Inorg. Chem. **1992**, *31*, 1411–1416

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Metal Template Synthesis of a 14-Membered *trans*-P_2S_2 Chelating Macrocycle

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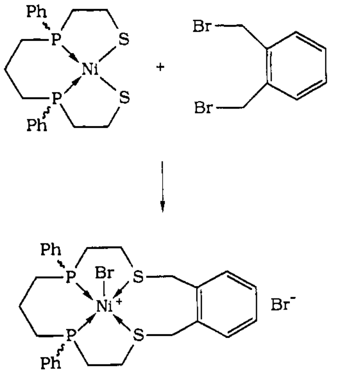
The R^*,R^* and R^*,S^* forms of the 14-membered *trans*-P_2S_2 chelating macrocycle 5,6,7,9,14,15,16,18-octahydro-5,14-dimethyldibenzo[*e,l*][1,8,4,11]dithiadiphosphacyclotetradecin have been isolated in low yields from the dimerization of deprotonated (±)-(2-mercaptoethyl)(2-methoxybenzyl)methylphosphine on platinum(II) in the presence of boron tribromide. The crystal structure of the monoacetone solvate of the nickel(II) perchlorate derivative of the R^*,R^* diastereomer of the macrocycle has been determined. Crystal data for $C_{23}H_{32}Cl_2NiO_9P_2S_2$: monoclinic, $P2_1/n$, $a = 8.988$ (1) Å, $b = 23.660$ (3) Å, $c = 14.257$ (2) Å, $\beta = 94.15$ (1)°, $Z = 4$, and $R = 0.040$. The complex is formed stereoselectively with the relative helicities of the four chiral donor stereocenters being R^*_P, R^*_P, S^*_S, and S^*_S because of exo coordination of the nickel(II) ion to the macrocyclic ring. The byproducts of the metal-template synthesis are seven-membered (±)-2-methyl-2-phospha-5-thiabicyclo[5.4.0]undeca-1(7),8,10-triene and its boron tribromide adduct; the latter is the principal product of the reaction, and its crystal structure has been determined. Crystal data for $C_{10}H_{13}BBr_3PS$: monoclinic, $P2_1/c$, $a = 14.200$ (2) Å, $b = 17.074$ (3) Å, $c = 13.429$ (2) Å, $\beta = 113.14$ (1)°, $Z = 8$, and $R = 0.038$.

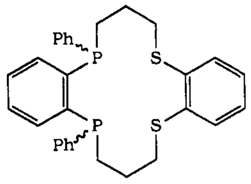
Introduction

The first macrocyclic complex containing phosphorus donors was prepared in 1970, according to eq 1.[1]



(1)

Since then a number of other *cis*- and *trans*-P_2S_2 macrocycles have been prepared, including 14-membered **1**–**3**.[2,3]



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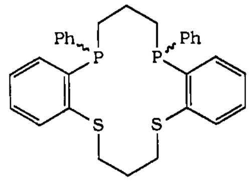

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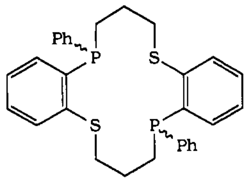
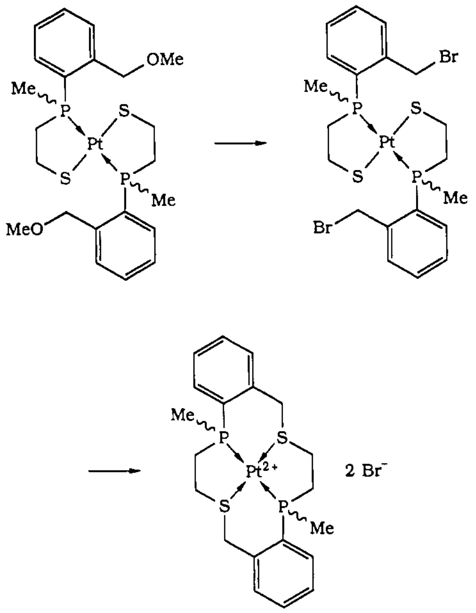
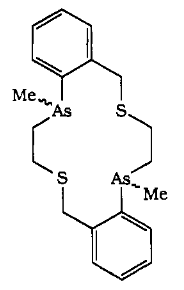


3

Scheme I



Compounds **1** and **2** behave as quadridentates for bivalent nickel, palladium, and platinum, giving complexes with stereochemistries between square-planar and trigonal-bipyramidal depending upon the relative helicities of the two chiral phosphorus stereocenters present,[4] viz. R^*,R^* or R^*,S^*. Unexpectedly, **3** did not function as quadridentate for the metal ions tried, preferring instead to chelate as a bidentate through the phosphorus donors. We have shown that the metal-template strategy can be used for the stereoselective dimerization of appropriate deprotonated 2-mercaptoethyl-substituted tertiary arsines on palladium(II) giving the 14-membered *trans*-As_2S_2 macrocycle **4** in diastereomerically homogeneous or optically pure forms with racemic or optically active (±)-AsS substrates (Figure 1).[5]



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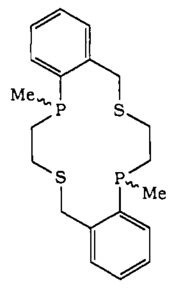

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The diastereomers and enantiomers of similar *trans*-As_2N_2 macrocycles have also been prepared by dimerizations of (±)-AsN substrates.[6]

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[1] Marty, W.; Schwarzenbach, G. *Chimia* **1970**, *24*, 431.

[2] Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S.; McPaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *22*, 1875. Kyba, E. P.; Chou, S.-S. P. *J. Org. Chem.* **1981**, *46*, 860.

[3] Kyba, E. P.; Clubb, C. N.; Larson, S. B.; Schueler, V. J.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 2141.

[4] Kyba, E. P.; Davis, R. E.; Fox, M. A.; Clubb, C. N.; Lui, S.-T.; Reitz, G. A.; Schueler, V. J.; Kashyap, R. P. *Inorg. Chem.* **1987**, *26*, 1647.

[5] Kerr, P. G.; Leung, P.-H.; Wild, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 4321.

[6] Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346.

