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Optically Active (2-Aminoethyl)methylphenylarsine and (2-Aminoethyl)butylphenylarsine and Their Palladium(II) and Platinum(II) Complexes

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The chiral bidentate ligands, (2-aminoethyl)methylphenylarsine (mpan) and (2-aminoethyl)butylphenylarsine (bpan) were prepared and resolved by preparing their palladium(II) complexes containing, respectively, (*R*)-*N*,*N*-dimethyl-1-(2-naphthyl)ethylamine and (*S*)-*N*,*N*-dimethyl-α-methylbenzylamine. The optically actaive free arsine ligands can be readily liberated from the palladium(II) complexes, and complexes of the type, [M^{II}X$_2$L] (M^{II}=Pd, Pt; X=Cl, Br, I; L= *R*-mpan, *S*-bpan) were prepared. The absorption and circular dichroism (CD) spectra of these and related complexes were recorded, and the absolute configurations of the arsenic atoms were assigned by comparing the CD spectra with those of analogous phosphine complexes. The optically active arsines in diethyl ether solution racemize by the addition of hydrochloric acid at room temperature, but their palladium(II) complexes in acetonitrile–ethanol solution containing hydrochloric acid are very optically stable and do not racemize by refluxing for a long time.

Otsuka *et al.* resolved chiral tertiary phosphines by fractional crystallization of their diastereomeric palladium(II) complexes containing optically active ortho-metallated *N*,*N*-dimethyl-α-methylbenzylamine or its analogs.[1,2] This method has been successfully applied to the resolution of bidentate chiral phosphines[3–6] and arsines.[5–8] The bidentate arsine ligands so far resolved, however, have a rigid framework such as *o*-phenylene[6–8] and quinolyl groups,[5] and no sterically flexible one such as (aminoalkyl)arsines has been reported, although several optically active metal complexes containing a flexible, linear quadridentate tetraarsine having two chiral arsenic donor atoms have been isolated.[9] We have succeeded in resolving (2-aminoethyl)methylphenylarsine (mpan) and (2-aminoethyl)butylphenylarsine (bpan) by use of (−)$_{589}$-di-μ-chloro-bis[(*R*)-*N*,*N*-dimethyl-1-(2-naphthyl)ethylamine-3*C*,*N*]dipalladium(II) and (+)$_{589}$-di-μ-chloro-bis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]dipalladium(II), respectively. In this paper, we describe the preparation of these optically active arsines and their metal complexes of the type, [M^{II}X$_2$L] (M^{II}=Pd, Pt; X=Cl, Br, I; L=mpan, bpan) as well as the analogous (2-aminoethyl)diphenylarsine (dpan) complexes, absorption and circular dichroism (CD) spectra of these complexes, and the absolute configurations and racemization of the chiral arsenic atoms.

Experimental

Free (aminoalkyl)arsines were handled under a nitrogen atmosphere until they formed air-stable palladium(II) and platinum(II) complexes. Tetrahydrofuran was dried with sodium and deoxygenated by distillation in a stream of nitrogen. Absorption, CD, and ^{1}H NMR spectra were recorded on a Hitachi 323 spectrophotometer, a JASCO J-40CS spectropolarimeter, and a JEOL JNM PMX 60 spectrometer, respectively. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter.

Diphenylarsine. Diphenylarsine was prepared by the method of Aquiar and Archibald,[10] and distilled under reduced pressure, bp 103—104 °C (133 Pa) (lit,[11] 87—90 °C (33 Pa)). ^{1}H NMR (CDCl$_3$) δ=4.97 (1H, s, AsH) and 7.13—7.76 (10H, m, C$_6$H$_5$).

(2-Aminoethyl)diphenylarsine, dpan. This compound was prepared by a method similar to that for (2-aminoethyl)diphenyl phosphine.[12,13] To a stirred solution of diphenylarsine (15.2 g, 66 mmol) in tetrahydrofuran (300 cm^3) was added a 15% (w/w) solution of butyllithium in hexane (45 cm^3, 73 mmol) over a period of 30 min at room temperature. After 1 h, aziridine (4.5 cm^3, 87 mmol) was added to the solution at 0 °C over a 15 min period. The mixture was heated at 50 °C for 1 h, then refluxed for 6 h, and allowed to stir at room temperature for 12 h. To the resulting brown solution was added deoxygenated water (2.5 cm^3), and after a while anhydrous sodium sulfate to remove excess water. After a few hours, the desiccant was filtered off, the solvent was removed by distillation, and the residual oil was distilled *in vacuo* to give (2-aminoethyl)diphenylarsine as a pale yellow viscous oil, bp 151—153 °C (133 Pa) (lit,[13] 140 °C (53 Pa)). Yield: 12.6 g (70%), ^{1}H NMR (CDCl$_3$) δ=1.25 (2H, s, NH$_2$), 2.15 (2H, t, AsCH$_2$), 2.91 (2H, t, NCH$_2$), and 7.17—7.77 (10H, m, C$_6$H$_5$).

(2-Aminoethyl)methylphenylarsine, mpan. Small pieces of sodium (2.4 g, 0.10 mol) were dissolved in liquid ammonia (150 cm^3). To this deep blue solution dpan (14.3 g, 5.2 mmol) was added with stirring. After 3 h, methyl iodide (18.2 g, 0.13 mol) was added to the resulting deep red solution, the color of which turning orange. Liquid ammonia was evaporated, and the residue was shaken with deoxygenated water–diethyl ether (60 cm^3–60 cm^3). The ethereal layer was separated and dried with anhydrous sodium sulfate. The desiccant was filtered off, the ether evaporated, and the residue was distilled at 95—98 °C and 133 Pa to give a colorless liquid. Yield: 7.0 g (63%). ^{1}H NMR (CDCl$_3$) δ=1.07 (2H, s, NH$_2$), 1.20 (3H, s, AsCH$_3$), 1.81 (2H, t, AsCH$_2$), 2.82 (2H, t, NCH$_2$), and 7.18—7.75 (5H, m, C$_6$H$_5$).

(2-Aminoethyl)butylphenylarsine, bpan. This compound was prepared by the same method as for mpan except that butyl bromide was used instead of methyl iodide. Bp 105—107 °C (133 Pa). Yield: 40%. ^{1}H NMR (CDCl$_3$)

δ=0.88 (3H, t, butylic CH_3), 1.1—1.8 (m, butylic $-CH_2-$), 1.23 (s, NH_2), 1.87 (t, $AsCH_2$), 2.87 (2H, t, NCH_2), and 7.23-7.77 (5H, m, C_6H_5).

