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1,3,6-Azadiphosphacycloheptanes: A Novel Type of Heterocyclic Diphosphines

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ABSTRACT: *The novel type of seven-membered cyclic diphosphines, namely 1,3,6-azadiphosphacycloheptanes, has been synthesized by condensation of 1,2-bis(phenylphosphino)ethane, formaldehyde, and primary amines (aniline, p-toluidine, benzylamine, and 5-aminoisophthalic acid) as a mixture of rac- and meso-stereoisomers. The structures of rac-stereoisomers of N-tolyl and N-(3′,5′-dicarboxyphenyl)-substituted diphosphines were investigated by X-ray crystal structure analyses. The stereoisomers of N-(3′,5′-dicarboxyphenyl)-substituted compound were separated at a preparative scale, and their platinum(II) dichloride complexes were obtained. The corresponding meso-isomer readily forms P,P-chelate complex with [PtCl$_2$(cod)], whereas the rac-stereoisomer forms oligomeric complex.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:125–132, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20397

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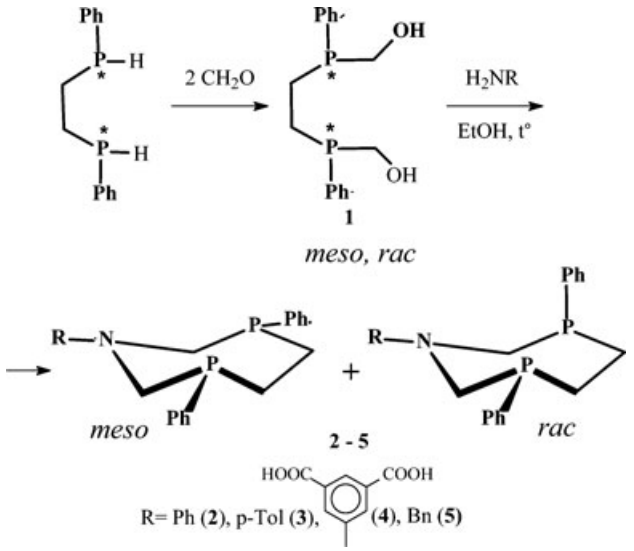
INTRODUCTION

Phosphine ligands are an excellent tool to obtain metal complexes with tailor-made properties, and they have been widely used in several fields such as water-soluble and asymmetric metal complexes [1,2]. The chelating diphosphines draw the special attention because of the stability of their metal complexes. However, to date, studies involving diphosphine ligands and especially hybrid functional diphosphines have mostly been focused on linear compounds [1,2]. In contrast, heterocyclic diphosphines in which the phosphorus atoms are incorporated into the ring have not been extensively investigated, though such incorporation leads to essential differences in the structures and the properties of acyclic and cyclic compounds [3]. The main specific feature of the cyclic diphosphines is the appearance of the cis–trans isomers of the substituents on the phosphorus atoms [3]. Indeed, 1,3- and 1,4-diphosphacyclohexanes [4], -cycloheptanes [5], and 1,4- and 1,5-diphosphacyclooctanes [6] exist as a mixture of cis- and trans- (or meso- and rac-)stereoisomers, only cis-isomers being able to act as chelating ligands as it was shown for 1,5-diphosphacyclooctanes [7]. In total, the eight-membered diphosphines are the most studied type of such ligands. A wide range of bidentate cyclic eight-membered aminomethylphosphines, namely 1,5-diaza-3,7-diphosphacyclooctanes ligands, has been synthesized by the Mannich-like reactions of arylphosphine, formaldehyde, and primary amines

[8–14]. It should be mentioned that only cis-stereoisomers (or meso-stereoisomers) of these diphosphines are formed. The similar approach was also successfully used for the synthesis of 1,3,5-azadiphosphacyclohexanes [15] on the basis of the secondary bis(arylphosphino)methane, but only a few examples of the seven-membered cyclic aminomethylphosphines were described. Most of these compounds include only one phosphorus center [16–18], but the condensation of hydroxymethyl derivatives of 1,2-diphosphinoethane and 1,2-diphosphinobenzene with amino acids led to the bicyclic diphosphines, where bridgehead phosphorus atoms are included simultaneously into the seven- and eight-membered heterocycles [19]. The complexes of 1,5-diaza-3,7-diphosphacyclooctanes with different transition metals (Cu^{I}[9,20,21], Re^{I}[12], Pt^{II}[9,12,13,22], and Pd^{II} [9,12–14]) were synthesized, and the structure of these complexes in the solid state and dynamic processes in solution as well as catalytic activity in the hydrogenation of alkynes [23], copolymerization of alkenes and carbon monoxide [24] have been studied. Although the chelating type of the coordination was predominant [9,12–14,20–22], these diphosphines appeared to be also able to form the binuclear complexes as the bridging ligands in spite of the cis-mutual orientation of the electron lone pairs on the phosphorus atoms [9,22]. For relatively small and rigid 1-aza-3,5-diphosphacyclohexanes, only the formation of oligonuclear complexes with bridging ligand was found for both trans- and cis-stereoisomers [15]. It indicates that inclusion of donor atoms in heterocyclic structures reduces their chelation ability, and sometimes the oligomerization becomes the predominant process. In this connection, the synthesis and study of the complexation properties of the intermediate-sized seven-membered N-containing diphosphines is of special interest, so that we assumed that the use of 1,2-bis(phenylphosphino)ethane [25] as a starting reagent will give possibly seven-membered cyclic diphosphines. Unlike unchelating bicyclic diphosphine ligands described in [19], the cis- (or meso-) stereoisomers of the monocyclic N-containing diphosphines may probably form chelate complexes whereas trans- (or rac-) ones may become the basis for the formation of polynuclear structures.