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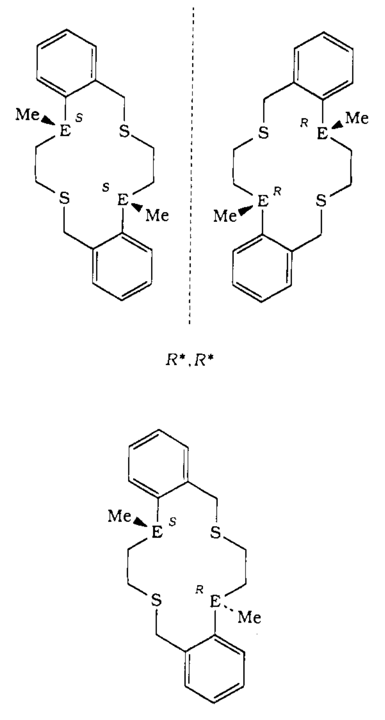
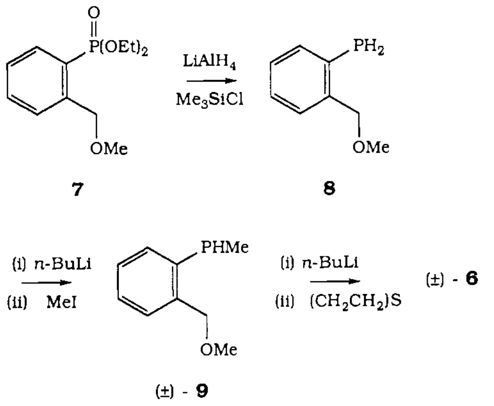


*R**,*R**

*R**,*S**

Figure 1. Diastereomers of **4** (E = As) and **5** (E = P).

Scheme II

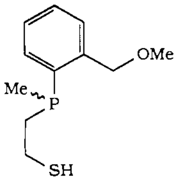


In this paper we report the metal-template synthesis of the *trans*-P_2S_2 macrocycle **5** on platinum(II), according to Scheme I.

Results

The various aspects of the work will be introduced in the sections that follow.

(a) Synthesis of Macrocycle Precursor Ligand (±)-6. The phosphine–thiol (±)-**6** was prepared from the phosphate ester **7** in three steps, as indicated in Scheme II. The key compound **7** was obtained by an Arbusov–Michaelis-type reaction involving 2-bromobenzyl methyl ether and triethyl phosphite in the presence of anhydrous nickel(II) chloride.[7] Compound **7**, when treated with lithium aluminum hydride in the presence of trimethylsilyl chloride,[8] gave the primary phosphine **8**, which, in two steps, was converted into the desired light-sensitive[9] phosphine–thiol (±)-**6**, a colorless oil, bp 98–100 °C (0.05 mmHg).



(±) - **6**

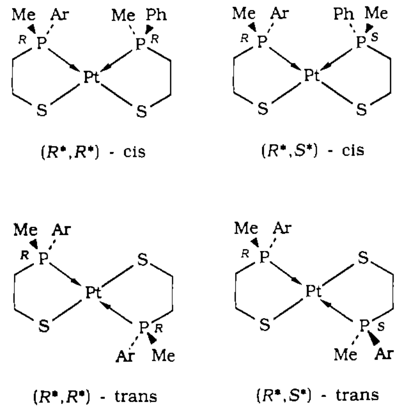
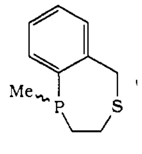


Figure 2. Diastereomers of [Pt(PS)$_2$] (**10**). *R* enantiomers of *R**,*R** are diastereomers depicted.

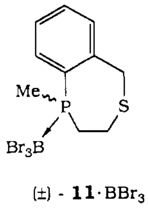
(b) Synthesis of Macrocycle Precursor Complex 10. The reaction of (±)-**6** with an aqueous alkaline solution of potassium tetrachloroplatinate(II) afforded the complex [Pt(PS)$_2$] (**10**) as a mixture of four diasteromers with relative amounts 1:1:3:4 (*R**,*R**)-*cis*/(*R**,*S**)-cis/(*R**,*R**)-*trans*/(*R**,*S**)-*trans* (Figure 2).[10] The proportions of the diastereomers did not change over 48 h at 25 °C in CD_2Cl_2. When dissolved in dichloromethane and diluted with diethyl ether, the initial mixture of diastereomers yielded lemon crystals of (*R**,*R**)-*trans*- and (*R**,*S**)-*trans*-**10** as an equimolar mixture (ca. 40% yield). (A small quantity of the pure (*R**,*R**)-*trans*-**10** was obtained by a further recrystallization of the equimolar mixture.)

(c) Cyclization of (*R,*R**)-*trans*/(*R**,*S**)-*trans*-10.** Treatment of the equimolar mixture of the *trans*-[Pt(PS)$_2$] complexes in dichloromethane with 6 equiv of boron tribromide, followed by stirring of the reaction mixture for 2 h at 20 °C and for a further 16 h at 40 °C, resulted in ca. 84% cyclization at sulfur. The phosphine products were isolated by treating the reaction mixture with aqueous hydroxide, followed by aqueous potassium cyanide, and extracting the aqueous layer with dichloromethane. The phosphines were then separated by column chromatography on a silica gel plate with dichloromethane–*n*-hexane as eluent. Four fractions were collected; the products were isolated and identified as described below.

(±)-2-Methyl-2-phospha-5-thiabicyclo[5.4.0]undeca-1(7),8,10-triene ((±)-11). The first fraction to be eluted from the plate contained 7-membered (±)-**11** having mp 79–81 °C (6% yield). The monomeric formulation of the compound was confirmed by a molecular weight determination in dichloromethane.



(±) - **11**



(±) - **11**·BBr_3

(9*R,18*S**)-5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin ((*R**,*S**)-5).** The second fraction collected contained the meso diastereomer of the desired *trans*-P_2S_2 macrocycle, (*R**,*S**)-**5**, which was isolated as colorless needles of the 0.25 dichloromethane solvate from dichloromethane, mp 202–204 °C. The yield was 0.5%. The

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[7] Tavs, P. *Chem. Ber.* **1970**, *103*, 2428.

[8] Kyba, E. P.; Liu, S.-T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.

[9] Leung, P.-H.; Willis, A. C.; Wild, S. B. *Inorg. Chem.*, previous paper in this issue.

[10] Leung, P.-H.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3396.

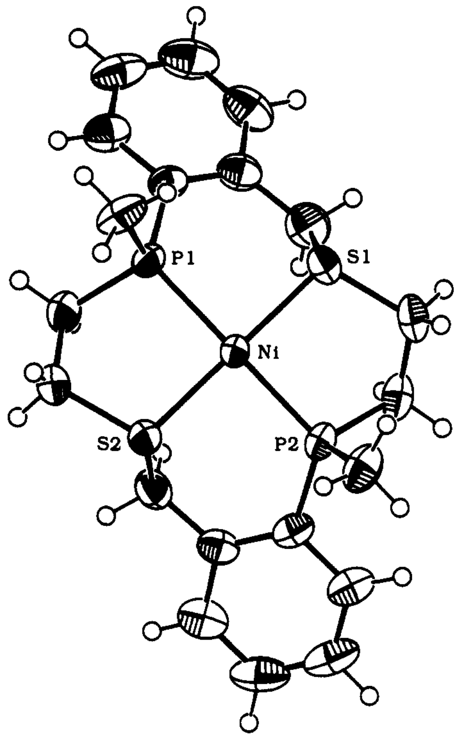
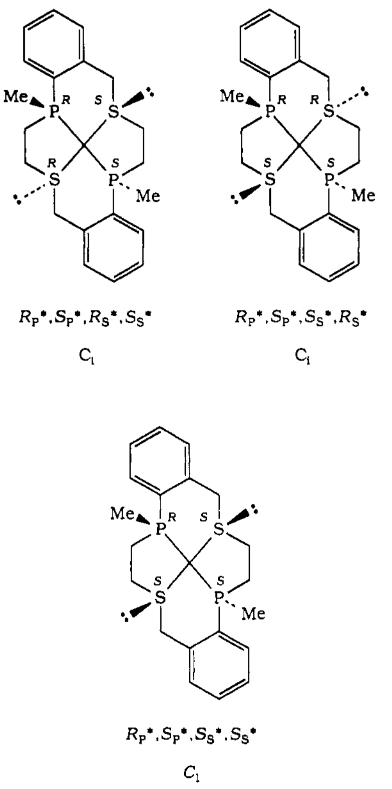


