Resolutions using Metal Complexes. Resolution of (*RR,SS*)-*ortho*-Phenylenebis(methylphenylarsine) using internally Diastereoisomeric Palladium Complexes

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The dissymmetric chelating agent (*RR,SS*)-*ortho*-phenylenebis(methylphenylarsine) has been resolved into its enantiomers by fractionally crystallising internally diastereoisomeric palladium complexes containing the ditertiary arsine and optically active *ortho*-metallated dimethyl(α-methylbenzyl)amine. The full procedure is described and constitutes the first satisfactory route to optically active ditertiary arsines containing asymmetric arsenic atoms. The optically active ditertiary arsines, α(589 nm, CH_2Cl_2) ± 95°, are air-stable crystalline solids, m.p. 75—76 °C, and the absolute configuration of the enantiomer with a positive rotation at the sodium D line (589 nm) has been established as *RR* by a single-crystal *X*-ray determination of the structure of the internally diastereoisomeric palladium complex containing (*S*)(−)-dimethyl(α-methylbenzyl)amine. The *meso* diastereoisomer undergoes a halide-ion assisted epimerisation in acidic methanol solution and may be converted, under suitable conditions, into the less soluble *racemic* diastereoisomer thereby effecting a second-order asymmetric transformation between the diastereoisomeric ditertiary arsines.

THE separation of a pair of internally diastereoisomeric metal complexes containing a co-ordinated optically active resolving agent provides an important means of resolving chiral molecules which behave as ligands.[1] First applied to the resolution of *trans*-cyclo-octene,[2] this method is particularly appropriate to the resolution of tertiary arsines and phosphines because of the wide variety of transition-metal complexes available and because of the mild conditions required to liberate the resolved ligand from the metal complex. In the case of square-planar complexes of bivalent palladium and platinum the resolution procedure does not depend on any inherent chirality of the metal complex, but simply on the ability of the metal atom to simultaneously co-ordinate the resolving agent and the molecule to be resolved.

Previous work by us[1] in this area described an efficient method of resolving the unidentate ligand (*R,S*)-ethylmethylphenylarsine which involved the fractional crystallisation of bivalent platinum complexes containing the tertiary arsine and either (*RR*)- or (*SS*)-stilbenediamine. A procedure based on this approach for the resolution of chiral ditertiary arsines has hitherto been lacking. Accordingly, we describe here details of a method for the large-scale resolution of *rac*-*o*-phenylenebis(methylphenylarsine) wherein internally diastereoisomeric bivalent palladium complexes of the ditertiary arsine and optically active *ortho*-metallated dimethyl(α-methylbenzyl)amines are fractionally crystallised. This method is superior to that previously described[3] where the resolution relied upon the fractional crystallisation of diastereoisomeric benzylarsonium D(−)-dibenzoylhydrogentartrate salts of the ditertiary arsine.

RESULTS AND DISCUSSION

A single recrystallisation of the equimolar mixture of the *racemic* and *meso* diastereoisomers[4] of *o*-phenylenebis(methylphenylarsine) (1), (*RR,SS*-1) and (*RS*-1), respectively, formed in the reaction between Na[AsMePh] and $C_6H_4Cl_2$-*o* in tetrahydrofuran,[3] from diethyl ether–methanol solution led to an 80% recovery of the pure *racemic* diastereoisomer, (*RR,SS*-1), m.p. 88—88.5 °C. The *meso* diastereoisomer (*RS*-1) was partially separated from the remaining racemic material by forming the complex [Ni(*RS*-1)$_2$Cl]Cl (2) which is very much less soluble in ethanol than the corresponding nickel complexes formed by (*RR,SS*-1), *viz.* [Ni(*RR*-1)$_2$Cl]Cl and its enantiomer.[5] The free *meso* diastereoisomer was subsequently liberated from complex (2) by treating it with concentrated aqueous ammonia [equation (1)].

$$[\mathrm{Ni}(RS\text{-}1)_2\mathrm{Cl}]\mathrm{Cl} + 6\mathrm{NH}_3 \longrightarrow [\mathrm{Ni}(\mathrm{NH}_3)_6]\mathrm{Cl}_2 + 2(RS\text{-}1) \quad (1)$$

Pure (*RS*-1) distils as a viscous liquid, b.p. 160 °C (0.01 mmHg),† and was obtained as white leaflets, m.p. 61—62 °C, after seeding with the corresponding ditertiary phosphine,[5] which was easier to crystallise in the first instance. An additional 5% of (*RR,SS*-1) was recovered from the purple filtrate remaining from the separation of (2) by displacing the co-ordinated ditertiary arsines with ammonia and then fractionally crystallising the mixture as described above.

The *meso* diastereoisomer epimerises under acidic conditions in the presence of halide ions into an equilibrium 53 : 47 mixture of the *racemic* and *meso* ditertiary arsines, respectively. The rate of the epimerisation is halide-ion dependent and increases in the order $Cl^- < Br^- < I^-$, the process presumably involving the rapid pseudo-rotation of a five-co-ordinate arsenic species.[6] The detailed kinetics of the reaction (an asymmetric transformation of the first kind) is currently under investigation. Because the *racemic* diastereoisomer is less soluble than the *meso* compound in methanol, however, it was possible, under acidic conditions in the presence of iodide ions, to convert the *meso* sample into the *racemic* form, thereby effecting a second-order transformation between the diastereoisomers of the ditertiary arsine [equation (2)].

