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Resolutions Involving Metal Complexation. Resolution of (±)-1-Amino-2-(methylphenylarsino)ethane and Its Phosphorus Analogue. Stereochemistry and Stability of Square-Planar Bis(bidentate) Complexes of Bivalent Palladium and Platinum

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The asymmetric bidentates (±)-1-amino-2-(methylphenylarsino)ethane and its phosphorus analogue have been resolved by fractional crystallization of internally diastereoisomeric palladium(II) complexes containing optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine. Optically pure enantiomers of both ligands were obtained from the separated diastereoisomers in stereospecific displacements as high-boiling air-sensitive oils with $[\alpha]_D(CH_2Cl_2)$ ±13° (arsine) and ±16° (phosphine). Absolute configurations have been assigned to the enantiomers by a ^1H NMR method involving a comparison of the spectra of the diastereoisomeric intermediates with others of known structure. The ligands form bis(bidentate) derivatives of palladium(II) and platinum(II) in which like donor atoms are cis to one another. The arsine complexes of both metals undergo facile ligand redistribution under ambient conditions, but the phosphine compounds are stable in this respect in the absence of free ligand. Indeed, condensation reactions take place between the platinum–arsine complexes and acetone, giving cations containing novel quadridentate ligands: these are the first examples of reactions of this type on platinum(II).

Introduction

The versatility of ortho-metalated palladium(II) derivatives of optically active dimethyl(α-methylbenzyl)- and dimethyl(1-ethyl-α-naphthyl)amines as resolving agents for both asymmetric and dissymmetric bidentates containing tertiary phosphorus and arsenic atoms has been convincingly demonstrated in our laboratories in recent years.[1-4] The present work concerns the resolution of 2-aminoethyl functionalized tertiary arsines and phosphines that are potential precursors to a variety of optically active phosphorus and arsenic species by conversion of the primary amino group. The new compound (±)-1-amino-2-(methylphenylarsino)ethane ((±)-**1**) has been prepared and the phosphorus analogue ((±)-**2**)[5] obtained by an improved method. Both substances have been resolved by fractional crystallization of internally diastereoisomeric palladium(II) complexes containing ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine.[3] A previous attempt to resolve (±)-**2** by use of the corresponding palladium complex of dimethyl(α-methylbenzyl)amine was unsuccessful,[5] although an incomplete resolution of (±)-1-amino-2-(*n*-butylphenylphosphino)ethane by the same authors has been described.[6]

Results and Discussion

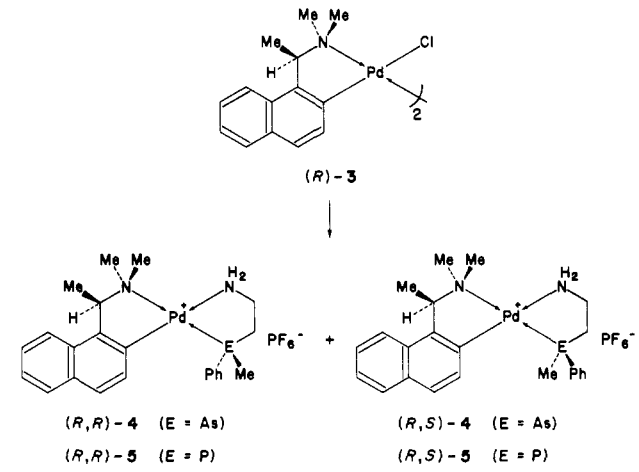
Ligand (±)-**1**, bp 84–86 °C (0.1 mmHg), was prepared in 81% yield from (2-chloroethyl)amine and sodium methylphenylarsenide in liquid ammonia:

$$Na[AsMePh] + ClCH_2CH_2NH_2 \rightarrow PhMeAsCH_2CH_2NH_2 + NaCl$$
$$(\pm)\text{-}\mathbf{1}$$

The corresponding tertiary phosphine was prepared by methylation of sodium (2-aminoethyl)phenylphosphide[7] in tetrahydrofuran at −10 °C:

$$Na[PhPCH_2CH_2NH_2] + MeI \rightarrow PhMePCH_2CH_2NH_2 + NaI$$
$$(\pm)\text{-}\mathbf{2}$$

Scheme I



The yield of (±)-**2**, bp 76-78 °C (0.02 mmHg), was 83%. Kashiwabara and co-workers[5] have isolated the same compound in 25% yield by reaction of lithium methylphenylphosphide with aziridine, followed by hydrolysis of the resulting anion.

The resolutions of (±)-**1** and (±)-**2** were based upon the separation of pairs of internally diastereoisomeric palladium(II) complexes derived from bis(μ-chloro)bis[(*R*)-2-[1-(dimethylamino)ethyl]naphthyl-*C*,*N*]dipalladium(II) ((*R*)-**3**), as shown in Scheme I. The diastereoisomeric chlorides were first produced and then subsequently converted into the less soluble hexafluorophosphate salts. The resulting mixture was fractionally crystallized from acetone. Diastereoisomers (*R*,*R*)-**4** and (*R*,*R*)-**5** crystallized as acetone solvates from acetone by the addition of diethyl ether. The solvent of crystallization was subsquently removed by recrystallization of the complexes from dichloromethane. (This precaution was taken in order to avoid possible condensation of the displaced ligand with the acetone in a subsequent step.) No evidence was found of the alternative pair of diastereoisomers with trans-nitrogen atoms. Less soluble salts (*R*,*R*)-**4** and (*R*,*R*)-**5** were obtained in ca. 80% yield as colorless prisms with $[\alpha]_D$ values of +42.4 and +36.6° (acetone), respectively. The more soluble components of the mixtures were obtained from the mother liquors by first removing the solvent and then recrystallizing the residues from

(1) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.
(2) Roberts, N. K.; Wild, S. B. *J. Chem. Soc. Dalton Trans.* **1979**, 2015.
(3) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007.
(4) Salem, G.; Wild, S. B. *Inorg. Chem.* **1983**, *22*, 4049.
(5) Kashiwabara, K.; Kinoshita, I.; Ito, T.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 725.
(6) Kinoshita, I.; Kashiwabara, K.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3715.
(7) Issleib, K.; Oehme, H. *Chem. Ber.* **1967**, *100*, 2685.

