

## Reactions of Coordinated Ligands. 13.<sup>1</sup> Template Syntheses of 14- to 16-Membered Tetraphosphacycloalkanes Using Bis(tertiary phosphines) with Protected Carbonyl Groups in the Alkyl Side Chains

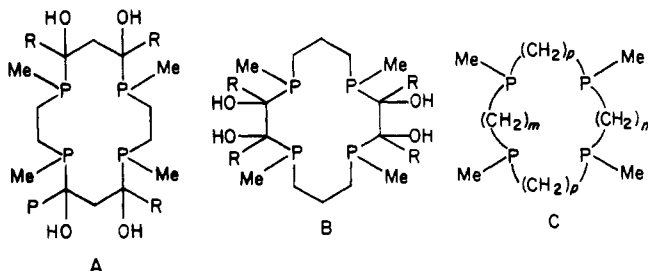
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Received November 2, 1983

Bis(tertiary phosphines) [(RO)<sub>2</sub>R'CCH<sub>2</sub>CH<sub>2</sub>PMe]<sub>2</sub>(CH<sub>2</sub>)<sub>m</sub> (L) (R = Et; R<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>; R' = H, Me; m = 2, 3), obtained by free-radical addition of (RO)<sub>2</sub>R'CCH=CH<sub>2</sub> to (HPMe)<sub>2</sub>(CH<sub>2</sub>)<sub>m</sub>, form stable complexes MLX<sub>2</sub> (M = Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>, Zn<sup>II</sup>; X = Cl, Br). On reaction with the secondary phosphines (HPMe)<sub>2</sub>(CH<sub>2</sub>)<sub>m</sub>, the halides are replaced, giving the ionic complexes [ML(HMeP)<sub>2</sub>(CH<sub>2</sub>)<sub>m</sub>]<sup>2+</sup>X<sub>2</sub><sup>-</sup>. After the carbonyl protecting groups (RO)<sub>2</sub> are removed by treatment with hydrochloric or hydrobromic acid, the macrocyclic ring system is formed by addition of the carbonyl groups to the PH bonds of the coordinated bis(secondary phosphine). The products are obtained as a mixture of diastereoisomers representing the spin systems AA'BB' or ABCD in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra. Careful spectral analysis reveals the number of the diastereoisomers formed. The degree of diastereoselectivity of the ring-closure reactions depends on ring size (n, m) and substituents R'.

### Introduction

Oligophosphacycloalkanes, the phosphorus analogues of crown ethers and macrocyclic polyamines like cyclam, are of current interest.<sup>2,3</sup> Recently we showed that complexes of such ligands are accessible in good yields by addition of dialdehydes or diketones to coordination compounds of bis(secondary phosphines).<sup>1,4</sup> The macrocycles formed contain two -CR(OH)(CH<sub>2</sub>)<sub>n</sub>CR(OH)- bridges (n = 0, 1; R = H, Me, Ph) in which each carbon atom in an α position to phosphorus is chiral (see A and B), giving a total of eight chiral centers.



Consequently, the reaction products should be obtained as a mixture of diastereoisomers. By suitable choice of the substituents R in the dicarbonyl compounds RC(O)(CH<sub>2</sub>)<sub>n</sub>C(O)R (R = H, Me, Ph; n = 0, 1), however, the diastereoselectivity of this reaction may be increased drastically. Instead of the numerous diastereoisomers expected, only two or three are formed respectively.

One serious disadvantage of this synthetic route lies in the fact that only symmetric 14-membered ring systems of type A or B may be obtained in good yields. Larger macrocycles of type C are not accessible by this method.

The ligand properties of macrocyclic polydentate donors, however, are strongly dependent on ring size and sequence of the donor atoms. This has been shown quite convincingly for the tetraazacycloalkanes by determination of stability constants, thermodynamic parameters, and redox potentials of

their complexes<sup>5,6</sup> and should also apply for the phosphorus analogues. Therefore, it seemed interesting to synthesize complexes with ligands of type C and study their coordination chemistry.

If the addition of carbonyl groups to coordinated secondary phosphine serves as the ring-closure reaction, two chiral centers are created for each new P-C bond formed. In order to limit the possibly broad diastereoisomeric distribution of the reaction products, the number of steps necessary for the formation of the macrocyclic ring system must be reduced. This should be achieved by using complexes of bis(tertiary phosphines), with the carbonyl groups in the alkyl side chains in a protected form, e.g. R'C(OC<sub>2</sub>H<sub>4</sub>O)(CH<sub>2</sub>)<sub>2</sub>PMe(CH<sub>2</sub>)<sub>n</sub>PMe(CH<sub>2</sub>)<sub>2</sub>C(OC<sub>2</sub>H<sub>4</sub>O)R' (R' = H, Me; n = 2, 3). Starting with these ligands, a two-step addition of only 1 equiv of a bis(secondary phosphine) HMeP(CH<sub>2</sub>)<sub>m</sub>PMeH (m = 2, 3) should give (after removal of the protecting ketal or acetal groups) complexes of macrocyclic 14- to 16-membered tetradentate phosphines with only six chiral centers (four P and two C atoms).

### Experimental Section

**Materials.** The bis(secondary phosphines) HMeP(CH<sub>2</sub>)<sub>m</sub>PMeH (m = 2, 3) have been prepared as reported in the literature.<sup>7</sup> The ethylene ketal of methyl vinyl ketone has been obtained by elimination of HCl from 4-chloro-2-butanone ethylene ketal.<sup>8</sup> All other chemicals were reagent grade materials and were used without further purification. All reactions were carried out in a nitrogen atmosphere.