*The Diastereomers of [(*R)-N,N-*Dimethyl-1-(2-naphthyl)ethylamine-3*C,N*][(2-aminoethyl)methylphenylarsine]palladium(II) Complex,* ***1a*** *and* ***1b****.* To a solution of $(-)_{589}$-di-μ-chloro-bis[(*R*)-*N*,*N*-dimethyl-1-(2-naphthyl)ethylamine-3*C*,*N*]dipalladium(II)[2) (2.04 g, 3.00 mmol) in benzene–methanol (10 cm^3–2 cm^3) was added a solution of mpan (1.28 g, 6.06 mmol) in benzene (3 cm^3). The mixture was stirred for 2 h at room temperature and then evaporated at 35 °C under reduced pressure until a small amount of white precipitate began to form. The precipitate was dissolved by heating at 45 °C, and the solution was allowed to stand overnight to yield colorless crystals. They were collected by filtration and recrystallized from methanol by adding benzene. No change in the $\Delta\varepsilon$ value was observed by repeated recrystallization. Yield (**1a**): 1.08 g. Found: C, 52.08; H, 5.82; N, 4.42%. Calcd for $PdC_{26.5}H_{35}N_2AsClO_{0.5}$=[Pd{(*R*)-$C_{10}H_6CH(CH_3)N(CH_3)_2$}(*R*-mpan)]Cl·1/2$CH_3OH$·1/2$C_6H_6$: C, 52.49; H, 5.82; N, 4.62%. $[\alpha]^{23}_{589}$ +135° (c 0.16, CH_3OH). Mp 175—179 °C. ^{1}H NMR ($CDCl_3$) δ=1.81 (3H, d, C–CH_3), 1.96 (3H, s, As–CH_3), 2.1—2.8 (4H, m, $-CH_2-$), 3.06 (6H, s, N–CH_3), 3.48 (1.5H, s, $C\underline{H}_3OH$), 3.93 (1H, q. $-\overset{|}{C}H-$), 5.20 (2H, broad s, NH_2), and 7.2—8.1 (14H, m, $C_{10}H_6$, C_6H_5, and C_6H_6).

The mother liquor was evaporated to a volume of *ca.* 10 cm^3, and an aqueous solution (2 cm^3) of ammonium hexafluorophosphate (*ca.* 70 mg) was added to form a white precipitate. The mixture was heated at 50 °C and methanol was added dropwise until the precipitate dissolved completely. The solution was then allowed to stand at room temperature to yield a white powder. It was collected and recrystallized from methanol by adding benzene. Yield (**1b**): 0.69 g. Found: C, 42.74; H, 4.79; N, 3.67%. Calcd for $PdC_{23}H_{30}N_2AsPF_6$=[Pd{(*R*)-$C_{10}H_6CH(CH_3)N(CH_3)_2$}(*S*-mpan)]$PF_6$: C, 41.81; H, 4.58; N, 4.24%. $[\alpha]^{23}_{589}$ −229° (c 0.095, CH_3OH). Mp 208—211 °C (dec). ^{1}H NMR (CD_2Cl_2) δ=2.00 (3H, s, As–CH_3), 1.72 (3H, d, C–CH_3), 2.1—2.6 (4H, m, $-CH_2-$), 2.73 (3H, s, N–CH_3), 2.90 (3H, s, N–CH_3), 3.16 (2H, broad s, NH_2), 4.13 (1H, q, $-\overset{|}{C}H-$), and 7.1—8.1 (11H, m, C_6H_5 and $C_{10}H_6$).

*The Diastereomers of [(*S)-N,N-*Dimethyl-α-methylbenzylamine-2*C,N*][(2-aminoethyl)butylphenylarsine]palladium(II) Complex,* ***2a*** *and* ***2b****.* To a solution of $(+)_{589}$-di-μ-chloro-bis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]-dipalladium(II)[2,3) (1.13 g, 1.95 mmol) in benzene (10 cm^3) was added a solution of bpan (1.00 g, 3.95 mmol) in benzene (5 cm^3), and the mixture was stirred for 2 h at room temperature. Hexane (3 cm^3) was added with stirring. The mixture was allowed to stand for 1 h at room temperature to yield colorless crystals, and then cooled at 0 °C for 1 h to complete precipitation. The crystals were collected, washed with hexane, and recrystallized repeatedly from methanol by adding benzene until no change in the $\Delta\varepsilon$ values was observed. Yield (**2a**): 0.68 g. Found: C, 48.67; H, 6.39; N, 5.39%. Calcd for $PdC_{22}H_{34}N_2AsCl$=[Pd{(*S*)-$C_6H_4CH(CH_3)$-$N(CH_3)_2$}(*S*-bpan)]Cl: C, 48.64; H, 6.31; N, 5.16%. $[\alpha]^{23}_{589}$ +37° (c 0.042, CH_3OH). Mp 203—207 °C. ^{1}H NMR ($CDCl_3$) δ= 0.86 (3H, t, butylic CH_3) 1.1—2.8 (m, $-CH_2-$), 1.72 (d, $-CHC\underline{H}_3-$), 3.08 (6H, s, N–CH_3), 3.72 (1H, q, $-\overset{|}{C}H-$), 5.20 (2H, broad s, NH_2) and 6.7—8.1 (9H, m, C_6H_4 and C_6H_5).

The mother liquor was evaporated to dryness. The residue was mixed with boiling water (200 cm^3), and the mixture was reduced in volume to about 40 cm^3. Ammonium hexafluorophosphate (*ca.* 60 mg) was added to yield a white precipitate. It was dissolved in a minimum amount of methanol, and the solution was allowed to evaporate slowly at room temperature to form colorless crystals, which were collected and recrystallized from methanol by adding benzene. Yield (**2b**): 0.89 g. Found: C, 40.56; H, 5.24; N, 4.29%. Calcd for $PdC_{22}H_{34}N_2AsPF_6$=[Pd{(*S*)-C_6H_4CH-$(CH_3)N(CH_3)_2$}(*R*-bpan)]PF_6: C, 40.48; H, 5.25; N, 4.29%. $[\alpha]^{23}_{589}$ +75° (c 0.098, CH_3OH). Mp 169—173 °C. ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, butylic CH_3), 1.2—2.6 (m, $-CH_2-$), 1.62 (d, $-CHC\underline{H}_3-$), 2.73 (3H, s, N–CH_3), 2.92 (3H, s, N–CH_3), 3.20 (2H, broad s, NH_2), 4.03 (1H, q, $-\overset{|}{C}H-$), and 6.3—8.1 (9H, m, C_6H_5 and C_6H_4).

