Synthesis of first representatives of 46-membered P,N,O-containing cyclophanes and their transition metal complexes*

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A condensation of phenyl- or *l*-menthylphosphine with formaldehyde and 4,4´-bis-(4´-aminophenoxy)biphenyl proceeding as a covalent self-assembly gave rise to the first representatives of 46-membered P,N,O-containing cyclophanes, namely, $1^3,1^7,8^3,8^7$-tetra-R-3,6,10,13-tetraoxa-1,8(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphanes (R = Ph (**1**), *l*-Ment (**2**)). The cage macrocyclic tetraphosphine **2** reacted with (cyclooctadiene)dichloroplatinum(II) and -palladium(II), as well as with (tetrahydrofuran)pentacarbonyltungsten(0) with the formation of binuclear complexes, in which the metal atoms are coordinated to 1,5-diaza-3,7-diphosphacyclooctane fragments by the P,P-chelate mode.

Key words: cyclophanes, phosphines, 4,4´-bis(4´-aminophenoxy)biphenyl, condensation, covalent self-assembly, metal complexes.

Macrocycles containing tricoordinated phosphorus atoms, in particular, macrocyclic phosphines, are of interest first of all as polydentate ligands with soft donor centers capable of binding transition metals.[1—3] They can be a basis for the development of catalytic systems, in which active centers are inside the macrocyclic cavity or in its close proximity. In such structures, there are preconditions for secondary interactions of the cavity with the substrates and reagents in the course of the catalytic processes, that increases their efficiency and, especially, selectivity. The metal complexes with macrocycles with phosphorus atoms in the main chain were found to possess specific catalytic properties.[1,3—10]

Earlier, the processes of covalent self-assembly in the systems "primary phosphine—formaldehyde—diamine with spatially separated groups" were used to synthesize a number of P,N-containing cyclophanes of different size (28-, 36-, and 38-membered), each including two 1,5-diaza-3,7-diphosphacyclooctane fragments.[3,11,12] However, there was no answer to the question: which limitations do exist related to the spacer length between the amino groups and, therefore, to the sizes of the cyclophane formed, for the processes of the covalent self-assembly of macrocycles in the condensation in the systems of such a type?

To test a possibility of the synthesis of the large-size macrocycles, we studied the condensation reactions of bis(hydroxymethyl)organylphosphines with diamines with a spacer bearing four *para*-phenylene fragments. 4,4´-Bis-(4´-aminophenoxy)biphenyl with the central linear biphenylene fragment was chosen as such a diamine. Its structure and conformational behavior resemble those of 1,4-di-[α-(4´-aminophenyl)isopropyl]- and 1,4-bis(4´-aminophenoxy)benzenes, the use of which in these reactions leads to a predominant formation of macrocyclic products of [2+2] condensation *via* covalent self-assembly.[13,14] Based on this, we expected the formation of similar cage cyclophanes in the reactions with 4,4´-bis(4´-aminophenoxy)biphenyl, though, the longer spacer and its additional conformational lability due to the rotation around the central C—C bond of the biphenylene fragment would play a negative role. Both "traditional" arylphosphines and chiral *l*-menthylphosphine were chosen for the phosphine component. In the first step of the synthesis, two equivalents of formaldehyde were added to the corresponding primary phosphine (phenyl-, mesityl-, 2,4,6-tri(isopropyl)phenyl-, and *l*-menthylphosphine). To do this, a mixture of a phosphine and solid paraformaldehyde was heated at 110—115 °C until homogenization was achieved (Scheme 1). Further reaction of thus obtained bis(oxymethyl)organylphosphine with 4,4´-bis(4´-aminophenoxy)biphenyl was carried out in DMF at 110 °C (in the case of *P*-phenyl- and *P*-mesityl-substituted compounds) or in toluene at 100 °C (in the case of phosphines with bulky hydrophobic triisopropylphenyl and menthyl substituents). The concentration of the starting phosphines was 0.2—0.3 mol L^{-1}. The reaction

