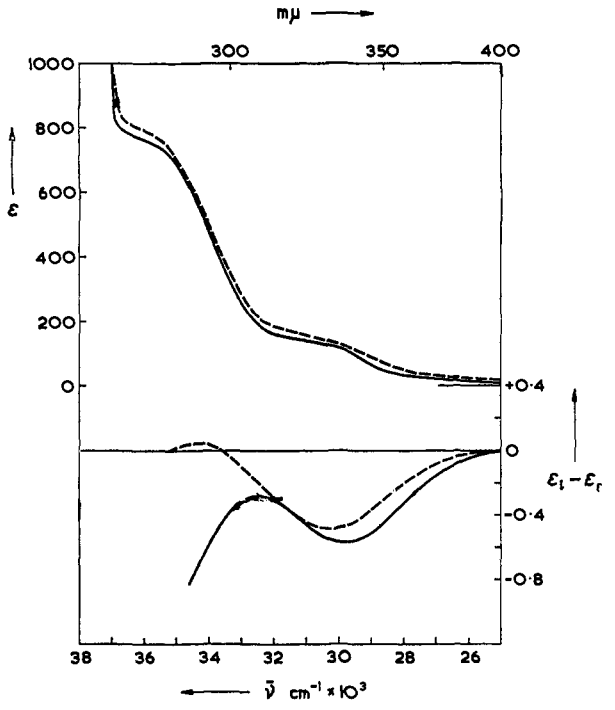

Figure 2. The absorption and circular dichroism spectra of the two complexes [PtCl(−)-MeEtPhAs(−)-stien]Cl (- - - -) and [PtCl(+)-MeEtPhAs(−)-stien]Cl (——) in methanol solutions (2×10^{-3} *M*).

In Figure 2 we show the absorption and circular dichroism spectra of the two complexes [PtCl(+)-MeEtPhAs(−)-stien]Cl and [PtCl(−)-MeEtPhAs(−)-stien]Cl. It can be seen that, as expected, the two absorption spectra are almost identical. However, although the circular dichroism is the same sign for the low energy band ($^1A_{1g} \rightarrow {}^1A_{2g}$ in D_{4h}), it is reversed in sign for the higher energy component ($^1A_{1g} \rightarrow {}^1E_g$ in D_{4h}).

In the preparation of these salts from the dimeric compound it was observed that the salts did not begin to precipitate from solution until exactly a 0.5 molar equivalent of active stilbenediamine had been added. The material obtained at this stage, however, consisted of an equal mixture of the two isomers and it would appear that, under the conditions used, the reaction is thermodynamically controlled. Recently it has been shown[10] that dissymmetric π complexes of platinum(II) could be resolved by forming internal diastereoisomers with optically active α-phenylethylamine. We have prepared the yellow *trans*-[$PtCl_2$(±)-MeEtPhAs(−)-α-phenylethylamine] complex, but after exhaustive chromatography and fractional crystallization procedures were unable to obtain any separation. This prompts us to speculate that, as in the dissymmetric π complexes, it is probably easier to obtain resolution if the two active ligands are disposed *cis* rather than *trans*. The use of the symmetrical bidentate ligand stilbenediamine ensures a *cis* interaction of the optically active centers.

The two optically pure arsines were obtained from the complex salt by reaction with cyanide ions in aqueous methanol. The ether extract contained both arsine

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and stilbenediamine, which was not removed before distillation. Both active tertiary arsines distilled at 31° (0.08 mm), which is approximately 10° lower than that of the racemic compound. The two isomers had rotations of $[\alpha]^{20}D$ +3.26 ± 0.1 and −3.05 ± 0.1° (in ether). These values are much higher than those reported for the arsines prepared by electrolytic reductions. However, the values reported by Horner are for solutions in methanol, and hence the results are not strictly comparable. We have been unable to obtain sufficient concentrations of the arsine in methanol to measure rotations to any reasonable accuracy. Horner[11] has shown that optically active methylethylphenylarsine exhibits no racemization after 10 hr at 200°, and that quaternization does not lead to inversion or racemization.

Separation of the Isomers of Ethylene-1,2-bis(methylphenylarsine)

It was shown by Chatt and Mann[12] that dichloroethylene-1,2-bis(*n*-butylphenylarsine)palladium existed in two crystalline modifications, which they succeeded in separating mechanically. They surmised that these two crystalline forms represented the *meso* and racemic isomers, which they believed to be stabilized by complex formation, and that if the ligands were set free, they would rapidly interconvert by pyrimidal inversion. We show here that the analogous diarsine, ethylene-1,2-bis(methylphenylarsine) (Dias), can be separated from its palladium complex without any interconversion of the forms; indeed, the two isomers are stable to distillation at 150°.

