

magnetic field) gives the g_{\parallel} component and the intensities of the g_{\perp} component are lessened to one-half. Therefore, the averaged z-axis of Cu(Zincon) molecules is situated parallel to the film plane: that is, Cu(Zincon) molecule is inserted vertically into the bilayer. The number of the negative charge in Cu(Zincon) is only one, in contrast to the six negative charges in Cu(Tiron)₂. This structural difference might be the cause of the different arrangement of these Cu(II) chelates in the bilayer membrane.

Cast multilayer films of double-chain, ammonium amphiphiles are similarly useful as matrices. A mixed cast film containing a covalently bound Cu(II) chelate gave also anisotropic ESR spectra.⁵ Thus, magnetically anisotropic thin films are obtainable from Cu(II) chelates that are either covalently or noncovalently bound to multilayer matrices. We are looking at further examples to establish how general this phenomenon might be.

Implications of the present results are as follows: (1) Macroscopic orientations of electron spins can be achieved by using anionic Cu(II) chelates embedded into cast films of ammonium bilayers. (2) Doping with the Cu(II) chelates is a very good means to probe the macroscopic and microscopic orders of multilayered cast films. The ESR technique is more flexible and convenient than the X-ray diffraction method we used previously.⁴ (3) Conversely, the mode of binding of metal chelates at the bilayer surface is readily inferred from ESR spectra. It does correlate with the molecular structure of bound chelates. (4) ESR spectroscopy of the cast film is a new, powerful methodology for studying the electronic structure of metal complexes. The magnetic anisotropy of metal complexes has been investigated by doping of single crystals⁷ and liquid crystals.⁸ These techniques possess, however, serious limitations such as the structural matching in the former and limited orientations in the latter. The present method is superior in both aspects.

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Aza- and Oxaphosphands, a New Class of Hard/Soft Binucleating Phosphine Macrocycles

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In recent years considerable effort has been devoted to the design and synthesis of binucleating macrocyclic ligands capable of binding two metals in close proximity.¹ Various bimetallic complexes have been synthesized by using ligands that contain two chelating subunits, such as aza, thia, phospho,² Schiff base,³

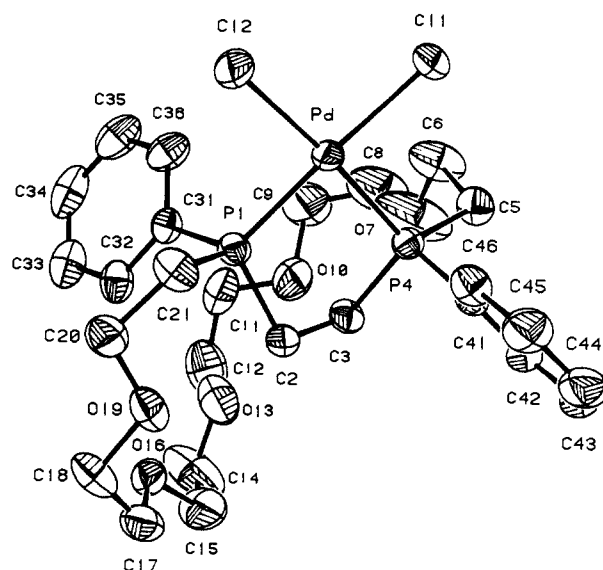
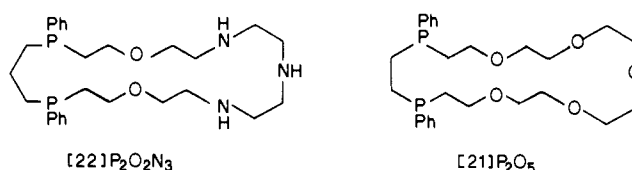