RESULTS AND DISCUSSION

The starting 1,2-bis(phenylphosphino)ethane contained two asymmetric phosphorus centers, so that it was, in fact, a mixture of rac- and meso-



SCHEME 1

diastereomers. Its interaction with paraformaldehyde at 100–110°C smoothly led to the mixture of *rac*- and *meso*-1,2-bis[(hydroxymethyl)phenylphosphino)ethanes **1**, which was further used without additional purification. Condensations of **1** with primary arylamines, namely aniline, *p*-toluidine and 5-aminoisophthalic acid, and benzylamine, were carried out in ethanol. The ^{31}P NMR spectra of the final reaction mixtures showed two prevailing peaks at δ_P − 25 and −27 ppm in the case of arylamines and at −33.5 and −31.8 ppm in the case of benzylamine. The spontaneous crystallization led to the isolation of the crystalline products **2–5** (Scheme 1), which were air stable and soluble in benzene, chloroform, acetone, and DMF. The compound **4** with a dicarboxyphenyl substituent was satisfactorily soluble in water in the presence of 2 equivalents of inorganic base.

The structure elucidation of these compounds was based on ^{31}P and ^{1}H NMR, IR and mass spectra, and elemental analysis. The absence of the absorption bands of hydroxyl (excluding dicarboxyphenyl-substituted compound **4**) and amino groups in the IR spectra of **2–4** indicated the formation of the cyclic compounds. The mass spectra of **4** and **5** showed the peak for the molecular ion of the corresponding 1,3,6-azadiphosphacycloheptanes with m/z 451.2 and 377.2, respectively. The ^{31}P NMR spectra of crude compounds **2–4** showed two narrow singlets in the region between −25 and −27 ppm that coincided with the main signals of reaction mixture's spectra and indicated the crystallization of a mixture of meso- and rac-stereoisomers. In the case of *N*-benzyl-substituted compound **5**, the spectrum

showed only one signal at δ_P −33.5 ppm due to spontaneous crystallization of the individual stereoisomer from the reaction mixture. Concentration of the filtrate gave rise to the stereoisomeric mixture, and along with the predominant signal of the first stereoisomer the minor peak of the second stereoisomer was also observed at δ_P −31.8 ppm. The intensity ratio was 5:1. The ^{1}H NMR spectra of crude compounds **2–4** also showed the double set of signals for the expected groups of protons and indicated the formation of 1,3,6-azadiphosphacycloheptanes.

The fractional crystallization of **4** from the DMF–acetone mixture led to the isolation of its individual stereoisomer. Only one peak at δ_P −25.7 ppm was observed in its ^{31}P NMR spectrum. On the contrary, the corresponding filtrate appeared to be essentially enriched by another meso-stereoisomer (δ_P −26.7 ppm), its content was about 80%. The X-ray analysis of the monocrystal of the isolated individual stereoisomer showed that it was rac-stereoisomer (Fig. 1).

Henderickson [26,27] proposed variants of the assignment of the carbocycle conformations according to the sequence of the signs of torsional angles of the cycle. This sequence allows one to describe the conformation of the cycle **4** as twist-chair (Table 1). The cycle includes the planar five-atom fragment N1C2P3C5P6. The atoms C4 and C7 are deviated from this planar fragment to the opposite sides (Fig. 2). The phenyl substituents on the phosphorus atoms are in pseudoequatorial positions and directed to the opposite sides of the medium plane of the cycle, so that the electron lone pairs are in axial positions and have the opposite directions. The nitrogen atom is coordinated in a near trigonal-planar fashion (the sum of its bond angles is 353.84°) due to conjugation of its electron lone pair with the π-systems of the aryl substituent, which is pseudoaxial.

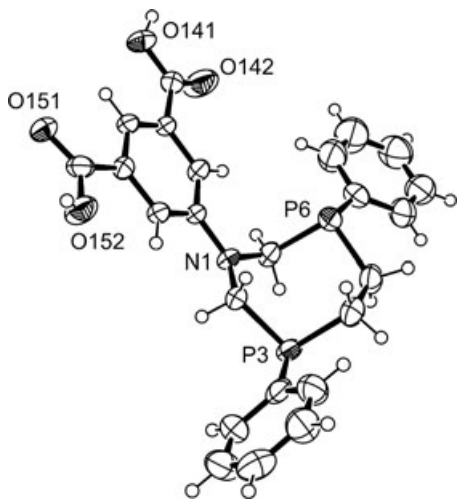


FIGURE 1 An ORTEP view of *rac*-(SS) isomer **4**.