Figure 3. ORTEP view of the cation of [Ni{(R^*,R^*)-**5**}]$(ClO_4)_2$·Me_2CO, showing the atom-labeling scheme for selected non-hydrogen atoms. The *R* enantiomer of the racemate is depicted. Thermal ellipsoids enclose 35% probability levels.



R_P^*,S_P^*,R_S^*,S_S^* C_i

R_P^*,S_P^*,S_S^*,R_S^* C_i

R_P^*,S_P^*,S_S^*,S_S^* C_1

Figure 4. Diastereomers of [Ni{(R^*,S^*)-**5**}]$^{2+}$. One enantiomer of the C_1 diastereomer is shown.

Table I. Crystallographic Data for [Ni{(R^*,R^*)-**5**}]$(ClO_4)_2$·Me_2CO and (±)-**11**·BBr_3

chem formula	$C_{23}H_{32}Cl_2NiO_9P_2S_2$	$C_{10}H_{13}BBr_3PS$
fw	708.12	446.77
space group	$P2_1/n$	$P2_1/c$
a, Å	8.988 (1)	14.200 (2)
b, Å	23.660 (3)	17.074 (3)
c, Å	14.257 (2)	13.429 (2)
β, deg	94.15 (1)	113.14 (1)
V, Å^3	3023.9	2993.9
Z	4	8
T, °C	25	20 ± 2
λ, Å	0.71069	0.71069
d_{calcd}, g cm^{-3}	1.555	1.982
μ, cm^{-1}	11.0	82.2
R, %	0.040	0.038
R_w, %	0.043	0.039

Table II. Final Positional Parameters for [Ni{(R^*,R^*)-**5**}]$(ClO_4)_2$·Me_2CO

atom	*x/a*	*y/b*	*z/c*	U_{eq},[a] Å^2
Ni	0.52440 (7)	0.14745 (3)	0.14783 (5)	0.0337 (4)
S(1)	0.5092 (2)	0.23576 (6)	0.1827 (1)	0.0437 (9)
S(2)	0.5422 (2)	0.05844 (6)	0.1144 (1)	0.0412 (9)
P(1)	0.7041 (2)	0.16718 (6)	0.0591 (1)	0.0378 (9)
P(2)	0.3748 (2)	0.12722 (6)	0.2559 (1)	0.0381 (8)
C(1)	0.6920 (7)	0.2510 (3)	0.2408 (5)	0.062 (4)
C(2)	0.8151 (6)	0.2562 (2)	0.1757 (4)	0.049 (4)
C(3)	0.9245 (8)	0.2974 (3)	0.1986 (5)	0.066 (5)
C(4)	1.0484 (8)	0.3033 (3)	0.1502 (6)	0.077 (5)
C(5)	1.0689 (7)	0.2679 (3)	0.0760 (6)	0.065 (5)
C(6)	0.9639 (6)	0.2275 (3)	0.0502 (4)	0.052 (4)
C(7)	0.8366 (6)	0.2211 (2)	0.0994 (4)	0.038 (3)
C(8)	0.6466 (7)	0.1862 (3)	−0.0602 (4)	0.062 (4)
C(9)	0.8067 (6)	0.1009 (3)	0.0550 (5)	0.055 (4)
C(10)	0.6982 (7)	0.0535 (2)	0.0391 (5)	0.061 (4)
C(11)	0.6186 (6)	0.0283 (2)	0.2249 (4)	0.047 (4)
C(12)	0.5026 (6)	0.0195 (2)	0.2947 (4)	0.043 (4)
C(13)	0.5016 (7)	−0.0314 (3)	0.3412 (5)	0.062 (4)
C(14)	0.4050 (9)	−0.0426 (3)	0.4102 (5)	0.072 (5)
C(15)	0.3079 (8)	−0.0020 (3)	0.4326 (4)	0.066 (5)
C(16)	0.3013 (7)	0.0497 (3)	0.3873 (4)	0.053 (4)
C(17)	0.3994 (6)	0.0608 (2)	0.3181 (4)	0.042 (3)
C(18)	0.1810 (6)	0.1298 (3)	0.2143 (4)	0.058 (4)
C(19)	0.4019 (7)	0.1847 (3)	0.3401 (4)	0.053 (4)
C(20)	0.3972 (7)	0.2397 (3)	0.2841 (4)	0.056 (4)
Cl(1)	0.2417 (2)	0.11830 (6)	0.9459 (1)	0.0475 (9)
O(1)	0.1703 (5)	0.0759 (2)	0.9979 (3)	0.067 (3)
O(2)	0.3536 (6)	0.0928 (2)	0.8948 (4)	0.097 (4)
O(3)	0.1304 (6)	0.1450 (2)	0.8849 (3)	0.097 (4)
O(4)	0.3095 (4)	0.1597 (2)	1.0088 (3)	0.063 (3)
Cl(2)	0.1220 (2)	0.87082 (9)	0.6039 (1)	0.069 (1)
O(5)	0.0028 (8)	0.8353 (3)	0.5839 (5)	0.142 (6)
O(6)	0.2419 (7)	0.8587 (3)	0.5527 (5)	0.151 (6)
O(7)	0.0765 (7)	0.9274 (3)	0.5860 (5)	0.135 (5)
O(8)	0.1634 (7)	0.8670 (2)	0.7025 (4)	0.107 (4)
C(21)	−0.016 (1)	0.9084 (4)	0.3284 (8)	0.130 (9)
C(22)	0.086 (1)	0.9158 (4)	0.2536 (8)	0.095 (7)
C(23)	0.076 (1)	0.9704 (4)	0.2049 (6)	0.104 (7)
O(9)	0.1685 (8)	0.8797 (3)	0.2350 (6)	0.162 (6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

macrocycle formed a bright orange derivative with nickel(II) perchlorate, but the crystals were unsuitable for X-ray crystallography. The ^1H NMR spectrum of the complex in dimethyl sulfoxide-d_6 contained a singlet P*Me* resonance at δ 2.10 with $^2J_{PH}$ = 3.2 Hz, and in the ^{31}P NMR spectrum of the complex, a singlet resonance at δ 57.2 was observed. There are three possible diastereomers of the square-planar complex [Ni{(R^*,S^*)-**5**}]$(ClO_4)_2$ (Figure 4); the NMR data are consistent with the presence of either of the two centrosymmetrical diastereomers. The arsenic ligand (R^*,S^*)-**4** forms a similar palladium(II) complex that crystallizes as conglomerate or as a compound of the two centrosymmetrical diastereomers.[5,11]

