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Diastereomerism in Square-Planar Complexes of Bivalent Nickel, Palladium, and Platinum Containing Asymmetric 2-Mercaptoethyl-Substituted Tertiary Arsines and Phosphines

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The racemic and optically active forms of the asymmetric bidentate (±)-(2-mercaptoethyl)methylphenylarsine, (±)-AsSH, and the racemic form of the corresponding tertiary phosphine, (±)-PSH, have been used to prepare a series of square-planar complexes of the type $[M(AsS)_2]$ and $[M(PS)_2]$ for M = Ni, Pd, or Pt. Ligand redistribution is rife in solutions of these complexes under ambient conditions, especially for the nickel and palladium derivatives of the tertiary arsine, as evidenced by facile intermolecular asymmetric transformations between racemic and meso diastereomers of the same complex. Furthermore, it has been shown that although stereoelectronic factors govern the distribution of product diastereomers in solution, these effects are frequently outweighed by lattice effects in isolated solids, where a single diastereomer of a particular complex can be isolated by a crystallization-induced disequilibration.

Introduction

The reactions of chelating deprotonated (mercaptoalkyl)-phosphines with elements of the cobalt and nickel triads have been extensively studied over many years by the groups of Schwarzenbach[1] and of Issleib,[2] although only work from the latter source appears to have been reported in detail. Tertiary arsines of a similar type are also long known,[3] and they, along with the phosphines, have been shown to have a rich coordination chemistry. The ligands are powerful sequesterers of bi- and trivalent metal ions, giving neutral complexes that contain terminal thiolato donors. Such sulfurs retain a considerable nucleophilicity, as demonstrated by ready alkylation[1,2,4] and a propensity for bridging to other metal centers.[5,6] The characterization of metal chelates of this type and investigations of their reactivity have been the primary aims of earlier work, with little attention being given to the importance of ligand-based stereoelectronic effects in determining product stereochemistries. An understanding of the latter may bear heavily on the design of synthetic analogues of certain sulfur-containing metalloproteins.[7]

In this paper we show that bis chelates of bivalent nickel, palladium, and platinum with deprotonated (2-mercaptoethyl)-methylphenylarsine and -phosphine display an unusually high lability with respect to ligand redistribution, with mixtures of up to four diasteromers of a complex ensuing in certain cases. With use of ^1H and ^{31}P NMR spectroscopy and the pure enantiomers of the tertiary arsine,[8] we have been able to unambiguously identify by NMR spectroscopy each of the diasteromers present for all three metals under a variety of conditions and thereby obtain the first direct estimate of the importance of stereoelectronic effects in such complexes.

Results and Discussion

Stereochemical Considerations. Square-planar complexes containing 2 equiv of deprotonated (±)-(2-mercaptoethyl)-methylphenylarsine or its phosphorus analogue (Figure 1) exhibit diastereomerism from two sources: (1) the relative arrangement of the like pairs of donor atoms results in cis-trans isomerism (electronic contribution); (2) the relative helicities of the asymmetric phosphorus or arsenic donor centers in each of the cis and trans diastereomers leads to racemic-meso diastereomerism (steric contribution). Thus, metal chelates of this type may exist as mixtures of up to four diastereomers (Figure 2).[9] Bidentates that give rise to this situation have C_1 symmetry and are accordingly classified as *asymmetric bidentates*. A study of the proportions of the various diastereomers present for a particular metal under a given set of conditions will therefore provide an estimate of the importance of stereoelectronic effects in such systems.[11] For labile complexes the presence or absence of particular diastereomers may be diagnostic of the nature of the reaction. Thus, cis-trans isomerism may be either intra- or intermolecular in origin, but racemic-meso interconversion is necessarily an intermolecular process: it is a measure of the extent of ligand redistribution in a particular system and is ipso facto a measure of the metal-ligand bond strength. It is obvious that this type of information is crucial to the rational development of metal-assisted organic reactions, such as ligand-based coupling reactions or asymmetric syntheses involving coordinated substrates.

General Strategy. Bis(bidentate) derivatives of all three metals were prepared with the optically active and racemic forms of the tertiary arsine and with the racemic form of the corresponding phospine. The cis and trans diastereomers of each complex containing the phosphine were readily identified by ^1H and ^{31}P NMR spectroscopy. In cis complexes of this type the PMe resonance appears as a doublet ($^2J_{PP'}$ = ca. 0 Hz) or as a "filled-in" doublet ($0 < {}^2J_{PP'} << |{}^2J_{PH} + {}^4J_{P'H}|$), but in trans complexes, the PMe groups are usually observed as deceptively simple triplets, due to virtual coupling between the trans phosphorus nuclei ($^2J_{PP'} >> |{}^2J_{PH} + {}^4J_{P'H}|$).[12] Additionally, the value of $^1J_{PtP}$ is diagnostic of geometry in platinum complexes.[13] Thus, with use of the tertiary phosphine ligand, cis and trans isomers of a particular complex are readily identified by NMR spectroscopy. In the present series of complexes cis diastereomers were found to exhibit PMe or AsMe chemical shifts upfield of those of the corresponding trans diasteromers. The identification of racemic and meso diastereomers was then achieved by comparing the NMR spectra of complexes derived from both the optically active and the racemic forms of the tertiary arsine ligand. (Racemic diastereomers under normal conditions have NMR spectra in achiral solvents identical with those of the corresponding optically active species). In the