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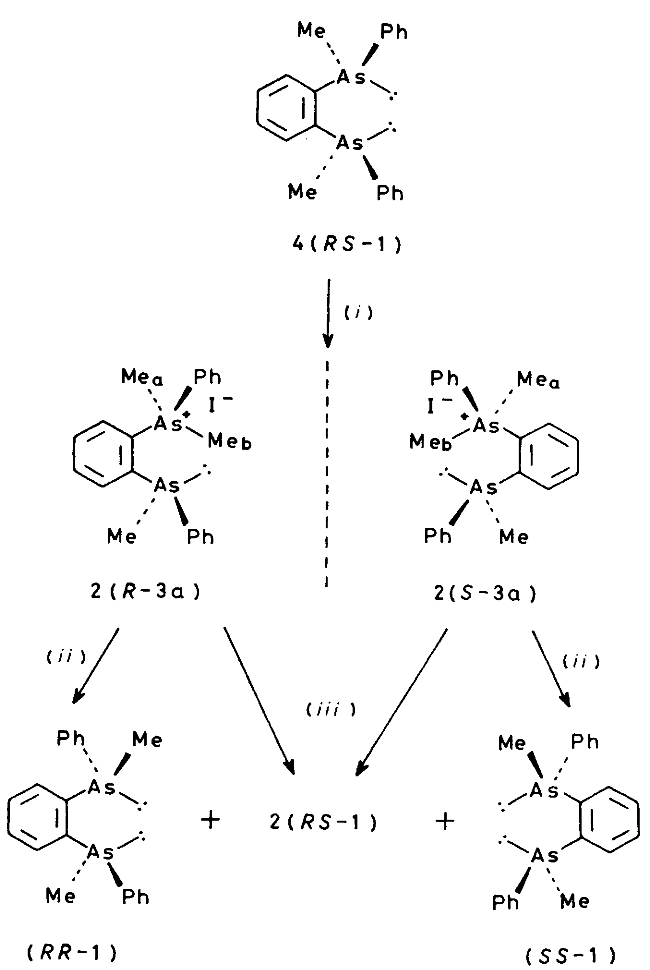
† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

Quaternisation of (*RS*-1) with iodomethane affords in good yield the *racemic* salt dimethyl[2-(*R*,*S*)-(methylphenylarsino)phenyl]phenylarsonium iodide (*R*,*S*-3a).

$$2(RS\text{-}1) \rightleftharpoons (RR,SS\text{-}1) + \underset{\text{(solution)}}{(RS\text{-}1)} \longrightarrow (RR,SS\text{-}1)_{(s)} \qquad (2)$$

Although the ^{1}H n.m.r. spectrum of (*R*,*S*-3a) shows the expected pair of singlet resonances for the diastereotopic methyls of the $\overset{+}{\mathrm{As}}\mathrm{Me}_2$ group, the chemical-shift difference between the signals is small (1.0 Hz). This is consistent with the results of the thermal decomposition of (*R*,*S*-3a), however, where only a minor discrimination was observed in the elimination of the iodomethane, a *ca.* 1 : 1 mixture of the *racemic* and *meso* ditertiary arsines being produced in high yield (94%) [(*RR*,*SS*-1) : (*RS*-1) = 53 : 47] (Scheme 1). Since (*RR*,*SS*-1) and (*RS*-1) are readily separated by fractional crystallisation, this procedure is also convenient for the conversion of (*RS*-1) into resolvable material.



SCHEME 1 (*i*) 4MeI; (*ii*) heat, $-\mathrm{Me_aI}$; (*iii*) heat, $-\mathrm{Me_bI}$

Resolution of (*RR*,*SS*-1).—The known [7] chloro-bridged dimer (*S*-4) was prepared in 94% yield from (*S*)(−)-dimethyl(α-methylbenzyl)amine and lithium tetrachloropalladate(II) in methanol. The dimer was suspended in methanol and treated with 2 equivalents of (*RR*,*SS*-1) whereupon the reactants dissolved to give a solution of the internally diastereoisomeric chlorides (*S*,*SS*-5) and (*S*,*RR*-5) (Scheme 2). The addition of 1 equivalent of an aqueous solution of $[\mathrm{NH_4}][\mathrm{PF_6}]$ to this solution selectively precipitated in high yield the less soluble hexafluorophosphate salt (*S*,*SS*-6) in a state of high optical purity, α(589 nm, acetone) + 273°.* Recrystallisation from acetone–benzene solution brought this material to its maximum optical purity, α(589 nm, acetone) +287°, large white prisms, m.p. 205 °C (decomp.). The combination of high chemical yield (>95%), overall stability, and low solubility of (*S*,*SS*-6) relative to (*S*,*RR*-6) facilitates its purification and makes it an excellent intermediate in the resolution procedure. Pure (*S*,*SS*-6) has the expected ^{1}H n.m.r. spectrum in $\mathrm{CH_2Cl_2}$ and behaves as a 1 : 1 electrolyte in nitrobenzene solution.

A single-crystal *X*-ray analysis [8] of $(+)_{589}$-(*S*,*SS*-6) clearly established the absolute configuration of the ditertiary arsine relative to the co-ordinated (*S*)(−)-dimethyl(α-methylbenzyl)amine. Furthermore, refinement of the structure established the overall chirality of the molecule, thereby confirming the absolute configuration of the ditertiary arsine and of the amine which had previously been inferred from optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) studies.[9]