**Bis(tertiary phosphines) 1, 3, and 4 and Derivative 2: 1,1,10,10-Tetraethoxy-4,7-dimethyl-4,7-diphosphadecane (1), 2,11-Bis(ethylenedioxy)-5,8-dimethyl-5,8-diphosphadodecane (3), and 2,12-Bis(ethylenedioxy)-5,9-dimethyl-5,9-diphosphatridecane (4).** The bis(secondary phosphine) HMeP(CH<sub>2</sub>)<sub>2</sub>PMeH (4.18 g; 34.26 mmol) was added to 8.92 g (68.52 mmol) of acrolein diethyl acetal, and the mixture was heated to 60 °C. After addition of ca. 0.1 g α,α'-azobisisobutyronitrile (AIBN), the mixture was stirred for 24 h. After separation of all volatile products at 20 °C (0.1 bar), **1** was obtained as a highly viscous oil; yield 12.83 g (98%). Compounds **3** and **4** were

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Table I. Elemental Analyses and Conductivity Data for 1-18b

color	molar conductivities <sup>a</sup> $\Lambda_M, \Omega^{-1}$ $\text{cm}^2 \text{mol}^{-1}$	$M_r$	anal., %								
			found				calcd				
			C	H	Cl	P	C	H	Cl	P	
1	colorless, highly viscous oil	$\text{C}_{18}\text{H}_{40}\text{O}_4\text{P}_2$	382.37	55.96	10.51		16.52	56.53	10.53		16.19
2	colorless	$\text{C}_{18}\text{H}_{40}\text{O}_4\text{P}_2\text{S}_2$	446.49	48.07	8.95			48.42	9.02		
3	colorless, highly viscous oil	$\text{C}_{16}\text{H}_{32}\text{O}_4\text{P}_2$	350.38	54.76	9.11			54.85	9.21		
4	colorless, highly viscous oil	$\text{C}_{17}\text{H}_{34}\text{O}_4\text{P}_2$	364.41	55.92	9.29			56.03	9.40		
5	orange	3.4 $\text{C}_{18}\text{H}_{40}\text{Cl}_2\text{NiO}_4\text{P}_2$	511.98	42.10	7.84			42.22	7.86		
6	light yellow	5.3 $\text{C}_{18}\text{H}_{40}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	559.67	38.34	6.99	12.71		38.62	7.19	12.66	
7	colorless	4.7 $\text{C}_{18}\text{H}_{40}\text{Cl}_2\text{O}_4\text{P}_2\text{Zn}$	518.64	48.07	8.95			48.41	9.02		
8	brownish green	$\text{C}_{16}\text{H}_{32}\text{Br}_2\text{NiO}_4\text{P}_2$	568.91	32.41	5.64			33.78	5.67		
9	pale yellow	0.4 $\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	527.68	36.45	6.15	13.33		36.42	6.11	13.44	
10	colorless	$\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{O}_4\text{P}_2\text{Pt}$	616.37	30.77	5.04			31.18	5.23		
11	colorless	1.4 $\text{C}_{17}\text{H}_{34}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	541.71	37.68	6.35			37.69	6.33		
12	colorless	0.06 $\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{O}_4\text{P}_2\text{Zn}$	486.65	38.59	6.55			39.49	6.63		
13a	orange	138 $\text{C}_{14}\text{H}_{34}\text{Cl}_2\text{NiO}_3\text{P}_4$	503.84	33.38	7.03	13.42		33.34	6.74	14.07 <sup>b</sup>	
13b	orange	195 $\text{C}_{15}\text{H}_{38}\text{Cl}_2\text{NiO}_4\text{P}_4$	535.84	33.86	7.16	11.28		33.59	7.09	13.23 <sup>c</sup>	
14a	light yellow	209 $\text{C}_{14}\text{H}_{32}\text{Cl}_2\text{O}_2\text{P}_4\text{Pd}$	533.53	31.00	6.35	13.25		31.51	6.03	13.28	
14b	light yellow	208 $\text{C}_{15}\text{H}_{34}\text{Cl}_2\text{O}_2\text{P}_4\text{Pd}$	547.55	32.51	6.44	12.51		32.90	6.25	12.94	
15	orange-brown	198 $\text{C}_{17}\text{H}_{38}\text{Br}_2\text{NiO}_4\text{P}_4$	616.91	33.14	6.63			33.10	6.21		
16a	colorless	203 $\text{C}_{18}\text{H}_{43}\text{Cl}_2\text{O}_4\text{P}_4\text{Pd}$	624.74	34.20	6.77	11.01		34.50	7.02	11.34 <sup>d</sup>	
16b	colorless	212 $\text{C}_{19}\text{H}_{45}\text{Cl}_2\text{O}_4\text{P}_4\text{Pd}$	638.77	35.00	7.32	11.10		35.63	7.19	11.09 <sup>d</sup>	
17a	light yellow	230 $\text{C}_{16}\text{H}_{36}\text{Cl}_2\text{O}_2\text{P}_4\text{Pt}$	650.35	29.52	5.82	10.85		29.55	5.58	10.90	
17b	yellow	226 $\text{C}_{17}\text{H}_{38}\text{Cl}_2\text{O}_2\text{P}_4\text{Pt}$	664.38	30.46	6.01	10.18		30.73	5.77	10.67	
18a	colorless	234 $\text{C}_{19}\text{H}_{45}\text{Cl}_2\text{O}_4\text{P}_4\text{Pd}$	638.77	35.17	7.13	11.18		35.63	7.19	11.09 <sup>d</sup>	
18b	light yellow	264 $\text{C}_{18}\text{H}_{40}\text{Cl}_2\text{O}_4\text{P}_4\text{Pd}$	589.72	36.60	6.72	11.68		36.66	6.84	12.02	

<sup>a</sup> Ca.  $10^{-3}$  m solutions in water at 20 °C. <sup>b</sup> Calculated for 13a·2H<sub>2</sub>O. <sup>c</sup> Calculated for 13b·2H<sub>2</sub>O. <sup>d</sup> Calculated for complex·H<sub>2</sub>O·EtOH.

synthesized in an analogous way. Thus reaction of 5.75 g (47.1 mmol) or 1.37 g (10 mmol), respectively, of the ethylene ketal of 3-buten-2-one with 11.82 g (94.3 mmol) or 2.8 g (20 mmol) of the bis(secondary phosphine) HMeP(CH<sub>2</sub>)<sub>2</sub>PMeH or HPMe(CH<sub>2</sub>)<sub>3</sub>PMeH, respectively, gave 15.6 g (94.4%) of 3 or 2.5 g (68.6%) 4 as a colorless, viscous oil.

**1,1,10,10-Tetraethoxy-4,7-dimethyl-4,7-diphosphadecane 4,7-Di-sulfide (2).** To a solution of 8.10 g (21.18 mmol) of 1 in benzene was added 1.36 g (42.36 mmol) of sulfur with vigorous stirring. The mixture was stirred at 60 °C for 12 h. After removal of the solvent at reduced pressure (20 °C (0.1 bar)), 9.36 g (99%) of 2 was obtained as a colorless solid.