*[(*R)-N,N-*Dimethyl-1-(2-naphthyl)ethylamine-3*C,N*][(2-aminoethyl)diphenylarsine]palladium(II) Chloride, 3.* To a stirred solution of $(-)_{589}$-di-μ-chloro-bis[(*R*)-*N*,*N*-dimethyl-1-(2-naphthyl)ethylamine-3*C*,*N*]dipalladium(II)[2) (200 mg, 2.94×10^{-4} mol) in benzene (8 cm^3) was added a benzene solution (3 cm^3) of dpan (180 mg, 6.59×10^{-4} mol). After 2 h, hexane (2 cm^3) was added and the mixture was allowed to cool at 0 °C for 30 min to yield a white precipitate. It was collected by filtration, and recrystallized from methanol by adding benzene. Yield: 0.36 g. Found: C, 54.77; H, 5.83; N, 4.69%. Calcd for $PdC_{28}H_{32}N_2AsCl$=[Pd{(*R*)-$C_{10}H_6$-$CH(CH_3)N(CH_3)_2$}(dpan)]Cl: C, 54.83; H, 5.26; N, 4.57%. $[\alpha]^{23}_{589}$ −42° (c 0.103, CH_3OH). Mp 218—222 °C (dec). ^{1}H NMR ($CDCl_3$) δ=1.76 (3H, d, C–CH_3), 2.5—3.0 (4H, m, $-CH_2-$), 3.07 (3H, s, N–CH_3), 3.11 (3H, s, N–CH_3), 3.99 (1H, q, $-\overset{|}{C}H-$), 5.31 (2H, broad s, NH_2), and 6.9—7.9 (16H, m, C_6H_5 and $C_{10}H_6$).

*[(*S)-N,N-*Dimethyl-α-methylbenzylamine-2*C,N*][(2-aminoethyl)diphenylarsine]palladium(II) Chloride Monohydrate, 4.* This complex was prepared from $(+)_{589}$-di-μ-chloro-bis-[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]dipalladium-(II)[2,3) and dpan by a method similar to that used for **3**. Yield: 90%. Found: C, 49.32; H, 5.52; N, 4.68%. Calcd for $PdC_{24}H_{32}N_2AsClO$=[Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$-}(dpan)]Cl·H_2O: C, 49.59; H, 5.55; N, 4.82%. $[\alpha]^{23}_{589}$ +41° (c 0.093, CH_3OH). Mp 208—211 °C (dec). ^{1}H NMR ($CDCl_3$) δ=1.66 (3H, d, C–CH_3), 2.4—2.9 (4H, m, $-CH_2-$), 3.04 (3H, s, N–CH_3), 3.12 (3H, s, N–CH_3), 3.86 (1H, q, $-\overset{|}{C}H-$), 5.18 (2H, broad s, NH_2), 6.5—7.9 (14H, m, C_6H_5 and C_6H_4).

[$PdCl_2$(R-mpan)]. A mixture of **1a** (56 mg, 9.20×10^{-5} mol) and sodium cyanide (45 mg, 9.18×10^{-4} mol) in water–diethyl ether (10 cm^3–10 cm^3) was stirred vigorously for 10 min and allowed to stand for a while. The ethereal phase was added to a stirred solution of palladium(II) chloride (17 mg, 9.59×10^{-5} mol) in acetonitrile (30 cm^3), the color of the mixture changing from orange to yellow. The mixture was stirred for 6 h at room temperature and then filtered. The filtrate was evaporated to a volume of *ca.* 5 cm^3, and the concentrate was applied on a column (ϕ12 mm×50 mm) of acid alumina. The product was eluted with 4:1 acetonitrile–ethanol. The eluate containing the main yellow band was collected and evaporated to a small volume to give yellow flocculent crystals of the palladium(II) complex. Yield: 28 mg. Found: C, 28.20; H, 3.61; N, 4.06%. Calcd for $PdC_9H_{14}NAsCl_2$: C, 27.83; H, 3.63; N, 3.61%.

[$PdCl_2L$] (L=S-bpan and dpan). These complexes were prepared by a method similar to that for [$PdCl_2$(*R*-mpan)]. Yields: *ca.* 70%. Found: C, 33.55; H, 4.41; N, 3.17%. Calcd for $PdC_{12}H_{20}NAsCl_2$=[$PdCl_2$(*S*-bpan)]: C, 33.48; H, 4.68; N, 3.25%. Found: C, 37.46; H, 3.56; N, 3.33%. Calcd for $PdC_{14}H_{16}NAsCl_2$=[$PdCl_2$(dpan)]: C, 37.32; H, 3.58; N, 3.11%.

[$PdBr_2L$] (L=R-mpan, S-bpan, and dpan). These complexes were prepared by methods similar to those for the corresponding dichloro complexes using palladium(II) bromide instead of palladium(II) chloride. The complexes were isolated as orange crystals in 60—90% yields. Found: C, 22.64; H, 2.93; N, 2.94%. Calcd for $PdC_9H_{14}NAsBr_2$=[$PdBr_2$(*R*-mpan)]: C, 22.65; H, 2.94; N, 2.93%. Found: C, 27.10; H, 3.60; N, 2.55%. Calcd for $PdC_{12}H_{20}NAsBr_2$=[$PdBr_2$(*S*-bpan)]: C, 27.75; H, 3.88; N, 2.70%. Found: C, 31.79; H, 2.97; N, 2.94%. Calcd for $PdC_{14}H_{16}NAsBr_2$=[$PdBr_2$(dpan)]: C, 31.17; H, 2.99; N, 2.60%.

[PdI_2L] (L=R-mpan, S-bpan, and dpan). These complexes were prepared from [$PdCl_2L$] and NaI by metathesis. To a stirred solution of [$PdCl_2L$] (L=*R*-mpan, *S*-bpan, dpan; 9.0×10^{-5} mol) in 2:1 acetonitrile–ethanol (7 cm^3) was added an excess of sodium iodide (0.2 g, 1.33×10^{-3} mol), the color of the solution changing immediately from yellow to orange red. The solution was stirred for 1 h at 40 °C, and then evaporated to dryness. The residue was dissolved in a small amount of acetonitrile, and the solution was applied on a column (ϕ12 mm×60 mm) of acid alumina. On elution with 10:1 acetonitrile–ethanol, two red bands developed. The eluate containing the slower moving main band was collected and evaporated to a small volume to form red crystals in 50—65% yield. Found: C, 19.22; H, 2.33; N, 2.62%. Calcd for $PdC_9H_{14}NAsI_2$=[PdI_2(*R*-mpan)]: C, 18.92; H, 2.47; N, 2.45%. Found: C, 24.37; H, 3.15; N, 2.64%. Calcd for $PdC_{12.5}H_{20.75}N_{1.25}AsI_2$=[$PdI_2$(*S*-bpan)]$\cdot$1/4$CH_3CN$: C, 24.07; H, 3.35; N, 2.81%. Found: C, 27.05; H, 2.64; N, 2.66%. Calcd for $PdC_{14}H_{16}NAsI_2$=[PdI_2(dpan)]: C, 26.55; H, 2.55; N, 2.21%.