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(9) No evidence was found in the present work of a contribution to the diastereomerism arising from the adoption by the two nonplanar chelate rings of different relative local helicities, viz., $\delta\delta$, $\lambda\lambda$, or $\delta\lambda$, which, in principle, could have doubled the number of observable diastereomers. Nevertheless, the usual factors governing the stabilities of various ring conformations undoubtedly apply to these systems.[10]
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Table I. Thermodynamic Populations in $CDCl_3$ at 25 °C (in Parentheses) and δ (EMe) of Diastereomers of $[M(PS)_2]$ and $[M(AsS)_2]$

compd	diasteromer[a]			
	racemic-cis	meso-cis	racemic-trans	meso-trans
(±)-$[Ni(PS)_2]$			1.77 t (50%), J_{PH} = 7.3 Hz[b]	1.81 t (50%), J_{PH} = 7.3 Hz
(±)-$[Ni(AsS)_2]$			1.73 s (50%)	1.76 s (50%)
(+)-$[Ni(AsS)_2]$			1.73 s (100%)	...
(±)-$[Pd(PS)_2]$	1.19 d (26%), J_{PH} = 8.8 Hz	1.71 d (13%), J_{PH} = 8.4 Hz	1.84 t (30.5%), J_{PH} = 6.3 Hz	1.87 t (30.5%), J_{PH} = 6.3 Hz
(±)-$[Pd(AsS)_2]$	1.27 s (11%)	1.71 s (5%)	1.80 s (42%)	1.82 s (42%)
(+)-$[Pd(AsS)_2]$	1.27 s (20%)		1.80 s (80%)	
(±)-$[Pt(PS)_2]$	1.30 d (100%),[c] J_{PH} = 9.8 Hz, J_{PtH} = 29.4 Hz	1.84 d (100%),[d] J_{PH} = 9.5 Hz, J_{PtH} = 29.3 Hz		
(±)-$[Pt(AsS)_2]$	1.35 s (61%), J_{PtH} = 17.3 Hz	1.82 s (23%), J_{PtH} = 18.0 Hz	1.87 s (8%), J_{PtH} = 20.0 Hz	1.89 s (8%), J_{PtH} = 20.2 Hz
(+)-$[Pt(AsS)_2]$	1.35 s (83%), J_{PtH} = 17.3 Hz		1.87 s (17%), J_{PtH} = 20.0 Hz	

[a] ^1H NMR spectra chemical shift values of EMe in ppm, relative to internal Me_4Si for ca. 0.05 M solutions. [b] $J_{PH} = |^2J_{PH} + {}^4P_{P'H}|$. [c] Isolated kinetically stable product. [d] Not isolated.

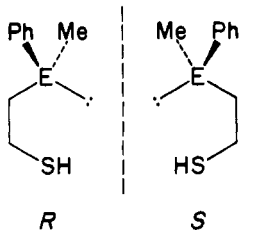

Figure 1. Enantiomers of (±)-$PhMeECH_2CH_2SH$ (where E = P or As).

present system, the shielding by phenyl groups of neighboring methyl groups was of considerable assistance in making the structural assignments. Thus, it is evident that from Figure 2 that the methyl groups of the *cis*-[*S*-(*R**,*R**)] diastereomer will be shielded relative to those of the corresponding trans-[*S*-(*R**,*R**)] diastereomer, and from this factor alone, it is clear that the racemic-cis diasteromer will have the E*Me* ^1H NMR chemical shift value to highest field in an optically inactive mixture of the four diastereomers. The ordering of chemical shifts in trans diastereomers cannot be predicted as simply, however: it was found in the present series of compounds that the racemic-trans diastereomer EMe resonance occurred upfield of the signal of the corresponding meso-trans diastereomer. The ordering of EMe chemical shifts for the four diastereomers is thus racemic-cis (highest field), meso-cis, racemic-trans, and meso-trans.

As intimated in the Introduction, the ease with which diastereomers interconvert may reflect either internal or external stability of the metal-ligand interaction or both. Thus, for a particular complex, if intermolecular racemic–meso interconversion can be shown to be slow on the NMR time scale, the observation of rapid cis–trans isomerization in the corresponding optically active complex under the same conditions implies that the latter process is intramolecular. Ideally, therefore, all diastereomers of a particular complex should be isolated and separately studied in stability studies of this type. It is worth noting, however, that is often more convenient to prepare the racemic form of a particular diastereomer by mixing together equal amounts of the corresponding pure enantiomers than by physically separating a racemic–meso mixture.

Metal Complexes. (a) Nickel(II) Derivatives. The neutral bivalent nickel derivatives were prepared by adding a solution of $[Ni(H_2O)_6](NO_3)_2$ in methanol to a solution containing 2 equiv of the appropriate form of the ligand in the same solvent in the