TABLE 1 The Selected Torsional Angles of the Molecules *rac*-**3** and *rac*-**4**

Molecule **3**		*Molecule* **4**	
Torsion Angle	τ *(deg)*	*Torsion Angle*	τ *(deg)*
C4P3C2N1	58.5(4)	N1C2P3C4	99.72
C2P3C4C5	−69.5(5)	C2P3C4C5	−69.77
P3C4C5P6	106.5(4)	P3C4C5P6	73.79
C7P6C5C4	−67.6(4)	C4C5P6C7	−84.94
C5P6C7N1	−12.7(5)	C5P6C7N1	79.45
C2N1C7P6	88.6(6)	P6C7N1C2	−16.30
C7N1C2P3	−97.4(5)	C7N1C2P3	−73.62

Both isomers of **4** are stable in 5% aqueous solution of sodium hydroxide and do not undergo the oxidation or the hydrolysis according to their ^{31}P and ^{1}H NMR spectra.

In the case of compounds **2** and **3**, the analogous fractional crystallization led only to enrichment of the mixture by one of stereoisomers. The successful separation of rac- and meso-isomers of **4** allowed us to attribute the signals of both stereoisomers for all compounds **2–4** because their proton signal's pictures of P—CH_2—N fragments were similar. In all cases for rac-stereoisomers, the signals of one proton are doublet of doublets with coupling constants $^2J_{HH}$ 13.7–13.8 Hz and $^2J_{PH}$ 9.2–11.2 Hz, whereas the signals of another proton are doublets of multiplets with small pseudocoupling constants J_{PH} 0–5 Hz due to the presence of complex and partially degenerated AA′BB′XX′ spin system. For the meso-stereoisomers of these compounds, the corresponding signals are two doublets of doublets with the coupling constants $^2J_{HH}$ 14.4–14.9 Hz and $^2J_{PH}$ 5.3–5.6 and 21.95–24.9 Hz. The unusually high value of one of stereospecific geminal constants indicates the eclipse of the phosphorus lone electron pair and

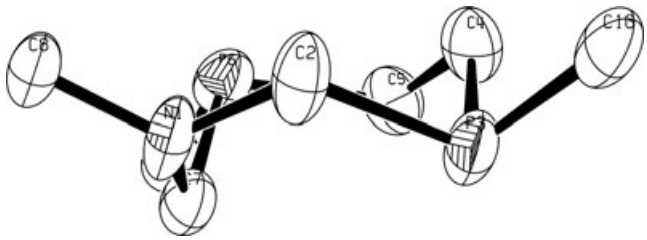


FIGURE 2 The conformation of the cycle of *rac*-(SS) isomer of **4** (the substituents on the heteroatoms and hydrogen atoms are omitted for clarity).

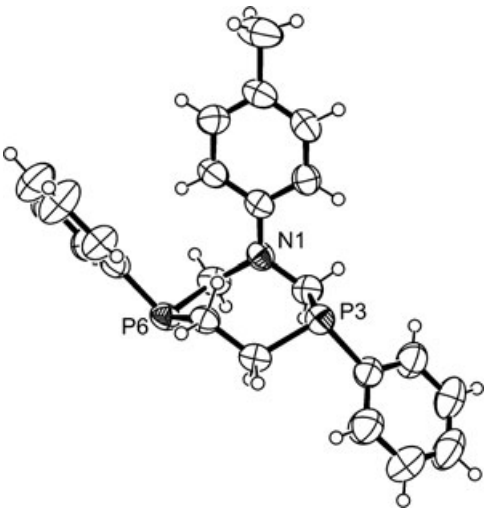


FIGURE 3 An ORTEP view of *rac*-(SS) isomer **3**.

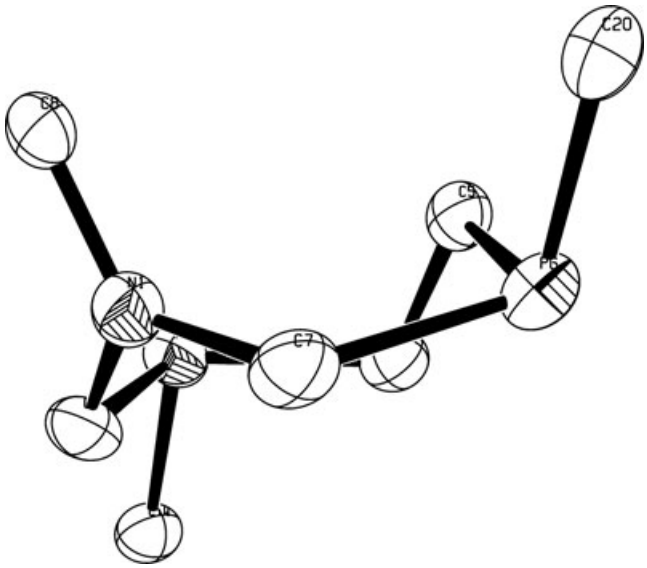


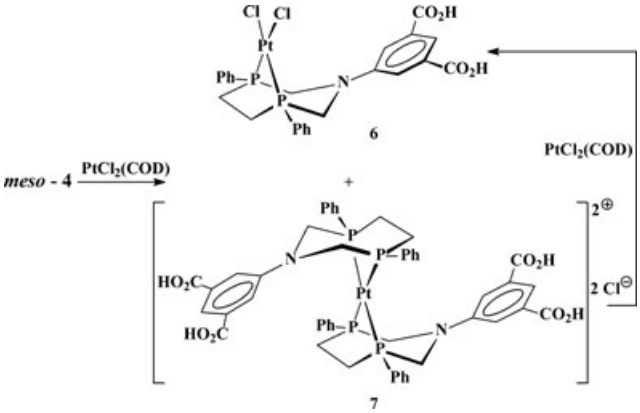
FIGURE 4 The conformation of the cycle of *rac*-(SS) isomer of **3** (the substituents on the heteroatoms and hydrogen atoms are omitted for clarity).

one of the C—H bonds in the predominant conformations of meso-isomers **2–4** (the torsion angles must not be more than 20° [28]). The spectra give the evidence that for **2** and **3** rac-isomers were predominant after the recrystallization (the ratios of rac- and meso-isomers were about 2:1); in the case of compound **3**, the monocrystal of the predominant rac-isomer was isolated.

