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Synthesis, Characterization, and Reactivity toward Nickel(II) of the New Saturated 14-Membered P_2S_2 Macrocycles *cis*- and *trans*-1,8-Diphenyl-1,8-diphospha-4,12-dithiacyclotetradecane

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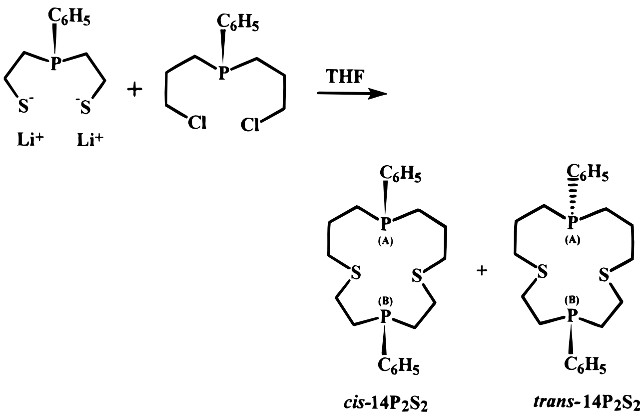
Introduction

Multidentate phosphorus containing macrocycles are interesting ligands which form very stable complexes, and several synthetic strategies have been used to obtain them.[1] It has been reported that introduction of sulfur donor atoms in these systems could modulate their complexing abilities,[2] and several macrocycles containing a mixed phosphorus−sulfur donor set of atoms could be found in the literature. Most of them incorporate aromatic rings fused in the macrocyclic chain,[2−4] but saturated ring systems containing exclusively P_xS_y donor set of atoms have been less developed.[5,6] The present work deals with the synthesis of the first saturated 14-membered diphosphadithia macrocycle $14P_2S_2$ (Scheme 1), the separation of its *cis* and *trans* isomers, and reactions of these isomers with hydrated Ni(II) perchlorate.

Results and Discussion

Scheme 1



The new macrocyclic ligand $14P_2S_2$ has been synthesized by reaction of equimolar amounts of the dilithium salt of 3-phenyl-3-phosphapentane-1,5-dithiol and bis(3-chloropropyl)phenylphosphine as shown in Scheme 1. The $^{31}P\{^1H\}$ NMR spectrum of the crude ligand displays two pairs of signals which suggest that the product obtained is a mixture of the *cis* and *trans* isomers. By comparing the positions of these resonances with the displacements reported for related compounds[4c,7] we have assigned the signals appearing at −26.66 and −27.51 ppm (vs 85% H_3PO_4) to the propyl-linked phosphine groups and those appearing at −24.43 and −25.04 ppm to ethyl-linked ones ($P_{(A)}$ and $P_{(B)}$ respectively, in Scheme 1).

The *cis* and *trans* isomers were separated by adding small portions of toluene to a cooled solution of the initial isomeric mixture in diethyl ether. The separation process is easily monitored by $^{31}P\{^1H\}$ NMR because the less soluble isomer shows a unique pair of signals at −24.43 and −26.66 ppm, whereas the more soluble one exhibits them at −25.04 and −27.51 ppm. With these spectroscopic data it is not possible to assign unequivocally the conformation of the compounds present in each fraction. So, we have solved the crystal structure of the less soluble product, which is the *trans*-$14P_2S_2$ isomer.

Figure 1 shows the molecular geometry and the atomic labeling scheme for the *trans*-$14P_2S_2$ macrocycle. The structure is partly disordered because the noncentrosymmetric molecule is situated across the crystallographic center of inversion, and thus bond parameters for the disordered part are only apparent. Owing to the symmetry, orientation of the phenyl groups is *trans*. The bond lengths and bond angles show the usual values found in organic compounds, and the values of torsional angles indicate lack of considerable strain in the molecule. The four donor atoms are oriented away from the intracyclic cavity and the intramolecular S···S and P···P distances (6.287(4) and 7.244(3) Å, respectively) are quite large. All of this reveals the poor preorganization of the free macrocyclic ligand toward metal ion coordination.

