Since much effort is currently devoted to antitumor testing of platinum diammines, it is clearly important for compounds to be well characterized by a wide range of physical techniques.

Acknowledgment. We thank the Cancer Research Campaign (Grant SP 1384 to S.N.), the SERC and Johnson Matthey Ltd. (CASE award to I.M.I.) for support, Professor C. J. L. Lock (McMaster University) for a preprint of his work on compound I, and Heather Robbins for technical assistance.

Registry No. I, 31246-66-9; II, 31246-62-5; III, 31246-63-6.

Supplementary Material Available: Listings of the anisotropic thermal parameters of non-hydrogen atoms and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Contribution from Fachbereich 9, Anorganische Chemie,
Bergische Universität-Gesamthochschule-Wuppertal, D-5600 Wuppertal 1, West Germany

Reactions of Coordinated Ligands. 12.[1] Single-Stage Template Syntheses of Tetradentate Macrocyclic Phosphine Complexes

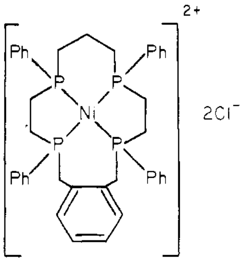
RAINER BARTSCH, SIBBELE HIETKAMP, STEPHEN MORTON, HELMUT PETERS, and OTHMAR STELZER*

Received December 28, 1982

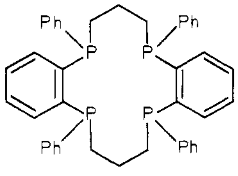
Square-planar complexes of nickel(II) and palladium(II) containing 14-membered macrocyclic tetradentate phosphine ligands are accessible by single-stage template-moderated ring-closure reactions between the complexes $[M(HMeP(CH_2)_nPMeH)_2]X_2$ (M = Ni, Pd; n = 2, 3; X = Cl, Br) and dialdehydes or diketones $RC(O)(CH_2)_nC(O)R$ (n = 0, 1; R = H, Me). For R = Me the formation of the macrocycles proceeds with high diastereoselectivity. The crystal and molecular structure of the two isomeric complexes **9a** and **9b** obtained by the reaction of acetylacetone and $[Pd(HMeP(CH_2)_2PMeH)_2]Cl_2$ shows the presence of a 14-membered ring system in both cases. Isomer **9a** crystallizes in the space group $C2/c$ with a = 18.819 (6) Å, b = 11.607 (2) Å, c = 13.600 (4) Å, β = 90.81 (4)°, T = 21 °C, λ = 0.71069 Å (Mo Kα), and Z = 4. The four phosphorus atoms display a square-planar coordination geometry at Pd(II) in the dication with the macrocyclic ring system in the trans-III (*RSSR*) arrangement. In isomer **9b**, in space group $P2_1$ with a = 10.891 (3) Å, b = 15.766 (6) Å, c = 8.163 (2) Å, β = 108.4 (2)°, T = 21 °C, λ = 0.71069 Å (Mo Kα), and Z = 2, the four phosphorus atoms and one chlorine atom form a square pyramid, the Pd atom being 0.26 Å above the basal plane. The configuration of the macrocyclic ring system may be assigned to the trans-I (*RSRS*) isomer.

Introduction

The first preparation of a macrocyclic ring system with four phosphorus atoms was carried out by Horner and co-workers,[2,3] who also proposed a template synthesis for ligands of this type or their complexes.[4] This synthetic method was, however, first successfully applied to phosphorus macrocycles by DelDonno and Rosen.[5] After a synthesis involving several steps, they were able to carry out the critical ring-closure reaction in the coordination sphere of nickel(II) to obtain complex I in low yield.



I



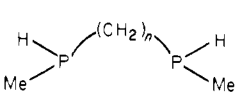
II

In 1977 Kyba, Hudson, McPhaul, and John described the synthesis of the macrocyclic, multidentate phosphine ligand II, which has two rigid *o*-phenylene bridges.[6] Of the five possible isomers (three meso and two *dl* pairs), one (cis-syn-cis) was investigated by X-ray structural analysis.[7]

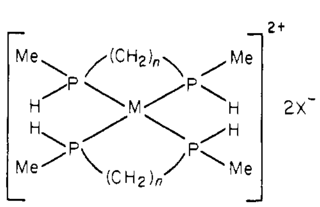
All syntheses of such ligands or of their complexes so far reported involve many reaction steps and give only poor yields.

The importance of macrocyclic multidentate phosphine ligands as phosphorus analogues of the crown ethers and the possible catalytic activity of their complexes make an easier access desirable.

In this paper we report a synthesis analogous to that for macrocyclic amines[8] and imines.[9] The multistep synthetic route is replaced by a template synthesis starting with suitable complexes of bidentate PH-functional phosphines, e.g.



1: $n = 2$
1a: $n = 3$



2: M = Ni, $n = 2$
3: M = Pd, $n = 2$
3a: M = Pd, $n = 3$

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(1) Part 11: Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *Angew. Chem.* **1982**, *94*, 367.

(2) Horner, L.; Kunz, H.; Walach, P. *Phosphorus Relat. Group V Elem.* **1975**, *6*, 63.

(3) Horner, L.; Walach, P.; Kunz, H. *Phosphorus Sulfur* **1978**, *5*, 171.

(4) Horner, L.; Kunz, H. *Chem. Ber.* **1971**, *104*, 717.

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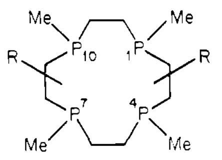
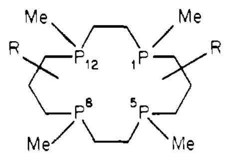
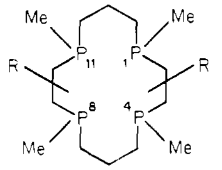
If the independent phosphorus atoms in cis positions are connected by ethylene or trimethylene chains bearing substituents R, the following macrocyclic tetradentate phosphine ligands may be formed:



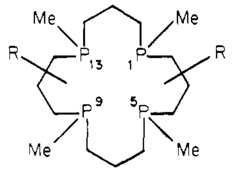
[12]tetraphos-1,4,7,10



[14]tetraphos-1,5,8,12



[14]tetraphos-1,4,8,11



[16]tetraphos-1,5,9,13

Experimental Section

Materials. The ligands **1**[10] and **1a**[11] were prepared as described in the literature. All other chemicals were reagent-grade materials and were used without further purification. All reactions were carried out under an atmosphere of dry nitogen.

2,5-Bis(hydroxymethyl)-2,5-diphosphahexane, $HOCH_2(Me)P(CH_2)_2P(Me)CH_2OH$ (1b). A mixture of $HMeP(CH_2)_2PMeH$ (5.21 g, 43 mmol) and paraformaldehyde (2.58 g, 86 mmol) was treated with a small quantity (0.1 g) of α,α'-azobis(isobutyronitrile) (AIBN) and heated to 60 °C (16 h). All volatile components were removed under vacuum (0.1 torr, 25 °C). The product was obtained as a colorless oil and was used without purification for further reactions; yield 7.53 g (97%). Anal. Calcd for $C_6H_{16}O_2P_2$: C, 39.57; H, 8.84. Found: C, 38.49; H, 8.70.

General Procedure for the Preparation of the Complexes 2–5. Two mole equivalents of the appropriate ligand were dissolved in 25 mL of ethanol. This solution was added dropwise in the course of 2 h to a solution or suspension of 1 mol equiv of $NiBr_2 \cdot 3H_2O$, K_2PdCl_4, or $PdCl_2$ in ca. 50 mL of ethanol. The reaction mixture was stirred for a further 16 h and then filtered. The solvent was removed under vacuum (0.1 torr, 20 °C), and the residue was washed with ether and dried under vacuum. In each case a product having the composition $M(bidentate)_2X_2$ was obtained.

Dibromobis[1,2-bis(methylphosphino)ethane]nickel(II) (2). Using 4.47 g (36.7 mmol) of **1** and 5.0 g (18.3 mmol) of $NiBr_2 \cdot 3H_2O$ gave 7.5 g (88%) of **2** as a brownish red powder. Anal. Calcd for $C_8H_{24}Br_2NiP_4$: C, 20.76; H, 5.22; Br, 34.34. Found: C, 20.98; H, 5.32; Br, 34.14. UV/vis spectrum (in nm, numbers in parentheses are molar absorptivities) (CH_3OH): 366 (483).

