Synthesis of new acyclic aminophosphites and their chelate complexes with rhodium(I) and palladium(II)

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New acyclic aminophosphites $(RO)_2POCH_2CH_2NMe_2$ (PN) (R= Et, Pr^i, or adamantyl) characterized by various steric requirements of the phosphorus center were synthesized. The reactions of the aminophosphites with $Pd(COD)Cl_2$ (COD is 1,5-cyclooctadiene) and $[Rh(CO)_2Cl]_2$ afforded the stable chelate mononuclear complexes $PdCl_2(PN)$ and RhClCO(PN), respectively. The structures of the resulting compounds were established by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy, X-ray diffraction analysis, laser and plasma desorption mass spectrometry, X-ray photoelectron spectroscopy, and sedimentation analysis.

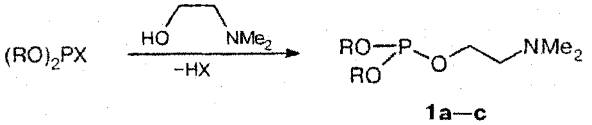
Key words: acyclic aminophosphites, palladium complexes, rhodium complexes, coordination, metal chelates, chelate-forming ligands.

P,N-Bidentate ligands, which are derivatives of phosphorous acid, *viz.*, aminophosphites and aminophosphoramidites, are synthetically available compounds stable to oxidative destruction. Their phosphorus centers have a pronounced π-acceptor character. Owing to these facts, these compounds are convenient and attractive ligands in the coordination chemistry of platinum metals.[1—5] Recently, the successive use of these systems in enantioselective catalytic reactions of allylic substitution[6,7] and conjugated addition[8] have been reported. At the same time, all the above-mentioned compounds contain a cyclic (generally, phospholane) phosphorus center. Only several acyclic aminophosphites, *viz.*, derivatives of *N,N*-dimethylaminoethanol[9,10] $(RO)_2POCH_2CH_2NMe_2$ (R = Ph, bornyl, menthyl, or cholesteryl) and quinine[11] $(RO)_2$PQuinine (R = $C_{10}H_{21}$ or $C_{16}H_{33}$), which were used in the synthesis of palladium(II) and rhodium(I) complexes, are known. Let us also mention the potentially P,N-bidentate $(Pr^iO)_2PN(CH_3)CH_2CH_2NMe_2$[12] and $(MeO)_2POCHCH_2C(Me_2)NHC(Me_2)CH_2$[13] ligands.

In the present work, we report the synthesis of new representatives of acyclic aminophosphites, which differ substantially from the viewpoint of the steric requirements of the phosphorus center, and the results of studies of their coordination to palladium(II) and rhodium(I). Chlorocarbonyl rhodium(I) complexes containing alkyl substituents in the acyclic phosphite center were synthesized for the first time.

Results and Discussion

New acyclic aminophosphites were synthesized according to the following general scheme:



1a—c

X = Cl, R = Ad (**a**); X = NEt_2, R = Pr^i (**b**); X = Cl, R = Et (**c**)

Generally, phosphorylation of *N,N′,N′*-trimethylethylenediamine is performed with the use of phosphorochloridite $(Pr^iO)_2PCl$.[12] We attempted to use phosphoramidite $(Pr^iO)_2PNEt_2$ for this purpose. However, this attempt was not quite successful because the corresponding phosphoramidite $(AdO)_2PNEt_2$ (Ad is adamantyl) exhibits weak phosphorylating activity and ~20% of this compound remained unconsumed even after refluxing of the reaction mixture in toluene for 4 h (according to a procedure analogous to the synthesis of **1b**), a substantial amount of admixtures being formed along with compound **1a**. Because of this, we synthesized **1a** according to another procedure, *viz.*, through the corresponding phosphorochloridite $(AdO)_2PCl$ prepared *in situ*. This approach allowed us to obviate the need for the isolation of this labile phosphorylating agent; however, in this case $(AdO)_3P$ was also formed as

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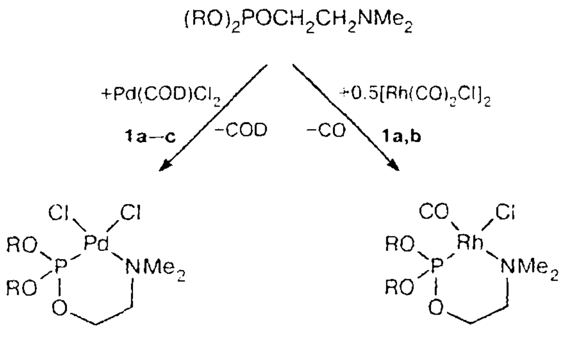
a by-product. This by-product can be separated only by double fractional distillation. Aminophosphite **1c** was prepared with the use of $(EtO)_2PCl$.[14]

The complexation with aminophosphites **1a—c** afforded stable mononuclear chelate compounds **2a—c** and **3a,b**.