[$PtCl_2$(R-mpan)]$\cdot$1/4CH_3CN. This complex was prepared by a method similar to that for the corresponding palladium(II) complex. A mixture of **1a** (250 mg, 4.12×10^{-4} mol) and sodium cyanide (200 mg, 4.08×10^{-3}mol) in water–diethyl ether (40 cm^3–40 cm^3) was stirred for 10 min, and then allowed to stand for a while. The ethereal layer was added to a stirred suspension of platinum(II) chloride (120 mg, 4.51×10^{-4} mol) in acetonitrile (300 cm^3). The resulting yellow solution was refluxed for 1 h, and then filtered. The filtrate was evaporated to a small volume to give a pale yellow precipitate. It was collected by filtration, dissolved in a small amount of acetonitrile, and the solution was applied on a column (ϕ12 mm×100 mm) of Toyopearl HW-40 (fine). The product was eluted with acetonitrile. The eluate containing the main yellow band was collected and evaporated to *ca.* 10 cm^3. The concentrate was applied again on a column (ϕ12 mm×100 mm) of acid alumina. By elution with acetonitrile–ethanol (5:1) the column showed a single pale yellow band. The yellow eluate was collected and evaporated slowly at room temperature to give pale yellow crystals. Yield: 50%. Found: C, 23.59; H, 3.00; N, 3.63%. Calcd for $PtC_{9.5}H_{14.75}N_{1.25}AsCl_2$: C, 23.41; H, 3.05; N, 3.59%.

[$PtCl_2$(dpan)]. This complex was prepared by a method similar to that for [$PtCl_2$(*R*-mpan)]$\cdot$1/4CH_3CN. When a solution of dpan in diethyl ether was mixed with a suspension of platinum(II) chloride in acetonitrile, a white precipitate formed. The mixture was refluxed for 2 h to give a clear pale yellow solution, from which the complex was obtained and purified in the same way as the above *R*-mpan complex. Yield: 50%. Found: C, 31.33; H, 2.90; N, 2.76%. Calcd for $PtC_{14}H_{16}NAsCl_2$: C, 31.19; H, 2.99; N, 2.60%.

[$PtBr_2$(R-mpan)]$\cdot$1/2CH_3CN. To a solution of [$PtCl_2$(*R*-mpan)]$\cdot$1/4CH_3CN (40 mg, 8.21×10^{-5} mol) in acetonitrile–ethanol (30 cm^3–30 cm^3) was added lithium bromide monohydrate (130 mg, 1.25×10^{-3} mol). The mixture was stirred at 60—65 °C for 3 h, cooled to room temperature, and then evaporated to dryness under vacuum. The residue was mixed with dichloromethane–H_2O (1:1) to extract the complex into the organic solvent. The dichloromethane was evaporated to 2 cm^3 and the concentrate was mixed with acetonitrile (1 cm^3) to give pale yellow crystals. They were purified by the same method as that for [$PtCl_2$(*R*-mpan)]$\cdot$1/4CH_3CN. Yield: 50%. Found: C, 20.97; H, 2.68; N, 3.24%. Calcd for $PtC_{10}H_{15.5}N_{1.5}AsBr_2$: C, 20.48; H, 2.66; N, 3.58%.

[PtI_2(R-mpan)]. This complex was prepared by a method similar to that for [$PtBr_2$(*R*-mpan)]$\cdot$1/2CH_3CN using sodium iodide instead of lithium bromide. The complex was isolated as brownish orange plates in a 60% yield. Found: C, 16.47; H, 2.04; N, 2.03%. Calcd for $PtC_9H_{14}NAsI_2$: C, 16.38; H, 2.14; N, 2.12%.

[PtI_2(dpan)]. This complex was prepared from [$PtCl_2$(dpan)] by a method analogous to that for [PtI_2(*R*-mpan)]. Yield: 65%. Found: C, 23.34; H, 2.32; N, 1.61%. Calcd for $PtC_{14}H_{16}NAsI_2$: C, 23.29; H, 2.23; N, 1.94%.

*Recemization of R-mpan**, [$PdCl_2$(R-mpan)], and [$PdCl_2$(S)-bpan)].* A mixture of **1a** (50 mg, 8.25×10^{-5} mol) and sodium cyanide (40 mg, 8.16×10^{-4} mol) in water–diethyl ether (15 cm^3–15 cm^3) was stirred for 30 min. After a while, the ethereal phase was withdrawn and mixed with hydrochloric acid (*ca.* 0.08 cm^3, *ca.* 10^{-3} mol). The mixture was stirred for 1h at room temperature, and then mixed with a solution of palladium(II) chloride (15 mg, 8.46×10^{-5} mol) in acetonitrile (40 cm^3). The mixture was stirred for 2 h and then filtered. The filtrate was evaporated to *ca.* 20 cm^3, and neutralized with an ethanol solution of sodium hydroxide. The resulting yellow solution was applied on a column (ϕ12 mm×60 mm) of acid alumina, and the product was eluted with acetonitrile–ethanol (5:1). The eluate containing the main yellow band was confirmed to contain [$PdCl_2$(mpan)] by the absorption spectrum. However, the eluate showed no detectable CD in the region of 500—200 nm.

Solutions of [$PdCl_2$(*R*-mpan)] in acetonitrile–ethanol (4:1) and in the same solvent saturated with LiCl were refluxed for 4 h, and then the CD spectra were measured. Either spectrum was the same as that of the starting solution. To a solution of the complex in acetonitrile–ethanol (4:1) was added an excess of hydrochloric acid. The color of the solution changed immediately from yellow to red, indicating the formation of [$PdCl_3$(*R*-Hmpan)], where Hmpan represents $^+NH_3CH_2CH_2As(CH_3)(C_6H_5)$ coordi-

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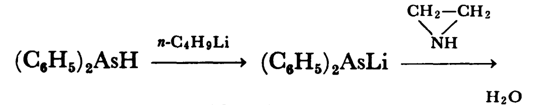
** The notation of the absolute configurations, *R* and *S*, for the tertiary arsine ligand is reversed upon liberation from a metal complex according to the rule.[14] However, the same notation as that for the coordinated arsine is used for the uncoordinated one throughout this paper.

nated to the Pd^{II} ion only through the arsenic atom. The solution was refluxed for 6 h, and then neutralized with an ethanol solution of sodium hydroxide. The resulting solution showed the same CD spectrum as that of the starting solution. The CD spectrum of [PdCl$_2$(*S*-bpan)] did not change by the same experiments, either.