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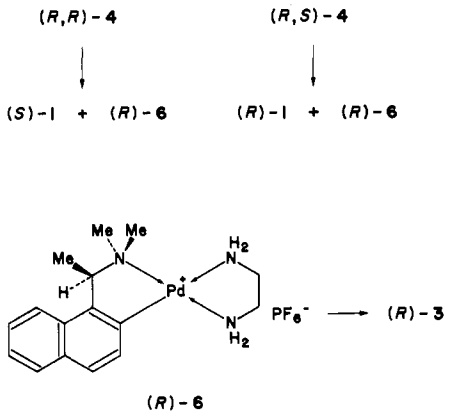
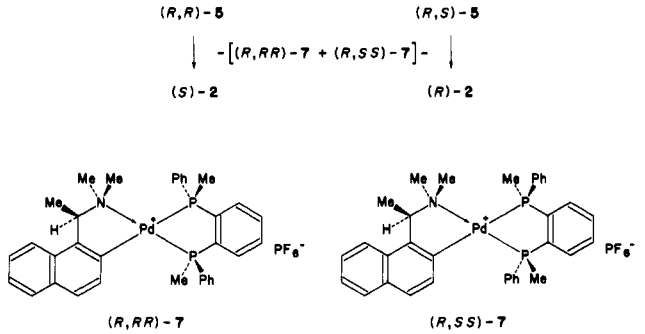
Scheme II



Scheme III



a 2-butanone–diethyl ether mixture. After several recrystallizations ca. 80% yields of each of (*R,S*)-**4** and (*R,S*)-**5** were obtained as colorless needles with $[\alpha]_D$ values of −129 and −119°, respectively.

Liberation of the resolved ligands from the diastereoisomers was carried out as indicated in Schemes II and III. The optically pure enantiomers of the tertiary arsine were displaced from (*R,S*)-**4** and (*R,R*)-**4** by 1,2-diaminoethane with formation of the complex (*R*)-**6**: this compound is insoluble in dichloromethane and can be reconverted into (*R*)-**3** by treatment with hydrochloric acid.[3] Enantiomers (*R*)- and (*S*)-**1** had $[\alpha]_D$ values of −13.1 and +13.0° in dichloromethane, respectively.

The liberation of the tertiary phosphines from (*R,S*)-**5** and (*R,R*)-**5** required a reagent more strongly coordinating than 1,2-diaminoethane: we found it convenient to use (*R*,R**)-(±)-1,2-bis(methylphenylphosphino)benzene.[1] Treatment of either of the diastereoisomers with the bis(tertiary phosphine) in dichloromethane solution resulted in immediate displacement of (*R*)- and (*S*)-**2**. The free ligands were readily separated from the mixture of diastereoisomeric bis(tertiary phosphine) complexes (*R,RR*)- and (*R,SS*)-**7**, and had $[\alpha]_D$ values of −16.3° (*R*) and +16.4° (*S*). The optically active phosphines cannot be distilled without racemization.

Absolute Configurations. The assignment of absolute configurations to (±)-**1** and (±)-**2** was based upon an analysis of the ^{1}H NMR spectra of the internally diastereoisomeric complexes (*R,R*)-**4**, (*R,R*)-**5** and (*R,S*)-**4**, (*R,S*)-**5**. In other work on related compounds containing the *R*-naphthylamine, we showed that the γ aromatic ring proton adjacent to the metalated carbon atom was shifted upfield (to ca. 7 ppm) when an adjacent phenyl-substituted phosphorus or arsenic donor atom had the *S* absolute configuration.[3] The origin of the shielding is evident in the structure of a compound of this type determined by X-ray analysis: puckering in the organometallic ring causes the γ-proton to protrude into the face of the neighboring phenyl group in the *R,S* but not in the *R,R* diastereoisomer. Furthermore, the orthogonal relationship of the adjacent aromatic rings in the *R,S* diastereoisomers results in a strong deshielding of the pair of the ortho protons of the phenyl group attached to the arsenic or phosphorus atom. In the present compounds it is the *R,R* diastereoisomers, viz. (*R,R*)-**4** and -**5**, that show the pronounced shielding effects, since it is in these that the arrangement of the aromatic rings is orthogonal.[8] Thus, the γ organometallic ring proton in (*R,R*)-**4** appears as a doublet centered at δ 6.73 ($^3J_{HH}$ = 8 Hz) and the pair of ortho aromatic ring protons on the arsenic atom as a pair of doublets centered at δ 8.03 and 8.04 ($^3J_{HH}$ = 7 Hz). Compound (*R,R*)-**5** shows additional phosphorus coupling to the shielded γ ring proton (through-space effect, $^3J_{PH}$ = 5 Hz)[3] and deshielded ortho aromatic ring protons of the phosphorus–phenyl group ($^3J_{PH}$ = 12 Hz).

Bis(bidentate) Complexes of Pd(II) and Pt(II). (i) Stereochemistry. Square-planar complexes of the type [M(bidentate)$_2$](PF$_6$)$_2$ were prepared from the racemic and optically active forms of **1** and **2** and their stereochemistry and stability toward redistribution of ligands examined by NMR spectroscopy. The ^{31}P NMR spectrum of (+)-[Pt(*R*)-**2**)$_2$](PF$_6$)$_2$ consisted of a singlet at δ 21.8 with platinum satellites ($^1J_{PtP}$ = 3321 Hz); the ^{1}H NMR spectrum of the same material contained a doublet for the PMe groups centered at δ 1.65 ($^2J_{PH}$ = 11.7 Hz, $^3J_{PtH}$ = 39.2 Hz). The large value of J_{PtP}[10] and the absence of virtual coupling in the ^{1}H NMR spectrum are both diagnostic of a cis structure for the complex. The ^{1}H NMR spectrum of the corresponding palladium(II) complex was similar. The optically active complexes of the tertiary arsine for both metals have also been assigned structures on the basis of the similarity in the chemical shifts of the As*Me* resonances in each case with those of the corresponding phosphine complexes.