Ethylene-1,2-bis(methylphenylarsine) reacts with chloropalladate(II) in methanol solution to give a quantitative yield of the bright yellow colored complex [PdDiasCl$_2$]. This compound separates on silica gel when eluted with 5% tetrahydrofuran–methylene dichloride to give two compounds. The first species to be eluted is the *rac*-[PdDiasCl$_2$] complex, and the more slowly moving fraction contains the *meso*-[PdDiasCl$_2$] complex. After separation, the individual complexes are much less soluble in methanol or methylene dichloride than the original mixture; despite the fact that the *meso* form is less soluble in these solvents than the racemic form, it was not found possible to obtain any separation by fractional crystallization. All of the several different preparations and separations of these salts gave an almost equal mixture of the two isomers. The electronic absorption spectra of the two forms are almost identical, although their melting points and ir and nmr spectra are distinctly different.

The two pure isomeric diarsines are obtained by reacting the respective complexes with aqueous sodium cyanide solution and, after extraction of the aqueous solution with ether, both forms may be distilled at about 150° without interconversion. The racemic diarsine, like the original mixture, is a liquid at room temperature, while the *meso* arsine is a white solid melting at 41°. We have shown that distillation of the free diarsines does not lead to the interconversion by repreparing the dichloropalladium complexes. Thin layer chromatography and comparison of the physical and chemical properties of the complexes showed that no interconversion had taken place.

In Figure 3 we show the nmr spectra of the racemic and the *meso* diarsines and the corresponding spectra of the two dichloropalladium complexes. At low resolution it can be seen from the spectra that there is very little difference between either of the two forms of the ligand or between the two forms of the complex. The chemical shifts and the coupling constants of the methylene protons appear to be of a similar magnitude, and we have not been able to carry out a first-order analysis of the spectra in order to assign the two structural forms. However, it will be noted that the methylene protons of the *rac*-[PdDiasCl$_2$] are more spread out than the corresponding protons of the *meso*-[PdDiasCl$_2$] complex. If we assume that the ethane linkage in the chelate ring is puckered and that the bulkier phenyl groups will prefer an equatorial disposition, we may interpret the methylene signals in the following way. In the racemic complex the puckered ring allows both of the phenyl groups to be equatorial, and thus the environment of the methylene protons is constant. In the *meso* complex, however, the puckered ring does not allow both phenyl groups to be equatorial at the same time, and thus it is likely that the ring system is mobile, allowing the methyl and phenyl groups to become equivalent on an nmr time scale (Figure 3). Further, because the chelate ring is "flipping," the distinction between axial and equatorial methylene protons is lost and the environment they experience will tend to equalize. Thus, because there is greater distinction between the environments of the methylene protons of the racemic complex than those of the corresponding protons of the *meso* complex, we would expect, as is observed, the protons of the racemic complex to be more spread out than those of the *meso* complex. A similar situation is observed for *cis*- and *trans*-2,3-dichloro-1,4-dioxane systems.[13]

In a study of cyclization reactions of tertiary arsines Jones and Mann[14] reacted ethylene-1,2-bis(methylphenylarsine) with ethylene dibromide to form the cyclic diarsonium salt 1,4-dimethyl-1,4-diphenyldiethylenediarsonium dibromide. Although the diarsine consists of a mixture of racemic and *meso* isomers, they were only able to isolate one diarsonium salt. The reaction has been repeated in this laboratory, using the two pure isomers of the diarsine, and it has been found that the product is the same starting from either the racemic or the *meso* diarsine. That this is so has been confirmed by the high resolution (100 Mc) nmr spectra of the cyclic diarsonium salts in D_2O and their infrared spectra, which are identical. The yield, however, is low (10%) and the remaining material in the reaction mixture is not the cyclic diarsonium salt, but probably consists of a mixture of quaternary arsonium polymers. The authors have been unable to determine which of the two isomers (or both) is formed, although the product has a similar melting point to that observed by Jones and Mann. Under similar conditions, however, reaction between methylene dibromide and the two isomers of the diarsine does not give the cyclic 1,3-dimethyl-1,3-diphenylmethyleneethylenediarsonium bromide. This behavior of the diarsine is in marked contrast to

