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Synthesis, Isomer Separation, and Metal Complexation Studies of Aza- and Oxaphosphands, a Class of Hard/Soft Dinucleating Phosphine Macrocycles

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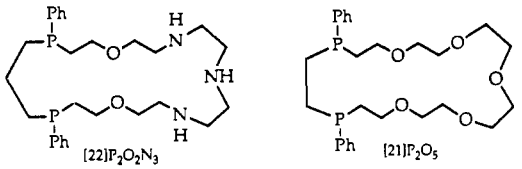
Two hybrid, asymmetric phosphine macrocycles, $[22]P_2O_2N_3$ and $[21]P_2O_5$, have been synthesized in high-dilution macrocyclization reactions. In THF solution, 1,3-bis(phenylphosphino)propane and 6,9,12-tris(*p*-tolylsulfonyl)-1,17-dichloro-3,15-dioxa-6,9,12-



triazaheptadecane react in the presence of lithium hexamethyldisilazide (LHDS) giving 16,20-diphenyl-4,7,10-tritosyl-1,13-dioxa-16,20-diphospha-4,7,10-triazacyclodocosane, $[22]P_2O_2N_3Ts_3$, in good yield (68%). Similarly, oxaphosphand $[21]P_2O_5$, 1,4-diphenyl-7,10,13,16,19-pentaoxa-1,4-diphosphacycloheneicosane, was prepared under high-dilution conditions from 1,2-bis(phenylphosphino)ethane and 1,19-ditosyl-1,4,7,10,13,16,18-heptaoxanonadecane. The two $[22]P_2O_2N_3Ts_3$ diastereoisomers, anti (racemic) and syn (meso), were separated through selective precipitation of their respective nickel complexes, *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ and *syn*-$\langle P_2Ni(NCS)_2|N_3\rangle Ts_3$, and subsequent cyanolysis to remove nickel. The oxaphosphand $[21]P_2O_5$ diastereoisomers, anti and syn, were separated as their nickel thiocyanate complexes, *anti*-$\langle P_2Ni(NCS)_2|O_5\rangle$ and *syn*-$\langle P_2Ni(NCS)_2|O_5\rangle$, by using preparative flash chromatographic techniques and subsequently demetalated with cyanide ion. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data established the isomeric purity of both racemic and meso forms of the macrocycles. The diastereomers *anti*- and *syn*-$[22]P_2O_2N_3Ts_3$ isomerize upon fusion to give an approximately equimolar isomeric mixture. Removal of the protecting tosyl groups was effected at −78 °C by sodium naphthalenide in glyme (DME) containing *tert*-butyl alcohol as a proton source to afford the azaphosphands $[22]P_2O_2N_3$. The ligands *anti*- and *syn*-$[22]P_2O_2N_3Ts_3$ and *anti*- and *syn*-$[21]P_2O_5$ form complexes with group 10 transition metals to yield species of the general formulas *anti*- and *syn*-$\langle P_2M(XY)|N_3\rangle Ts_3$ and *anti*- and *syn*-$\langle P_2M(XY)|O_5\rangle$. In no case does the protected amine portion of the macrocycle bind to transition-metal centers. The structure of *anti*-$\langle P_2PdCl_2|O_5\rangle$ was determined by single-crystal X-ray diffraction analysis. Resolution of *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ enantiomers was achieved by the method of Pasteur. From solutions of dissolved single crystals in 1:1 CH_3CN–CH_3OH the following specific rotations were found: $[\alpha]^{25}_D = +15 \pm 2°$; $[\alpha]^{25}_D = -18 \pm 2°$.

Introduction

We are interested in macrocyclic ligands capable of binding two metals independently with sufficient intervening space to bind and activate substrate molecules or to transfer reactive species from one metal coordination sphere to another.[1] Metal complexes of such dinucleating ligands could exhibit unique chemistry, reactivity, and selectivity compared to analogous mononuclear species as a result of cooperativity and may provide insight into bimetallic centers involved in chemical and biological catalysis.[2]

Reports of phosphine-functionalized crown ethers capable of holding hard Lewis acid cations adjacent to transition metals have appeared, and there are indications that such derivatized ethers will promote CO activation.[3] In particular, the ether component of polyether polyphosphinite ligands[4] and monophosphine ethers[3] were found to enhance nucleophilic attack of metal-bound car-

Table I. Crystallographic Data for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$[a,b]

	anti-$\langle P_2Ni(NCS)_2\|H_2N_3\rangle(NCS)_2$	*anti*-$\langle P_2PdCl_2\|O_5\rangle$
chem formula	$C_{31}H_{45}N_7O_2S_4P_2Ni$	$C_{26}H_{38}PdCl_2P_2O_5$
fw	796.7	669.84
space group	$P2_12_12_1$	$P2_1/c$
a, Å	12.345 (2)	10.503 (2)
b, Å	12.830 (1)	14.472 (2)
c, Å	24.224 (3)	19.368 (2)
α, deg	90	90
β, deg	90	93.00 (1)
γ, deg	90	90
V, Å^3	3836.8	2939.9
Z, Å^3	4	4
T, °C	23	19.5
λ, Å	0.71069	0.71069
ρ_{obsd}, g cm^{-3}		1.50 (1)
ρ_{calcd}, g cm^{-3}	1.379	1.513
μ, cm^{-1}	7.30	8.60
transm coeff	NA[f]	0.78–0.83
R_1[c,d]	0.053	0.0355
R_2[c,e]	0.075	0.0485

[a] From a least-squares fit to the setting angles of 22 reflections with $2\theta \geq 31°$. [b] For typical procedures, see ref 22. [c] F_o and $\sigma(F_o)$ were corrected for background, attenuation, and Lorentz and polarization effects of X-radiation as described in ref 22. [d] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [f] Not applied.

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bonyls by alkyllithium reagents. Monophosphine aza crown ethers[3,5] also form complexes in which intramolecular coordination occurs between a metal–acyl group and the crown ether held cation. Various macrocyclic ligands have been developed that provide the requisite subunits to form heterodinuclear complexes incorporating a soft, redox-active site and a hard, Lewis acid metal ion center.[6-10]

Our studies of dinucleating macrocyclic ligands have focused on the coordination properties of homodinucleating hexaamine macrocycles[11] and the chemistry of dicopper(I), dicopper(II), and dirhodium tropocoronand complexes.[12] The latter has led to novel regiospecific enantioselective organocuprate-catalyzed conjugate addition of Grignard reagents to 2-cyclohexenone.[13] We have now developed a convenient synthetic method for preparing two new classes of phosphorus-containing heterodinucleating macrocycles, designated azaphosphand and oxaphosphand, respectively, exemplified by specific molecules $[22]P_2O_2N_3$ and $[21]P_2O_5$.[14,15] These ligands were designed to form heteronuclear dimetallic complexes with sufficient flexibility such that adjacent metal centers can bind small molecule substrates. The main interest in these particular asymmetric ligands stems from their ability to assemble dimetallic complexes containing both "hard" and "soft" metal centers. To date, there is only one reported example of a phospha macrocycle capable of coordinating two transition-metal ions.[6h] Here we describe the synthesis of aza- and oxaphosphands, their reaction with group 10 metal ions to yield mononuclear complexes, and chemistry that enables ligand diastereoisomers to be separated.

Experimental Section

Materials. *N,N',N''*-Tris(*p*-tolylsulfonyl)diethylenetriamine[16] and hexamethylene glycol ditosylate[17] were prepared by literature methods. The phosphand precursors diethylenetriamine (Strem), 1,3-bis(phenylphosphino)propane (Strem; this material was contaminated with 5–10% of $PhP(CH_2)_3PPh$ and used without purification), 1,2-bis(phenylphosphino)ethane (Pressure), bis(2-chloroethyl) ether, and hexaethylene glycol (Aldrich) were purchased and used as received. Naphthalene (Baker), *p*-toluene sulfonyl chloride (Aldrich), lithium hexamethyldisilazide (LHDS) (1.0 M in THF solution; Aldrich), *t*-BuOK (Callery), NaH (80% solid dispersion in mineral oil) (Aldrich), $NiCl_2 \cdot 6H_2O$ (Fisher), NaSCN (Fisher), KCN (Mallinckrodt), *t*-BuOH (Aldrich), and DME (Aldrich) were obtained, as were all other reagents and solvents, from commercial sources. *p*-Toluenesulfonyl chloride was recrystallized from $CHCl_3$/petroleum ether as described in the literature and vacuum-dried overnight at 30 °C.[18] Naphthalene was recrystallized from hot methanol and vacuum-dried. NaH (in mineral oil) was washed with hexane before use. THF (tetrahydrofuran) and DME (1,2-dimethoxyethane) were obtained dry by distillation from sodium benzophenone ketyl under N_2; *t*-BuOH was dried by distillation from CaO under N_2 and stored over molecular sieves. The prepared *N,N',N''*-tris(*p*-tolylsulfonyl)diethylenetriamine was recrystallized from ethanol. The metal complex $[Pd(COD)Cl_2]$ (Strem) was used as received. The metal reactants $[Pt(NCPh)_2Cl_2]$,[19] $[Pt(COD)Cl_2]$,[20] [Pt(COD)ClMe],[21] and $[Pt(COD)Me_2]$[21] were prepared by literature procedures and recrystallized before use.

Physical Measurements. Infrared (IR) spectra were recorded as KBr pellets or on thin films in mineral oil with a Beckman Acculab 10 spectrophotometer or an IBM Instruments IR32 Fourier transform (4800–400 cm^{-1}) spectrometer. ^1H NMR spectra were recorded on Varian T-60, Bruker 250, or Varian XL-300 instruments by using the residual proton resonances of $CDCl_3$ (δ 7.24 vs TMS) or CD_2Cl_2 (δ 5.32 vs TMS) as well as other solvents as internal standards or by referencing with internal TMS. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX 90Q spectrometer at 36.20 and 22.50 MHz, respectively, or a Varian XL-300 instrument at 121.425 and 75.432 MHz, respectively. $^{31}P\{^1H\}$ NMR chemical shifts were referenced in parts per million relative to external 85% H_3PO_4. $^{13}C\{^1H\}$ NMR spectra were referenced to the

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(15) Nomenclature: The phosphine coronands described here are assigned the name phosphand, modified to azaphosphand and oxaphosphand upon incorporation of metal-binding heteroatoms, N or O, within the macrocycle. For the azaphosphand two generic formulas are used. The first, *anti-* or *syn*-$[22]P_2O_2N_3Ts_3$, identifies diastereoisomers of the ligand in its amine-protected form. The tosyl groups preclude the binding of metals to the nitrogen pole of the macrocycle. The other formula, *anti-* or *syn*-$[22]P_2O_2N_3$, indicates detosylated diastereomers capable of metal binding at both poles of the macrocycle. Metal–macrocycle complexes are designated as follows: $(A_nML_x|L'_yM'B_m)$, 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 that possess bridging ligands.

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chemical shifts of the deuteriohydrocarbon solvent used. Elemental analyses were carried out by Atlantic Microlab, Inc. (Atlanta, GA), and Spang Microanalytical Laboratory (Eagle Harbor, MI).

General Methods. Unless noted, all reactions were carried out under an atmosphere of dry nitrogen or argon with subsequent workup being performed aerobically. Air-sensitive liquids were handled in a Vacuum Atmospheres drybox maintained under a N_2 atmosphere. A Sage syringe pump (Model 355), employing 22-gauge needles, was used for high-dilution work.

X-ray Structural Work. All data were collected on an Enraf-Nonius CAD-4F diffractometer with monochromatized Mo Kα (λ = 0.710 73 Å) radiation and $\theta/2\theta$ scans, with the use of procedures typically employed in our laboratory.[22]

Azaphosphand and Oxaphosphand Syntheses. A. Macrocycle Precursors. Preparation of 6,9,12-Tris(*p*-tolylsulfonyl)-1,17-dichloro-3,15-dioxa-6,9,12-triazaheptadecane (I). A 250-mL, three-necked, round-bottomed flask equipped with a thermometer, a gas outlet tube connected to a bubbler, and a condenser fitted with a nitrogen inlet adapter, was charged with *N,N',N''*-tris(*p*-tolylsulfonyl)diethylenetriamine (17.0 g, 30.0 mmol), bis(2-chloroethyl) ether (100 mL, 853 mmol), and NaH (3.0 g of 80% solid dispersion in mineral oil, 100 mmol). The resulting mixture was stirred and allowed to warm to 70 °C in an oil bath for approximately 30 min until the evolution of hydrogen ceased. The gas outlet tube was removed and replaced by a rubber septum, and the resulting clear solution was heated to 120 °C for 6 h. Upon completion of the reaction, the mixture was cooled to room temperature; then the cloudy solution was filtered to remove the NaCl that had formed, thereby yielding a pale yellow solution. The reaction solution was then poured into 800 mL of hexane with stirring, and after being stirred for 30 min the cloudy solution was allowed to settle, whereupon two layers separated. The supernatant layer was decanted and combined with 2 × 200 mL quantities of subsequent hexane washings, concentrated, and distilled to retrieve any unreacted bis(2-chloroethyl) ether. The remaining viscous yellow solution was then heated to 100 °C under reduced pressure until no more bis(2-chloroethyl) ether was distilled from the product. The thick, yellow, oily residue was cooled to room temperature and dissolved in 200 mL of methanol. After the alcoholic solution was stirred for approximately 30 min and cooled to 0 °C, the solution turned cloudy and a cream-colored solid precipitated. The crude product, 6,9,12-tris(*p*-tolylsulfonyl)-1,17-dichloro-3,15-dioxa-6,9,12-triazaheptadecane (I) was collected by filtration, washed with hexane, and dried in vacuo. The methanolic filtrate was concentrated to near dryness and triturated with diethyl ether to give a second crop of I. Recrystallization of the material could be achieved by stirring the crude product in THF (50 mL) and filtering a light tan solid from the pale yellow saturated solution. The clear solution obtained was added to 400 mL of an ethanol–diethyl ether (3:1) solvent mixture and the combined solutions were cooled to −10 °C for 16 h. The fluffy white crystalline solid that deposited was collected by filtration, washed with diethyl ether and pentane, and dried in vacuo. Further quantities of product I could be obtained by taking the alcoholic solution to dryness and recrystallizing the residue from THF–ethanol–diethyl ether (1:6:2). Overall yield: 17.54 g (75%). MP: 88–89 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 7.27–7.35, 7.71–7.75 (m, 12 H, phenyl H); 3.60–3.69 (m, 8 H, CH_2O); 3.56 (t, 4 H, CH_2Cl); 3.32–3.40 (m, 12 H, CH_2N); 2.42, 2.45 (s, 9 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.23, 129.71, 129.79, 134.71, 135.92, 143.45, 143.62 (aromatic C); 69.88, 71.00 (C–O); 49.04, 49.22, 49.44 (C–N); 42.65 (C–Cl); 21.40 (CH_3). Anal. Calcd for $C_{33}H_{45}N_3S_3O_8Cl_2$: C, 50.89; H, 5.82; N, 5.40; Cl, 9.10. Found: C, 50.66; H, 5.82; N, 5.38; Cl, 9.15.