The liberation of the ditertiary arsine from (*S*,*SS*-6) was performed in two steps. The first involved boiling a solution of the complex in acetone containing hydrochloric acid to remove the resolving agent, which could then be recovered [equation (3)]. The square-planar

$$(S,SS\text{-}6) + 2\mathrm{HCl} \longrightarrow \underset{(SS\text{-}7)}{[\mathrm{PdCl_2}(SS\text{-}1)]} + (S)(-)[\mathrm{NMe_2}\{\mathrm{CH(Me)Ph}\}\mathrm{H}][\mathrm{PF_6}] \qquad (3)$$

complex (*SS*-7) deposits from the reaction mixture in almost quantitative yield as yellow microcrystals, m.p. 305 °C (decomp.), α(589 nm, $\mathrm{CH_2Cl_2}$) −68.2°. The equally pure enantiomer (*RR*-7) was obtained similarly from the enantiomeric internal diastereoisomer (*R*,*RR*-6). Only mild conditions were required for the final step which involved the liberation of the optically active ditertiary arsines from the palladium complexes (*RR*-7) and (*SS*-7). Thus, for example, a solution of (*SS*-7) in dichloromethane was stirred for a few minutes with an excess of K[CN] in water and the colourless organic layer separated and dried. Removal of the solvent followed by a recrystallisation of the colourless residue from aqueous methanol afforded large friable rods, m.p. 75—76 °C, of the air-stable optically pure ditertiary arsine (*RR*-1), α(589 nm, $\mathrm{CH_2Cl_2}$) +95°. The pure optically active product may be distilled [b.p. 180—200 °C (0.2 mmHg)] without loss of optical activity. Although perfectly stable in the solid state, the ditertiary arsines are somewhat air-sensitive in solution and reactions involving them were carried out in a nitrogen atmosphere. The optical rotations of (*RR*-1) and (*SS*-1) are remarkably

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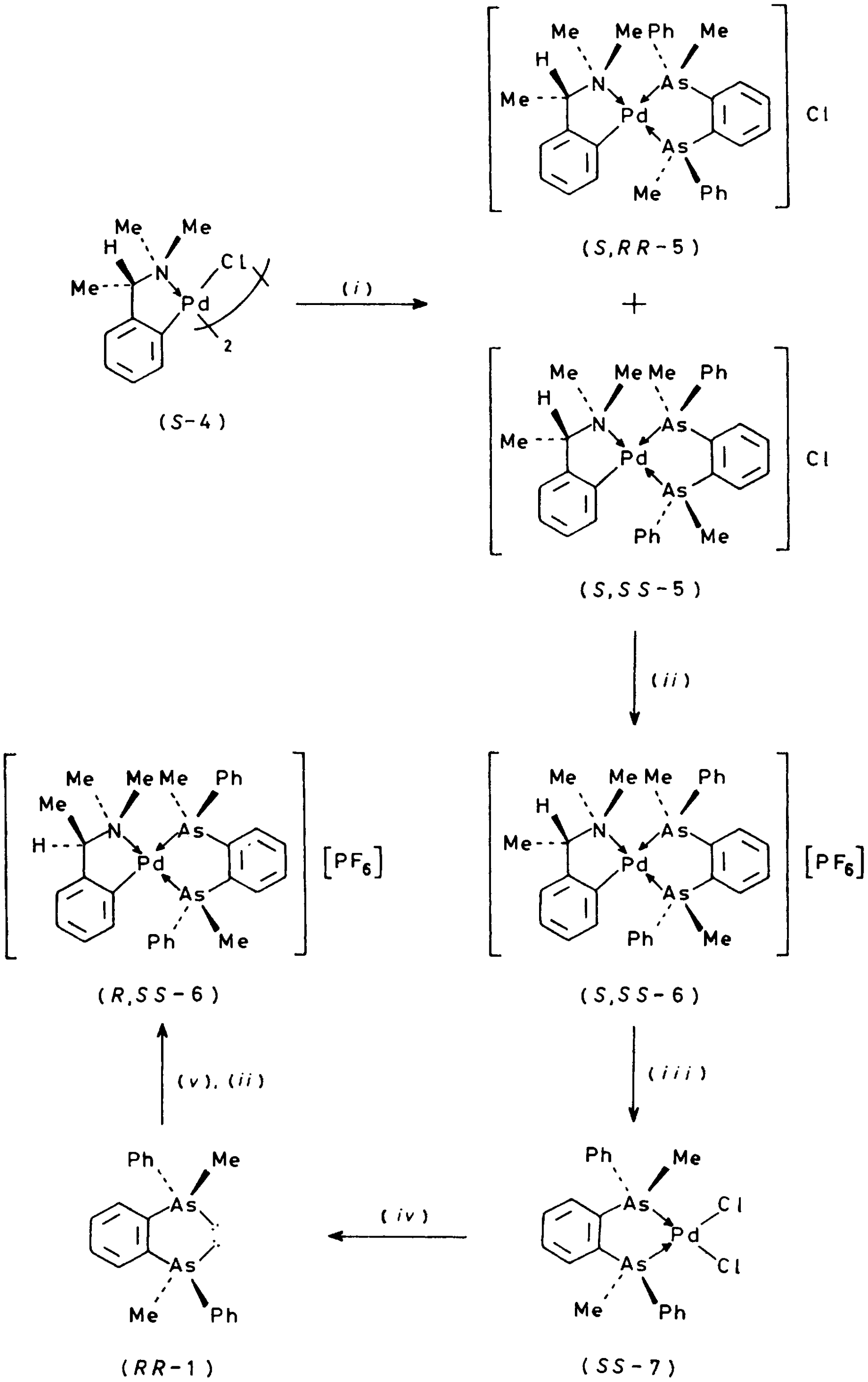
* α(589 nm) refers to the optical rotation at the sodium D line at 20 °C.

solvent dependent. For example, the following values of α(589 nm) for 10 g l^{-1} solutions of (*SS*-1) were obtained: −99.7 (Me_2CO), −95 (CH_2Cl_2), −57.5 (C_6H_6), −57.4 (Et_2O), and −55.3 ($CHCl_3$).