The structure of the rac-isomer of compound **3** was investigated by X-ray analysis (Fig. 3). The phosphorus atoms configurations in the studied crystal of **3** corresponded to (SS)-enantiomer. According to the method [26,27], the conformation of the cycle of the compound **3** may also be described as twist-chair (Table 1). The fragment N1P3C4P6C7 is near planar. The atoms C2 and C5 are located on the opposite sides of this plane (Fig. 4). Like the rac-isomer of **4**, the phenyl substituents on the phosphorus atoms are in pseudoequatorial positions and are directed to the opposite sides of the medium plane of the cycle, and the tolyl group on the nitrogen atom is pseudoaxial. The nitrogen atom is coordinated in a trigonal-planar fashion (the sum of the bond angles is 359.48°).

In the case of the isolated stereoisomer of *N*-benzyl substituted compound **5**, the proton spectrum picture of P—CH_2—N fragments in the region of 3–4 ppm looks slightly different from those ones of both stereoisomers of the compounds **2–4**: the signals are broad doublet (the coupling constants $^2J_{HH}$ 13.8 Hz and $^2J_{PH}$ near 0 Hz) and the doublet of multiplets (the coupling constants $^2J_{HH} = 13.8$ Hz and pseudoconstants J_{PH} 0–4 Hz). Since the values of the coupling constants were closer to the corresponding values of the rac-stereoisomers of the compounds **2–4**, we concluded that the isolated compound was also the rac-stereoisomer of the heterocycle **5**, but its predominant conformation probably differed from those of N-aryl-substituted compounds.

It is possible to expect that the type of complexation of transition metals by rac- and meso-stereoisomers of 1,3,6-azadiphosphacycloheptanes is completely different because their rac-isomers with opposite-directed electron lone pairs may act only as bridging ligands, whereas the meso-isomers may form chelate complexes. However, in the case of 1,3,5-azadiphosphacyclohexanes, both stereoisomers acted only as bridging ligands to form oligonuclear complexes with Pt(II) dichloride because of the high-sterical strain of four-membered chelate complexes and the rigidity of six-membered cycle [15]. Since the most complete isomer's separation was provided in the case of 1,3,5-azadiphosphacycloheptane **4**, the complexation reactions of its both stereoisomers were studied. The reaction of meso-isomer of **4** with (cyclooctadiene)platinum(II) dichloride in DMF led to the formation of two types of complexes. The ^{31}P NMR spectrum of the reaction mixture showed two peaks at δ_P 37.5 and 42.4 ppm with the ratio 1:1 and indicated the formation of two different metal complexes. The unusually high-downfield shifts of both signals in comparison with the signal of ligand ($\Delta\delta = 64.2$ and $\Delta\delta = 69.1$ ppm, respectively) indicated that both complexes formed chelate five-membered cycles. The corresponding coupling constants $^1J_{PtP}$ are strongly different (3342



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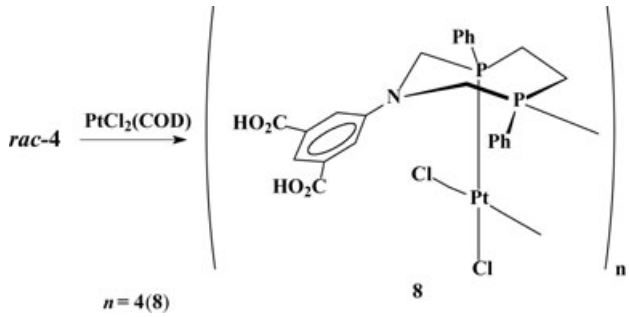

SCHEME 3

and 2195.4 Hz) perhaps due to the formation of cis-$LPtCl_2$ and $[L_2Pt]^{2+}\cdot 2Cl^-$ structures **6** and **7** (Scheme 2). A low-field peak of the complex **7** disappears in the ^{31}P NMR spectrum of the reaction mixture, when treating the crude product with the excess of (cyclooctadiene)platinum(II) dichloride in DMF at 70°C. The crystallization of the product from DMSO led to the isolation of individual complex **6** with metal–ligand ratio 1:1. Its ^{31}P NMR spectrum showed only the upfield peak at δ_P 37.5 with coupling constant $^1J_{PtP}$ 3342 Hz, which was typical for cis-chelate P,P-complexes of cyclic aminomethylphosphines. The proton signals of P—CH_2—N fragments are two broad doublets with coupling constant $^2J_{PH}$ near 0 Hz, which correspond to torsion angles Pt—P—C—H values of 70°–80°. These data give the evidence that the compound **6** is typical mononuclear cis-P,P-chelate complex. So, on the contrary to 1,3,5-azadiphosphacyclohexanes, the meso-isomers of 1,3,6-azadiphosphacyclooctanes are chelating P,P-ligands. It should be mentioned that the formation of chelate complexes **6** and **7** additionally confirmed the structure attribution of the stereoisomers.