(ii) Stability. The ^{1}H NMR spectrum of an equimolar mixture of (+)-*cis*-[Pt((*R*)-**2**)$_2$](PF$_6$)$_2$ and (−)-*cis*-[Pt(*S*)-**2**)$_2$](PF$_6$)$_2$ in Me$_2$CO-d_6 was identical with that of either of the individual enantiomers in the same solvent and remained so for 3 days at 25 °C. Addition of a trace of (*S*)-**2** to the mixture, however, caused the appearance of a new P*Me* doublet centered at δ 2.34 ($^2J_{PH}$ = 11.35 Hz, $^3J_{PtH}$ = 40.8 Hz) due to the presnece of the complex *meso-cis*-[Pt((*R*)-**2**)-((*S*)-**2**)](PF$_6$)$_2$. Equilibrium was established within 0.3 h at 25 °C with racemic:meso = 2.5:1. The palladium(II) compounds behaved similarly, but the redistribution was slower: the mixture of enantiomers in the absence of free ligand remained unaltered over a 3-day period at 25 °C but had changed into a racemic:meso = 12:1 mixture of cis complexes within 8 days at 25 °C in the presence of added ligand.

As expected, redistribution was more rapid in complexes of the tertiary arsine. A mixture of pure (+)-*cis*-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$ and its enantiomer in Me$_2$CO-d_6 initially showed an As*Me* resonance at δ 2.24 due to the chiral cations present, but within 6 h at 25 °C ligand redistribution had resulted in a racemic:meso = 1.5:1 mixture of diastereoisomers. Indeed, pure (±)-*cis*[Pt((*R,S*)-**1**)$_2$](PF$_6$)$_2$ could be crystallized from the mixture at equilibrium. Redistribution of bidentates occurred still faster for the palladium(II)–arsine complexes, an equilibrium racemic:meso = 1.4:1 mixture of cis complexes being established within 30 min of mixing of equimolar quantities of the pure enantiomers at 25 °C.

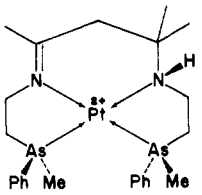
Condensation Reactions. Condensation reactions of acetone with labile amine complexes of Co(II), Ni(II), and Cu(II) are relatively common.[11] Similar reactions on Pd(II) and Pt(II)

(8) The apparent anomaly in the assignment of the absolute configurations between the two sets of compounds is a consequence of the priority rules.[9]

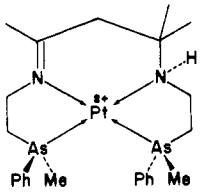
(9) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(10) Heaton, B. T.; Pidcock, A. *J. Organomet. Chem.* **1968**, *14*, 235. Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

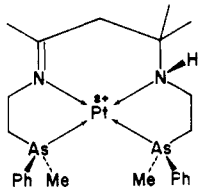
have hitherto not been reported, although they do occur on Pt(IV).[12] The complex (+)-*cis*-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$, when it was stirred for 16 h in acetone at 25 °C in the presence of a trace of (*S*)-**1**, produced **8** in high yield. The reaction does



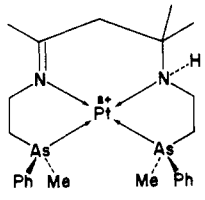
8a



8b



8c



8d

not take place in the absence of free ligand. The ^{1}H NMR spectrum of the product is exceedingly complex, but the ^{13}C NMR spectrum and IR data are consistent with the presence of epimers **8a** and **8b** in equal proportions. A complete assignment of the proton-decoupled ^{13}C NMR spectrum of the mixture was possibly by use of the INEPT procedure,[13] which provides a means of distinguishing between resonances due to methylene and methyl carbon atoms. The chemical shift of the AsCH$_2$ carbon atoms in (+)-*cis*-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$ occurs at δ 30.48 and the N-CH$_2$ nuclei at δ 44.12, the assignment of the latter resonance being consistent with observations on related 1,2-diaminoethane compounds.[15] In the condensation product there is a doubling up of all ^{13}C resonances: four INEPT-sensitive signals in the region δ 26.9–29.3 (AsCH$_2$), another four between δ 52 and 59 (NCH$_2$), and a pair having δ 46.54 and 47.36 (CCH$_2$). Nevertheless, it was not possible to assign a set of resonances to each particular epimer of the inseparable mixture.

Reaction of the racemic complex (±)-*cis*-[Pt((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$ with acetone under the same conditions afforded a mixture of condensation products derived from the racemic-cis and meso-cis forms of the starting complex. The two condensates were separated by fractional crystallization, and each component was shown by ^{13}C NMR spectroscopy to be an equimolar mixture of NH epimers. The more soluble component of the mixture had a ^{13}C NMR spectrum identical with that of the corresponding optically active material and was accordingly identified as a mixture of the racemic forms of **8a** and **8b**. Complexes **8** are extremely stable and can be recovered unchanged from hot concentrated nitric acid: they also appear to be unaffected by base, and the imino group was not reduced by borohydride. This behavior is reminiscent of the properties of related macrocycles on nickel(II) and copper(II), but not of the corresponding linear quadridentates on these metals, which are susceptible to hydrolysis under mild conditions.[11]

Experimental Section

Reactions involving air-sensitive compounds were run under a positive pressure of argon. ^{1}H NMR spectra were recorded at 34 °C on JEOL FX 200 (200 MHz) and Bruker HFX 270 (270 MHz) spectrometers. A JEOL FX 200 spectrometer operating at 50.3 MHz was used to obtain the ^{13}C NMR spectra; ^{31}P NMR spectra were recorded on a Bruker 3220 (24.28 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported as δ values relative to internal Me$_4$Si; ^{31}P NMR chemical shifts are in ppm relative to external 85% H$_3$PO$_4$. Optical rotations were measured on the specified solutions in a 1-dm cell with a Perkin-Elmer Model 241 polarimeter. Infrared spectra were obtained in Nujol mulls between KBr plates by use of a Perkin-Elmer Model 683 spectrophotometer. Conductivities were determined on 10^{-3} M solutions in acetone. Elemental analyses were performed by staff within the Research School of Chemistry.

Optically active primary amines were purchased from Norse Laboratories, Inc., Santa Barbara, CA, and methylated by standard procedures. Bis(μ-chloro)bis[(*R*)-2-[1-(dimethylamino)ethyl]-naphthyl-*C*,*N*]dipalladium(II) ((*R*)-**3**)[3] was prepared from Li$_2$[PdCl$_4$] by treatment with 1 equiv each of (*R*)-[1-(dimethylamino)ethyl]-naphthalene and triethylamine in methanol (yield 92%).

