Heteroatom Chemistry
Volume 17, Number 6, 2006

Synthesis, Structure, and Transition Metal Complexes of Amphiphilic 1,5-Diaza-3,7-diphosphacyclooctanes

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Received 19 September 2005; revised 21 February 2006

ABSTRACT: *Amphiphilic 1,5-diaza-3,7-diphosphacyclooctanes have been synthesized by condensation of hydrophobic primary arylphosphines, formaldehyde, and functionalized hydrophilic primary arylamines (5-aminoisophthalic acid and the sodium salt of sulfanilic acid). These compounds readily form P,P-chelate complexes with [$PtCl_2$(cod)], which are stable in water. The catalytic activity of palladium catalysts with 1,5-diaza-3,7-diphosphacyclooctane ligands was studied in the copolymerization of ethylene and carbon monoxide.* Heteroatom Chem 17:499–513, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20272

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Contract grant sponsor: International Association for the Promotion of Cooperation with Scientists from the New Independent States (NIS) of the former Soviet Union.
Contract grant number: 00-00677.
Contract grant sponsor: Russian Federation for Basic Research.
Contract grant numbers: 03-03-33085, 04-03-32671, and 04-03-97252.
Contract grant sponsor: Deutsche Forschungsgemeinschaft.
Contract grant number: 436RUS113/724/0-1.
Contract grant sponsor: Russian Science Support Foundation.

INTRODUCTION

The synthesis of cyclic bisphosphines and their coordination chemistry have attracted considerable interest because phosphines are excellent ligands for transition metals [1–4]. The incorporation of phosphorus into a ring changes its coordination ability directly by modifying its Tolman angle through electronic effects resulting from a change in the C–P–C intracyclic angle, and by preventing a perfect overlap between the orbitals of the P donor and the metal [1–3]. The Mannich-type condensation of phosphines appears to be a powerful method of constructing heterocyclic bisphosphines and macroheterocyclic tetraphosphine ligands for transition metal coordination chemistry [5–7]. Interesting

compounds of this type include diazadiphosphacyclooctanes, which can act as bidentate bisphosphine chelate ligands. A wide variety of substituents on the phosphorus and nitrogen atoms open the opportunity for ligand design and preparation of tailor-made complexes. During the last decade, chiral [8], unsaturated [9], ferrocenylmethyl [10], *o*-oxyphenyl [11,12], phosphinomethyl [13], and amino acid [14] fragments have been incorporated into bisphosphine ligands to give a number of asymmetric [8], polymetallic [10], water-soluble [10,11,12,14,15] and chelate [16–19] transition metal complexes.

The advantages of homogeneous over heterogeneous catalysis with respect to 1) activity (relative to metal content), 2) selectivity (particularly enantioselectivity), 3) mildness of reaction conditions, 4) lack of diffusion problems, 5) sensitivity toward catalyst poisons, 6) variability of steric and electronic properties of catalysts, and 7) mechanistic understanding of processes are well established. However, problems with the separation of very expensive catalysts from the products often present major obstacles to industrial applications [20–23]. The main method of overcoming this problem is to "heterogenize" a homogeneous catalyst by utilizing a liquid–liquid (usually water–organic solvent) biphasic system, in which the solutions of the catalyst and of the substrate are separated by a phase barrier [20,24]. This approach has aroused great interest in water-soluble ligands, especially phosphines [24–28].

The Mannich-type reaction of *p*-aminobenzoic acid with bis(hydroxymethyl)arylphosphines leads to the corresponding diazadiphosphacyclooctanes with good to excellent yields [11,12]. However, only derivatives of *o*-phosphinophenols demonstrated water solubility suitable for catalysis [11,12]. Recently, we obtained aminomethylphosphines based on 5-aminoisophthalic acid and (ferrocenylmethyl)phosphine [10], as well as their chelate complexes with late transition metals, which exhibit higher solubility in water.

In addition, variation of the steric demands of the ligands is also important because the stereoselectivity of catalytic reactions is highly sensitive to the nature of the ligands attached to the transition metal.

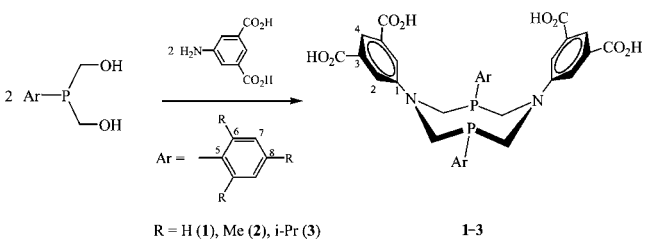
We now report the synthesis, molecular structure, and transition metal complexes of a number of novel water-soluble cyclic bisphosphines with bulky substituents on the phosphorus atoms based on the condensation reaction of 5-aminoisophthalic acid or the sodium salt of sulfanilic acid with bis(hydroxymethyl)arylphosphines (aryl = phenyl (Ph), mesityl (Mes), and 2,4,6-triisopropylphenyl (Tipp)).

RESULTS AND DISCUSSION

In spite of the presence of an additional acidic group in comparison with aminobenzoic acid, the amino group of 5-aminoisophthalic acid is still reactive in the Mannich-type condensations. The standard procedure for the synthesis of 1,5-diaza-3,7-diphosphacyclooctanes (in situ preparation of bis(oxymethyl)arylphosphine, 1:1 molar ratio of reagents, refluxing in ethanol) [5,8,11,12] was used to prepare several 1,5-bis(3,5-dicarboxyphenyl)-3,7-diaryl-1,5-diaza-3,7-diphosphacyclooctanes (**1–3**) in good yield (Scheme 1).

The condensation reaction appeared to be highly selective. Thus, the reaction of mesitylphosphine even with three equivalents of formaldehyde and two equivalents of 5-aminoisophthalic acid led to the formation of compound **2** in 87% yield, but only ca. 10% of the expected 1,3-diaza-5-phosphorinane was formed according to the ^{31}P NMR spectrum of the reaction mixture. Phosphine **2** was isolated in 78% yield from this mixture.

The bisphosphines **1–3** are air-stable bright yellow compounds. The chemical shifts in the ^{31}P NMR spectra of compounds **1–3** decrease in this order with increasing steric hindrance of the substituent at the phosphorus atom. Compound **1** exhibits good solubility in DMF, DMSO, and water, while the cyclic bisphosphines **2** and **3** demonstrate only limited solubility in these solvents. They are, however, soluble in water in the presence of at least four equivalents of base (NaOH or KOH). Compound **2** is sufficiently soluble in water, but readily crystallized from both DMF and DMSO. In agreement with the increasing hydrophobic effect of the bulky substituent on the phosphorus atom, **3** is much more soluble in DMF, but forms emulsions in water when its concentration is higher than 0.01 M, and is practically insoluble in DMSO.



SCHEME 1

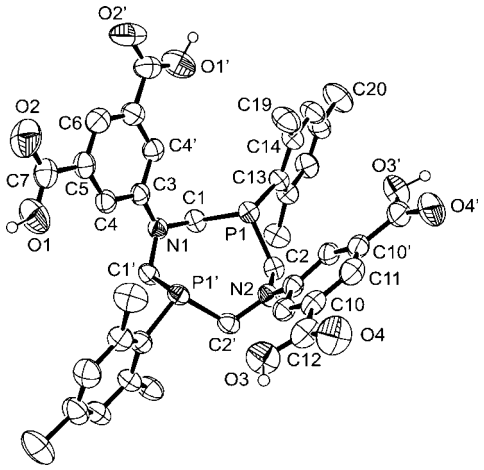


FIGURE 1 An ORTEP view of **2** (molecules of DMSO and hydrogen atoms other than OH are omitted for clarity).

The X-ray analysis of **2** and **3** confirmed the proposed structures. Only isomers with axially oriented lone pairs of electrons on the phosphorus atoms are present. The heterocyclic molecules have a crown (chair–chair) conformation. Compound **2** is located on a crystallographic mirror plane, perpendicular to the eight-membered central ring, on which N1, N2, C3, C6, C8 and C11 are located (Fig. 1). In **3**, the molecule lies on a twofold axis and two crystallographic mirror planes (site symmetry 2*mm*); the latter incorporate P1, P1′, C1–C6, C7, C9, C11 or N1, N1′, C14, C17 (Fig. 2). In both cases, solvent molecules (DMSO for **2** and DMF for **3**) are bonded via hydrogen bonds to the carboxyl groups. Additional solvent molecules are located in hydrophobic cavities along the *c*-axis, pointing toward the center of the eight-membered ring without any noticeable strong interactions.

The nitrogen atoms are in an almost planar environment, and their hydrophilic substituents are in pseudoaxial positions. The bulky aryl groups on phosphorus are perpendicular to the central eight-membered ring to minimize steric hindrance, with the lone pairs of electrons of both phosphorus atoms pointing toward the center of the cavity. In the lattice, **2** and **3** form stacks along the *c*-axis, in which the molecules are separated by two DMSO molecules for **2** and one DMF molecule for **3** (Fig. 2). No intermolecular hydrogen bonding is observed in **2** and **3** despite the presence of carboxyl groups, which are usually liable to the formation of strong intermolecular hydrogen bonds [29–32].