2a—c **3a,b**

The data of ^{31}P NMR and IR spectroscopy (Tables 1 and 2, respectively) are in good agreement with the suggested structures of the complexes. Thus the presence of the Pd—P bond in compounds **2a—c** is confirmed by substantial coordination shifts $\Delta\delta_P$ observed in the range from δ –60.4 to –68.0. The δ_P values in the region δ 62—78 are characteristic of six-membered palladium chelates with acyclic aminophosphites.[9,10] Note that, unlike the NMR spectra of aminophosphine palladium(II) *cis*-dichloride complexes, the spectra of the corresponding aminophosphite complexes have regular upfield coordination shifts $\Delta\delta_P$ because the π-acceptor character of the phosphorus center is responsible for shielding of the phosphorus nucleus. In the long-wavelength regions of the IR spectra of compounds **2a—c**, two ν(Pd—Cl) absorption bands with equal intensities are observed. These bands correspond to the *cis* configuration of the Cl^- ligands and to different *trans* effects of the phosphorus and nitrogen centers. The spin-spin coupling constants ^1J(P,Rh) and the ν(CO) bands (see Tables 1 and 2, respectively) for compounds **3a,b** are characteristic of the *cis* orientation of the phosphorus and nitrogen atoms at the rhodium atom and of the *trans*-carbonyl ligand and the amino group (see Ref. 4 and references cited therein).

The data of ^{13}C NMR spectroscopy (Table 3) agree well with the structures suggested for chelate complexes **2a—c** and **3a,b**. A comparison of the spectral parameters of the free and coordinated aminophosphites revealed substantial downfield coordination shifts of the signals for the carbon atoms at the phosphorus ($\Delta\delta_C$ 5—12) and nitrogen ($\Delta\delta_C$ 3—9) donor centers. Analogous regularities are also observed in the ^1H NMR spectra (Table 4). For example, the downfield shift $\Delta\delta_H$ of the resonance signals for the protons of the methyl groups at the nitrogen atom are 0.4—0.8 ppm. Note also the pronounced homology of the ^1H and ^{13}C NMR spectral characteristics (see Tables 3 and 4, respectively) of compounds **2a—c** and **3a,b**, which is attributed to the similarity of their chelate structures.

Table 1. ^{31}P NMR spectra (δ, *J*/Hz) of compounds **1a—c**, **2a—c**, and **3a,b**

Compound	Solvent	δ_P	$\Delta\delta_P$*	$^1J_{P,Rh}$
1a	$CDCl_3$	129.5	—	—
1b	$CDCl_3$	138.8	—	—
1c	$CDCl_3$	139.3	—	—
	DMF-d_7	138.8	—	—
2a	$CDCl_3$	61.5	–68.0	—
2b	$CDCl_3$	74.9	–63.9	—
	DMF-d_7	76.9	—	—
2c	DMF-d_7	78.4	–60.4	—
3a	$CDCl_3$	113.9	–15.6	266.8
3b	$CDCl_3$	127.1	–12.2	261.7
	Me_2CO	127.5	—	260.2

* $\Delta\delta_P = \delta_P$ (complex) – δ_P (ligand).

Table 2. IR spectra (ν/cm^{-1}) of complexes **2a—c** and **3a,b**

Compound	ν(M—Cl) (conditions of measurements of the spectrum)	ν(CO) (conditions of measurements of the spectrum)
2a	340, 284 (Nujol)	—
	344, 278 ($CHCl_3$)	—
2b	337, 285 (Nujol)	—
	342, 284 ($CHCl_3$)	—
2c	338, 284 (Nujol)	—
3a	300 (Nujol)	2000 (KBr), 2014 ($CHCl_3$)
3b	286 (Nujol)	2000 (KBr), 2022 ($CHCl_3$)