The reaction of equimolar amounts of *trans*-$14P_2S_2$ and hydrated $Ni(ClO_4)_2$ in a $CH_2Cl_2−CH_3CN$ mixture affords the red-violet crystalline solid **1** of formula [Ni(*trans*-$14P_2S_2$)(CH_3CN)]$(ClO_4)_2$. However, when the same reaction is carried out using the *cis*-$14P_2S_2$ isomer as ligand, only noncharacterizable oily materials could be isolated. Complex **1** slowly changes when exposed to the atmosphere to a yellow solid, probably due to loss of the coordinated acetonitrile molecule. This yellow solid dissolves in acetonitrile affording a red-yellow solution from which the solid complex **1** was recovered. The $^{31}P\{^1H\}$ NMR spectrum of **1** recorded in acetonitrile solution shows a pair of doublets centered at 0.08 and 121.38 ppm,

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(1) Caminade, A. M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183.

(2) (a) Kyba, E. P.; Davis, R. E.; Hudson, C. W.; John, A. M.; Brown, S. B.; McPhaul, M. J.; Liu, L.-K.; Glover, A. C. *J. Am. Chem. Soc.* **1981**, *103*, 1875. (b) Kyba, E. P.; Chou, S.-S. P. *J. Org. Chem.* **1981**, *46*, 860. (c) Kyba, E. P.; Clubb, C. N.; Larson, S. B.; Schueler, V. J.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 2141. (d) Kyba, E. P.; Davis, R. E.; Fox, M. A.; Clubb, C. N.; Liu, S.-T.; Reitz, G. A.; Scheuler, V. J.; Kashyap, R. P. *Inorg. Chem.* **1987**, *26*, 1647.

(3) Jones, T. L.; Willis, A,; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1411.

(4) (a) Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053. (b) Kyba, E. P.; Chou, S. S. P. *J. Chem. Soc., Chem. Commun.* **1980**, 449. (c) Kyba, E. P.; John, A. M.; Brown, B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139. (d) Kyba, E. P.; Chou, S. S. P. *J. Am. Chem. Soc.* **1980**, *102*, 7012. (e) Fox, M. A.; Campbell, K. A. Kyba, E. P. *Inorg. Chem.* **1981**, *20*, 4163. (f) Kyba, E. P.; Liu, S. T. *Inorg. Chem.* **1985**, *24*, 1613.

(5) Ciampolini, M. *Pure Appl. Chem.* **1986**, *58*, 1429 and references therein.

(6) (a) Märkl, G.; Hoferer, M. *Tetrahedron Lett.* **1992**, *33*, 3621. (b) Toto, S. D.; Olmstead, M. M.; Arbuckle, B. W.; Bharadwaj, P. K.; Musker, W. K. *Inorg. Chem.* **1990**, *29*, 691. (c) Smith, R. J.; Powell, A. K.; Barnard, N.; Dilworth, J. R.; Blower, P. J. *J. Chem. Soc., Chem. Commun.* **1993**, 54.

(7) Marchand, A. P., Ed *Methods in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis 8; VCH Publishers Inc.: Deerfield Beach, FL, 1987.

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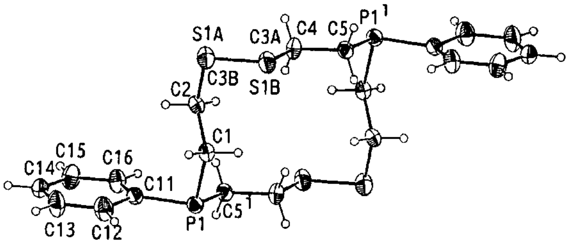

Figure 1. ORTEP plot of *trans*-$14P_2S_2$ showing 30% displacement ellipsoids. In the disordered part of the molecule the atom labeled S(1A) and C(3B), as well as S(1B) and C(3A) describe averaged positions of the two close atom positions.