The linear absorption spectra of complexes (*RR*-7) and (*SS*-7) (Figure 1) show two definite regions of absorption. The band centred at 360 nm (ε = 3 920 dm^3 mol^{-1} cm^{-1}) may reasonably be attributed[10] to predominantly *d–d* transitions and the more intense peak at higher energy (not shown in Figure), which is resolved into two components ($\lambda_{max.}$ 237, ε = 17 100; and $\lambda_{max.}$ 264 nm, ε = 18 400 dm^3 mol^{-1} cm^{-1}), to aromatic and charge-transfer (Pd–As and Pd–Cl) transitions. The intensity of the *d–d* band in these complexes is greater than in similar compounds of palladium containing ' hard ' donor atoms although a similar effect has been observed previously[11] in the spectra of cobalt(III) complexes containing ' hard ' and ' soft ' donor atoms. The c.d.



SCHEME 2 (*i*) 2(*RR*,*SS*-1) in MeOH; (*ii*) $[NH_4][PF_6]$ in water; (*iii*) conc.HCl in Me_2CO; (*iv*) K[CN] in water; (*v*) ½(*R*-4) in MeOH spectra of the two optical isomers are enantiomorphic and contain several bands within the region 280—450 nm. The intensity of these bands appears to indicate a strong vicinal effect [12] of the asymmetric donor atoms on the metal chromophores. The u.v. absorption and c.d. spectra of the free ligand are complicated (Figure 2) and are presumably the result of overlapping absorption peaks associated with the aromatic *o*-phenylene and arsenic–phenyl moieties.

The internally diastereoisomeric palladium chlorides (*R*,*RR*-5) and (*R*,*SS*-5), and their enantiomers could not be isolated from the reaction mixture or prepared in a satisfactory state directly from the optically active ditertiary arsines. They are moderately hygroscopic amorphous solids which appear to associate in solution as evidenced by spectral and conductivity measurements in solvents of different polarity. For example, solutions of both diastereoisomers were yellow in benzene but colourless in methanol in which they behaved as 1 : 1 electrolytes. The soluble diastereoisomers were accordingly prepared directly and characterised as their hexafluorophosphate salts, which are air-stable crystalline solids, m.p. 194—197 °C, α(589 nm, acetone) ±151°, for (*R*,*SS*-6) and (*S*,*RR*-6), respectively [equations (4) and (5)].

$$(RR\text{-}1) + \tfrac{1}{2}(R\text{-}4) \longrightarrow (R,SS\text{-}5) \longrightarrow (R,SS\text{-}6) \quad (4)$$

$$(SS\text{-}1) + \tfrac{1}{2}(S\text{-}4) \longrightarrow (S,RR\text{-}5) \longrightarrow (S,RR\text{-}6) \quad (5)$$

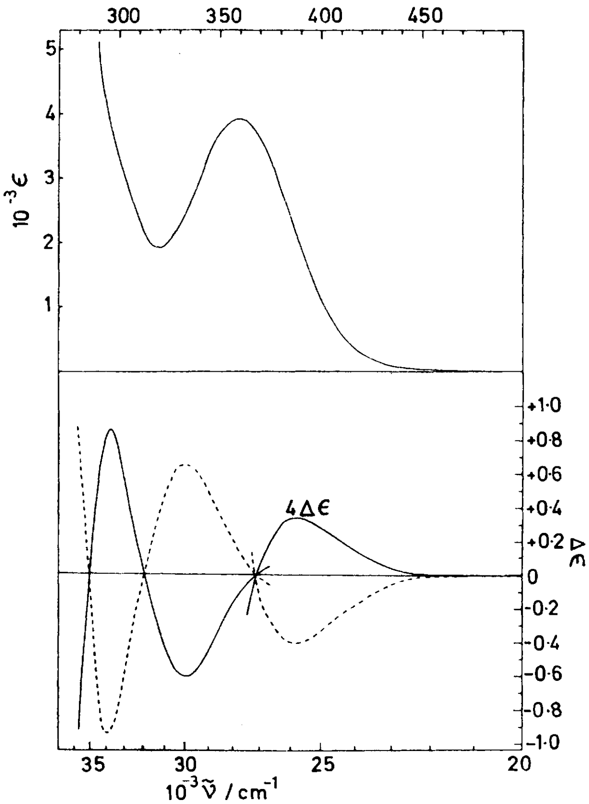


FIGURE 1 Absorption and c.d. spectra of $(+)_{589}$-(*RR*-7) (——) and $(-)_{589}$-(*SS*-7) (– – – –)

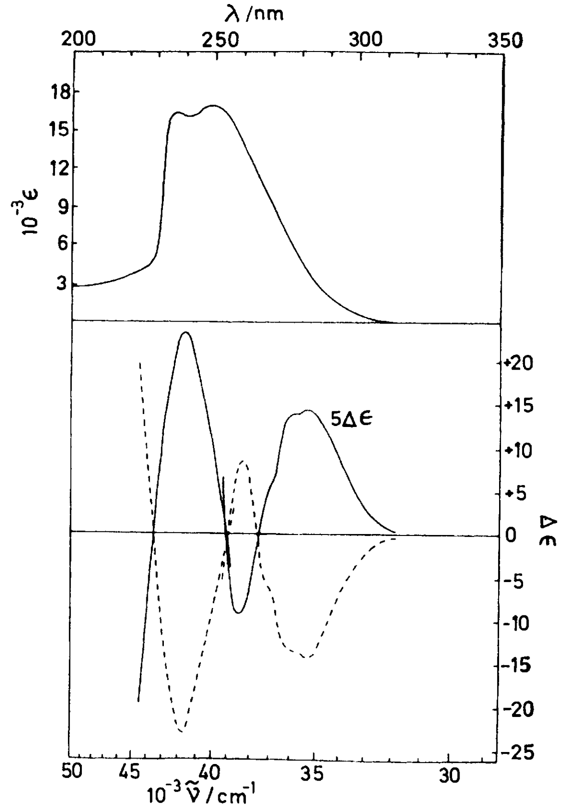


FIGURE 2 Absorption and c.d. spectra of $(+)_{589}$-(*RR*-1) (——) and $(-)_{589}$-(*SS*-1) (– – – –)