Dichlorobis[1,2-bis(methylphosphino)ethane]palladium(II) (3). A 7.42-g (61.2 mmol) amount of **1** and 10.0 g (30.6 mmol) of K_2PdCl_4 gave 11.91 g (92%) of **3** as colorless crystals. Anal. Calcd for $C_8H_{24}Cl_2P_4Pd$: C, 22.62; H, 5.73; Cl, 17.36. Found: C, 22.79; H, 5.73; Cl, 16.82.

Dichlorobis[1,3-bis(methylphosphino)propane]palladium(II) (3a). A 9.67-g (71.1 mmol) amount of **1a** reacted with 11.61 g (35.6 mmol) of K_2PdCl_4 to yield 14.7 g (92%) of **3a** as colorless crystals. Anal. Calcd for $C_{10}H_{28}Cl_2P_4Pd$: C, 26.72; H, 6.27; Cl, 15.77. Found: C, 26.51; H, 6.29; Cl, 15.68.

Dibromobis[2,5-bis(hydroxymethyl)-2,5-diphosphahexane]nickel(II) (4). A 2.67-g (14.7 mmol) amount of **1b** and 2.0 g (7.3 mmol) of $NiBr_2 \cdot 3H_2O$ gave 2.0 g (81%) of complex **4** as a red powder. Anal. Calcd for $C_{12}H_{32}Br_2NiO_4P_4$: C, 24.73; H, 5.52; Br, 27.42. Found: C, 24.98; H, 5.47; Br, 26.68. IR spectrum: 3300 cm^{-1} (ν_{OH}). UV/vis spectrum (in nm, numbers in parentheses are molar absorptivities) (CH_3OH): 395 (1250).

Dichlorobis[2,5-bis(hydroxymethyl)-2,5-diphosphahexane]palladium(II) (5). A 4.51-g (24.8 mmol) amount of the ligand **1b** and 2.20 g (12.4 mmol) of K_2PdCl_4 gave 6.03 g (90%) of complex **5** as a pale yellow powder. Anal. Calcd for $C_{12}H_{32}Cl_2O_4P_4Pd$: C, 26.61; H, 5.94; Cl, 13.09. Found: C, 26.42; H, 5.99; Cl, 13.23. IR spectrum: 3200 cm^{-1} (ν_{OH}).

Preparation of Complex 5. Second Method. A solution of 3.0 g (7.1 mmol) of **3** in ca. 50 mL of ethanol was treated with paraformaldehyde (0.68 g; 28.28 mmol). A small quantity of AIBN was added to the reaction mixture, which was then heated to 70 °C (12 h). The product **5** precipitates from solution and was isolated by filtration, washed with ether, and dried under vacuum. The product thus obtained proved by $^{31}P\{^1H\}$ NMR spectroscopy to be identical with that obtained by the previous method.

$[Ni(Me_3SiO)MeP(CH_2)_2PMe(OSiMe_3)_2]Br_2$ (6). A 1.02-g (1.7 mmol) amount of **4** was suspended in $HN(SiMe_3)_2$[12] (10.0 g, 62.0 mmol) and the reaction mixture heated to 100 °C (16 h), during which time ammonia escaped from the suspension. Excess $HN(SiMe_3)_2$ was removed under vacuum (0.1 torr, 25 °C). The complex **6**, an intensely red solid, was purified by recrystallization from a mixture of dichloromethane and diethyl ether at −20 °C; yield 1.06 g (70%). Anal. Calcd for $C_{24}H_{64}Br_2NiO_4P_4Si_4$: C, 33.08; H, 7.39; Cl, 18.33. Found: C, 33.45; H, 7.21; Cl, 18.04. UV/vis spectra (in nm, numbers in parenthesis are molar absorptivities) (CH_2Cl_2): 400 (1780).

Synthesis of Macrocyclic Phosphine Complexes. 1. Dichloro[2,4,9,11-tetrahydroxy-1,5,8,12-tetramethyl-1,5,8,12-tetraphosphacyclotetradecane-P^1,P^5,P^8,P^{12}]palladium(II) (7). Malonaldehyde tetramethyl acetal (1.55 g, 9.48 mmol) was added to a solution of **3** (2.0 g, 4.74 mmol) in 50 mL of ethanol. Water (5 mL) and 0.1 mL of 0.1 N HCl were added. The solution was stirred at 60–70 °C for 12 h. The complex **7** was deposited as a fine white precipitate during the course of the reaction: it was filtered, washed with a mixture of ethanol and tetrahydrofuran (1:1), and dried under vacuum; yield 3.32 g (91%). Anal. Calcd for $C_{14}H_{32}Cl_2O_4P_4Pd$: C, 29.73; H, 5.69; Cl, 12.53. Found: C, 30.14; H, 5.83; Cl, 12.64. IR spectrum: 3400, 3230 cm^{-1} (ν_{OH}).

2. Dibromo[2,4,9,11-tetrahydroxy-1,2,4,5,8,9,11,12-octamethyl-1,5,8,12-tetraphosphacyclotetradecane-P^1,P^5,P^8,P^{12}]nickel(II) (8). Method A. A solution of **2** (2.36 g, 5.09 mmol) in a mixture of ethanol (10 mL) and water (20 mL) was treated with acetylacetone (1.02 g, 10.22 mmol). The reaction mixture was stirred at 70 °C for 3 days. The solvent was removed under vacuum (0.1 torr, 25 °C) and the residue washed with three 20-mL portions of diethyl ether and dried under vacuum. The product, a light yellow solid, was obtained in 89% yield (1.52 g). Anal. Calcd for $C_{18}H_{40}Br_2NiO_4P_4$: C, 32.61; H, 6.03; Br, 24.11. Found: C, 32.22; H, 5.91; Br, 24.24.

Method B. Nickel acetylacetonate dihydrate ($Ni(CH_3C(O)CHC(O)CH_3)_2 \cdot 2H_2O$)[13] (1.33 g, 4.55 mmol) was suspended in 20 mL of ethanol. After addition of 2 equiv of the di(secondary phosphine) **1** (1.11 g, 9.1 mmol) a red solution was obtained. Two equivalents of aqueous concentrated HCl was added, and the mixture was stirred for 2 weeks at 65 °C. The product formed was shown to be identical with that prepared according to method A (by means of ^{31}P NMR). IR spectrum: 3400, 3180 cm^{-1} (ν_{OH}). UV/vis spectrum (in nm, numbers in parenthesis are molar absorptivities) (CH_3OH): 356 (1120).

3. Dichloro[2,4,9,11-tetrahydroxy-1,2,4,5,8,9,11,12-octamethyl-1,5,8,12-tetraphosphacyclotetradecane-P^1,P^5,P^8,P^{12}]palladium(II) (9). Method A. A solution of **3** (4.12 g, 19.5 mmol) in 50 mL of ethanol was treated with 3.92 g (39 mmol) of acetylacetone and stirred at 60 °C for 12 h. After the solution cooled to room temperature, **9a** was deposited as a fine white precipitate (1.2 g, 20%), which could be recrystallized from water as the tetrahydrate **9a**$\cdot 4H_2O$. After removal of the solvent from the filtrate **9b** was obtained as a colorless powder. It was further purified by recrystallization from an ethanol–THF mixture. A 4.3-g (70%) amount of **9b** was obtained. Anal. Calcd for $C_{18}H_{40}Cl_2O_4P_4Pd$: C, 34.78; H, 6.47; Cl, 11.41. Found for **9a**: C, 34.56; H, 6.67; Cl, 11.48. Found for **9b**: C, 34.25; H, 6.73; Cl, 11.48. IR spectra: **9a**, 3180 cm^{-1}; **9b**, 3200 cm^{-1} (ν_{CO}).

Method B. Palladium acetylacetonate[14] (9.72 g, 31.93 mmol) in 150 mL of ethanol was treated with 7.79 g (63.85 mmol) of **1**. Concentrated HCl (10 mL) was added to the red solution, which became pale yellow. Isomer **9a** (identified by elemental analysis and

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its ^{31}P NMR spectrum) was formed in 95.7% crude yield (19.0 g). Isomer **9b** was not formed.