Figure 1. Structure of *anti*-(P₂PdCl₂O₅) showing the 40% probability thermal ellipsoids and atom labeling scheme and omitting hydrogen atoms. Selected interatomic distances (Å) and angles (deg) are as follows: Pd-P1 2.237 (1); Pd-P4 2.232 (1); Pd-C11 2.352 (1); Pd-C12 2.357 (2); P1-C2 1.824 (5); C2-C3 1.535 (7); C3-P4 1.825 (5); P4-Pd-C12 175.12 (5); C11-Pd-C12 93.62 (5); Pd-P1-C2 108.3 (2); P1-C2-C3 108.3 (3); C2-C3-P4 107.2 (3); C3-P4-Pd 107.5 (2). The deviations for P1 and P4 from the PdCl₂ plane are -0.11 and +0.10 Å, respectively.

or tetrapyrrole⁴ macrocycles or compartmentalized ligands.⁵ Previous studies in our laboratory have focused on the chemistry of dicopper(I), dicopper(II), and dirhodium(I) tropocoronand complexes⁶ and the coordination properties of homobinucleating hexaamine macrocycles.⁷ We have now developed a convenient, practical synthesis for two new, heterobinucleating azaphospha and oxaphospha macrocycles, [22]P₂O₂N₃ and [21]P₂O₅, re-



spectively, designated as "phosphands".⁸ Here we report details of the ligand syntheses, the high-yield separation of ligand diastereoisomers, the preparation and X-ray structural characterization of metal complexes *anti*-(P₂PdCl₂O₅) and *rac,anti*-(P₂Ni(NCS)₂[H₂N₃](NCS)₂), and the optical resolution of the latter by the method of Pasteur.⁹

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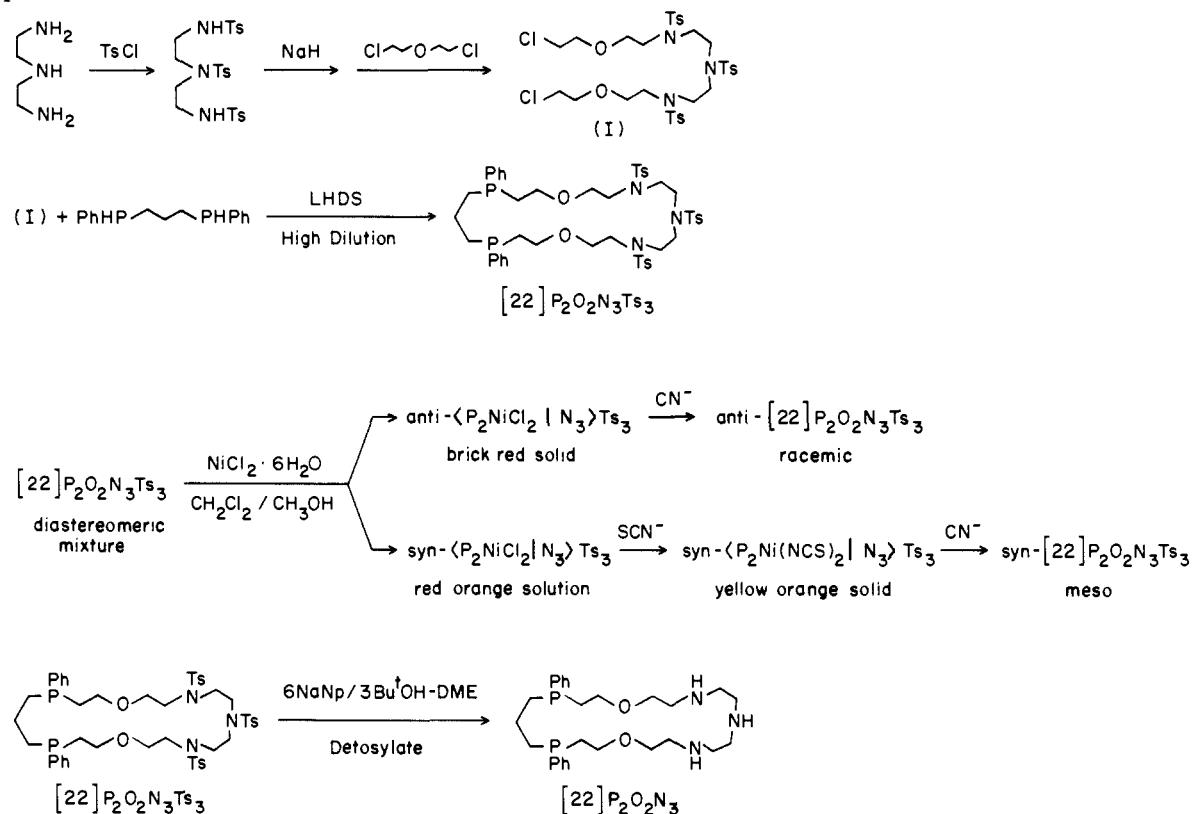
(8) Nomenclature: The phosphine coronands presented here are assigned the name phosphand, modified to azaphosphand and oxaphosphand upon incorporation of metal-binding heteroatoms, N or O, within the macrocycle. Metal-macrocycle complexes are designated as follows: (A_nML₂[L'_mM'_m]), where the angular brackets denote the main ring of the macrocycle; (n, m, ...) denote the number of potentially coordinating atoms (A_n, B_m, ...) placed at the poles of the phosphand cavity along with the particular metal(s) (M, M', ...) and auxiliary ligands (L_x, L'_y, ...); and a single vertical line illustrates that no bridging ligand is present. Two parallel vertical lines flanking a substrate (S), i.e., (|S|), are used to denote bimetallic systems which possess bridging ligands.