**Nickel, Palladium, Platinum, and Zinc Complexes 5-12 Containing the Bis(tertiary phosphines) 1, 3, and 4: (1,1,10,10-Tetraethoxy-4,7-dimethyl-4,7-diphosphadecane-*P*<sup>4</sup>,*P*<sup>7</sup>)nickel(II) Dichloride (5), -nickel(II) Dibromide (5a), -palladium(II) Dichloride (6), and -zinc(II) Dichloride (7), (2,11-Bis(ethylenedioxy)-5,8-dimethyl-5,8-diphosphadecane-*P*<sup>5</sup>,*P*<sup>8</sup>)nickel(II) Dibromide (8), -palladium(II) Dichloride (9), -platinum(II) Dichloride (10), and -zinc(II) Dichloride (12), and (2,12-Bis(ethylenedioxy)-5,9-dimethyl-5,9-diphosphatridecane-*P*<sup>5</sup>,*P*<sup>9</sup>)palladium(II) Dichloride (11).** The preparative procedure is essentially the same for all complexes. It is presented here for the palladium complex 9. The bis(tertiary phosphine) 3 (9.2 g; 26.3 mmol), dissolved in ca. 100 mL of dichloromethane, was added with magnetic stirring to a solution of 10.08 g (26.3 mmol) of bis(benzonitrile)palladium(II) dichloride<sup>9</sup> in 250 mL of dichloromethane. The color of the solution changed from dark red to yellow. After 12 h the solvent was stripped off under reduced pressure (20 °C (0.1 bar)), and the residue was washed with 20 mL of diethyl ether and dried in vacuo; yield 12.6 g (90.5%). Use of palladium chloride instead of PdCl<sub>2</sub>(PhCN)<sub>2</sub> in this reaction gave almost the same yield. For the preparation of the nickel complexes 5 and 8, NiBr<sub>2</sub>·3H<sub>2</sub>O or NiCl<sub>2</sub> was employed with ethanol as a solvent. Metathetical reaction between 3 and bis(pyridine)platinum(II) dichloride<sup>9</sup> in CH<sub>2</sub>Cl<sub>2</sub> afforded the platinum complex 10. The zinc complexes 7 and 12 were obtained by reaction between anhydrous zinc chloride and equimolar amounts of 1 and 3, respectively, in a procedure analogous to that reported for the synthesis of 9. The yields in all these reactions ranged from 80 to ca. 95%. Analytical data are given in Table I.

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Table II. <sup>31</sup>P{<sup>1</sup>H} NMR Data<sup>a</sup> for 1-12 and the Intermediate Complexes 5b-11b

	$\delta_P^b$		$\delta_P^b$
1	-38.2	7	-30.0
2	+44.0	8	+47.0
3	-37.23, -37.32	9	+69.11, 68.44
4	-42.23	10	+40.61, 40.22
5	+59.0	11	+8.65, +7.17
6	+68.4, +68.7	12	-30.9
	$\delta_{P_1, P_2}^c$		$\delta_{P_3, P_4}^c$
5b	+59 to +53		+15 to +10
6a	+58 to +47		+8 to -6
6b	+58 to +46		-43 to -58
8a	+55 to +48		-25 to -37
9a	+55 to +44		+7 to -2
9b	+55 to +44		-49 to -58
10a	+48 to +39 (2360) <sup>d</sup>		3.4 to -7.9 (2280) <sup>d</sup>
10b	+47 to +39 (2340) <sup>d</sup>		-57 to -65 (2110) <sup>d</sup>
11b	-7.9 to -17		-45 to -55

<sup>a</sup> Phosphorus-31 chemical shifts in ppm, relative to 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> Solvent dichloromethane. <sup>c</sup> Shift ranges for the signal multiplets assigned to either coordinated tertiary or secondary phosphine. For notation, see Scheme 1. Solvent methanol. <sup>d</sup> Phosphorus-31-platinum-195 coupling constants in Hz.

**Ring-Closure Reactions. Complexes with 14-Membered Rings: (2,11-Dihydroxy-1,5,8,12-tetramethyl-1,5,8,12-tetraphosphacyclotetradecane-*P*<sup>1</sup>,*P*<sup>2</sup>,*P*<sup>8</sup>,*P*<sup>12</sup>)nickel(II) Dichloride (13a) and -palladium(II) Dichloride (14a) and (2,11-Dihydroxy-1,2,5,8,11,12-hexamethyl-1,5,8,12-tetraphosphacyclotetradecane-*P*<sup>1</sup>,*P*<sup>5</sup>,*P*<sup>8</sup>,*P*<sup>12</sup>)palladium(II) Dichloride (16a) and -platinum(II) Dichloride (17a). Complexes with 15-Membered Rings: (2,11-Dihydroxy-1,5,8,12-tetramethyl-1,5,8,12-tetraphosphacyclopentadecane-*P*<sup>1</sup>,*P*<sup>5</sup>,*P*<sup>8</sup>,*P*<sup>12</sup>)nickel(II) Dichloride (13b) and -palladium(II) Dichloride (14b), (2,11-Dihydroxy-1,2,5,8,11,12-hexamethyl-1,5,8,12-tetraphosphacyclopentadecane-*P*<sup>1</sup>,*P*<sup>5</sup>,*P*<sup>8</sup>,*P*<sup>12</sup>)nickel(II) Dichloride (15), -palladium(II) Dichloride (16b), and -platinum(II) Dichloride (17b), and (2,12-Dihydroxy-1,2,5,9,12,13-hexamethyl-1,5,9,13-tetraphosphacyclopentadecane-*P*<sup>1</sup>,*P*<sup>2</sup>,*P*<sup>9</sup>,*P*<sup>13</sup>)palladium(II) Dichloride (18a). Complex with a 16-Membered Ring: (2,12-Dihydroxy-1,2,5,9,12,13-hexamethyl-**