4. Dichloro[2,3,9,10-tetrahydroxy-1,4,8,11-tetramethyl-2,3,9,10-tetraphenyl-1,4,8,11-tetraphosphacyclotetradecane-*P*^{1},*P*^{4},*P*^{8},*P*^{11}]palladium(II) (10) and Dichloro[2,3,9,10-tetrahydroxy-1,2,3,4,8,9,10,11-octamethyl-1,4,8,11-tetraphosphacyclotetradecane-*P*^{1},*P*^{4},*P*^{8},*P*^{11}]palladium(II) (11). Biacetyl (1.17 g, 13.66 mmol) or benzil (2.83 g, 13.48 mmol) was respectively added to a suspension of **3a** (3.07 g, 6.83 mmol, or 3.03 g, 6.74 mmol, respectively) in 50 mL of ethanol and the reaction mixture stirred for 4 days at 70 °C. In the case of the benzil reaction **10** was precipitated as a fine crystalline solid. After the precipitate was filtered and washed with ether, **10** was dried in vacuo (10^{-2} torr, 20 °C). Further purification could be achieved by recrystallization from dichloromethane; yield 4.14 g (71%). **11** was obtained after removal of the solvent from the reaction mixture as a white solid; yield 3.92 g (92%). Anal. Calcd for $C_{38}H_{48}Cl_2O_4P_4Pd$ (**10**): C, 52.46; H, 5.55; Cl, 8.12. Found: C, 52.11; H, 5.67; Cl, 8.34. Anal. Calcd for $C_{18}H_{40}Cl_2O_4P_4Pd$ (**11**): C, 34.78; H, 6.47; Cl, 11.41. Found: C, 35.20; H, 6.84; Cl, 10.05. IR spectra: **10**, 3200 cm^{-1}; **11**, 3200 cm^{-1} (ν_{OH}).

Instrumentation and Physical Measurements. Proton magnetic resonance spectra were measured on a Varian EM 390 spectrometer using Me_4Si as internal reference. Proton-decoupled Fourier transform phosphorus-31 NMR spectra were obtained from a Varian FT 80A spectrometer operating at 32.2 MHz. Some of the ^{31}P NMR spectra were measured on Bruker WP 300 spectrometer. The samples were run in 10-mm tubes with deuterated solvents providing an internal deuterium lock. Phosphoric acid (85%) was used as external reference. Positive chemical shifts are measured downfield from H_3PO_4. IR spectra were recorded on a Perkin-Elmer Model 580 grating spectrometer from 250 to 4000 cm^{-1} as Nujol mulls between polished potassium bromide plates. UV/visible spectra were obtained with a Beckman Acta V spectrophotometer using 1.0-cm quartz cells. Conductivity measurements were made with a Knick digital conductometer. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany.

Crystal Structure Determination of the Isomers 9a and 9b. Isomer **9a** was recrystallized from water and isomer **9b** from ethanol–THF. The crystals were initially investigated by oscillation and Weissenberg photography. Intensities were collected with use of θ–2θ scans at room temperature on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation. All independent reflections with $2\theta \leq 55°$ were collected. An empirical absorption correction was applied to the data. All reflections with $I > 0$ were used in structure solution and refinement. The palladium atoms were located by Patterson syntheses; all other atoms were located by a series of difference-Fourier syntheses, and parameters were refined by full-matrix least-squares methods. The quantity minimized was $\sum w\Delta^2$, with $\Delta = |F_o - F_c|$ and $w^{-1} = |\sigma^2(F_o) + gF_o^2|$. The final value of g was 0.001 for **9a** and 0.004 for **9b**. Scattering factors for uncharged atoms were taken from ref 15. Methyl and methylene hydrogen atoms were placed in geometrically calculated positions with d(C–H) = 1.08 Å.[16]

Structure calculation and refinements were carried out with the programs SHELX-76 (G. M. Sheldrick), ORTEP-2 (Johnson), XANADU (Robert and Sheldrick), and local programs.

Isomer 9a. After location and least-squares refinement of the main structure component a strong Fourier peak remained (R_w was 0.11 at this stage). Careful examination showed this peak to be the palladium atom at a disordered location of the cation. The phosphorus and chlorine atoms of the disorder component could also be identified. The atoms belonging to the disorder component were refined freely, all refined to positions close to y/b + 0.378 from the corresponding atoms in the main component. The exact nature of the disorder remains somewhat unclear. After least-squares refinement a final difference-Fourier synthesis showed no peaks >0.7 e Å^{-3}; some of the larger peaks could tentatively be assigned as hydroxyl hydrogen atoms or carbon atoms of the minor component, but these were not used in further refinement. Crystal data are summarized in Table I; positional parameters are given in Table II.

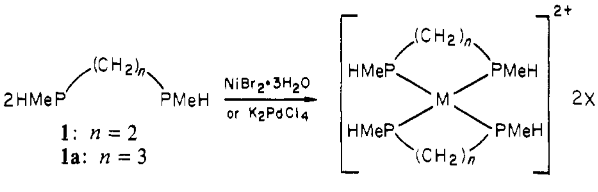
Isomer 9b. After refinement with all non-hydrogen atoms anisotropically a difference-Fourier synthesis revealed the positions of the four hydroxyl hydrogen atoms as four of the nine strongest peaks. These were introduced into the structure with d(O–H) constrained to 0.96 ± 0.01 Å.[17] A final difference-Fourier synthesis revealed no peaks with >1.0 e Å^{-3}. Crystal data are given in Table I and positional parameters in Table III.

Table I. Crystallographic Data

parameter	isomer **9a**	isomer **9b**
formula	$C_{18}H_{40}Cl_2O_4P_4Pd \cdot 4H_2O$	$C_{18}H_{40}Cl_2O_4P_4Pd$
fw	693.78	621.72
a, Å	18.819 (6)	10.891 (3)
b, Å	11.607 (2)	15.766 (6)
c, Å	13.600 (4)	8.163 (2)
β, deg	90.81 (4)	108.41 (2)
Z	4	2
d_{calcd}, g cm^{-3}	1.56	1.55
μ, cm^{-1}	9.95	10.97
space group	$C2/c$	$P2_1$
$I > 0$	3383	3133
R $(=\Sigma\|\Delta\|/\Sigma\|F_o\|)$	0.047	0.068
R_w $(=\Sigma w\Delta^2/\Sigma F_o^2]^{1/2})$	0.049	0.062

Results and Discussion

The Complexes M[HMeP(CH$_2$)$_n$PMeH]$_2$X$_2$ (M = Ni, Pd; *n* = 2, 3) (2, 3, 3a). The twofold-substituted nickel(II) and palladium(II) complexes of the di(secondary phosphines) MeHP(CH$_2$)$_n$PMeH (n = 2, 3) (**1**, **1a**)[10,11] suggested themselves as suitable starting materials for the synthesis of macrocyclic tetradentate phosphine ligands. These complexes already contain stable five- or six-membered chelate rings and possess reactive PH functions; they are easily obtained by the reaction of the appropriate di(secondary phosphine) with nickel(II) bromide or potassium tetrachloropalladate(II) (eq 1).



1: $n = 2$
1a: $n = 3$

(1)

2: M = Ni, X = Br, n = 2
3: M = Pd, X = Cl, n = 2
3a: M = Pd, X = Cl, n = 3

The complexes are highly soluble in water and stable with respect to atmospheric oxygen even in solution. Their electrical conductivity in dilute aqueous solution (ca. 10^{-3}–10^{-4} mol L^{-1}) shows them to be 1:2 electrolytes.[18] In contrast to **3** and **3a**, **2** is only moderately soluble in ethanol.

The complexes exhibit slightly broadened $^{31}P\{^1H\}$ NMR spectra, showing a series of partially overlapping signals which could not be assigned to the five diastereomers. With use of a diastereomeric mixture of the ligands **1** or **1a** for the synthesis of the complexes **2**, **3**, and **3a**, a statistical mixture of the diastereoisomers racemic (SS)$_2$, meso (SS, RR), ($RSRR$), anti (RS)$_2$, and syn (RS)$_2$[19] has to be expected.

Addition of excess ligand to the solutions of the complexes in ethanol does not result in separate signals for coordinated and free ligand: instead the $^{31}P\{^1H\}$ signals are slightly broadened and appear at a frequency between that of the complex and of free ligand, showing exchange between free and coordinated diphosphine to be rapid at room temperature. In solutions containing **3** and **3a** rapid ligand exchange does

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[19] Roberts, N. K.; Wild, B. S. *Inorg. Chem.* **1981**, *20*, 1892.