(±)-1-Amino-2-(methylphenylarsino)ethane ((±)-1). A solution of sodium methylphenylarsenide was prepared from methylphenylarsine (31.6 g) and sodium (4.5 g) in liquid ammonia (500 mL), and this solution was treated with a twofold excess of (2-chloroethyl)amine in diethyl ether over 1 h. (The (2-chloroethyl)amine was generated from the *hydrochloride* by reaction with an excess of solid potassium hydroxide suspended in diethyl ether.) After the addition, the ammonia was allowed to boil off; diethyl ether (500 mL) and then water (200 mL) were added to the residue, and the organic layer was separated and dried (MgSO$_4$). Distillation yielded the pure product as a colorless oil: bp 84–86 °C (0.1 mmHg); yield 32 g (81%). Anal. Calcd for C$_9$H$_{14}$AsN: C, 51.2; H, 6.7. Found: C, 51.2; H, 6.7. ^{1}H NMR (CDCl$_3$): δ 1.13 (s, 2, NH$_2$), 1.18 (s, 3, AsMe), 1.56–2.04 (m, 2, AsCH$_2$), 2.81 (t, 2, J_{HH} = 7 Hz, NCH$_2$), 7.04–7.72 (m, 5, aromatics).

(±)-1-Amino-2-(phenylphosphino)ethane. This compound was obtained in ca. 80% yield by use of the method of Issleib and Oehme[7] or by the reaction of sodium phenylphosphide with a twofold excess of (2-chloroethyl)amine in tetrahydrofuran at −78 °C.

(±)-1-Amino-2-(methylphenylphosphino)ethane ((±)-2). A solution of sodium (2-aminoethyl)phenylphosphide was prepared from (±)-1-amino-2-(phenylphosphino)ethane (23.4 g) and sodium (foil, 3.9 g) in tetrahydrofuran (150 mL). The reaction mixture was stirred at room temperature for 1 h and then heated under reflux for 30 min; it was then filtered and the filtrate treated with iodomethane (22.7 g) at −10 °C. After 1 h of stirring at room temperature, the reaction mixture was filtered. Distillation of the filtrate yielded the desired tertiary phosphine as a colorless oil: bp 76–78 °C (0.02 mmHg); yield 21 g (83%). Anal. Calcd for C$_9$H$_{14}$NP: C, 64.7; H, 8.4; P, 18.5. Found: C, 65.5; H, 8.7; P, 18.2. ^{1}H NMR (CDCl$_3$): δ 1.22 (s, 2, NH$_2$), 1.32 (d, 3, $^2J_{PH}$ = 4 Hz, PMe), 1.60–2.12 (m, 2, PCH$_2$), 2.64–2.96 (m, 2, NCH$_2$), 7.08–7.84 (m, 5, aromatics).

Resolution of (±)-1. Formation and Separation of Internal Diastereoisomers [*SP*-4-2-(*R*,*R*)]- and [*SP*-4-2-(*R*,*S*)]-[1-Amino-2-(methylphenylarsino)ethane-*As*,*N*][1-[1-(dimethylamino)ethyl]-naphthyl-*C*,*N*]palladium(II) Hexafluorophosphate ((*R*,*R*)-4 and (*R*,*S*)-4, Respectively). A solution of (±)-**1** (21.8 g) in methanol (50 mL) was added to a suspension of (*R*)-**3** (35.1 g) in the same solvent (100 mL), and the mixture was stirred until complete solution had occurred (ca. 1 h at 25 °C). An excess of NH$_4$PF$_6$ (20 g) in water (200 mL) was then added: after 30 min the granular white precipitate was filtered off and washed with water. The product was dissolved in dichloromethane and the solution dried (MgSO$_4$). Evaporation of the solvent from the dried solution yielded a mixture of (*R*,*R*)-**4** and (*R*,*S*)-**4** as a glass (67.2 g, 98%): $[\alpha]_D$ −33.6° (*c* 1.30, Me$_2$CO). The mixture was dissolved in hot acetone (100 mL) and the solution allowed to cool slowly to 20 °C, whereupon it stood at 5 °C for 16 h. Pure (*R*,*R*)-**4** crystallized as large colorless prisms of the mono(acetone) solvate (24.6 g). Concentration of the filtrate (to ca. 30 mL) yielded more of the same diastereoisomer (4 g): $[\alpha]_D$ +40.4°