**1,5,9,13-tetraphosphacyclohexadecane-*P*<sup>1</sup>,*P*<sup>5</sup>,*P*<sup>9</sup>,*P*<sup>13</sup> palladium(II) Dichloride (18b).** The preparative procedure is the same for all complexes. It is presented here for **16a**. Complex **9** (3.1 g; 5.88 mmol) was suspended in 50 mL of ethanol, and 0.74 g (6.1 mmol) of the bis(secondary phosphine) HMeP(CH<sub>2</sub>)<sub>2</sub>PMeH was added dropwise to the mixture. Thereby, **9** was dissolved gradually with formation of **9a**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this solution showed two groups of signals, as indicated in Table II. After addition of ca. 0.1 mL of concentrated HCl, the reaction mixture was heated to 65–80 °C with stirring. The progress of the reaction was checked by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. After completion of the reaction, the solvent was removed in vacuo (20 °C (0.1 bar)), and the residue was washed several times with diethyl ether (a total of ca. 50 mL). The products could not be successfully recrystallized. Separation of the diastereoisomers was, however, possible using a Sephadex C 25 cation exchanger and KCl or KBr (0.04 *m*) as eluents. The reaction time was shortest for **18b** and extended to ca. 3 months for **15**. Normally it took ca. 70 h to complete the ring-closure reaction. Yields ranged from 91 to 95%. All complexes showed broad absorption bands in the 3200–3400-cm<sup>-1</sup> region, which may be assigned to OH stretching vibrations of the α-OH groups of the macrocyclic rings or/and the water molecules coordinated to the metallic center.

**Instrumentation and Physical Measurements.** Proton magnetic resonance spectra were measured on a Varian EM 390 spectrometer using Me<sub>4</sub>Si as internal reference. Proton-decoupled Fourier transform phosphorus-31 NMR spectra were obtained from a Varian FT 80 A spectrometer operating at 32.2 MHz. Some of the <sup>31</sup>P NMR spectra were measured on a Bruker WP 300 spectrometer at 121.49 MHz and a Varian XL 200 spectrometer at 80.98 MHz. The samples were held in 10-mm tubes with deuterated solvents providing an internal deuterium lock. Phosphoric acid (85%) was used as external reference. Positive chemical shifts were measured downfield from H<sub>3</sub>PO<sub>4</sub>. IR spectra were recorded on a Perkin-Elmer Model 580 grating spectrometer from 250 to 4000 cm<sup>-1</sup> as Nujol mulls between polished potassium bromide plates. Conductivity measurements were made by using a Knick digital conductometer. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany.

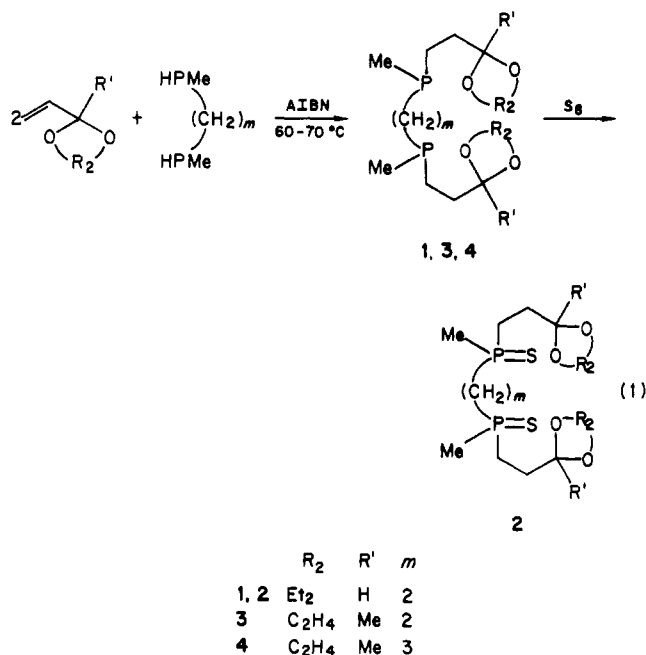
## Results and Discussion

**Bis(tertiary phosphines) with Protected Carbonyl Groups and Their Complexes.** Diamines with carbonyl groups in γ positions to nitrogen in the alkyl side chains have been used quite successfully as starting materials for the syntheses of 14- to 16-membered tetraaza macrocycles.<sup>10</sup>

Bis(tertiary phosphines) with carbonyl groups in the alkyl side chains are expected to function in a similar way in the macrocyclization according to Scheme I. They are introduced into the template in a protected form as acetals or ketals. These derivatives permit a stepwise ring closure, thus preventing side reactions like the formation of oligomeric and polymeric complexes. Compounds **1**, **3**, and **4** are obtained by free-radical addition of 2 equiv of acrolein diethyl acetal or 3-buten-2-one ethylene ketal,<sup>8,11</sup> respectively, to 1 equiv of the bis(secondary phosphine) MeHP(CH<sub>2</sub>)<sub>m</sub>PMeH (*m* = 2,3).<sup>7,12</sup>

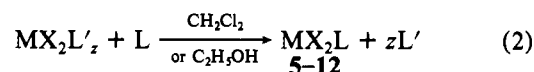
With elemental sulfur these ligands form phosphine sulfides as shown for **1** in eq 1.

Phosphines with carbonyl groups in β positions to phosphorus have been synthesized by Sokolov and Issleib<sup>13</sup> and Brunner et al.<sup>14</sup> (e.g. Ph<sub>2</sub>PCH<sub>2</sub>C(O)R; R = alkyl, -CH<sub>2</sub>PPh<sub>2</sub>). γ-Ketophosphines (e.g. RR'PCHPhCH<sub>2</sub>C(O)R''; R, R', R'' = alkyl, aryl; R' = H) have been obtained by



addition of alkali-metal phosphides RR'PM (M = alkali metal) to α,β-unsaturated ketones with subsequent hydrolysis.<sup>15</sup>

Stable complexes of composition MX<sub>2</sub>L (M = Ni, Pd, Pt, Zn; X = Cl, Br; L = **1**, **3**, **4**) are formed on treating the ligands L with NiCl<sub>2</sub>, NiBr<sub>2</sub>·3H<sub>2</sub>O, ZnCl<sub>2</sub>, bis(benzonitrile)-palladium(II) dichloride,<sup>9</sup> or bis(pyridine)platinum(II) dichloride,<sup>9</sup> respectively (eq 2).