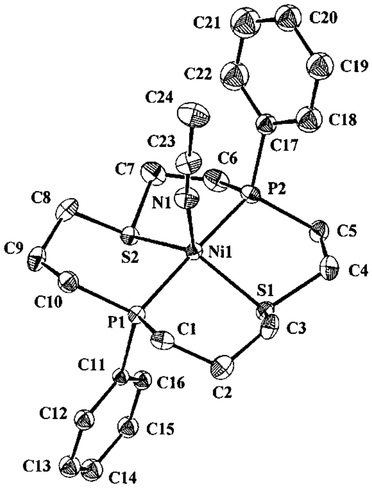

Figure 2. ORTEP plot of **1** showing 30% displacemnte ellipsoids. Hydrogen atoms are omitted for clarity.

respectively with a *trans* coupling constant of 191,9 Hz. These data are in accord with those reported for Ni(II) complexes of similar 14-membered phosphorus-containing macrocycles.[8,9]

The crystal structure of **1** consists of discrete $[Ni(trans\text{-}14P_2S_2)(CH_3CN)]^{2+}$ cations and ClO_4^- anions without significant interactions between them. Figure 2 shows the molecular geometry and the atomic labeling scheme for the $[Ni(CH_3CN)(trans\text{-}14P_2S_2)]^{2+}$ cation. In this cation the Ni(II) atom adopts a pentacoordinated environment defined by the four donor atoms of the ligand *trans*-$14P_2S_2$ and the nitrogen atom of one coordinated acetonitrile molecule. The coordination polyhedra of Ni(II) can be described as a distorted trigonal bipyramid with the phosphorus atoms situated at axial positions, whereas the two sulfur and the nitrogen atoms are located at the equatorial plane. The P−Ni−P angle is almost linear (174.1(1)°) but equatorial angles vary from 109.1(3) to 137.4(1)°. The Ni−P and Ni−S bond distances are similar, ranging from 2.181(3) to 2.193(3) Å, and are in agreement with the values found in the literature for pentacoordinated[10] or square-planar[2d,3,11] Ni(II) complexes in related P_2S_2 environments. The simultaneous coordination of the four macrocyclic donor atoms to the Ni(II) atom defines two five-membered and two six-membered chelate rings in half-chair and chair conformations, respectively.

Several examples of structurally characterized Ni(II) complexes with all-phosphorus or mixed sulfur−phosphorus tetradentate macrocycles have been reported. These data indicate that reaction of $P_{4-n}S_n$ ($n = 0-3$) macrocycles and Ni(II) salts of noncoordinating anions favors the formation of tetracoordinate Ni(II) complexes with square-planar geometry.[2d,3] However, if strongly coordinating anions (halides, cyanide or thiocyanate) are used as counter-ions, then pentacoordinate Ni(II) complexes are obtained.[2d,8,9] Nevertheless the *trans*-$14P_2S_2$ macrocycle seems to impose pentacoordination to the Ni(II) ion. This behavior encourages further research on reactivity and catalytic properties of this macrocycle.

Experimental Section

General Methods. Syntheses were carried out using standard Schlenk techniques under dry dinitrogen atmosphere. Solvents were dried by conventional methods and distilled under dinitrogen. Dilithium 3−phenyl-3-phosphapentane-1,5-dithiolate[12] and bis(3-chloropropyl)phenylphosphine[13] were obtained by previously described procedures. Elemental analyses were performed by the Service of Chemical Analysis of the Universitat Autònoma de Barcelona with a Carlo Erba EA-1108 instrument. NMR spectra were carried out by the Service of NMR of the Universitat Autònoma de Barcelona. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker 400 MHz AC instrument. $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker 250 MHz AC instrument and chemical shifts are given as ppm relative to 85% H_3PO_4.

Synthesis of 1,8-Diphenyl-1,8-diphospha-4,12-dithiacyclotetradecane ($14P_2S_2$). A solution of dilithium 3-phenyl-3-phosphapentane-1,5-dithiolate (4.40 g, 18.1 mmol) in THF (100 cm^3) was mixed with a solution of bis(3-chloropropyl)phenylphosphine (4.80 g, 18.1 mmol) in THF (100 cm^3) over THF (500 cm^3) at a rate of 20 $cm^3 \cdot h^{-1}$. After the addition was completed, the reaction mixture was stirred at room temperature for 48 h and then evaporated to dryness. The resulting oily material was treated with diethyl ether (100 cm^3), affording a white solid (LiCl) which was filtered off and discarded. The ether solution was then evaporated to 5 cm^3 and chromatographed over neutral Al_2O_3. The fraction eluted with toluene−diethyl ether (1:1) was collected and evaporated to obtain a mixture of *cis*- and *trans*-$14P_2S_2$ as a white solid. Yield: 0.35 g (4.4%). Anal. Calcd for $C_{22}H_{30}P_2S_2$, C, 62.83; H, 7.14; S, 14.73. Found: C, 62.3; H, 7.1; S, 14.6. ^1H NMR (400 MHz, $CDCl_3$): δ 1.61−2.82 (m, 20, $-CH_2-$), 7.05−7.90 (m, 10, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.3−26.6 (m, $CH_2-S-CH_2-CH_2$), 32.5 (m, $P-CH_2$), 127.0−138.1 (m, Ph). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −24.43, −25.04, −26.66, −27.51.