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(12) Brawner, S. A.; Lin, I. J. B.; Kim, J.-H.; Everett, G. W. *Inorg. Chem.* **1978**, *17*, 1304. Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4562.
(13) INEPT (Insensitive Nuclei Enhanced by Polarization Transfer).[14]
(14) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760. Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6388.
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(c 1.09, Me_2CO); 84% combined yield. The filtrate was then evaporated to dryness and the residue was dissolved in 2-butanone (50 mL). The careful addition of diethyl ether to this solution, followed by cooling of the mixture (3 h at 25 °C and 16 h at 5 °C), yielded the more soluble (*R,S*)-**4** (10.2 g): $[\alpha]_D$ −128.8° (c 1.27, Me_2CO). The filtrate at this stage was taken to dryness and the residue subjected to several alternate recrystallizations from acetone and from 2-butanone, giving additional crystalline material. The combined fractions of (*R,R*)-**4** and (*R,S*)-**4** were given a final recrystallization from acetone–diethyl ether and 2-butanone–diethyl ether, respectively. (*R,R*)-**4**·Me_2CO: Overall yield 32.9 g (90%); colorless prisms; mp 165–169 °C; $[\alpha]_D$ + 42.4° (c 1.04, Me_2CO). Anal. Calcd for $C_{26}H_{36}AsF_6N_2OPPd$: C, 43.4; H, 5.1; N, 3.9. Found: C, 43.4; H, 5.0; N, 3.8. ^1H NMR (Me_2SO-d_6): δ 1.76 (d, 3, $^3J_{HH}$ = 6 Hz, CH*Me*), 1.93 (s, 3, AsMe), 2.10 (s, 6, Me_2CO), 2.1–2.4 (m, 2, $AsCH_2$), 2.88 (br s, 6, NMe_2), 2.8–3.2 (m, 2, NCH_2), 4.1–4.3 (m, 1, NH), 4.55–4.75 (m, 1, NH), 4.58 (q, 1, $^3J_{HH}$ = 6 Hz, C*H*Me), 6.9–8.1 (m, 11, aromatics). Λ_M = 139 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Two recrystallizations of the *solvate* from dichloromethane afforded the nonsolvated (*R,R*)-**4** as colorless prisms in 98% yield: mp 166–168 °C. Anal. Calcd for $C_{23}H_{30}AsF_6N_2PPd$: C, 41.8; H, 4.6; N, 4.2. Found: C, 41.9; H, 4.6; N, 4.0. ^1H NMR (Me_2SO-d_6): δ 1.77 (d, 3, $^3J_{HH}$ = 6 Hz, CH*Me*), 1.95 (s, 3, AsMe), 2.18–2.42 (m, 2, $AsCH_2$), 2.88 (br s, 6, NMe_2), 2.8–3.2 (m, 2, NCH_2), 4.1–4.3 (m, 1, NH), 4.55–4.75 (m, 1, NH), 4.58 (q, 1, $^3J_{HH}$ = 6 Hz, C*H*Me), 6.9–8.1 (m, 11, aromatics). Λ_M = 153 Ω^{-1} cm^2 mol^{-1} (10^{-3} M in Me_2CO at 20 °C). (*R,S*)-**4**: overall yield 27.5 g (82%); colorless prisms; mp 224–228 °C; $[\alpha]_D$ −129° (c 1.14, Me_2CO). Anal. Calcd for $C_{23}H_{30}AsF_6N_2PPd$: C, 41.8; H, 4.6; N, 4.2. Found: C, 41.7; H, 4.5; N, 4.2. ^1H NMR (Me_2SO-d_6): δ 1.80 (d, 3, $^3J_{HH}$ = 6 Hz, CH*Me*), 2.10 (s, 3, AsMe), 2.4–2.7 (m, 2, $AsCH_2$), 2.79 (s, 3, NMe), 2.87 (s, 3, NMe), 2.81–3.1 (m, 2, NCH_2), 4.10–4.25 (m, 1, NH), 4.55–4.75 (m, 1, NH), 4.58 (q, 1, $^3J_{HH}$ = 6 Hz, C*H*Me), 7.1–7.9 (m, 11, aromatics). Λ_M = 134 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

(*S*)-1-Amino-2-(methylphenylarsino)ethane ((*S*)-1). A solution of (*R,R*)-**4** (17.7 g) in dichloromethane (500 mL) was treated with 1,2-diaminoethane (9.0 g, 10 mL) at room temperature: after ca. 30 min diethyl ether (350 mL) was added to the reaction mixture and compound (*R*)-**6** was filtered off and washed with diethyl ether. The filtrate was evaporated to dryness to yield pure (*S*)-**1** as a colorless oil: bp 74–76 °C (0.02 mmHg); yield 5.2 g (92%); $[\alpha]_D$ +13.0° (c 2.63, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.13 (s, 2, NH_2), 1.18 (s, 3, AsMe), 1.46–2.08 (m, 2, $AsCH_2$), 2.81 (t, 2, J_{HH} = 7.5 Hz, NCH_2), 7.04–7.72 (m, 5, aromatics).

(*R*)-1-Amino-2-(methylphenylarsino)ethane ((*R*)-1). By displacement from (*R,S*)-**4** with 1,2-diaminoethane as described above, pure (*R*)-**1** was obtained as a colorless oil, bp 74–76 °C (0.02 mmHg), in 90% yield: $[\alpha]_D$ −13.0° (c 4.76, CH_2Cl_2). ^1H NMR ($CDCl_3$): identical with that of its enantiomer.

Resolution of (±)-2. Formation and Separation of Internal Diastereoisomers [*SP*-4-2-(*R,R*)]- and [*SP*-4-2-(*R,S*)]-[1-Amino-2-(methylphenylphosphino)ethane-*N,P*][2-[1-(dimethylamino)ethyl]-naphthyl-*C,N*]palladium(II) Hexafluorophosphate ((*R,R*)-5 and (*R,S*)-5, Respectively). A solution of (±)-**2** (7.02 g) in methanol (50 mL) was added to (*R*)-**3** (14.5 g) in methanol (150 mL), and the mixture was stirred for 2 h at 20 °C. The clear solution was then filtered and treated with NH_4PF_6 (11.5 g) in water (250 mL). The pale yellow solid was filtered off, washed with water, and then dissolved in dichloromethane and dried ($MgSO_4$) and the solution taken down to dryness. The resulting pale yellow glass (23.5 g, 91%) had $[\alpha]_D$ −39° (c 2.54, Me_2CO). The glass was dissolved in acetone (30 mL) and the solution diluted with diethyl ether until it was slightly turbid, whereupon the mixture stood for 2 h at 20 °C and 16 h at 5 °C. Pale yellow crystals of (*R,R*)-**5** crystallized as an acetone hemisolvate. After three similar crystallizations from successively smaller volumes of acetone, a total of 8.3 g (85%) of pure (*R,R*)-**5**·0.5Me_2CO was obtained: mp 172–180 °C; $[\alpha]_D$ +37° (c 1.03, acetone). Anal. Calcd for $C_{24.5}H_{33}F_6O_{0.5}N_2P_2Pd$: C, 45.6; H, 5.2; N, 4.3. Found: C, 45.2; H, 5.2; N, 4.2. ^1H NMR (Me_2SO-d_6): δ 1.75 (d, 3, $^3J_{HH}$ = 6 Hz, CH*Me*), 1.98 (d, 3, $^2J_{PH}$ = 11 Hz, PMe), 2.10 (s, 3, Me_2CO), 2.2–2.4 (m, 2, PCH_2), 2.80 (s, 3, NMe), 2.84 (s, 3, NMe), 2.9–3.2 (m, 2, NCH_2), 4.3–4.5 (m, 1, NH), 4.58 (q, 1, $^3J_{HH}$ = 6 Hz, C*H*Me), 4.7–4.9 (m, 1, NH), 6.9–8.3 (m, 11, aromatics). Λ_M = 127 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Solvent-free (*R,R*)-**5** was obtained from the acetone hemisolvate after it had been recrystallized from dichloromethane: colorless crystals; mp 172–174 °C. Anal. Calcd. for $C_{23}H_{30}F_6N_2P_2Pd$: C, 44.8; H, 4.9; N, 4.5. Found: C, 44.7; H, 4.8; H, 4.5. ^1H NMR (Me_2SO-d_6): as for solvate, but minus Me_2CO peak. Λ_M = 139 Ω^{-1} cm^2 mol^{-1} (Me_2CO). The combined filtrates were evaporated to dryness, and the residue was crystallized from chloroform (300 mL) by the addition of diethyl ether (150 mL). The product was then recrystallized from acetone (25 mL) by the addition of propan-2-ol (800 mL) as colorless needles (3.75 g). Additional material was recovered from the filtrate by successive crystallizations from butan-2-one–diethyl ether mixtures. Fractions of crude (*R,S*)-**5** having $[\alpha]_D$ values greater than +110° (acetone) were combined for a final crystallization from the same solvent mixture. (*R,S*)-**5**: total yield 6.45 g (72%); mp 237–241 °C dec; $[\alpha]_D$ −119.3° (c 0.91, Me_2CO). Anal. Calcd for $C_{23}H_{30}F_6N_2P_2Pd$: C, 44.8; H, 4.9; N, 4.5. Found: C, 45.0; H, 5.0; N, 4.4. ^1H NMR (Me_2SO-d_6): δ 1.79 (*d*, 3, $^3J_{HH}$ = 6 Hz, CH*Me*), 2.17 (*d*, 3, $^2J_{PH}$ = 10 Hz, PMe), 2.39 (br t, $^2J_{PH}$ = 11 Hz, PCH_2), 2.71 (s, 3, NMe), 2.85 (br s, 3, NMe), 2.9–3.2 (m, 2, NCH_2), 4.35–4.45 (m, 1, NH), 4.56 (q, 1, $^3J_{HH}$ = 6 Hz, C*H*Me), 4.7–4.9 (br m, 1, NH), 7.0–7.9 (m, 11, aromatics). Λ_M = 146 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