Table II. Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for 9a

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Pd1	5000	4059 (1)	7500	P1	4196 (1)	2636 (1)	7195 (1)
P2	4194 (1)	5475 (1)	7165 (1)	C1	4705 (2)	1297 (3)	7108 (2)
C2	3727 (1)	2876 (3)	5997 (2)	C3	3333 (2)	4046 (2)	5951 (2)
C4	3742 (1)	5201 (2)	5960 (2)	C5	4714 (2)	6806 (2)	7088 (2)
C6	3532 (2)	2361 (3)	8116 (2)	C7	3195 (2)	1910 (3)	5796 (3)
C8	3227 (2)	6159 (3)	5703 (3)	C9	3506 (2)	5781 (3)	8049 (2)
O1	4279 (1)	2872 (2)	5287 (1)	O2	4297 (1)	5215 (2)	5244 (2)
O3	4318 (2)	937 (2)	4158 (2)	O4	825 (2)	4059 (2)	9605 (2)
Cl1	3247 (1)	−969 (1)	7367 (1)	Pd2	5000	7833 (4)	7500
P3	5800 (5)	6388 (9)	7838 (7)	P4	5806 (6)	9245 (10)	7801 (8)
Cl2	3237 (7)	2871 (13)	7378 (10)				

Table III. Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for 9b

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Pd1	773 (1)	2500	2771 (1)	Cl1	1319 (3)	3458 (2)	150 (3)
Cl2	6788 (3)	3365 (2)	6939 (4)	P1	2060 (2)	3337 (2)	4931 (3)
P2	2408 (2)	1536 (2)	3122 (3)	P3	9442 (2)	1490 (2)	1111 (3)
P4	9093 (2)	3311 (2)	2979 (3)	C1	1004 (11)	4088 (7)	5616 (15)
C2	2947 (9)	2716 (6)	6920 (12)	C3	3788 (10)	2004 (6)	6579 (14)
C4	3185 (9)	1243 (6)	5447 (13)	C5	1719 (11)	572 (7)	1960 (15)
C6	272 (11)	491 (6)	1788 (15)	C7	7803 (11)	1360 (7)	1381 (1)
C8	7080 (9)	2200 (6)	1212 (12)	C9	7480 (9)	2832 (6)	2702 (12)
C10	9624 (10)	3754 (7)	5165 (12)	C11	3296 (1)	3993 (8)	4463 (17)
C12	3804 (11)	3314 (8)	8292 (13)	C13	4224 (10)	561 (7)	5597 (15)
C14	3730 (12)	1800 (8)	3202 (16)	C15	−780 (12)	1602 (8)	−1175 (11)
C16	−3012 (12)	748 (9)	−13 (20)	C17	6469 (11)	3526 (7)	2427 (15)
C18	−1198 (11)	4220 (7)	1538 (15)	O1	1949 (7)	2336 (5)	7503 (9)
O2	2169 (9)	840 (5)	5976 (10)	O3	8006 (9)	937 (5)	2972 (11)
O4	7573 (8)	2383 (6)	4261 (9)	H(O1)	2156 (119)	2777 (59)	8363 (106)
H(O2)	1832 (126)	1289 (60)	6505 (154)	H(O3)	7767 (127)	1385 (56)	3609 (146)
H(O4)	7194 (96)	2368 (97)	5194 (112)				

not occur; however, if roughly equimolar amounts of **3** and **3a** are dissolved in water, the formation of mixed species, $[Pd(MeHP(CH_2)_2PHMe)(MeHP(CH_2)_3PMeH)]Cl_2$, in equilibrium with the starting materials, could be observed by $^{31}P\{^1H\}$ NMR spectroscopy. Equilibrium was achieved after ca. 2 h. This reaction may be catalyzed by traces of base or free ligand.

The hydrogen atoms bound to phosphorus are sufficiently active to undergo slow exchange with hydrogen of solvent water. If **3a** is dissolved in deuterium oxide, the formation of **3a**-d_4 may be observed by $^{31}P\{^1H\}$ NMR spectroscopy, equilibrium being reached after ca. 30 min. A similar effect has been reported by us for $Pd[(MeHP(CH_2)_3)_2PPh]Cl_2$.[20]

There are thus three mechanisms by which the most favorable isomers of **2**, **3**, or **3a** may be formed from an originally statistical mixture of all isomers: (i) by rapid ligand exchange during the formation of the complexes; (ii) by slow ligand exchange in solutions of the pure complexes, and (iii) by inversion on phosphorus during proton exchange as demonstrated for $Pd[(MeHP(CH_2)_3)_2PPh]Cl_2$.[20]

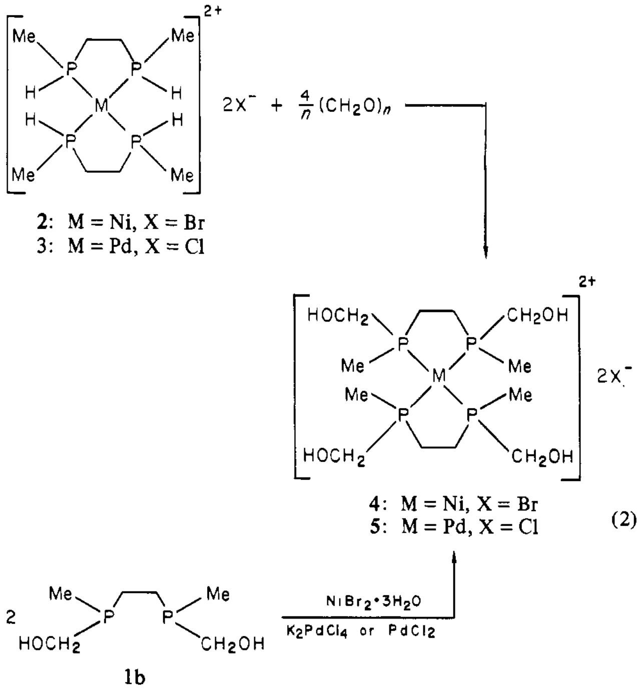
The complexes **2**, **3**, and **3a** are acidic enough to react with bases such as OH^- or NEt_3 with the formation of phosphido complexes. These complexes have not yet been fully characterized.

Ligand-exchange reactions and acid/base equilibria play an important role in the chemistry of these complexes as will be shown below.

The addition of carbonyl compounds on phosphine and primary and secondary phosphines[21a] and their complexes[21b] has been reported in the literature. We planned to convert the complexes **2**, **3**, or **3a** into macrocyclic tetradentate ligands by addition of 2 mol of α- or β-dicarbonyl compounds. The chelate ring systems thus formed would contain OH groups in the α position relative to each phosphorus atom.

In order to determine the best reaction conditions (temperature, catalyst, solvent, etc.), the reaction of **2** and **3** with formaldehyde was first studied.

Formaldehyde was used in the form of paraformaldehyde, and the products **4** and **5** were obtained in clean reactions (eq 2). The addition of various bases (pyridine, triethylamine,



2: M = Ni, X = Br
3: M = Pd, X = Cl

4: M = Ni, X = Br
5: M = Pd, X = Cl

(2)

1b

etc.) in catalytic or in stoichiometric quantities, however,

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[20] Baacke, M.; Hietkamp, S.; Morton, S.; Stelzer, O. *Chem. Ber.* **1981**, *114*, 2568.

[21] (a) Maier, L. "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, p 1 ff. (b) Stelzer, O. *Top. Phosphorus Chem.* **1977**, *9*, 1. Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *J. Organomet. Chem.* **1981**, *222*, 263.

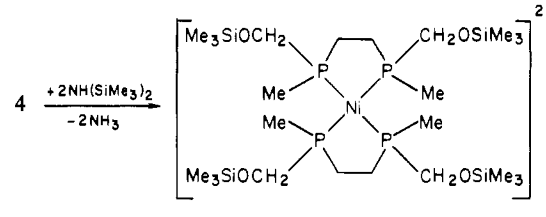
always leads to the formation of poorly defined products.

5 was also prepared by a different route using $(HOCH_2)MeP(CH_2)_2PMe(CH_2OH)$ and K_2PdCl_4.

The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** each show two strong signals indicating the formation principally of two isomers with symmetrical (A_4) spin systems. Further weak signals may indicate the presence of an isomer with an asymmetric (ABCD)[22b] spin system.

4 and **5** are practically insoluble in all organic solvents tried by us (alcohols, ether, chlorinated hydrocarbons, acetonitrile, dimethylsulfoxide, acetone, etc.) so that NMR studies were restricted to water as solvent.

The OH functions in **4** may be converted to $OSiMe_3$ groups by treatment with hexamethyldisilazane[12] (eq 3).