Much attention was given to the determination of the molecular weights of the new complex compounds. We chose rhodium complexes **3a,b** for the mass-spectrometric analysis because we have observed intense recombining ions for *cis*-dichloride palladium(II) complexes with aminophosphites and aminophosphoramidites many times. These ions substantially hinder the interpretation of the results (even when "mild" methods of mass spectrometry, *viz.*, field and plasma desorption and fast-atom bombardment (FAB), are used).[2,9] On the whole, the results of mass spectrometry of compounds **3a,b** do not contradict their structures. Thus the mass spectrum of compound **3a** (plasma desorption (PD) method) has the following signals, *m/z* (I_{rel} (%)): 560 $[M - CO]^+$ (3), 524 $[M - Cl - CO]^+$ (8), 392 $[L - 2 Me + H]^+$ (10), 135 $[adamantyl]^+$ (45), 72 $[CH_2CH_2NMe_2]^+$ (100), 58 $[CH_2NMe_2]^+$ (35); in the laser desorption (LD) mass spectrum: 523 $[M - CO - Cl - H]^+$ (100), 389 $[L - 2 Me - 2 H]^+$ (41). An analogous situation is also typical of compound **3b** (LD mass spectrum, *m/z* (I_{rel} (%)): 368 $[M - Cl]^+$ (16), 340 $[M - Cl - CO]^+$ (2), 297 $[M - Cl - CO - Pr^i]^+$ (20), 152 $[L - 2 Pr^i + H]^+$ (4), 72 $[CH_2CH_2NMe_2]^+$ (100), 58 $[CH_2NMe_2]^+$ (40)). However, the PD mass spectrum

Table 3. ^{13}C NMR spectra (δ, $J_{C,P}$/Hz) of compounds **1a—c**, **2a—c**, and **3a,b**

Molecular fragment	**1a**	**2a**	**3a**	**1b**	**2b**	**3b**	**1c**	**2c**
	CDCl$_3$						DMF-d$_7$	
C_{quat}	75.03 (^2J = 8.9)	87.23 (^2J = 13.3)	82.92 (^2J = 11.9)					
OCH$_2$	59.72 (^2J = 3.6)	64.29 (^2J = 6.9)	64.58 (^2J = 6.7)	59.74 (^2J = 4.5)	64.61 (^2J = 6.5)	65.26 (^2J = 7.8)	61.60 (^2J = 4.3)	68.17 (^2J = 2.1)
CH$_2$N	56.40	61.72 (^3J = 3.2)	61.40 (^3J = 4.4)	58.77 (^3J = 5.2)	62.07 (^3J = 3.2)	61.85 (^3J = 4.5)	59.30 (^3J = 10.7)	67.80 (^3J = 4.5)
NMe$_2$	45.60	52.55	48.93	45.66	52.59	48.99	47.11	56.21
OCCH$_2$	44.72 (^3J = 8.4)	44.19 (^3J = 4.6)	44.52 (^3J = 4.2)					
CH$_2$	35.86	35.53	35.55					
CH	30.83	31.26	30.85					
CO			186.0 ($^1J_{C,Rh}$ = 73.8; $^2J_{C,P}$ = 20.3)			185.50 ($^1J_{C,Rh}$ = 71.0, $^2J_{C,P}$ = 20.9)		
OCH				66.31 (^2J = 15.4)	77.44 (^2J = 4.1)	70.4		
CH$_3$				24.38 (^3J = 4.0); 24.33 (^3J = 3.6)	23.72 (^3J = 3.6) 23.46 (^3J = 5.8)	23.80 (^3J = 3.2) 23.70 (^3J = 4.9)	18.32 (^3J = 4.7)	20.0 (^3J = 6.7)
O$\underline{C}$H$_2$CH$_3$							61.80 (^2J = 11.0)	68.80 (^2J = 2.0)

Table 4. ^1H NMR spectra (δ, J/Hz, CDCl$_3$) of compounds **1b,c**, **2b,c**, and **3b**

Molecular fragment	**1b**	**2b**	**3b**	**1c**	**2c**
OCH	4.34 m ($^3J_{H,P}$ = 8.8)	5.12 m ($^3J_{H,P}$ = 9.8)	4.89 m ($^3J_{H,P}$ = 10.4)		
OCH$_2$	3.84 q (^3J = 6.4; $^3J_{H,P}$ = 6.8)	4.12 dt (^3J = 4.0; $^3J_{H,P}$ = 18.4)	4.12 dt (^3J = 4.0; $^3J_{H,P}$ = 18.0)	3.86 m (^3J = 6.2; $^3J_{H,P}$ = 7.4)	4.19 dt (^3J = 4.1; $^3J_{H,P}$ = 17.9)
CH$_2$N	2.48 t (^3J = 6.4)	2.76 t (br) (^3J = 4.0)	2.69 m (br)	2.49 t (^3J = 6.2)	2.80 dt (^3J = 4.1; $^4J_{H,P}$ = 3.1)
NMe$_2$	2.22 s	2.98 s	2.64 s	2.23 s	3.02 s
CH$_3$	1.22 d (^3J = 1.2) 1.20 d (^3J = 1.6)	1.37 d (^3J = 6.0) 1.31 d (^3J = 6.4)	1.31 t (^3J = 6.0; ^3J = 4.4)	1.23 t (^3J = 7.1)	1.38 t (^3J = 7.0)
OC$\underline{H}_2$CH$_3$				3.84 m (^3J = 7.1)	4.43 m (^3J = 7.0)