Results and Discussion

Preparation and Characterization of the Arsine Ligands and the Complexes. The known compound, (2-aminoethyl)diphenylarsine (dpan) was prepared in fairly high yield (70%) by reaction of lithium diphenylarsenide with aziridine:



$$(C_6H_5)_2AsH \xrightarrow{n\text{-}C_4H_9Li} (C_6H_5)_2AsLi \xrightarrow{\text{CH}_2\text{—CH}_2\text{ (NH)}} (C_6H_5)_2AsCH_2CH_2NHLi \xrightarrow{H_2O} \text{dpan}$$

This method is analogous to that for the corresponding phosphine.[12,13] To obtain dpan in good yield, it is essential to use pure AsH(C$_6$H$_5$)$_2$ isolated by distillation. New chiral (2-aminoethyl)methylphenylarsine (mpan) and (2-aminoethyl)butylphenylarsine (bpan) were prepared from dpan in liquid ammonia by a method similar to that for the corresponding phosphine analogs:[4]

$$\text{dpan} \xrightarrow{Na} NaC_6H_5AsCH_2CH_2NH_2 \xrightarrow[(RX=CH_3I,\ n\text{-}C_4H_9Br)]{RX} RC_6H_5AsCH_2CH_2NH_2$$

The chiral arsines, mpan and bpan were resolved into their enantiomers by fractional crystallization of the diastereomeric palladium(II) complexes, **1a** and **1b**, and **2a** and **2b**, containing, respectively, ortho-metallated (*R*)-*N*,*N*-dimethyl-1-(2-naphthyl)-ethylamine and (*S*)-*N*,*N*-dimethyl-α-methylbenzylamine. The less soluble **1a** and **2a** were isolated as the chlorides, whereas the more soluble **1b** and **2b** as the hexafluorophosphates. Except **2b** the diastereomers were separated in high purity as confirmed by the ^{1}H NMR and CD spectra. The separation of pure **2b** was difficult.

The optically active free (aminoalkyl)arsines were obtained from the diastereomers by treating with sodium cyanide in water, and by extracting with diethyl ether. The liberated ligands were used to prepare the [PdX$_2$L] (X=Cl, Br) and [PtCl$_2$L] complexes. The other halogeno complexes, [PdI$_2$L] and [PtX$_2$L] (X=Br, I), were prepared by metatheses from the dichloro complexes and sodium iodide or lithium bromide.

For complexes **1** and **2**, there are two possible geometrical isomers; the two nitrogen atoms can be either in the cis or trans positions to each other. For each complex only one of the geometrical isomers was formed as confirmed by ^{1}H NMR spectra. Kinoshita *et al.*[4] resolved (2-aminoethyl)butylphenylphosphine by forming a pair of diastereomeric palladium(II) complexes, **2a′** and **2b′**, with ortho-metallated (*S*)-*N*,*N*-dimethyl-α-methylbenzylamine. They assigned both diastereomers to the *cis*(*N*,*N*) isomer, since the ^{1}H NMR and ^{13}C NMR spectra exhibit large long-range couplings between the ^{31}P atom and the *N*-methyl protons ($^4J_{PPdNCH}$), and the *N*-methyl carbons ($^3J_{PPdNC}$), respectively. Such long-range couplings would be very small for the *trans*(*N*,*N*) configuration. Although such argument on couplings cannot be applied to the arsine complexes, the results that isomers **2a** and **2a′**, and **2b** and **2b′**, respectively show very similar ^{1}H NMR patterns strongly suggest that **2a** and **2b** also have the *cis*(*N*,*N*) configuration.

Since the σ-bonded carbon and the arsenic atoms induce the stronger trans effect than the amine nitrogen atom, the formation of the *cis*(*N*,*N*) isomer would be more favorable than the *trans*(*N*,*N*) one. Examination of molecular models indicates that the *trans*(*N*,*N*) isomer involves considerable steric interactions between the *N*-methyl groups and the substituent on the arsenic atom. Thus, all isomers **1a**—**4** can be assigned as the *cis*(*N*,*N*) configuration. Recently Allen *et al.*[5] resolved methylphenyl-(8-quinolyl)phosphine and its arsenic analog with di-μ-chloro-bis[(*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine-C^2,*N*]dipalladium(II). In each case only one of geometrical isomers was formed, and X-ray crystal structure analysis of one of the diastereomers revealed the *cis*(*N*,*N*) configuration.

The optical activity of diastereomers **1a**—**2b** can be explained as a superposition of the two effects; one from the chiral arsine ligand and the other from the chiral ortho-metallated amine ligand. The observation that the CD spectra are nearly enantiomeric between diastereomers **1a** and **1b**, and between **2a** and **2b** suggests that the chiral arsine ligand has a dominating influence on the CD spectra (Figs. 1 and 2). In fact, the corresponding dpan complexes, **3** and **4** whose arsenic atoms are achiral show very weak CD. Thus the absolute configurations of the chiral arsenic atoms can be assigned from the CD spectra of the diastereomers. The CD pattern of **2a** is similar to that of the phosphine analog, **2a′** of the known absolute configuration (*S*(P)).[4] Thus the absolute configuration of the arsenic atom of **2a** is assigned as *S*. Diastereomer **1b** which shows a similar CD pattern to that of **2a** can be assigned to have the *S* configuration. Accordingly, the absolute configurations of the arsenic atoms of **2b** and **1a** can be assigned as *R*. Half the sum of the CD spectra of a pair of diastereomers should give the contribution due to the amine ligand. Actually, the calculated CD curves, $1/2[\Delta\varepsilon(\mathbf{1a})+\Delta\varepsilon(\mathbf{1b})]$ and $1/2[\Delta\varepsilon(\mathbf{2a})+\Delta\varepsilon(\mathbf{2b})]$ are similar to the observed spectra of **3** and **4**, respectively over the whole region (Figs. 1 and 2), indicating that the additivity in CD between the two effects holds for the diastereomers, and that