In contrast to crystals of **2** and **3** obtained from DMF or DMSO, solid samples of **1–3** obtained from ethanol exhibit very broad ν(OH) bands centered near 2950 cm^{-1} in their IR spectra (Fig. 3) with

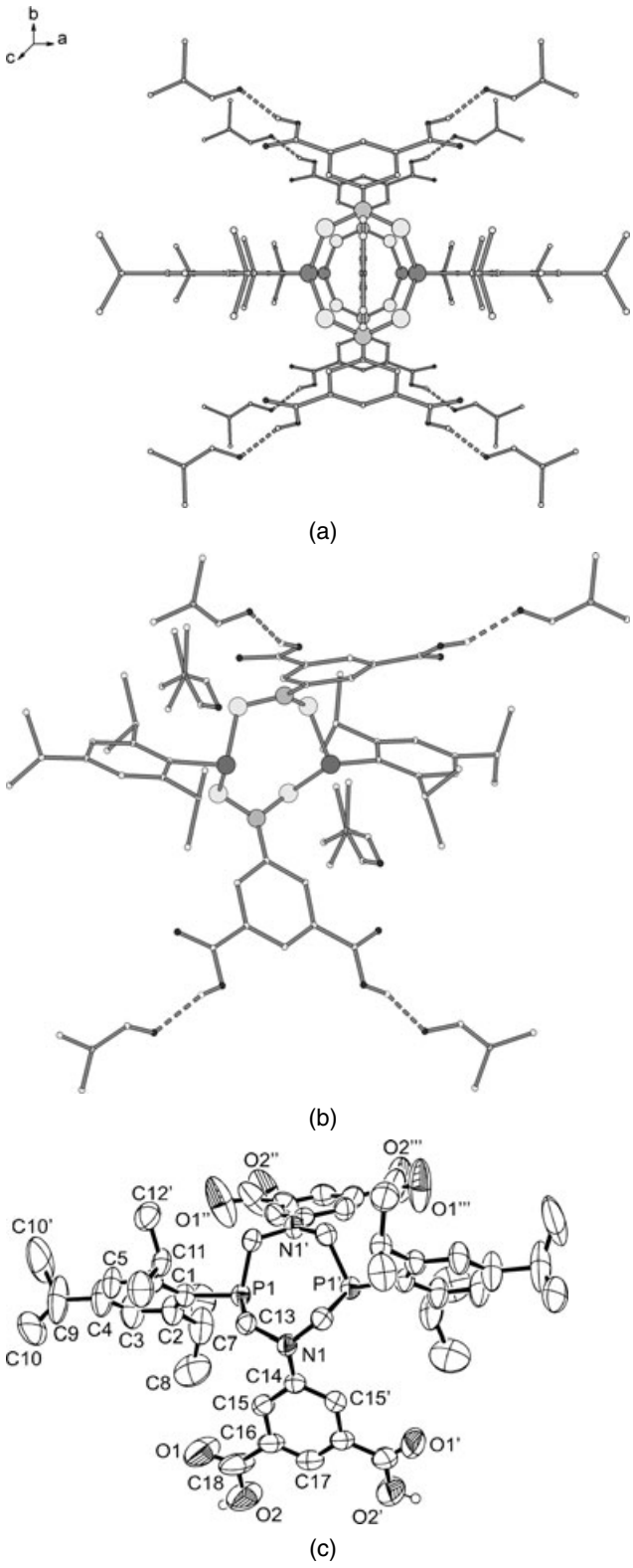


FIGURE 2 An ORTEP view of **3** (c). Disordered DMF is located in hydrophobic cavities along the *c*-axis, pointing toward the center of the eight-membered ring or bonded via hydrogen bonds ((a) and (b)). A perspective view along the *c*-axis illustrating the stacking (a). Hydrogen atoms other than OH are omitted for clarity.

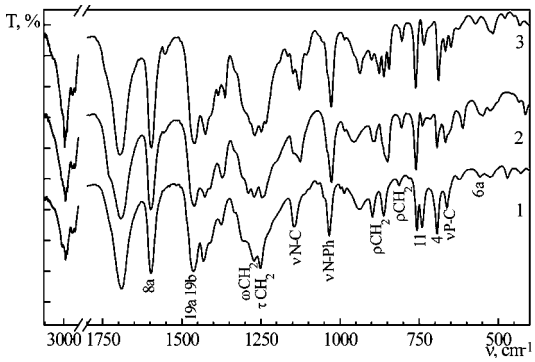


FIGURE 3 IR spectra of **1–3**. Wilson's notation (4, 6a, 8a, 11, 19a, 19b) [31,32] is used for the vibrations of the 3,5-dicarboxyphenyl rings.

distinctive submaxima at ca. 2550 and 2650 cm^{-1}, ν(C=O) at about 1690 cm^{-1}, and a broad band at ca. 940 cm^{-1} that can be regarded as the evidence for a very strong hydrogen bond [29–32] of the type C=O···HO(C=O). At the same time, no traces of ethanol absorption bands are observed in the IR spectra. In the structures of **2** and **3** crystallized from DMSO or DMF, the DMSO or DMF molecules interact with the CO_2H groups and are located in hydrophobic cavities along the *c*-axis pointing toward the center of the eight-membered ring. Apparently, in the absence of molecules of solvation, a different type of molecular packing results for **1–3** in which the carboxyl groups of neighboring molecules exhibit strong intermolecular hydrogen bonding.

To confirm the proposed structure of **1** and to find out whether the differences in the preparation of the samples result in any changes in the intramolecular structure of the compounds, we studied the normal modes of **1** by the scaled quantum mechanical (SQM) method [33] on the basis of density functional theory (DFT) [34] calculations. According to our computations, the crown conformation with axially oriented lone pairs of electrons on the phosphorus atoms is the most energetically stable conformation of **1**; the energy of the chair–boat conformation is ca. 4 kcal/mol higher. These DFT calculations give an insight into why 1,5-diaza-3,7-diphosphacyclooctanes and their complexes exist exclusively in these two conformations (the results of the detailed conformational analysis of these compounds will be published elsewhere). The calculated structural and vibrational characteristics of the crown conformation of **1** are in good agreement with the experimental data (see Tables 1A and 2A). The absence of vibrations of the other conformers implies conformational homogeneity of the sample of **1**.

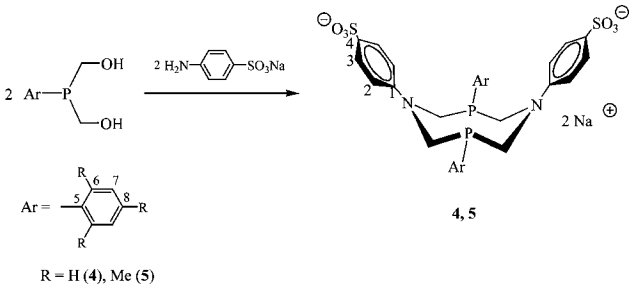
The major part of the IR spectrum of **1** consists of the vibrations of the substituents at phosphorus and nitrogen (Fig. 3). The frequencies of the vibrations involving the heterocyclic core of the molecules **1–3** practically coincide. This means that not only the constitution but also the conformation of the heterocycles coincide for all three compounds.

The NMR experiments showed that no noticeable hydrolysis or oxidation occurred in water. The chemical shifts in the ^{31}P NMR spectra of **1–3** in water and organic solvents are similar, and the ^{1}H NMR spectra (orientation-dependent $^{2}J_{PH}$ in the P-CH_2-N fragments) are consistent with a predominant crown conformation of the 1,5-diaza-3,7-diphosphacyclooctanes with equatorial positions of the aryl groups on the phosphorus atoms. In the ^{1}H and ^{13}C NMR spectra of compounds **2** and **3**, very broad signals or even double sets of signals of the atoms in ortho and meta positions of the bulky substituents are observed, which indicate restricted rotation around the exocyclic P—C bond.

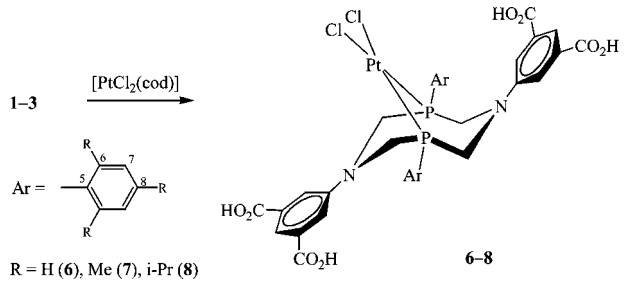
Because **1–3** are soluble in water only under basic conditions, we also prepared water-soluble sulfonated aminomethylphosphines using the same synthetic approach. Sulfanilic acid is not reactive in condensation reactions due to the protonated amino group (zwitterion), and its salts are insoluble in most of the organic solvents used for Mannich-type condensation reactions. Therefore, an aqueous solution of the corresponding sodium salt was used, and the 1,5-diaza-3,7-diphosphacyclooctanes **4** and **5** were obtained in good yield in spite of the known reversibility of the condensation reaction in water (Scheme 2).

The bisphosphines were isolated as white microcrystalline compounds, which are readily soluble in water and practically insoluble in most organic solvents (excluding DMSO). The similarity of the NMR data of **4** and **5** to those of **1** and **2** indicates similar behavior in solution. No hydrolysis or oxidation occurs in water, even after exposure to air for several days.

It was shown previously that 3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane [16–19] and 3,7-bis(ferrocenylmethyl)-1,5-diaza-3,7-diphosphacyclooctane [10] form chelate complexes with various



SCHEME 2



SCHEME 3

transition metals. However, complexation of compounds with bulky substituents on the phosphorus atoms was not studied previously.

Like other 1,5-diaza-3,7-diphosphacyclooctanes, the bisphosphines **1–3** readily act as bidentate ligands to form cis-chelate complexes (**6–8**) on reaction with $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene, Scheme 3).

While the molecular structures of **6** (Fig. 4) and **7** (Fig. 5) are mainly as expected for square-planar cis complexes with 1,5-diaza-3,7-diphosphacyclooctanes [14], there are also some differences. In both cases, the heterocyclic ligands have chair–boat conformations with Pt–P–C(Ar) bond angles of ca. 120° and P—Pt—P bond angles of ca. 85°. The deviation of the Pt—P bonds from the centroid of the three P—C bonds by about 10° indicates some distortion [16–19]. In **6**, both phenyl groups on the phosphorus atoms are eclipsed with one of the neighboring endocyclic P—C bonds (torsion angle ca. 11°), whereas the mesityl substituents on the phosphorus atoms in **7** are nearly perpendicular to the PtP_2Cl_2 plane (dihedral angle ca. 70°), in such a way that the *ortho*-methyl groups of the mesityl rings are situated above and below the PtP_2Cl_2 plane. The nitrogen atoms of complex **7** have trigonal-pyramidal coordination (sums of C—N—C bond angles are 339 and 345°) in contrast to complex **6** (sums of C—N—C bond angles are 353 and 360°) and previously described $PtCl_2$ complexes of 1,5-diaza-3,7-diphosphacyclooctanes [16–19], which show trigonal-planar coordination of the nitrogen atoms. Perhaps the sp^3 hybridization of the nitrogen atoms in **7** is the result of the steric interaction of the substituents on nitrogen with the bulky mesityl groups on phosphorus.