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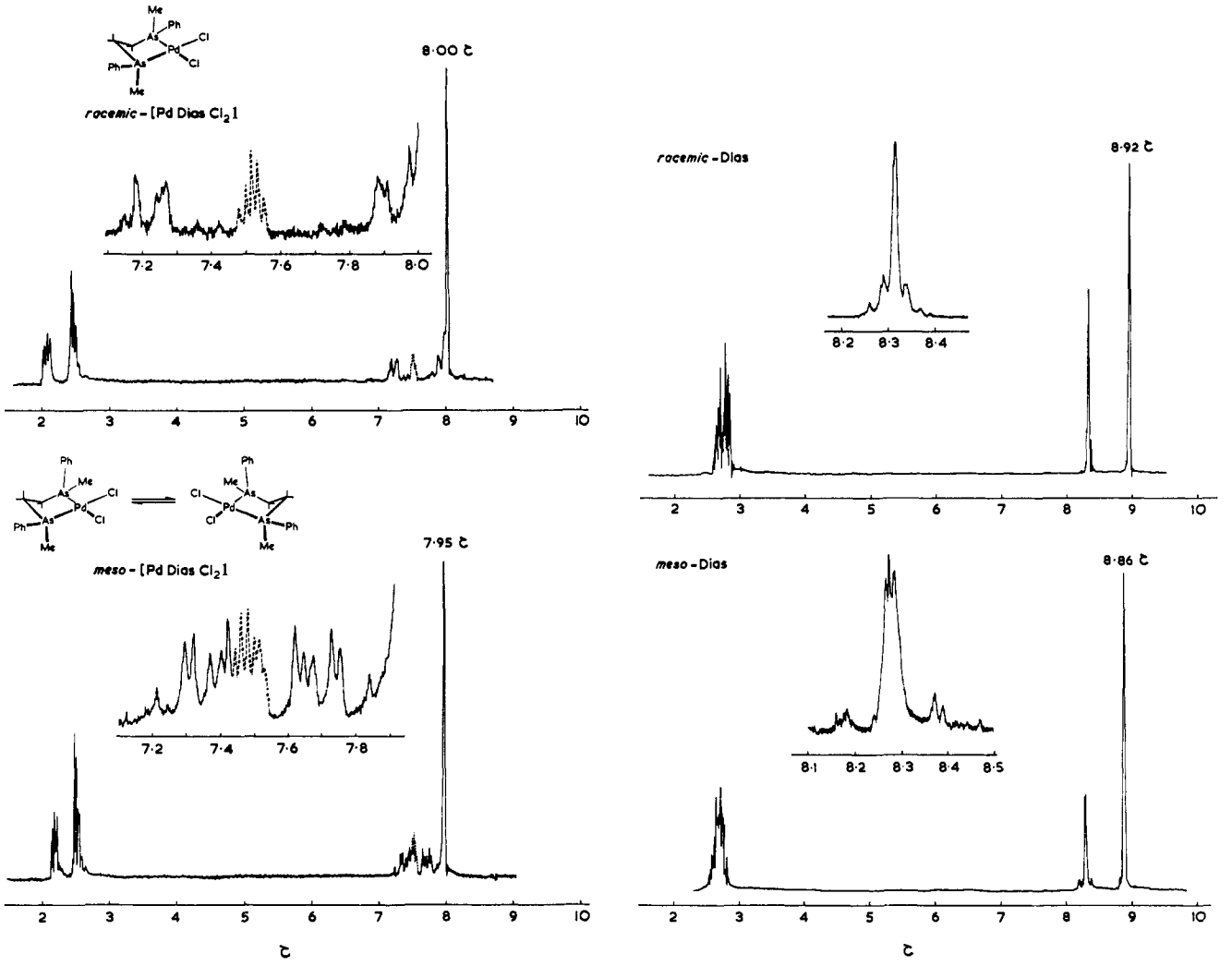

Figure 3. The nmr spectra of the racemic and *meso* diarsines, ethylene-1,2-bis(methylphenylarsine), in $CDCl_3$, and those of the corresponding dichloropalladium complexes in $(CD_3)_2SO$. The inset shows the spectra of the methylene protons at higher sensitivity and on expanded scale together with the proposed conformational structures of the two dichloropalladium complexes. Dashed lines indicate absorption due to partially deuterated solvent.

that observed for the corresponding diphosphine, ethylene-1,2-bis(methylphenylphosphine).[15] The reaction between ethylene dibromide and the two forms of the diphosphine gives the two isomers of the cyclic diphosphonium salts, whereas the cyclic salts formed by reaction with methylene dibromide give only the *meso* cyclic diphosphonium compound, irrespective of which isomer of the diphosphine is employed.