An alternative method that worked equally well involved the intermediate use of *t*-BuOK in place of NaH. In this procedure, the reaction between the base *t*-BuOK (11.72 g, 104 mmol) and *N,N',N''*-tris(*p*-tolylsulfonyl)diethylenetriamine (17.0 g, 30.0 mmol) was performed in 200 mL of anhydrous ethanol. The dipotassium salt prepared was then isolated as a white solid by removing the alcoholic solvents under reduced pressure. This salt was then heated with 150 mL of neat bis(2-chloroethyl) ether (183.0 g, 1.28 mmol) at 130 °C for 2 h. The KCl deposited from the reaction was filtered and the pale yellow ethereal solution worked up as previously described for the NaH procedure. Yield: 72%. The material obtained had ^{1}H and $^{13}C\{^1H\}$ NMR spectra identical with those of an authentic sample of I.

1,19-Bis(*p*-tolylsulfonyl)-1,4,7,10,13,16,19-heptaoxanonadecane (Hexaethylene Glycol Ditosylate) (II). This hexaethylene glycol was prepared by using a procedure similar to one described in the literature;[17] however, the modified synthesis used by us is outlined below for clarity.

A 200-mL round-bottomed flask was charged with hexaethylene glycol (25.0 g, 88.5 mmol) and 75 mL of pyridine and cooled to 0 °C in an ice bath. Purified, solid *p*-toluenesulfonyl chloride (35.5 g, 186 mmol) was added slowly over 10 min to the stirring solution without the reaction temperature exceeding 10 °C. The resulting yellowish mixture was kept stirring at 10 °C for 2 h and then at room temperature for 2 h more and was poured into an ice cold 3 N HCl (500 mL) solution to give white oil drops that were separated from the aqueous phase by careful decanting. The aqueous phase was then extracted with 2 × 100 mL of CH_2Cl_2, and the combined organic phases and oil drops were washed with 1 × 250 mL of 2 N HCl, 2 × 250 mL of saturated $NaHCO_3$, and 1 × 250 mL of NaCl solutions. The organic layer was dried with $MgSO_4$, filtered, concentrated to dryness, and vacuum-dried at 60 °C for 2 days to give 44.5 g (85% yield) of the hexaethylene glycol ditosylate as a colorless oil, which was shown to be pure by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies and used without further purification. Analytically pure samples were obtained by column chromatography using silica and 5% MeOH–CH_2Cl_2 as eluant. ^{1}H NMR ($CDCl_3$): δ 7.34, 7.80 (dd, 8 H, phenyl H); 4.16 (t, 2 H, CH_2–OTs); 3.68 (t, 2 H, O–*CH_2*–CH_2–OTs); 3.50–3.65 (m, 16 H, CH_2–O); 2.44 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.27, 129.33, 132.37, 144.28 (aromatic C); 69.85, 68.87, 67.90 (C–O); 20.98 (Me). Anal. Calcd for $C_{26}H_{38}O_{11}S_2$: C, 52.87; H, 6.48. Found: C, 52.91; H, 6.44.

B. Preparation of Diastereoisomer Mixtures of Aza- and Oxaphosphands. Synthesis of *anti*- and *syn*-16,20-Diphenyl-4,7,10-tritosyl-1,13-dioxa-16,20-diphospha-4,7,10-triazacyclodocosane, *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$. 1,3-Bis(phenylphosphino)propane (5.56 g, 20 mmol, 7% impurity) and the dichloride I (15.51 g, 19.91 mmol) were weighed into separate 100-mL volumetric flasks, which were filled to their marks with THF. The flasks were stoppered with rubber septa and sealed with electrical tape. A 1-L one-necked, round-bottomed flask containing a rubber septum was charged with 80 mL of lithium hexamethyldisilazide (LHDS) in THF (1.0 M, 80 mmol) and 700 mL of dry THF. The two stock solutions previously prepared (0.2 M, 100 mL, 20 mmol) were loaded into 50 mL disposable syringes, which were then inserted into the flask with the needle tips far apart and mounted on a syringe pump. At room temperature, the two reactants were added into the stirring solution at a rate of 20–25 drops/min (syringe pump reading: 15% × 1/100, equivalent to 0.12 mL/min) over a period of 7 h. The procedure was repeated under identical conditions. The resulting yellow solution was quenched with 20 drops of H_2O and concentrated with a rotary evaporator. The resulting yellow oil was then extracted with 200 mL of CH_2Cl_2 and 200 mL of 5 N NH_4Cl. The aqueous phase was separated and extracted with 100 mL of CH_2Cl_2, and the combined organic phases were washed with 200 mL of 5 N NH_4Cl and saturated NaCl solution, then dried over $MgSO_4$, filtered, and concentrated. The resulting oil contained 86% of the desired products, *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$, as judged by integration of the $^{31}P\{^1H\}$ NMR spectrum. This oil was then redissolved in 50 mL of CH_2Cl_2 and added dropwise to 750 mL of rapidly stirred pentane. The resulting cream-colored solid was filtered from the clear solution, and the solid was washed with more pentane. The original pentane solution and washings were combined and taken to dryness under reduced pressure to give a thick pale yellow oil (1.91 g), which contained a little (<5%) of the desired azaphosphand along with the impurity from the 1,3-bis(phenylphosphino)propane starting material. The cream-colored solid is a mixture of *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ diastereomers. It was shown by $^{31}P\{^1H\}$ NMR spectroscopy to be approximately 85% pure (syn:anti ~ 1:1) with the other 15% being higher macrocyclic oligomers. Final purification of the crude product was achieved by dissolving the impure tosylated macrocycle in a minimum volume of CH_2Cl_2 and slowly adding pentane to the solution until the cloud point was reached. At this point, the solution was allowed to settle for a few minutes until a clear yellow oil deposited from solution. The addition of more pentane to reach the cloud point again removed some of the yellow color (impurity) in the supernatant liquor. This procedure was performed a number of times until the solution over the yellow oil was colorless. In this manner, it was possible to obtain ≥98% pure [22]$P_2O_2N_3Ts_3$ (both isomers) in the colorless layer with the yellow oil containing almost all the more highly oligomeric macrocycles with a small percentage of the [1 + 1] macrocycles [22]$P_2O_2N_3Ts_3$. The yield of the *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ mixture was 13.9 g (72%). This product was then deemed to be of sufficient purity so as to be used as a starting material for the separation of the diastereoisomers (vide infra). On one occasion, the product was obtained as a fluffy crystalline solid, mp 63–70 °C. The anti and syn isomers are both stable to air in the solid state, but solutions of the latter are air-sensitive. IR (KBr): 3340 (m), 3040 (w), 2820–2940 (m), 1580 (w), 1470 (sh), 1450 (m), 1430 (m), 1335 (s, HSO_2), 1150 (s, $\nu_{S=O}$), 1105 (m, ν_{C-O-C}), 1090, 970–1010 (m), 930 (w), 810 (m), 740, 720, 700 (s), 650 (m), 530 (m) cm^{-1}. Mass spectrum (FD, M^+): m/z 965. ^{1}H NMR (CD_2Cl_2): δ 7.2–7.5, 7.5–7.8 (m, 22 H, phenyl H); 3.2–3.7 (m, 20 H, CH_2N, O); 2.42 (m, 9 H, CH_3); 1.25–1.50, 1.65–2.05 (m, 10 H, CH_2–P). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.432

(22) Silverman, L. D.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379–3383.

MHz): δ 126.98, 127.23, 129.53, 129.60, 135.33, 135.77, 135.83, 143.15, 143.28 (tosyl aromatic C); 128.05, 128.15, 128.35, 131.65, 131.79, 131.92, 137.96, 138.15, 138.33 (P-aromatic C); 69.50, 68.43, 68.19 (C-O); 49.72, 49.56, 49.30, 49.17, 49.05 (C-N); 29.08 (m, P-*C*-C-C-P); 27.98 (m, C-P); 22.31 (t, O-C-*C*-P, J_{PC} = 16 ± 3 Hz); 21.31 (t, C-*C*-C, $^2J_{PC}$ = 12 ± 3 Hz); 21.31, 21.25 (Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -29.28, -30.22. The ^{31}P NMR data indicate a mixture of syn and anti isomers. Molecular weight measurement (osmometry): calcd, 966; found, 1013.

Synthesis of *anti*- and *syn*-1,4-Diphenyl-1,4-diphospha-7,10,13,16,19-pentaoxacycloheneicosane, *anti*- and *syn*-[21]P_2O_5. Two 50-mL stock solutions containing 25 mmol of 1,2-bis(phenylphosphino)ethane and ditosylated hexaethylene glycol were prepared. A 1-L flask fitted with a rubber septum was evacuated and charged with THF (500 mL) and 100 mmol of lithium hexamethyldisilazide (100 mL of 1.0 M THF solution). The stock solutions were transferred to 50-mL syringes and added dropwise via syringe pump to the stirred solution under dinitrogen over a period of 12 h. Addition of water (2 mL) to quench the remaining base in this clear blood red solution resulted in a clear golden-yellow solution. Following the macrocyclization procedure, all manipulations were carried out in air. The THF solution containing the mixture of *anti*- and *syn*-[21]P_2O_5 (plus higher oligomers) was evaporated to dryness to give a thick yellow oil, which was redissolved in CH_2Cl_2 (200 mL). This organic solution was washed twice with saturated aqueous NH_4Cl (200 mL), dried with $MgSO_4$, filtered, and evaporated to give the oxaphosphand [21]P_2O_5 as an impure yellow oil. From integration of the $^{31}P\{^1H\}$ NMR spectrum, the resultant oil was estimated to contain approximately 64% of the desired oxaphosphand diastereomeric mixture. The oil was then triturated with 3 × 100 mL of pentane. The combined triturants were concentrated, triturated with 2 × 50 mL of pentane, and concentrated once again to give 6.03 g of *anti*- and *syn*-[21]P_2O_5 as a colorless oil. The product was shown to be pure by ^{31}P NMR spectroscopy and used without further purification (estimated at greater than 90% purity, anti:syn = 64:36; 49% yield). Small quantities of analytically pure samples were obtained either by low-temperature crystallization from pentane at 0 °C or by column chromatography on alumina (3% MeOH-CH_2Cl_2). ^1H NMR ($CDCl_3$, TMS): δ 7.20-7.35 (m, 20 H, phenyl H); 3.30-3.65 (m, 20 H, CH_2-O); 1.50-2.05 (m, 8 H, CH_2-P). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.432 MHz, TMS): δ 138.53, 138.43, 138.36, 138.24, 138.18, 132.32, 132.19, 132.15, 132.07, 132.01, 131.92, 128.64, 128.44, 128.40, 128.32, 128.26 (aromatic C); 71.08, 70.73, 70.60, 70.51 (C-O); 69.07, 69.02, 68.92, 68.87, 68.79, 68.73 (O-*C*-C-P); 28.86 (O-C-*C*-P, dd, J_{PC} = 7.0, 5.5 Hz); 27.73 (O-C-*C*-P, t, J_{PC} = 8.2 Hz); 24.13 (*C*-P, s, J_{PC} = 0 Hz); 23.25 (C'-P, d, J_{PC} = 4.7 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -22.45, -23.83 (anti:syn = 64:36). MS (FD, M^+): *m/z* 492. Anal. Calcd for $C_{26}H_{38}O_5P_2$: C, 63.40; H, 7.78. Found: C, 63.64; H, 7.73. The diastereomeric separation of *anti*- and *syn*-[21]P_2O_5 on a preparative scale is outlined below.

Diastereomeric Separation of *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ via Nickel Complexation. A solution of $NiCl_2 \cdot 6H_2O$ (3.0 g, 12.6 mmol) dissolved in 50 mL of methanol was added dropwise to a solution of [22]$P_2O_2N_3Ts_3$ (anti and syn isomers) (10.25 g, 10.61 mmol) in 50 mL of CH_2Cl_2 and the resultant solution mixture stirred at room temperature for 30 min. During this time, another 200 mL of methanol was added to the dark red-orange solution so as to precipitate selectively from solution the compound *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3. After an additional 15 min of stirring, the precipitate was allowed to settle and the brick red microcrystalline solid was then collected by filtration, washed with methanol and diethyl ether, and dried in vacuo; yield 4.77 g, 41%. As a check on the effectiveness of the separation process, methanol (50 mL) was added to the clear orange-red filtrate to ensure that all the *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3 had been deposited from solution. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ +4.28 (v br). Anal. Calcd for $C_{48}H_{61}Cl_2N_3NiO_8P_2S_3$: C, 52.61; H, 5.61; N, 3.83. Found: C, 52.78; H, 5.61; N, 3.79.