of compound **3b** contains signals of heavier ions: 772 [2 M − Cl]$^+$ (10), 751 [2 M − 2 CO]$^+$ (7), 717 [2 M − 2 CO − Cl + H]$^+$ (3). Apparently, these ions were formed as a result of gas-phase reactions proceeding under conditions of mass spectrometry. Thus the [2 M − Cl]$^+$ peak can appear due to an interaction between the M molecule and the [M − Cl]$^+$ ion, as was demonstrated by the FAB mass spectrum of the [RhL(CO)Cl] chelate complex, where L is the pyridylphosphine P,N-bidentate ligand.[15] This fact is further evidence that the results of mass spectrometry of complexes with P,N-bidentate ligands should be interpreted with caution.

For this reason, solutions of complexes **2a—c** and **3a,b** were studied by sedimentation analysis, which confirmed a mononuclear character of these compounds (Table 5) because the determined M_Z values and the calculated M_r values coincide to within the experimental error (±7%). The curves of the equilibrium sedimentation distribution are typical of monodisperse compounds and indicate that admixtures with other molecu-

Table 5. Results of sedimentation analysis of complexes **2a—c** and **3a,b**

Compound	Molecular weight		d^a/Å	
	M_Z^{b} experiment	M_r calculation	I	II
2a	596 (DMF)	599	10.4 (DMF)	11.4
2b	441 (DMF)	414	9.8 (DMF)	9.2
2c	385 (DMF)	387	8.8 (DMF)	9.4
3a	632 (DMSO)	588	13.4 (DMSO)	11.9
3b	—	404	9.2 (acetone)	9.7

[a] *d* is the diameter of the sphere in which the molecule can be inscribed; I, according to the results of the determination of the diffusion coefficient; II, according to the results of calculations by the MM2 method.

[b] The solvent is given in parentheses.

lar weights, for example, dimers, are absent. The only exception is complex **3b** for which sedimentation was not equilibrated during the standard time of the run (2—4 h) whatever solvent was used (DMSO, DMF, or acetone). In addition, the diameters of the spheres in which the molecules can be inscribed were determined for all complexes by measuring the diffusion coefficients (see Table 5). The obtained estimates of the particle sizes agree well with the results of calculations of the equilibrium geometry of the complex molecules by the MM2 method[16] (only in the case of complex **3a**, the error was larger than 10%). In the case of compound **2c**, this estimate (9.182 Å) agrees also with the results of X-ray diffraction analysis (see below). This convincing agreement has also been mentioned previously,[9] which indicates, in our opinion, that the above-mentioned approach to the determination of the degree of nucleation of metal complexes is sufficiently reliable.

Complexes **2a—c** and **3a,b** are characterized by high stability in organic media, including coordinatively active media. This is evidenced by the fact that the ^{31}P NMR spectral characteristics obtained in the studies of freshly prepared solutions are identical to those of solutions stored over a long period. For example, the ^{31}P NMR spectrum of a solution of compound **2c** in DMF-d_7 stored for 4 days has the same singlet at δ_P 76.9.

Compound **2c** was studied by X-ray photoelectron spectroscopy. The determined bond energies (E_{bond}/eV) are as follows: Pd (3d5/2), 336.8; P (2p), 132.2; Cl (2p), 197.9 and 198.9; and N (1s), 398.8. These values are rather typical of dichloride palladium(II) complexes,[17] including those with aminophosphites and aminophosphoramidites.[18] Note the presence of two maxima in the curve of the Cl 2p bond energy due to the asymmetry of the bond lengths in the $PdCl_2$ fragment.[2]

The structure of complex **2c** was conclusively established by X-ray diffraction analysis (Fig. 1). Analysis of the bond lengths and bond angles (Table 6) demonstrated that these values are close to the corresponding parameters in the $Cl_2Pd(BlO)_2POCH_2CH_2NMe_2$ complex (Bl is bornyl) studied previously.[9] The Pd(1)—Cl(2) bond length (2.380(2) Å) is larger than the Pd(1)—Cl(1) bond length (2.294(2) Å). This is attributable to the stronger *trans* effect of the P atom compared to that of the N atom. The results of calculations of the Pd—Cl bond lengths (2.401 and 2.313 Å) according to the Badger equation based on the ν(Pd—Cl) vibration frequencies in the IR spectrum of compound **2c** (see Table 2) agree well with the data of X-ray diffraction study. The deviation of the calculated values from the structural data (0.02 Å) is numerically equal to the average value of the absolute errors.[19] The Pd(1)—P(1) distance (2.194(2) Å) is smaller than the known corresponding bond lengths in dichloride palladium complexes with P,N-bidentate ligands that form six-membered metallocycles (2.208—2.241 Å; see Ref. 9 and references cited therein) and is slightly larger than the shortest known Pd(1)—P(1) bond length (2.189(1) Å) in the $Cl_2Pd[(BlO)_2POCH_2CH_2NMe_2]$ complex,[9] which reflects the pronounced π-acceptor nature of the phosphite center.