6

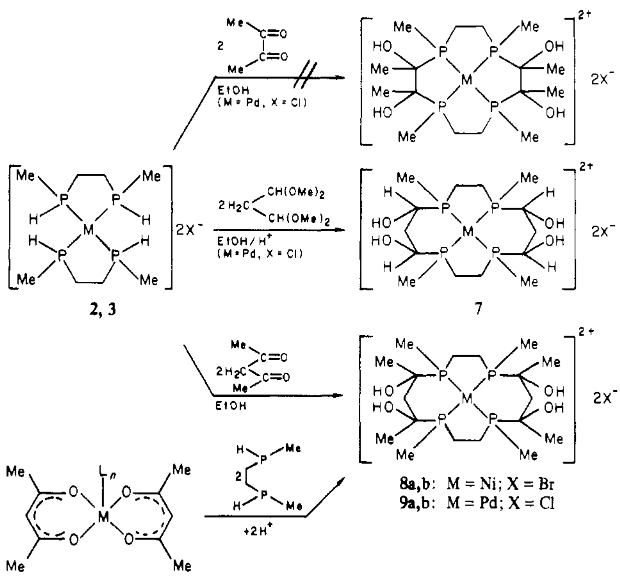
(3)

The silyl compound **6** is, in contrast to **4**, soluble in organic solvents such as dichloromethane. It is a 1:2 electrolyte. Solid **4** and **5** are probably extensively linked by intermolecular hydrogen bonds which only a very strongly hydrogen-bonding solvent such as water is able to break. By contrast **6** can form no hydrogen bonds and has much more lipophilic character. Curiously **5** may not be converted into the trimethylsilyl derivative by the above method. Treatment with a mixture of hexamethyldisilazane and trimethylchlorosilane also gave no reaction. The starting material could be recovered unchanged.

The $^{31}P\{^1H\}$ NMR spectra of **4**, **5**, and **6** showed in each case the existence mainly of two isomers. The presence of four asymmetric phosphorus atoms in the cations of **4**, **5**, and **6** should lead to five configurational isomers if square-planar coordination on nickel or palladium is assumed. Steric effects apparently favor the formation of mainly two isomers by the reaction of **2** or **3** with paraformaldehyde.

Ring-Closure Reactions on 2 and 3. In the application of the above results to analogous reactions between complexes of di(secondary phosphines) and α- or β-dicarbonyl compounds the following points need to be considered: (a) The α-carbon atoms in the two newly formed chelate rings are asymmetrically substituted. Thus, the macrocycle formed has four asymmetric carbon atoms and four asymmetric phosphorus atoms—a total of eight centers of asymmetry. It is desirable to achieve a stereospecific ring closure by the choice of suitable substituents on the dicarbonyl component. (b) In addition to the formation of the macrocycle the formation of a bridge between the two phosphorus atoms of the same ligand might be expected to occur. (c) In the newly formed chelate ring the bridge $-C(OH)R(CH_2)_nC(OH)R-$ (R = H, Me; n = 0, 1) must be able to span the cis-phosphorus atoms with a minimum of ring strain.

In an attempt to synthesize a complex with the 12-membered chelate ring [12]-tetraphos-1,4,7,10, we treated **3** with 2 equiv of biacetyl (eq 4). However, only ill-defined products were obtained, showing groups of signals at +60 and +20 ppm in the $^{31}P\{^1H\}$ NMR spectra. Obviously no ring closure had taken place as indicated by the ^{31}P NMR signals at +20 ppm, which may be assigned to a secondary phosphine coordinated to Pd(II) ($-CH_2PMeHPd-$).



(4)

(5)

(6)

(7)

M = Ni, L_n = $(H_2O)_2$
M = Pd, n = 0

8a,b: M = Ni; X = Br
9a,b: M = Pd; X = Cl

If, however, **3** is treated with malonaldehyde tetramethyl acetal and a trace of HCl to convert the acetal used into the free aldehyde, a smooth ring-closure reaction with the formation of **7** takes place (eq 5). Complex **7** is highly soluble in water and is a 1:2 electrolyte. Its $^{31}P\{^1H\}$ NMR spectrum, which no longer shows signals in the region of the starting material, is extraordinarily complex—this may be attributed to the existence of several configurational isomers each giving a spectrum of higher order (AA'BB'[22a] or ABCD[22b]). The spectrum could not be successfully analyzed.

If one replaces the aldehyde hydrogen atoms in malonaldehyde by larger groups, it might be expected that the steric interaction of the substituents on phosphorus and on the carbonyl component would lead to a diastereospecific ring closure—this indeed proved to be the case.

When **2** or **3** is treated with acetylacetone in place of malonaldehyde, **8** or **9** is obtained in each case as a mixture of only two isomers, which each give only a singlet in the $^{31}P\{^1H\}$ NMR spectrum. If one excludes the possibility of accidentally degenerate spectra in all cases, it is clear that in each case the four phosphorus atoms must be chemically and magnetically equivalent. Interestingly **9** may be prepared by the reaction of $Pd(acac)_2$[14] with $HMeP(CH_2)_2PMeH$ (**1**) and HCl. Only *one* isomer is formed in this case. Two isomers of **8**, however, are obtained by the corresponding reaction between $Ni(acac)_2 \cdot 2H_2O$[13] and the di(secondary phosphine) **1**. The ratio between the two isomers was approximately 1:3.

The rate of reaction was slower in case of the syntheses of the nickel complexes **8a** and **8b** by either route. This is probably due to the lower reactivity of the PH bonds in the starting material **2**. This may be inferred from the lower rate of H/D exchange in CH_3OD for **2** as compared to **3**.

It should be mentioned that anhydrous nickel(II) acetylacetonate, which is trimeric,[23] with bis(methylphosphino)ethane did not lead to **8a** or **8b**. No pure products could be isolated from the reaction mixture. Since in the trimer the acetylacetonate forms bridges between different nickel atoms, one should expect to get di- or trinuclear species as a result of the reaction with the bidentate phosphine.

The $^{31}P\{^1H\}$ NMR spectra of the products obtained according to reactions 6 and 7 indicate the formation of mononuclear species as a mixture of two isomers.

However, none of the spectroscopic methods usually available for transition-metal phosphine complexes, in par-

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(22) (a) Emsley, J. M.; Feeney, J.; Suttcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: New York, 1965; Vol. 1, p 425. (b) See ref 22a, p 339.

(23) Buller, J. G.; Mason, R.; Pauling, P. *Inorg. Chem.* **1965**, *4*, 456.

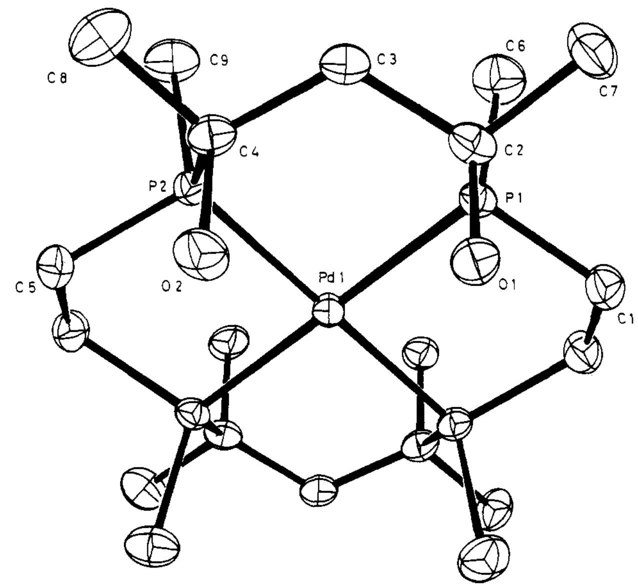
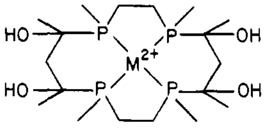
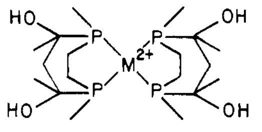


Figure 1. ORTEP view of the dication **9a** without hydrogen atoms.

ticular ^1H, $^{31}P\{^1H\}$, or $^{13}C\{^1H\}$ NMR spectroscopy, are able to distinguish between the desired structure with a 14-membered chelate ring (A) and a structure with two bidentate seven-membered chelate rings (B).



A



B

Since good crystals of **9** (**9a** and **9b**) could be obtained, an X-ray structural investigation was carried out.

Crystal Structure of the Isomers 9a and 9b. The X-ray structural analysis of the isomers **9a** and **9b** confirmed in both cases the formation of a tetradentate macrocyclic ligand in the coordination sphere of Pd(II).