(9R^*,18R^*)-5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin ((R^*,R^*)-5). The racemic diastereomer of the macrocycle was the third compound to be eluted from the thin-layer plate; it was isolated in 1% yield as colorless needles having mp 141–143 °C. The macrocycle reacted with nickel(II) perchlorate in acetone to give

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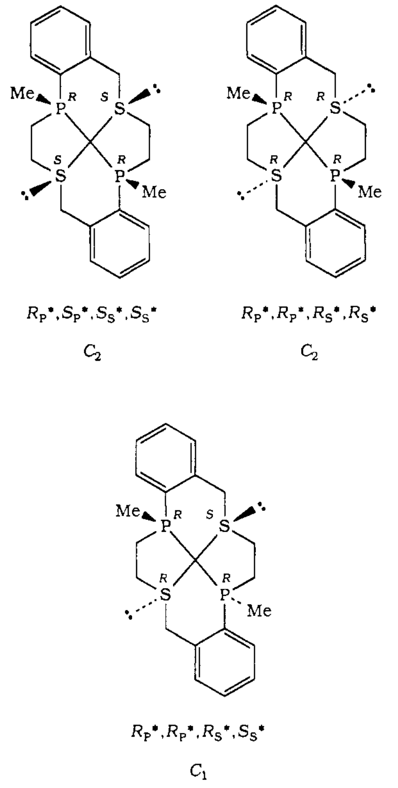
(11) Harrowfield, J. M.; Patrick, J. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 159.

Table III. Selected Bond Distances and Angles

[Ni{(R^*,R^*-**5**}](ClO_4)$_2$·Me_2CO		($\pm$)-**11**·BBr_3^{a}	
	Bond Lengths (Å)		
Ni-P(1)	2.173 (2)	P-B	1.954, 1.952 (9)
Ni-P(2)	2.171 (2)	P-C(1)	1.824, 1.813 (8)
Ni-S(1)	2.154 (2)	P-C(2)	1.809, 1.803 (9)
Ni-S(2)	2.168 (2)	P-C(3)	1.807, 1.799 (7)
	Bond Angles (deg)		
P(1)-Ni-S(1)	89.31 (6)	B-P-C(1)	111.2, 110.8 (4)
P(1)-Ni-S(2)	90.62 (6)	B-P-C(2)	112.8, 112.3 (4)
P(1)-Ni-P(2)	170.15 (6)	B-P-C(3)	109.7, 109.8 (4)
P(2)-Ni-S(1)	89.84 (6)	C(1)-P-C(2)	111.3, 111.1 (4)
P(2)-Ni-S(2)	90.08 (6)	C(1)-P-C(3)	105.3, 104.9 (4)
S(1)-Ni-S(2)	179.17 (7)	C(2)-P-C(3)	106.1, 107.6 (4)

^{a}Two independent molecules in crystallographic asymmetric unit.



R_P^*,S_P^*,S_S^*,S_S^*
C_2

R_P^*,R_P^*,R_S^*,R_S^*
C_2

R_P^*,R_P^*,R_S^*,S_S^*
C_1

Figure 5. Diastereomers of [Ni{(R^*,R^*)-**5**}]$^{2+}$. One enantiomer of each diastereomer is depicted.

Table IV. Final Positional Parameters for ($\pm$)-**11**·BBr_3

atom	x/a	y/b	z/c	U_{eq},^{a} Å^2
P(1)	0.2315 (1)	0.7786 (1)	0.8323 (1)	0.0336 (8)
C(1)	0.1112 (6)	0.7746 (5)	0.7160 (6)	0.050 (3)
C(11)	0.2196 (5)	0.8578 (4)	0.9159 (5)	0.034 (3)
C(12)	0.1240 (6)	0.8712 (4)	0.9165 (6)	0.046 (3)
C(13)	0.1078 (6)	0.9303 (5)	0.9782 (7)	0.053 (4)
C(14)	0.1880 (7)	0.9774 (4)	1.0392 (6)	0.053 (4)
C(15)	0.2843 (6)	0.9654 (4)	1.0401 (6)	0.047 (4)
C(16)	0.3018 (5)	0.9052 (4)	0.9787 (5)	0.037 (3)
C(17)	0.4079 (6)	0.8947 (4)	0.9832 (6)	0.044 (3)
S(1)	0.4296 (2)	0.9391 (1)	0.8718 (2)	0.057 (1)
C(18)	0.3381 (6)	0.8869 (4)	0.7589 (6)	0.047 (4)
C(19)	0.3277 (5)	0.8004 (4)	0.7778 (6)	0.040 (3)
B(1)	0.2583 (6)	0.6777 (5)	0.9069 (7)	0.038 (4)
Br(11)	0.39971 (6)	0.67794 (5)	1.02370 (7)	0.0531 (4)
Br(12)	0.24727 (8)	0.59617 (5)	0.79600 (8)	0.0671 (5)
Br(13)	0.15185 (6)	0.66093 (5)	0.96746 (7)	0.0528 (4)
P(2)	0.2474 (1)	0.3015 (1)	0.2636 (1)	0.0373 (8)
C(2)	0.3300 (6)	0.2966 (5)	0.4049 (6)	0.060 (4)
C(21)	0.3097 (5)	0.3619 (4)	0.1975 (6)	0.042 (3)
C(22)	0.4159 (6)	0.3537 (5)	0.2325 (7)	0.056 (4)
C(23)	0.4718 (7)	0.3978 (6)	0.1876 (9)	0.074 (5)
C(24)	0.4210 (9)	0.4479 (6)	0.1065 (9)	0.082 (6)
C(25)	0.3174 (8)	0.4571 (5)	0.0701 (7)	0.065 (5)
C(26)	0.2597 (6)	0.4145 (4)	0.1135 (6)	0.047 (4)
C(27)	0.1455 (7)	0.4251 (5)	0.0664 (6)	0.059 (4)
S(2)	0.0958 (2)	0.4879 (1)	0.1434 (2)	0.061 (1)
C(28)	0.1376 (6)	0.4368 (5)	0.2707 (7)	0.064 (4)
C(29)	0.1309 (5)	0.3473 (5)	0.2601 (6)	0.047 (3)
B(2)	0.2196 (7)	0.1961 (5)	0.2027 (7)	0.046 (4)
Br(21)	0.12243 (6)	0.20492 (5)	0.04689 (6)	0.0530 (4)
Br(22)	0.15446 (7)	0.13667 (5)	0.28794 (8)	0.0673 (4)
Br(23)	0.35207 (7)	0.14778 (6)	0.21661 (9)	0.0745 (5)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