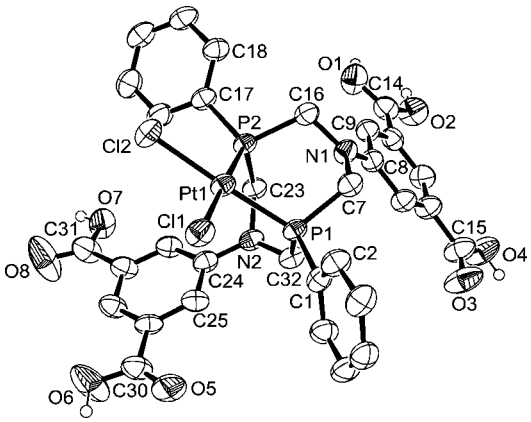


FIGURE 4 An ORTEP view of **6** (DMF molecules are omitted for clarity).

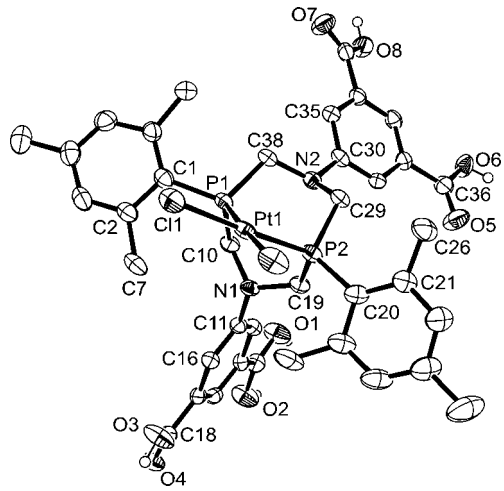
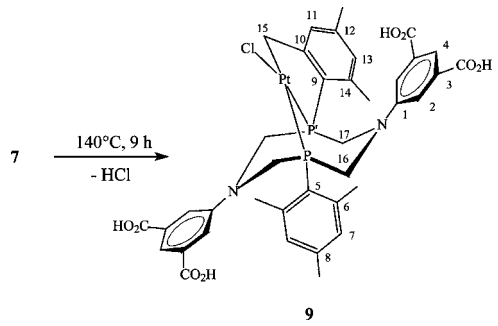
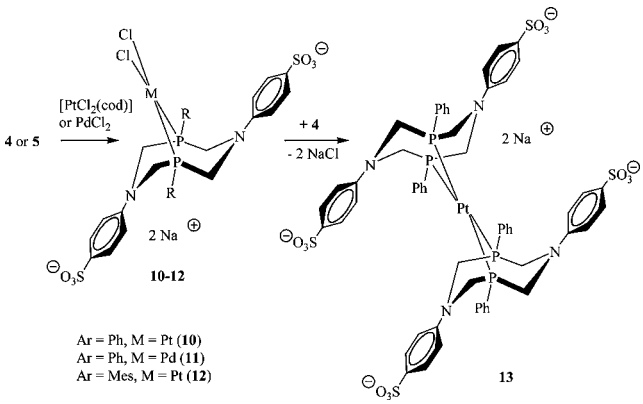


FIGURE 5 An ORTEP view of **7** (DMF molecules are omitted for clarity).

The ^{31}P NMR data for the complexes **6–8** in DMF ($\Delta\delta$ values ($\delta_{complex} - \delta_{ligand}$) ca. 40–45 ppm and $^1J_{PtP}$ ca. 3050 Hz) are similar to those reported previously for related complexes with 1,5-diaza-3,7-diphosphacyclooctanes [16–19]. Complexes **6–8** are soluble in water in the presence of at least four equivalents of base (KOH or NaOH). Their solubility depends on the substituents in the phosphorus atoms and varies from 0.1 mol/L for **6** to 0.01 mol/L for **8**. In the ^{31}P NMR spectra of **6–8** in water, the signals are shifted slightly (by ca. 6 ppm) to higher field and the PtP coupling constants are lower (by ca. 50 Hz) in comparison with DMF solutions due to deprotonation of the carboxyl groups. In the case of **6**, two additional doublets ($\delta_{P1} = -17.0$, $^1J_{PtP} = 2929$ Hz and $\delta_{P2} = -18.7$ ppm, $^1J_{PtP} = 2792$ Hz, $^2J_{P1P2} = 9$ Hz) were observed in the ^{31}P NMR spectrum along with the signal of complex **6**. The additional high-field shift (by ca. 2 ppm) and smaller coupling constant $^1J_{PtP}$ (by ca. 50 Hz) for one of these doublets in comparison with **6** indicates the formation of the partially hydrolyzed compound [PtCl(OH)(L^1-κ^2P,P')] (L^1 = **1**) in water (ca. 25%) [35]. For complex **7** ($\delta_{P1} = -3.0$, $^1J_{PtP}$ ca. 2900 Hz and $\delta_{P2} = -5.2$, $^1J_{PtP} = 2700$ Hz, $^2J_{P1P2} = 24$ Hz), the corresponding product [PtCl(OH)(L^2-κ^2P,P')] (L^2 = **2**) was formed to an extent of less than 8%, which indicates some steric protection of the metal center.



SCHEME 4



SCHEME 5

Complexes **7** and **8** have lower thermal stability than **6**. Heating of **7** to 120°C for 3 h in DMF gave the ortho-metallated compound **9** in ca. 25% yield (^{31}P NMR: $\delta_{P1} = 25.0$, $^{1}J_{PtP} = 3620$ Hz and $\delta_{P2} = 18.8$, $^{1}J_{PtP} = 1441$ Hz, $^{2}J_{P1P2} = 19$ Hz). After heating to 140°C for 9 h, ca. 80% of complex **9** was formed along with some other thermal decomposition products (Scheme 4). Only a few crystals of pure **9** were obtained from the reaction mixture and studied by X-ray crystallography.

The heterocyclic ligand has a slightly distorted chair–boat conformation similar to that of **6** and **7**. The Pt–P2 bond (2.162 Å) is shorter and the Pt–P1 bond (2.328 Å) longer than the mean value observed for $PtCl_2$ complexes with 1,5-diaza-3,7-diphosphacyclooctane ligands (ca. 2.23 Å) [17–19] because of the chelate formation and the trans effect of the organic ligand. The Pt–P1–C(Mes) bond angle is 124.2°, but Pt–P2–C20 is only 108.3° without noticeable deviation of the Pt–P bond from the $PtClP_2C$ plane. The involvement of one of the mesityl substituents in the metallocycle leads to decreased steric hindrance and, in contrast to **7**, both nitrogen atoms are in an almost planar environment (sum of CNC bond angles: 350° for N1 and 352° for N2).

In the ^{1}H NMR spectrum of **9**, the signals of the Pt-CH_2 group are observed as well as the two sets of signals for the nonequivalent P-CH_2-N fragments in accordance with the cycloplatinated structure [36–38]. Similarly, cyclometallation occurred when a toluene solution of trimesitylphosphine and bis(benzonitrile)dichloroplatinum(II) was refluxed for 6 h in the presence of triethylamine [38].

The bisphosphine ligands **4** and **5** readily react with $[PtCl_2(cod)]$ or $PdCl_2$ to give the P,P′-chelate complexes **10–12** according to ^{31}P and ^{1}H NMR spectra (Scheme 5).

In solution, **10** slowly transforms into the dianionic bis-chelate complex **13**. Complex **13** was obtained in pure state by adding one equivalent of **4** to a solution of **10** in DMF. The same behavior was previously observed for the platinum complex of chiral 1,5-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane [8]. Complexes **10–13** demonstrate relatively high solubility in water (up to 0.2 M) in comparison to complexes **6–8**. No signals due to partial hydrolysis or oxidation of **10–13** were observed in the ^{31}P NMR spectra in water, and this demonstrates the stability of these complexes.

It is well known that palladium(II) complexes with bidentate bisphosphines or nitrogen-containing phosphines catalyze the copolymerization of alkenes with carbon monoxide [8,39–44]. However, only a few examples of copolymerization in water or biphasic systems (water–organic phase) were described [44–46].

The copolymerization of C_2H_4 with carbon monoxide, catalyzed by palladium-based systems containing the water-soluble ligands **1–5**, palladium(II) acetate ([Pd]), an organic acid (*p*-toluenesulfonic (*p*-TSA) or trifluoroacetic acid (TFA)) as promoters and alkali metal hydroxides for

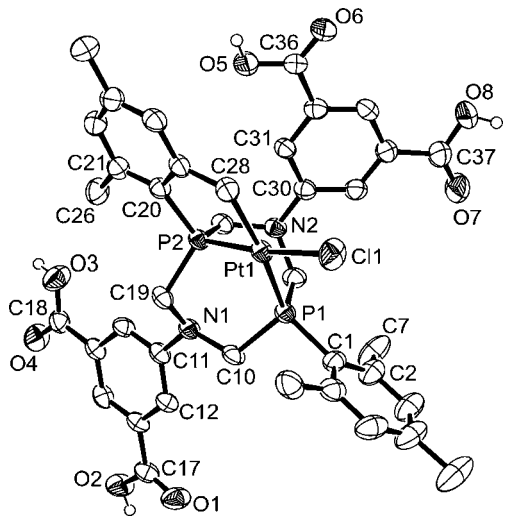


FIGURE 6 An ORTEP view of the **9** (DMF molecules are omitted for clarity).