(*S*)-1-Amino-2-(methylphenylphosphino)ethane ((*S*)-2). A solution containing (*R,R*)-**5** (6.9 g) and (*R*,R**)-(±)-1,2-phenylenebis(methylphenylphosphine) (3.2 g) in dichloromethane (300 mL) stood for 2 h at 25 °C and then was concentrated to ca. 25 mL and diluted with *n*-hexane (200 mL). The white precipitate was filtered off and washed with *n*-hexane: it was shown by ^1H NMR spectroscopy to be an equimolar mixture of (*R,RR*)- and (*R,SS*)-**7** (7.95 g, 98%). Optically active (*S*)-**2** was recovered from the filtrate after removal of solvent as a pale yellow oil: $[\alpha]_D$ +16.3° (c 0.96, CH_2Cl_2); 1.35 g (82%). ^1H NMR ($CDCl_3$): δ 1.22 (s, 2, NH_2), 1.32 (d, 3, $^2J_{PH}$ = 4 Hz, PMe), 1.60–2.12 (m, 2, PCH_2), 2.64–2.96 (m, 2, NCH_2), 7.08–7.83 (m, 5, aromatics).

(*R*)-1-Amino-2-(methylphenylphosphino)ethane ((*R*)-2). By use of a similar procedure optically active (*R*)-**2** was obtained from (*R,S*)-**5** in 81% yield: $[\alpha]_D$ −16.4° (c 0.99, CH_2Cl_2). ^1H NMR ($CDCl_3$): identical with that of its enantiomorph.

Preparation of Complexes. [*SP*-4-2-(*S,S*)]-Bis[1-amino-2-(methylphenylarsino)ethane]palladium(II) Hexafluorophosphate, (±)-*cis*-[Pd((*S*)-1)$_2$](PF$_6$)$_2$. A solution of (*R*)-**1** (0.71 g) in dichloromethane (20 mL) was added to solution of lithium chloropalladate(II) prepared from palladous chloride (0.29 g) and lithium chloride (0.2 g) in methanol (20 mL). The yellow solution was evaporated to dryness and the residue taken up in water (20 mL) and treated with NH_4PF_6 (1 g). The pale yellow precipitate was filtered off and then recrystallized from a dichloromethane–diethyl ether mixture as pale yellow microcrystals: mp 225 °C dec; yield 0.90 g, 75%; $[\alpha]_D$ −288° (c 1.0, Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pd$: C, 26.4; H, 3.5; N, 3.4. Found: C, 26.4; H, 3.4; N, 3.3. ^1H NMR (Me_2CO-d_6): δ 1.65 (s, 3, AsMe), 2.56–2.94 (m, 2, $AsCH_2$), 3.04–3.45 (m, 2, NCH_2), 4.92–5.28 (m, 2, NH_2), 7.6–7.9 (m, 5, aromatics). Λ_M = 206 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

The following compounds were prepared similarly in high yield. **[*SP*-4-2-(*R,R*)]-Bis[1-amino-2-(methylphenylarsino)ethane]palladium(II) hexafluorophosphate, (+)-*cis*-[Pd((R)-1)$_2$](PF$_6$)$_2$**: pale yellow crystals; mp 225 °C dec; $[\alpha]_D$ +292° (c 1.0, Me_2CO); Λ_M = 204 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pd$: C, 26.4; H, 3.5; N, 3.4. Found: C, 26.4; H, 3.4; N, 3.6. ^1H NMR (Me_2CO-d_6): identical with that of its enantiomorph. **[*SP*-4-2]-(±)-Bis[1-amino-2-(methylphenylarsino)ethane]palladium(II) hexafluorophosphate, (±)-*cis*-[Pd((*R,S*)-1)$_2$](PF$_6$)$_2$**: pale yellow crystals; mp 200–202 °C; yield 46%; Λ_M = 206 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pd$: C, 26.4; H, 3.5; N, 3.4. Found: C, 26.6; H, 3.5; N, 3.6. ^1H NMR (Me_2CO-d_6): δ 1.69 (s, 1.8, AsMe, racemic, 58%), 2.24 (s, 1.2, AsMe, meso, 42%), 2.46–2.94 (m, 2, $AsCH_2$), 3.1–3.5 (m, 2, NCH_2), 4.8–5.5 (m, 2, NH_2), 7.1–7.9 (m, 5, aromatics). **[*SP*-4-2-(*S,S*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]palladium(II) hexafluorophosphate, (−)-*cis*-[Pd((*S*)-2)$_2$](PF$_6$)$_2$**: pale yellow crystals; mp 230–233° dec; $[\alpha]_D$ −337° (c 0.5, Me_2CO); Λ_M = 203 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}F_{12}N_2P_4Pd$: C, 29.6; H, 3.9; N, 3.8. Found: C, 29.8; H, 4.0; N, 3.8. ^1H NMR (Me_2CO-d_6): δ 1.55 (d, 3, $^2J_{PH}$ = 11 Hz, PMe), 2.4–2.7 (m, 2, PCH_2), 3.1–3.6 (m, 2, NCH_2), 4.85–5.25 (m, 2, NH_2), 7.6–7.9 (m, 5, aromatics). **[*SP*-4-2-(*R,R*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]palladium(II) hexafluorophosphate, (+)-*cis*-[Pd((*R*)-2)$_2$](PF$_6$)$_2$**: pale yellow crystals; mp 230 °C dec; $[\alpha]_D$ +343° (c 0.5, Me_2CO); Λ_M = 204 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}F_{12}N_2P_4Pd$: C, 29.6; H, 3.9; N, 3.8. Found: C, 29.6;