The orange filtrate, which only contained *syn*-⟨$P_2NiCl_2|N_3$⟩Ts_3, changed to a murky yellow color upon addition of KSCN (2.20 g, 22.6 mmol) to form *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3, which partially precipitated from solution. This complex was prepared because it could be more easily purified than the chloride analogue and is diamagnetic, facilitating study by NMR spectroscopy. The methanolic mixture was taken to dryness at 40 °C under reduced pressure and the orange-yellow solid dried thoroughly in vacuo for 12 h. The solid was then washed with 125 mL of CH_2Cl_2 to extract *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3, and the other nickel(II) salts were collected by filtration and discarded. The orange-yellow clear filtrate was taken to dryness, and the solid obtained was washed with diethyl ether and collected by filtration (yield 6.24 g). The purity of the complex was investigated at this point by TLC using silica plates and 5% CH_3OH-CH_2Cl_2 as eluant. The dirty yellow solid was found to be composed of one major, colored component, *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3, together with two spots visible under UV light. The solid was then stirred in 350 mL of diethyl ether-ethanol (2:1) to remove the unwanted products, possibly other ligands and oxidized azaphosphand. The diethyl ether-ethanol solution turned yellow after being stirred at room temperature for 16 h. The remaining yellow solid was collected by filtration, rinsed with diethyl ether, and dried in vacuo (yield 3.52 g, 30%). TLC analysis of this material on silica (5% MeOH-CH_2Cl_2) showed mainly one colored band corresponding to *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 and only traces of non-metalated components barely visible under UV light. Analysis of the ethanolic filtrate by TLC revealed only organic materials and a colored component that did not migrate from the origin. The *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 product could be obtained as red-orange needles by crystallization from dichloromethane-pentane, or the yellow solid could be used directly in the demetalation procedure to obtain free *syn*-[22]$P_2O_2N_3Ts_3$ (vide infra). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ +7.14. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.17 (P-C-*C*-C-P, t); 21.65, 21.69 (tosyl CH_3); 28.50 (P-*C*-C-C-P or P-*C*-C-O, t); 28.67 (P-*C*-C-C-P or P-*C*-C-O, t); 50.07, 50.12, 50.56 (C-N); 66.62, 69.94 (C-O); 127.55, 127.93, 128.26, 128.56, 129.36, 129.52, 129.61, 129.67, 130.04, 130.28, 130.39, 132.23, 132.56, 135.22, 135.87, 144.30, 144.78 (aromatic C). Anal. Calcd for $C_{50}H_{61}N_5NiO_8P_2S_5$: C, 52.63; H, 5.39; N, 6.14. Found: C, 52.64; H, 5.41; N, 6.06.

Note: In one particular case, *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3 could be metathesized to *anti*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 with NaSCN in methanol solution. Anal. Calcd for $C_{50}H_{61}N_5NiO_8P_2S_5$: C, 52.63; H, 5.39; N, 6.14. Found: C, 52.64; H, 5.41; N, 6.06.

Separation of *anti*- and *syn*-[21]P_2O_5 Diastereoisomers via Nickel Complexation. A quantity of impure *anti*- and *syn*-[21]P_2O_5 (25 mmol, assuming quantitative conversion) obtained directly from the macrocyclization reaction was dissolved in 20 mL of CH_2Cl_2. To this oxaphosphand mixture was added dropwise $NiCl_2 \cdot 6H_2O$ (5.94 g, 25.0 mmol) dissolved in 20 mL of methanol. Addition of the nickel salt was accompanied by a rapid color change from pale yellow to a deep red-orange. After the reaction was stirred for 5 min, the solution was evaporated to dryness under reduced pressure, redissolved in a small amount of CH_2Cl_2 (25 mL), and filtered to remove any unreacted nickel(II) salts and the CH_2Cl_2 removed in vacuo. The dark yellow-brown, thick oily product was dissolved in 50 mL of methanol, and solid KSCN (3.26 g, 33.5 mmol) was added to the stirred solution. Almost immediately, the clear, dark orange-brown solution became cloudy and a white precipitate formed. After the reaction mixture was stirred for 5 min, it was evaporated to dryness, dissolved in CH_2Cl_2, filtered, and taken to dryness under reduced pressure. The orange-brown material, a mixture of *anti*- and *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩, was dissolved in a minimum of CH_2Cl_2 and separated by flash chromatography[23] through a silica gel column (200-300 mesh; 7 cm × 22.5 cm) with a 20:6:1 CH_2Cl_2-diethyl ether-methanol mixture. The eluted materials were collected in 12-mL aliquots, and the fractions were examined by TLC to determine their content. The R_f values for the *anti*- and *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩ diastereomers are 0.61 and 0.32, respectively, as determined on silica gel plates by using the same eluant as for the column. The fractions corresponding to each diastereomeric isomer were combined and evaporated to dryness, yielding *anti*-⟨$P_2Ni(NCS)_2|O_5$⟩ (2.90 g, 4.35 mmol) and *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩ (1.55 g, 2.32 mmol). The overall yield following macrocyclization and diastereomeric purification steps was 26.7%. The properties of *anti*-⟨$P_2Ni(NCS)_2|O_5$⟩ are as follows: mp 193-195 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.89. IR (KBr): 2079 cm^{-1} (ν_{NCS}). Anal. Calcd for $C_{28}H_{38}N_2NiO_5P_2S_2$: C, 50.39; H, 5.74; N, 4.20; S, 9.61. Found: C, 50.59; H, 5.74; N, 4.29; S, 9.69. For *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩: mp 193-195 °C. ^{31}P NMR ($CDCl_3$): δ 64.89. IR (KBr): 2081 (ν_{NCS}) cm^{-1}. Anal. Calcd for $C_{28}H_{38}N_2NiO_5P_2S_2$: C, 50.39; H, 5.74; N, 4.20; S, 9.61. Found: C, 50.66; H, 5.75; N, 4.30; S, 9.75.

Preparation of Pure *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ Diastereoisomers. Isolation of *anti*-[22]$P_2O_2N_3Ts_3$. A quantity of *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3 (4.01 g, 3.66 mmol) was added with stirring to 150 mL of CH_2Cl_2, yielding a deep red solution. Addition of an aqueous solution of KCN (4.0 g, 61.4 mmol) in 50 mL of H_2O to the *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3 solution led to a yellow aqueous solution and a pale red CH_2Cl_2 layer. The entire reaction mixture was transferred to a 250-mL separatory funnel and shaken vigorously until the CH_2Cl_2 layer was colorless. The *anti*-[22]$P_2O_2N_3Ts_3$ dissolved in the organic layer was extracted twice more with aqueous KCN (4.0 g/50 mL) and the CH_2Cl_2 layer washed twice with distilled H_2O as the final purification step. The CH_2Cl_2 was dried over $MgSO_4$ and evaporated to dryness to give a white flocculent solid, *anti*-[22]$P_2O_2N_3Ts_3$, in 90% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -30.2. ^1H NMR ($CDCl_3$, TMS): δ 7.6-7.85, 7.2-7.4 (phenyl and tosyl protons, 22 H); 3.2-3.7 (CH_2-O, N, 2 H); 2.4 (tosyl CH_3); 1.8-2.0 (CH_2-P, 6 H); 1.73 (H_α, 2 H, $^2J_{HH}$ = 16 Hz, $^3J_{HH}$ = 8 Hz); 1.36 (-CH_2-, 2 H, $^2J_{PH}$

(23) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

= 9.2 Hz (triplet from 2D COSY), $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.58, 21.64 (tosyl CH_3); 22.03 (t, J_{PC} = 12.6 Hz, P-C-C-C-P); 28.57 (d, J_{PC} = 15.5 Hz, P-C-C-C-O); 29.48 (t, J_{PC} = 11.3 Hz, P-C-C-C-P); 49.57, 49.77, 50.18 (C-N); 68.88 (d, J_{PC} = 16.9 Hz, C-O); 69.98 (C-O); 127.47, 127.69, 128.58, 128.68, 128.81, 130.08, 130.22, 132.18, 132.46, 136.13, 136.54, 138.91, 139.10, 143.89, 144.02 (aromatic C). Anal. Calcd for $C_{48}H_{61}N_3O_8P_2S_3$: C, 59.67; H, 6.36; N, 4.35; S, 9.96. Found: C, 59.81; H, 6.36; N, 4.35; S, 10.06.

Isolation of *syn*-[22]$P_2O_2N_3Ts_3$. The following procedure was carried out in an inert atmosphere. The azaphosphand complex *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 (3.52 g, 3.08 mmol) was dissolved in a small amount of CH_2Cl_2 (25 mL), and this solution was then added dropwise to a nearly saturated methanolic KCN solution (10 equiv, 2.01 g, 30.9 mmol). The mixture was stirred for 30 min and then evaporated to dryness. The pale pink solid was extracted with CH_2Cl_2 (25 mL), and the yellow-orange solution again was added dropwise to a KCN solution (2.00 g in 50 mL of methanol). Pure *syn*-[22]$P_2O_2N_3Ts_3$ was obtained by evaporating the methanolic solution to dryness and extracting the product with CH_2Cl_2. The *syn*-[22]$P_2O_2N_3Ts_3$ was isolated as colorless cubes by removing the CH_2Cl_2 under vacuum and redissolving the *syn*-[22]$P_2O_2N_3Ts_3$ in a small volume of acetonitrile (15 mL). When the *syn*-[22]$P_2O_2N_3Ts_3$ was allowed to crystallize from this solution upon standing at room temperature, very pure material was isolated. Yield: 2.47 g (83%). ^{31}P NMR ($CDCl_3$): δ −29.3. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.63, 21.67 (tosyl CH_3); 22.95 (t, J_{PC} = 16.6 Hz, P-C-C-C-P); 28.63 (d, J_{PC} = 15.2 Hz, P-C-C-O); 29.83 (t, J_{PC} = 12.9 Hz, P-C-C-C-P); 49.76, 49.95, 50.38 (C-N); 68.95 (d, J_{PC} = 17.1 Hz, C-O); 70.00 (C-O); 127.52, 127.80, 128.63, 128.72, 128.89, 130.14, 130.28, 132.26, 132.49, 136.07, 136.46, 143.98, 144.10 (aromatic C). Anal. Calcd for $C_{48}H_{61}N_3O_8P_2S_3$: C, 59.67; H, 6.36; N, 4.35. Found: C, 59.61; H, 6.45; N, 4.21.

Cyanolysis of *anti*- and *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩ To Give *anti*- and *syn*-[21]P_2O_5 Diastereoisomers. Demetalation of *anti*-⟨$P_2Ni(NCS)_2|O_5$⟩. A 100-mL recovery flask was charged with *anti*-⟨$P_2Ni(NCS)_2|O_5$⟩ (0.564 g, 8.45 × 10^{-4} mol) and CH_2Cl_2 (10 mL). KCN (0.36 g, 5.53 mmol) dissolved in distilled H_2O (15 mL) was added to the vigorously stirred CH_2Cl_2 solution. The CH_2Cl_2 and aqueous layers were separated, and the former was extracted twice more with saturated KCN solution until the organic layer was colorless. After the CH_2Cl_2 layer was washed twice with an equal volume of distilled water, the solution was dried with $MgSO_4$ and the CH_2Cl_2 removed at reduced pressure to yield *anti*-[21]P_2O_5 as a colorless oil, yield 0.254 g (61%). ^{31}P NMR ($CDCl_3$): δ −22.45. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.38, 138.27, 138.19, 132.18, 132.05, 131.93, 128.53, 128.25, 128.21, 128.17 (aromatic C); 70.91, 70.57, 70.51, 70.43 (C-O); 68.80 (d, $J_{PC} \approx$ 9 Hz, O-C-C-P); 68.67 (d, $J_{PC} \approx$ 9 Hz, O-C-C-P); 28.76 (d, $J_{PC} \approx$ 12 Hz, O-C-C-C-P); 28.66 (d, $J_{PC} \approx$ 12 Hz, O-C-C-C-P); 23.94 (s, P-C); 23.9 (t, J_{PC} = 29 Hz, P-C-C).

Demetalation of *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩. A quantity of *syn*-⟨$P_2Ni(NCS)_2|O_5$⟩ (0.982 g, 1.471 mmol) was dissolved in CH_2Cl_2 (50 mL) and extracted twice with 200 mL of a saturated NaCN aqueous solution. The original orange-red solution produced a clear pale yellow organic layer and a yellow-orange aqueous layer after the first washing. The second cyanide washing led to a clear, colorless organic layer and a cloudy, colorless aqueous layer. The CH_2Cl_2 layer was then washed with distilled water (100 mL) to remove any residual NaCN. The organic solution containing *syn*-[21]P_2O_5 was dried with $MgSO_4$ and the CH_2Cl_2 removed under reduced pressure to yield the oxaphosphand as a clear, colorless oil. Yield: 70%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.83. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.97, 137.83, 137.78, 131.78, 131.63, 131.52, 128.08, 128.00, 127.93, 127.85 (aromatic C); 70.69, 70.35, 70.12 (C-O); 68.59 (d, J_{PC} = 11 Hz, O-C-C-P); 68.45 (d, J_{PC} = 11 Hz, O-C-C-P); 27.40 (d, J_{PC} = 7 Hz, P-C-C-O); 27.30 (d, J_{PC} = 7 Hz, P-C-C-O); 22.88 (t, J_{PC} = 29 Hz, P-C-C-C-P); 22.80 (s, P-C-C-C-P).