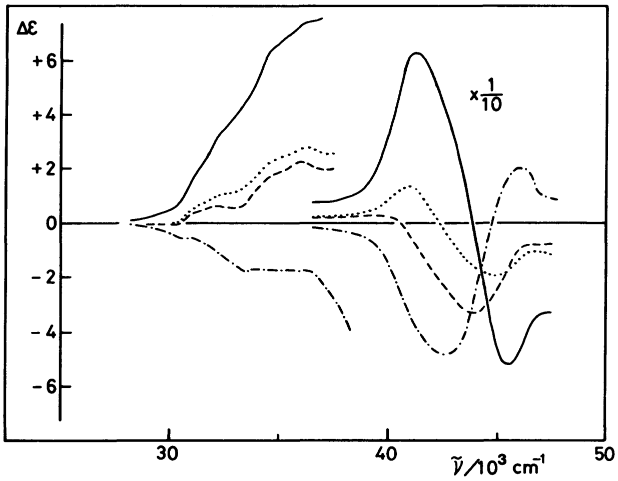


Fig. 1. CD spectra of [Pd{(*R*)-$C_{10}H_6CH(CH_3)N(CH_3)_2$}-(*R*-mpan)]Cl·1/2$CH_3OH$·1/2$C_6H_6$(**1a**, ——), [Pd{(*R*)-$C_{10}H_6CH(CH_3)N(CH_3)_2$}(*S*-mpan)]$PF_6$(**1b**, —·—), and [Pd{(*R*)-$C_{10}H_6CH(CH_3)N(CH_3)_2$}(dpan)]Cl(**3**, ----), and the mean CD curve of the two spectra for **1a** and **1b**.(······).

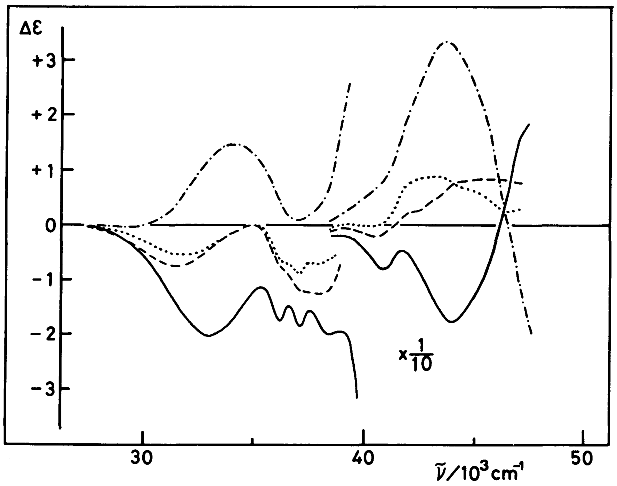


Fig. 2. CD spectra of [Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}-(*S*-bpan)]Cl(**2a**, ——), [Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}(*R*-bpan)]PF_6(**2b**, —·—), and [Pd{(*S*)-$C_6H_4CH(CH_3)N(CH_3)_2$}(dpan)]Cl(**4**, ----), and the mean CD curve of the two spectra for **2a** and **2b**(······).

TABLE 1. ABSORPTION AND CD SPECTRA OF THE COMPLEXES IN ACETONITRILE

Complex	Absorption: $\tilde{\nu}_{max}/10^3\ cm^{-1}$ (log ε)	CD: $\tilde{\nu}_{ext}/10^3\ cm^{-1}$ ($\Delta\varepsilon$)
[PdCl$_2$(*R*-mpan)]	27.25(3.17) 36.1(3.84) a) 40.52(4.05)	25.99(+0.76) 29.25(−0.63) 32.81(+0.066) 39.68(−12.75)
[PdBr$_2$(*R*-mpan)]	25.97(3.25) 32.0(3.38) a) 37.50(4.12)	24.30(+0.28) 27.51(−0.45) 30.85(+0.43) 36.50(−9.93) 44.15(+19.25)
[PdI$_2$(*R*-mpan)]	22.96(3.53) 26.5(3.21) a) 33.56(4.12) 41.2(4.29) a)	24.27(−0.33) 28.05(+0.62) 32.73(−8.26) 36.5(+3.58) a) 40.65(+16.69)
[PdCl$_2$(*S*-bpan)]	27.10(3.19) 35.7(3.80) a) 40.50(4.06)	25.79(−0.64) 29.34(+0.78) 32.57(+0.14) 39.40(+12.28)
[PdBr$_2$(*S*-bpan)]	25.77(3.29) 31.01(3.43) 37.11(4.16)	24.27(−0.34) 27.74(+0.61) 30.77(+0.070) 36.36(+11.43) 43.48(−13.78)
[PdI$_2$(*S*-bpan)]-¼CH_3CN	22.99(3.47) 26.74(3.22) 33.64(4.07) 41.2(4.32) a)	20.83(−0.035) 24.21(+0.30) 28.01(−0.26) 32.79(+7.07) 36.7(−0.39) a) 41.24(+13.7)
[PdCl$_2$(dpan)]	26.67(3.23) 35.1(3.89) a) 38.31(4.08)	
[PdBr$_2$(dpan)]	25.37(3.30) 30.40(3.40) 35.95(4.21)	
[PdI$_2$(dpan)]	22.17(3.55) 26.0(3.13) a) 32.63(4.17) 41.0(4.33) a)	
[PtCl$_2$(*R*-mpan)]-¼CH_3CN	29.0(2.35) a) 33.22(3.00) 43.1(4.12) a) 46.1(4.19) a)	25.00(+0.044) 27.03(−0.031) 32.89(+0.57) 36.90(−0.45) 39.68(+0.30) 44.84(−13.1)
[PtBr$_2$(*R*-mpan)]-½CH_3CN	27.0(2.20) a) 32.31(3.01) 41.7(4.02) a) 45.5(4.29) a)	24.21(+0.030) 26.67(−0.037) 31.55(+0.21) 34.06(+1.09) 43.86(−7.42)
[PtI$_2$(*R*-mpan)]	23.0(2.03) a) 28.25(3.43) 33.19(3.13) 41.2(4.31) a)	25.97(−0.26) 28.65(−0.013) 30.86(−0.20) 33.90(+1.03) 39.76(−12.09)
[PtCl$_2$(dpan)]	28.5(2.38) a) 32.79(3.05) 42.0(4.16) a) 45.10(4.37)	
[PtI$_2$(dpan)]	22.7(2.08) a) 27.59(3.46) 32.89(3.13) 40.03(4.39)	

a) Shoulder.

the contribution from the chiral amine ligand is small.