The structures of the two isomeric diarsines have been established by the resolution of the *rac*-ethylene-1,2-bis(methylbenzylphenylarsonium) ion by means of its di-D(−)-dibenzoylhydrogentartrate salt.

Experimental Section

All rotations refer to the sodium D-line, and the specific rotations were calculated by correcting for the density of the solvent. Manipulations of the free arsines were carried out under purified nitrogen, and all distillations were performed using a 5-in. vacuum-jacketed column. Melting points are uncorrected. The absorption spectra were measured using a Unicam SP 800 (recording) spectrophotometer, and the circular dichroism spectra using a Roussel-Jouan Dicrographe (sensitivity 1.5×10^{-4}). The nmr spectra were recorded at 29° by means of a Varian HA100 spectrometer.

(±)-Methylethylphenylarsine. This compound was prepared according to the method of Burrows and Turner:[16] bp 54° (0.1 mm). *Anal.* Calcd for $C_9H_{13}As$: C, 55.1; H, 6.7. Found: C, 55.2; H, 6.7.

***cis*-Dichlorobis(methylethylphenylarsine)platinum(II).** A solution of potassium chloroplatinite (10 g) in water (150 ml) was treated with a solution of methylethylphenylarsine (10 g) in ethanol (10 ml) and the mixture shaken for 2 hr. The product separated as an oil which was extracted into CH_2Cl_2 (200 ml) and the extract dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The pale yellow oily residue was dissolved in methanol (50 ml) and slowly diluted with ether to give very pale lemon crystals of the pure product (14.1 g), mp 112–114°. *Anal.* Calcd for $C_{18}H_{26}As_2Cl_2Pt$: C, 32.9; H, 4.0; Cl, 10.8. Found: C, 33.0; H, 4.0; Cl, 10.9.

Bis(methylethylphenylarsine)dichloro-μ,μ'-dichloro-diplatinum(II). *cis*-$(MeEtPh)_2PtCl_2$ (29 g) and $PtCl_2$ (11.8 g) were finely ground together and then dispersed in solid naphthalene (100 g). The mixture was slowly stirred and heated on an oil bath until a clear red solution resulted. The reaction occurred between 80 and 110°. This molten solution was carefully poured, with stirring, into petroleum ether (bp 60–80°; 1 l.) to give a quantitative yield of the orange dimer, which was filtered off and washed several times with hot petroleum ether. This compound is suitable for the next step. A small portion recrystallized from benzene to give large orange crystals which after pumping (25°, 0.1 mm) for several hours gave the mononaphthalene solvate, $(MeEtPhAs)_2Pt_2Cl_4 \cdot C_{10}H_8$, mp 111–

(15) L. Horner and J. P. Bercv, *Tetrahedron Lett.*, 5783 (1966).

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114°. The presence of naphthalene is confirmed by nmr and mass spectra. *Anal.* Calcd for $C_{28}H_{34}As_2Cl_4Pt_2$: C, 32.0; H, 3.5. Found: C, 31.5; H, 3.3. Extensive pumping (3 hr at 100°, 0.005 mm) of the mononaphthalene solvate gave the heminaphthalene solvate. The presence of naphthalene is confirmed by nmr and mass spectra, $(MeEtPhAs)_2Pt_2Cl \cdot 0.5C_{10}H_8$, mp 106–107°. *Anal.* Calcd for $C_{23}H_{20}As_2Cl_4Pt_2$: C, 27.95; H, 3.05; Cl, 14.35. Found: C, 28.8; H, 3.25; Cl, 14.0.

[PtCl(±)-MeEtPhAs(−)-stien]Cl. (−)-Stilbenediamine[17] ($[\alpha]^{20}D$ −108° (CH_3OH); 18.4 g) in benzene (800 ml) was added dropwise to a cold, well-stirred solution of $(MeEtPhAs)_2Pt_2Cl_4 \cdot C_{10}H_8$ (42 g) in benzene (450 ml). The reaction is almost instantaneous, and after the addition of half of the diamine the white product began to separate. Stirring was continued for 30 min after the addition was completed. The product was filtered off, washed with benzene and ether, and dried (53 g).