Separation of the *cis*- and *trans*-Isomers of $14P_2S_2$. The mixture of *cis*- and *trans*-$14P_2S_2$ (0.30 g, 0.71 mmol) was dissolved in diethyl ether (5 cm^3). Toluene (1 cm^3) was added, and the resulting mixture was kept for 5 min at −70 °C. A white precipitate of *trans*-$14P_2S_2$ appeared, which was filtered off and vacuum-dried. Yield: 0.095 g, (0.23 mmol). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −24.43, −26.66. To the filtrate was added toluene (1 cm^3), and the mixture was cooled again at −70 °C to afford a second crop of precipitate (0.11 g), which was a mixture of *cis*- and *trans*-$14P_2S_2$ isomers, according to the ^{31}P NMR. An additional portion of toluene (1 cm^3) was added to the remaining solution which was cooled to −70 °C to afford a third fraction of precipitate corresponding to the pure *cis*-$14P_2S_2$ isomer. Yield: 0.081 g (0.21 mmol). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ −25.04, −27.51.

Synthesis of (Acetonitrile)*(trans*-1,8-diphenyl-1,8-diphospha-4,12-dithiacyclotetradecane)nickel(II) Diperchlorate, $[Ni(trans\text{-}14P_2S_2)(CH_3CN)](ClO_4)_2$ (1). A solution of *trans*-$14P_2S_2$ (0.050 g, 0.12 mmol) in dichloromethane (2 cm^3) was slowly added to a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.043 g, 0.12 mmol) in acetonitrile (10 cm^3). The mixture, which changed immediately from blue to dark red, was maintained under stirring at room temperature for 30 min. After that, diethyl ether (4 cm^3) was added. Red-violet needles separated from the solution and were filtered off and vacuum dried. Yield: 0.045 g (45%). Anal. Calcd for $C_{24}H_{33}P_2S_2NCl_2O_8Ni$, C, 40.08; H, 4.62; N, 1.95; S, 8.92. Found: C, 39.8; H, 4.2; N, 1.9; S, 8.9. ^1H NMR (400 MHz, CD_3CN): δ 0.91−4.32 (m, 20, $-CH_2-$), 7.45−8.21 (m, 10, Ph). $^{31}P\{^1H\}$ NMR (101 MHz, CD_3CN): δ 0.08 (d, $^3J_{PP} = 191{,}9$ Hz), 121.38 (d, $^3J_{PP} = 191{,}9$ Hz).

X-ray Structure Determinations for *trans*-$14P_2S_2$ and 1. Single-crystal data collections for both compounds were performed with

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(8) Brauer, D. J.; Dörrenbach, F.; Lebbe, T.; Stelzer, O. *Chem. Ber.* **1992**, *125*, 1785.

(9) Brauer, D. J.; Lebbe, T.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 438.

(10) Bertinsson, G. I. *Acta Crystallogr.* **1983**, *C39*, 698.

(11) Aurivillius, K; Bertinsson, G. I. *Acta Crystallogr.* **1981**, *B37*, 72.

(12) Muñoz, J. A.; Escriche, L.; Casabó, J.; Kivekäs, R; Sillanpää, R. *Inorg. Chim. Acta*, submited for publication.

(13) Green, L. M.; Meek, D. W. *Polyhedron* **1990**, *9*, 35.