Isomerization of *anti*-[22]$P_2O_2N_3Ts_3$ To Generate a Diastereomeric Mixture of Separable Tosylated Azaphosphands. A pear-shaped 25-mL flask containing pure *anti*-[22]$P_2O_2N_3Ts_3$ (1.0 g, 1.035 mmol) was heated in an oil bath under dinitrogen until the colorless solid melted. The flask was heated to a temperature of 200 °C and then cooled to 160 °C. After 90 min, the vessel was cooled to room temperature whereupon the melted ligand formed a pale yellow glass. A small amount of CH_2Cl_2 was added to the reaction pot and the solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy, revealing the material to be a diastereomeric mixture of the [22]$P_2O_2N_3Ts_3$ azaphosphand. The dichloromethane solution was taken to dryness to give the usual flocculent solid. As expected from the above chemistry, the *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ isomers could be separated from one another through metalation and subsequent nickel removal via cyanolysis, following the procedures given above. The isomeric mixture of ligands was dissolved in 10 mL of CH_2Cl_2 and 10 mL of methanol. To this solution was added $NiCl_2·6H_2O$ (1.1 equiv, 0.271 g, 1.140 mmol) in 10 mL of methanol. Methanol was then added in 10-mL aliquots to achieve a 70 mL total volume of solvent and cause selective precipitation of the brick red *anti*-⟨$P_2NiCl_2|N_3$⟩Ts_3. The solid (0.485 g, 4.43 × 10^{-4} mol, 43% yield) was filtered, washed with 5 mL of methanol and 25 mL of diethyl ether, and dried in vacuo. The orange-brown solution of *syn*-⟨$P_2NiCl_2|N_3$⟩Ts_3 was added to a flask containing KSCN (3.0 equiv, 0.302 g, 3.11 mmol), resulting in a yellow precipitate of *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 and a pale yellow solution. The whole reaction mixture was taken to dryness under reduced pressure and the *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 extracted from all the other salts present with CH_2Cl_2. The contents of the yellow solution were investigated by using TLC (alumina, 5% methanol-CH_2Cl_2) and shown to consist of the main product, *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 plus some noncolored organic impurities. After the solid *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 was obtained by removal of the CH_2Cl_2, the product was finally purified by stirring the solid in a 2:1 diethyl ether-ethanol solution (30 mL) for 16 h at room temperature. The *syn*-⟨$P_2Ni(NCS)_2|N_3$⟩Ts_3 was then purified by stirring the solid in a solution of ethanol-diethyl ether (1:2) for 16 h in an effort to remove the last organic impurities present. The yellow-orange solid was filtered from the ethanolic solution, washed with diethyl ether, and dried in vacuo; yield 0.466 g (40%).

The *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ azaphosphand ligands were obtained by cyanolysis of the requisite nickel complexes separated above to give *anti*-[22]$P_2O_2N_3Ts_3$ and *syn*-[22]$P_2O_2N_3Ts_3$ in 85% and 72% yields, respectively.

Detosylation of *anti*- or *syn*-[22]$P_2O_2N_3Ts_3$ by Sodium Naphthalenide (NaNap) To Prepare *anti*- or *syn*-[22]$P_2O_2N_3$. A quantity of *anti*-[22]$P_2O_2N_3Ts_3$ (1.0 g, 1.035 mmol) was placed in a three-necked 50-mL round-bottomed flask and dissolved in 15 mL of a *t*-BuOH-DME solution (0.25 M). A magnetic stir bar was added and the three necks of the flask were equipped with a thermometer, a rubber septum, and a gas inlet tube. Detosylation was carried out by using a freshly prepared 1.0 M solution of NaNap in DME. The reducing agent was added dropwise to the azaphosphand solution, the temperature of which was maintained close to −78 °C, until the characteristic green color of the NaNap persisted, indicating that the reductive cleavage of the protecting tosyl groups was complete. The reaction mixture was stirred at −50 °C for 30 min and then slowly allowed to warm to room temperature. At ~10 °C, the greenish hue dissipated and a pale yellow precipitate deposited. The reaction mixture was taken to dryness under reduced pressure. The detosylated azaphosphand ligand was recovered by washing the off-white solid with pentane (50 mL) to extract *anti*-[22]$P_2O_2N_3$, and any insoluble salts were removed by filtration. Naphthalene formed in the reaction was also soluble in the pentane, but pure *anti*-[22]$P_2O_2N_3$ could be obtained by evaporating the solution to dryness and subliming the naphthalene from the product, which was isolated as a thick colorless oil. Yield: 86%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −30.06. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.73 (t, J_{PC} = 13.9 Hz, P-C-C-C-P); 28.09 (d, J_{PC} = 12.5 Hz, P-C-C-O); 29.25 (t, J_{PC} = 13.9 Hz, P-C-C-C-P); 48.84, 48.91, 48.97 (C-N); 68.01 (d, J_{PC} = 18.4 Hz, C-O); 69.7 (C-O); 127.86 (d, J_{PC} = 7.1 Hz, aromatic C3); 128.10 (aromatic C4); 131.60 (d, J_{PC} = 20.0 Hz, aromatic C2); 138.04 (d, J_{PC} = 13.9 Hz, aromatic C1 (ipso)).

In a similar manner, *syn*-[22]$P_2O_2N_3Ts_3$ could be detosylated by following the above procedure to yield pure *syn*-[22]$P_2O_2N_3$ in good yield. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −27.65. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.92 (t, J_{PC} = 15.1 Hz, P-C-C-C-P); 29.04 (d, J_{PC} = 13.5 Hz, P-C-C-O); 30.36 (t, J_{PC} = 13.5 Hz, P-C-C-C-P); 49.56, 49.75 (C-N); 68.68 (d, J_{PC} = 18.2 Hz, C-O); 70.59 (C-O); 128.70 (d, J_{PC} = 7.9 Hz, aromatic C3); 128.80 (aromatic C4); 132.46 (d, J_{PC} = 17.4 Hz, aromatic C2); 139.63 (d, J_{PC} = 151.1 Hz, aromatic C1 (ipso)).

In general, the detosylated azaphosphands *anti*- and *syn*-$P_2O_2N_3$ were purified to the extent required for subsequent metalation experiments, and under normal circumstances, the naphthalene formed during the reduction process was not removed from the reaction medium.

Complexation Chemistry of *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ and *anti*- and *syn*-[21]P_2O_5. *anti*- and *syn*-⟨$P_2PdCl_2|N_3$⟩Ts_3. A solution of *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ (1:1) in dichloromethane (10 mL) was added to a solution of [$PdCl_2$(COD)] (0.23 g, 0.81 mmol) in dichloromethane (10 mL). The clear, yellow solution was allowed to stand undisturbed at room temperature for 16 h. The pale yellow crystals of *anti*-⟨$P_2PdCl_2|N_3$⟩Ts_3 that deposited were collected by filtration, washed with 2 × 20 mL of diethyl ether, and dried in vacuo. Yield: 0.41 g, 45% (R_f = 0.17; 5% MeOH-CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 12.49. ^1H NMR ($CDCl_3$, TMS): δ 7.1-7.9 (phenyl protons, 22 H); 3.0-4.2, 1.6-2.3 (methyl protons, 30 H); 2.35, 2.40 (tosyl CH_3, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.77, 142.70, 137.63, 137.01, 129.54, 129.34, 127.19, 127.12 (tosyl aromatic C); 131.64 (s); 133.06 (d, J_{PC} = 8.1 Hz); 129.88 (d, J_{PC} = 5 Hz); 128.77 (d, J_{PC} = 11.0 Hz); 68.38, 64.17 (C-O); 46.23, 45.94 (C-N); 28.80 (C-P, d, J_{PC} = 28.9 Hz); 23.68 (C_α-P, dd, $|^2J_{PC} + {}^3J_{PC}|$ = 33 Hz); 17.80 (C_β-P, s); 21.43, 21.38 (tosyl CH_3). Anal. Calcd for $C_{48}H_{61}N_3O_8P_2S_3Cl_2Pd$: C, 50.42; H, 5.38; N, 3.67; Cl, 6.20. Found: C, 50.69; H, 5.57; N, 3.62; Cl, 5.95.

Further concentration of the mother liquor to half its initial volume afforded a second crop of crystals, 0.180 g (20%), comprising a mixture of anti and syn diastereoisomers when analyzed by TLC. To the filtrate was added diethyl ether (20 mL), and the yellow solid produced was collected by filtration. The solid, which contained a small amount of the anti isomer, was further purified by column chromatography to afford the *syn*-$\langle P_2PdCl_2|N_3\rangle Ts_3$ (0.350 g, 38%) complex as a light yellow solid (R_f = 0.42; 5% MeOH–CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ 10.77. ^1H NMR ($CDCl_3$, TMS) δ 7.0–7.9 (phenyl protons, 22 H); 2.8–4.3, 1.1–2.5 ($-CH_2-$, broad, 30 H); 2.3, 2.5 (tosyl CH_3, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (selected) 69.48, 67.16 (C–O); 50.10, 49.84, 49.77 (C–N); 29.24 (C–P, filled-in doublet, $|^1J_{PC} + {}^3J_{PC}|$ = 40.5 Hz); 29.92 (C_α–P, filled-in doublet, $|^1J_{PC} + {}^3J_{PC}|$ = 37.0 Hz); 18.33 (C_β–P, s); 21.54, 21.44 (tosyl CH_3).

Preparation of *anti*- and *syn*-$\langle P_2M(XY)|N_3\rangle Ts_3$ (M(XY) = $NiCl_2$, $PdCl_2$, $PtCl_2$, PtClMe, $PtMe_2$). A general procedure was adopted for preparing metal complexes of the tosylated azaphosphand macrocycle. Since metals cannot bind the tosylated amine pole of the phosphand, the only complexes that form are of the generic stoichiometry *anti*- or *syn*-$\langle P_2M(XY)|N_3\rangle Ts_3$. These complexes could be characterized quite readily by their $^{31}P\{^1H\}$ NMR spectra (vide infra). The method employed was to react the azaphosphand (*anti*- or *syn*-[22]$P_2O_2N_3Ts_3$) with the metal species of choice, e.g., $NiCl_2\cdot 6H_2O$, $[Pd(COD)Cl_2]$, $[Pt(NCPh)_2Cl_2]$, $[Pt(COD)Cl_2]$, $[Pt(COD)Me_2]$, or [Pt(COD)ClMe], in suitable solvents, e.g., methanol, dichloromethane, and acetonitrile, with a slight excess of the macrocycle present. After the reaction was complete, solutions were evaporated to dryness and the product was recrystallized if necessary to yield the *anti*- or *syn*-$\langle P_2M(XY)|N_3\rangle Ts_3$ complexes in quantitative yield, based on the amount of metal present. The nickel complexes, *anti*- and *syn*-$\langle P_2NiCl_2|N_3\rangle Ts_3$, could be readily converted to *anti*- and *syn*-$\langle P_2Ni(NCS)_2|N_3\rangle Ts_3$ by metathesis with SCN^- ion.

Similarly, the pure *anti*- and *syn*-[21]P_2O_5 diastereomers reacted directly with transition-metal complexes to generate *anti*- and *syn*-$\langle P_2M(XY)|O_5\rangle$ under analogous conditions. Examples of these preparations are given below for *anti*- and *syn*-$\langle P_2NiCl_2|O_5\rangle$ and *anti*- and *syn*-$\langle P_2PdCl_2|O_5\rangle$.

Preparation of *anti*-$\langle P_2NiCl_2|O_5\rangle$. A 50-mL round-bottomed flask was charged with *anti*-[21]P_2O_5 (0.848 g, 1.72 mmol) and CH_2Cl_2 (10 mL). A solution of $NiCl_2\cdot 6H_2O$ (0.644 g, 2.709 mmol) in methanol (10 mL) was added to the stored oxaphosphand solution. Immediately upon addition of the metal salt, the solution turned a dark orange. After the reaction was stirred for 10 min, the solvent was removed under reduced pressure, and the orange solid was redissolved in CH_2Cl_2 and dried over $MgSO_4$. The dried solution was filtered, evaporated to dryness, and collected by filtration after being washed with diethyl ether. Yield: 0.951 g (89%) of a bright orange powder. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.63. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.31, 133.26, 133.16, 131.21, 128.66, 128.62, 128.52, 126.59 (aromatic C); 70.92, 70.21, 69.74, 69.38 (C–O); 65.56 (O–*C*–C–P); 27.98 (t, P–C–*C*–C–P, J = 16 Hz); 26.451, 26.203, 25.88 (P–C). Anal. Calcd for $C_{26}H_{38}Cl_2NiO_5P_2$: C, 50.19; H, 6.16; Cl, 11.40. Found: C, 50.33; H, 6.23; Cl, 11.32.

Preparation of *syn*-$\langle P_2NiCl_2|O_5\rangle$. The *syn*-$\langle P_2NiCl_2|O_5\rangle$ complex was prepared by a procedure similar to that described above. *syn*-[21]P_2O_5 (0.725 g, 1.472 mmol) was dissolved in methanol (10 mL), and $NiCl_2\cdot 6H_2O$ (0.5 g, 2.103 mmol) was added directly to this stirred solution, resulting in the formation of a dark orange solution. A dark orange viscous oil was obtained upon evaporation of the methanol. This oil was then dissolved in CH_2Cl_2, filtered to remove any unreacted nickel salts, and evaporated to dryness to give an orange solid that was dried in vacuo. Yield: 0.642 g (70%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.12. Anal. Calcd for $C_{26}H_{38}Cl_2NiO_5P_2$: C, 50.19; H, 6.16; Cl, 11.40. Found: C, 50.30; H, 6.14; Cl, 11.32.

Preparation of *anti*-$\langle P_2PdCl_2|O_5\rangle$. A quantity of *anti*-[21]P_2O_5 (1.797 g, 3.65 mmol) was placed in a 50-mL round-bottomed flask and dissolved in a 1:1 mixture of CH_2Cl_2–acetone (25 mL). $[Pd(COD)Cl_2]$ (1.320 g, 4.62 mmol) was added to the stirred oxaphosphand solution, and after 5 min, a white solid precipitated. The reaction mixture was stirred for a total of 4.5 h, and then the solids (a fine white powder and a small quantity of unreacted starting material) were removed by filtration. The mixture of solids was redissolved in a minimum of methylene chloride, and to this solution was added acetone (70 mL), which induced crystallization. White microcrystals deposited from this pale yellow solution in about 15 min. After 30 min, more acetone was added, the solution was filtered, and the precipitate of *anti*-$\langle P_2PdCl_2|O_5\rangle$ was washed with acetone before being dried in vacuo. Yield: 0.994 g (41%). The compound was identified by its spectra, which agreed perfectly with those of analytically pure material prepared by a different procedure (vide infra).