[PtCl(+)-MeEtPhAs(−)-stien]Cl. The mixture of diastereoisomers (53 g) was stirred in chloroform (3 l.) (analar chloroform (Fisons), which contains 2% ethanol as stabilizer) for 30 min and the suspension let stand overnight. The insoluble material was filtered off, washed with chloroform (200 ml), and the filtrate diluted with ether (2 l.) to give a voluminous white crystalline precipitate of the (+)(−) isomer (26.5 g), $[\alpha]^{20}D$ −65.7° (CH_3OH); *c*, 10.0 g/l. Subsequent dissolution of this compound in chloroform (2.5 l.) followed by dilution with ether (2 l.) gave the pure diastereoisomer as plates (22.7 g) (these crystals darken but do not melt below 290°), $[\alpha]^{20}D$ −63.03 (CH_3OH); *c*, 10.07 g/l. *Anal.* Calcd for $C_{23}H_{29}N_2AsCl_2Pt$: C, 41.1; H, 4.1; N, 4.2; Cl, 10.5. Found: C, 41.0; H, 4.2; N, 4.2; Cl, 10.2.

[PtCl(−)-MeEtPhAs(−)-stien]Cl. The chloroform insoluble fraction from the above extraction was dissolved in methanol (450 ml), filtered, and the filtrate diluted with ether (2.5 l.), and on standing, needles of the pure (−)(−) isomer (13.32 g) separated, $[\alpha]^{20}D$ −129.6° (CH_3OH); *c*, 10.2 g/l. Recrystallization of this sample (13.32 g) from methanol (120 ml) by dilution with ether (600 ml) gave similar needles (10.1 g), $[\alpha]^{20}D$ −129.5° (CH_3OH); *c*, 9.98 g/l.), and a further dilution of the filtrate with ether gave an additional sample of the pure isomer (1.4 g): mp >290°; $[\alpha]^{20}D$ −130.1° (CH_3OH); *c*, 10.2 g/l. *Anal.* Calcd for $C_{23}H_{29}N_2AsCl_2Pt$: C, 41.1; H, 4.1; N, 4.2; Cl, 10.5. Found: C, 40.75; H, 4.35; N, 4.2; Cl, 10.2.

The filtrate from this recrystallization was evaporated to near-dryness and diluted with ether to give a white precipitate of a mixture containing both (+)(−) and (−)(−) isomers (12.05 g): $[\alpha]^{20}D$ −109.2° (CH_3OH); *c*, 10.07 g/l. The mixture was stirred in chloroform (400 ml) for 5 hr, the insoluble fraction collected (8.99 g), and the filtrate diluted with ether (400 ml) to give a flocculent precipitate of slightly impure [PtCl(+)-MeEtPhAs(−)-stien]Cl (2.7 g): $[\alpha]^{20}D$ −70.1° (CH_3OH); *c*, 10.10 g/l. The chloroform insoluble material was dissolved in methanol (80 ml), the solution filtered, and the filtrate diluted with ether (300 ml) to give needles of [PtCl(−)-MeEtPhAs(−)-stien]Cl (7.4 g): $[\alpha]^{20}D$ −127.3° (CH_3OH); *c*, 9.9 g/l; total yield: [PtCl(−)-MeEtPhAs(−)stien]Cl, 25.4 g; [PtCl(−)-MeEtPhAs(−)-stien]Cl, 20.7 g.

[PtCl(±)-MeEtPhAs(+)-stien]Cl. The mixture of diastereoisomers was prepared from $(MeEtPhAs)_2Pt_2Cl_4$ and (+)-stilbenediamine in an identical manner to the above. Separation of the diastereoisomers by their differential solubility in chloroform gave the pure diastereoisomers.

[PtCl(+)-MeEtPhAs(+)-stien]Cl: needles; mp >290°; $[\alpha]^{20}D$ +121.3° (CH_3OH); *c*, 10.06 g/l. *Anal.* Calcd for $C_{23}H_{29}N_2AsCl_2Pt$: C, 41.1; H, 4.1; N, 4.2; Cl, 10.5. Found: C, 40.0; H, 4.6; N, 4.1; Cl, 10.6.

[PtCl(−)-(MeEtPhAs(+)-stien]Cl: plates; mp (darken but do not melt below 290°); $[\alpha]^{20}D$ +64.73° (CH_3OH); *c*, 10.07 g/l. *Anal.* Calcd for $C_{23}H_{29}As_2Cl_2Pt$: C, 41.1; H, 4.1; N, 4.2; Cl, 10.5. Found: C, 40.8; H, 4.3; N, 4.3; Cl, 10.2.