an orange complex that crystallized from dimethyl sulfoxide as a bis(dimethyl sulfoxide) solvate. From acetone, a mono(acetone) solvate was isolated; this compound crystallized in a form suitable for X-ray structural analysis (Figure 3). Crystal data for [Ni{(R^*,R^*)-**5**}](ClO_4)$_2$·Me_2CO are given in Table I, and Table II lists positional parameters employing the atom-numbering scheme of Figure 1 of the supplementary material. Table III lists the most important bond distances and angles in the complex. The sulfur stereocenters in the complex are pyramidal with the free lone pairs on the sulfur atoms lying on the same side of the square-plane as the methyl groups on the phosphorus atoms. The relative absolute configuration of the four donor stereocenters in the complex is thus R^*_P,R^*_P,S^*_S,S^*_S (Figure 5). This configuration of the macrocycle permits coordination of metal ions outside of the macrocycle cavity in a pyramidal arrangement. The arsenic analogue, (R^*,R^*)-**4**, forms a palladium(II) complex of the same stereochemistry as the kinetic product of the template synthesis, which was shown subsequently to be the thermodynamically most stable of the three possible diastereomers of the complex.[5,8] It appears that the R^*_P,R^*_P,S^*_S,S^*_S stereochemistry for [Ni{(R^*,R^*)-**5**}](ClO_4)$_2$·Me_2CO is retained in solution. Thus, a singlet P*Me* resonance at δ 2.10 ($^2J_{PH}$ = 3.2 Hz) was observed for the complex in dimethyl sulfoxide-d_6, and in the ^{31}P NMR spectrum in the same solvent, a peak at δ 42.66 was observed. It is noteworthy that the *exo coordination* of metal ions by 14-membered macrocyclic quadridentates is *necessarily* stereoselective. Thus, (R^*,R^*)-**4** forms a platinum(II) complex of similar stereochemistry, as does 1,4,8,11-tetrathiacyclodecane (and its 6,6,13,13-tetramethyl derivative) with rhodium(II)[12] and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane with nickel(II).[13]

($\pm$)-2-Methyl-2-phospha-5-thiabicyclo[5,4,0]undeca-1(7),8,10-triene–Boron Tribromide (($\pm$)-11·BBr_3). When the plate was eluted with neat dichloromethane, the adduct ($\pm$)-**11**·BBr_3 was obtained. This compound was the principal product of the synthesis, being isolated in 76% yield as colorless plates; it was also prepared by adding boron tribromide to ($\pm$)-**11** and by treating the precursor platinum complex with a large excess of boron tribromide. The adduct is remarkably stable and can be recovered unchanged from dichloromethane solution after exposure to 2 M NaOH. The crystal structure of ($\pm$)-**11**·BBr_3 has been determined (Figure 6); crystal data are given in Table I, and Table IV lists positional parameters employing the atom-labeling scheme of Figure 2 of the supplementary material. Table III lists the most important bond distances and angles in the compound.

At least 6 equiv of boron tribromide was necessary for the formation of the macrocycle from the precursor complex. When the stoichiometric quantity of boron tribromide was used in the reaction (2 equiv), the *benzyl alcohol* ($\pm$)-**12** was isolated in 57% yield.

Epimerization (R^*,R^*)-5 $\rightleftarrows$ (R^*,S^*)-5. When heated for 2 h at 160 °C, (R^*,R^*)-**5** (mp 141–143 °C) epimerizes at phosphorus; the melt crystallizes upon cooling with 6:4 (R^*,R^*)-**5**/(R^*,S^*)-**5**. This result is consistant with the relatively low barrier

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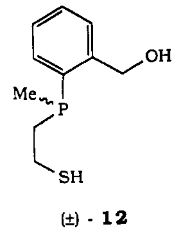

(±) - **12**

to inversion of tertiary phosphines (E_{inv} ca. 30 kcal mol^{-1}).[14] In a similar fashion, (R^*,R^*)- or (R^*,S^*)-**2**, when heated in boiling toluene for 3 h, undergoes epimerization at phosphorus with 3:7 (R^*,R^*-**2**/(R^*,S^*)-**2** being observed in the solidified melt.

Experimental Section

Preparations were carried out under an argon atmosphere; the phosphine–thiol (±)-**6** was stored in the dark. ^{1}H NMR spectra were recorded on Jeolco FX 200 and Bruker CXP 200 spectrometers; ^{31}P NMR spectra were recorded on Bruker CXP 200 and Varian VXR 300 S spectrometers. Elemental analyses were performed by staff within the Research School of Chemistry. Molecular weights were determined by the Signer method of isothermal distillation.[15]

Diethyl (2-(Methoxymethyl)phenyl)phosphinate (7). A mixture of 2-bromobenzyl methyl ether[16] (415 g, 2.0 mol) and anhydrous nickel(II) chloride (41 g) was heated at 155 °C for 30 min under an argon atmosphere. Triethyl phosphite (339 g, 2.0 mol) was then added slowly over 1 h. This mixture was heated with stirring at 155 °C for 40 h, and then it was cooled to 20 °C. The dark brown reaction mixture was distilled (0.20 mmHg) to give some byproducts (bp 50–90 °C), followed by the desired product, a colorless oil: bp 112–114 °C; yield 252 g (56%). Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.8; H, 7.4. Found: C, 55.8; H, 7.5. ^{1}H NMR ($CDCl_3$): δ 1.33 (t, 6 H, OCH_2*Me*), 3.47 (s, 3 H, OMe), 4.08–4.14 (m, 4 H, OC*H_2*Me), 4.79 (s, 2 H, benzyl CH_2), 7.33–7.98 (m, 4 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 18.38 (s).