Preparation of *syn*-$\langle P_2PdCl_2|O_5\rangle$. A 25-mL round-bottomed flask was charged with *syn*-[21]P_2O_5 (0.70 g, 1.421 mmol) and acetone (10 mL). A methylene chloride solution of $[Pd(COD)Cl_2]$ was then added dropwise to the oxaphosphand solution, and the reaction mixture was stirred for 2 h. After the solvent was removed under reduced pressure, the yellow solid obtained was redissolved in a minimum quantity of methylene chloride. Hexane was added to the *syn*-$\langle P_2PdCl_2|O_5\rangle$ solution to achieve the cloud point, and the mixture was cooled to −20 °C. After 2 days, a pale yellow powder was collected by filtration and recrystallized from CH_2Cl_2–hexane. Repeated recrystallizations of *syn*-$\langle P_2PdCl_2|O_5\rangle$ were required to remove the last traces of $[Pd(COD)Cl_2]$. Final purification was achieved by dissolving a pale yellow solid sample of *syn*-$\langle P_2PdCl_2|O_5\rangle$ in a minimum amount of methylene chloride and adding hexane until a cloudiness persisted in the solution. The solution was stirred overnight to yield a pale yellow solution and a white powder. The mixture was filtered to remove white *syn*-$\langle P_2PdCl_2|O_5\rangle$ (0.143 g, 15%). The compound was identified by spectral comparison with analytically pure material prepared by the method in the following paragraph.

Reaction of a Diastereomeric Mixture of [21]P_2O_5 Oxaphosphand with $[Pd(COD)Cl_2]$. Chromatographic Separation of *anti*- and *syn*-$\langle P_2PdCl_2|O_5\rangle$. To a mixture of oxaphosphand diastereoisomers (anti:syn = 7:3, 0.35 g, 0.71 mmol) in dichloromethane (3 mL) was added $[Pd(COD)Cl_2]$ (0.200 g, 0.70 mmol) in dichloromethane (5 mL). Fractional crystallization from CH_2Cl_2–Et_2O gave a pale yellow solid and a colorless solution. The solution was filtered, concentrated, and chromatographed on silica by using 5% MeOH–CH_2Cl_2 as an eluant. *anti*-$\langle P_2PdCl_2|O_5\rangle$ eluted first (R_f = 0.61, 7.5% MeOH–CH_2Cl_2) and the syn isomer second (R_f = 0.45, 7.5% MeOH–CH_2Cl_2) from the column. The separated isomers were collected and dried in vacuo to afford 0.29 g (61%) and 0.11 g (23%) yields of *anti*- and *syn*-$\langle P_2PdCl_2|O_5\rangle$, respectively. Anal. Calcd for *anti*-$\langle P_2PdCl_2|O_5\rangle$, $C_{26}H_{38}O_5P_2PdCl_2$: C, 46.62; H, 5.72; Cl, 10.59. Found: C, 46.83; H, 5.74; Cl, 10.99. Anal. Calcd for *syn*-$\langle P_2PdCl_2|O_5\rangle$, $C_{26}H_{38}O_5P_2PdCl_2$: C, 46.62; H, 5.72. Found: C, 47.04; H, 5.63.

Synthesis of *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$. To a quantity of detosylated azaphosphand, *anti*- and *syn*-[22]$P_2O_2N_3$ (0.52 g, 1.03 mmol), prepared in situ at 0 °C, was added dropwise a degassed methanol (15 mL) solution of $NiCl_2\cdot 6H_2O$ (0.333 g, 1.401 mmol). The resulting yellowish mixture was stirred for 5 min, after which time $HBF_4\cdot Et_2O$ (3 mL) was added to form a clear, dark red solution. Addition of diethyl ether (30 mL) to the reaction mixture caused a precipitate to form, which was collected by filtration. The product was washed with 2 × 20 mL of diethyl ether and recrystallized from a 1:2 mixture of CH_3CN–Et_2O to afford an orange-pink powder (0.556 g, 67%). This complex was tentatively assigned the formula *anti*- and *syn*-$\langle P_2NiCl_2|H_2N_3\rangle(BF_4)_2$ (vide infra). Following metathesis of *anti*- and *syn*-$\langle P_2NiCl_2|H_2N_3\rangle(BF_4)_2$ (20 mL of 1:1 CH_3CN–MeOH solution) with excess NaNCS (2.43 g, 30 mmol) in methanol (40 mL), an orange solution formed that was concentrated to half its original volume. Addition of diethyl ether (30 mL) gave a precipitant that was filtered from the reaction mixture, washed with 2 × 10 mL of H_2O, and recrystallized from CH_3CN–Et_2O (1:2) to give an orange solid. Recrystallization of the orange solid with a 1:1 CH_3CN–MeOH solvent mixture provided microcrystals. Larger crystals suitable for X-ray structure determination were grown by slow evaporation of a 1:1 CH_3CN–MeOH solution or by the vapor diffusion of diethyl ether into DMF. The crystal used for the X-ray structure determination was selected from the latter batch. All analyses showed that those orange-red crystals were of the composition *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$. ^{31}P NMR (1:1 CH_3CN–MeOH): δ 4.63. ^{31}P NMR (DMF): δ 10.5 (broad). UV–vis (1:1 CH_3CN–MeOH): 425.4, 291.0, 271.4, 258.6, 233.8, 215.2 nm. IR (KBr pellet): 3180 (s), 3293 (w, N–H), 2700–2900 (m, CH_2), 2071, 2088 (s, NCS), 1360 (w), 1110 (s), 750 (w), 705 (m) cm^{-1}. Anal. Calcd for $C_{31}H_{45}N_7O_2S_4P_2Ni$: C, 46.74; H, 5.69; N, 12.31. Found: C, 46.28; H, 5.68; N, 12.10.

X-ray Crystallography. Collection and Reduction of X-ray Data for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$. An orange crystal was grown from slow evaporation of a 1:1 CH_3CN–MeOH solution at room temperature. The crystal used for data collection was a block of dimensions 0.3 × 0.2 × 0.1 mm mounted in a capillary tube. Study on the diffractometer indicated *mmm* Laue symmetry and systematic absences $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$) and $00l$ ($l = 2n + 1$), uniquely consistent with space group $P2_12_12_1$ (D_2^4, No. 19).[24a] Open-counter ω-scans of several strong low-angle reflections showed no structure ($\Delta\bar{\omega}_{1/2}$ = 0.18°), and the crystal quality was deemed acceptable. Data collection and reduction procedures were those standard to our laboratory.[22] Crystal data are presented in Table I.

Solution and Refinement of the Structure of *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$. The structure was solved by standard heavy-atom techniques and refined by full-matrix least-squares methods.[22] The function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights w = 5.893 $[\sigma^2(F_o)$

(24) *International Tables for Crystallography*; D. Reidel: Dordrecht, Holland, 1983; Vol. A: (a) pp 196–197. (b) pp 174–176.

Table II. Final Non-Hydrogen Positional Parameters for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$[a]

atom	x	y	z
Ni	0.22480 (10)	0.47060 (10)	0.37010 (10)
S1	0.4818 (3)	0.5500 (3)	0.2374 (2)
S2	0.6967 (4)	0.2286 (4)	0.0006 (2)
P1	0.0890 (2)	0.4317 (3)	0.42160 (10)
P2	0.2027 (3)	0.3432 (3)	0.31340 (10)
O5	0.4011 (7)	0.3358 (7)	0.3902 (3)
O9	0.0819 (7)	0.6389 (7)	0.3527 (3)
N1	0.3278 (7)	0.5191 (7)	0.3191 (4)
N2	0.2646 (8)	0.5734 (7)	0.4241 (4)
N6	0.9685 (8)	0.4967 (8)	0.9147 (4)
N7	0.5035 (11)	0.6967 (11)	0.3638 (6)
N8	0.2783 (9)	0.7669 (7)	0.3349 (4)
C1	0.3913 (9)	0.5317 (9)	0.2835 (5)
C2	0.2811 (10)	0.6356 (9)	0.4568 (5)
C31	0.1249 (6)	0.4231 (7)	0.4936 (2)
C32	0.2090 (6)	0.3552 (7)	0.5073 (2)
C33	0.2364 (6)	0.3391 (7)	0.5625 (2)
C34	0.1797 (6)	0.3910 (7)	0.6041 (2)
C35	0.0956 (6)	0.4588 (7)	0.5904 (2)
C36	0.0682 (6)	0.4749 (7)	0.5352 (2)
C37	0.0171 (12)	0.3046 (13)	0.4122 (5)
C38	0.0080 (12)	0.2703 (13)	0.3498 (6)
C39	0.1092 (11)	0.2375 (11)	0.3281 (5)
C41	0.1614 (7)	0.3870 (7)	0.2453 (3)
C42	0.0758 (7)	0.4575 (7)	0.2413 (3)
C43	0.0404 (7)	0.4909 (7)	0.1895 (3)
C44	0.0906 (7)	0.4537 (7)	0.1418 (3)
C45	0.1762 (7)	0.3831 (7)	0.1459 (3)
C46	0.2116 (7)	0.3497 (7)	0.1977 (3)
C48	0.3362 (10)	0.2761 (11)	0.3024 (5)
C49	0.3881 (11)	0.2450 (11)	0.3570 (5)
C51	0.4769 (11)	0.3232 (10)	0.4332 (5)
C52	0.4910 (11)	0.4241 (10)	0.4610 (5)
C61	0.5708 (13)	0.6084 (11)	0.4426 (6)
C62	0.5934 (12)	0.6828 (12)	0.3978 (6)
C71	0.4739 (13)	0.8009 (11)	0.3473 (6)
C72	0.3833 (13)	0.7984 (12)	0.3078 (6)
C81	0.1857 (11)	0.7547 (13)	0.2966 (6)
C82	0.0826 (12)	0.7384 (12)	0.3266 (6)
C91	0.0056 (13)	0.6299 (11)	0.3973 (6)
C92	−0.0188 (12)	0.5210 (12)	0.4080 (6)
S3	0.7992 (6)	0.5371 (7)	0.2773 (3)
N3	0.7145 (10)	0.3995 (8)	0.3423 (5)
C3	0.7391 (13)	0.462 (2)	0.3236 (8)
S4	0.7634 (4)	0.4147 (4)	0.5216 (2)
N4	0.771 (2)	0.4512 (14)	0.1034 (6)
C4	0.7546 (16)	0.5044 (12)	0.0706 (6)

[a] Numbers in parentheses are errors in the last significant digit(s).

$+ 0.000625(F_o)^2$]. The structure converged to the R factors reported in Table I. All non-hydrogen atoms were anisotropically refined with the exception of N3 of a thiocyanate counter ion, which did not refine well, possibly due to end-for-end disorder. The largest residual peak in the final difference map (0.7 e Å^{-3}) was close to N73 and C73 of this thiocyanate ion. Hydrogen atoms were placed in calculated positions (d_{C-H}, d_{N-H} = 0.95 Å) and given a fixed common isotropic thermal parameter.

Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms and scattering factors for hydrogen atoms were taken from refs 25 and 26, respectively. Final non-hydrogen positional, hydrogen positional and thermal, and non-hydrogen thermal parameters are given in Tables II, S1, and S2 (supplementary material), respectively, and observed and calculated structural factors are given in Table S3.

Collection and Reduction of X-ray Data for *anti*-$\langle P_2PdCl_2|O_5\rangle$. A clear colorless crystal grown from a 5:1 acetone–dichloromethane solution at room temperature was used for the diffraction study. The crystal, a parallelepiped of approximate dimensions 0.53 mm × 0.23 mm × 0.23 mm, bounded by {100}, {010}, and {001}, was mounted on a glass fiber and coated with epoxy. Study on the diffractometer showed the crystal to belong to the monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14).[24b] Open-counter ω-scans of several strong, low-angle reflections showed no

Table III. Final Non-Hydrogen Atom Positional Parameters for *anti*-$\langle P_2PdCl_2|O_5\rangle$[a]

atom	x	y	z
Pd	0.15624 (3)	0.34551 (3)	0.85742 (2)
Cl1	−0.06635 (12)	0.34220 (11)	0.83650 (7)
Cl2	0.18519 (14)	0.46565 (11)	0.77759 (8)
P1	0.36741 (12)	0.33620 (9)	0.87817 (6)
P4	0.14321 (12)	0.23645 (8)	0.93825 (6)
O7	0.1260 (6)	0.0267 (5)	0.8705 (4)
O10	0.3709 (4)	−0.0211 (3)	0.8436 (2)
O13	0.5879 (4)	0.0622 (3)	0.9222 (3)
O16	0.7207 (3)	0.2175 (2)	0.98098 (18)
O19	0.6083 (3)	0.3969 (3)	0.97057 (19)
C2	0.3987 (4)	0.2624 (3)	0.9535 (2)
C3	0.3006 (5)	0.1837 (3)	0.9508 (3)
C5	0.0230 (5)	0.1477 (3)	0.9232 (3)
C6	0.0328 (6)	0.0950 (5)	0.8557 (3)
C8	0.1539 (9)	−0.0244 (7)	0.8148 (4)
C9	0.2732 (8)	−0.0162 (7)	0.7911 (4)
C11	0.4886 (8)	−0.0009 (5)	0.8181 (3)
C12	0.5925 (8)	−0.0123 (6)	0.8725 (5)
C14	0.6945 (8)	0.0550 (6)	0.9647 (6)
C15	0.6999 (7)	0.1340 (6)	1.0152 (4)
C17	0.7468 (5)	0.2917 (5)	1.0278 (3)
C18	0.7396 (5)	0.3794 (4)	0.9885 (3)
C20	0.5838 (5)	0.4505 (4)	0.9114 (3)
C21	0.4407 (5)	0.4488 (3)	0.8946 (3)
C31	0.4481 (5)	0.2814 (3)	0.8090 (3)
C32	0.5739 (5)	0.2540 (4)	0.8184 (3)
C33	0.6366 (6)	0.2134 (4)	0.7654 (4)
C34	0.5723 (8)	0.1976 (4)	0.7029 (4)
C35	0.4466 (8)	0.2225 (5)	0.6933 (3)
C36	0.3831 (6)	0.2649 (4)	0.7460 (3)
C41	0.1093 (4)	0.2816 (3)	1.0223 (2)
C42	0.0987 (5)	0.2227 (4)	1.0790 (3)
C43	0.0683 (5)	0.2576 (6)	1.1424 (3)
C44	0.0467 (6)	0.3497 (6)	1.1503 (3)
C45	0.0599 (6)	0.4078 (5)	1.0966 (3)
C46	0.0893 (5)	0.3754 (4)	1.0321 (3)

[a] Numbers in parentheses are errors in the last significant digit(s).

structure ($\Delta\bar{\omega}_{1/2}$ = 0.17°), and the crystal quality was deemed acceptable. Data collection and reduction proceeded by methods standard in our laboratory, the details of which are presented in Table I.