Structure of Isomer 9a. Bond lengths and angles are given in Table IV; Figure 1 shows the numbering system used. The atoms O3 and O4 belong to the two crystallographically independent molecules of water of crystallization, and the atoms Pd2, P3, P4, and Cl2 belong to the minor structural component. The site occupation factor of this component was 5.6 (1)%. The dication in **9a** lies on a crystallographic twofold axis; the ion has exact C_2 and approximate C_{2h} symmetry. The coordination geometry at palladium is almost exactly square planar, with no deviations of more than 0.02 Å from the plane. The Pd–P bond lengths are within the normal range for Pd(II). The chelate five- and six-membered rings have the expected twist and chair conformations. The bond angles in the chelate rings are, with the exception of C2–C3–C4 (121.5 (2)°), normal. The corresponding angles in isomer **9b** are also very large; presumably this methylene group is the position of greatest flexibility in the 14-membered chelate ring, enabling the palladium atom to be coordinated well while steric interactions are reduced in the macrocycle, in particular between the axial oxygen atoms, to a minimum. There are a number of short O···O and O···Cl distances in **9a** (Table IV). O1, O2, and Cl1 each have two short contacts, O3 has four, and O4 has three. Although such O···O and O···Cl distances cannot be regarded as *proof* of hydrogen-bonding interactions in systems where the hydrogen atoms could not be definitely identified (the sum of two oxygen van der Waals radii is 2.8 Å,[17] and the molecular geometry requires O1···O2 to be short) the O···O and O···Cl distances are in close agreement with values reported in systems known from neutron diffraction data to be hydrogen bonding,[24] and it is reasonable to assume that all hydroxyl hydrogen atoms are involved in hydrogen bonding in this structure.

Table IV. Bond Lengths and Bond Angles within the Cation of **9a**[a]

	Bond Distances (A)		
Pd1–P1	2.274 (1)	Pd1–P2	2.278 (1)
P1–C1	1.830 (3)	P1–C2	1.863 (3)
P1–C6	1.811 (3)	P2–C4	1.863 (3)
P2–C5	1.831 (3)	P2–C9	1.815 (3)
C1–C1′	1.528 (6)	C2–C3	1.548 (4)
C2–C7	1.526 (4)	C3–C4	1.546 (4)
C4–C8	1.513 (4)	C5–C5′	1.544 (6)
C2–O1	1.428 (3)	C4–O2	1.437 (3)
Pd2–P3	2.30 (1)	Pd2–P4	2.27 (1)
	Bond Angles (deg)		
P1–Pd1–P2	92.8 (1)	P1–Pd1–P1′	86.8 (1)
P1–Pd1–P2′	179.0 (1)	P2–Pd1–P2′	87.6 (1)
Pd1–P1–C1	106.4 (1)	Pd1–P1–C2	110.9 (1)
Pd1–P1–C6	117.8 (1)	Pd1–P2–C4	110.3 (1)
Pd1–P2–C5	105.4 (1)	Pd1–P2–C9	119.2 (1)
C1–P1–C2	108.2 (1)	C1–P1–C6	105.2 (2)
C2–P1–C6	108.0 (1)	C4–P2–C5	109.3 (1)
C4–P2–C9	107.2 (1)	C5–P2–P9	105.0 (2)
P1–C1–C1′	109.3 (2)	P1–C2–C3	112.8 (2)
P2–C4–C3	112.1 (2)	P2–C5–C5′	109.1 (2)
P1–C2–C7	110.4 (2)	P1–C2–O1	104.5 (2)
P2–C4–C8	111.1 (2)	P2–C4–O2	105.5 (2)
C2–C3–C4	121.5 (2)	C3–C2–C7	108.9 (2)
C3–C2–O1	109.2 (2)	C7–C2–O1	111.0 (2)
C3–C4–C8	108.5 (2)	C3–C4–O2	111.8 (2)
C8–C4–O2	107.7 (2)	P3–Pd2–P4	93.2 (3)
P3–Pd2–P3′	86.2 (4)	P3–Pd2–P4′	178.6 (6)
P4–Pd2–P4′	87.4 (6)		
	Hydrogen-Bonding Contacts (A)		
	Intramolecular		
	O1···O2	2.72	
	Intermolecular		
Cl1···O3	3.14	Cl1···O4	3.22
O1···O3	2.72	O2···O2	2.78
O3···O4	2.77	O3···O4	2.89

[a] The number in parentheses following each data is the estimated standard deviation in the last significant figure.

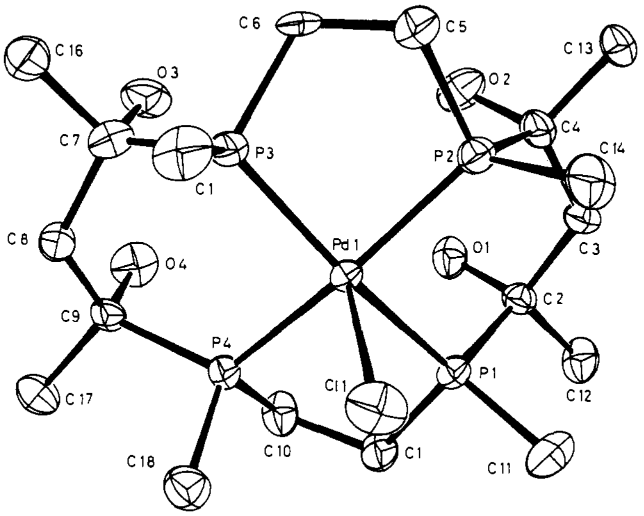


Figure 2. ORTEP view of the cation **9b** without hydrogen atoms.

Structure of Isomer 9b. Bond lengths and angles are given in Table V; Figure 2 shows the numbering system used. In contrast to the (for palladium(II) typical) square-planar geometry in **9a**, **9b** exhibits square-pyramidal coordination geometry; the four phosphorus atoms form the base of the

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(24) Olovsson, I.; Jönsson, P. G. "The Hydrogen Bond"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: New York, 1976; Vol. 2, p 395.

Table V. Bond Lengths and Bond Angles within Isomer **9b**[a]

Bond Distances (Å)			
Pd1-Cl1	2.831 (3)	Pd1-P1	2.291 (2)
Pd1-P2	2.290 (3)	Pd1-P3	2.287 (2)
Pd1-P4	2.282 (3)	P1-C1	1.86 (1)
P1-C2	1.881 (9)	P1-C11	1.83 (2)
P2-C4	1.88 (1)	P2-C5	1.82 (1)
P2-C14	1.82 (2)	P3-C6	1.81 (1)
P3-C7	1.88 (1)	P3-C15	1.81 (1)
P4-C9	1.86 (1)	P4-C10	1.83 (1)
P4-C18	1.82 (1)	C1-C10	1.52 (2)
C2-C3	1.53 (2)	C2-C12	1.54 (1)
C3-C4	1.53 (1)	C4-C13	1.54 (2)
C5-C6	1.54 (2)	C7-C8	1.52 (2)
C7-C16	1.54 (2)	C8-C9	1.53 (1)
C9-C17	1.52 (2)	C2-O1	1.45 (1)
C4-O2	1.45 (2)	C7-O3	1.41 (2)
C9-O4	1.43 (1)		
Bond Angles (deg)			
Cl1-Pd1-P1	92.9 (1)	Cl1-Pd1-P2	96.2 (1)
Cl1-Pd1-P3	99.7 (1)	Cl1-Pd1-P4	97.0 (1)
P1-Pd1-P2	91.3 (1)	P1-Pd1-P3	167.3 (1)
P1-Pd1-P4	86.0 (1)	P2-Pd1-P3	86.2 (1)
P2-Pd1-P4	166.7 (1)	P3-Pd1-P4	93.5 (1)
Pd1-P1-C1	108.2 (3)	Pd1-P1-C2	112.8 (3)
Pd1-P1-C11	118.4 (5)	Pd1-P2-C4	112.0 (4)
Pd1-P2-C5	108.2 (4)	Pd1-P2-C14	118.5 (4)
Pd1-P3-C6	105.2 (3)	Pd1-P3-C7	117.0 (4)
Pd1-P3-C15	113.3 (4)	Pd1-P4-C9	120.8 (3)
Pd1-P4-C10	105.8 (4)	Pd1-P4-C18	111.9 (5)
C1-P1-C2	105.7 (5)	C1-P2-C11	105.6 (6)
C2-P1-C11	105.2 (5)	C4-P2-C5	107.5 (5)
C4-P2-C14	105.8 (5)	C5-P2-C14	104.1 (6)
C6-P3-C7	105.7 (5)	C6-P3-C15	106.8 (6)
C7-P3-C15	108.0 (6)	C9-P4-C10	105.6 (5)
C9-P4-C18	106.1 (5)	C10-P4-C18	105.5 (5)
P1-C1-C10	111.3 (8)	P1-C2-C3	113.5 (7)
P2-C4-C3	112.8 (7)	P2-C5-C6	110.9 (8)
P3-C6-C5	110.7 (7)	P3-C7-C8	112.2 (8)
P4-C9-C8	112.6 (8)	P4-C10-C1	110.6 (8)
P1-C2-C12	109.8 (7)	P1-C2-O1	105.4 (6)
P2-C4-C13	109.8 (8)	P2-C4-O2	105.4 (6)
P3-C7-C16	109.2 (9)	P3-C7-O3	106.3 (7)
P4-C9-C17	109.7 (7)	P4-C9-O4	107.1 (6)
C2-C3-C4	121.2 (9)	C7-C8-C9	119.0 (7)
C3-C2-C12	108.8 (8)	C3-C2-O1	108.2 (8)
C12-C2-O1	111.2 (9)	C3-C4-C13	109.6 (8)
C3-C4-O2	112.6 (9)	C13-C4-O2	106.3 (8)
C8-C7-C16	108.4 (8)	C8-C7-O3	114.8 (10)
C16-C7-O3	105.6 (10)	C8-C9-C17	110.0 (7)
C8-C9-O4	108.0 (8)	C17-C9-O4	109.4 (9)
C2-O1-H(O1)	85 (8)	C4-O2-H(O2)	104 (8)
C7-O3-H(O3)	99 (6)	C9-O4-H(O4)	141 (8)
Hydrogen-Bonding Contacts (Å)[b]			
H(O1)···Cl1	2.2	O1···Cl1	3.03
H(O2)···O1	1.8	O1···O2	2.71
H(O3)···O4	1.7	O3···O4	2.62
H(O4)···Cl2	2.3	O4···Cl2	3.02