TABLE 1 Best Results in the copolymerization of C_2H_4 and CO ([Pd] = 5 $\times 10^{-4}$ mmol/L, $T = 90°C$, $p = 4$ MPa)

Ligand (L)	*Stoichiometry* $C_{[Pd]}:C_L:C_{p\text{-}TSA}:C_{KOH}$	*Solvent*	*Reaction Time (min)*	*Copolymer (g)*	*W ($g/g_{Pd}\cdot h$)*
1	1:1.3:11:6	100 mL MeOH	62	4.9	891
1	1:1.3:11:6	70 mL MeOH 20 mL H_2O 10 mL acetone	79	3.8	547
1	1:1.2:11:20	5 mL MeOH 95 mL H_2O	289	2.6	102
1	1:1.3:11:5	100 mL MeOH	60	6.72	1263[a]
4	1:2:5	100 mL MeOH	60	3.83	720[a]
4	1:2:5	50 mL MeOH 50 mL H_2O	60	4.63	870

[a]In the presence of 5 equivalents of benzoquinone to 1 equivalent of [Pd].

dissolving the ligands **1–3** in water, was investigated. The reactions were carried out in methanol, H_2O or methanol/H_2O and with variation of the stoichiometry of the catalyst components. The catalytic activity of the systems based on bisphosphine **1** is moderate in comparison with similar tertiary bisphosphine ligands [43–46]. The best results are listed in Table 1.

The catalyst containing **1** is stable in water only under basic conditions. To the best of our knowledge, this is the first example of a copolymerization catalyst working under basic conditions. The effectiveness of the catalyst increased in the presence of benzoquinone, perhaps because of the deceleration of free-radical organometallic intermediate decomposition. The catalytic systems containing ligands **2** and **3** showed only low activity, probably because of the steric shielding of the palladium atom by the bulky substituents on the phosphorus atoms. The activity of the catalysts based on ligand **4** in the copolymerization of C_2H_4 and CO in H_2O/CH_3OH is moderate in comparison with those of tertiary bisphosphines [43–46]. The catalyst system containing **5** showed noticeably lower activity. Unexpectedly, catalyst systems containing ligands **4** and **5** appeared to be practically inactive in water.

EXPERIMENTAL

All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. NMR spectra: Avance DRX 400 (Bruker), standards: ^{1}H NMR (400 MHz): internal solvent, ^{13}C NMR (100.6 MHz): internal solvent, ^{31}P NMR (162 MHz): external 85% H_3PO_4. The IR spectra were recorded as KBr mulls on a Perkin-Elmer FT-IR spectrometer System 2000 in the range 350–4000 cm^{-1}. The melting points were determined in sealed capillaries and were uncorrected. $PhPH_2$ [47], $MesPH_2$ [48,49], $(Tipp)PH_2$ [50,51], and $[PtCl_2(cod)]$ [52,53] were prepared according to literature procedures. Paraformaldehyde, $PdCl_2$, sulfanilic acid, and 5-aminoisophthalic acid are commercially available.

Crystal Data

The data for compounds **3, 6, 7**, and **9** were collected on a Siemens CCD diffractometer (SMART; ω-scan rotation). Data reduction was performed with SAINT including the program SADABS for empirical absorption correction. The data for **2** were collected on a Stoe-IPDS imaging plate diffractometer in ϕ scan mode with numerical absorption correction (X-RED). Radiation for all measurements was Mo K_α ($\lambda = 71.073$ pm). The structures were solved by direct (**2, 3**, and **9**) or Patterson (**6** and **7**) methods, and the refinement of all non-hydrogen atoms was performed with SHELX97. H atoms were calculated on idealized positions. Figures 1, 2, and 4–6 were generated with ORTEP and DIAMOND-3 [54]. CCDC-275047 (**2**), 275046 (**3**), 275044 (**6**), 275045 (**7**), and 275043 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$C_{52}H_{82}N_2O_{15}P_2S_7$ (**2**). $M = 1261.56$, orthorhombic, space group, $Pnma$, $a = 2135.4(4)$ pm, $b = 1947.7(4)$ pm, $c = 1553.8(3)$ pm, $V = 6.46(1)$ nm^3, $T = 213(2)$ K; $Z = 4$, $D_{calc} = 1.297$ Mg/m^3; μ(Mo K_α) = 0.354 mm^{-1}; 53904 reflections collected, 8059 independent reflections. Final $R1 = 0.0508$ and $wR2 = 0.1233$ [$I \geq 2\sigma(I)$]; $R1 = 0.1148$ and $wR2 = 0.1370$ for all data.

$C_{59}H_{85}N_5O_{11}P_2$ (**3**). $M = 1102.26$, tetragonal, space group $I4_1md$, $a = b = 2505.6(1)$ pm, $c = 1097.43(7)$ pm, $V = 6.8898(6)$ nm^3, $T = 208(2)$ K; $Z = 4$, $D_{calc} = 1.063$ Mg/m^3; μ(Mo K_α) = 0.117 mm^{-1}; 19,980 reflections collected, 3577 independent reflections. Final $R1 = 0.0659$ and $wR2 = 0.1841$

$[I \geq 2\sigma(I)]$; $R1 = 0.0920$ and $wR2 = 0.2081$ for all data.

$C_{44}H_{56}Cl_2N_6O_{12}P_2Pt$(**6**). $M = 1188.88$, triclinic, space group $P\bar{1}$, $a = 1311.5(1)$ pm, $b = 1320.4(1)$ pm, $c = 1627.7(2)$ pm, $\alpha = 105.869(2)^\circ$, $\beta = 94.667(2)^\circ$, $\gamma = 111.462(2)^\circ$, $V = 2.4709(4)$ nm^3, $T = 217(2)$ K; $Z = 2$, D_{calc} 1.598 Mg/m^3; μ(Mo K_α) = 3.078 mm^{-1}; 15,416 reflections collected, 11,323 independent reflections. Final $R1 = 0.0475$ and $wR2 = 0.1271$ $[I \geq 2\sigma(I)]$; $R1 = 0.0651$ and $wR2 = 0.1452$ for all data.

$C_{53}H_{75}Cl_2N_7O_{13}P_2Pt$ (**7**). $M = 1346.13$, triclinic, space group $P\bar{1}$, $a = 1349.5(3)$ pm, $b = 1491.5(3)$ pm, $c = 1746.4(4)$ pm, $\alpha = 96.427(4)^\circ$, $\beta = 111.026(4)^\circ$, $\gamma = 109.103(4)^\circ$, $V = 2.994(1)$ nm^3, $T = 220(2)$ K; $Z = 2$, $D_{calc} = 1.493$ Mg/m^3; μ(Mo K_α) = 2.551 mm^{-1}; 19,824 reflections collected, 13,765 independent reflections. Final $R1 = 0.0408$ and $wR2 = 0.0851$ $[I \geq 2\sigma(I)]$; $R1 = 0.0644$ and $wR2 = 0.0915$ for all data.

$C_{50}H_{67}ClN_6O_{12}P_2Pt$ (**9**). $M = 1236.58$, triclinic, space group $P\bar{1}$, $a = 1317.5(2)$ pm, $b = 1332.8(2)$ pm, $c = 1627.2(2)$ pm, $\alpha = 96.691(2)^\circ$, $\beta = 98.762(2)^\circ$, $\gamma = 99.328(2)^\circ$, $V = 2.7573(7)$ nm^3, $T = 220(2)$ K; $Z = 2$, $D_{calc} = 1.489$ Mg/m^3; μ(Mo K_α) = 2.714 mm^{-1}; 29,337 reflections collected, 13,017 independent reflections. Final $R1 = 0.0415$ and $wR2 = 0.1163$ $[I \geq 2\sigma(I)]$; $R1 = 0.0578$ and $wR2 = 0.1278$ for all data.

Computations

All DFT calculations were carried out using the Gaussian 98 suite of programs [55]. Becke's three-parameter exchange functional [56] in combination with the Lee–Yang–Parr correlation functional [50,51] (B3LYP) and standard 3-21G* and 6-31G* basis sets were used. All stationary points were characterized as minimal by analysis of the Hessian matrices. The calculated force fields were transformed to internal coordinates, and the scaling procedure was applied with the use of the program described in [43]. Transferable scaling factors, employed for this purpose, are summarized in Table 3A. It was demonstrated earlier that their application to calculated force constants allowed a priori quantitative prediction of the IR and Raman spectra of organic molecules, including the atoms H, C, N, O [33,34, 55–58], and P [59].

Synthesis

1,5-Bis(meta-dicarboxyphenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1**) A solution of bis(oxymethyl)phenylphosphine (2.57 g, 15 mmol) and 5-aminoisophthalic acid (2.73 g, 15 mmol) in 40 mL of ethanol was refluxed for 6 h. The resulting yellow crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 4.5 g (95%); mp >250°C (decomp.). Anal. Calcd for $C_{32}H_{28}N_2O_8P_2$ [630]: C, 60.95; H, 4.44; N, 4.44. Found: C, 60.3; H, 4.8; N, 4.2.

^{1}H NMR (DMSO-d_6): 4.24 (dd, $^2J_{HH} = 12.7$ Hz, $^2J_{PH} = 13.2$ Hz, 4H, P-CH_2^A-N), 4.73 (d, br, $^2J_{HH} = 12.7$ Hz, 4H, P-CH_2^B-N), 7.68 (s, 4H, H^2 in C_6H_3), 7.54 (m, 6H, H^6, and H^8 in C_6H_5), 7.70 (m, br, 4H, H^7 in C_6H_5), 7.79 (s, br, 2H, H^4 in C_6H_3), 12.98 (s, br, 4H, CO_2H). ^{13}C NMR (DMSO-d_6): 56.1 (td, $^1J_{HC} = 140.6$ Hz, $^1J_{PC} = 13.4$ Hz, P-CH_2-N), 116.8 (d, $^1J_{HC} = 161.7$ Hz, C^2 in C_6H_3), 117.4 (d, $^1J_{HC} = 160.4$ Hz, C^4 in C_6H_3), 129.1 (d, $^1J_{HC} = 161.3$ Hz, C^7 in C_6H_5), 129.6 (d, $^1J_{HC} = 161.3$ Hz, C^8 in C_6H_5), 131.5 (s, C^3 in C_6H_3), 132.5 (dd, $^1J_{HC} = 160.5$ Hz, $^3J_{PC} = 19.4$ Hz, C^6 in C_6H_5), 135.6 (d, br, $^1J_{PC} = 13.2$ Hz, C^5 in C_6H_5), 145.2 (s, C^1 in C_6H_3), 166.9 (s, CO_2H). ^{31}P{^{1}H} NMR (DMSO-d_6): −50.3 (s).