	5	5a	6	7	8
M	Ni	Ni	Pd	Zn	Ni
L'		H <sub>2</sub> O			H <sub>2</sub> O
z		3			3
X	Cl	Br	Cl	Cl	Br
L	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>3</b>

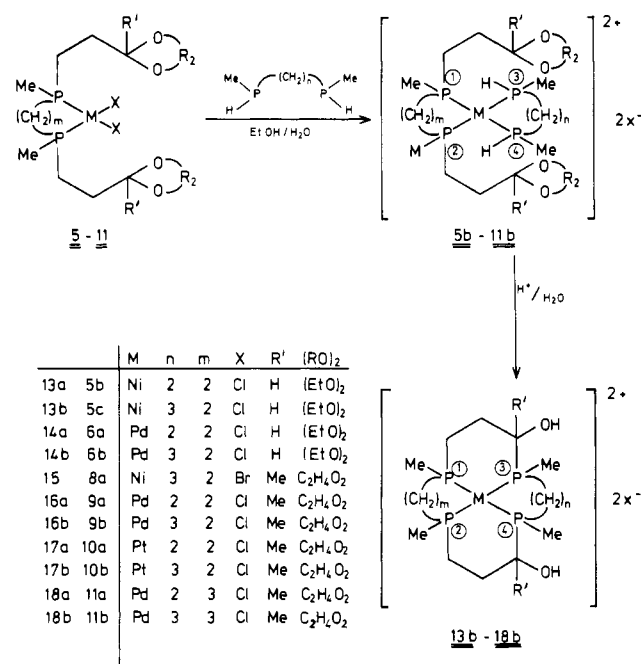
	9	10	11	12
M	Pd	Pt	Pd	Zn
L'	PhCN	py	PhCN	
z	2	2	2	
X	Cl	Cl	Cl	Cl
L	<b>3</b>	<b>3</b>	<b>4</b>	<b>3</b>

A <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic investigation of the reaction mixtures shows that the formation of **9** and **10** possibly proceeds via ionic complexes of the type [ML<sub>2</sub>]<sup>2+</sup>X<sub>2</sub><sup>-</sup> or [ML<sub>2</sub>X]<sup>+</sup>X<sup>-</sup> (M = Pd, Pt; X = Cl; L = **3**). In addition to the signals of the two diastereoisomers of the complexes MX<sub>2</sub>L, resonances at higher field were observed that were assigned to [ML<sub>2</sub>]<sup>2+</sup>X<sub>2</sub><sup>-</sup> or [ML<sub>2</sub>X]<sup>+</sup>X<sup>-</sup>, respectively (e.g. for [Pd(3)<sub>2</sub>]Cl<sub>2</sub> δ<sub>P</sub> = +44.0). This is in agreement with the phosphorus–platinum coupling constants <sup>1</sup>J(<sup>31</sup>P–<sup>195</sup>Pt) of about 2300 Hz observed for [Pt(3)<sub>2</sub>]Cl<sub>2</sub> (δ<sub>P</sub> = 35.5). For [Pt(PMe<sub>2</sub>Ph)<sub>4</sub>]Cl<sub>2</sub><sup>16</sup> or [Pt(HMeP(CH<sub>2</sub>)<sub>3</sub>PMeH)<sub>2</sub>]Cl<sub>2</sub><sup>17</sup> with square-planar coordination geometry at platinum <sup>1</sup>J(<sup>31</sup>P–<sup>195</sup>Pt) is about 2340 or 2300 Hz, respectively, while the complexes *cis*-PtCl<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub><sup>18</sup> (R = alkyl, aryl) show much higher (3400–3600 Hz) values.

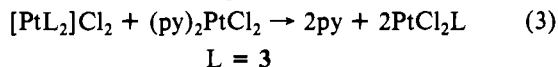
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Scheme I



The ionic complexes  $[ML_2]X_2$  or  $[ML_2X]X$  formed as intermediates may further react with the starting materials, e.g.  $(py)_2PtCl_2$ , to give the final products; for example:



In dichloromethane or methanol **5–12** are nonelectrolytes. Electrolytic dissociation with formation of Magnus salt type complexes  $[ML_2][MX_4]$  ( $M = Ni, Pd, Pt$ )<sup>19</sup> or halogen-bridged dimers  $[LM(\mu-Cl)_2ML]Cl_2$ <sup>20</sup> may therefore be excluded. This was an important prerequisite for the macrocyclization reaction presented in Scheme I.

**Formation of the Macrocyclic Complexes.** The influence of metal ions on ring-closure reactions is well-known.<sup>21</sup> Diamines and glyoxal, for instance, do not form cyclic products in the absence of a metal ion even after several days.<sup>22</sup> Similarly, the formation of tetraphosphacycloalkanes is promoted by suitable transition-metal coordination centers.<sup>23,24</sup> In the syntheses presented in Scheme I, the transition metal was expected to act as a template in an analogous manner.

In ethanol solution **5, 6, and 8–11** react with 1 equiv of the bis(secondary phosphines)  $HMeP(CH_2)_nPMeH$  ( $n = 2, 3$ ) to give ionic complexes **5b–11b**. The replacement of the halogens **X** by the bis(secondary phosphines) is indicated by an increase in the conductivity, which reaches a maximum value at a ca. 1:1 stoichiometric ratio of complex (**5, 6, or 8–11**) to bis(secondary phosphine).

The  $^{31}P\{^1H\}$  NMR spectra of **5b–11b** show two groups of signals (Table II). One group may be assigned to the bis(secondary phosphines) coordinated to Ni(II), Pd(II), or Pt(II)

in a square-pyramidal or square-planar arrangement.<sup>1,4</sup>

The P–H coupling observed in the  $^{31}P$  NMR spectra supports this assignment. No signals due to  $[M(HMeP(CH_2)_nPMeH)_2]X_2$ , however, appear in the spectra. The other group of signals corresponds to the bis(tertiary phosphine) ligand **1, 3, or 4** coordinated to the transition metals. This may be inferred from a comparison of the phosphorus-31 shift values for **5b–11b** and those for **5, 6, and 8–11** (see Table II). In case of **10a** and **10b** both groups of signals show  $^{31}P$ – $^{195}Pt$  coupling. The values for  $^1J(^{31}P$ – $^{195}Pt)$  are within the range typical for square-planar platinum(II) complexes (2300–2500 Hz).<sup>17,18</sup>

Formation of complexes  $[ML_2]X_2$  ( $L = 1, 3, 4; X = Cl, Br$ ) or  $[M(HMeP(CH_2)_nPMeH)_2]X_2$  ( $n = 2, 3; X = Cl, Br$ )<sup>1,17</sup> by ligand-scrambling reactions in **5b–11b** may therefore be excluded.