Table 1. Crystallographic Data and Structure Refinement Parameters

	trans-14P_2S_2	(1)
chem formula	$C_{22}H_{30}P_2S_2$	$C_{22}H_{30}Cl_2NNiO_8P_2S_2$
fw	420.52	719.20
a, Å	12.294(3)	13.372(2)
b, Å	5.672(2)	12.729(5)
c, Å	16.703(4)	18.470(4)
β, deg	109.55(2)	102.86(2)
V, Å^3	1097.6(6)	3065(1)
Z	2	4
space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
T, °C	21	21
λ, Å	0.710 69	0.710 69
ρ_{calc}, g·cm^{-3}	1.272	1.559
ρ_{obsd}, g·cm^{-3}	1.28	1.56
μ, cm^{-1}	3.9	10.9
transm coeff		0.86−1.00
R^a	0.080	0.058
$R_w{}^b$	0.080	0.058

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [(\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

Table 2. Selected Atomic Coordinates and Equivalent Displacement Parameters for *trans*-14P_2S_2

	x	y	z	$U_{eq}{}^a$
P(1)	0.1316(2)	0.4469(4)	0.4073(1)	0.0434(7)
S(1A)[b]	0.2820(2)	0.0355(7)	0.6494(2)	0.062(1)
S(1B)[b]	0.1508(2)	0.0615(6)	0.6819(2)	0.059(1)
C(1)	0.1793(6)	0.348(1)	0.5196(4)	0.042(3)
C(2)	0.2342(6)	0.104(1)	0.5421(4)	0.045(3)
C(4)	0.0708(6)	−0.184(1)	0.6298(4)	0.049(3)
C(5)	−0.0429(6)	−0.198(1)	0.6485(4)	0.045(3)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j\mathbf{U}_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] Site occupation parameter 0.69.

Rigaku AFC5S diffractometer using monochromatized Mo $K\alpha$ radiation ($\lambda = 0.710\ 69$ Å) and $\omega-2\theta$ scan mode at room temperature.

The structure of *trans*-14P_2S_2 was solved by direct methods using the SHELXS86 program.[14] Least-squares refinements and all subsequent calculations were performed using the XTAL[15] crystallographic software package. Because the molecule lacks an inversion center and Z is 2, it is disordered, with two molecules sharing four equivalent positions. Of the non-hydrogen atoms only S(1) and C(3) are disordered, each occupying two positions. The disordered atoms are labeled in Figure 1 as S(1A), S(1B), C(3A), and C(3B). As the real positions of S(1A) and C(3B) are very close, as well as the positions of S(1B) and C(3A), the close positions could not be distinguished. Therefore partially occupied sulfur atoms S(1A) and S(1B) (site occupation parameter 0.69) were used in the calculations. The non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at their calculated positions [C−H = 0.95 Å and U(H) = 1.2U_{eq}(host atom)].

The structure of **1** was solved by direct methods using the MITRIL program.[16] Least-squares refinements and all subsequent calculations were performed using the TEXSAN program package.[17] Non-hydrogen atoms, except the phenyl carbons, were refined with anisotropic displacement parameters. Phenyl groups were refined as rigid groups, and hydrogen atoms were placed at their calculated positions [C-H=0.95 Å and U(H) equal to 1.2xU of host atom].

For both compounds neutral atomic scattering factors were those included in the programs. The figures were plotted with ORTEP.[18] Crystallographic data for *trans*-14P_2S_2 and **1** are presented in Table 1.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-14P_2S_2[a]

P(1)−C(1)	1.854(7)	S(1A)−S(1B)	1.872(5)
P(1)−C(11)	1.835(8)	S(1A)−C(2)	1.733(7)
P(1)−C(5)^i	1.837(7)	S(1B)−C(4)	1.759(8)
C(1)−P(1)−C(11)	100.4(3)	S(1A)−C(2)−C(1)	115.2(5)
C(1)−P(1)−C(5)^i	102.4(3)	S(1B)−C(4)−C(5)	109.6(6)
C(11)−P(1)−C(5)^i	103.1(3)	C(4)−C(5)−P(1)^i	111.2(5)
S(1B)−S(1A)−C(2)	104.8(3)	P(1)−C(11)−C(12)	115.8(6)
S(1A)−S(1B)−C(4)	100.8(3)	P(1)−C(11)−C(16)	127.2(6)
P(1)−C(1)−C(2)	119.0(5)		

[a] Equivalent position: (i) $-x$, $-y$, $1 - z$.