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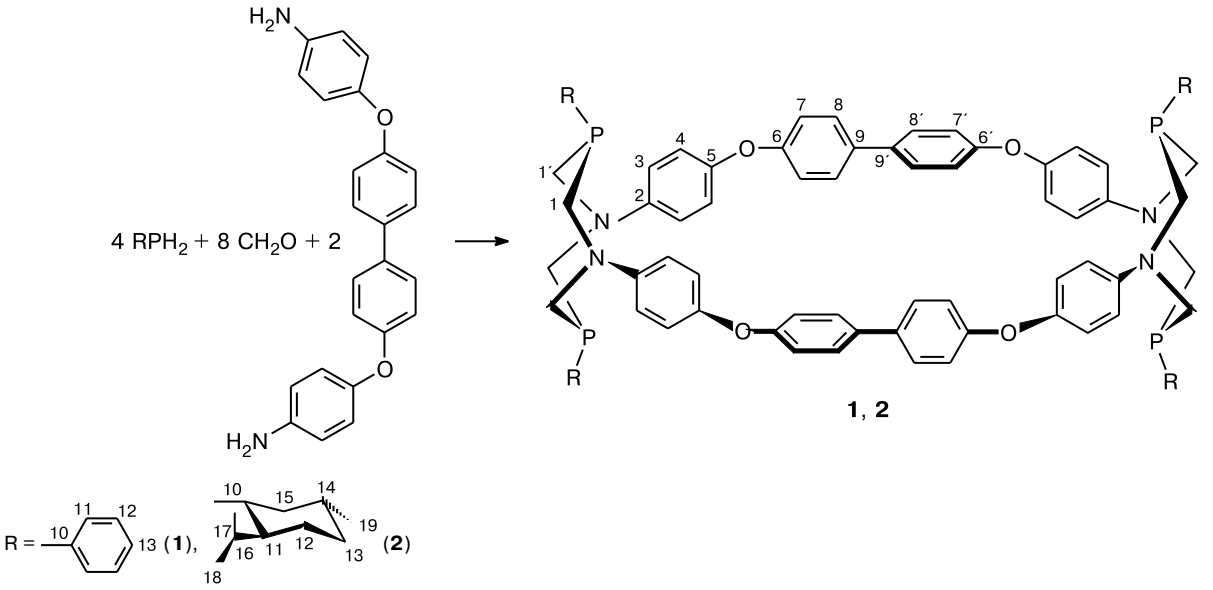
Scheme 1



progress was monitored by ^{31}P NMR spectra of the reaction mixtures.

The reaction of bis(oxymethyl)phenylphosphine or (*l*-menthyl)bis(oxymethyl)phosphine with 4,4′-bis(4′-aminophenoxy)biphenyl was accompanied by a gradual formation of a finely crystalline precipitate and reached completion within 1.5 and 2.5 days, respectively. In the first case, the ^{31}P NMR spectrum of the reaction mixture exhibited a predominant narrow signal of the main product, the corresponding 3,6,10,13-tetraoxa-1,8(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane (**1**), at δ_P −50.21, *i.e.*, in the region characteristic of *P*,*P*-diphenyl-1,5-diaza-3,7-diphosphacyclooctanes.[15] The content of the main product in the reaction mixture was ~80%. Apart from that, in the same region of the spectrum there were minor signals corresponding to different oligomers with 1,5-diaza-3,7-diphosphacyclooctane units, whereas the signals attributed most likely to acyclic and macrocyclic oligomers with linear aminomethylphosphine fragments were present in the region of δ_P −(30—38). After completion of the second reaction, the ^{31}P NMR spectrum of the soluble part of the reaction mixture exhibited a strong narrow signal at δ_P −50.55 attributed apparently to a similar cage *P*-menthyl-substituted macrocycle **2**, as well as a group of signals of other oligomers in the region of δ_P −(49.8—50.2) It should be noted that the content of the main macrocyclic product was higher than the content of each of the other oligomers, however, the content of the last mentioned compounds was ~70% of the condensation products remained in the solution, *i.e.*, the selectivity of the condensation decreased on going from *P*-phenyl- to *P*-menthyl-substituted phosphine. Our attempts to obtain similar macrocycles based on other arylphosphines (mesityl- and 2,4,6-triisopropylphenylphosphine) were unsuccessful because of the low solubility and ahead-of-time precipitation of the intermediate products of aminomethylation.