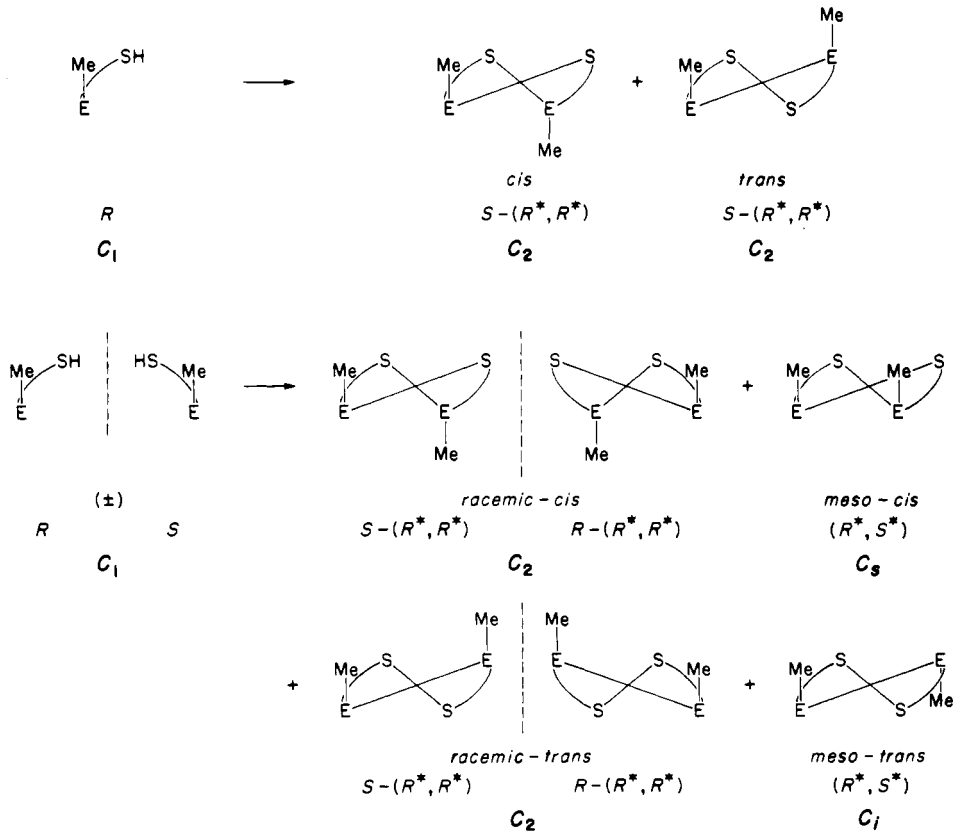

Figure 2. Diastereomers of square-plane complexes of the type $[M(SCH_2CH_2EMePh)_2]$. The phenyl groups on each of the asymmetric tertiary phosphorus or arsenic donor stereocenters have been omitted for clarity.

presence of base (sodium hydroxide, 2 equiv). The products precipitated from the reaction mixtures as brightly colored air-stable solids. In each case, the ^1H NMR spectrum of the initial material was recorded prior to recrystallization. Selected physical and spectroscopic properties for the recrystallized products $[Ni(PS)_2]$ and $[Ni(AsS)_2]$ are given in Table I.

The 200-MHz ^1H NMR spectrum of a freshly prepared sample of the tertiary phosphine complex (±)-$[Ni(PS)_2]$ exhibited a sharp 1:2:1 PMe triplet in $CDCl_3$ centered at δ 1.77 (J_{PH} = 7.3 Hz), which indicated a single diastereomer of trans stereochemistry. After ca. 24 h, however, the same solution was found to exhibit an additional 1:2:1 PMe triplet at δ 1.81 with J_{PH} = 7.3 Hz. At equilibrium ($t_{1/2}$ ca. 12 h), both peaks were of equal intensity. The ^{31}P NMR spectra were consistent with these results. A freshly prepared sample of the complex in $CDCl_3$ gave a singlet at δ 55.8 in the ^{31}P NMR spectrum, with an additional singlet of equal intensity at δ 55.1 being present at equilibrium (asymmetric equilibration in solution).[14] When a solution of the mixture at equilibrium was taken to dryness, the residue was shown to consist of a 1:1 mixture of the two trans complexes, although the relatively slow recrystallization of the mixture always ended in the preferential crystallization of the original single trans diastereomer (crystallization-induced asymmetric disequilibration).[14] The identification of this trans diastereomer was achieved by analyzing the ^1H NMR spectra of the corresponding tertiary arsine derivatives, for which both racemic and optically active forms of the ligand are available.[8] Thus, (*R*)-(−)-AsSH produced an optically pure complex that gave a single sharp AsMe resonance at δ 1.73 in $CDCl_3$, whereas racemic (±)-AsSH gave a product showing a pair of AsMe resonances of equal intensity at δ 1.73 and 1.76. Because of the similarity of the chemical shifts of the AsMe signals to those of the PMe signal of the trans phosphine complex, both arsine complexes were considered to possess trans stereochemistry. Furthermore, since the product from (*R*)-(−)-AsSH exhibited the signal to higher field, the initial product from the phosphine reaction was undoubtedly the corresponding racemic-trans diastereomer (see Note Added in Proof). Thus, in the reaction of (±)-PSH with the Ni(II) ion the *rac-trans*-bis(bidentate) diastereomer is formed stereospecifically (kinetic product), although both this and the corresponding meso-trans diastereomer have similar energies within experimental error at equilibrium. It can also be concluded from the above that the rearrangement occurs by an intermolecular redistribution of the bidentate ligands:

$$\textit{rac-trans}\text{-}[Ni(PS)_2] \rightleftharpoons \textit{meso-trans}\text{-}[Ni(PS)_2]$$

Interestingly, the corresponding crystalline tertiary arsine compound, that is, the product from the reaction of Ni^{2+} with (±)-AsSH, was also shown to be the racemic-trans diastereomer. Thus, when a sample of $[Ni(AsS)_2]$ was dissolved in dichloromethane-d_2 at −78 °C, only the AsMe signal at δ 1.69 was observed. Warming of this solution to 25 °C resulted in the appearance of a new signal of equal intensity at δ 1.72; recooling of the sample to −78 °C did not alter the equilibrium 1:1 ratio of trans diastereomers.

The regiospecificity of coordination of the P, As, and S donors to nickel(II) (to give trans complexes), together with the ready attainment of racemic–meso equilibria by asymmetric equilibrations in both cases (absence of diastereoselectivity), makes such complex derivatives ideal for the determination of optical purities. It should be noted in a general sense, however, that if the method of metal complexation is to be used for the determination of the optical purity of a ligand, it must first be established with use of the racemic form of the same ligand that the *meso*-bis(bidentate) complex is indeed stable under the same conditions in the solvent chosen, since intermolecular asymmetric equilibrations of this type often show a marked solvent and temperature dependence.[15]