The zinc complexes **7** and **12** react only very slowly with the bis(secondary phosphines). The products obtained are ill-defined and have not been studied further.

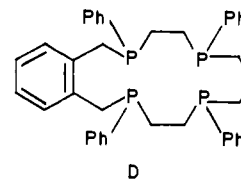
Cleavage of the acetal or ketal groups in **5b–11b** by hydrochloric or hydrobromic acid makes the free carbonyl groups accessible for the addition of the P–H bonds within the template. As a result complexes **13a–18b** are obtained (Scheme I) as a mixture of diastereoisomers (see Table III) in good yields.

The rate of these ring-closure reactions strongly depends on the substituents  $R'$  at the carbonyl groups. If H is replaced by Me (**1** vs. **3** or **4**), the rate of reaction is decreased drastically. There is also a pronounced effect of the coordination center. The formation of the macrocycle with nickel as a template center proceeds much more slowly than the corresponding reaction of the palladium or platinum analogues.

The reaction between diketones  $RC(O)(CH_2)_nC(O)R$  and phosphine complexes, e.g. *cis*-(CO)<sub>4</sub>Cr(PH<sub>3</sub>)<sub>2</sub>, has been reported by Klabunde.<sup>25</sup> There was no indication of a Buckler–Trippett type rearrangement<sup>26</sup> of the PC(OH)R- fragments in the ligand system  $PC(OH)R(CH_2)_nC(OH)RP$ .

Conductivity measurements in ethanolic solution (concentration ca.  $10^{-5} m$ ) show complexes **13a–18b** to be 2:1 electrolytes.<sup>27</sup> In cases (**14a, 14b, 15, 17a, 17b**) where no water or ethanol was coordinated to the metal, the rather broad band observed in the infrared spectra at ca.  $3400 cm^{-1}$  may be assigned unambiguously to the OH stretching vibration of the  $\alpha$ -OH groups.

The tetradentate macrocyclic phosphines formed by the template syntheses presented in Scheme I are strong-field ligands. They are not replaced by cyanide ions even on prolonged treatment of **13a–18b** with a concentrated aqueous solution of KCN at ca. 80 °C. In contrast to this extraordinary stability, demetalation occurs if the nickel complex of ligand **D** is treated with excess KCN in aqueous solution.<sup>23,24</sup> The



lower  $\sigma$ -donor power<sup>28</sup> of the aryl-substituted phosphorus atoms

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Table III.  $^{31}\text{P}\{^1\text{H}\}$  NMR Data for Complexes 13a–18b

	$\delta_{\text{P}}^{\text{a}}$				$J_{\text{PP}}^{\text{b}}$ Hz						
	P1	P2	P3	P4	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	
13a	+55 to +45 <sup>c</sup>										
14b	broad signals from -50 to +50										
14a	+50 to +40 <sup>c</sup>										
14b	isomer 1, AA'BB' <sup>d</sup>	+47.8	+47.8	-12.4	-12.4	-5.0	-45.3	293.9			-30.7
	isomer 2, AA'BB'	+47.8	+47.8	-14.7	-14.7	-8.5	-40.9	289.8			-24.5
	isomer 3, AA'BB'	+37.5	+37.5	-16.3	-16.3	-7.8	-42.8	288.8			-26.1
	isomer 4, AA'BB'	+35.9	+35.9	-11.8	-11.8	-5.7	-42.7	291.5			-28.6
	isomer 5, AA'BB'	+35.8	+35.8	-10.2	-10.2	-6.3	-46.5	292.5			-21.2
	isomer 6, ABCD	+36.9	+49.5	-23.1	-13.9	-8.2	-42.6	286.4	291.3	-43.6	-25.0
15	isomer 1, AA'BB'	+49.2	+49.2	-8.3	-8.3	-36.1	-84.8	168.5			-53.8
	isomer 2, AA'BB'	+44.2	+44.2	-0.1	-0.1	-39.7	-91.4	180.9			-51.6
	isomer 3, AA'BB'	+43.0	+43.0	-5.9	-5.9	-43.7	-89.7	179.4			-54.9
	isomer 4, ABCD	+42.8	+43.2	-0.3	-6.3	-42.1	-89.8	180.1	176.3	-86.7	-53.9
16a	isomer 1, AA'BB'	+45.6	+45.6	+55.2	+55.2	-8.1	-42.9	299.8			-8.1
	isomer 2, AA'BB'	+42.2	+42.2	+56.4	+56.4	-6.9	-42.4	293.4			-6.9
	isomer 3, ABCD	+48.7	+45.8	+63.9	+59.1	-10.5	-43.7	306.5	296.7	-43.6	-4.8
16b	isomer 1, AA'BB'	+41.4	+41.4	-2.0	-2.0	-7.2	-47.3	284.6			-19.7
	isomer 2, AA'BB'	+43.8	+43.8	-3.7	-3.7	-7.2	-47.1	288.4			-21.1
	isomer 3, AA'BB'	+39.0	+39.0	-7.5	-7.5	-3.8	-49.2	295.7			-15.6
	isomer 4, AA'BB'	+40.9	+40.9	-13.4	-13.4	-5.2	-45.3	289.7			-21.4
	isomer 5, ABCD	+39.9	+39.1	-2.6	-7.6	-4.9	-49.2	294.9	285.7	-47.3	-18.1
	isomer 6, ABCD	+45.0	+40.6	-6.2	-13.0	-6.0	-46.8	294.0	284.5	-44.3	-21.3
17a	isomer 1, AA'BB'	+38.5	+38.5	+49.0	+49.0	-8.5	-27.7	269.2			-8.5
	isomer 2, AA'BB'	+37.2	+37.2	+51.9	+51.9	-10.5	-28.1	268.0			-10.5
	isomer 3, ABCD	+41.3	+37.9	+54.4	+51.8	-10.0	-26.8	266.5	256.9	-27.4	-9.7
	isomer 4, ABCD	+41.3	+38.8	+55.2	+52.6	-8.8	-27.8	274.7	263.9	-28.2	-7.2
17b	isomer 1, AA'BB'	+34.7	+34.7	-9.7	-9.7	-6.6	-32.7	255.7			-23.8
	isomer 2, AA'BB'	+34.7	+34.7	-7.0	-7.0	-13.2	-27.4	249.4			-8.9
	isomer 3, AA'BB'	+29.8	+29.8	-13.6	-13.6	-9.7	-34.3	269.0			-23.9
	isomer 4, AA'BB'	+29.6	+29.6	-18.9	-18.9	-7.5	-33.9	264.3			-24.8
	isomer 5, ABCD	+34.2	+30.6	-11.9	-17.9	-6.6	-33.4	266.5	255.7	-33.0	-24.5
	isomer 6, ABCD	+30.3	+31.8	-13.1	-8.9	-9.6	-33.6	257.5	267.3	-33.7	-23.2
18a <sup>e</sup>	isomer 1, AA'BB'	-20.8	-20.8	+47.6	+47.6	-26.2	-42.5	288.5			-3.3
	isomer 2, AA'BB'	-17.3	-17.3	+50.3	+50.3	-25.0	-44.8	295.4			-3.3
	isomer 3, AA'BB'	-16.6	-16.6	+54.8	+54.8	-29.4	-43.7	282.4			-2.5
	isomer 4, ABCD	-20.2	-17.8	+47.4	+55.3	-27.6	-41.9	281.5	290.3	-44.1	-3.9
18b		-16.0	-14.4	+49.7	+56.1	-27.3	-43.6	285.0	295.0	-44.6	-4.4
		-19 to -32 <sup>c</sup>									