(+)-Methylethylphenylarsine. A stirred solution of [PtCl(+)-MeEtPhAs(+)-stien]Cl (5.0 g), $[\alpha]^{20}D$ +121.3° (CH_3OH), in methanol (20 ml) was treated with a solution of KCN (2.45 g) in water (100 ml). The reaction mixture became cloudy and stirring was continued for 2 hr. The aqueous layer was extracted with ether (3 × 100 ml) and the combined ether fraction extracted with water (2 × 100 ml). The ether extract was dried over anhydrous $MgSO_4$, filtered, and evaporated to a small volume, and the oily residue transferred to the distillation apparatus with the aid of small portions of ether. The ether was removed *in vacuo* at room temperature and the residue distilled to give pure (+)-MeEtPhAs: bp 31° (0.1 mm, 0.66 g); $[\alpha]^{20}D$ +3.26 ± 0.1° (Et_2O); *c*, 41.93 g/l. *Anal.* Calcd for $C_9H_{13}As$: C, 55.1; H, 6.7. Found: C, 55.5; H, 6.85.

(−)-Methylethylphenylarsine. A stirred solution of [PtCl(−)-MeEtPhAs (+)-stien]Cl (11.6 g) in methanol (30 ml) was treated with NaCN (5.66 g) in water (20 ml) and methanol (20 ml), and the solution stirred for 30 min. Water (150 ml) was added and the cloudy suspension was extracted as before and distilled. In this way pure (−)-MeEtPhAs, bp 32° (0.09 mm), 2.6 g, was obtained: $[\alpha]^{20}D$ −3.05 ± 0.1° (Et_2O); *c*, 36.9 g/l. *Anal.* Calcd for $C_9H_{13}As$: C, 55.1; H, 6.7. Found: C, 55.55; H, 6.85.

***trans*-Dichloro(±)-methylethylphenylarsine(−)-α-phenylethylamine-platinum(II).** Dropwise addition of (−)-α-phenylethylamine (2.8 g) in chloroform (30 ml) to a solution of $(MeEtPhAs)_2Pt_2Cl_4 \cdot C_{10}H_8$ (10 g) in chloroform (100 ml) cooled to 0° gave a bright yellow solution of the product. After removal of the solvent and recrystallization of the residue from hot chloroform (35 ml) and petrol (bp 40–60°, 25 ml) the pure product separated as large yellow prisms (9.76 g): mp 138–140°; $[\alpha]^{20}D$ −62.65° (CH_2Cl_2), *c*, 10.0 g/l. *Anal.* Calcd for $C_{17}H_{24}NAsCl_2Pt$: C, 35.0; H, 4.15; N, 2.4; Cl, 12.15. Found: C, 35.2; H, 4.2; N, 2.1; Cl, 11.8.

Ethylene-1,2-bis(methylphenylarsine) was prepared in 71% yield from $Ph(Cl)As(CH_2)_2As(Cl)Ph$[18] by treatment with MeMgI,[12] bp 140–155° (0.05 mm), and characterized as the dimethiodide, $[PhMe_2As(CH_2)_2AsMe_2Ph]I_2$, long needles, mp 284–285°. *Anal.* Calcd for $C_{18}H_{26}As_2I_2$: C, 33.5; H, 4.05. Found: C, 33.4; H, 4.05.

Dichloroethylene-1,2-bis(methylphenylarsine)palladium(II). Its Preparation and Separation into *meso* and Racemic Forms. Preparation. Palladous chloride (17.5 g) was stirred in hot methanol (400 ml) with lithium chloride (24 g) until all of the $PdCl_2$ had dissolved. The chloropalladite solution was filtered and cooled and then treated with a solution of the diarsine (34.3 g) dissolved in a mixture of ether (50 ml) and methanol (50 ml). A red gum separated immediately, which dissolved on heating to rapidly precipitate the yellow product. After refluxing for 2 hr the solution was cooled and diluted with water (200 ml) and the mixture of *meso*- and *rac*-[PdDiasCl$_2$] filtered off and washed with methanol and ether (51 g).