(b) Palladium(II) Derivatives. Ligand (±)-PSH reacted with $[Pd(MeCN)_4](NO_3)_2$[16] in the presnce of triethylamine in acetonitrile to give a yellow product that exhibited PMe peaks due to the four possible diastereomers of the neutral bis(bidentate) complex in the 200-MHz ^1H NMR spectrum in $CDCl_3$: two doublets centered at δ 1.19 and 1.71 (cis diastereomers), and two triplets at δ 1.84 and 1.87 (trans diastereomers). The intensities of the peaks, respectively 6:3:7:7, did not alter over a 48-h period. Thus, whereas coordination of (±)-PSH to nickel(II) is regiospecific (to give trans diastereomers), coordination to palladium(II) is regioselective (cis:trans = 9:14) with trans diastereomers nevertheless predominating. Diastereoselectivity was absent (racemic-trans:meso-trans = 1:1) in the trans palladium(II) compounds (as for nickel(II)) but was exhibited in the cis diastereomers (racemic-cis:meso-cis = 2:1), presumably due to the proximity of the asymmetric stereocenters. When the original mixture was stirred in neat methanol, the residue after a rapid recrystallization from a dichloromethane–methanol mixture was shown to be the pure high-field yellow racemic-cis diasteromer (δ 1.19, d, PMe). The methanol extract after concentration yielded a crop of the more deeply colored high-field racemic-trans diasteromers (δ 1.84, t, PMe). Redistribution of the bidentates was found to be relatively slow for each of the isolated diastereomers; both isolated diastereomers required 48 h to reach the 6:3:7:7 equilibrium condition. At this stage the analogous tertiary arsine complexes were prepared in order to determine the racemic-meso shielding order in the cis and trans diastereomers.

The derivatives of (*S*)-(+)- or (*R*)-(−)-AsSH and of (±)-AsSH were prepared by adding the tetrachloropalladate(II) ion (in solutions containing excess chloride $[PdCl_5]^{3-}$ may also be present) in methanol to a solution of the appropriate form of the ligand in the same solvent with added NaOH. The ^1H NMR spectrum of the orange precipitate obtained from (±)-AsSH in $CDCl_3$ contained four AsMe singlets at δ 1.27, 1.71, 1.80, and 1.82 in the ratio of 2:1:8:8. The proportions of the four diastereomers are similar to those found for the corresponding phosphine complex. The spectrum of the corresponding optically active complex under the same conditions exhibited two AsMe singlets at δ 1.27 and 1.80 in the ratio of 1:4. The peaks at δ 1.71 and 1.82 in the optically inactive mixture were thus due to the two meso diastereomers. With the knowledge from the corresponding phosphine complexes that the PMe resonances of cis diastereomers occur upfield of those of the corresponding trans diasteromers it was then possible to unambiguously assign the methyl resonances of the four diastereomers in both sets of compounds. The assignments are given in Table I.

Intermolecular rearrangement between the diastereomers of the complex $[Pd(AsS)_2]$ is facile at 25 °C. Indeed, equilibrium concentrations of the meso diastereomers (cis and trans) of the complex were evident within the time of mixing of equal amounts of the pure enantiomorphic optically active complexes in $CDCl_3$ at 25 °C. We were able to show subsequently, however, that the yellow needles obtained from the crystallization of the optically active material, (+)-$[Pd(AsS)_2]$, were indeed the pure cis diastereomer. Thus, when a sample of the needles was dissolved in CD_2Cl_2 at −78 °C, a single AsMe peak at δ 1.26 was observed in the ^1H NMR spectrum. As the temperature of the solution was raised a new AsMe peak at δ 1.80 due to the trans diastereomer emerged. At 25 °C cis:trans = 7:11. Recooling of the sample to −60 °C did not detectably affect the equilibrium ratio. Interestingly, the crystalline inactive complex, (±)-$[Pd(AsS)_2]$, was bright orange in color. Dissolution of the orange inactive material in CD_2Cl_2 at −78 °C revealed that it was the corresponding meso-trans diasteromer, thus emphasizing the subtlety of the stereochemical effects in these systems. At −78 °C, (±)-$[Pd(AsS)_2]$ in CD_2Cl_2 exhibited a single AsMe peak at δ 1.86. Signals due to the three other possible diastereomers subsequently emerged in the spectrum as the temperature was raised. At 25 °C the equilibrium racemic-cis:meso-cis:racemic-trans:meso-trans ratio was ca. 2:1:2:2. The equilibrium ratio of diastereomers was

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not altered by recooling the solution to −60 °C. Consistent with this observation, the structure of a similar orange complex containing deprotonated (±)-(2-mercaptoethyl)(2-methoxybenzyl)methylarsine was shown by X-ray crystallography in other work to be the meso-trans diastereomer.[17]

The solubilities of pure yellow (+)-*cis*-[Pd(AsS)$_2$] and orange *meso-trans*-[Pd(AsS)$_2$] are quite different. Whereas the latter is quite soluble in benzene, the former is insoluble. In hot benzene, however, yellow (+)-*cis*-[Pd(AsS)$_2$], with $[\alpha]_D$ + 323° (CH_2Cl_2), dissolved to give an orange solution that was shown by ^{1}H NMR spectroscopy to contain only (+)-*trans*-[Pd(AsS)$_2$] and that had an $[\alpha]_D$ of +334° in this solvent. It was not found possible, however, to isolate the orange trans complex from the benzene solution. In solvents more polar than benzene, both the optically active cis and inactive trans diastereomers are soluble, although the diastereomeric ratios in the different solvents vary. Thus, for the optically active compound the following values of the cis:trans ratio were found at 25 °C: 0:1 (benzene-d_6), 1:4 ($CDCl_3$), 7:11 (dichloromethane-d_2), 1:1 (Me_2SO-d_6), 2:3 ($PhNO_2$-d_5).

(c) Platinum(II) Derivatives. The reaction of (±)-PSH with K_2PtCl_4 in the presence of base yielded a pale yellow precipitate from which pure *rac-cis*-[Pt(PS)$_2$] with δ(PMe) of 1.30 was recovered in 45% yield after recrystallization of the original material from hot ethanol. The mother liquor was subsequently shown to contain a mixture of the isolated *rac*-cis diastereomer (ca. 60%) and the corresponding meso-cis compound (ca. 40%) with δ(PMe) of 1.84. The latter was not isolated in a pure state. The ^{1}H NMR spectrum of the pure racemic-cis diastereomer in $CDCl_3$ did not change over a 5-day period.