^{1}H NMR (D_2O + 5% NaOH): 3.76 (dd, $^2J_{HH} = 15.4$ Hz, $^2J_{PH} = 4.6$ Hz, 4H, P-CH_2^A-N), 4.03 (dd, $^2J_{HH} = 15.4$ Hz, $^2J_{PH} = 9.4$ Hz, 4H, P-CH_2^B-N), 7.20 (s, 4H, H^2 in C_6H_3), 7.32–7.37 (m, 6H, H^6, and H^8 in C_6H_5), 7.44 (m, br, 4H, H^7 in C_6H_5), 7.56 (s, br, 2H, H^4 in C_6H_3). ^{31}P{^{1}H} NMR (D_2O + 5% NaOH): −50.6 (s).

IR ($\tilde{\nu}$/cm^{-1}): 1597 (aryl), 1691 (CO, aryl), 3440 (OH).

1,5-Bis(meta-dicarboxyphenyl)-3,7-dimesityl-1,5-diaza-3,7-diphosphacyclooctane (**2**). A mixture of mesitylphosphine (1.52 g, 10 mmol) and paraformaldehyde (0.60 g, 20 mmol) was heated to 110°C for 3 h, then 20 mL of ethanol and 5-aminoisophthalic acid (1.81 g, 10 mmol) were added, and the reaction mixture was refluxed for 2 h. The resulting yellow crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 3.0 g (78%); mp >250°C (decomp.). Anal. Calcd for $C_{38}H_{40}N_2O_8P_2$ [715]: C, 63.86; H, 5.64; N, 3.92. Found: C, 63.37; H, 5.73; N, 4.12.

^{1}H NMR (DMSO-d_6): 2.29 (s, 6H, C^8-CH_3), ca. 2.50 (obscured by DMSO, C^6-CH_3), 4.23 (dd, $^2J_{HH} = 15.2$ Hz, $^2J_{PH} = 5.9$ Hz, 4H, P-CH_2^A-N), 5.18 (dd, br, $^2J_{HH} = 15.2$ Hz, $^2J_{PH} = 3.6$ Hz, 4H, P-CH_2^B-N), 6.95 (s, 4H, H^2), 7.08 (s, 4H, H^7), 7.73 (s, br, 2H, H^4), 13.00 (s, br, 4H, CO_2H). ^{31}P{^{1}H} NMR (DMSO-d_6): −44.1 (s); (DMF-d_7): −43.6 (s).

^{1}H NMR (D_2O + 5% NaOH): 2.00 (s, 6H, C^8-CH_3), 2.04 (s, 12H, C^6-CH_3), 4.04 (d, 4H, $^2J_{HH} = 15.4$ Hz, P-CH_2^A-N), 4.40 (d, 4H, $^2J_{HH} = 15.4$ Hz, P-CH_2^B-N), 6.95 (s, 4H, H^2), 7.04 (s, 4H, H^7), 7.71 (s, 2H, H^4). ^{31}P{^{1}H} NMR (5% NaOH, D_2O): −45.8 (s).

IR ($\tilde{\nu}$/cm^{-1}): 1598 (aryl), 1695 (CO, aryl), 3435 (OH).

*1,5-Bis(meta-dicarboxyphenyl)-3,7-bis(2,4,6-triisopropylphenyl)-1,5-diaza-3,7-diphosphacyclooctane (**3**).* A mixture of 2,4,6-triisopropylphenylphosphine (2.89 g, 12 mmol) and paraformaldehyde (0.74 g, 24 mmol) was heated to 110°C for 3 h, then 50 mL of ethanol and 5-aminoisophthalic acid (2.22 g, 12 mmol) were added, and the reaction mixture was refluxed for 2 h. The resulting yellow crystals were collected by filtration, washed with ethanol and dried in vacuum. Yield: 4.5 g (83%); mp >250°C (decomp.). Anal. Calcd for $C_{50}H_{64}N_2O_8P_2$ [882]: C, 68.03; H, 7.26; N, 3.18. Found: C, 68.4; H, 7.4; N, 3.5.

^{1}H NMR (DMF-d_7): 1.14–1.29 (m, 36H, CH_3 in *i*-Pr), 2.91 (m, 2H, C^8-C<u>H</u>Me_2), 3.40 (m, br, 2H, C^6-C<u>H</u>Me_2), 4.10 (m, br, 2H, C^6-C<u>H</u>Me_2), 4.38 (dd, 4H, $^2J_{HH} = 15.2$ Hz, $^2J_{PH} = 6.6$ Hz, P-CH_2^A-N), 5.34 (dd, 4H, $^2J_{HH} = 15.2$ Hz, $^2J_{PH} = 2.2$ Hz, P-CH_2^B-N), 7.18 (s, 4H, H^2), 7.29 (s, 4H, H^7), 7.88 (s, 2H, H^4), 12.5 (s, 4H, CO_2H). ^{13}C{^{1}H} NMR (DMSO-d_6): 23.35 (s, C^8-CH<u>C</u>H_3), 24.66, (s, C^6-CH<u>C</u>H_3), 25.35 (s, C^6-CH<u>C</u>H_3), 31.96 (s, br, C^8-<u>C</u>HCH_3), 32.36 (s, C^6-<u>C</u>HCH_3), 33.34 (s, C^6-<u>C</u>HCH_3), 54.44 (d, $^1J_{PC} = 19.4$ Hz, P-CH_2-N), 116.79 (s, C^2 in C_6H_3), 117.75 (s, C^4 in C_6H_3), 121.88 (s, br, C^7), 123.13 (s, br, C^7), 129.14 (d, $^1J_{PC} = 25.2$ Hz, C^5), 132.32 (s, C^3 in C_6H_3), 146.09 (s, C^1 in C_6H_3), 150.61 (s, C^8), 154.47 (s, br, C^6), 156.72 (m, br, C^6), 167.2 (s, CO_2H). ^{31}P{^{1}H} NMR (DMF-d_7): −42.5 (s); (5% NaOH, D_2O): −45.0 (s).

IR ($\tilde{\nu}$/cm^{-1}, KBr): 1597 (aryl), 1697 (CO, aryl), 3439 (OH).

*Disodium 1,5-Bis(para-sulfophenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane dihydrate (**4**).* A solution of bis(oxymethyl)phenylphosphine (1.85 g, 11 mmol) in ethanol (20 mL) was added while stirring with a solution of the sodium salt of sulfanilic acid (2.12 g, 11 mmol) in water (8 mL). The mixture was stirred for 3 h, and then 10 mL of water was added to dissolve the gray precipitate formed, and the reaction mixture was stirred overnight. The resulting slightly gray crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 1.96 g (52%), mp >260°C. Anal. Calcd for $C_{28}H_{26}N_2Na_2O_6P_2S_2{\cdot}2H_2O$ [692]: C, 48.55; H, 4.33, N, 4.05. Found: C, 48.1; H, 4.5; N, 3.9.

^{1}H NMR (DMSO-d_6): 4.20 (dd, $^2J_{HH} = 14.6$ Hz, $^2J_{PH} = 12.4$ Hz, 4H, P-CH_2^A-N), 4.53 (dd, $^2J_{HH} = 14.6$ Hz, $^2J_{PH} = 5.2$ Hz, 4H, P-CH_2^B-N), 6.59 (d, $^3J_{HH} = 9.0$ Hz, 4H, H^2 in C_6H_4), 7.42 (d, $^3J_{HH} = 9.0$ Hz, 4H, H^3 in C_6H_4), 7.50 (m, 6H, H^6, and H^8 in C_6H_5), 7.69 (m, 4H, H^7 in C_6H_5). ^{13}C{^{1}H} NMR (DMSO-d_6): 55.5 (d, $^1J_{PC} = 15.3$ Hz, P-CH_2-N), 110.9 (s, C^2 in C_6H_4), 126.3 (s, C^3 in C_6H_4), 128.7 (s, C^7 in C_6H_5), 129.1 (s, C^8 in C_6H_5), 132.5 (d, $^3J_{PC} = 19.1$ Hz, C^6 in C_6H_5), 135.9 (d, br, $^1J_{PC} = 15.3$ Hz, C^5 in C_6H_5), 136.1 (s, C^4 in C_6H_4), 145.3 (s, C^1 in C_6H_4). ^{31}P{^{1}H} NMR (DMSO-d_6): −49.4 (s).

^{1}H NMR (D_2O): 4.11 (s, 8H, P-CH_2-N), 6.52 (d, $^3J_{HH} = 8.9$ Hz, 4H, H^2 in C_6H_4), 7.49 (m, 10H, C_6H_5), 7.55 (d, 4H, $^3J_{HH} = 8.9$ Hz, H^3 in C_6H_4). ^{31}P{^{1}H} NMR (D_2O): −46.7 (s).