Absorption and CD Spectra of [M^{II}X$_2$L] (M^{II}=Pd, Pt; X=Cl, Br, I; L=R-mpan, S-bpan). The elemental analyses and a comparison of the absorption spectral data (Table 1) with those of related complexes of dpan[15,16] support that these complexes are four-coordinate and square-planar. The low energy absorption bands with intensities $\log \varepsilon = 3.0$—3.5 may be assigned to predominantly a d-d transition, while those observed at energies higher than 30×10^3 cm^{-1} for the palladium(II) complexes and 35×10^3 cm^{-1} for the platinum(II) complexes will be assigned to charge-transfer transitions[15,17] (Figs. 3—6). The platinum(II) complexes show a shoulder ($\log \varepsilon \approx 2.3$) at the low energy side of the d-d absorption band, and the absorption may be assigned to the spin-forbidden transition. The patterns of the absorption spectra of [PtX$_2$(*R*-mpan)] (X=Cl, Br, I) are similar to those of the corresponding palladium(II) complexes, although all the bands of the former complexes are shifted by 5000—7000 cm^{-1} toward higher energy compared to the corresponding bands of the latter complexes. The spin-forbidden band at the lowest energy is pronounced for platinum(II) complexes (Figs. 4 and 6). In any series [M^{II}X$_2$L] (M^{II}=Pd, Pt), the energy of the d-d absorption band decreases in the order Cl>Br>I. When the phenyl group attached to the arsenic atom is replaced by an alkyl group, the d-d absorption band shifts to higher energy. Thus, the spectrochemical series of the arsine ligands is mpan≧bpan>dpan. For a series of bis(acetylacetonato)cobalt(III) complexes with analogous phosphine ligands a similar order has been reported; $NH_2CH_2CH_2P(CH_3)(C_6H_5) \geqq NH_2CH_2CH_2P(n\text{-}C_4H_9)(C_6H_5) > NH_2$-

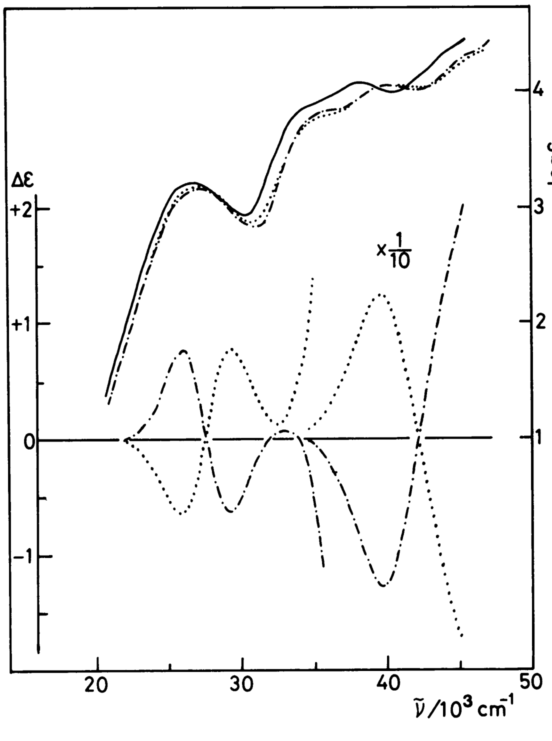


Fig. 3. Absorption and CD spectra of [PdCl$_2$(*R*-mpan)](—·—) derived from **1a**, and [PdCl$_2$(*S*-bpan)] (……) derived from **2a**, and absorption spectrum of [PdCl$_2$(dpan)](——).

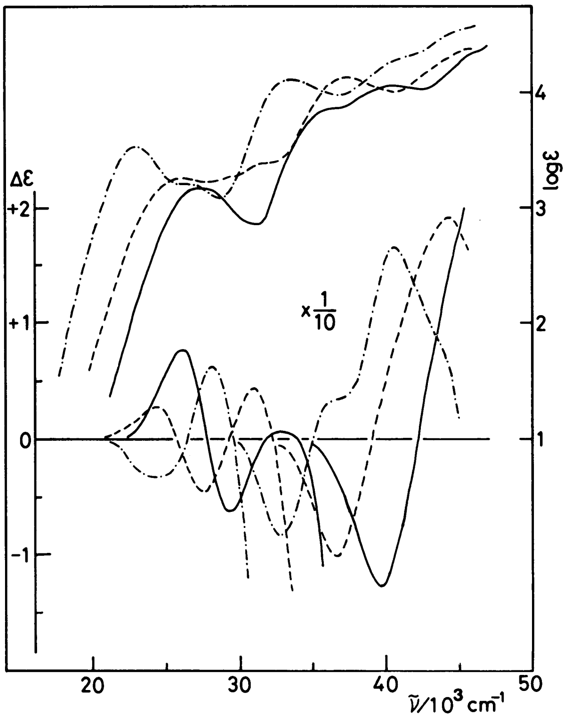


Fig. 4. Absorption and CD spectra of [PdX$_2$(*R*-mpan)], X=Cl(——), Br(----), and I(—·—).

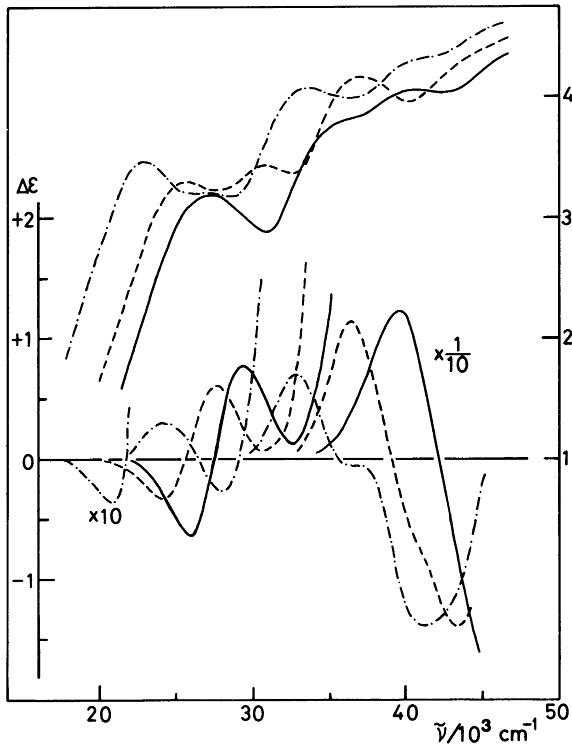


Fig. 5. Absorption and CD spectra of [PdX$_2$(*S*-bpan)], X=Cl(——), Br(----), and I(—·—).