Table 6. Principal bond lengths (*d*) and bond angles (ω) in the structure of **2c**

Bond	*d*/Å	Angle	ω/deg
Pd(1)—N(1)	2.120(6)	N(1)—Pd(1)—P(1)	95.0(2)
Pd(1)—P(1)	2.194(2)	N(1)—Pd(1)—Cl(1)	179.1(2)
Pd(1)—Cl(1)	2.294(2)	P(1)—Pd(1)—Cl(1)	84.29(8)
Pd(1)—Cl(2)	2.380(2)	N(1)—Pd(1)—Cl(2)	91.9(2)
P(1)—O(2)	1.538(8)	P(1)—Pd(1)—Cl(2)	172.51(8)
P(1)—O(3)	1.560(7)	Cl(1)—Pd(1)—Cl(2)	88.82(8)
P(1)—O(1)	1.569(6)	O(2)—P(1)—O(3)	100.4(5)
		O(2)—P(1)—O(1)	101.0(4)
		O(3)—P(1)—O(1)	106.5(4)
		O(2)—P(1)—Pd(1)	118.9(3)
		O(3)—P(1)—Pd(1)	111.4(3)
		O(1)—P(1)—Pd(1)	116.7(3)
		C(8)—N(1)—Pd(1)	106.9(7)
		C(2)—N(1)—Pd(1)	116.5(5)
		C(7)—N(1)—Pd(1)	105.4(6)

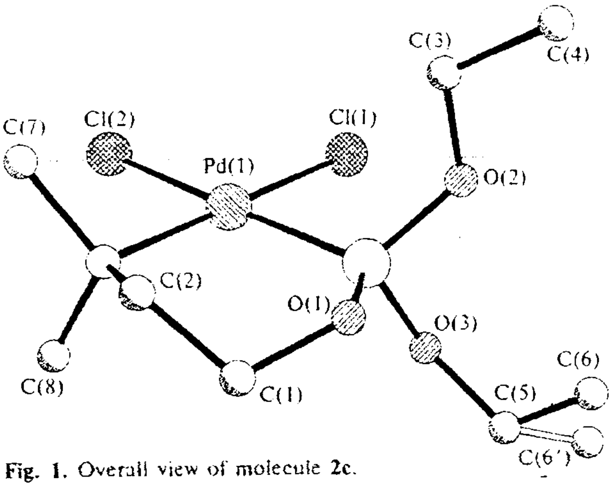


Fig. 1. Overall view of molecule **2c**.

The palladium atom is characterized by the planar-square configuration. The six-membered metallocycle adopts a boat conformation with the C(1) and C(2) atoms deviating from the mean plane by 0.46 Å and 0.31 Å, respectively.

In conclusion, note that the parameters of the phosphorus centers in compounds **1a—c** differ substantially. As an example we refer to the results of calculation of the steric requirements of the phosphorus atom performed by the semiempirical quantum-mechanical AM1 method[19] with the use of the procedure for the determination of the cone angle[20]: **1a** (177°), **1b** (138°), and **1c** (118°). However, all these acyclic aminophosphites form chelate rhodium(I) and palladium(II) complexes of the same type.