*Disodium 1,5-Bis(para-sulfophenyl)-3,7-dimesityl-1,5-diaza-3,7-diphosphacyclooctane dihydrate (**5**).* A mixture of mesitylphosphine (0.84 g, 5.5 mmol) and 0.9 mL of formalin (0.33 g, 11 mmol of formaldehyde) was stirred in 5 mL of ethanol for 5 h. A solution of the sodium salt of sulfanilic acid (1.08 g, 5.5 mmol) in water (2 mL) was added, and the solution was stirred for 2 h. The resulting slightly gray crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 1.2 g (59%); mp 260°C (decomp.). Anal. Calcd for $C_{34}H_{38}N_2Na_2O_6P_2S_2{\cdot}2H_2O$ [778]: C, 52.44; H, 5.40; N, 3.60. Found: C, 52.3; H, 5.7; N, 3.7.

^{1}H NMR (DMSO-d_6): 2.27 (s, 6H, C^8-CH_3), 2.50 (obscured by DMSO, C^6-CH_3), 4.20 (dd, $^2J_{HH} = 14.7$ Hz, $^2J_{PH} = 3.9$ Hz, 4H, P-CH_2^A-N), 5.01 (dd, br, $^2J_{HH} = 14.7$ Hz, $^2J_{PH} = 0.5$ Hz, 4H, P-CH_2^B-N), 6.13 (d, $^3J_{HH} = 8.4$ Hz, 4H, H^2 in C_6H_4), 6.98 (s, 4H, H^7 in Mes), 7.33 (d, $^3J_{HH} = 8.4$ Hz, 4H, H^3 in C_6H_4). ^{13}C{^{1}H} NMR (DMSO-d_6): 20.6 (s, C^8-<u>C</u>H_3), 23.2 (s, br, C^6-<u>C</u>H_3), 52.5 (d, $^1J_{PC} = 19.7$ Hz, P-CH_2-N), 111.3 (s, C^2 in C_6H_4), 126.3 (s, C^3 in C_6H_4), 128.8 (C^7 in Mes), 129.9 (s, C^7 in Mes), 130.5 (d, br, $^1J_{PC} = 25.9$ Hz, C^5 in Mes), 135.8 (s, C^4 in C_6H_4), 139.1 (s, C^8 in Mes), 143.1 (s, C^6 in Mes), 144.5 (br, C^6 in Mes), 145.7 (s, C^1 in C_6H_4). ^{31}P{^{1}H} NMR (DMSO-d_6): −40.0 (s).

*cis-{P,P′-1,5-Bis(meta-dicarboxyphenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane}dichloroplatinum(II) (**6**).* Solid [$PtCl_2$(cod)] (0.19 g, 0.51 mmol) was added to a solution of **1** (0.32 g, 0.51 mmol) in 20 mL of DMF. The resulting white crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 0.41 g (62%); mp >250°C (decomp.). Anal. Calcd for $C_{32}H_{28}Cl_2N_2O_8P_2Pt$ [896]: C, 42.86; H, 3.13; N, 3.13. Found: C, 42.39; H, 3.32; N, 3.24%.

^{1}H NMR (DMF-d_7): 4.74 (dd, $^2J_{HH} = 14.7$ Hz, $^2J_{PH} = 7.4$ Hz, 4H, P-CH_2^A-N), 4.87 (d, br, $^2J_{HH} = 14.7$ Hz, 4H, P-CH_2^B-N), 7.59 (s, br, 6H, H^2 in C_6H_3 and H^8 in C_6H_5), 8.05 (m, br, 4H, H^6 in C_6H_5), 8.24 (s, br, 4H, H^7 in C_6H_5), 8.28 (s, br, 2H, H^4 in C_6H_3), 13.59 (s, v br, 4H, CO_2H). ^{31}P{^{1}H} NMR (DMF-d_7): −9.6 ($^1J_{PtP} = 3060$ Hz); (5% NaOH, D_2O): −16.4 ($^1J_{PtP} = 2999$ Hz).

IR ($\tilde{\nu}$/cm^{-1}, KBr): 1596 (aryl), 1640, 1718 (CO, aryl), 3486 (OH); ($\tilde{\nu}$/cm^{-1}, CsI): 296, 316 (Pt-Cl).

*cis-{P,P′-1,5-Bis(meta-dicarboxyphenyl)-3,7-bis-mesityl-1,5-diaza-3,7-diphosphacyclooctane}dichloroplatinum(II) (**7**).* Solid [$PtCl_2$(cod)] (0.37 g, 1 mmol) was added to a solution of **2** (0.76 g, 1 mmol) in 10 mL of DMF. The solvent was evaporated, 10 mL of acetone was added, and the resulting white crystals were collected by filtration, washed with acetone, and dried in vacuum. Yield: 0.51 g (52%); mp >250°C (decomp.). Anal. Calcd for $C_{38}H_{40}N_2Cl_2O_8P_2Pt$ [980]: C, 46.53; H, 4.08; N, 2.86. Found: C, 46.28; H, 4.13; N, 2.17.

^{1}H NMR (DMF-d_7): 2.27 (s, 6H, C^8-CH_3), 2.72 (partly obscured by DMF, C^6-CH_3), 4.53 (d, $^2J_{HH}$ = 13.7 Hz, 4H, P-CH_2^A-N), 4.77 (dd, br, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ ca. 1 Hz, 4H, P-CH_2^B-N), 6.95 (s, 4H, H^2), 8.22 (s, 4H, H^7), 8.30 (s, br, 2H, H^4), 13.30 (s, br, 4H, CO_2H). ^{31}P{^{1}H} NMR (DMF-d_7): 1.3 ($^1J_{PtP}$ = 3022 Hz).

^{1}H NMR (D_2O + 5% NaOH): 1.96 (s, 6H, C^8-CH_3), 2.46 (s, 12H, C^6-CH_3), 3.98 (d, 4H, $^2J_{HH}$ = 13.7 Hz, P-CH_2^A-N), 4.17 (d, br, 4H, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ ca. 1–2 Hz, P-CH_2^B-N), 6.74 (s, 4H, H^2), 7.70 (s, 4H, H^7), 8.24 (s, 2H, H^4). ^{31}P{^{1}H} NMR (5% NaOH, D_2O): 3.4 ($^1J_{PtP}$ = 2985 Hz).

IR ($\tilde{\nu}$/cm^{-1}, KBr): 1612 (aryl), 1630–1730 (CO, aryl), 3400 (OH); ($\tilde{\nu}$/cm^{-1}, CsI): 292, 312 (Pt-Cl).

*cis-{P,P′-1,5-Bis(meta-dicarboxyphenyl)-3,7-bis(2,4,6-triisopropylphenyl)-1,5-diaza-3,7-diphosphacyclooctane}dichloroplatinum(II) (**8**).* Solid [$PtCl_2$(cod)] (0.37 g, 1 mmol) was added to a solution of **3** (0.88 g, 1 mmol) in 10 mL of DMF. The solvent was evaporated, 10 mL of acetone was added, and the resulting yellow crystals were collected by filtration, washed with acetone, and dried in vacuum. Yield: 0.62 g (55%); mp >250°C (decomp.). Anal. Calcd for $C_{50}H_{64}Cl_2N_2O_8P_2Pt$ [1148]: C, 52.27; H, 5.58; N, 2.44, P, 5.40. Found: C, 52.67; H, 5.43; N, 2.48; P 5.23.

^{1}H NMR (DMF-d_7): 1.19 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C^8-CH$\underline{Me}_2$), 1.29 (d, 12H, $^3J_{HH}$ = 6.4 Hz, C^6-CH$\underline{Me}_2$), 1.31 (d, 12H, $^3J_{HH}$ = 6.4 Hz, C^6-CH$\underline{Me}_2$), 2.86–2.92 (m, obscured by DMF, C^6-C$\underline{H}Me_2$), 3.44 (m, br, 2H, C^8-C$\underline{H}Me_2$), 4.47 (d, 4H, $^2J_{HH}$ = 13.2 Hz, P-CH_2^A-N), 4.62 (dd, br, 4H, $^2J_{HH}$ = 13.2 Hz, $^2J_{PH}$ ca. 1–2 Hz, P-CH_2^B-N), 7.19 (s, 4H, H^2), 8.21 (s, 4H, H^7), 8.36 (s, 2H, H^4), 13.70 (s, 4H, CO_2H). ^{13}C{^{1}H} NMR (DMF-d_7): 23.77 (s, C^6-CH$\underline{C}H_3$), 24.28 (s, C^6-CH$\underline{C}H_3$), 26.34 (s, C^8-CH$\underline{C}H_3$), (C^6-$\underline{C}$HCH$_3$ and C^8-$\underline{C}$HCH$_3$ obscured by DMF), 55.78 (d, $^1J_{PC}$ = 51.3 Hz, P-CH_2-N), 122.40 (d, $^1J_{PC}$ = 56.8 Hz, C^5), 123.65 (s, C^2 in C_6H_3), 126.38 (s, C^4 in C_6H_3), 127.61 (s, C^7), 133.49 (s, C^3 in C_6H_3), 151.98 (s, C^1), 153.38 (m, br, C^6), 154.40 (m, br, C^8), 167.1 (s, CO_2H). ^{31}P{^{1}H} NMR (DMF-d_7): 1.7 ($^1J_{PtP}$ = 3068 Hz).

IR ($\tilde{\nu}$/cm^{-1}, KBr): 1598 (aryl), 1646, 1719 (CO), 3439 (OH); ($\tilde{\nu}$/cm^{-1}, CsI): 285, 306 (Pt-Cl).

*Cycloplatinated Compound **9**.* Heating of complex **7** in DMF at 140°C for 9 h led to the predominant formation of **9** (up to 80% according to a ^{31}P NMR spectrum of the reaction mixture). However, only a few crystals of **9** were isolated in relatively pure state: mp >250°C (decomp.).