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Scheme I



The synthesis of the azaphosphand $[22]P_2O_2N_3$ was accomplished as shown in Scheme I. Reaction of tris(*p*-tolylsulfonyl)diethylenetriamine¹⁰ with a 15-fold excess of bis(2-chloroethyl) ether in the presence of NaH afforded the dichloride I¹¹ in 75% yield. The macrocycle $[22]P_2O_2N_3Ts_3$ was obtained in 68% yield by the high-dilution condensation of I with 1,3-bis(phenylphosphino)propane using lithium hexamethyldisilazide (LHDS) in THF solution. Additionally, we prepared the oxaphosphand $[21]P_2O_5$ ¹¹ from 1,2-bis(phenylphosphino)ethane and hexaethylene glycol ditosylate under similar conditions.

Both macrocycles, $[22]P_2O_2N_3Ts_3$ and $[21]P_2O_5$, contain two chiral phosphorus centers and both can and do exist as meso (*syn*) and racemic (*anti*) diastereoisomers with distinguishable ³¹P NMR spectra.¹¹ The *anti*- and *syn*- $[22]P_2O_2N_3Ts_3$ diastereoisomers were separated, as shown in Scheme I. Addition of $NiCl_2 \cdot 6H_2O$ to an isomeric ligand mixture in 4:1 CH_3OH/CH_2Cl_2 led immediately to precipitation of pure *anti*- $\langle P_2NiCl_2 | N_3 \rangle Ts_3$ as brick-red microcrystals.¹¹ The air-stable *anti*- $[22]P_2O_2N_3Ts_3$ ligand¹¹ was quantitatively obtained following decomplexation of the nickel complex by aqueous potassium cyanide. The more soluble *syn* isomer remaining in the reaction mixture was isolated following metathesis with thiocyanate to precipitate *syn*- $\langle P_2Ni(NCS)_2 | N_3 \rangle Ts_3$.¹¹ The air-sensitive free ligand¹¹ was obtained by cyanolysis under nitrogen in methylene chloride. The two $[22]P_2O_2N_3Ts_3$ diastereoisomers could be equilibrated to an equimolar mixture upon fusion of either *syn* or *anti* form, and after several cycles of thermal isomerization followed by diastereomeric separation the original mixture could be converted largely into either the *rac* or *meso* diastereoisomer. Detosylation of *syn*- or *anti*- $[22]P_2O_2N_3Ts_3$ was achieved without isomerization by addition of 6 equiv of sodium naphthalenide in 1,2-dimethoxyethane (DME)¹² in the presence of 3 equiv of *tert*-butyl alcohol at $-45^\circ C$.