Experimental

The IR spectra were recorded on Specord M-80 and Nicolet 750 instruments in $CHCl_3$ and in Nujol mulls in polyethylene cells and between CsI plates as well as in KBr pellets. The ^{31}P NMR spectra were measured on a Bruker AMX-400 instrument operating at 161.98 MHz and on a Bruker AC-200 instrument operating at 81.0 MHz relative to 85% H_3PO_4 as the external standard. The ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument operating at 100.61 MHz relative to $CDCl_3$ (δ_C 76.91). The ^1H NMR spectra were measured on the same instrument operating at 400.13 MHz relative to Me_4Si. Plasma desorption (PD) mass spectrometry was performed on an MS-VKh time-of-flight mass spectrometer with ionization by nuclear fragments of ^{252}Cf. Laser desorption (LD) mass spectrometry was carried out on a Thermobioanalysis Vision 2000 instrument by the matrix-free ionization method with the use of an UV laser (337 nm). The electron impact (EI) mass spectra were recorded on a Varian MAT 311 instrument with direct introduction of the sample. The data of sedimentation analysis and the results of measurements of the diffusion coefficients were obtained on an MOM 3180 analytical ultracentrifuge with the Philpot—Swensson optics in two-compartment and boundary-forming cells according to known procedures.[9] The data of X-ray photoelectron spectroscopy were obtained on a Kratos XSAM 800 spectrometer; calibration against Ag (line at 84.0 eV), the charging of the sample was taken into account (285.0 eV); the accuracy of the determined maximum of the spectral line was ±0.1 eV.

X-ray diffraction study of a single crystal of compound **2c** ($C_8H_{20}Cl_2NO_3PPd$) was carried out at 153 K on an automated four-circle Siemens P3 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta < 60°$). The crystals are monoclinic, at 153 K: $a = 6.006(1)$, $b = 9.835(2)$, $c = 12.635(2)$ Å, $\beta = 98.59(2)°$, $V = 738.0(3)$ Å^3, $d_{calc} = 1.739$ g cm^{-3}, $\mu = 17.20$ mm^{-1}, $F(000) = 388$, M = 386.52, space group Pc, $Z = 2$. A total of 3550 independent reflections were measured of which 3497 reflections were used in the structure refinement.

The structure was refined by the full-matrix least-squares method in the anisotropic-isotropic approximation based on F^2. The positions of the hydrogen atoms were calculated geometrically. Analysis of the difference Fourier syntheses revealed additional peaks in the region of the ethyl group at the O(3) atom. These peaks were attributed to the disorder of the terminal atom.

The final R factors were as follows: $wR_2 = 0.1320$, GOF = 0.946 using all 3497 measured reflections ($R_1 = 0.0485$ using 2187 reflections with $I > 2\sigma(I)$ based on F). All calculations were carried out on an IBM PC/AT computer with the use of the SHELXTL PLUS program package (version 5).

All reactions were performed under an atmosphere of dry argon. The solvents were dried according to known procedures[21] and stored over 3 Å and 4 Å molecular sieves. The phosphorylating reagents were distilled immediately before use. *N,N*-Dimethylaminoethanol was twice distilled over KOH and then over a small amount of $LiAlH_4$ immediately before use. Adamant-1-ol (Merck) was sublimed *in vacuo* (1 Torr) immediately before use. The initial $Pd(COD)Cl_2$ and $[Rh(CO)_2Cl]_2$ complexes were prepared according to known procedures.[22,23]

Di(adamant-1-yl) *N,N*-diethylphosphoramidite. Adamantan-1-ol (5.214 g, 0.034 mol) and $P(NEt_2)_3$ (4.236 g, 0.017 mol) were dissolved in toluene (20 mL). The resulting solution was heated to boiling with intense stirring and refluxed for 3 h. Then the solvent was distilled off (together with $HNEt_2$) to approximately one-half of the initial volume and the remaining solution was concentrated *in vacuo* (40 Torr). The resulting product was evacuated (10 Torr) at 80 °C for 0.5 h and distilled. B.p. 218—220 °C (0.8 Torr), n_D^{20} 1.4634. The yield was 4.475 g (65%). A viscous colorless liquid. Found (%): C, 71.27; H, 10.03; N, 3.50; P, 7.81. $C_{24}H_{40}NO_2P$. Calculated (%): C, 71.08; H, 9.94; N, 3.45; P, 7.64. ^{31}P NMR ($CDCl_3$), δ: 129.8. ^{13}C NMR ($CDCl_3$), δ: 73.61 (d, C_{quat}, $^2J = 9.0$ Hz); 44.62 (d, $O\underline{C}CH_2$, $^3J = 8.5$ Hz); 37.19 (d, NCH_2, $^2J = 21.7$ Hz); 36.0 (s, CH_2); 30.71 (s, CH); 14.68 (d, $NCH_2\underline{C}H_3$, $^3J = 3.6$ Hz).