^{1}H NMR (DMF-d_7): 2.26 (s, 3H, C^8-C$\underline{H}_3$), 2.34 (s, 3H, C^{12}-C$\underline{H}_3$), 2.66 (s, 6H, C^6-C$\underline{H}_3$), 2.67 (s, 3H, C^{14}-C$\underline{H}_3$), 3.10 (m, br, $^2J_{PtH}$ ca. 85 Hz, 2H, Pt-$C^{15}H_2$), 4.52 (d, br, $^2J_{HH}$ = 14.7 Hz, 2H, P-$C^{16}H_2^A$-N), 4.67 (d, br, $^2J_{HH}$ = 15.2 Hz, 2H, P-$C^{17}H_2^A$-N), 4.75 (dd, $^2J_{HH}$ = 14.7 Hz, $^2J_{PH}$ = 4.9 Hz, 2H, P-$C^{16}H_2^B$-N), 4.85 (dd, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 4.9 Hz, 2H, P-$C^{17}H_2^B$-N), 6.93 (s, br, 4H, H^2), 7.10 (s, br, 1H, H^{11}), 7.78 (s, br, 3H, H^4, and H^{13}), 8.10 (s, 2H, H^7), 13.40 (s, br, 4H, CO_2H). ^{31}P{^{1}H} NMR (DMF-d_7): 18.8 ($^1J_{PtP}$ = 1441 Hz, $^2J_{PP'}$ = 19 Hz), 25.0 ($^1J_{PtP}$ = 3620 Hz, $^2J_{PP'}$ = 19 Hz).

*Disodium cis-{P,P′-1,5-Bis(para-sulfophenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane}dichloroplatinum(II) dihydrate (**10**).* Solid [$PtCl_2$(cod)] (0.065 g, 0.19 mmol) was added to a solution of **4** (0.13 g, 0.19 mmol) in 10 mL of water. The solvent was evaporated, 10 mL of ethanol was added, and the resulting yellow crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 0.09 g (50%); mp >250°C (decomp.). Anal. Calcd for $C_{28}H_{30}Cl_2N_2Na_2O_8P_2PtS_2$ [960]: C, 35.00; H, 3.12; N, 2.92. Found: C, 34.6; H, 3.3; N, 2.7.

^{1}H NMR (DMSO-d_6): 4.36 (dd, $^2J_{HH}$ = 14.6 Hz, $^2J_{PH}$ = 5.4 Hz, 4H, P-CH_2^A-N), 4.70 (d, br, $^2J_{HH}$ = 14.6 Hz, 4H, P-CH_2^B-N), 7.15 (s, br, 2H, H^8), 7.24 (d, $^2J_{HH}$ = 8.3 Hz, 4H, H^2), 7.59 (d, $^2J_{HH}$ = 8.3 Hz, 4H, H^3), 7.63 (s, br, 4H, H^6), 7.87 (s, br, 4H, H^7). ^{31}P{^{1}H} NMR (DMSO-d_6): −11.9 ($^1J_{PtP}$ = 3071 Hz); (D_2O): −10.6 ($^1J_{PtP}$ = 3147 Hz).

*Disodium cis-{P,P′-1,5-Bis(para-sulfophenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane}dichloropalladium(II) dihydrate (**11**).* Solid $PdCl_2$ (0.02 g, 0.12 mmol) was added to a solution of **4** (0.09 g, 0.13 mmol) in 5 mL of water. The solvent was evaporated, 10 mL of ethanol was added, and the resulting brown crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 0.07 g (64%); mp >250°C (decomp.). Anal. Calcd for $C_{28}H_{30}Cl_2N_2Na_2O_8P_2PdS_2$ [871]: C, 38.58; H, 3.44; N, 3.21. Found: C, 38.9; H, 3.3; N, 2.9.

^{1}H NMR (D_2O): 4.24 (d, br, $^2J_{HH}$ = 14.6 Hz, $^2J_{PH}$ = 0 Hz, 4H, P-CH_2^A-N), 4.34 (d, br, $^2J_{HH}$ = 14.6 Hz, $^2J_{PH}$ = 0 Hz, 4H, P-CH_2^B-N), 6.88 (s, br, 2H,

H^8), 7.08 (d, $^2J_{HH} = 8.3$ Hz, 4H, H^2), 7.59 (d, $^2J_{HH} = 8.3$ Hz, 4H, H^3) 7.20 (t, br, $^2J_{HH} \cong {}^2J_{PH} \cong 7.0$ Hz, 4H, H^6), 7.87 (t, br, $^2J_{HH} \cong {}^2J_{HH} \cong 7.4$ Hz, 4H, H^7). $^{31}P\{^1H\}$ NMR (D_2O): −8.8.

*Disodium cis-{P,P′-1,5-Bis(para-sulfophenyl)-3,7-dimesityl-1,5-diaza-3,7-diphosphacyclooctane}dichloroplatinum(II) dihydrate (**12**).* Solid $[PtCl_2(cod)]$ (0.19 g, 0.5 mmol) was added to a solution of **5** (0.38 g, 0.5 mmol) in 6 mL of DMF. The solvent was evaporated, 10 mL of acetone was added, and the resulting white crystals were collected by filtration, washed with acetone, and dried in vacuum. Yield: 0.40 g (50%); mp >250°C (decomp.). Anal. Calcd for $C_{34}H_{42}Cl_2N_2Na_2O_8P_2PtS_2$ [1044]: C, 39.08; H, 4.02; N, 2.68. Found: C, 39.3; H, 3.7; N, 2.7.

^1H NMR (DMSO-d_6): 2.28 (s, 6H, C^8-CH_3), 2.57 (s, 12H, C^6-CH_3), 4.22 (d, br, $^2J_{HH} = 13.7$ Hz, $^2J_{PH} = 0$ Hz, 4H, P-CH_2^A-N), 4.38 (d, br, $^2J_{HH} = 13.7$ Hz, 4H, P-CH_2^B-N), 6.96 (s, 4H, H^7 in Mes), 7.20 (d, $^3J_{HH} = 8.8$ Hz, 4H, H^2 in C_6H_4), 7.53 (d, $^3J_{HH} = 8.8$ Hz, 4H, H^3 in C_6H_4). $^{13}C\{^1H\}$ NMR (DMSO-d_6): 20.3 (s, C^8-$\underline{C}H_3$), 24.0 (s, br, C^6-$\underline{C}H_3$), 52.5 (d, $^1J_{PC} = 51.3$ Hz, P-CH_2-N), 118.2 (s, C^2 in C_6H_4), 126.7 (d, $^1J_{PC} = 38.0$ Hz, C^5 in Mes), 126.9 (s, C^3 in C_6H_4), 129.7 (s, C^7 in Mes), 139.9 (s, C^4 in C_6H_4), 141.5 (s, br, C^6 in Mes), 142.5 (s, C^8 in Mes), 152.0 (s, C^1 in C_6H_4). $^{31}P\{^1H\}$ NMR (DMSO-d_6): 1.8 ($^1J_{PtP} = 3029$).

*Disodium Bis{P,P′-1,5-bis(para-sulfophenyl)-3,7-bisphenyl-1,5-diaza-3,7-diphosphacyclooctane} platinum(II) dihydrate (**13**).* Solid **4** (0.020 g, 0.03 mmol) was added to a solution of **10** (0.028 g, 0.03 mmol) in 1 mL of DMF. The solvent was evaporated, 1 mL of ethanol was added, and the resulting yellow crystals were collected by filtration, washed with ethanol, and dried in vacuum. Yield: 0.02 g (50%); mp >250°C (decomp.). Anal. Calcd for $C_{56}H_{56}N_4Na_2O_{14}P_4PtS_4$ [1547]: C, 43.44; H, 3.62; N, 3.62. Found: C, 44.2; H, 3.2; N, 3.7.

^1H NMR (DMF-d_7): 4.58 (d, br, $^2J_{HH} = 14.2$ Hz, $^2J_{PH} = 0$ Hz, 8H, P-CH_2^A-N), 4.76 (d, br, $^2J_{HH} = 14.2$ Hz, 8H, P-CH_2^B-N), 7.27 (m, $^2J_{HH} = 9.4$ Hz, 12H, H^2, and H^8), 7.38 (s, br, 8H, H^6), 7.46 (s, br, 8H, H^7), 7.83 (d, $^2J_{HH} = 9.4$ Hz, 8H, H^3). $^{31}P\{^1H\}$ NMR (DMF-d_7): −12.7 ($^1J_{PtP} = 2193$ Hz); (D_2O): −12.4 ($^1J_{PtP} = 2041$ Hz).

Copolymerisation of Ethylene with CO

A solution of $Pd(CH_3COO)_2$ ($[Pd(CH_3COO)_2] = 5 \times 10^{-4}$ mol/L), ligands or their potassium salts, and CF_3COOH or *p*-$CH_3C_6H_4SO_3H$ in CH_3OH/H_2O (100 mL) was placed in a 200-mL mechanically stirred steel autoclave, which was then charged with an equimolar mixture of ethylene and carbon monoxide ($p_{co} = 4.0$ MPa). The reaction mixture was stirred at 90°C for the time shown in Table 1, after which the remaining carbon monoxide and ethylene were vented off. Then the copolymer precipitated by the addition of heptane was then collected by filtration and dried under vacuum. After copolymerization, the surface of the autoclave was coated with black Pd. According to ^1H and ^{13}C NMR and elemental analysis data, the synthesized copolymers were strictly alternating copolymers [29]. Their intrinsic viscosities in *m*-cresol are in the range of 0.3–0.6 dL/g at 30°C).