Polarimetry provided a sensitive and accurate means of monitoring the optical purity of the less soluble diastereoisomer because of the large and opposite values of α for the different diastereoisomers, *viz.* +287 and −151° for (*S*,*SS*-6) and (*S*,*RR*-6), respectively.

Quaternisation of (*RR*-1) or (*SS*-1) is stereospecific. The reaction of (*RR*-1) with benzyl bromide gives a 95% yield of the mono salt *threo*-(*S*)(+)-benzyl(methyl)[2-(*R*)-(methylphenylarsino)phenyl]phenylarsonium bromide, (8a), α(589 nm, CH_2Cl_2) +108.7, which is readily converted into the corresponding hexafluorophosphate salt, (8b), α(589 nm, acetone) +102.8°. The optically active quaternary salts are of interest in connection with various problems of asymmetric synthesis. For example, preliminary work [13] has shown that ylides derived from the optically active salts (8a) and (8b) react with prochiral aldehydes to give *trans*-2,3-diaryloxiranes in high chemical yields and with optical purities of between 4.7 and 38% depending upon the nature and position of substituents on the benzyl and aromatic groups of the reacting species.

EXPERIMENTAL

Reactions involving air-sensitive reagents were carried out in an atmosphere of pure nitrogen using the Schlenk technique. Solvents were dried in the usual way and degassed by distillation through a stream of pure nitrogen. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Hydrogen-1 n.m.r. spectra were recorded at 90 MHz using a Bruker HX-90 spectrometer; chemical shifts are quoted relative to tetramethylsilane as internal standard. The optical rotations were recorded using a Perkin-Elmer 141 polarimeter and a 10 cm cell thermostatted at 20 °C. The c.d. spectra were obtained using a Jasco model ORD/UV-5 ORD recorder fitted with a Sproul Scientific SS20 CD modification.

racemic- *and* -meso-o-*Phenylenebis(methylphenylarsine)*, (*RR*,*SS*-1) *and* (*RS*-1).—An equimolar mixture of the two diastereoisomeric ditertiary arsines was obtained in 78% yield using the method previously described [3] which involves the reaction of Na[AsMePh] with *o*-dichlorobenzene in tetrahydrofuran solution.

Separation of (*RR*,*SS*-1) *and* (*RS*-1).—The mixture of diastereoisomers (100 g) was dissolved in hot methanol (1 300 cm^3) containing diethyl ether (52 cm^3). Slow cooling of the solution afforded large flakes of (*RR*,*SS*-1) which after recrystallisation from methanol (1 060 cm^3) had m.p. 88—88.5 °C, yield 40 g (80%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.31 (6 H, s, AsMe), 7.17—7.49 p.p.m. (14 H, br m, aromatics). The solvents were removed from the original mother liquor and the oil which remained (60 g) was dissolved in hot ethanol (35 cm^3) and added to a stirred solution of $[Ni(OH_2)_6]Cl_2$ (18 g) in ethanol (110 cm^3). An immediate purple colour developed in the solution. The reaction mixture was filtered and concentrated to *ca.* 100 cm^3 whereupon green crystals of the complex [Ni(*RS*-1)$_2$Cl]Cl (2) began to separate. The precipitation of (2) was completed by adding light petroleum (b.p. 60—70 °C, 30 cm^3). The crude nickel complex (30 g) was purified by Soxhlet extraction into CH_2Cl_2 (2 l). The purple extract was stirred and concentrated to *ca.* 300 cm^3 and the suspension diluted with light petroleum (300 cm^3). Pure (2) separated as green microcrystals, m.p. 262—263 °C, yield 29 g (49%) (Found: C, 50.4; H, 4.0 $C_{40}H_{40}As_4Cl_2Ni$ requires C, 50.6; H, 4.2%). A full description of the properties of (2) will appear in a forthcoming paper. The co-ordinated ditertiary arsine (*RS*-1) was liberated from (2) by treating the complex with aqueous ammonia. Thus, a suspension of (2) (12.6 g) in CH_2Cl_2 (100 cm^3) was vigorously stirred while aqueous ammonia (30% w/w, 5 cm^3) was added. Purple $[Ni(NH_3)_6]Cl_2$ precipitated and was filtered off. The filtrate was dried (Mg[SO$_4$]), the solvent removed, and the residual oil re-dissolved in hot light petroleum (350 cm^3) and once again filtered and freed from solvent. The resulting oil (10.7 g, 98%) was crystallised by dissolving it in boiling methanol (145 cm^3), cooling the solution to room temperature, and seeding with crystalline *meso-o*-phenylenebis(methylphenylphosphine).[5] Pure (*RS*-1) was obtained as white leaflets, m.p. 61—62 °C, yield 9.5 g (87%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.46 (6 H, s, AsMe), 7.07—7.37 p.p.m. (14 H, br m, aromatics).