[a] The number in parentheses following each data is the estimated standard deviation in the last significant figure.
[b] The shortest non-hydrogen-bonding Cl···H distances are 2.7 Å; the shortest O···H distance is 2.5 Å.

pyramid, with palladium 0.26 Å above the plane (cf. 0.29 Å in $[NiMeHPC_3H_6PMeC_2H_4PMeC_3H_6PMeH]^+Br^-$)[25] and chlorine in the apical position. The cation has approximate C_{2v} symmetry if the twist conformations of the chelate five-membered rings are ignored. However, whereas the Pd–P bond lengths are normal for palladium(II), the Pd–Cl bond is, at 2.831 (3) Å, very much longer than normal (ca. 2.2–2.4 Å).[26]

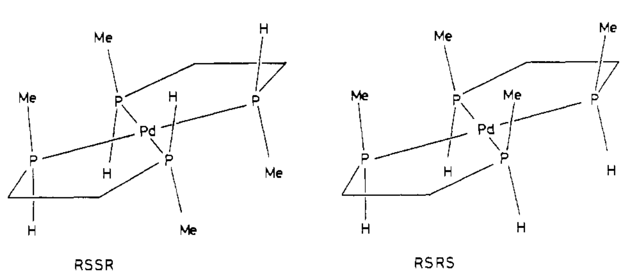
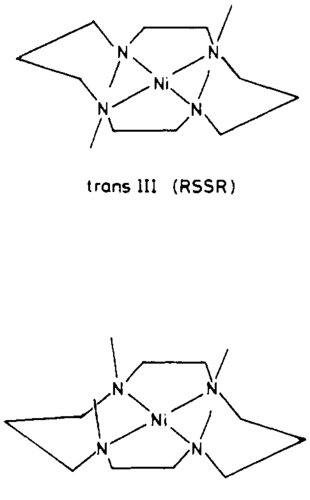


Figure 3. Diastereoisomers of **2** or **3**.



trans III (RSSR)

trans I (RSRS)

Figure 4. Two isomers of nickel(II) 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

In the structure of $Pd[PPhMe_2]_3Cl_2$[27] there is one short (2.434 (3) Å) and one long (2.956 (3) Å) Pd–Cl bond; the latter is 0.125 Å longer than in **9b**. In this complex, which the authors describe as intermediate between square planar and trigonal bipyramidal, the Pd atom lies only 0.18 Å from the plane defined by the three P atoms and the strongly bound Cl atom.

We are inclined to believe that the ligand in **9b** is not able to achieve exact square-planar coordination at palladium and that, since the palladium is forced somewhat out of plane, the fifth coordination position is slightly activated. The chelate five- and six-membered rings have the expected twist and chair configurations. Since the hydroxyl hydrogen atoms in **9b** could be located, it is possible to make certain definite statements about the hydrogen bonding in **9b** (Table V). Two of the hydroxyl hydrogen atoms, H(O2) and H(O3), are involved in intraionic hydrogen bonding to O1 and O4. H(O1) hydrogen bonds to the chlorine atom of the previous cation, forming endless chains of ions running through the crystal in the *x* direction. H(O4) hydrogen bonds to the chlorine ion. In both these hydrogen bonds to chlorine the O···Cl and H···Cl distances agree well with neutron diffraction data for hydrogen bonds to chlorine,[24] and the O–H···Cl unit is roughly linear. The O–H···O units are also normal.[24]

In contrast to the situation for **9a** all the methyl groups on phosphorus in **9b** are in the cis position. In both isomers the OH groups occupy the axial positions and the methyl groups the equatorial positions on the α-C atoms in the six-membered chelate rings.

Isomer **9a** may be regarded as derived from the *RSSR* form of the starting material **3**, whereas isomer **9b** is derived from the *RSRS* form (Figure 3).

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Table VI. $^{31}P\{^1H\}$ NMR and Conductivity Data

	δ_P[a]	J_{PP}, Hz	conductivities,[b] Ω^{-1} cm^{-1} mol^{-1}
1b	−33.7		
2	~+7.6[c]		200[h]
3	~+21[c]		217[h]
3a	~−45[c]		242[h]
4	~+53[c]		162[h]
5	~+45.5[c]		174[h]
6	~+54[c]		52[i]
7	~+60[c]		185[h]
8 isomer **8a**	+69.1		250[h]
isomer **8b**	+64.3		
9 isomer **9a**	+63.4		187[h]
isomer **9b**	+60.6		197[h]
10[e] isomer **10a**	+56.2[d] (A_4)		160[j]
isomer **10b**	+58.6[e] (AA′BB′)	−34.7 ($J_{1,2}$)[f]	
		−25.6 ($J_{1,3}$)	
	+56.4	+294.6 ($J_{1,4}$)	
		−34.7 ($J_{3,4}$)	
isomer **10c**	+59.0 (AA′BB′)	+300 ($J_{1,4}$)	
		−36.1 ($J_{1,2}$)	
	+55.3	23.7 ($J_{1,3}$)	
		+292.3 ($J_{2,3}$)	
11[e] isomer **11a**	*g* (A_4)		195[h]
isomer **11b**	54.0 (AA′BB′)		
isomer **11c**	52.3 (AA′BB′)	+251.3 ($J_{1,4}$)	
		−30.2 ($J_{1,2}$)	
		−29.6 ($J_{1,3}$)	
		+260.0 ($J_{2,3}$)	

[a] Phosphorus-31 chemical shifts are relative to 85% H_3PO_4 with positive values being downfield from the reference, solvent CH_3OH. [b] ca. 10^{-3} M solutions, 298 K. [c] Mixture of diastereomers. [d] Very low concentration, singlet, A_4 spin system. [e] Analyzed after measuring on a Bruker WP 300 NMR spectrometer. [f] For notation see formula 8. [g] Assignment of a single line for isomer **11a** was not possible due to impurities, the value given for isomer **11b** corresponds to the center of the AA′BB′ spectrum. [h] Solvent H_2O. [i] Solvent dichloromethane. [j] Solvent methanol.

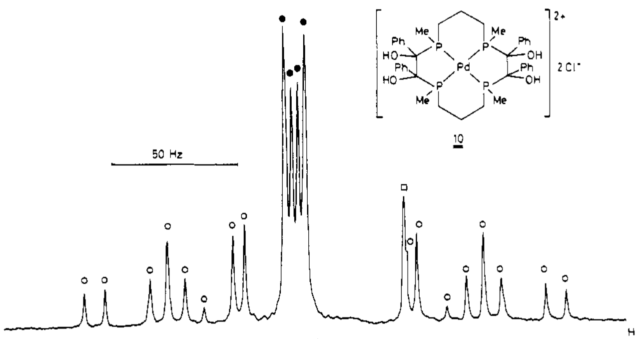


Figure 5. $^{31}P\{^1H\}$ NMR spectrum (30 MHz) of **10**, solvent methanol: (□) isomer **10a**; (●) isomer **10b**; (○) isomer **10c**.