Determination and Refinement of the Structure of *anti*-$\langle P_2PdCl_2|O_5\rangle$. The structure was solved by standard Patterson and difference Fourier methods. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogen atoms of the phenyl rings were placed at calculated positions (d_{C-H} = 0.95 Å) and constrained to "ride" on the carbon atoms to which they were attached. These hydrogen atoms were refined with a common isotropic temperature factor. The hydrogen atoms of the 14 methylene carbons in the macrocycle were also placed at calculated positions and refined isotropically with a separate, but common, thermal parameter.[22] Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms and hydrogen atom scattering factors were obtained from refs 25 and 26, respectively. Least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ where weights were set at $w = 1.4784\ [\sigma^2(F_o) + 0.000625(F_o)^2]^{-1}$ and converged to the R factors reported in Table I. The large anisotropic thermal parameters of O7 suggest some possibly unresolved disorder. A final difference map showed a peak of 2.10 e Å^{-3} at 1.50 Å from O7. We attempted to model O7 as being disordered over two sites, with the 2.10 e Å^{-3} peak chosen as the second site. The bond distances and angles associated with this second site were unreasonable, however, and this model was abandoned. Final non-hydrogen atom positional and thermal parameters are given in Tables III and S4, respectively, final hydrogen positional and thermal parameters are given in Table S5, and a listing of observed and calculated structure factors is given in Table S6.

Results and Discussion

Ligand Syntheses—General Strategy. The synthesis of phosphorus-containing macrocyclic ligands and studies of their ability to coordinate transition metals in their soft ligating sites has been an active area of research in recent years.[7d,e,27-31] The rather

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sparse field of phospha macrocycles was greatly expanded through the development of one-pot syntheses employing high-dilution apparatus. This approach facilitates the condensation of phosphorus (or sulfur) nucleophiles with halogenated or tosylated hydrocarbon units to produce 11-membered P_3 and mixed P_2S, PS_2, and P_2N cycles, as well as 14-membered P_4, P_2S_2, P_2N_2, and P_2O_2 macrocyclic ligands.[32] A crown ether-type phosphorus macrocycle, 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane ([18]P_4O_2), was obtained in 18% yield in one step by treating the dilithio derivative of 1,2-bis(phenylphosphino)ethane with bis(chloroethyl) ether.[33] The coordination chemistry of the five diastereoisomers of this macrocycle and related sulfur[15,34] and aza[35] analogues has been reported. The ligand synthesis was not performed under high-dilution conditions, however, which may have adversely affected the yields; experimental complications can arise when manipulating air-sensitive phosphides for the high-dilution reaction. Many other workers have successfully employed "template" reactions to promote phospha macrocycle syntheses.[7c-f,28-31]

In the present work, we have developed a reaction for preparing dinucleating phospha macrocycles, termed "phosphands", by the macrocyclization reaction shown in Scheme I. In this approach, a 2-fold excess of LHDS base is loaded at the start of the reaction into the high-dilution reservoir and the reagents, 1,3-bis(phenylphosphino)propane and dichloride I or 1,2-bis(phenylphosphino)ethane and hexaethylene glycol ditosylate, are added by syringe as THF solutions. This procedure generates phosphides in situ in the presence of base which then react immediately with electrophiles. The azaphosphand and oxaphosphand macrocycles have been prepared in good yield by using this high-dilution approach, which facilitates rapid ring closure while avoiding the buildup of sensitive phosphide intermediates.

The use of the above strategy, the simplicity of the apparatus, and the ability of the reaction to tolerate adventitious moisture are significant advances. The synthetic scheme employs efficient reactions leading to asymmetric macrocycles and may permit, in the future, incorporation of different chain lengths in order to vary the distance between the sets of donor atoms and, ultimately, the coordination of the disparate metals in the macrocycle cavity itself.

Preparation of Oxaphosphands and Tosylated Azaphosphands. Scheme I indicates that the 21-membered oxa- and 22-membered azaphosphands are synthesized from readily available starting materials. In the azaphosphand procedure, diethylenetriamine was first protected with *p*-toluenesulfonyl chloride to generate the *N,N',N''*-tris(*p*-tolylsulfonyl)triethylenetriamine,[16] which was then allowed to react with a 50-fold excess of bis(chloroethyl) ether in the presence of 2.5 equiv of base (NaH or *t*-BuOK) to afford dichloride I in 75% yield. This dichloride component was designed such that its reaction with the diphosphine subunit would form pentamethylene linker chains to bridge the diethylenetriamine moiety. Indeed, the desired ring, 16,20-diphenyl-4,7,10-tritosyl-1,13-dioxa-16,20-diphospha-4,7,10-triazacyclodocosane ([22]$P_2O_2N_3Ts_3$), was obtained in 72% isolated yield by the condensation of the bis(electrophile) I with 1,3-bis(phenylphosphino)propane. In the synthesis, solutions of the two reactants are added very slowly and simultaneously to a large volume of THF solution that contains an excess of the base LHDS, which generates the reactive dilithio reagent in situ. Under the conditions employed, the local concentration of the reacting species is very low, and the probability of 1:1 condensation to form phosphand is maximized. The ring-closure step is quite effective, as judged by $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture. The ratio of tosylated macrocyclic to polymeric material is approximately 85:15.

Modification of the above azaphosphand route resulted in the synthesis of the oxaphosphand [21]P_2O_5 (Scheme I). In the oxaphosphand protocol, the linker chains of the macrocycle are provided by hexaethylene glycol. First, the diol was protected with *p*-toluenesulfonyl chloride to give the macrocycle precursor, 1,19-bis(*p*-tolylsulfonyl)-1,4,7,10,13,16,19-heptaoxanonadecane (II). The ditosylated derivative, when condensed with 1,2-bis(phenylphosphino)ethane by using LHDS under high-dilution conditions, leads directly to the oxaphosphand 1,4-diphenyl-7,10,13,16,19-pentaoxa-1,4-diphosphacycloheneicosane ([21]P_2O_5) in overall 36–40% isolated yield. In this case, the crude cyclization products, obtained from equimolar mixtures of the reactants, contain a higher proportion of oligomers than of the desired monomacrocycle [21]P_2O_5.

The additional products formed during the macrocyclization of the tosylated azaphosphand and oxaphosphand were considerably less soluble in the solvents used and were readily separated. They consistently exhibited $^{31}P\{^1H\}$ NMR resonances 1–2 ppm upfield from those of the primary cyclized products [22]$P_2O_2N_3Ts_3$ and [21]P_2O_5 and, presumably, are higher order oligomers. In one instance, a material separated from [22]$P_2O_2N_3Ts_3$ during the purification procedure that was further characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. The spectral patterns were comparable to those seen in the azaphosphand [22]$P_2O_2N_3Ts_3$ case, consistent with their being higher oligomers. No efforts have been made to study these larger phosphands, which may have ring sizes of 44 members or more.

Ligand Stereochemistry. Both macrocycles, [22]$P_2O_2N_3Ts_3$ and [21]P_2O_5, contain two chiral phosphine centers, and since inversion barriers for tertiary phosphines are in the range 32–35 kcal mol^{-1},[36] the phosphands can and do exist as racemic (anti) and meso (syn) diastereomers with distinguishable $^{31}P\{^1H\}$ NMR spectra. For the diastereomeric tosylated azaphosphand isolated from the macrocyclization reaction, two sharp singlets in an approximate 1:1 ratio (48:52; $^{31}P\{^1H\}$ NMR δ −29.28, −30.22) are observed, consistent with the occurrence of two isomers. In the case of the analogous oxaphosphand, however, the $^{31}P\{^1H\}$ NMR spectrum

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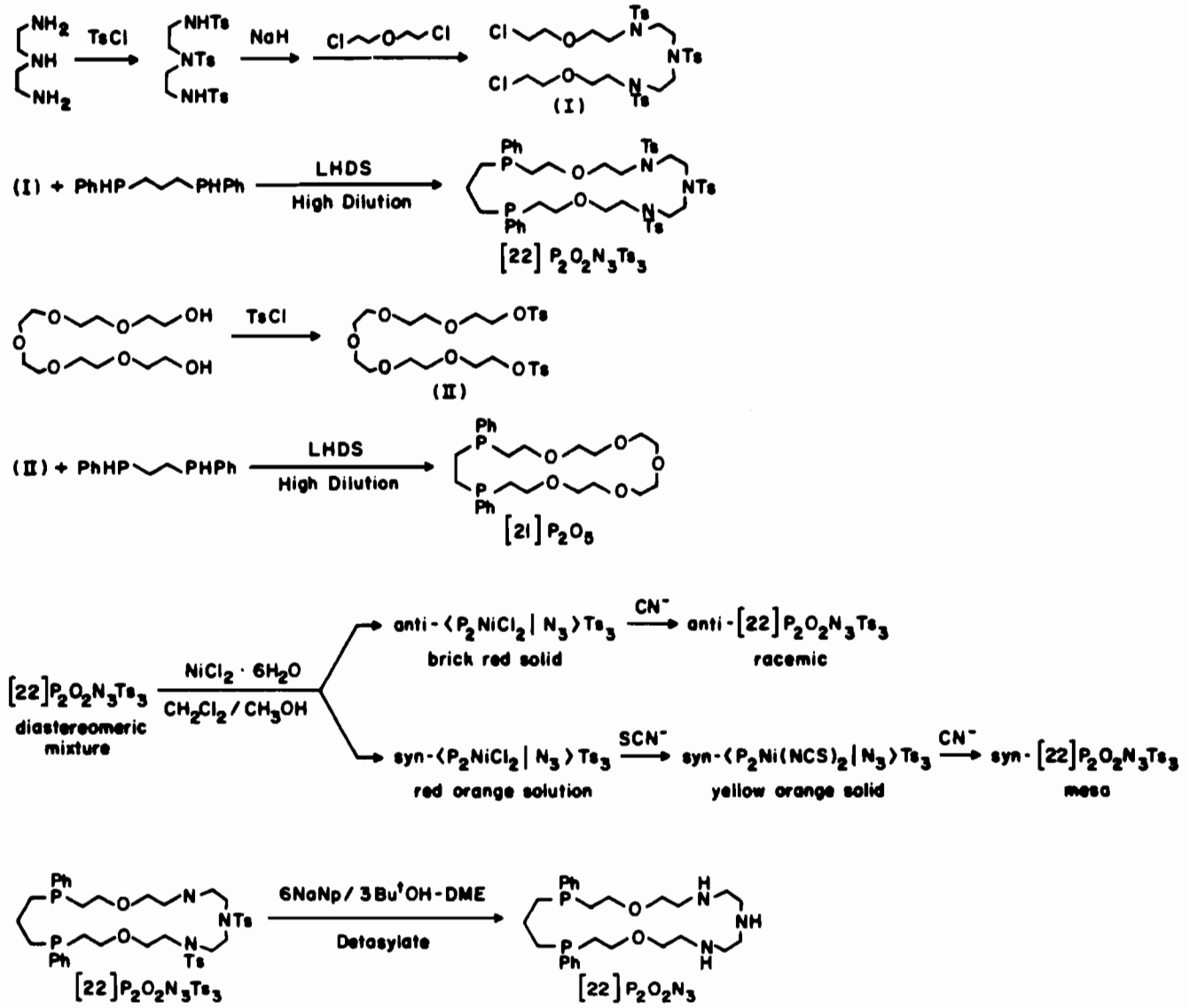
Scheme I



is composed of two sharp singlets in an approximate 2:1 ratio (64:36; $^{31}P\{^1H\}$ NMR δ −22.45, −23.83). Although aza- and oxaphosphands have conformational flexibility, the diastereomer distributions are significantly different and could be due to kinetic resolution at the final ring-closure step. The major isomer has anti stereochemistry, an assignment made after the structure of the dichloropalladium(II) complex was determined (vide infra).

The preferential cyclization of the $[21]P_2O_5$ oxaphosphand in the anti form is reminiscent of other systems, notably those involving 11- and 14-membered tertiary arsine and phosphine macrocycles,[33d,e,h,i] in which steric interactions presumably play a dominant role in *cis*-Ph_2 formation.[33e] Inspection of CPK space-filling and Dreiding models suggests that the precursor species resulting in *syn*-$[21]P_2O_5$ formation may have considerably more nonbonding steric interactions compared to the analogous precursor for the anti isomer. The steric bulk of phenyl groups contributes to this steric preference. In addition, the ethylene chain connecting the phosphorus centers may influence the cyclization such that more anti oxaphosphand than syn product is formed. In the analogous azaphosphand macrocyclization step, whatever conformational factors are operative at the crucial intramolecular nucleophilic substitution reaction are such that nearly equal amounts of the *anti*- and *syn*-$[22]P_2O_2N_3Ts_3$ diastereomers are generated.

Separation of Ligand Diastereoisomers. Typically, phosphine-containing macrocyclic isomers are very difficult to separate chromatographically, and direct separation of diastereoisomers of some polyphosphine and other phosphand-type ligands has rarely been achieved.[32k,37] In the present azaphosphand system, the *anti*- and *syn*-$[22]P_2O_2N_3Ts_3$ diastereoisomers were separated, as shown in Scheme I, by taking advantage of the very different solubilities of their nickel(II) complexes. Similar metalation and subsequent separation procedures have worked well previously for a variety of phosphands as a method of ligand purification and diastereomeric resolution, including the phosphine–ether macrocycle $[18]P_4O_2$, the equilibrium mixture of which was comprised of five diastereoisomers.[33]

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. The *anti*-$[22]P_2O_2N_3Ts_3$ ligand tritosylate was quantitatively obtained as an air-stable, colorless, flocculent solid 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*-$\langle P_2Ni(NCS)_2|N_3\rangle Ts_3$. The air-sensitive tosylated free ligand, *syn*-$[22]P_2O_2N_3Ts_3$, was obtained by cyanolysis under nitrogen in methylene chloride. In this latter case, the azaphosphand could be obtained as colorless clear blocks when purified by using acetonitrile as the solvent of crystallization.