Table 4. Selected Atomic Coordinates and Equivalent Displacement Parameters for **1**

	x	y	z	$B_q{}^a$
Ni(1)	0.4273(1)	0.0727(1)	0.74558(7)	2.17(5)
S(1)	0.2646(2)	0.1126(2)	0.7077(2)	2.8(1)
S(2)	0.5748(2)	0.1536(2)	0.7623(2)	2.6(1)
P(1)	0.4206(2)	0.1192(2)	0.8587(1)	2.2(1)
P(2)	0.4357(2)	0.0435(2)	0.6307(2)	2.7(1)
N(1)	0.4404(7)	−0.0850(7)	0.7755(5)	3.6(4)
C(1)	0.3139(8)	0.0554(8)	0.8890(5)	2.7(5)
C(2)	0.2074(8)	0.076(1)	0.8388(6)	3.8(5)
C(3)	0.1919(7)	0.0342(9)	0.7600(6)	3.5(5)
C(4)	0.2266(8)	0.059(1)	0.6139(6)	4.6(6)
C(5)	0.3116(8)	0.0841(9)	0.5725(6)	3.6(5)
C(6)	0.5425(9)	0.1239(9)	0.6146(6)	4.0(6)
C(7)	0.6284(9)	0.119(1)	0.6829(7)	4.3(6)
C(8)	0.6608(7)	0.0903(9)	0.8385(6)	3.6(5)
C(9)	0.6347(8)	0.1211(9)	0.9120(6)	3.6(5)
C(10)	0.5338(8)	0.0731(9)	0.9251(5)	3.3(5)
C(23)	0.4498(9)	−0.172(1)	0.7783(6)	3.8(6)
C(24)	0.461(1)	−0.288(1)	0.7784(7)	5.6(7)

[a] $B_{eq} = (3/4)\Sigma_i\Sigma_j\beta_{ij}{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 5. Selected bond lengths (Å) and angles (deg) for **1**

Ni(1)−S(1)	2.192(3)	S(1)−C(3)	1.81(1)
Ni(1)−S(2)	2.185(3)	S(1)−C(4)	1.82(1)
Ni(1)−P(1)	2.193(3)	S(2)−C(7)	1.82(1)
Ni(1)−P(2)	2.181(3)	S(2)−C(8)	1.80(1)
Ni(1)−N(1)	2.079(9)	N(1)−C(23)	1.12(2)
S(1)−Ni(1)−S(2)	137.4(1)	Ni(1)−P(1)−C(11)	115.5(2)
S(1)−Ni(1)−N(1)	109.1(3)	Ni(1)−P(2)−C(17)	119.0(3)
S(2)−Ni(1)−N(1)	113.4(3)	Ni(1)−N(1)−C(23)	167(1)
P(1)−Ni(1)−P(2)	174.1(1)		

Selected atomic coordinates and bond parameters for *trans*-14P_2S_2 are listed in Tables 2 and 3, and for **1** the same data are presented in Tables 4 and 5. Further details of the X-ray analyses are included in the Supporting Information.

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Supporting Information Available: Text giving the details of X-ray structure analyses and complete listings of bond distances and angles, thermal parameters, and hydrogen coordinates for *trans*-14P_2S_2 and **1** (26 pages). Ordering information is given on any current masthead page.

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(14) Sheldrick, G. M. SHELXS86. Program for Crystal Structure Solution. University of Göttingen, Germany, 1986.

(15) Hall, S. R., Flack, H. D., Stewart, J. M., Eds., *XTAL3.2 User's Guide*; Universities of Western Australia, Geneva, and Maryland: Nedlands, Australia, Geneva, Switzerland, and College Park, MD, 1992.

(16) Gilmore, C. J. *J. Appl. Crystallogr.* **1982**, *17*, 42.

(17) *(17) TEXSAN-TEXRAY: Single Crystal Structure Analysis Software*, Version 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989.

(18) Johnson, C. K. *ORTEP II.* Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.