(2-(Methoxymethyl)phenyl)phosphine (8). A suspension of $LiAlH_4$ (15.0 g) in diethyl ether (500 mL) was cooled to −78 °C and treated cautiously with Me_3SiCl (52.5 g). The mixture was allowed to warm to 20 °C, and then it was stirred for 2 h at that temperature, recooled to −78 °C, and treated with a solution of **7** (30.0 g, 0.12 mol) in diethyl ether (150 mL). This mixture was warmed to 20 °C and stirred for 36 h. After this period, the reaction mixture was cooled to 0 °C and treated cautiously with degassed water (120 mL). The gray solid that precipitated was separated by decantation and washed with dichloromethane (5 × 50 mL); the combined organic extracts were dried over $MgSO_4$ and distilled. The product was isolated as a colorless pyrophoric oil: bp 54 °C (0.05 mmHg); 13.6 g; 76% yield. Anal. Calcd for $C_8H_{11}OP$: C, 62.3; H, 7.2. Found: C, 61.8; H, 7.2. ^{1}H NMR ($CDCl_3$): δ 3.38 (s, 3 H, OMe), 3.88 (d, 2 H, $^2J_{PH}$ = 206 Hz, PH_2), 4.49 (s, 2 H, benzyl CH_2), 7.17–7.52 (m, 4 H, aromatics). ^{31}P NMR ($CDCl_3$): δ − 34.39 (s).

(±)-(2-(Methoxymethyl)phenyl)methylphosphine ((±)-(9)). A solution of **8** (52.5 g, 0.34 mol) in diethyl ether (400 mL) was cooled to −78 °C and treated with a solution of *n*-BuLi in *n*-hexane (212.8 mL, 1.6 M, 0.34 mol) with stirring. The mixture was then allowed to warm to 20 °C. The orange organophosphide solution was added dropwise to a solution of methyl iodide (21.25 mL, 48.34 g, 0.34 mol) in diethyl ether (250 mL) at −78 °C. Stirring was continued for a further 16 h at 20 °C. Water (200 mL) was then added to the mixture to extract the lithium iodide. The aqueous phase was separated and washed with dichloromethane (5 × 100 mL), and the combined organic fraction was dried ($MgSO_4$) and filtered. The slightly turbid oil that remained after evaporation of the filtrate was distilled to give the product as a colorless air-sensitive liquid: bp 55 °C (0.03 mmHg); 47.5 g (83% yield). ^{1}H NMR (CD_2Cl_2): δ 1.35 (d of d, 3 H, $^2J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7.5 Hz, PMe), 3.36 (s, 3 H, OMe), 4.14 (d of q, 1 H, $^2J_{PH}$ = 212 Hz, $^3J_{HH}$ = 7.6 Hz, PH), 4.49–4.57 (m, 2 H, benzyl CH_2), 7.12–7.52 (m, 4 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −79.36 (s).

(±)-1-Mercapto-2-[(2-(methoxymethyl)phenyl)methylphosphino]ethane ((±)-6). A solution of (±)-**9** (35.6 g, 0.21 mol) in diethyl ether (400 mL) was cooled to 78 °C and treated with a solution of *n*-BuLi in *n*-hexane (132 mL, 1.6 M, 0.21 mol). The mixture was then warmed to 20 °C and recooled to −78 °C before treating with a solution of ethylene sulfide (12.7 g, 0.21 mol) in diethyl ether (200 mL). The reaction mixture was warmed to room temperature and stirred for 2 h before being treated with a solution of ammonium chloride (15 g) in water (150 mL). The phases were separated, and the aqueous phase was washed with diethyl ether (3 × 100 mL). The combined organic fraction was dried ($MgSO_4$) and filtered, and the solvent was evaporated to give the crude product, which was purified by distillation. The desired product was obtained as a colorless air-sensitive liquid: bp 98–100 °C (0.05 mmHg); 42 g (87% yield). Anal. Calcd for $C_{11}H_{17}OPS$: C, 57.9; H, 7.5. Found: C, 55.8; H, 7.5. ^{1}H NMR (CD_2Cl_2): δ 1.30 (d, 3 H, $^2J_{PH}$ = 4.1 Hz, PMe), 1.54–1.72 (m, 1 H, SH), 1.89–2.11 (m, 2 H, PCH_2), 2.43–2.64 (m, 2 H, SCH_2), 3.39 (s, 3 H, OMe), 4.59–4.75 (m, 2 H, benzyl CH_2), 7.20–7.55 (m, 4 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −51.03 (s).

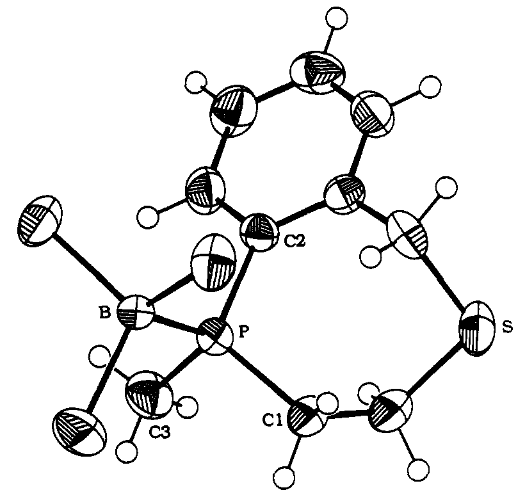

Figure 6. ORTEP view of **11**·BBr_3, showing the atom-labeling scheme for selected non-hydrogen atoms. The *R* enantiomer of the racemate is depicted. Thermal ellipsoids enclose 35% probability levels.

[*SP*-4-1-(R^*,R^*),(R^*,S^*)]/[*SP*-4-2-(R^*,R^*),(R^*,S^*)]-Bis[2-methyl(2-(methoxymethyl)phenyl)phosphino)ethanethiolato-*P*,*S*]platinum(II) ((R^*,R^*)-*trans*/(R^*,S^*)-*trans*-10; (R^*,R^*)-*cis*/(R^*,S^*)-*cis*-10). $K_2[PtCl_4]$ (2.23 g, 5.39 mmol) in water (30 mL) was added dropwise to a solution of (±)-**6** (2.46 g, 10.78 mmol) in ethanol (20 mL) containing 1 M NaOH (10 mL). After the mixture was stirred for 4 h, the solvent was removed from the reaction mixture, the residue was dissolved in dichloromethane (50 mL), and the solution washed with water (2 × 50 mL), dried ($MgSO_4$), and filtered. The crude product was obtained from the filtrate as a mixture of four diastereomers: yellow glass; mp 139–141 °C; 3.0 g (86% yield). Anal. Calcd for $C_{22}H_{32}O_2P_2PtS_2$: C, 40.7; H, 5.0; P, 9.5; S, 9.9. Found: C, 40.6; H, 5.0; P, 9.9; S, 10.2. ^{1}H NMR (CD_2Cl_2): δ 1.63–2.15 (m, 24 H, PMe), 2.15–2.86 (m, 32 H, CH_2CH_2), 3.39 (s, 6 H, OMe), 3.43 (s, 6 H, OMe), 3.44 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 4.75–5.44 (m, 16 H, benzyl CH_2), 6.95–7.82 (m, 32 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ 36.45 (t, $^1J_{PtP}$ = 2707 Hz), 37.07 (t,$^1J_{PtP}$ = 2713 Hz), 45.92 (t, $^1J_{PtP}$ = 2689 Hz), 46.14 (t, $^1J_{PtP}$ = 2670 Hz).