<sup>a</sup> Phosphorus-31 chemical shifts relative to 85%  $\text{H}_3\text{PO}_4$ . Solvent is ethanol unless stated otherwise. <sup>b</sup> For the notation of the phosphorus nuclei see Scheme I. <sup>c</sup> The spectrum could not be analyzed. <sup>d</sup> 270 lines in the low-field region and 111 lines in the high-field part of the spectrum could not be assigned to individual spin systems. <sup>e</sup> For an additional AA'BB' isomer, only the high field part could be assigned.

together with the poorer fit of the seven-membered chelate ring may be taken as an explanation for the lower ligand field strength of D compared to that of the ligands bound in 13a–18b.

$^{31}\text{P}\{^1\text{H}\}$  NMR Spectra of Complexes 13a–18b. The skeletons of the 14- to 16-membered tetraphosphacycloalkanes in 13a–18b contain two pairs of chemically nonequivalent phosphorus atoms. By combination of these four centers of chirality, six diastereoisomers are obtained for a square-planar coordination geometry.<sup>29</sup> The two OH groups in  $\alpha$  positions to phosphorus may be arranged in four different ways relative to a plane defined by the four phosphorus atoms. Taking into account the four pairs of enantiomeric arrangements of the (P)Me and (C)OH groups, 20 diastereoisomers result from the six centers of chirality (four P and two C atoms).

In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra they give rise to AA'BB' or ABCD spin systems.<sup>30</sup> Normally configurational isomers of complexes related to 13a–18b hardly differ in their phosphorus-31 chemical shift values.<sup>29,31</sup> If all diastereoisomers of 13a–18b were formed in a statistical ratio, very complicated

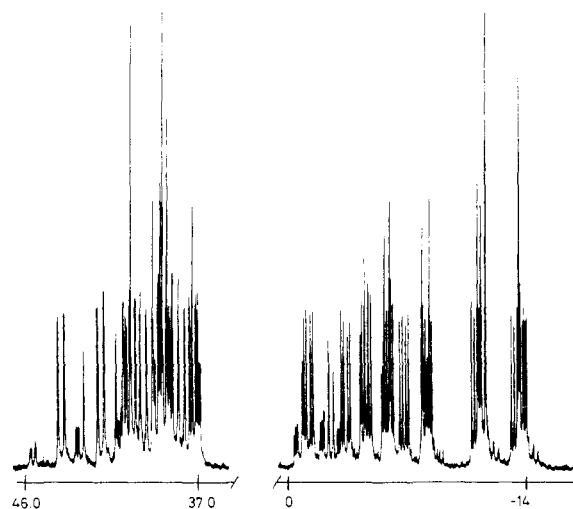
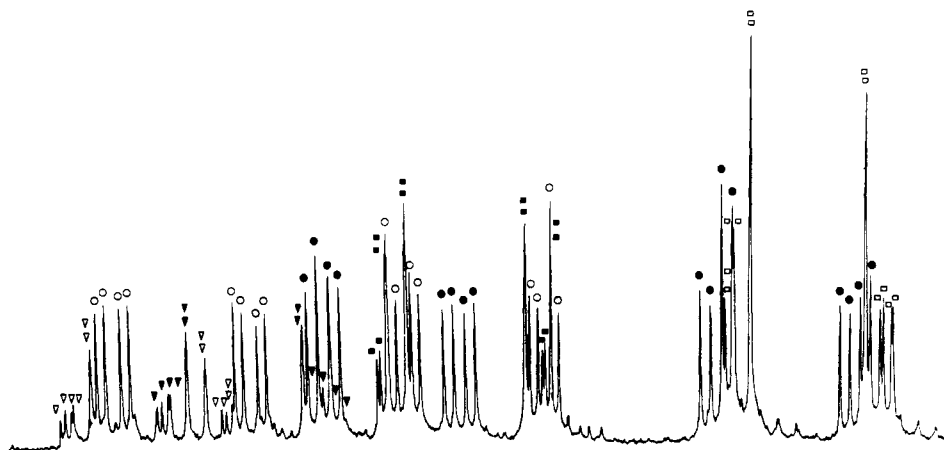


Figure 1. 80.98-MHz  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 16b (solvent  $\text{CD}_3\text{OH}$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra with partial resonance overlap must be expected; clearly, the analysis of such spectra would be quite difficult. For 13a, 13b, 14a, and 18b it was impossible, indeed, to interpret the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in terms of an assignment of the observed lines to the AA'BB' or ABCD spin systems expected for the various diastereoisomers. In the very complicated spectrum of 14b, six sets of lines for the spin

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**Figure 2.** High-field part of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **16b**: (▽) isomer 1; (▼) isomer 2; (■) isomer 3; (□) isomer 4; (○) isomer 5; (●) isomer 6.