Because of the similar solubilities of the uncomplexed oxaphosphands and their nickel(II) complexes, chromatographic resolution of the two isomers was found to be the best method

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Table IV. Metrical Details for *anti*-$\langle P_2PdCl_2|O_5\rangle$ and *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$: Bond Lengths (Å) and Angles (deg) for Both Compounds and Torsion Angles (deg) for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$

Bond Lengths for *anti*-$\langle P_2PdCl_2|O_5\rangle$[a]							
Palladium Coordination Sphere							
Pd–Cl1	2.352 (1)	Pd–P1	2.237 (1)	Pd–Cl2	2.357 (2)	Pd–P4	2.232 (1)
Oxaphosphand Macrocycle Framework							
P1–C2	1.824 (5)	C3–C2	1.535 (7)	O13–C14	1.36 (1)	C14–C15	1.50 (1)
P4–C3	1.825 (5)	P4–C5	1.814 (5)	C15–O16	1.401 (9)	O16–C17	1.423 (7)
C5–C6	1.520 (8)	O7–C6	1.41 (1)	C17–C18	1.480 (9)	C18–O19	1.427 (6)
O7–C8	1.35 (1)	C8–C9	1.36 (1)	O19–C20	1.397 (7)	C20–C21	1.522 (8)
C9–O10	1.409 (9)	O10–C11	1.386 (9)	C21–P1	1.823 (5)	P1–C31	1.805 (5)
C11–C12	1.48 (1)	C12–O13	1.45 (1)	P4–C41	1.808 (5)		
C31–C32	1.382 (7)	C32–C33	1.381 (9)	C41–C42	1.398 (7)	C42–C43	1.380 (8)
C33–C34	1.37 (1)	C34–C35	1.37 (1)	C43–C44	1.36 (1)	C44–C45	1.350 (9)
C35–C36	1.391 (9)	C31–C36	1.388 (7)	C45–C46	1.384 (8)	C41–C46	1.388 (7)
Bond Angles for *anti*-$\langle P_2PdCl_2|O_5\rangle$[a]							
Palladium Coordination Sphere							
P4–Pd–P1	85.87 (5)	P4–Pd–C11	90.55 (5)	P1–Pd–Cl2	90.09 (5)	Cl1–Pd–Cl2	93.62 (5)
P4–Pd–Cl2	175.12 (5)	P1–Pd–Cl1	175.36 (6)				
Oxaphosphand Macrocycle Geometry							
C21–P1–Pd	112.5 (2)	C31–P1–Pd	113.1 (2)	C3–P4–Pd	107.5 (2)	C5–P4–Pd	117.1 (2)
C41–P4–Pd	113.5 (1)	C2–P1–Pd	108.3 (2)				
C31–P1–C2	105.3 (2)	P1–C2–C3	108.3 (3)	C14–O13–C12	107.0 (6)	O13–C14–C15	109.8 (7)
C2–C3–P4	107.2 (3)	C3–P4–C5	110.1 (2)	O16–C15–C14	110.5 (7)	C15–O16–C17	112.3 (5)
C3–P4–C41	104.6 (2)	C41–P4–C5	103.5 (2)	O16–C17–C18	108.5 (4)	O19–C18–C17	107.5 (4)
P4–C5–C6	114.6 (4)	O7–C6–C5	104.8 (5)	C20–O19–C18	115.7 (4)	O19–C20–C21	107.7 (4)
C8–O7–C6	113.5 (6)	O7–C8–C9	117.5 (8)	C20–C21–P1	117.1 (4)	C21–P1–C2	109.1 (2)
C8–C9–O10	113.6 (6)	C11–O10–C9	111.2 (5)	C31—P1–C21	108.2 (2)		
O10–C11–C12	111.1 (6)	O13–C12–C11	109.9 (6)				
C32–C31–P1	120.7 (4)	C36–C31–P1	120.0 (4)	C35–C34–C33	120.1 (6)	C34–C35–C36	120.8 (6)
C33–C32–C31	120.9 (5)	C34–C33–C32	119.6 (6)	C31–C36–C35	119.2 (6)	C32–C31–C36	119.3 (5)
C46–C41–P4	121.0 (4)	C42–C41–P4	121.0 (4)	C45–C44–C43	120.0 (6)	C44–C45–C46	121.4 (6)
C43–C42–C41	120.4 (5)	C44–C43–C42	120.4 (6)	C45–C46–C41	119.8 (5)	C46–C41–C42	118.1 (4)
Bond Lengths for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$[a]							
Nickel Coordination Sphere							
Ni–N1	1.879 (9)	Ni–N2	1.922 (9)	Ni–P1	2.149 (3)	Ni–P2	2.152 (4)
Azaphosphand Macrocycle							
S1–C1	1.60 (1)	S2–C2	1.60 (1)	C32–C33	1.395	C33–C34	1.395
P1–C92	1.79 (2)	P1–C31	1.803 (6)	C34–C35	1.395	C35–C36	1.395
P1–C37	1.87 (2)	P2–C41	1.816 (8)	C37–C38	1.58 (2)	C38–C39	1.42 (2)
P2–C39	1.82 (1)	P2–C48	1.88 (1)	C41–C46	1.395	C41–C42	1.395
O5–C51	1.41 (1)	O5–C49	1.42 (2)	C42–C43	1.395	C43–C44	1.395
O9–C82	1.42 (2)	O9–C91	1.44 (2)	C44–C45	1.395	C45–C46	1.395
N1–C1	1.18 (1)	N2–C2	1.14 (2)	C48–C49	1.52 (2)	C51–C52	1.47 (2)
N6–C61	1.58 (2)	N6–C52	1.59 (2)	C61–C62	1.47 (2)	C71–C72	1.47 (2)
N7–C62	1.39 (2)	N7–C71	1.44 (2)	C81–C82	1.48 (2)	C91–C92	1.45 (2)
N8–C81	1.48 (2)	N8–C72	1.51 (2)	S3–C3	1.65 (2)	N3–C3	0.97 (3)
C31–C32	1.395	C31–C36	1.395	S4–C4	1.59 (2)	N4–C4	1.07 (2)
Interatomic Distances (Nonbonded)							
O5···N6	2.768	N8···O9	2.948	N7···N8	3.013	Ni···O9	2.849
N6···N7	2.809	Ni···O5	2.843				
Bond Angles for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$[a]							
Nickel Coordination Sphere							
N1–Ni–N2	92.7 (4)	N1–Ni–P1	170.7 (3)	N2–Ni–P2	171.2 (3)	P1–Ni–P2	95.5 (1)
N1–Ni–P2	85.3 (3)	N2–Ni–P1	87.9 (3)				
Azaphosphand Macrocycle							
C92–P1–C31	113.6 (6)	C92–P1–C37	100.6 (7)	C49–C48–P2	111.5 (9)	O5–C49–C48	109 (1)
C92–P1–Ni	109.0 (5)	C31–P1–C37	100.4 (5)	O5–C51–C52	108 (1)	C51–C52–N6	106.0 (9)
C31–P1–Ni	112.6 (3)	C37–P1–Ni	120.1 (4)	C62–C61–N6	107 (1)	N7–C62–C61	112 (1)
C41–P2–C39	103.3 (5)	C41–P2–C48	105.0 (5)	N7–C71–C72	111 (1)	C71–C72–N8	112 (1)
C41–P2–Ni	112.4 (3)	C39–P2–C48	104.1 (6)	N8–C81–C82	112 (1)	O9–C82–C81	110 (1)
C39–P2–Ni	121.5 (4)	C48–P2–Ni	109.1 (4)	O9–C91–C92	110 (1)	C91–C92–P1	120 (1)
C1–N1–Ni	168.0 (9)	C2–N2–Ni	175 (1)	C32–C31–C36	120.0	C33–C32–C31	120.0
N1–C1–S1	177 (1)	N2–C2–S2	176 (1)	C32–C33–C34	120.0	C35–C34–C33	120.0
C51–O5–C49	113 (1)	C82–O9–C91	114 (1)	C34–C35–C36	120.0	C35–C36–C31	120.0
C61–N6–C52	109.8 (9)	C62–N7–C71	119 (1)	C46–C41–C42	120.0	C41–C42–C43	120.0
C81–N8–C72	115 (1)	C32–C31–P1	116.8 (5)	C44–C43–C42	120.0	C43–C44–C45	120.0
C36–C31–P1	123.1 (6)	C38–C37–P1	113 (1)	C44–C45–C46	120.0	C41–C46–C45	120.0
C39–C38–C37	112 (1)	C38–C39–P2	114 (1)	N3–C3–S3	160 (2)	N4–C4–S4	177 (2)
C46–C41–P2	121.4 (7)	C42–C41–P2	118.5 (6)				

Table IV (Continued)

Torsion Angles for *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$[b]

δ Side-Chain Pocket

Ni-P2-C48-C49	52.46	g	C91-C92-P1-Ni	-38.65	-g	C51-C52-N6-C61	-167.52	a	C72-N8-C81-C82	-168.93	-a
P2-C48-C49-O5	-57.19	-g	O9-C91-C92-P1	55.61	g	C52-N6-C61-C62	-174.24	a	C71-C72-N8-C81	-174.78	a
C48-C49-O5-C51	-162.35	a	C82-O9-C91-C92	155.03	a	N6-C61-C62-N7	55.47	g	N7-C71-C72-N8	71.61	g
C49-O5-C51-C52	174.92	a	C81-C82-O9-C91	158.07	a	C61-C62-N7-C71	134.92	a	C62-N7-C71-C72	173.48	a
O5-C51-C52-N6	-58.10	-g	N8-C81-C82-O9	-66.60	-g						

Chelate Ring

P2-Ni-P1-C37	10.70	C39-P2-Ni-P1	-12.49	P1-C37-C38-C39	72.07	C37-C38-C39-P2	-77.52
Ni-P1-C37-C38	-37.89	C38-C39-P2-Ni	46.66				

[a] See Figures 1 and 2 for atom labels. Numbers in parentheses are estimated standard deviation(s) in the first figure(s) listed. [b] g = gauche; a = anti.

of isolating and characterizing both diastereoisomers in pure form. A diastereoisomeric mixture of prepurified [21]P_2O_5 was allowed to react with 1 equiv of $NiCl_2{\cdot}6H_2O$, leading to a reaction mixture containing *anti*- and *syn*-$\langle P_2NiCl_2|O_5\rangle$. The components of this mixture were separated by flash chromatography[22] on silica of their thiocyanate complexes, *anti*- and *syn*-$\langle P_2Ni(NCS)_2|O_5\rangle$, prepared by metathesis of the $NiCl_2$–oxaphosphand mixture with KSCN. With use of the protocol developed for the azaphosphand synthesis, cyanolysis of the nickelated oxaphosphand with aqueous cyanide solutions led to the uncomplexed [21]P_2O_5 ligands in very pure diastereomeric form.

The two [22]$P_2O_2N_3Ts_3$ diastereomers could be equilibrated to an equimolar mixture upon fusion of either the syn or the anti form. In both cases, inversion at the asymmetric phosphorus atoms leads to the same final mixture. In principle, several cycles of thermal isomerization followed by diastereomeric separation could be used to convert the original mixture largely into either the racemic or the meso diastereoisomer.

Detosylation of the Protected Azaphosphand Diastereomers. In order to render the tosylated azaphosphands capable of binding metals at both poles, various detosylation methods were attempted. Acid hydrolysis with concentrated H_2SO_4 at 95 °C[16b,35] resulted in the desired detosylation, but the phosphine stereochemistry was not retained. Also, since oxidation of the phosphine centers occurred quite readily in the case of the rather vulnerable *syn*-[22]$P_2O_2N_3Ts_3$, this approach was therefore abandoned. Instead, protecting tosyl groups were removed by reductive detosylation[39] through the addition of 6 equiv of NaNap in DME in the presence of 3 equiv of *tert*-butyl alcohol at −78 °C. This method is a modification of the published procedure that markedly improves the overall yield. The known tendency for sodium naphthalenide (NaNap) to cleave phosphorus–carbon bonds,[40] particularly those involving aryl substituents, was suppressed by using a low reaction temperature where the NaNap detosylation predominates. Three equivalents of *tert*-butyl alcohol was supplied as the proton source. Fortunately, the rate[39] of proton–NaNap (acid–base) neutralization was slow compared to the detosylation (electron-transfer) reaction rate at low temperature, facilitating this whole detosylation process. Analogous use of proton sources is well-known in the comparable Birch reductions[41] but, to our knowledge, has not been applied to cases such as the present one. An additional major advantage of the NaNap reductive cleavage step over other methods, apart from its efficiency and quantitative nature, is its ability to preserve anti and syn phosphine configurations.

Formation and Characterization of Ni, Pd, and Pt Complexes. Complexation of transition metals within the tosylated aza- and oxaphosphands was conveniently monitored by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopies. Reaction of *anti*- and *syn*-[22]$P_2O_2N_3Ts_3$ with $NiCl_2{\cdot}6H_2O$ gave rise to the brick red and red-orange complexes *anti*- and *syn*-$\langle P_2NiCl_2|N_3\rangle Ts_3$, respectively (vide supra). Both these nickel species are paramagnetic and give rise to broadened signals in the $^{31}P\{^1H\}$ NMR spectra. An X-ray structure determination[42] was performed for a dark red crystal of *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$, grown by slow evaporation of a dichloromethane solution. In the latter stages of refinement, however, it was not possible to model the disorder of the solvent molecules that were present in the lattice. The results clearly revealed, however, that the nickel atom in *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ is bonded to the diphosphine chelate and two chlorides to give a square-planar arrangement of atoms. A pseudooctahedral geometry is defined by close contacts between the nickel and ether oxygens of the macrocycle linker chain (Ni···O = 3.15 Å) (see Figure S1, supplementary material). The phenyl rings of the chelating diphosphine unit of the macrocycle are in the anti orientation with respect to the six-membered chelate ring.