The two conformations of the fourfold hydroxyl-substituted 1,4,8,11-tetraphosphacyclotetradecane found by us have been observed in the nickel(II) complexes of the analogous 1,4,8,11-tetraazacyclotetradecane.[28-30]

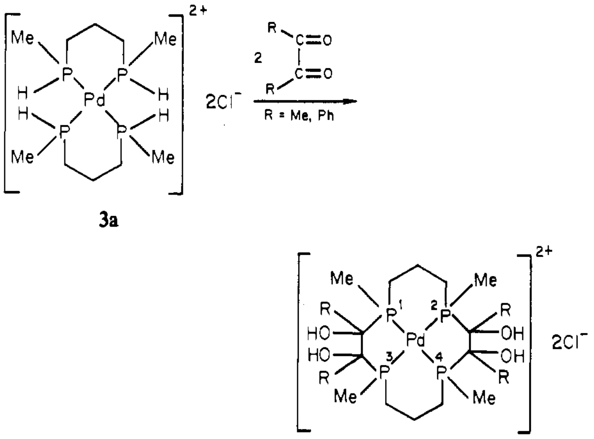
The trans-I isomer is easily capable of forming five-coordinated square-pyramidal complexes.[31,32] This property of the cyclic amine complex resembles that of **9b**, which covalently bonds a chlorine atom in the solid state (Figure 4).

In dilute aqueous solution both **9a** and **9b** have conductivities cooresponding to 2:1 electrolytes, so that the covalently bound chlorine in solid **9b** must be dissociated in dilute solution. The conformations of chelate rings do not usually play a role on the time scale of an NMR experiment.[33,34] It is thus clear from the X-ray structural data that both isomers must give a singlet in the $^{31}P\{^1H\}$ NMR spectrum.

Ring-Closure Reactions on 3a. In the analogous complexes **3** and **3a** the distance between the neighboring phosphorus atoms in the two independent ligands is determined by the chelate ring size. At the same time this defines limits for the orientation of the P–C vectors in the chelate ring which would be formed in the cyclization. In order to study the importance of these factors in the ring closure, the reactions of **3a**, which contains two six-membered chelate rings, with α- and β-diketones were investigated.

Whereas **3**, with five-membered chelate rings, and acetylacetone react with the formation of the two isomeric complexes containing macrocyclic ligands, no reaction occurs between **3a** and acetylacetone. Also, the free ligands, HMeP$(CH_2)_n$PMeH (n = 2, 3) (**1**, **1a**), do not react with acetylacetone under the same conditions.

If, however, one treats **3a** with an α-diketone, cyclization occurs with addition of the PH function on the C═O double bond (eq 8).



3a

10: R = Ph
11: R = Me

(8)

The complex **10** is only poorly soluble in ethanol; in dilute solution it is a 1:2 electrolyte. The $^{31}P\{^1H\}$ NMR spectrum is dominated by the transitions of two AA′BB′ spin systems. These two sets of lines correspond to two symmetrical isomers. The remaining line of low intensity may be attributed to a third isomer with an A_4 spin system in the $^{31}P\{^1H\}$ NMR spectrum (Figure 5).

10 was, like **9**, formed principally as a mixture of two isomers. A separation of the two isomers has not yet been achieved. When **10** is recrystallized from chlorinated hydrocarbons, variable amounts of solvent are bound as solvate molecules in the crystal.

The reaction of **3a** with biacetyl is less smooth than that with benzil. The $^{31}P\{^1H\}$ NMR spectrum of the raw product still showed some signals with chemical shifts similar to that of the starting material. However, after recrystallization from ethanol–THF, **11** could be obtained in satisfactory analytical purity. Apart from a very small residual impurity the $^{31}P\{^1H\}$ NMR spectrum showed the presence of two AA′BB′ spin systems in the region from +49 to +59 ppm in a way analogous to that for **10**.

The analysis of the $^{31}P\{^1H\}$ NMR spectra of **10** and **11** shows that for one isomer the trans-phosphorus atoms are chemically identical. Since the trans couplings are very large for the

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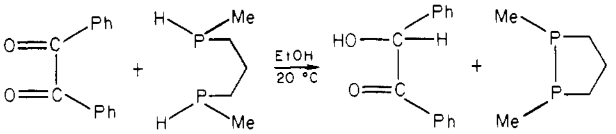
palladium complexes, $K = J_{AA'} + J_{BB'}$ becomes very large (~500 Hz) and the outer lines vanish. So, for the trans coupling constants an arbitrary value of 300 Hz was taken. Analysis of the $^{31}P\{^1H\}$ NMR spectrum of the other isomer (with an AA′BB′-type appearance) indicated P1 and P2 are chemically identical.

Clearly the steric conditions in **3a** encourage the formation of two additional five-membered chelate rings with the formation of the macrocyclic tetradentate ligand, [14]-tetraphos-1,4,8,11. The greater steric bulk of the phenyl groups in benzil in comparison to the methyl groups in biacetyl does not adversely affect the ring-closure reaction. The coupling of two six-membered chelate rings in **3a** over two three-carbon-atom bridges could not, however, be achieved.

If the free di(secondary phosphine) $HMeP(CH_2)_3PMeH$ (**1a**) is treated with benzil, a redox reaction occurs in which the main products are benzoin and 1,2-dimethyl-1,2-diphospholane[11,35] (eq 9).



(9)

1a

Ligand Displacement Reactions. One of the aims of the template synthesis of macrocyclic polydentate phosphine ligands was the preparation of the free ligand after displacement from the coordination sphere of palladium in **8–11**.

The extreme chelate effect of the tetradentate ligand stabilizes the complexes **8–11** with respect to displacement by monodentate ligands. However, because of its strong ligand field, we expected the cyanide ion to be able to displace the ligands.

Complex **9a** reacts rapidly with aqueous KCN, the macrocycle is broken up, and free $HMeP(CH_2)_2PMeH$ (**1**) is re-formed. By contrast **9b** reacts only slowly with cyanide. In the course of a few hours a mixture of uncharacterized complexes is formed. $HMeP(CH_2)_2PMeH$ (**1**) is only formed in traces. The complexes **10** and **11** are not destroyed by CN^- ions in aqueous or alcoholic solution.

Further experiments concerning ligand-exchange and ligand-replacement reactions on these complexes are currently investigated.

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Registry No. **1a**, 87137-74-4; **2**, 87137-65-3; **3a**, 87137-73-3; **3**, 81643-57-4; **4**, 87137-66-4; **5**, 87137-67-5; **6**, 87137-68-6; **7**, 87137-69-7; **8a**, 87137-70-0; **8b**, 87173-26-0; **9a**, 87173-24-8; **9b**, 87173-25-9; **10a**, 87137-71-1; **10b**, 87173-27-1; **10c**, 87173-28-2; **11a**, 87137-72-2; **11b**, 87173-29-3; **11c**, 87173-70-4.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221,
and the Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Synthesis and Characterization of a S-Bonded Sulfenamide–Cobalt(III) Complex. Single-Crystal X-ray Structure of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$. Kinetics of the NH_3OSO_3 Oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$

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Oxidation of (2-mercaptoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) with excess hydroxylamine-*O*-sulfonic acid yields (2-aminoethanesulfenamido-*N*,*S*)bis(ethylenediamine)cobalt(III) in good yield. The mixed perchlorate/oxalate salt of this sulfenamide product has been characterized by single-crystal X-ray structural analysis. Crystals of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$ are monoclinic, $P2_1/c$, with $a = 7.350$ (1) Å, $b = 17.290$ (5) Å, $c = 15.590$ (3) Å, $\beta = 100.76$ (2)°, and $Z = 4$. The structure was solved by direct methods and was refined to $R = 0.072$ based on 1715 reflections with $|F_o| > 4\sigma(|F_o|)$. Despite a somewhat short Co–S bond length of 2.250 (3) Å, the neutral S-bonded sulfenamide ligand does not induce a structural trans effect. The oxidation reaction follows the rate law $k_2[(en)_2Co(SCH_2CH_2NH_2)^{2+}][NH_3OSO_3]$ with $k_2 = a/(1 + b[H^+])$. At 25 °C, $\mu = 1.00$ M ($LiClO_4$ in aqueous media), $a = 3.2 \pm 0.1$ M^{-1} s^{-1} and $b = 16.4 \pm 0.6$ M^{-1}. The observed rate law is interpreted in terms of nucleophilic attack by the coordinated sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ on the N–O linkage of $NH_2OSO_3^-$. In this reaction the thiolato complex is as reactive a nucleophile as thiourea or triphenylphosphine.

Introduction

The chemistry of coordinated sulfur has been reviewed in detail, with special attention being given to the oxidation of thiols coordinated to cobalt(III).[3] These reactions (1) are facile, (2) often proceed via nucleophilic attack of the coordinated sulfur atom with concomitant atom or group transfer from the oxidant to the sulfur atom,[4] and (3) result in an oxidized ligand that is often considerably more stable than is the corresponding noncoordinated species. These generalizations are nicely illustrated by oxidations of the prototype thiolato cobalt(III) complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$

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