The interaction of rac-isomer of **4** with (cyclooctadiene)platinum(II) dichloride led to the formation of the crystalline product with the metal–ligand ratio 1:1. One very broad peak at δ_P 1.2 ppm with the coupling constant $^1J_{PtP}$ 3519 Hz was observed in its ^{31}P NMR spectrum. The relatively low complexation shift of the signal in the comparison with the ligand's signal ($\Delta\delta$ 27 ppm) and the typical coupling constant value for cis-nonchelate P,P-complexes of aminomethylphosphines [29] proves the formation of the oligomeric polynuclear complexes with the bridging P,P-ligands. The absence of the signals of uncomplexed three-coordinated terminal phosphorus atoms may correspond to the formation of both linear oligomers of high-molecular weights and some cyclic oligomer, but the satisfactory solubility of the complex indicates that the cyclic structure is more probable. On keeping of the starting ligand conformation, the geometrical parameters of the subunits (namely the antiparallel electron pair's direction of the ligand and the turning angles of the metal centers of about 90°) make the formation of tetranuclear macrocyclic complex **8** the most probable [30]; however, one cannot exclude the formation of other oligomers (Scheme 3).

The results obtained show that the condensation of 1,2-bis[(hydroxymethyl)aryl-phosphino]ethanes with primary amines may be considered as a general and convenient method of the synthesis of a novel type of cyclic diphosphines—1,3,6-azadiphosphacycloheptanes, which are formed as the mixtures of meso- and rac-stereoisomers. These stereoisomeric mixtures may be separated, and the different stereoisomers act as different types of ligands: the meso-isomers are chelating P,P-ligands, and the rac-isomers are bridging ones to form oligonuclear metal complexes.

EXPERIMENTAL

All manipulations involving 1,2–bis(phenylphosphino)ethane and 1,2-bis[(hydroxymethyl)phenylphosphino]ethane were carried out under an inert atmosphere. NMR-spectra: MSL-400 (Bruker), standards: ^{31}P NMR (161 MHz): external 85% H_3PO_4; ^1H MNR (400 MHz): internal solvent; ^{13}C NMR (100.6 MHz); WM-250 (Bruker): ^1H NMR (250 MHz): internal solvent; CXP-100: ^{31}P NMR (36.47 MHz): external 85% H_3PO_4. The IR spectra were recorded as Nujol mulls on a Specord M-80 spectrometer in the range 400–4000 cm^{-1}. The EI mass spectra were obtained on a TRACE MS "Finnigan MAT" spectrometer (electron energy 70 eV, ion source temperature 200°C, the direct injection system). The treatment of mass spectral data was carried out with the use of "Xcalibur" program. The melting points were done on a Boetius apparatus and are uncorrected.

Crystal Data

The X-ray data for crystals **3** and **4** were collected on a CAD-4 Enraf–Nonius automatic diffractometer at 20°C. The stability of crystal and of experimental conditions was checked every 2 h using three control reflections, whereas the orientation was monitored every 200 reflections by centering two standards. Decay corrections were not necessary. Corrections for Lorentz and polarization effects were applied. Twenty five centered reflections were used to determine unit cell dimensions.

Crystals **3**: $C_{23}H_{25}NP_2$, M 377.38, $F(000)$ 800, monoclinic, a 10.577(1), b 14.212(4), c 14.685(3) Å, β 110.100(5)°, V 2073.0(14) Å^3, d_{calc} 1.21 g cm^{-3}, Z 4, space group $P2_1/a$. A total of 4192 unique reflections were measured in the range $2° \leq \theta \leq 26°$ using graphite monochromated λ Mo Kα radiation and $\omega/2\theta$ scan mode, of which 1667 were with $I > 2\sigma$. Empirical absorption correction was not applied (μ Mo 2.16 cm^{-1}).

Crystals **4**: $C_{27}H_{30}N_2O_5P_2$, M 524.47, $F(000)$ 1104, monoclinic, a 9.919(4), b 10.691(7), c 24.65(2) Å, β 96.24(6)°, V 2599(3) Å^3, d_{calc} 1.34 g cm^{-3}, Z 4, space group $P2_1/c$. A total of 5050 unique reflections were measured in the range $2° \leq \theta \leq 26°$ using graphite monochromated λ Mo Kα radiation and $\omega/2\theta$ scan mode, of which 2098 were with $I > 2\sigma$. Empirical absorption correction was not applied (μ Mo 2.08 cm^{-1}).

The structure was solved by the direct method using the SIR [31] program and refined by the full matrix least-squares using SHELXL97 [32] program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated position with thermal parameters 30% larger than atom to which they attached. The final agreement factors are R 0.058, R_w 0.115 based on 4192 reflections with $F^2 > 3\sigma$ for crystal **3** and R 0.098, R_w 0.252 based on 5050 reflections with $F^2 > 3\sigma$ for crystal **4**. All calculations were performed on PC using WinGX [33] program. Cell parameters, data collection, and data reduction were performed on Alpha Station 200 computer using MoLEN [34] program.

CCDC no. 622121 and 622122 contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK; fax: +44-1223 336033 or deposit@ccdc.cam.ac.uk).