[*SP*-4-1-(R^*,R^*),(R^*,S^*)]-Bis[2-(methyl(2-(methoxymethyl)phenyl)phosphino)ethanethiolato-*P*,*S*]platinum(II) ((R^*,R^*)-*trans*/(R^*,S^*)-*trans*-10). The mixture of cis and trans diastereomers (see above) was dissolved in dichloromethane (20 mL), and the solution was diluted with diethyl ether. Upon standing, lemon yellow crystals separated; these were filtered off, washed with diethyl ether, and dried under high vacuum. The crystals consisted of an equimolar mixture of the (R^*,R^*)-*trans* and (R^*,S^*)-*trans* isomers of **10**: mp 162–164 °C, 0.87 g (25% yield). ^{1}H NMR (CD_2Cl_2): δ 1.88 (t, 6 H, PMe (R^*,R^*)-*trans*), 1.91 (t, 6 H, PMe (R^*,S^*)-*trans*), 1.99–2.85 (m, 16 H, CH_2CH_2), 3.43 (s, 6 H, OMe (R^*,R^*)-trans), 3.44 (s, 6 H, OMe (R^*,S^*)-*trans*), 4.75–5.44 (m, 8 H, benzyl CH_2), 7.37–7.83 (m, 16 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ 45.92 (t, $^1J_{PtP}$ = 2689 Hz, (R^*,S^*)-*trans*), 46.14 (t, $^1J_{PtP}$ = 2670 Hz, (R^*,R^*)-*trans*).

The solvent was removed from the mother liquor, the residue was dissolved in dichloromethane (10 mL), and the solution was diluted with diethyl ether. A second crop of yellow crystals, identical to those described above, separated: 0.51 g (15% yield). The crystalline fractions were combined and redissolved in dichloromethane (20 mL), and the solution was diluted with diethyl ether. Yellow crystals of the pure (R^*,R^*)-*trans* diastereomer separated: mp 172–174 °C, 0.21 g (15% yield). Anal. Calcd for $C_{22}H_{32}O_2P_2PtS_2$: C, 40.7; H, 5.0; P, 9.5; S, 9.9; Pt, 30.0. Found: C, 40.1; H, 5.1; P, 9.6; S, 9.8; Pt, 30.0. ^{1}H NMR (CD_2Cl_2): δ 1.88 (t, 6 H, PMe), 1.98–2.86 (m, 8 H, CH_2CH_2), 3.43 (s, 6 H, OMe), 4.75–5.45 (m, 4 H, benzyl CH_2), 7.36–7.81 (m, 8 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ 46.14 (t, $^1J_{PtP}$ = 2670 Hz).

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Cyclization of (*R,*R**)-*trans*/(*R**,*S*)-*trans*-10.** A 1:1 mixture of (*R**,*R**)-*trans*/(*R**,*S**)-*trans*-**10** (5.0 g, 7.7 mmol) was dissolved in dichloromethane (150 mL), and the solution was treated with BBr_3 (5.0 mL, 13.25 g, 7.0 equiv) over 5 min. The reaction mixture was stirred for 2 h at 20 °C and for another 16 h at 40 °C. At this stage, the mixture was cooled to room temperature and treated with aqueous NaOH (100 mL, 1 M) over 30 min, followed by a solution of KCN (5 g) in water (25 mL). The mixture was stirred for 1 h, and the colorless organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL), and the organic layers were combined and washed with water, dried ($MgSO_4$), and evaporated to dryness. The white glassy material that remained was subjected to radial thin-layer chromatography on silica gel (Merck 60 PF_{254}) with use of dichloromethane–*n*-hexane (1:3 v/v) as eluent, giving three products that were isolated and identified as follows.

(±)-2-Methyl-2-phospha-5-thiabicyclo[5.4.0]undeca-1(7),8,10-triene ((±)-11). The first fraction (R_f 0.6) contained (±)-**11**, which was isolated as a colorless oil that crystallized on standing: colorless needles; mp 79–81 °C; 0.090 g (6% yield). Anal. Calcd for $C_{10}H_{13}PS$: C, 61.2; H, 6.7; S, 16.3. Found: C, 60.2, H, 7.0; S, 16.2. ^1H NMR (CD_2Cl_2): δ 1.41 (d, 3 H, $^2J_{PH} = 3.17$ Hz, PMe), 1.87–2.06 (m, 2 H, SCH_2), 2.81–3.50 (m, 2 H, PCH_2), 3.62–4.35 (m, 2 H, benzyl CH_2), 7.06–7.31 (m, 4 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −31.97 (s). Mol wt (CH_2Cl_2): 194 (found), 196.2 (calcd).

(9*R,18*S**)-5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin–0.25-Dichloromethane ((*R**,*S**)-5·0.25CH_2Cl_2).** The second fraction to be eluted from the plate (R_f 0.5) contained the *R**,*S** diastereomer of the *trans*-P_2S_2 macrocycle: colorless needles of the 0.25 dichloromethane solvate after recrystallization from dichloromethane; mp 202–204 °C; 0.0145 g (0.5% yield). Anal. Calcd for $C_{20.25}H_{26.5}Cl_{0.5}P_2S_2$: C, 58.8; H, 6.5; S, 15.5. Found: C, 58.7; H, 6.8; S, 16.0. ^1H NMR (CD_2Cl_2): δ 1.20 (d, 6 H, $^2J_{PH} = 4.4$ Hz, PMe), 1.54–2.49 (m, 8 H, CH_2CH_2), 3.50–4.82 (m, 4 H, benzyl CH_2), 7.32–7.59 (m, 8 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −53.05 (s). Mol wt (CH_2Cl_2): 403 (found), 413.7 (calcd).

(9*R,18*R**)-5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin ((*R**,*R**)-5).** The *R**,*R** diastereomer of the macrocycle was obtained (R_f 0.3) as a colorless solid that crystallized from dichloromethane as colorless needles, mp 141–143 °C, 0.032 g (1% yield). Anal. Calcd for $C_{20}H_{26}P_2S_2$: C, 61.2; H, 6.7; S, 16.3. Found: C, 60.6; H, 7.1; S, 15.9. ^1H NMR (CD_2Cl_2): δ 1.18 (d, 6 H, $^2J_{PH} = 4.39$ Hz, PMe), 1.75–2.56 (m, 8 H, CH_2CH_2), 3.48–4.68 (m, 4 H, benzyl CH_2), 7.06–7.34 (m, 8 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −53.30 (s). Mol wt (CH_2Cl_2): 386 (found), 392.5 (calcd).