The aza- and oxaphosphand ligands bind soft transition metals preferentially at the phosphine pole to form 1:1 complexes. The same reaction procedures were used for both aza- and oxaphosphand ligands to prepare species of formulas *anti*- and *syn*-$\langle P_2M(XY)|N_3\rangle Ts_3$ or *anti*- and *syn*-$\langle P_2M(XY)|O_5\rangle$, by simply reacting free ligand with the desired metal complex in a suitable solvent, specifically $NiCl_2{\cdot}6H_2O$, [Pd(COD)Cl_2], [Pt(COD)Cl_2], [Pt(COD)ClMe], [Pt(COD)Me_2], or [Pt(NCPh)$_2Cl_2$].

Although *anti*-[22]$P_2O_2N_3Ts_3$ and *anti*-[21]P_2O_5 metal complexes crystallize quite readily from various solvents, the syn complexes have thus far afforded only amorphous powders or fibers upon recrystallization. In most cases, the anti macrocyclic complexes were obtained with solvents of crystallization, which is rather typical of these types of molecules. This latter property of the anti tosylated azaphosphand, as mentioned above, complicated the X-ray structure determinations, but sufficient information could be obtained from diffraction data to enable valuable geometric details to be obtained.

The structure of *anti*-$\langle P_2PdCl_2|N_3\rangle Ts_3{\cdot}CH_3CN{\cdot}H_2O$ was fully solved,[43] and the molecular geometry is shown in Figure S2 (supplementary material). In this case, the palladium atom is in a distorted square-planar environment with two phosphorus and two chloride ligands in a cis geometry and the azaphosphand phenyl rings oriented to opposite sides of the main ring of the macrocycle. Deviations of the chlorides from the P_2Pd plane are substantial,[44] ±0.496 Å from that plane, and the dihedral angle between the $PdCl_2$ and P_2Pd planes is ~16°. These values may

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(42) The compound *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 13.465 (2) Å, b = 25.255 (8) Å, c = 19.530 (5) Å, β = 107.25 (2)°, V = 6343 Å^3, and Z = 4.

(43) The compound *anti*-$\langle P_2PdCl_2|N_3\rangle Ts_3{\cdot}CH_3CN{\cdot}H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 13.864 (2) Å, b = 34.218 (7) Å, c = 13.625 (4) Å, β = 116.77 (2)°, V = 5771 Å^3, and Z = 4; R_1 = 0.084 and R_2 = 0.113 for 3534 unique reflections.

(44) (a) For general discussion and some structure details of Pd(II) and Pt(II) complexes, see: Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973. (b) Such a deviation from planarity is rather rare (unknown for P_2MX_2 (M = Pd, Pt)). For example, see: Schneider, M. L.; Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1973**, 354–356.

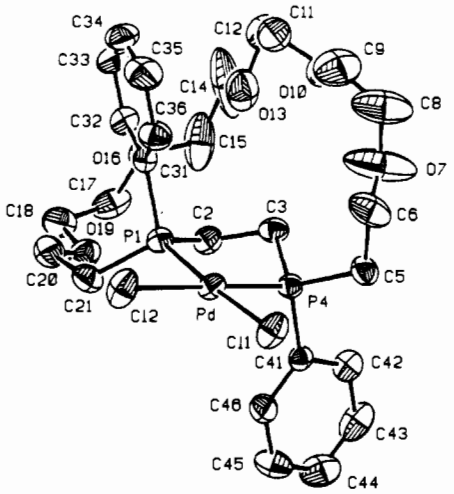

Figure 1. Molecular structure of *anti*-$\langle P_2PdCl_2|O_5\rangle$.

be compared to a value of ±0.312 Å for $[PdCl_2(dppp)]$.[45] We attribute the geometric deformation to the intramolecular repulsion with the linker chains. Close nonbonded contacts also exist at axial coordination sites involving Pd and O8 and O20 of the ether linkages.

In one instance, complexation between a diastereomeric mixture of $[21]P_2O_5$ and $[Pd(COD)Cl_2]$ in acetone–CH_2Cl_2 (3:1) solution afforded crystals of *anti*-$\langle P_2PdCl_2|O_5\rangle$ upon slow evaporation of the solvents. The molecular structure of this latter species, shown in Figure 1, contains a palladium atom in the center of an approximate square plane composed of the two phosphorus and two chloride atoms. The chloride atoms are in cis positions as required by the geometry of bidentate chelating diphosphine. The average deviation of atoms from the mean plane defined by Pd, Cl1, Cl2, P1, and P4 is only 0.05 Å. The range of C–C and C–O bond distances are those normally observed for crown ether complexes.[46] Further metrical details are given in Table IV.

Interestingly, the molecular structures of *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ or *anti*-$\langle P_2PdCl_2|N_3\rangle Ts_3$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$ represent the two distinct possible topologies for anti phosphand metal complexes, namely the inward form (endogenous) and outward form (exogenous) topologies. These two topologies describe the relative orientations of the metal coordination sphere towards or away from the second, vacant coordinating pocket of the macrocycle. Since the X-ray structures determined reveal the two different topological forms in the solid state, they do not necessarily reflect the only macrocyclic geometries adopted in solution.

Azaphosphand *anti*- or *syn*-$[22]P_2O_2N_3$, obtained in situ from the NaNap detosylation procedure, was relatively soluble in organic solvents. Various attempts were made to isolate the detosylated free ligand in different forms. For instance, white solids of HCl salts (very hygroscopic) and HBF_4 salts could be obtained; however, they exhibited considerable air sensitivity, and the materials obtained were not identified.

Addition of $NiCl_2·6H_2O$ in methanol to the diastereomeric mixture of azaphosphands prepared in situ afforded light yellow precipitates, subsequent protonation of which by excess $HBF_4·Et_2O$ led to *anti*- and *syn*-$\langle P_2NiCl_2|H_2N_3\rangle(BF_4)_2$. The affinity of Ni(II) for amine donors is well-known. As a result, initial binding of Ni(II) to the macrocycle is likely to include the amine sites, as implied by the characteristic yellow color of products. Addition of the strong Brønsted acid, i.e. $HBF_4·Et_2O$, switches the coordination exclusively to the phosphines, a transformation consistent with the HSAB (hard–soft and acid–base) principle,[47] where harder acid (H^+) and softer metal (Ni(II)) bind amine (hard) and phosphine (soft) donors, respectively.

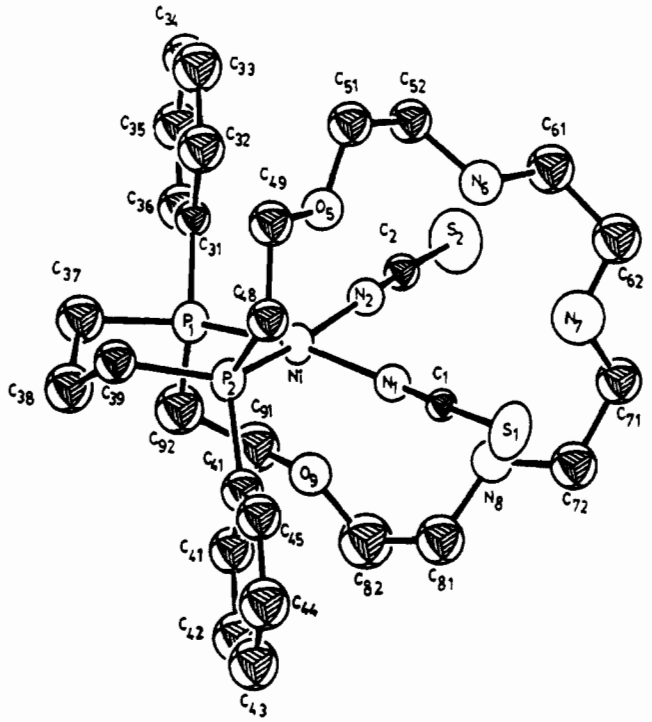

Figure 2. Molecular structure of *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$.

Thiocyanate metathesis of *anti*- and *syn*-$\langle P_2NiCl_2|H_2N_3\rangle(BF_4)_2$ led to very stable products, *anti*- and *syn*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$. The molecular structure of *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ is presented in Figure 2. Individual bond lengths, angles and torsion angles are listed in Table IV. A notable feature of this structure is the double protonation of the triamine pole, a preference reflecting the pK_a values for polyamine macrocycles.[48] Presumably, electrostatic repulsion between ammonium centers is the primary reason preventing full protonation, since excess acid was used. The $\{NiP_2N_2\}^{2+}$ coordination unit encapsulated by the macrocyclic ligand can be regarded as having endogenous, or inward, topology. The nickel atom is in the center of a distorted square composed of two phosphorus and two nitrogen atoms, a common geometry for nickel(II) bis(phosphine) complexes. The deviations of atoms N43 and N53 from the mean plane defined by NiP_1P_5 are 0.238 Å and −0.283 Å, respectively. The geometric deformation in the present structure appears to be dictated by the macrocycle side chains.

A novel aspect of the structure results from the fact that space group $P2_12_12_1$ has no center of symmetry. Thus, the compound *anti*-$\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ is an example whereby spontaneous resolution from a racemic mixture occurs upon crystallization. Although the absolute configuration of the crystal structure could not be determined, crystals were of a suitable size to allow polarimetry measurements to be made on individual crystals, following their separation by the method of Pasteur.[49] Optical rotations were determined on CH_3CN–CH_3OH (1:1) solutions prepared from 1-mg single crystals and found to be $[\alpha]^{25}_D = 15° \pm 2$ and $[\alpha]^{25}_D = -18° \pm 2$. Furthermore, the circular dichroism spectra of these individual crystals were mirror images of one another, confirming the occurrence of two optical isomers.

Summary. Synthetic routes have been developed for the stepwise formation of the asymmetric aza- and oxaphosphand macrocycles *anti*- and *syn*-$[22]P_2O_2N_3Ts_3$, *anti*- and *syn*-$[22]P_2O_2N_3$, and *anti*- and *syn*-$[21]P_2O_5$. Procedures for separating ligand diastereoisomers by metal complexation–decomplexation steps are described. The utility of these and related ligands for the bimetallic activation of substrates relevant to both homo- and heterogeneous catalysis is currently being investigated.

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A particularly novel approach to the detosylation of protected amines was also demonstrated. Low-temperature NaNap reductive cleavage of amine-sulfonamide bonds *in the presence of alcohol* was found to be quite efficient and quantitative. In addition, preservation of the diastereomeric integrity of the detosylated species was maintained, and no oxidation of the vulnerable phosphine atoms was observed. Several Ni^{II}, Pd^{II}, and Pt^{II} complexes were prepared and characterized. A subsequent paper will demonstrate that two metals may be incorporated within the azaphosphands to create Pt-Cu bimetallic species.[50]

(50) Bell, A.; Gibson, D.; Lippard, S. J. Unpublished results.

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Supplementary Material Available: Listings of hydrogen atom positional and thermal parameters (Tables S1 and S5) and non-hydrogen atom thermal parameters (Tables S2 and S4) for $\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$ and ORTEP diagrams for *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ and *anti*-$\langle P_2PdCl_2|N_3\rangle Ts_3 \cdot CH_3CN \cdot H_2O$ (Figures S1 and S2) (6 pages); listings of observed and calculated structure factors (Tables S3 and S6) for $\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$ (25 pages). Ordering information is given on any current masthead page.

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Infrared Matrix Isolation Studies of Molecular Interactions: Complexes of Trichlorosilane, $HSiCl_3$, with Selected Bases

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The matrix isolation technique and twin-jet deposition have been employed to isolate and characterize the reaction products of the codeposition of trichlorosilane with bases containing nitrogen and oxygen donor atoms. The infrared spectra of these initial reaction products indicate that a complex is formed in which the donor atom of the base interacts with the silicon center on $HSiCl_3$. These complexes were characterized by a blue shift of the Si-H stretching mode and red shifts for the Cl-Si-H bending and Si-Cl stretching modes. In addition, the Si-N stretching mode in the complex was identified near 700 cm^{-1} for the amine complexes. Also, when the amines were codeposited with $HSiCl_3$, a red-shifted and broadened Si-H stretching mode was detected, providing tentative evidence for a second, isomeric form of the complex. In this complex, the nitrogen of the base is weakly hydrogen-bonded to the Si-H bond of $HSiCl_3$. Attempts to isolate analogous complexes of CH_3SiCl_3 were unsuccessful, in accord with the results of earlier studies.

Introduction

The chemical reactions of trichlorosilane, $HSiCl_3$, are very sensitive to the solvent.[1] Consequently, there is interest in a complete characterization of the intermolecular interactions of this species with electron donors. By analogy with chloroform, which is well-known[2-5] to serve as a proton donor in hydrogen-bonding interactions with strong bases, one might anticipate hydrogen-bond formation involving the Si-H bond. Also, several studies have demonstrated the stability of the $SiCl_3^-$ anion in both the gas phase and in solution.[6,7] Consequently, trichlorosilane may have some ability to act as a proton donor, although the increased metallic character and lower electronegativity of silicon relative to carbon weakens this analogy. In any event, the role of the Si-H bond in hydrogen bonding is not well established, although this bond is a very important moiety in organosilicon chemistry.

Voronkov and Lebedeva[8,9] have investigated the intermolecular interactions in solutions of halosilane hydrides. In these binary systems, three types of interactions were found: (1) the formation of a hydrogen bond involving the Si-H bond to ethers and ketones; (2) coordination of the solvent molecules to the silicon center on the silane; (3) dipole-dipole interactions. It is known[10-12] that $HSiCl_3$ is able to form complexes with nitrogen-containing bases in solution, and researchers have preferred[13-15] to invoke a three-center interaction rather than formation of a coordinate bond or a hydrogen bond. In addition, it has been reported that a number of halosilanes[16,17] serve as Lewis acids and form five-coordinate complexes with medium-to-strong bases. The interaction of a strong base with $HSiCl_3$ might be through hydrogen bonding to the Si-H bond, coordination to the central Si, or formation of a three-center interaction.

Infrared spectroscopy has emerged as one of the most effective experimental tools for the study of hydrogen bonding, in that hydrogen-bond formation gives rise to distinct, readily identifiable spectral features.[2] The matrix isolation technique[18-20] has been used often for the study of weakly bound, intermediate complexes,[21-23] including hydrogen-bonded complexes.[24-29] Matrix

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