Synthesis

1,2-Bis(phenylphosphino)ethane. The solution of 1,2-bis[(isopropyloxy)phenyl-phosphoryl]ethane [35] (31 g, 0.07 mol) in dry ether (200 mL) was added dropwise with the vigorous stirring to the suspension of lithium aluminum hydride (5.9 g, 0.15 mol) in dry ether (150 mL) at 0°C. The reaction mixture was then heated under reflux with vigorous stirring for 4 h, cooled to the ambient temperature, and 15% aqueous hydrochloric acid (70 mL) was added dropwise up to pH 2. The organic layer was separated, the aqueous layer was extracted by ether (100 mL), and the combined organic extracts were dried with sodium sulfate for 3 days. The solvent was removed in vacuum; the residue was distilled to give 8.5 g (44%) of 1,2-bis(phenylphosphino)ethane [25] with the boiling point 160°C/0.05 mm. ^{1}H NMR ($CDCl_3$): 1.86–2.2 (m, 4H, CH_2), 3.95 (d, $^1J_{PH}$ = 209.7 Hz, 2H, PH), 7.19–7.45 (m, 10H, C_6H_5). ^{31}P NMR ($CDCl_3$): −46.91 ($^1J_{PH}$ = 209.7 Hz), −47.10 ($^1J_{PH}$ = 209.7 Hz).

*1,2-Bis[(hydroxymethyl)phenylphosphino]ethane (**1**).* Solid paraformaldehyde (0.24 g, 8.1 mmol) was added to 1,2-bis(phenylphosphino)ethane (1 g, 4.1 mmol), and the reaction mixture was heated at 90°C until the mixture became homogeneous. The yield of **1** was 1.24 g (100%). ^{31}P{^{1}H} NMR (C_6D_6): –18.1, –19.43.

*General Procedure for the Synthesis of (**2**)–(**5**)*

The solution of **1** (3.0 mmol) and the corresponding primary amine (3.0 mmol) in ethanol (10–30 mL) was stirred at 80°C for 2–4 h and cooled to the ambient temperature. In the case of compound **2**, the solvent was partially removed in vacuum, in the case of compound **3** the reaction mixture was allowed to stand for 2 days at 0°C for the crystallization. The precipitate formed was filtered off, washed by ethanol, and dried at 0.1 Torr for 2–4 h.

*1,3,6-Triphenyl-1-aza-3,6-diphosphacycloheptane (**2**).* Recrystallized from ethanol. Yield 0.32 g, 29%; mp 80–82°C. ^{1}H NMR (C_6D_6): 1.91–2.13 (m, 4H + 4H, P—CH_2, *meso* + *rac*), 3.26 (dd, $^2J_{HH}$ = 14.7 Hz, $^2J_{PH}$ = 5.4 Hz, 2H, P—CH_2^A—N, *meso*), 3.85 (dd, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ = 11.2 Hz, 2H, P—CH_2^A—N, *rac*), 4.09 (dm, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH} \approx$ 5.0 Hz, 2H, P—CH_2^B—N, *rac*), 4.17 (dd, $^2J_{HH}$ = 14.7 Hz, $^2J_{PH}$ = 24.9 Hz, 2H, P—CH_2^B—N, *meso*), 6.69–6.95 (m, 3H +3H, *o*-H + *p*-H in NC_6H_5, *meso* + *rac*), 7.00–7.45 (m, 12H + 12H, PC_6H_5 + *m*-H in NC_6H_5, *meso* + *rac*).

$^{31}P\{^1H\}$ NMR (C_6D_6): –25.8 (*meso*), –26.6 (*rac*). IR ($\tilde{\nu}$ (cm^{-1}), Nujol): 1593 (aryl), 3050 (aryl). Anal. Calcd for $C_{22}H_{23}NP_2$ [363]: C, 72.70; H, 6.33; N, 3.85; P, 17.07. Found: C, 72.93; H, 6.57; N, 3.65; P 16.65.

*1-p-Tolyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane (**3**).* Recrystallized from ethanol: acetone (20:1). Yield 0.30 g, 27%; mp 80–84°C. ^1H NMR ($CDCl_3$): 2.24 (s, 3H, CH_3, *meso*), 2.28 (s, 3H, CH_3, *rac*), 2.36–2.51 (m, 4H + 4H, P—CH_2, *meso* + *rac*), 3.63 (dd, $^2J_{HH} = 15.04$ Hz, $^2J_{PH} = 5.6$ Hz, 2H, P—CH_2^A—N, *meso*), 3.93 (dd, $^2J_{HH} = 13.8$ Hz, $^2J_{PH} = 9.9$ Hz, 2H, P—CH_2^A—N, *rac*), 4.20 (m, $^2J_{HH} = 13.8$ Hz, 2H, P—CH_2^B—N, *rac*), 4.34 (dd, $^2J_{HH} = 15.04$ Hz, $^2J_{PH} = 24.0$ Hz, 2H, P—CH_2^B—N, *meso*), 6.72 (d, $^3J_{HH} = 8.6$ Hz, 2H, *o*-C_6H_4, *rac*), 6.93 (d, $^3J_{HH} = 8.6$ Hz, 2H, *o*-C_6H_4, *meso*), 7.00 (d, $^3J_{HH} = 8.6$ Hz, 2H, *m*-C_6H_4, *rac*), 7.11 (d, $^3J_{HH} = 8.6$ Hz, 2H, *m*-C_6H_4, *meso*), 7.26–7.60 (m, 10H + 10H, C_6H_5, *meso* + *rac*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −25.3 (*meso*), −26.2 (*rac*). IR ($\tilde{\nu}$ (cm^{-1}), Nujol): 1612 (aryl), 3060 (aryl). Anal. Calcd for $C_{23}H_{25}NP_2$ [377]: C, 73.21; H, 6.63; N, 3.71; P 16.44. Found: C, 72.83; H, 6.19; N, 3.50; P, 16.02.