(±)-2-Methyl-2-phospha-5-thiabicyclo[5.4.0]undeca-1(7),8,10-triene–Tribromoboron(III) ((±)-11·BBr_3). The polarity of the eluent was increased (neat dichloromethane), whereupon (±)-**11**·BBr_3 was eluted (R_f 0.5) and subsequently isolated as a colorless powder that crystallized from dichloromethane as colorless prisms: 2.6 g (76% yield). Anal. Calcd for $C_{10}H_{13}BBr_3PS$: C, 26.9; H, 2.9; P, 6.9; S, 7.2; Br, 53.7. Found: C, 26.3; H, 2.9; P, 7.0; S, 7.1; Br, 53.4. ^1H NMR (CD_2Cl_2): δ 2.00 (d, $^2J_{PH} = 10.99$ Hz, 3 H, PMe), 2.61–3.21 (m, 4 H, CH_2CH_2), 3.65, 4.68 (AB q, $^1J_{HH} = 15.14$ Hz, 2 H, benzyl CH_2), 7.35–7.91 (m, 4 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ 1.22 (q, $^1J_{PB} = 148.5$ Hz). Mol wt (CH_2Cl_2): 455 (found), 446 (calcd).

(±)-1-Mercapto-2-[(2-(hydroxymethyl)phenyl)methylphosphino]ethane ((±)-12). Treatment of (*R**,*R**)-*trans*/(*R**,*S**)-*trans*-**10** with 2 equiv of BBr_3 resulted in the isolation of (±)-**12** as the major product. Compound (±)-**12** was eluted from the plate with the use of dichloromethane as a broad band from which the pure *benzyl alcohol* was obtained as a colorless oil in 57% yield. Anal. Calcd for $C_{10}H_{15}OPS$: C, 56.1; H, 7.1; S, 15.0. Found: C, 55.0; H, 7.0; S, 15.4. ^1H NMR (CD_2Cl_2): δ 1.23–1.48 (m, 4 H, PMe, SH), 1.89–2.14 (m, 2 H, PCH_2), 2.39–2.75 (m, 3 H, SCH_2, OH), 3.60–4.18 (m, 2 H, benzyl CH_2), 7.14–7.54 (m, 4 H, aromatics). ^{31}P NMR (CD_2Cl_2): δ −50.84 (s).

[*SP*-4-1-(1*R,8*R**,4*S**,11*S**)]-5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin-S^1,S^8,P^4,P^{11}]nickel(II) Perchlorate–2-Dimethyl Sulfoxide ([Ni{(*R**,*R**)-5}](ClO_4)$_2$·2Me_2SO).** A solution of (*R**,*R**)-**5** (0.006 g, 0.015 mmol) in dichloromethane (1 mL) was added dropwise to a solution of $[Ni(H_2O)_6]ClO_4)_2$ (0.005 g, 0.015 mmol) in acetone (1 mL). The solution immediately turned orange. During 30 min at room temperature the product separated as orange crystals. The pure product crystallized from dimethyl sulfoxide as orange rosettes of the bis(dimethyl sulfoxide) *solvate*: 0.007 g (78% yield); mp 258–262 °C. Anal. Calcd for $C_{24}H_{38}Cl_2NiO_8P_2S_4$: C, 35.7; H, 4.8; S, 15.9. Found: C, 34.5; H, 5.0; S, 15.2. ^1H NMR (Me_2SO-d_6): δ 2.10 (d, 6 H, $^2J_{PH} = 3.2$ Hz, PMe), 1.58–3.52 (m, 8 H, CH_2CH_2), 4.57–5.49 (m, 4 H, benzyl CH_2), 7.18–8.01 (m, 8 H, aromatics). ^{31}P NMR (Me_2SO-d_6): δ 42.66 (s).

[*SP*-4-1-[(4*R,11*S**)]-[5,7,8,9,14,16,17,18-Octahydro-9,18-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin-S^1,S^8,P^4,P^{11}]nickel(II) Perchlorate ([Ni{(*R**,*S**)-5}](ClO_4)$_2$).** A solution of (*R**,*S**)-**5**·0.25CH_2Cl_2 (0.018 g, 0.046 mmol) in dichloromethane (3 mL) was added dropwise to a solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.017 g, 0.046 mmol) in acetone (1 mL) with stirring. The solution immediately turned yellow. During 30 min at room temperature the product separated as fine yellow crystals. The pure product crystallized from acetonitrile as yellow needles: 0.025 g (92% yield); mp > 327 °C. Anal. Calcd for $C_{20}H_{26}Cl_2NiO_8P_2S_4$: C, 37.0; H, 4.0; S, 9.8. Found: C, 37.7; H, 4.1; S, 9.4. ^1H NMR (Me_2SO-d_6): δ 2.10 (d, H 6, $^2J_{PH} = 3.2$ Hz, PMe), 1.64–3.58 (m, 8 H, CH_2CH_2), 4.41–5.23 (m, 4 H, benzyl CH_2), 7.21–8.35 (m, 8 H, aromatics). ^{31}P NMR (Me_2SO-d_6): δ 57.2 (s).

Structural Analyses. Single crystals of [Ni{(*R**,*R**)-**5**}](ClO_4)$_2$·Me_2CO were obtained from acetone by slow evaporation of the solvent; the adduct **11**·BBr_3 crystallized from dichloromethane as prisms suitable for crystallography.

Computer Programs. Data reduction and refinement were performed with the program XTAL2.6.[16]

Registry No. (*R**,*R**)-**5**, 139376-97-9; (*R**,*S**)-**5**, 139377-03-0; (±)-**6**, 139376-98-0; **7**, 139376-99-1; **8**, 139377-00-7; (±)-**9**, 139377-01-8; (*R**,*S**)-*cis*-**10**, 139377-04-1; (*R**,*R**)-*cis*-**10**, 139490-62-3; (*R**,*R**)-*trans*-**10**, 139490-63-4; (*R**,*S**)-*trans*-**10**, 139490-64-5; (±)-**11**, 139377-05-2; **11**-BBr_3, 139377-06-3; (±)-**12**, 139377-02-9; [Ni{(*R**,-*R**)-**5**}](ClO_4)$_2$, 139377-08-5; [Ni{(*R**,*S**)-**5**}](ClO_4)$_2$, 139490-66-7; [Ni{(*R**,*R**)-**5**}](ClO_4)$_2$·Me_2CO, 139490-67-8; $K_2[PtCl_4]$, 10025-99-7; 2-bromobenzyl methyl ether, 52711-30-5; triethyl phosphite, 597-50-2.

Supplementary Material Available: For [Ni{(*R**,*R**)-**5**}](ClO_4)$_2$·Me_2CO and for **11**·BBr_3, textual descriptions of the crystal structure determinations, figures showing atom-labeling schemes, and tables of crystallographic parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, calculated hydrogen atom parameters, and least-square planes and torsion angles (31 pages); tables of observed and calculated structure factors for both structures (52 pages). Ordering information is given on any current masthead page.

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(17) Hall, S. R.; Stewart, J. M., Eds. XTAL2.6 User's Manual. Universities of Western Australia and Maryland, 1989.