Complexation between $[21]P_2O_5$ and $[Pd(COD)Cl_2]$ in acetone/dichloromethane solution afforded crystals¹³ of *anti*- $\langle P_2PdCl_2 | O_5 \rangle$, the molecular structure of which is shown in Figure 1. Reaction between $NiCl_2 \cdot 6H_2O$ and *anti*- $[22]P_2O_2N_3$, followed by addition of HBf_4 -etherate, gave *anti*- $\langle P_2NiCl_2 | H_2N_3 \rangle (BF_4)_2$. Metathesis of this latter complex with an excess of NaSCN resulted in the formation of the racemic diastereoisomer, *anti*- $\langle P_2Ni(NCS)_2 | H_2N_3 \rangle (NCS)_2$. Recrystallization of this compound from methanol/acetonitrile gave a racemic mixture of optically active crystals, and an X-ray structure determination was performed for one optically pure enantiomer.¹⁴ Circular dichroism studies of individual crystals confirmed the occurrence of two optical isomers, and polarimetric measurements on CH_3CN/CH_3OH (1:1) solutions prepared from ~ 1 mg of single crystals revealed $[\alpha]_D^{25}$ to be $+15 \pm 2^\circ$ and $-18 \pm 2^\circ$ for the two enantiomers.

A subsequent paper will demonstrate that two metals may be incorporated within the azaphosphands to create novel Pt-Cu bimetallic species, specifically *anti*- and *syn*- $\langle P_2PtMe_2 | LCuN_3 \rangle (BPh_4)$, where $L = CO$ or $CNCH_3$.¹⁵

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Supplementary Material Available: Tables of analytical and/or spectroscopic data for all compounds and atomic positional and thermal parameters for *anti*- $\langle P_2PdCl_2 | O_5 \rangle$ (4 pages). Ordering information is given on any current masthead page.

(13) Crystal data for $C_{26}H_{38}PdCl_2P_2O_5$; M_r 669.84, monoclinic, $P2_1/c$, $a = 10.503$ (2) Å, $b = 14.472$ (2) Å, $c = 19.368$ (2) Å, $\beta = 93.00$ (1)°, $V = 2939.8$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.514$ g cm⁻³, $\rho_{\text{obsd}} = 1.50$ (1) g cm⁻³. For 3304 unique observed $\{F_o \geq 4\sigma(F_o)\}$ reflections measured at 19.5 °C by diffractometer, the structure was solved and refined to a current value for the discrepancy indices, $R_1 = 0.0355$, $R_2 = 0.0485$. Anal. Calcd for $C_{26}H_{38}O_5P_2PdCl_2$: C, 46.62; H, 5.72; Cl, 10.59. Found: C, 46.83; H, 5.74; Cl, 10.57. ³¹P{¹H} NMR (28.70 MHz) δ +72.3.

(14) Crystal data for $C_{31}H_{44}N_7NiO_2P_2S_4$; $M_r = 767.59$, orthorhombic, $P2_12_12_1$, $a = 12.345$ (2) Å, $b = 12.830$ (1) Å, $c = 24.224$ (3) Å, $V = 3836.8$ Å³, $Z = 4$. For 1784 unique observed $\{F_o \geq 4\sigma(F_o)\}$ reflections measured at 24 °C by diffractometer, the structure was solved and refined to a value for discrepancy index $R_1 = 0.053$. An enantiomorph check was carried out, but no difference in R_2 value was observed. Details will be reported elsewhere.

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(11) Analytical and/or NMR spectroscopic data are given in the supplementary material.

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