The purple filtrate from the original separation of (2) was evaporated to dryness and the co-ordinated ditertiary arsines liberated with aqueous ammonia as described above. Recovery and fractional crystallisation of the mixture of diastereoisomers of (1) from this decomposition afforded an additional 5% of (*RR*,*SS*-1).

Second-order Transformation of (*RS*-1) *into* (*RR*,*SS*-1).—A suspension of (*RS*-1) (10 g) in methanol (100 cm^3) was heated (in a nitrogen atmosphere) until the solid had melted and sodium iodide (0.3 g) and HCl (10 mol dm^{-3}, 0.3 cm^3) added. The reaction mixture was seeded with (*RR*,*SS*-1) and allowed to crystallise at room temperature for 4 h with occasional stirring; the crystallisation was completed by cooling to −10 °C for 8 h. The product was collected under nitrogen, washed with dilute ammonia solution (3%, 100 cm^3), and then dissolved in diethyl ether (150 cm^3) containing concentrated ammonia (30%, 5 cm^3). The organic layer was separated, thoroughly washed with water, dried, and evaporated. The residue was recrystallised from hot methanol (200 cm^3) to yield white flakes of pure (*RR*,*SS*-1), m.p. 90 °C, yield 8.5 g (85%). The ^1H n.m.r. spectrum in $CDCl_3$ was identical with that of an authentic sample.

Dimethyl[2-(R,S)-(*methylphenylarsino*)*phenyl*]*phenylarsonium Iodide*, (*R*,*S*-3a), *and Hexafluorophosphate*, (*R*,*S*-3b).—A solution of (*RS*-1) (0.5 g) in iodomethane (1 cm^3) was diluted with propan-2-ol (10 cm^3) and the reaction mixture stood at room temperature for 8 h. The product was filtered off, washed with propan-2-ol, and dried to give pale yellow needles 0.54 g (82%), m.p. 145—146 °C (Found: C, 46.2; H, 4.3. $C_{21}H_{23}As_2I$ requires C, 45.7; H, 4.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.31 (3 H, s, AsMe), 2.98 (3 H, AsMe), 2.99 (3 H, s, AsMe), 6.97—8.06 p.p.m. (14 H, br m, aromatics). Metathesis of (*RS*-3a) with $[NH_4][PF_6]$ in aqueous methanol afforded, in 75% yield, the *hexafluorophosphate* (*R*,*S*-3b) as colourless fronds, m.p. 183—184 °C, after recrystallisation from CH_2Cl_2–Et_2O (Found: C, 44.0; H, 4.0. $C_{21}H_{23}As_2F_6P$ requires C, 44.2; H, 4.1%). Hydrogen-1 n.m.r. spectrum in CH_2Cl_2: δ 1.35 (3 H, s, AsMe), 2.59 (6 H, s, $\overset{+}{As}Me_2$), 7.01—7.75 p.p.m. (14 H, br m, aromatics).

Pyrolysis of (*R*,*S*-3a).—A sample of (*R*,*S*-3a) (0.23 g) was decomposed by heating it to 200 °C *in vacuo*. A colourless oil distilled, 0.16 g, b.p. *ca.* 180 °C (0.1 mmHg), which was shown by its ^1H n.m.r. spectrum to consist of an almost equimolar mixture of (*RR*,*SS*-1) and (*RS*-1) (*rac* : *meso* = 53 : 47) (94%).

Di-μ-chloro-bis[(R)-*dimethyl*(α-*methylbenzyl*)*aminato*-C^2N]*dipalladium*(II),* (*R*-4).—Following a procedure modified from that described by Otsuka *et al.*,[7] finely divided $[(PdCl_2)_n]$ (20.6 g) was dissolved in methanol (500 cm^3) containing LiCl (11.6 g) at 60 °C and the resulting solution filtered and treated with (*R*)(+)-NMe$_2$[CH(Me)Ph] (40 g, 2 equiv.), α(589 nm, neat) +56°. The granular yellow product separated at once but the reaction mixture was stirred for another 2 h and then cooled to −10 °C to complete the precipitation. The product was filtered off, thoroughly washed with cold methanol (0° C), and dried at 80 °C (0.01 mmHg) as a yellow powder, m.p. 195—200 °C (decomp.), 31.6 g (94%), α(589 nm, CH_2Cl_2, 6.5 g l^{-1}) −51.8° (Found: C, 41.5; H, 4.9; N, 5.0. $C_{20}H_{28}Cl_2N_2Pd_2$ requires C, 41.4; H, 4.9; N, 4.8%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.57 (3 H, d, *J* 6.8 Hz, $CHCH_3$), 2.64 (3 H, s, NMe) 2.91 (3 H, s, NMe), 3.87 (1 H, q, *J* 6.8 Hz, $CHCH_3$), 6.67—7.28 p.p.m. (4 H, br m, aromatics). The second equivalent of amine, which acted as the depronating agent in the *ortho*-metallation, was recovered from the filtrate by evaporating the solvent and extracting the *hydrochloride* into water, neutralising the extract with sodium hydroxide, and then extracting the optically pure amine into diethyl ether.

Di-μ-chloro-bis[(S)-*dimethyl*(α-*methylbenzyl*)*aminato*-C^2,*N*]-*dipalladium*(II), (*S*-4), was prepared in the same way but using (*S*)(−)-dimethyl(α-methylbenzyl)amine, α(589 nm, neat) −58°, to give a yellow powder, m.p. 195—200 °C

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* Di-μ-chloro-bis[(*R*)-2-(1-dimethylaminoethyl)phenyl-*C'N*]-dipalladium(II).