Separation. The mixture containing both *meso*- and *rac*-[PdDiasCl$_2$] (~25 g) was dissolved in methylene dichloride (350 ml) and transferred to a column (3 in. × 30 in.) containing silica gel (2 kg of "Sorbsil," J. Crosfield and Sons, Warrington, England) made up in 5% tetrahydrofuran–methylene dichloride. Elution with 5% THF–CH_2Cl_2 separated the mixture into two distinct bands. After the first fraction had been eluted the solvent mixture was stepped up to 15% THF–CH_2Cl_2 to remove the second fraction more quickly. Evaporation of the first fraction gave yellow, highly crystalline *rac*-[PdDiasCl$_2$], which recrystallized from methylene dichloride–methanol as prisms (11.3 g), mp 287–288° dec. *Anal.* Calcd for $C_{16}H_{20}As_2Cl_2Pd$: C, 35.6; H, 3.75; As, 27.75; Cl, 13.15. Found: C, 35.6; H, 3.8; As, 27.65; Cl, 13.05.

Similarly, evaporation of the second fractions gave the less soluble *meso*-[PdDiasCl$_2$] as a highly crystalline yellow solid (11.6 g), a small portion of which was recrystallized from methylene dichloride–methanol to yield prisms, mp 273–274° dec. *Anal.* Calcd for $C_{16}H_{20}As_2Cl_2Pd$: C, 35.6; H, 3.75; As, 27.75; Cl, 13.15. Found: C, 35.7; H, 3.75; As, 27.65; Cl, 13.15.

***rac*-Ethylene-1,2-bis(methylphenylarsine).** *rac*-[PdDiasCl$_2$] (19.5 g) was suspended in deoxygenated water (100 ml) and ether (100 ml) and treated with NaCN (9 g). After several minutes the complex had decomposed and the clear ether layer was separated. The aqueous layer was extracted with ether (2 × 50 ml) and the combined ether fraction extracted with water (50 ml). The ether extract was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness, and the oily residue transferred to the distillation apparatus with the aid of small portions of ether. The ether was removed *in vacuo* at room temperature and the residue distilled to give the racemic diarsine (11.1 g), bp 156–158° (0.1 mm). *Anal.* Calcd for $C_{16}H_{20}As_2$: C, 53.1; H, 5.6; As, 41.4. Found: C, 52.9; H, 5.85; As, 41.4.

Addition of a small portion of the diarsine to chloropalladite(II) in methanol gave *rac*-[PdDiasCl$_2$], identical with the original. *Anal.* Calcd for $C_{16}H_{20}As_2Cl_2Pd$: C, 35.6; H, 3.75. Found: C, 35.65; H, 4.0.

***meso*-Ethylene-1,2-bis(methylphenylarsine).** Decomposition of *meso*-[PdDiasCl$_2$] (17.1 g) with NaCN (8 g) by the same procedure

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gave the *meso* diarsine (8.55 g), bp 142° (0.05 mm), mp 40–41°. *Anal.* Calcd for $C_{16}H_{20}As_2$: C, 53.1; H, 5.6. Found: C, 52.9; H, 5.6.

Similarly, reaction of this diarsine with chloropalladite(II) solution gave *meso*-[PdDiasCl$_2$]. *Anal.* Calcd for $C_{16}H_{20}As_2Cl_2Pd$: C, 35.6; H, 3.75. Found: C, 35.7; H, 3.75.

1,4-Dimethyl-1,4-diphenyldiethylenediarsonium Dibromide. A solution of *rac*-ethylene-1,2-bis(methylphenylarsine) (0.5 g) and ethylene dibromide (0.3 g) in methanol (0.5 ml) was heated in a sealed tube at 108° for 19 hr. After this time the tube was opened and the contents diluted with absolute ethanol (2.5 ml) and cooled to give a crystalline precipitate. The product was filtered off, washed with absolute ethanol and ether, and recrystallized from methanol by addition of ether (0.052 g), mp 274–275°. *Anal.* Calcd for $C_{18}H_{24}As_2Br_2$: C, 39.3; H, 4.4; As, 27.2. Found: C, 39.3; H, 4.4; As, 27.15.

***rac*-Ethylene-1,2-bis(methylbenzylphenylarsonium) Diiodide. Its Preparation and Resolution. Preparation.** *rac*-Ethylene-1,2-bis-(methylphenylarsine) (3.95 g) was dissolved in excess benzyl bromide. After 30 min at room temperature the reaction mixture had become solid and the contents were ground with ether and filtered off. The hygroscopic diarsonium dibromide was quickly dissolved in hot water and the solution filtered into an aqueous solution containing excess sodium iodide, to precipitate the diarsonium diiodide. Recrystallization of this compound from hot methanol–ether gave white plates of the dibenziodide (6.72 g), mp 211–212°. *Anal.* Calcd for $C_{30}H_{34}As_2I_2$: C, 45.1; H, 4.3; As, 18.75. Found: C, 44.5; H, 4.4; As, 18.75.