A similar reaction of (*S*)-(+)- or (*R*)-(−)-AsSH with K_2PtCl_4 produced the corresponding optically active [Pt(AsS)$_2$] arsine complexes, respectively; both displayed a single sharp AsMe resonance at δ 1.35, which corresponded to the cis diastereomer in each case. When (±)-AsSH was used in the reaction, the predominant isolable product was the racemic-cis species, although a small quantity of the meso-cis diastereomer was observed in the mother liquor. No evidence of the trans diastereomers was found in freshly prepared solutions. Unlike the corresponding phosphorus compounds, however, the arsenic derivatives displayed a considerable lability with respect to the redistribution of ligands. For example, a $CDCl_3$ solution of the optically active cis diastereomer had rearranged within 18 h into a cis:trans = 5:1 equilibrium mixture. The pure racemic-cis species over a similar period rearranged into a diastereomeric mixture of equilibrium composition racemic-cis:meso-cis:racemic-trans:meso-trans = 8:3:1:1. The ^{1}H NMR data for the various diastereomers is given in Table I.

Experimental Section

All reactions were performed under an argon atmosphere. Routine ^{1}H NMR spectra were recorded at 25 °C by use of a JEOL FX 200 spectrometer; low-temperature and ^{31}P NMR spectra were obtained with use of a Bruker CXP-200 instrument. Optical rotations were measured on the specified solutions in a 1-dm cell at 20 °C by use of a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the Research School of Chemistry.

The ligand (±)-(2-mercaptoethyl)methylphenylarsine was prepared and resolved as described in ref 8. The ligand (±)-(2-mercaptoethyl)-methylphenylphosphine was described in the work by Marty and Schwarzenbach,[1] although details of its preparation do not appear to have been published.

(±)-(2-Mercaptoethyl)methylphenylphosphine ((±)-PSH). A solution of ethylene sulfide (4.8 g) in tetrahydrofuran (50 mL) was added over 30 min to a solution of Na[PMePh] at −78 °C that had previously been prepared from PHMePh (9.9 g) and sodium (foil, 2.7 g) in the same solvent. After the addition, the cooling medium was removed and the reaction mixture was stirred at room temperature for ca. 20 h. At this stage, the solvent was removed by distillation and the residue was treated with a solution of ammonium chloride (5 g) in water (200 mL). The product was extracted from the mixture with dichloromethane and subsequently isolated from the dried organic extract by distillation. Pure (±)-PSH was thus obtained (10.4 g, 71%) as a foul-smelling colorless oil, bp 80–81 °C (0.03 mmHg). Anal. Calcd for $C_9H_{13}PS$: C, 58.7; H, 7.1. Found: C, 58.9; H, 6.9. ^{1}H NMR ($CDCl_3$): δ 1.31 (d, 3 H, $^2J_{PH}$ = 3.4 Hz, PMe), 1.58 (d of t, 1 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.2 Hz, SH), 1.88–2.09 (m, 2 H, PCH_2), 2.41–2.60 (m, 2 H, SCH_2), 7.28–8.15 (m, 5 H, aromatics).

[*SP*-4-1-(*R,*R**)]-(±)-Bis[2-(methylphenylphosphino)ethanethiolato]nickel(II) (*rac-trans*-[Ni(PS)$_2$]).** A solution of $[Ni(H_2O)_6](NO_3)_2$ (0.52 g) in methanol (20 mL) was slowly added to a solution of (±)-PSH (1.0 g) in MeOH (20 mL) containing 1 M NaOH (5 mL). After ca. 30 min the deep red product was filtered off and was recrystallized from a dichloromethane–methanol mixture; the pure compound formed claret-colored needles, mp 198–200 °C (lit.[1] 199–202 °C) (82%). Anal. Calcd for $C_{18}H_{24}NiP_2S_2$: C, 50.9; H, 5.7. Found: C, 50.9; H, 5.7. ^{1}H NMR ($CDCl_3$): δ 1.77 (t, 6 H, J_{PH} = 7.3 Hz, PMe), 2.04–2.76 (m, 8 H, CH_2CH_2), 7.48–8.05 (m, 10 H, aromatics). ^{1}H NMR ($CDCl_3$, after 48 h): δ 1.77 (t, 3 H, J_{PH} = 7.3 Hz, PMe), 1.81 (t, 3 H, J_{PH} = 7.3 Hz, PMe), 2.04–2.76 (m, 8 H, CH_2CH_2), 7.48–8.50 (m, 10 H, aromatics).

The following compounds were prepared similarly. **[*SP*-4-1-[*R*-(*R**,*R**)]]-(+)-Bis[2-(methylphenylarsino)ethanethiolato]nickel(II) (*trans*-(+)-[Ni(AsS)$_2$])** was prepared from (*S*)-AsSH, $[\alpha]_D$ +16.7 ° (*c* 5, CH_2Cl_2)[8]: dark green plates, mp 177–178 °C, 75% yield, $[\alpha]_D$ +447° (*c* 0.25, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 6 H, AsMe), 2.06–2.73 (m, 4 H, $AsCH_2$), 2.48–2.71 (m, 4 H, SCH_2), 7.47–7.89 (m, 10 H, aromatics). The enantiomer *trans*-(−)-[Ni(AsS)$_2$], $[\alpha]_D$ −448° (*c* 0.25, CH_2Cl_2), had properties identical with the above. **[*SP*-4-1-(*R**,*S**)]-Bis[2-(methylphenylarsino)ethanethiolato]nickel(II) (*meso-trans*-[Ni(AsS)$_2$])** was prepared from (±)-AsSH: dark green prisms, mp 165–167 °C, 40% yield. ^{1}H NMR (CD_2Cl_2, −78 °C) δ 1.69 (s, 6, AsMe), 2.12–2.74 (m, 8, CH_2CH_2), 7.49–7.89 (m, 10, aromatics). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.69 (s, 3 H, AsMe), 1.72 (s, 3 H, AsMe), 2.13–2.74 (m, 8 H, CH_2CH_2), 7.49–7.84 (m, 10 H, aromatics). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 3 H, AsMe), 1.76 (s, 3 H, AsMe), 2.10–2.41 (m, 4 H, $AsCH_2$), 2.51–2.72 (7, 4 H, SCH_2), 7.47–7.89 (m, 10 H, aromatics).