(decomp.), α(589 nm, CH_2Cl_2, 9.2 g l^{-1}) +50.1° (Found: C, 41.4; H, 4.9; N, 4.8. $C_{20}H_{28}Cl_2N_2Pd_2$ requires C, 41.4; H, 4.9; N, 4.8%). The ^{1}H n.m.r. spectrum was identical with that of (*R*-4).

Resolution of (*RR,SS*-1): *Formation and Separation of the Internal Diastereoisomer* (*S,SS*-6).—A suspension of (*RR,SS*-1) (4.1 g, 10 mmol) and (*S*-4) (3.1 g, 5.35 mmol) in methanol (50 cm^3) was stirred for 2 h to form a clear, almost colourless, solution of the internally diastereoisomeric *chlorides* (*S,SS*-5) and (*S,RR*-5). The reaction mixture was filtered and a solution of $[NH_4][PF_6]$ (0.86 g, 5.4 mmol) in water (35 cm^3) slowly added (over 1 h) to the filtrate. After 12 h the crystalline precipitate was filtered off, washed with aqueous methanol (1 : 3, 15 cm^3) and diethyl ether, and then dried to give the almost pure internal diastereoisomer (*S,SS*-6), 4.15 g, α(589 nm, acetone, 10.8 g l^{-1}) +273°. This material was dissolved in acetone (100 cm^3), filtered, the filtrate concentrated to *ca.* 15 cm^3, and the solution stood aside for 3 h. Large prisms of the pure hexafluorophosphate (*S,SS*-6) slowly deposited and benzene (70 cm^3) was carefully added to complete the precipitation. The product was separated, washed with benzene, and dried as white prisms, m.p. 205 °C (decomp.), 3.82 g (95%), α(589 nm, acetone, 9.35 g l^{-1}) +287° (Found: C, 44.4; H, 4.3. $C_{30}H_{34}As_2F_6NPPd$ requires C, 44.5; H, 4.2%). Hydrogen-1 n.m.r. spectrum in CH_2Cl_2: δ 1.67 (3 H, d, *J* 6.5 Hz, CHC*H*$_3$), 2.09 (3 H, s, AsMe), 2.28 (3 H, s, AsMe), 2.79 (3 H, s, NMe), 2.94 (3 H, s, NMe), 3.98 (1 H, q, *J* 6.5 Hz, C*H*CH$_3$), 6.85—7.89 p.p.m. (18 H, br m, aromatics). Conductivity (5×10^{-4} mol dm^{-3} in $PhNO_2$ at 24 °C) = 28.4 ohm^{-1} cm^2 mol^{-1}.

The use of (*R*-4) as the resolving agent and following the same procedure afforded the enantiomeric *hexafluorophosphate* (*R,RR*-6), α(589 nm, acetone, 10.7 g l^{-1}) −287°.

Removal and Recovery of Resolving Agent: Conversion of (*S,SS*-6) *into Dichloro*[(SS)-o-*phenylenebis*(*methylphenylarsine*)]*palladium*(II), (*SS*-7).—A suspension of (*S,SS*-6) (3.0 g) in acetone (45 cm^3) was treated with hydrochloric acid (10 mol dm^{-3}, 15 cm^3) and the resulting yellow solution heated under reflux for 0.25 h. A yellow solid separated during this time. Water (15 cm^3) was then added to the reaction mixture and most of the acetone removed at the water pump. The bright yellow product was filtered off and washed successively with water, methanol, and diethyl ether, yield 2.63 g (96%), m.p. 305 °C (decomp.), α(589 nm, CH_2Cl_2, 9.8 g l^{-1}) −68.2° (Found: C, 41.0; H, 3.4. $C_{20}H_{20}As_2Cl_2Pd$ requires C, 41.0; H, 3.4%). Hydrogen-1 n.m.r. spectrum in CH_2Cl_2: δ 2.26 (6 H, s, AsMe), 7.43—7.74 p.p.m. (14 H, br m, aromatics). The filtrate was evaporated and the residue, mostly *amine hydrochloride*, dissolved in water. An excess of Na[OH] was added to this solution and the free *amine* extracted into diethyl ether. Almost all (*ca.* 90%) of the optically pure (*S*)(−)-dimethyl(α-methylbenzyl)amine, α(589 nm, neat) −57°, was recovered in this way from the diethyl ether after the usual drying and distillation.

Liberation of the Resolved Ditertiary Arsine (RR)(+)-o-*Phenylenebis*(*methylphenylarsine*), (*RR*-1).—A solution of (*SS*-7) (2.6 g) in CH_2Cl_2 (80 cm^3) was treated with an excess of K[CN] (3 g) in water (25 cm^3). The mixture was stirred until the yellow colour of the starting material had disappeared. The organic layer was separated, dried over $Mg[SO_4]$, and the solvent removed. The residual oil could be crystallised by the addition of a small quantity of diethyl ether but a better product was obtained by dissolving the oil in boiling methanol (112 cm^3) and carefully diluting with water (62 cm^3). The pure product, (*RR*-1), was thus obtained as large friable rods, m.p. 75—76 °C, 1.74 g (96%), α(589 nm, CH_2Cl_2, 8.8 g l^{-1}) +95° (Found: C, 58.9; H, 4.8. $C_{20}H_{20}As_2$ requires C, 58.6; H, 4.9%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.29 (6 H, s, AsMe), 7.10—7.50 p.p.m. (14 H, br m, aromatics).