Resolution. To a solution of the diarsonium diiodide (6.72 g) in hot methanol (300 ml) was added a suspension of silver D(−)-dibenzoylhydrogentartrate (7.83 g) in hot methanol (300 ml) and water (50 ml). The hot solution was stirred for 30 min. The solution was cooled and the precipitated silver iodide filtered off. The filtrate, on evaporation to dryness, left (±)-ethylenebis(methylbenzylphenylarsonium) di[D(−)-dibenzoylhydrogentartrate]. This mixture of diastereoisomers was suspended in boiling absolute ethanol (200 ml) and sufficient water (30 ml) added to obtain solution (30 ml). The solution was filtered, and after standing overnight at 0° yielded white crystals of (+)-ethylene-1,2-bis(methylbenzylphenylarsonium) di[D(−)-dibenzoylhydrogentartrate] (3.7 g): mp 160–162°; $[\alpha]^{20}D$ −68.3° (CH_3OH); *c*, 10.03 g/l. An additional 1.16 g of this same diastereoisomer remained after evaporation of the filtrate and extraction of the residue with boiling absolute ethanol (200 ml) for 30 min. *Anal.* Calcd for $C_{66}H_{60}As_2O_{16}$: C, 63.9; H, 5.25. Found: C, 62.2; H, 5.2.

(−)-Ethylene-1,2-bis(methylbenzylphenylarsonium) Di[D(−)-dibenzoylhydrogentartrate]. The absolute ethanol extract from the above was concentrated to ~30 ml and diluted with acetone (250 ml) to give a clear solution; careful addition of ether (10–20 ml) to this solution, with trituration, induced fine crystals to form. More ether was then carefully added to complete crystallization. The white (−)-diarsonium di[D(−)-dibenzoylhydrogentartrate] was collected, washed with ether, and dried (3.32 g): $[\alpha]^{20}D$ −106.2° (CH_3OH); *C*, 10.02 g/l. Recrystallization of a small portion (0.5 g.) from ho tabsolute ethanol (12 ml) with slow cooling gave the pure diastereoisomer (0.35 g): mp 139–141°; $[\alpha]^{20}D$ −113.8° (CH_3OH); *C*, 10.07 g/l. *Anal.* Calcd for $C_{66}H_{60}As_2O_{16}$: C, 63.9; H, 5.25. Found: C, 62.3; H, 5.3.

(+)-Ethylene-1,2-bis(methylbenzylphenylarsonium) Di(hexafluorophosphate). It was not found possible to exchange both dibenzoylhydrogen tartrate ions for iodide ions. (+)-Diarsoniumdi[D(−)-dibenzoylhydrogentartrate] (3.6 g) was ground in a mortar and pestle with a concentrated solution of LiI and then diluted with water (25 ml) whereupon the consistency of the insoluble mixture changed. The insoluble material was filtered off and ground again with concentrated LiI solution. This procedure was repeated three times. The product was then filtered off and washed quickly with ether (125 ml) to give a precipitate of, presumably, (+)-diarsonium [D(−)-dibenzoylhydrogentartrate] iodide (2.73 g): $[\alpha]^{20}D$ −54.4° (CH_3OH); *c*, 10.03 g/l. The presence of the dibenzoylhydrogentartrate was shown in the infrared spectrum. The hemiiodide was dissolved in a little methanol and added to a solution of aqueous KPF_6 and then excess water was added to precipitate all of the (+)-diarsonium di(hexafluorophosphate). Recrystallization of this compound from methanol–ether and then acetone–ether gave long needles of the desired product: mp 196°–200°; $[\alpha]^{20}D$ +5.22° (acetone); *c*, 40.03 g/l.) *Anal.* Calcd for $C_{30}H_{34}As_2F_{12}P_2$: C, 43.2; H, 4.11. Found: C, 43.1; H, 4.4.

(−)-Ethylene-1,2-bis(methylbenzylphenylarsonium) Di(hexafluorophosphate). The same procedure yielded the (−)-diarsonium di(hexafluorophosphate) as white needles: mp 191–193°; $[\alpha]^{20}D$ −7.74° (acetone); *c*, 40.06 g/l. *Anal.* Calcd for $C_{30}H_{34}As_2F_{12}P_2$: C, 43.2; H, 4.11. Found: C, 43.3; H, 4.2.

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