*1-(3′,5′-Dicarboxyphenyl)-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane (**4**).* Yield 0.98 g, 67%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −25.7 (*rac*), −26.7 (*meso*), the intensity ratio 1:1. IR ($\tilde{\nu}$ (cm^{-1}), Nujol): 1598 (aryl), 1696 (CO), 3060 (aryl), 3312 br (OH).

The crude **4** was recrystallized from the DMF–acetone mixture (1:1), washed with ethanol and dried at 0.1 Torr for 3 h to give 0.35 g (24%) of stereoisomerically pure *rac*-**4**, mp 232–236°C. ^1H NMR (DMF-d_7): 2.44–2.64 (m, 4H, P—CH_2), 4.10 (dd, $^2J_{HH} = 13.8$ Hz, $^2J_{PH} = 10.2$ Hz, 2H, P—CH_2^A—N), 4.30 (m, $^2J_{HH} = 13.8$ Hz, 2H, P—CH_2^B—N), 7.40–7.55 (m, 6H, *o*-H + *p*-H in C_6H_5), 7.60–7.75 (m, 6H, *m*-H in C_6H_5 + *o*-H in C_6H_3), 8.02 (s, 1H, s, 1H, *p*-H in C_6H_3). ^1H NMR (D_2O): 1.65–2.0 (m, 4H, P—CH_2), 3.61–3.70 (m, 2H, P—CH_2^A—N), 3.76 (d, $J = 12.4$ Hz, 2H, P—CH_2^B—N), 7.01–7.60 (m, 12H, C_6H_5 + *o*-H in C_6H_3), 8.34 (s, 1H, *p*-H in C_6H_3). $^{13}C\{^1H\}$ NMR (DMF-d_7): 25.14 (dd, $^1J_{PC} = 15.3$ Hz, $^3J_{PC} = 15.0$ Hz, P—CH_2), 53.98 (d, $^1J_{PC} = 15.3$ Hz, P—CH_2—N), 118.37 (s, *o*-C in C_6H_3), 119.39 (s, *p*-C in C_6H_3), 129.36 (d, $^3J_{PC} = 6.54$ Hz, *m*-C in C_6H_5), 129.64 (s, *p*-C in C_6H_5), 132.46 (d, $^2J_{PC} = 18.53$ Hz, *o*-C in C_6H_5), 132.92 (s, *m*-C in C_6H_3), 138.08 (d, $^1J_{PC} = 15.3$ Hz, *i*—C in C_6H_5), 150.20 (s, *i*-C in C_6H_3), 167.81 (s, COOH). $^{31}P\{^1H\}$ NMR (DMF-d_7): −25.7. ^{31}P NMR (D_2O): δ_p −27.14. MS EI (*m/z*): 451.2 (20) $[M]^+$, 423.2 (22) $[M—C_2H_4]^+$, 258.2 (40) $[M—CH_2NC_6H_3(COOH)_2]^+$, 230.2 (77) $[M—C_2H_4—CH_2NC_6H_3(COOH)_2]^+$, 108.2 (85) $[PhP]^+$. Anal. Calcd for $C_{24}H_{23}NO_4P_2$ [451]: C, 63.86; H, 5.10; N, 3.10; P, 13.75. Found: C, 63.28; H, 4.7; N, 3.00; P, 13.18.

The concentration of the filtrate after the recrystallization of **4** gave precipitate, which was filtered off, washed with ethanol, and dried at 0.1 Torr for 3 h. The precipitate was the mixture of *meso*-**4** (80%) and *rac*-**4** (20%). Yield 0.31 g (21%). Spectral data for *meso*-**4**: ^1H NMR (DMF-d_7): 2.11–2.25 (m, 2H, P—CH_2^A), 2.44–2.66 (m, 2H, P—CH_2^B), 4.11 (dd, $^2J_{HH} = 14.9$ Hz, $^2J_{PH} = 5.3$ Hz, 2H, P—CH_2^A—N), 4.49 (dd, $^2J_{HH} = 14.9$ Hz, $^2J_{PH} = 21.95$ Hz, 2H, P—CH_2^B—N), 7.39–7.55 (m, 6H, *o*-H + *p*-H in C_6H_5), 7.60–7.65 (m, 6H, *m*-H in C_6H_5+ *o*-H in C_6H_3), 8.01 (s, 1H, *p*-H in C_6H_3). ^1H NMR (D_2O): 1.54 (m, 2H, P—CH_2^A), 1.75 (m, 2H, P—CH_2^B), 2.85–3.05 (m, 2H, P—CH_2^A—N), 3.88–4.07 (m, 2H, P—CH_2^B—N), 6.80–7.70 (m, 13H, Ar). $^{13}C\{^1H\}$ NMR (DMF-d_7): 18.74 (s, P—CH_2), 57.22 (br s, P—CH_2—N), 118.24 (s, *o*-C in C_6H_3), 118.91 (s, *p*-C in C_6H_3), 129.06 (s, *p*-C in C_6H_5), 129.28 (d, $^3J_{PC} = 2.44$ Hz, *m*-C in C_6H_5), 132.07 (d, $^2J_{PC} = 17.10$ Hz, *o*-C in C_6H_5), 132.97 (s, *m*-C in C_6H_3), 138.0 (d, $^1J_{PC} = 15.3$ Hz, *i*-C in C_6H_5), 147.53 (s, *i*-C in C_6H_3), 167.95 (s, COOH). $^{31}P\{^1H\}$ NMR (DMF-d_7): −26.7. $^{31}P\{^1H\}$ NMR (D_2O): –27.34.