[*SP*-4-1-(*R,*R*)]-, [*SP*-4-1-(*R**,*S**)]-, [*SP*-4-2-(*R**,*R**)]-, and [*SP*-4-2-(*R**,*S**)]-Bis[2-(methylphenylphosphino)ethanethiolato]palladium(II) (*rac-trans*-, *meso-trans*-, *rac-cis*-, and *meso-cis*-[Pd(PS)$_2$]).** Tetrakis(acetonitrile)palladium(II) nitrate was generated in acetonitrile (100 mL) from $[PdCl_2(MeCN)_2]$ (0.71 g) and $AgNO_3$ (0.92 g) over 5 min in the dark. The AgCl was filtered off, and the filtrate was slowly added to a solution of (±)-PSH (1.0 g) and triethylamine (0.8 mL) in the same solvent (20 mL). After the reaction mixture was stirred for ca. 30 min, the solvent was removed, the yellow residue was dissolved in dichloromethane, and the resulting solution was washed with water and subsequently dried ($MgSO_4$). A rapid and total recrystallization of the crude product from a dichloromethane–methanol mixture gave pure [Pd(PS)$_2$], mp 193–200 °C, as a mixture of four diastereomers in 86% yield (1.1 g). Anal. Calcd for $C_{18}H_{24}P_2PdS_2$: C, 45.7; H, 5.1. Found: C, 46.0; H, 5.1. ^{1}H NMR ($CDCl_3$): δ 1.19 (d, 1.56 H, J_{PH} = 8.8 Hz, PMe), 1.71 (d, 0.78 H, J_{PH} = 8.4 Hz, PMe), 1.84 (t, 2.34 H, J_{PH} = 6.3 Hz, PMe), 1.87 (t, 2.34 H, J_{PH} = 6.3 Hz, PMe), 2.13–2.97 (m, 8 H, CH_2CH_2), 7.40–7.92 (m, 10 H, aromatics). The ^{1}H NMR spectrum of the solution was unaltered after 48 h.

[*SP*-4-2-(*R,*R**)]-(±)-Bis[2-(methylphenylphosphino)ethanethiolato]palladium(II) (*rac-cis*-[Pd(PS)$_2$]).** The mixture from above (1 g) was stirred in methanol (50 mL) for 15 min at room temperature. The undissolved material was filtered off and rapidly recrystallized from a dichloromethane–methanol mixture. After 4 h, the pure racemic-cis diastereomer was isolated in 16% yield as pale yellow needles, mp 229–230 °C. Anal. Calcd for $C_{18}H_{24}P_2PdS_2$: C, 45.7; H, 5.1. Found: C, 45.8; H, 5.1. ^{1}H NMR ($CDCl_3$): δ 1.19 (d, 6 H, J_{PH} = 8.8 Hz, PMe), 2.13–2.97 (m, 8 H, CH_2CH_2), 7.4–7.6 (m, 10 H, aromatics). The ^{1}H NMR spectrum of this solution after 48 h was identical with that of the initial product before fractional crystallization.

[*SP*-4-1-(*R,*R**)]-(±)-Bis[2-(methylphenylphosphino)ethanethiolato]palladium(II) (*rac-trans*-[Pd(PS)$_2$]).** The methanol extract from the above was concentrated on the steam bath. After ca. 2 h, it yielded 24% of the pure racemic-trans diastereomer as yellow needles, mp 193–195 °C. Anal. Calcd for $C_{18}H_{24}P_2PdS_2$: C, 45.7; H, 5.1. Found: C, 45.8; H, 5.1. ^{1}H NMR ($CDCl_3$): δ 1.84 (t, 6 H, J_{PH} = 6.3 Hz, PMe), 2.13–2.97 (m, 8 H, CH_2CH_2), 7.40–7.92 (7, 10 H, aromatics). The ^{1}H NMR spectrum of the solution after 48 h was identical with that of the initial mixture before recrystallization.

[*SP*-4-1-[*R*-(*R,*R**)]]-(+)-Bis[2-(methylphenylarsino)ethanethiolato]palladium(II) ((+)-*trans*-[Pd(AsS)$_2$]).** A solution of (*S*)-AsSH (1.0 g) in methanol (10 mL) containing 1 M NaOH (5 mL) was treated with a solution of $Li_2[PdCl_4]$ from $PdCl_2$ (0.4 g) and LiCl (0.4 g)] in the same solvent (30 mL). After 30 min, the orange precipitate was filtered off and washed with water, aqueous methanol, and diethyl ether. The crude product was then dissolved in ethanol (30 mL), and the solution was allowed to cool slowly, giving the deep yellow needles of the pure (+)-trans diasteromer in 85% yield; mp 204–206 °C, $[\alpha]_D$ +323° (*c* 1.0,

(17) Kerr, P. G.; Leung, P. H.; Wild, S. B., to be submitted for publication.

CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}As_2PdS_2$: C, 38.6; H, 4.3. Found: C, 38.5; H, 4.3. ^1H NMR (CD_2Cl_2, -78 °C): δ 1.26 (s, 6 H, AsMe), 1.90-2.88 (m, 8 H, CH_2CH_2), 7.01-7.47 (m, 10 H, aromatics). ^1H NMR (CD_2Cl_2, 25 °C): δ 1.26 (s, 2.3 H, AsMe), 1.80 (s, 3.7 H, AsMe), 1.93-2.91 (m, 8 H, CH_2CH_2), 7.01-7.80 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$): δ 1.27 (s, 1.2 H, AsMe), 1.80 (s, 4.8 H, AsMe), 2.30-2.89 (m, 4 H, CH_2CH_2), 7.37-7.80 (m, 10 H, aromatics). ^1H NMR (benzene-d_6): δ 1.37 (s, 6 H, AsMe), 1.93-2.91 (m, 8 H, CH_2CH_2), 7.01-7.80 (m, 10 H, aromatics). ^1H NMR (toluene-d_8): δ 1.38 (s, 6 H, AsMe), 2.09-2.94 (m, 8 H, CH_2CH_2), 7.04-7.73 (m, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5, 100 °C): δ 1.37 (s, 2.0 H, AsMe), 1.83 (s, 4.0 H, AsMe), 2.40-2.96 (m, 8 H, CH_2CH_2), 7.38-8.17 (m, 10 H, aromatics).

[*SP*-4-1-(*R,*S**)]-Bis[2-(methylphenylarsino)ethanethiolato]palladium(II) (*meso-trans*-[Pd(AsS)$_2$]).** This compound was isolated in 44% yield as orange prisms, mp 171-173 °C, with use of (±)-AsSH as ligand. Anal. Calcd for $C_{18}H_{24}As_2PdS_2$: C, 38.6; H, 4.3. Found: C, 38.7; H, 4.4. ^1H NMR (CD_2Cl_2, -78 °C): δ 1.86 (s, 6 H, AsMe), 2.32-2.87 (m, 8 H, CH_2CH_2), 7.30-7.87 (m, 10 H, aromatics). ^1H NMR (CD_2Cl_2, 25 °C): δ 1.26 (s, 1.71 H, AsMe), 1.73 (s, 0.87 H, AsMe), 1.80 (s, 1.71 H, AsMe), 1.86 (s, 1.71 H, AsMe), 2.32-2.87 (m, 8 H, $AsCH_2CH_2$), 7.30-7.87 (m, 10, aromatics). ^1H NMR (benzene-d_6): δ 1.374 (s, 3 H, AsMe), 1.378 (s, 3 H, AsMe), 1.93-2.91 (m, 8 H, $AsCH_2CH_2$), 7.01-7.80 (m, 10 Hz, aromatics). ^1H NMR ($CDCl_3$): δ 1.27 (s, 0.6 H, AsMe), 1.71 (s, 0.3 H, AsMe), 1.80 (s, 2.55 H, AsMe), 1.82 (s, 2.55 H, AsMe), 2.30-2.94 (m, 4 H, CH_2CH_2), 7.37-7.83 (m, 10 H, aromatics).

[*SP*-4-1-(*R,*R**)]-Bis[2-(methylphenylphosphino)ethanethiolato]palladium(II) (*rac-cis*-[Pt(PS)$_2$]).** A solution of K_2PtCl_4 (1.13 g) in water (15 mL) was slowly added to a solution of (±)-PSH (1.0 g) in ethanol (20 mL) containing 1 M NaOH (5 mL). The reaction mixture was stirred for 30 min, whereupon the pale yellow precipitate was filtered off and recrystallized from hot ethanol. The pure racemic-cis diastereomer was thus isolated as pale yellow needles in 46% yield (0.7 g); mp 248-252 °C. Anal. Calcd for $C_{18}H_{24}P_2PtS_2$: C, 3.5; H, 4.3. Found: C, 38.7; H, 4.4. ^1H NMR ($CDCl_3$): δ 1.30 (s, 6 H, J_{PH} = 9.8 Hz, $^3J_{PtH}$ = 29.4 Hz, PMe), 2.07-2.34 (m, 8 H, CH_2CH_2), 7.35-7.56 (m, 10 H, aromatics).

The following compounds were prepared similarly. **[*SP*-4-2-[*R*-(*R**,*R**)]]-(+)-Bis[2-(methylphenylarsino)ethanethiolato]platinum(II) ((+)-*cis*-[Pt(AsS)$_2$]):** pale yellow needles, mp 267-269 °C, 94% yield, $[\alpha]_D$ +368° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}AsPtS_2$: C, 33.3; H, 3.7. Found: C, 33.4; H, 3.9. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 2.20-2.60 (m, 8 H, CH_2CH_2), 6.73-6.59 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$, after 18 h): δ 1.35 (s, 5 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 1.87 (s, 1 H, $^3J_{PtH}$ = 20.0 Hz, AsMe), 2.20-2.62 (m, 8 H, CH_2CH_2), 6.73-6.59 (m, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5): δ 1.69 (s, 6 H, $^3J_{PtH}$ = 17.2 Hz, AsMe), 2.54-2.93 (m, 8 H, CH_2CH_2), 7.59-8.30 (7, 10 H, aromatics). ^1H NMR (nitrobenzene-d_5, 100 °C): δ 1.69 (s, 5 H, $^3J_{PtH}$ = 17.2 Hz, AsMe), 2.05 (s, 1 H, $^3J_{PtH}$ = 20.5 Hz, AsMe), 2.53-2.87 (m, 8 H, CH_2CH_2), 7.54-8.30 (m, 10 H, aromatics). **(-)-*cis*-[Pt(AsS)$_2$]:** $[\alpha]_D$ -367° (*c* 1.0, CH_2Cl_2). **[*SP*-4-2-(*R**,*R**)]-(±)-Bis[2-(methylphenylarsino)ethanethiolato]platinum(II) ((±)-*cis*-[Pt(AsS)$_2$]):** pale yellow needles, mp 217-222 °C, 85% yield. Anal. Calcd for $C_{18}H_{24}As_2PtS_2$: C, 33.3; H, 3.7. Found: C, 33.1; H, 3.7. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 2.20-2.65 (m, 8 H, CH_2CH_2), 6.37-6.59 (m, 10 H, aromatics). ^1H NMR ($CDCl_3$, after 18 h): δ 1.35 (s, 3.6 H, $^3J_{PtH}$ = 17.3 Hz, AsMe), 1.82 (s, 1.4 H, $^3J_{PtH}$ = 18.0 Hz, AsMe), 1.87 (s, 0.5 H, $^3J_{PtH}$ = 20.0 Hz, AsMe), 1.89 (s, 0.5 H, $^3J_{PtH}$ = 20.2 Hz, AsMe), 2.20-2.68 (m, 8 H, CH_2CH_2), 7.10-7.85 (m, 10 H, aromatics).