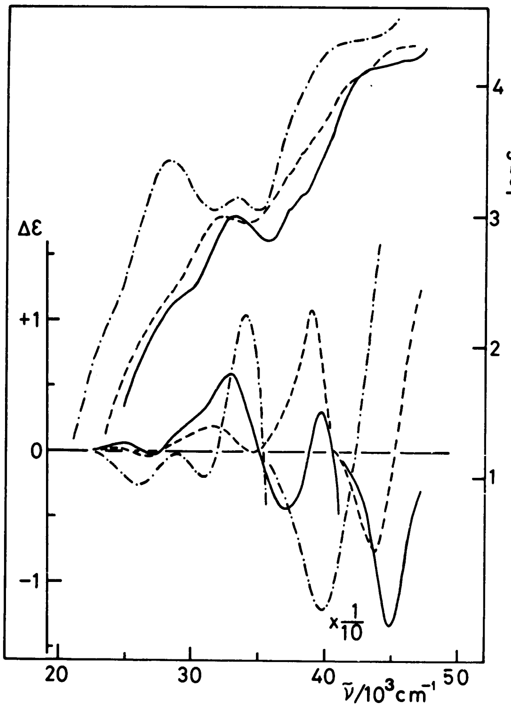


Fig. 6. Absorption and CD spectra of $[\mathrm{PtX_2}(R\text{-mpan})]$, X=Cl(——), Br(----), aud I(—·—).

$\mathrm{CH_2CH_2P(C_6H_5)_2}$.[18] The $[\mathrm{PdCl_2\{NH_2CH_2CH_2P}(n\text{-}\mathrm{C_4H_9)(C_6H_5)\}}]$ complex exhibits the d-d absorption band at a little higher energy than the corresponding bpan complex,[4] suggesting that an (aminoalkyl)phosphine ligand exerts a ligand field slightly greater than the corresponding arsine ligand.

Figure 3 shows the CD spectra of the dichloro-*R*-mpan and *S*-bpan palladium(II) complexes derived from **1a** and **2a**, respectively. The spectra are nearly enantiomeric over the whole region. The *S*-bpan complex shows the same CD pattern as that of $[\mathrm{PdCl_2}\{(S)\text{-}\mathrm{NH_2CH_2CH_2P}(n\text{-}\mathrm{C_4H_9)(C_6H_5)}\}]$; a negative and a positive band from lower wave numbers in the region of the first absorption band.[4] These results support the previous assignments for the absolute configurations of the arsenic atoms of **1a**—**2b**. It should be noted that the CD strength of the bpan complex is about 2.5—3 times smaller than that of the phosphine analog. A similar decrease in CD strength accompanying the change of donor atom from the third to the fourth-row atom has been observed for the vicinal effect of $\mathrm{NH_2CH_2CH(CH_3)X^-}$-*N,X* (X=S, Se) in the cobalt(III) complexes.[19]

In Figs. 4 and 5 the CD spectra of the complexes, $[\mathrm{PdX_2}(R\text{-mpan})]$ (X=Cl, Br, I) and $[\mathrm{PdX_2}(S\text{-bpan})]$ (X=Cl, Br, I), respectively, are shown. In either series of complexes all of the CD bands cause a systematic shift to smaller wave numbers as X proceeds from Cl through Br to I. The CD components in the region of the d-d absorption band decreases in magnitude in the order Cl>Br>I. For $[\mathrm{PdI_2}(R\text{-mpan})]$ no positive CD band could be observed at *ca.* 21000 $\mathrm{cm^{-1}}$, while the corresponding weak CD band for $[\mathrm{PdI_2}(S\text{-bpan})]$ was observed at 20830 $\mathrm{cm^{-1}}$.

The CD spectra of $[\mathrm{PtX_2}(R\text{-mpan})]$ (X=Cl, Br, I) are similar to those of the corresponding palladium(II) complexes except that the former spectra shift to higher energy side by 5000—7500 $\mathrm{cm^{-1}}$ compared to the latter ones. The spectra of the $\mathrm{Pt^{II}}$ complexes show CD bands in the spin-forbidden band region, the corresponding CD bands being not observed in the spectra of the $\mathrm{Pd^{II}}$ complexes (Figs. 4 and 6).

Racemization of R*-mpan and Attempted Racemization of* $[\mathrm{PdCl_2}(R\text{-mpan})]$ *and* $[\mathrm{PdCl_2}(S\text{-bpan})]$. It has been known that arsines and phosphines can be racemized catalytically, although in general they are thermally stable toward racemization.[21] For example, Horner and Hofer[21] reported that (+)-methylpropylphenylarsine in methanol solution racemizes in the presence of strong acid (HX). The rate is anion dependent and increases in the order $\mathrm{X{=}ClO_4^-{<}F^-{<}Cl^-{<}I^-}$, the process presumably involving the rapid pseudorotation of a five-coordinate arsenic species.[22] Roberts and Wild[7] showed that *meso-o*-phenylenebis(methylphenylarsine) undergoes a halide-ion assisted epimerization in acidic methanol solution. The optically active arsine ligand, *R*-mpan, liberated from the diastereomeric palladium(II) complex (**1a**) was allowed to react with hydrochloric acid in diethyl ether at room temperature. The $[\mathrm{PdCl_2(mpan)}]$ complex which was prepared from this mpan showed no detectable CD. The result shows that the arsine ligand undergoes racemization in the presence of hydrochloric acid.

Optically active quarternary phosphonium and arsonium salts also undego racemization in the presence of some anions such as $\mathrm{Cl^-}$ or $\mathrm{Br^-}$, acid being not required.[24] Here again a similar account in terms of rapidly pseudorotating five-coordinate arsenic may be applicable. A metal complex with a chiral arsine ligand might undergo a halide-ion assisted racemization at the arsenic atom, if the metal ion assumes the role of a proton of a tertiary arsine or an alkyl group of a quarternary arsonium ion. Epimerization of a coordinated tertiary arsine within a chelate ring has been observed in $[\mathrm{CoX_2(tetars)}]\mathrm{X}$ (X=Cl, Br; tetars=$[\mathrm{(CH_3)_2As(CH_2)_3As(C_6H_5)CH_2\text{-}}]_2$).[9,25] However, refluxing a solution of $[\mathrm{PdCl_2}(R\text{-mpan})]$ (or $[\mathrm{PdCl_2}(S\text{-bpan})]$) in acetonitrile–ethanol (4:1) for several hours in the presence of saturated lithium chloride or excess hydrochloric acid resulted in no racemization at a chiral arsenic center. These results indicate that the stability of chiral arsines toward racemization is greatly enhanced by coordination to a metal ion.

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