**Table IV.** Phosphorus-31-Platinum-195 Coupling Constants for Complexes **17a** and **17b**<sup>a</sup>

		P1-Pt	P2-Pt	P3-Pt	P4-Pt
<b>17a</b>	isomer 1, AA'BB'	2111.8		2063.4	
	isomer 2, AA'BB'	2087.9		2050.6	
	isomer 3, ABCD	2070.9	2045.9	1939.9	2055.9
	isomer 4, ABCD	2126.6	2100.0	2007.5	2114.9
<b>17b</b>	isomer 1, AA'BB'	1985.5		1924.5	
	isomer 2, AA'BB'	1867.6		1892.6	
	isomer 3, AA'BB'	2044.8		2078.1	
	isomer 4, AA'BB'	2042.4		2046.8	
	isomer 5, ABCD	2018.9	2006.7	1948.3	2037.7
	isomer 6, ABCD	2023.5	2008.5	2033.1	1963.2

<sup>a</sup> Solvent ethanol. For the notation of the phosphorus atoms see Scheme I. All coupling constants in Hz.

systems AA'BB' (five) and ABCD (one) (see Table III) could be identified. There are still a considerable number of lines left that could not be assigned so far (see Table III). In the case of **16a**–**18a**, however, a complete analysis of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra could be achieved. This is shown in Figures 1 and 2 for the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **16b**.

The number of diastereoisomers obtained in the ring-closure reactions according to Scheme I is lowest (3) for the 14-membered macrocycle **16a**. Obviously the ring formation in the 14-membered palladium complex **16a** has the lowest degree of stereochemical freedom. This may be due to the close fit of the 14-membered ring system to Pd(II).

For  $\text{R}' = \text{Me}$  the number of diastereoisomers formed is lower than theoretically calculated (20). The metallic coordination center has a pronounced effect not only on the rate of reaction but also on the number of isomers formed (cf. **16a** vs. **17a**). Similar observations were made for the formation of the macrocyclic tetradentate phosphine ligand by reaction of  $[\text{M}(\text{HMeP}(\text{CH}_2)_2\text{PMeH})_2]\text{X}_2$  and acetylacetone.<sup>1,17</sup>

It should be noted that the diastereoisomers of the nickel complex **15** could be separated by use of a Sephadex C 25 ion exchanger using aqueous sodium bromide solution (0.04 *m*) for elution. This chromatographic method has been used by us<sup>17</sup> and others<sup>3</sup> for the separation of ionic diastereoisomeric complexes. In addition to the four fractions eluted, there was

a fifth one which could not be further separated. The  $^{31}\text{P}$  NMR spectrum was, however, not conclusive and could not reasonably be analyzed for either an AA'BB' or ABCD spin system.

The NMR data collected in Table III indicate that the size of the chelate rings has a similar effect on  $\delta_{\text{P}}$  and  $^2J_{\text{PP}}(\text{cis})$  as discussed before for complexes of linear tetrakis(tertiary phosphines).<sup>29,31</sup> As the chelate ring size decreases from six to five, the  $\delta_{\text{P}}$  values are shifted downfield by about 50 ppm, the coupling constants  $^2J_{\text{PP}}(\text{cis})$  being significantly smaller in the case of the five-membered ring.

The pattern of the  $^{195}\text{Pt}$ – $^{31}\text{P}$  coupling constants (see Table IV) of **17a** and **17b** does not show any significant dependence on ring size. It is noteworthy, however, that the various diastereoisomers of **17a** and **17b** show differences in  $^1J_{\text{Pt-P}}$  for the corresponding phosphorus atoms.

**Acknowledgment.** The Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, und Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen are thanked for financial support of this work. Bayer AG and Hoechst AG-Werk Knapsack are thanked for generous gifts of chemicals. Dr. Hahn, Institut für Anorganische Chemie, Universität Köln, Köln, West Germany, is thanked for running NMR spectra on the Bruker WP 300 spectrometer.

**Registry No.** **1**, 91311-63-6; **2**, 91311-64-7; **3**, 91327-57-0; **4**, 91311-65-8; **5**, isomer I, 91311-67-0; **5**, isomer II, 91383-57-2; **5a**, isomer I, 91311-68-1; **5a**, isomer II, 91383-58-3; **5b**, 91311-69-2; **5c**, 91311-70-5; **6**, isomer I, 91311-71-6; **6**, isomer II, 91383-59-4; **6a**, 91311-72-7; **6b**, 91311-73-8; **7**, isomer I, 91311-74-9; **7**, isomer II, 91383-60-7; **8**, isomer I, 91311-75-0; **8**, isomer II, 91383-61-8; **8a**, 91311-76-1; **9**, isomer I, 91311-77-2; **9**, isomer II, 91383-93-6; **9a**, 91311-78-3; **9b**, 91311-79-4; **10**, isomer I, 91311-80-7; **10**, isomer II, 91383-62-9; **10a**, 91311-81-8; **10b**, 91311-82-9; **11**, isomer I, 91311-83-0; **11**, isomer II, 91383-63-0; **11a**, 91311-84-1; **11b**, 91311-85-2; **12**, isomer I, 91311-86-3; **12**, isomer II, 91383-64-1; **13a**, 91311-87-4; **13b**, 91327-58-1; **14a**, 91311-88-5; **14b**, 91311-89-6; **15**, 91311-90-9; **16a**, 91311-91-0; **16b**, 91311-92-1; **17a**, 91311-93-2; **17b**, 91311-94-3; **18a**, 91311-95-4; **18b**, 91311-96-5;  $\text{HMeP}(\text{CH}_2)_2\text{PHMe}$ , 91311-66-9;  $\text{HPMe}(\text{CH}_2)_3\text{PMeH}$ , 39564-18-6;  $\text{NiBr}_2$ , 13462-88-9;  $\text{NiCl}_2$ , 7718-54-9;  $\text{PdCl}_2$ , 7647-10-1;  $\text{ZnCl}_2$ , 7646-85-7;  $\text{PtCl}_2(\text{py})_2$ , 14872-21-0;  $\text{PdCl}_2(\text{PhCN})_2$ , 14220-64-5; acrolein diethyl acetal, 3054-95-3; ethylene ketal of 3-butene-2-one, 26924-35-6.