Diisopropyl *N,N*-diethylphosphoramidite. A solution of Cl_2PNEt_2 (7.337 g, 0.042 mol) in benzene (30 mL) was slowly added dropwise with intense stirring and cooling to 0 °C to a solution of Pr^iOH (5.04 g, 0.084 mol) and NEt_3 (8.484 g, 0.084 mol) in the same solvent (150 mL). Then the reaction mixture was heated to boiling and cooled, $Et_3N \cdot HCl$ that precipitated was filtered off, and the benzene was evaporated *in vacuo* (40 Torr). The resulting product was distilled. B.p. 67—68 °C (10 Torr), n_D^{20} 1.4269. The yield was 6.0 g (65%). A nonviscous colorless liquid. Found (%): C, 54.17; H, 10.62; N, 6.25; P, 14.12. $C_{10}H_{24}NO_2P$. Calculated (%): C, 54.28; H, 10.93; N, 6.33; P, 14.00. ^{31}P NMR ($CDCl_3$), δ: 144.9. ^{13}C NMR ($CDCl_3$), δ: 66.02 (d, OCH, $^2J = 17.9$ Hz); 37.01 (d, NCH_2, $^2J = 20.9$ Hz); 24.20 (d, $OCH\underline{C}H_3$, $^3J = 4.8$ Hz); 24.16 (d, $OCH\underline{C}H_3$, $^3J = 4.5$ Hz); 14.79 (d, $NCH_2\underline{C}H_3$, $^3J = 3.1$ Hz).

Di(adamant-1-yl) 2-(*N,N*-dimethylamino)ethyl phosphite (1a). A solution of adamant-1-ol (4.354 g, 0.0286 mol) and NEt_3 (2.888 g, 0.0286 mol) in benzene (100 mL) was slowly added dropwise with intense stirring and cooling to 0 °C to a solution of PCl_3 (1.966 g, 0.0143 mol) in the same solvent (50 mL). Then the reaction mixture was stirred at 25 °C for 1 h and $Et_3N \cdot HCl$ that precipitated was filtered off. A solution of *N,N*-dimethylaminoethanol (1.273 g, 0.0143 mol) and NEt_3 (1.444 g, 0.0143 mol) in benzene (30 mL) was added dropwise with intense stirring and cooling to 0 °C to the resulting filtrate over 0.5 h. Then the reaction mixture was heated to boiling and cooled. $Et_3N \cdot HCl$ that precipitated was filtered off, and the benzene was evaporated *in vacuo* (40 Torr). The resulting product was evacuated (10 Torr) at 80 °C for 0.5 h and twice distilled *in vacuo* to remove $(AdO)_3P$ that formed as a by-product, the fraction with the b.p. 210—220 °C and then the fraction with the b.p. 217—218 °C (0.8 Torr) being taken; n_D^{20} 1.4678. The yield was 2.227 g (37%). A viscous colorless liquid. Found (%): C, 68.11; H, 9.77; N, 3.30; P, 7.27. $C_{24}H_{40}NO_3P$. Calculated (%): C, 68.38; H, 9.56; N, 3.32; P, 7.35. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 405 [M − Me − H]$^+$ (4), 390 [M − 2 Me − H]$^+$ (10), 286 [M − Ad]$^+$ (11), 270 [M − AdO]$^+$ (65), 152 [AdOH]$^+$ (19), 135 [Ad]$^+$ (100), 72 [$CH_2CH_2NMe_2$]$^+$ (73), 58 [CH_2NMe_2]$^+$ (60).

Diisopropyl 2-(*N*,*N*-dimethylamino)ethyl phosphite (1b). *N*,*N*-Dimethylethanolamine (1.0 g, 0.011 mol) and $(Pr^iO)_2PNEt_2$ (2.51 g, 0.011 mol) were dissolved in toluene (20 mL). The resulting solution was heated to boiling with intense stirring and then refluxed for 3 h. Then the solvent was distilled off (together with $HNEt_2$) to approximately one-half of the initial volume and the remaining solution was concentrated *in vacuo* (40 Torr). The residue was dissolved in hexane (10 mL), the solution was filtered, and the hexane was evaporated *in vacuo* (40 Torr). The resulting product was evacuated (20 Torr) at 25 °C for 0.5 h and distilled. B.p. 102—103 °C (10 Torr), n_D^{20} 1.4290. The yield was 1.3 g (50%). A colorless nonviscous liquid. Found (%): C, 50.31; H, 10.26; N, 6.21; P, 12.84. $C_{10}H_{24}NO_3P$. Calculated (%): C, 50.62; H, 10.19; N, 5.90; P, 13.05. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 237 [M]$^+$ (1), 194 [M − Pr^i]$^+$ (1), 151 [M − 2 Pr^i]$^+$ (9), 135 [M − OPr^i − Pr^i]$^+$ (24), 106 [Pr^iOPO]$^+$ (77), 72 [$CH_2CH_2NMe_2$]$^+$ (15), 58 [CH_2NMe_2]$^+$ (100).