(SS)(−)-*Phenylenebis*(*methylphenylarsine*), (*SS*-1).—The filtrate from the original separation of (*S,SS*-6) was concentrated and treated with concentrated hydrochloric acid (10 mol dm^{-3}, 10 cm^3). The clear yellow solution was boiled for 0.25 h and further reduced in volume (to *ca.* 20 cm^3), cooled, and the yellow crystalline product filtered off and washed with methanol and diethyl ether. This was shown to be almost optically pure (*RR*-7), m.p. 300 °C (decomp.), 2.66 g (91%), α(589 nm, CH_2Cl_2, 10.9 g l^{-1}) +66.8°. The ^{1}H n.m.r. spectrum of this material was identical with that of (*SS*-7). Decomposition of the almost pure (*RR*-7) with K[CN] afforded (*SS*-1), 1.8 g (88%), m.p. 73—74 °C, α(589 nm, CH_2Cl_2, 11 g l^{-1}) −83°. This material was brought to optical purity by treating it with (*R*-4) and $[NH_4][PF_6]$ to give (*R,RR*-6) which, after one recrystallisation, had α(589 nm, acetone, 10.6 g l^{-1}) −287° and m.p. 205 °C (decomp.), yield 3.25 g (93%). The ^{1}H n.m.r. spectrum in CH_2Cl_2 was identical with that reported for its enantiomer (*S,SS*-6). After decomposition to the dichloro-complex (*RR*-7) [α(589 nm, CH_2Cl_2, 9.2 g l^{-1}) +68.7°] and cyanolysis of this complex optically pure (*SS*-1) was obtained, 1.54 g (93%), m.p. 75—76 °C, α(589 nm, CH_2Cl_2, 8.8 g l^{-1}) −95.2°. This yield represents 75% of the possible recovery of (*SS*-1).

The absolute stereospecificity of the cyanolysis was confirmed by re-preparing the complexes (*RR*-7) and (*SS*-7) from the ditertiary arsines (*SS*-1) and (*RR*-1), respectively. The complexes had optical rotations identical with those from which the optically active ditertiary arsines were liberated.

Preparation of the Soluble Internal Diastereoisomers (*R,SS*-6) *and* (*S,RR*-6).—A mixture of (*RR*-1) (0.21 g) and (*R*-4) (0.15 g) in methanol (5 cm^3) was stirred until solution was complete. The reaction mixture was filtered and a solution of $[NH_4][PF_6]$ (0.1 g) in water (2 cm^3) added, followed by the slow addition of more water (10 cm^3). The white precipitate was filtered off, thoroughly washed with water, and dried (60 °C, 0.01 mmHg) to give pure (*R,SS*-6), 0.4 g (98%), m.p. 194—197 °C (decomp.), α(589 nm, CH_2Cl_2, 8.0 g l^{-1}) +151° (Found: C, 44.2; H, 4.4. $C_{30}H_{34}As_2F_6NPPd$ requires C, 44.5; H, 4.2%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.55 (3 H, d, *J* 6.3 Hz, CHC*H*$_3$), 2.08 (3 H, s, AsMe), 2.21 (3 H, s, AsMe), 2.66 (3 H, s, NMe), 2.95 (3 H, s, NMe), 3.70 (1 H, q, *J* 6.3 Hz, C*H*CH$_3$), 6.70—7.96 p.p.m. (18 H, br m, aromatics). Conductivity (5×10^{-4} mol dm^{-3} in $PhNO_2$ at 24 °C) = 27.0 ohm^{-1} cm^2 mol^{-1}. The enantiomer (*S,RR*-6) was prepared similarly in 99% yield, m.p. 196—197 °C (decomp.), α(589 nm, CH_2Cl_2, 8.7 g l^{-1}) −152°. The ^{1}H n.m.r. spectrum in $CDCl_3$ was identical with that for (*R,SS*-6).

threo-(S)(+)-*Benzyl*(*methyl*)[2-(R)-(*methylphenylarsino*)-*phenyl*]*phenylarsonium Bromide Hemihydrate*, (8a), *and Hexafluorophosphate*, (8b).—A solution of (*RR*-1) (0.41 g) in benzyl bromide (1 cm^3) was allowed to stand at 20 °C for 48 h and then carefully diluted with light petroleum (b.p. 60—70 °C, 30 cm^3). The pure *bromide hemihydrate* separated as white microcrystals, m.p. 145—146 °C, after filtration and washing with light petroleum, yield 0.55 g (95%), α(589 nm,

CH_2Cl_2, 11.4 g l^{-1}) +108.7° (Found: C, 55.2; H, 5.0. $C_{27}H_2As_2BrO_{0.5}$ requires C, 55.0; H, 4.8%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.28 (3 H, s, AsMe), 2.71 (3 H, s, $\overset{+}{\mathrm{As}}$Me), 5.18 (2 H, s, PhCH_2), 6.93—7.98 p.p.m. (19 H, br m, aromatics). The bromide was converted into the *hexafluorophosphate* (8b) as follows. A solution of (8a) (0.1 g) in methanol (3 cm^3) was treated with $[NH_4][PF_6]$ (0.1 g) in water (1 cm^3) followed by the addition of water (10 cm^3). The white precipitate was filtered off, washed with water, and dried (50 °C, 0.01 mmHg). Recrystallisation of this material from acetone (3 cm^3), by the addition of diethyl ether (10 cm^3), afforded white crystals of the pure salt (8b), 0.19 g (86%), m.p. 144—145°C, α(589 nm, acetone, 10.2 g l^{-1}) +102.8°. Hydrogen-1 n.m.r. spectrum in $(CD_3)_2CO$: δ 1.26 (3 H, s, AsMe), 2.33 (3 H, s, $\overset{+}{\mathrm{As}}$Me), 4.49 (2 H, s, PhCH_2), 6.69—7.89 p.p.m. (19 H, br m, aromatics). The enantiomeric salts with equal and opposite optical rotations but otherwise identical physical properties may be prepared similarly from (*SS*-1).

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