APPENDIX

TABLE 1A A Comparison of the Results Obtained from the B3LYP/6-31G* Geometry Optimization (Bond Lengths in Å; Bond Angles in Deg) of **1** with the Corresponding X-ray Data of **3**

	3 *X-ray*	**1** *B3LYP/6-31G**
Bond lengths		
C1–C2	1.413	1.404
C1–C6	1.414	1.406
C1–P1	1.852	1.851
C2–C3	1.377	1.396
C3–C4	1.349	1.395
C4–C5	1.388	1.397
C5–C6	1.388	1.395
C13–N1	1.454	1.452
C13–P1	1.881	1.909
C14–N1	1.384	1.393
C14–C15	1.406	1.411
C15–C16	1.390	1.397
C16–C17	1.377	1.397
C16–C18	1.476	1.489
C18–O1	1.207	1.215
C18–O2	1.267	1.357
Bond angles		
C2–C1–C6	118.3	118.4
C2–C1–P1	116.8	117.4
C6–C1–P1	124.9	124.3
C3–C2–C1	118.8	120.9
C4–C3–C2	124.1	120.0
C3–C4–C5	117.6	119.8
C6–C5–C4	121.8	120.1
C5–C6–C1	119.4	120.8
N1–C13–P1	113.8	115.4
N1–C14–C15	121.5	121.5
C16–C15–C14	121.1	121.3
C17–C16–C15	120.8	121.1
C17–C16–C18	121.3	121.9
C15–C16–C18	117.9	116.8
O1–C18–O2	119.8	121.8
O1–C18–C16	122.1	125.0
O2–C18–C16	118.0	113.0
C14–N1–C13	121.4	120.8
C1–P1–yC13	103.3	98.9

TABLE 2A IR Data of 1

Crown					
Experiment	*Computations*		*Chair-Boat Computations*		
$\tilde{\nu}^a$ *(cm^{-1}) Int.*	$\tilde{\nu}$ *(cm^{-1})*	I_{IR} *(km/mol)*	$\tilde{\nu}$ *(cm^{-1})*	I_{IR} *(km/mol)*	Assignment[b]
~2950 v br	3611, 3611, 3611, 3611	322	3612, 3612, 3609, 3609	336	ν OH
	3127, 3127, 3120	8	3131, 3130, 3128	9	ν CH (ring)
	3120, 3119, 3119	19	3127, 3116, 3115	14	ν CH (ring)
3089 m	3072, 3072	56	3077, 3077	19	ν CH (ring)
3073 m	3063, 3063	53	3068, 3068	78	ν CH (ring)
3055 m	3055, 3055	24	3061, 3061	27	ν CH (ring)
3040 m, sh	3048, 3048	3	3053, 3053	6	ν CH (ring)
3030 m, sh	3036, 3036	15	3044, 3044	1	ν CH (ring)
			3000, 2999, 2998, 2995	**27**	**ν_{as} CH$_2$**
2956 m	**2959, 2958, 2953, 2952**	**48**			**ν_{as} CH$_2$**
			2949, 2946	**25**	**ν_{as} CH$_2$**
2923 s	**2912, 2910, 2907, 2903**	**118**	**2926, 2924**	**46**	**ν_{s} CH$_2$**
1690 vs	1751, 1751, 1746, 1744	952	1751, 1745, 1744, 1738	987	ν C═O[c]
1597 vs	1601, 1599	291	1599, 1598	280	8a
	1593, 1593	2	1591, 1591	3	8a
	1589, 1589	3	1589, 1585	3	8b
1560 w	1577, 1577	3	1576, 1575	2	8b
1484 m, sh	1496, 1495	8	1492, 1492	8	19a
			1471	**11**	**δ CH$_2$**
1475 m, sh	1470, 1469	28	1466, 1444	30, 65	19b
1463 vs	1468, 1466	284	1467, 1467	340	19a, ν N-Ph
1457 vs	**1452, 1447**	**206**	**1466, 1449**	**0, 75**	**δ CH$_2$**
	1444, 1444	13	1442, 1441	84	19b
1431 vs					
	1423, 1419	**74**	**1427**	**5**	**δ CH$_2$**
1424 m, sh					
	1325, 1325	124	1323, 1323	137	δ OH, ν C—O[c]
1409 m, sh					
	1391, 1383	710	1397, 1388	681	ν N-Ph, ν C-Ph
1375 m					
1365 m, sh	1350, 1347	111	1354, 1349	175	ν C—O
1335 w, sh	1340, 1339	28	1336, 1332	30	14
	1328, 1327	6	1328, 1324	5	3
	1303, 1302	11	1296, 1292	3	3
1305 m	**1302**	**7**			**ω CH$_2$**
	1291	**3**	**1289**	**23**	**ω CH$_2$**
	1277, 1277	12	1279, 1277	20	14
			1274	**9**	**ω CH$_2$**
1273 s	**1277, 1266**	**131**	**1268**	**75**	**ω CH$_2$**
			1257	**5**	**ω CH$_2$**
1251 vs	**1259, 1241**	**127**	**1246, 1245**	**146**	**τ CH$_2$**
1240 s, sh	**1236**	**190**			**τ CH$_2$**
1224 m, sh	**1228**	**300**	**1229, 1227**	**164, 319**	**τ CH$_2$**
1196 m, sh	1183, 1183	12	1181, 1181	1	9a
	1161, 1161	0	1159, 1159	0	15
1160 m, sh	1160, 1159	473	1160, 1158	484	δ OH, 9a
1145 vs	**1145**	**179**			**ν N—C**
1141 s	1139, 1138	220	1138, 1137	253	δ OH, 9b
1131 m, sh	1130, 1128	340	1130, 1128	435	δ C—O
			1124	**67**	
1113 w, sh	**1121**	**0**			**ν N—C**
			1121	**1**	
	1105	53	1103	59	ν C—O, ν N—C
1096 w, sh	1103, 1102	20	1098, 1098	19	ν P-Ph
	1101	0	1097	4	ν N—C, ν C—O

Continued

TABLE 2A Continued

	Crown				
Experiment	*Computations*		*Chair-Boat Computations*		
$\tilde{\nu}^a$ *(cm^{-1}) Int.*	$\tilde{\nu}$ *(cm^{-1})*	I_{IR} *(km/mol)*	$\tilde{\nu}$ *(cm^{-1})*	I_{IR} *(km/mol)*	Assignment[b]
1070 wv	1082, 1081	15	1083, 1082	11	18b
1051 m, sh	**1043**	**165**			**ν N-Ph, ν N—C**
			1031	**9**	**ν N-Ph, ν N—C**
	1029, 1028	4	1026, 1025	8	18a
1034 vs	**1026**	**309**	**1020**	**69**	**ν N-Ph, ν N—C**
1000 vw	994, 994	10	995, 995	10	12
987 w	989, 982	11	984, 980	13	12
	989, 987	0	991, 991	0	5
955 m, sh	961, 961	0	971, 969	4	17a
939 s, br	613, 614	0	612, 618	0	OH···O out-of-plane deformation[c]
	920, 920	0	931, 929	0	10b
			909, 909	**3**	**10b**
897 s	**903**	**58**			**ρ CH_2**
	903, 903	1	897, 895	92	17a
	900, 900	18	886, 885	12	5
	881, 879	21	881, 880	9	ν C-Ph
880 m, sh	**879, 878**	**39**			**10b**
862 s	**871**	**41**	**876**	**105**	**ρ CH_2**
			862	**1**	**ρ CH_2**
844 w, sh	851, 850	0	856, 856	18	10a
	849, 849	0	847, 842	10	ν C—N, ν N-Ph
			826	**7**	**ρ CH_2**
812 m	**804**	**18**			
					ρ CH_2
803 w, sh	**776**	**0**	**782**	**51**	
784 w	771, 771	0	778, 776	1	10a
757 vs	759, 756,	243	754, 754, 753,	264	11
739 vs	750, 749		752		
726 w	714, 691	2	693, 683	13	ν P—C
	706, 706	4	702, 701	1	ν P-Ph
702 m, sh	705, 697	68	707, 704	55	4
693 vs	**691, 689**	**70**			**4**
			676, 674	**19**	**4**
663 s	672, 670	186	672, 670	275	δ O=C—O
	659, 657	**70**	**650**	**6**	**ν P—C**
640 m, sh	640, 640	90	641, 640	103	ρ C=O, δ O=C—O
			633	**3**	**ν P—C**
630 w, sh	628, 628	10	627, 625	85	
					6b, ρ OH
623 m	618, 617	200	621, 619	136	
	612, 607	6	607, 604	6	δ N-Ph
557 m	575, 563	4	568, 552	2	6a
526 m	533, 520	94	529, 529	93	ρ OH
503 w	513, 511	1	524, 520	5	6b
	498, 490	379	500, 495	35	δ C—P—C
471 m	470, 464	4	477, 476	8	16b
	445, 444	0	449, 448	0	16a
	442	4	447	0	Breathing
428 m	441	14	433, 420	18	Skeletal
	402, 400	0	405, 405	0	16a

Computed frequencies and assignments of conformationally sensitive vibrations are printed in bold.

[a] w: weak; m: medium; s: strong; v: very; sh: shoulder; br: broad.

[b] ν: stretch; δ: bend; ω: wagging; τ: twisting; ρ: rocking; s: symmetric; as: antisymmetric. Wilson's notation is used for vibrations of phenyl rings [32].

[c] The deviations of frequencies of the vibrations of the C=O and OH groups, calculated for the isolated molecule, from the solid-state experimental data are apparently due to intermolecular hydrogen bonding in the **1**. See text.

TABLE 3A Scaling Factors for the Force Fields of Molecules **6** and **7**

Scaling Factor		*Value*
Stretch	C—C	0.9207 [33]
Stretch	C—N	0.9207 [33]
Stretch	C—O	0.9207 [33]
Stretch	C═O	0.9207 [33]
Stretch	P—C	1.040 [61]
Stretch	C—H (arom.)	0.915 [60]
Stretch	C—H (aliph.)	0.889 [60]
Stretch	O—H	0.9527 [33]
Bend	C—C—C	1.0144 [33]
Bend	C—N—C	1.0144 [33]
Bend	C—C—O	1.0144 [33]
Bend	C—C═O	1.0144 [33]
Bend	O—C═O	1.0144 [33]
Bend	N—C—P	1.0144 [33]
Bend	P—C—C	1.0144 [33]
Bend	C—P—C	1.070 [61]
Bend	C—O—H	0.876 [33]
Bend	C—C—H	0.950 [33]
Bend	H—C—H	0.9016 [33]
Torsion	All	0.9523 [33]
Out of plane	Ring-H	0.976 [33]

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