Diethyl 2-(*N*,*N*-dimethylamino)ethyl phosphite (1c). A solution of *N*,*N*-dimethylaminoethanol (3.204 g, 0.036 mol) and Et_3N (3.636 g, 0.036 mol) in Et_2O (20 mL) was slowly added dropwise with intense stirring and cooling to 0 °C to a solution of $(EtO)_2PCl$ (5.636 g, 0.036 mol) in Et_2O (70 mL). The reaction mixture was stirred at 25 °C for 1 h and kept for 12 h. Then $Et_3N \cdot HCl$ was filtered off, Et_2O was evaporated *in vacuo* (40 Torr), and the resulting product was distilled. B.p. 61—62 °C (1 Torr), n_D^{20} 1.4316. The yield was 3.536 g (47%). A colorless nonviscous liquid. Found (%): C, 46.00; H, 9.47; N, 6.75; P, 15.02. $C_8H_{20}NO_3P$. Calculated (%): C, 45.93; H, 9.63; N, 6.69; P, 14.80. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 208 [M − H]$^+$ (1), 194 [M − Me]$^+$ (1), 180 [M − Et]$^+$ (4), 152 [M − 2 Et + H]$^+$ (12), 72 [$CH_2CH_2NMe_2$]$^+$ (26), 58 [CH_2NMe_2]$^+$ (100).

Synthesis of palladium complexes 2a—c (general procedure). A solution of the corresponding ligand (0.001 mol) in CH_2Cl_2 (10 mL) was slowly added dropwise with intense stirring to a solution of $Pd(COD)Cl_2$ (0.001 mol) in CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was stirred for 1 h and concentrated *in vacuo* (40 Torr) to 2 mL. The complex was precipitated with an ether/hexane mixture (1 : 1 by volume). The precipitate that formed was carefully washed three times with ether until 1,5-cyclooctadiene was completely removed. The precipitate was separated by centrifugation and then dried in air and *in vacuo* (1 Torr).

***cis*-{Di(adamant-1-yl) [2-(*N*,*N*-dimethylamino)ethyl] phosphite-*P*,*N*}palladium dichloride (2a).** M.p. 118—120 °C. The yield was 87%. A light-yellow powder. Found (%): C, 48.0; H, 6.97; N, 2.10; P, 5.21. $C_{24}H_{40}Cl_2NO_3PPd$. Calculated (%): C, 48.13; H, 6.73; N, 2.34; P, 5.17.

***cis*-{Diisopropyl [2-(*N*,*N*-dimethylamino)ethyl] phosphite-*P*,*N*}palladium dichloride (2b).** M.p. 160—161 °C. The yield was 90%. A yellow powder. Found (%): C, 29.0; H, 6.12; N, 3.11; P, 7.62. $C_{10}H_{24}Cl_2NO_3PPd$. Calculated (%): C, 28.97; H, 5.83; N, 3.38; P, 7.47.

***cis*-{Diethyl [2-(*N*,*N*-dimethylamino)ethyl] phosphite-*P*,*N*}palladium dichloride (2c).** M.p. 155—156 °C. The yield was 79%. A yellow powder. Single crystals for X-ray diffraction study were prepared by slow evaporation of a solution of **2c** in $CHCl_3$. Found (%): C, 25.01; H, 5.32; N, 3.56; P, 8.04. $C_8H_{20}Cl_2NO_3PPd$. Calculated (%): C, 24.86; H, 5.22; N, 3.62; P, 8.01.

Rhodium complexes **3a,b** were synthesized according to the procedure for the preparation of complexes **2a—c** with the use of a solution of $[Rh(CO)_2Cl]_2$ (0.001 mol) in CH_2Cl_2 (20 mL) and a solution of the corresponding ligand (0.002 mol) in CH_2Cl_2 (20 mL).

{Di(adamant-1-yl) [2-(*N*,*N*-dimethylamino)ethyl] phosphite-*P*,*N*}carbonylrhodium chloride (3a). M.p. 148—149 °C. The yield was 88%. A light-yellow powder. Found (%): C, 51.22; H, 7.00; N, 2.31; P, 5.35. $C_{25}H_{40}ClNO_4PRh$. Calculated (%): C, 51.07; H, 6.86; N, 2.38; P, 5.27.

{Diisopropyl [2-(*N*,*N*-dimethylamino)ethyl] phosphite-*P*,*N*}carbonylrhodium chloride (3b). M.p. 74—75 °C. The yield was 83%. A brown powder. Found (%): C, 32.82; H, 6.05; N, 3.25; P, 7.72. $C_{11}H_{24}ClNO_4PRh$. Calculated (%): C, 32.73; H, 5.99; N, 3.47; P, 7.67.

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