H, 3.8; N, 3.8. ^{1}H NMR (Me_2CO-d_6): identical with that of its enantiomorph.

[*SP*-4-2-(*S*,*S*)]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) Hexafluorophosphate, (−)-*cis*-Pt((*S*)-1)$_2$](PF$_6$)$_2$. Potassium tetrachloroplatinate(II) (0.53 g) was dissolved in water (4 mL), and acetonitrile (15 mL) was added: the mixture was briefly heated at 60 °C and then a solution of (*R*)-**1** in acetonitrile (5 mL) was added. The colorless solution was filtered and the filtrate taken to dryness. The residue was redissolved in water and an excess of NH_4PF_6 was added: the product separated as a white precipitate that was recrystallized from dichloromethane–diethyl ether as colorless crystals: mp 258–260 °C (0.94 g, 89%); $[\alpha]_D$ −209° (*c* 0.95, Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pt$: C, 23.8; H, 3.1; N, 3.1. Found: C, 23.7; H, 3.1; N, 3.2. ^{1}H NMR (Me_2CO-d_6): δ 1.76 (s, 3, $^3J_{PtH}$ = 24 Hz, AsMe), 2.55 (m, 2, $AsCH_2$), 3.16 (m, 2, NCH_2), 5.74 (m, 2, NH_2), 7.5–7.9 (m, 5, aromatics). ^{13}C NMR (Me_2SO-d_6): δ 6.13 ($^2J_{PtC}$ = 61 Hz, AsMe), 30.48 ($^2J_{PtC}$ = 34 Hz, $AsCH_2$), 44.12 (NCH_2), 129.38, 131.43, 131.66 (aromatics). Λ_M = 221 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

The following compounds were prepared similarly in high yield. **[*SP*-4-2-(*R*,*R*)]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) hexafluorophosphate, (+)-*cis*-[Pt((*R*)-1)$_2$](PF$_6$)$_2$**: colorless crystals; mp 250–252 °C dec; $[\alpha]_D$ +206° (*c* 0.93, Me_2CO); Λ_M = 216 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pt$: C, 23.8; H, 3.1; N, 3.1. Found: C, 24.1; H, 3.1; N, 2.9. ^{1}H NMR (Me_2CO-d_6): identical with that of its enantiomorph. **(±)-[*SP*-4-2]-Bis[1-amino-2-(methylphenylarsino)ethane]platinum(II) hexafluorophosphate, (±)-*cis*-[Pt((*R*,*S*)-1)$_2$](PF$_6$)$_2$**: colorless needles from an acetone solution of an equimolar mixture of the enantiomers; mp 205–208 °C; 50% yield; Λ_M = 217 Ω^{-1} cm^2 mol^{-1} (Me_2CO). Anal. Calcd for $C_{18}H_{28}As_2F_{12}N_2P_2Pt$: C, 23.8; H, 3.1; N, 3.1. Found: 23.7; H, 3.1; N, 3.1. ^{1}H NMR (Me_2CO-d_6): identical with that of either pure enantiomer. **[*SP*-4-2-(*S*,*S*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorohosphate, (−)-*cis*-[Pt((*S*)-2)$_2$](PF$_6$)$_2$**: colorless crystals; mp 280° dec; $[\alpha]_D$ −224° (*c* 0.50, Me_2CO); Λ_M = 208 Ω^{-1} cm^2 mol^{-1} (Me_2CO). ^{1}H NMR (Me_2CO-d_6): δ 1.65 (d, 3, $^2J_{PH}$ = 11.7 Hz, $^3J_{PtH}$ = 39.6 Hz, PMe), 2.50 (m, 2, PCH_2), 3.29 (m, 2, NCH_2), 5.68 (m, 2, NH_2), 7.6–8.0 (m, 5, aromatics). ^{31}P NMR (Me_2CO-d_6): δ 21.8 (s, $^1J_{PtP}$ = 3221 Hz). **[*SP*-4-2-(*R*,*R*)]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorophosphate, (+)-*cis*-[Pt((*R*)-2)$_2$](PF$_6$)$_2$**: colorless crystals; mp 280° dec; $[\alpha]_D$ +227° (*c* 0.50, Me_2CO); Λ_M = 210 Ω^{-1} cm^2 mol^{-1} (Me_2CO). ^{1}H and ^{31}P NMR (Me_2CO-d_6): identical with that of its enantiomorph. **(±)-[*SP*-4-2]-Bis[1-amino-2-(methylphenylphosphino)ethane]platinum(II) hexafluorophosphate, (±)-*cis*-[Pt((*R*,*S*)-2)$_2$](PF$_6$)$_2$**: colorless crystals from acetone–propan-2-ol mixture; mp 252–254 °C. Anal. Calcd for $C_{18}H_{28}F_{12}N_2P_4Pt$: C, 26.4; H, 3.4; N, 3.4. Found: C, 26.7; H, 3.6; N, 3.5. Λ_M = 209 Ω^{-1} cm^2 mol^{-1} (Me_2CO). ^{1}H and ^{31}P NMR (Me_2CO-d_6): identical with that of enantiomers.