*1-Benzyl-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane (**5**).* Yield of *rac*-**5** 0.45 g, 39%; mp 86–88°C. ^1H NMR ($CDCl_3$): 2.25–2.51 (m, 4H, P—CH_2), 3.25 (br d, $^2J_{HH} = 13.8$ Hz, $^2J_{PH} \approx 0$ Hz, 2H, P—CH_2^A—N), 3.81 (m, $^2J_{HH} = 13.8$ Hz, 2H, P—CH_2^B—N), 3.95 (m, $^2J_{HH} = 12.9$ Hz, Ph—CH_2—N), 7.22–7.46 (m, 15H, C_6H_5). ^{31}P NMR $\{^1H\}$ ($CDCl_3$): −33.5. IR ($\tilde{\nu}$ (cm^{-1}), Nujol): 1588 (aryl), 3060 (aryl). MS EI (*m/z*): 377.2 (23) $[M]^+$, 349.2 (25) $[M—C_2H_4]^+$, 286.2 (35)) $[M—CH_2Ph]^+$, 258.2 (30) $[M—CH_2NCH_2Ph]^+$, 230.2 (32) $[M—C_2H_4—CH_2NCH_2Ph]^+$, 133.2 (62) [M–$PhPCH_2CH_2PPh]^+$, 108.2 (38) $[PhP]^+$, 91.1 (100) $[PhCH_2]^+$. Anal. Calcd for $C_{23}H_{25}NP_2$ [377]: C, 73.21; H, 6.63; N, 3.71; P 16.44. Found: C, 72.77; H, 6.27; N, 3.56; P 16.00.

The concentration of the filtrate of the reaction mixture gave the mixture of *rac*-**5** and *meso*-**5** in the ratio 5:1. Spectral data for *meso*-**5**: ^{31}P NMR $\{^1H\}$ ($CDCl_3$): −31.8.

*cis-(RS)-[P,P-1-(3′,5′-Dicarboxyphenyl)-3,6-diphenyl-1-aza-3,6-diphosphacycloheptane]-platinum (II) Dichloride (**6**).* The solution of (cyclooctadiene)platinum(II) dichloride (0.13 g, 0.3 mmol) in DMF (10 mL) was added dropwise to the solution of *meso*-**4** (0.17 g, 0.3 mmol, contained about 20% of *rac*-**4**) in DMF (5 mL).$^{31}P\{^1H\}$ NMR (DMF): δ_p 37.51 ($^1J_{PtP} = 3342.2$ Hz), 42.46 ($^1J_{PtP} = 2195$ Hz), the intensity ratio 1:1. (Cyclooctadiene)platinum(II) dichloride (0.02 g, 0.05 mmol) was added to the

reaction mixture, and it was stirred at 70°C for 10 h and cooled. The precipitate formed was filtered off and recrystallized from DMSO to give individual **6**. Yield 0.05 g (28%), mp >260°C. ^{1}H NMR (DMSO-d_6): 2.50 (m, 4H, P—CH_2), 4.15 (d, $^2J_{HH} = 14.9$ Hz, 2H, P—CH_2^A—N), 4.80 (d, $^2J_{HH} = 14.9$ Hz, 2H, P—CH_2^B—N), 7.59–8.02 (m, 13H, Ar). ^{31}P{^{1}H} NMR (DMSO-d_6): 37.51 ($^1J_{PtP} = 3342.2$ Hz). Anal. Calcd for $C_{24}H_{23}Cl_2NP_2PtO_4$ [717]: C, 40.17; H, 3.21; N, 1.95; P, 8.64. Found: C, 39.32; H, 2.97; N, 1.72; P 8.03.

The Interaction of rac-4 with (Cyclooctadiene)platinum(II) Dichloride. The solution of (cyclooctadiene)platinum(II) dichloride (0.14 g, 0.3 mmol) in DMF (10 mL) was added dropwise to the solution of *rac*-**4** (0.17 g, 0.3 mmol) in DMF (5 mL). The precipitate formed was filtered off and washed by ethanol. Yield 0.13 g (48.1%), mp >260°. ^{31}P{^{1}H} NMR (DMF): 1.26 (br s, $^1J_{PtP} \approx 3519$ Hz). Anal. Calcd for $[C_{24}H_{23}Cl_2NP_2PtO_4]_n$ [717]: C, 40.17; H, 3.21; N, 1.95; P, 8.64. Found: C, 39.46; H, 2.88; N, 1.78; P, 8.12.

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