Macrocycles **1** and **2** were isolated from the reaction mixtures in the individual state by spontaneous crystallization and did not require additional purification. It should be noted that the yield of cyclophane **2** (24%) due to its better crystallization from the reaction medium, turned out to be higher than the yield of cyclophane **1** (15%). Compounds **1** and **2** are high-melting-point finely crystalline powders, stable in air. Macrocycle **1** is satisfactorily soluble in DMF and DMSO, whereas macrocycle **2** is well soluble in chloroform and slightly in hot benzene and toluene. The mass spectra of both macrocycles exhibited peaks of their protonated molecular ions with *m*/*z* 1273 (**1**) and 1521 (**2**), whereas the spectrum of tetraphosphine **1** also has peaks corresponding to its protonated mono- (*m*/*z* 1289), di- (*m*/*z* 1305), and trioxides (*m*/*z* 1321). The ^{31}P NMR spectra of compounds **1** and **2** dissolved in DMSO-d_6 and $CDCl_3$, respectively, each exhibited a narrow signal with chemical shifts δ_P −51.20 (**1**) and −46.54 (**2**), which indicated a symmetric structure of the molecules and the equivalence of all the phosphorus atoms. In the ^1H NMR spectra of macrocycle **1**, the signals for the protons of the P—CH_2—N fragments were found as one $(AB)_2X$-spin system, whereas in the spectrum of **2**, because of the presence of chiral substituents at the phosphorus atoms,[14] as two $(AB)_2X$-systems. In pure $CDCl_3$, a partial degeneration of these signals was observed, whereas in a mixture of $CDCl_3$—DMSO-d_6 (10%) they are resolved better. The spin-coupling constants $^2J_{PH}$ for axial and equatorial protons of the ring (respectively, 0 and 11.2 Hz

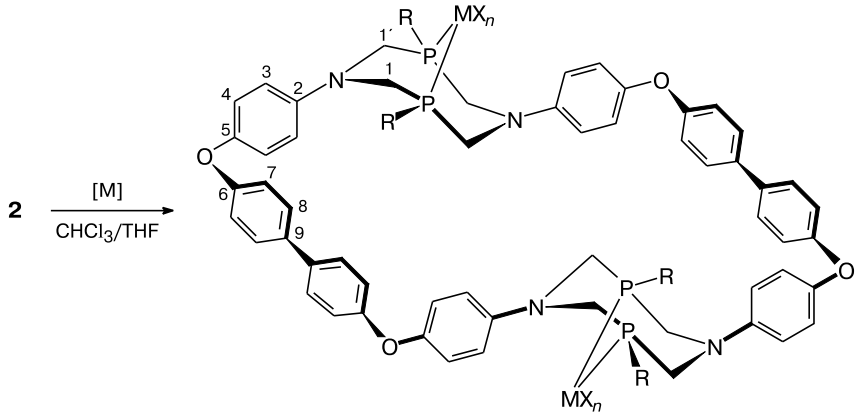
for compound **1**, 0—3.2 and 5.9—6.8 Hz for compound **2**) are typical of *P*-phenyl-[15] and *P*-menthyl-substituted diazadiphosphacyclooctanes[16] in the *chair—chair* conformation with the equatorial orientation of substituents at the phosphorus atoms and indicate a similar conformation of heterocyclic fragments of cyclophanes and the axial orientation of all the unshared pairs of electrons at the phosphorus atoms, which, as a result of this, are directed inside the macrocycle cavity. Such a conformation is typical of most compounds with diazadiphosphacyclooctane fragments[15—17] and, in particular, of earlier obtained cage cyclophanes including similar units.[3,11—14,18,19] The signals for the protons of the phenyl or menthyl substituents at the phosphorus atoms in **1** and **2** correspond to their structure. The signals for the protons of the phane fragments in cyclophane **2** were found as two AB-systems of terminal and central *para*-phenylene rings. The spectrum of cyclophane **1** is distinguished by the nonequivalence of the protons at atoms C(7) and C(7′) of the phenylene rings of the central biphenylene fragment, which were found as two doublets at δ 6.96 ($^3J_{HH}$ = 7.8 Hz) and 6.98 ($^3J_{HH}$ = 7.8 Hz). Apparently, this nonequivalence is caused by the fact that the planes of directly bonded phenylene rings are turned with respect to each other and the macrocycle in solution is generally characterized by a predominance of a twisted conformation.

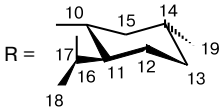
A spontaneous predominant formation of 46-membered P,N,O-containing macrocycles from six species proceeding at high concentrations of the starting reagents and in the absence of templates allows us to regard the condensation of bis(hydroxymethyl)organylphosphines with 4,4′-bis(4′-aminophenoxy)biphenyl as the processes of covalent self-assembly.