Condensation Reactions. [*SP*-4-4-(*R*,*R*)][1,9-bis(methylphenylarsino)-4,6,6-trimethyl-3,7-diazanon-3-ene]platinum(II) Hexafluorophosphate (8a/8b). A small quantity of (*S*)-**1** was added to a solution of (+)-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$ (0.1 g) in acetone (50 mL), and the reaction mixture was allowed to stand for 16 h at 25 °C. The volume of the solution was then reduced, and the product was precipitated by the addition of diethyl ether. Recrystallization of this material from an acetone–diethyl ether mixture gave the pure mixture of epimers **8a**/**8b** as colorless needles: mp 158–159 °C (0.08 g, 74%); $[\alpha]_D$ +107.1° (*c* 0.24, Me_2CO). Anal. Calcd for $C_{24}H_{36}As_2F_{12}N_2P_2Pt$: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.9; N, 2.9. ^{13}C NMR (Me_2SO-d_6): δ 4.98, 5.19, 5.64, 6.69 (AsMe), 20.79, 21.40, 25.32, 25.70, 25.75, 25.96 (CCH_3), 26.92, 27.07, 29.11, 29.06 ($AsCH_2$), 46.54, 47.36 (CH_2C(Me)=), 54.84, 55.48 (CMe_2), 55.13, 56.06, 56.50, 56.68 ($NHCH_2$, $=NCH_2$), 128.24–131.93 (m, aromatics), 182.96, 183.37 (C=N). IR (Nujol): 1644 cm^{-1} (br s, $\nu_{C=N}$). Λ_M = 214 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

(±)-8a/8b. This substance was isolated in 30% yield by fractional crystallization of the product obtained from use of (±)-[Pt((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$ as starting material: colorless crystals from acetone–diethyl ether; mp 258–260 °C dec. Anal. Calcd for $C_{24}H_{36}As_2F_{12}N_2P_2Pt$: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.9; N, 2.7. ^{13}C NMR (Me_2SO-d_6): identical with that of optically active material. Λ_M = 211 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

(±)-8c/8d: colorless crystals; mp 260 °C dec. Anal. Calcd for $C_{24}H_{36}As_2F_{12}N_2P_2Pt$: C, 29.2; H, 3.7; N, 2.8. Found: C, 29.3; H, 3.8; N, 2.8. ^{13}C NMR (Me_2SO-d_6): δ 6.31, 6.72, 6.92, 7.88 (AsMe), 20.82, 21.32, 25.11, 25.37, 25.72, 25.87 (CCH_3), 26.13, 26.28, 28.88, 29.08 ($AsCH_2$), 46.43, 47.52 (CH_2CH(Me)=), 54.78, 55.39 (CMe_2), 55.10, 55.92, 56.33, 56.68 ($NHCH_2$, $=NCH_2$), 127.45–131.69 (m, aromatics), 183.11, 183.43 (C=N). IR (Nujol): 1640 cm^{-1} (br s, $\nu_{C=N}$). Λ_M = 214 Ω^{-1} cm^2 mol^{-1} (Me_2CO).

Registry No. (±)-**1**, 90971-53-2; (*S*)-**1**, 91049-53-5; (*R*)-**1**, 91049-58-0; (±)-**2**, 90971-54-3; (*S*)-**2**, 91049-54-6; (*R*)-**2**, 91049-55-7; (*R*)-**3**, 80145-77-3; (*R*,*S*)-**4**, 90971-56-5; (*R*,*R*)-**4**, 91049-57-9; (*R*,*R*)-**5**, 90971-58-7; (*R*,*S*)-**5**, 91049-60-4; **8a**(PF$_6$)$_2$, 90971-68-9; **8b**(PF$_6$)$_2$, 91049-76-2; **8c**(PF$_6$)$_2$, 91049-78-4; **8d**(PF$_6$)$_2$, 91049-80-8; (−)-*cis*-[Pd((*S*)-**1**)$_2$](PF$_6$)$_2$, 90971-60-1; (+)-*cis*-[Pd((*R*)-**1**)$_2$](PF$_6$)$_2$, 91049-62-6; (±)-*cis*-[Pd((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$, 91049-64-8; (−)-*cis*-[Pd((*S*)-**2**)$_2$](PF$_6$)$_2$, 90971-62-3; (+)-*cis*-[Pd((*R*)-**2**)$_2$](PF$_6$)$_2$, 91049-66-0; (−)-*cis*-[Pt((*S*)-**1**)$_2$](PF$_6$)$_2$, 90971-64-5; (+)-*cis*-[Pt((*R*)-**1**)$_2$](PF$_6$)$_2$, 91049-68-2; (±)-*cis*-[Pt((*R*,*S*)-**1**)$_2$](PF$_6$)$_2$, 91049-70-6; (−)-*cis*-[Pt((*S*)-**2**)$_2$](PF$_6$)$_2$, 90971-66-7; (+)-*cis*-[Pt((*R*)-**2**)$_2$](PF$_6$)$_2$, 91049-72-8; (±)-*cis*-[Pt((*R*,*S*)-**2**)$_2$](PF$_6$)$_2$, 91049-74-0; $ClCH_2CH_2NH_2$, 689-98-5; MeI, 74-88-4; methylphenylarsine, 53979-86-5; (±)-1-amino-2-(phenylphosphino)ethane, 90971-69-0; lithium tetrachloropalladate(II), 15525-45-8; potassium tetrachloroplatinate(II), 10025-99-7; acetone, 67-64-1.

Contribution from the Departamento de Química Inorgánica y Química General, Facultad de Química, Universidad de Sevilla, Sevilla, Spain

Synthesis and Characterization of New Mononuclear and Dinuclear Complexes of Palladium(II) with Glycyl Chloride

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The complexes *cis*- and *trans*-$PdCl_2(NH_2CH_2COCl)_2$ and *trans*-$Pd_2Cl_4(NH_2CH_2COCl)_2$ are obtained in the reaction of $Pd(GlyO)_2$ with $SOCl_2$. Products have been characterized by elemental analysis and infrared and proton nuclear magnetic resonance spectroscopy. *cis*- and *trans*-$PdCl_2(NH_2CH_2COOH)_2$ have been prepared, similarly characterized, and studied by potentiometry.

Introduction

The importance of coordination compounds of transition-metal ions in the vital biological processes and their potential applications as antitumor agents have been stressed elsewhere.[1,2] The first complexes of Pd(II) with α-amino acids as ligands were described by Sharrat et al.[3] Shestanova[4]

(1) Williams, D. R. *Chem. Rev.* **1972**, *72*, 203.

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