Note Added in Proof. Ligand (±)-PSH has now been resolved by the method of metal complexation into its optical antipodes: use of the optically pure forms of the tertiary phosphine has validated structural assignments of diastereomers made on the basis of comparisons of chemical shift data between analogous phosphine and arsine complexes.

Registry No. (±)-PSH, 102782-08-1; *rac-trans*-[Ni(PS)$_2$], 102782-02-5; (+)-*trans*-[Ni(AsS)$_2$], 102782-03-6; *meso-trans*-[Ni(AsS)$_2$], 102850-01-1; *rac-trans*-[Pd(PS)$_2$], 102850-02-2; *meso-trans*-[Pd(PS)$_2$], 102782-04-7; *rac-cis*-[Pd(PS)$_2$], 102850-04-4; *meso-trans*-[Ni(PS)$_2$], 102850-05-5; *rac-trans*-[Ni(AsS)$_2$], 102850-06-6; (+)-*trans*-[Pd(AsS)$_2$], 102782-05-8; *meso-trans*-[Pd(AsS)$_2$], 102916-56-3; *rac-cis*-[Pt(PS)$_2$], 102782-06-9; (+)-*cis*-[Pt(AsS)$_2$], 102782-07-0; *rac-cis*-[Pt(AsS)$_2$], 102850-07-7; (-)-*trans*-[Ni(AsS)$_2$], 102850-03-3; *meso-cis*-[Pd(PS)$_2$], 102850-13-5; (-)-*cis*-[Pt(AsS)$_2$], 102850-12-4; *rac-cis*-[Pd(AsS)$_2$], 102850-10-2; *meso-cis*-[Pd(AsS)$_2$], 102850-11-3; *rac-trans*-[Pd(AsS)$_2$], 102916-58-5; (+)-*cis*-[Pd(AsS)$_2$], 102916-57-4; *meso-cis*-[Pt(PS)$_2$], 102850-09-9; *meso-cis*-[Pt(AsS)$_2$], 102850-15-7; *rac-trans*-[Pt(AsS)$_2$], 102916-49-4; *meso-trans*-[Pt(AsS)$_2$], 102850-14-6; (+)-*trans*-[Pt(AsS)$_2$], 102850-08-8; Na[PMePh], 55640-97-6; [$PdCl_2$(MeCN)$_2$], 14592-56-4; $Li_2[PdCl_4]$, 15525-45-8; $K_2[PtCl_4]$, 10025-99-7; ethylene sulfide, 420-12-2.

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Syntheses and Spectral Properties of Tropocoronands, a New Class of Versatile Metal-Complexing Macrocycles Derived from Aminotropone Imines

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The synthesis and spectral properties of tropocoronands, TC-*n*,*n*′, a new class of metal-complexing macrocycles derived from two aminotropone imine moieties bridged by two polymethylene linker chains (*n*,*n*′ = 2,2; 3,3; 4,4; 5,5; 6,6), two ether linker chains (*n*,*n*′ = 2-O-2,2-O-2), or two thioether linker chains (*n*,*n*′ = 2-S-2,2-S-2) are described. The tropocoronands were prepared by linking two tropone rings (Tp) through the reaction of 2-(tosyloxy)- or 2-chlorotropone with α,ω-diamino alkanes, ethers, or thioethers; the dimeric 2-aminotropone was then converted to dimeric 2-alkoxytropone imine and reacted with a second molecule of the α,ω-diamino linker to yield TC-*n*,*n*′. The condensation of Tp substituted at position 2 by $-NH(CH_2)_4NH_2$ with the aminotropone imine substituted by $=N(CH_2)_4NH_2$ and $-NH(CH_2)_4NH_2$ yielded TC-*n*,*n*′,*n*″ comprised of three aminotropone imine moieties joined by $-(CH_2)_4-$ linker chains. TC-*n*,*n*′ readily forms a complex with first-row transition-metal ions. Spectral data (^1H NMR, ^{13}C NMR, UV-vis) and single-crystal X-ray diffraction studies of the nickel(II) complexes reveal an interesting transition from nearly planar (diamagnetic) to nearly tetrahedral (paramagnetic) coordination geometry as the length of the linker chain is increased. The planar diamagnetic complexes (*n*,*n*′ = 3,3; 4,4) exhibit NMR resonances in the normal range while signals of tetrahedral paramagnetic complexes (*n*,*n*′ = 5,5; 6,6; 2-O-2,2-O-2) are spread out over field widths of 400 and 2000 ppm, respectively, for ^1H and ^{13}C.

Since their appearance more than two decades ago, nitrogen-containing macrocyclic ligands (coronands[1]) have attracted widespread interest.[2] Their metal-complexing abilities have been used extensively in coordination chemistry to convey unusual redox, spectroscopic, or reactivity properties onto transition-metal ions[3]

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