However, the introduction in similar condensation with bis(hydroxymethyl)phenylphosphine of longer and more flexible diamines containing an additional bridging group (2,2-bis[4′-(4′-aminophenoxy)phenyl]propane and bis[4-(4′-aminophenoxy)phenyl]sulfone) led to nonselective proceeding of the reactions with the formation of mixtures of different oligomers, mainly including diazadiphosphacyclooctane fragments. It is possible that this is caused by too large length and conformational lability of the spacer in the starting diamines, which make the entropy of macrocyclization unfavorable. To sum up, the processes of covalent self-assembly of macrocycles by condensation in the systems primary phosphine—formaldehyde—diamine have the limitations related to the structure of the starting diamine.

The satisfactorily soluble macrocyclic tetraphosphine **2** containing two chelating diazadiphosphacyclooctane fragments smoothly reacts with (cyclooctadiene)dichloroplatinum(II) and -palladium(II) in chloroform at room temperature, giving rise to metal complexes **3** and **4** with the metal—ligand composition of 2 : 1 (Scheme 2). The signal of the starting ligand completely disappeared in the ^{31}P NMR spectra of the reaction mixtures 2.5 h after beginning of the reaction, while one narrow signal emerged at δ_P –5.72 (**3**) and 16.51 (**4**), respectively, with the spin-coupling constant for the platinum complex $^1J_{PtP}$, being equal to 3178.8 Hz. These chemical shifts and spin-coupling constant values lie in the regions characteristic of *cis-P,P*-chelate platinum and palladium complexes of 1,5-diaza-3,7-diphosphacyclooctanes with the terminal metal—chlorine bonds.[15] Platinum complex **3** spontaneously crystallized from the reaction mixture as colorless crystals, which, apparently, were unstable solvate with

Scheme 2





[M] = (cod)$PtCl_2$, (cod)$PdCl_2$, (THF)$W(CO)_5$

Compound	M	X	*n*
3	Pt	Cl	2
4	Pd	Cl	2
5	W	CO	4

chloroform, since after washing with acetonitrile or drying the crystals became a powder. Palladium complex **4** crystallized from acetonitrile (after the removal of chloroform from the reaction mixture) as yellow microcrystals. Both complexes are stable in air, well soluble in dichloromethane, satisfactorily in chloroform. The yields of complexes **3** and **4** were 84 and 78%, respectively.

The reaction of ligand **2** with a solution of (tetrahydrofuran)pentacarbonyltungsten(0) in THF proceeded considerably slower, despite the use of excessive $(THF)W(CO)_5$. For the reaction to reach completion and the disappearance of the signals of tricoordinated phosphorus atoms in the ^{31}P NMR spectra, the solution was stirred for ~100 h at 50 °C. In the ^{31}P NMR spectrum of the reaction mixture, the signal at δ 6.95 with $^1J_{WP}$ = 204.4 Hz was predominant. The value of this spin-coupling constant close to the spin-coupling constant $^1J_{WP}$ observed for *P*,*P*-chelated [3,7-di(pyridin-2′-yl)-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane]tetracarbonyltungsten(0) (204 Hz)[20] allowed us to suggest that the complexation was accompanied by the loss from the starting $(THF)W(CO)_5$ not only easily leaving tetrahydrofuran ligand, but also one of the carbonyl ligands, and the formation of binuclear bis-*P*,*P*-chelated complex **5** (see Scheme 2), isolated as a finely crystalline colorless powder in 35% yield, rather than the expected tetranuclear complex.

The elemental analysis data for all the complexes **3**—**5** confirmed that they have the 2 : 1 metal—ligand composition. The ^{31}P NMR spectra of the complexes each exhibited one narrow signal at δ −5.72 ($^1J_{PtP}$ = 3178.8 Hz) (**3**), 16.51 (**4**), and 6.95 ($^1J_{WP}$ = 204.4 Hz) (**5**), that indicated the equivalence of all the phosphorus atoms. The spin-coupling constants $^1J_{PtP}$ and $^1J_{WP}$ indicated the square planar *cis*-coordination of platinum ions and the *cis*-*P*,*P*-chelate coordination of tungsten atoms and are typical of the *P*,*P*-chelated *cis*-complexes of diazadiphosphacyclooctanes with the corresponding metals.[15,20] It is possible that palladium complex **4** also has a similar *cis*-coordination of the metal ions. The presence of four stretching vibration bands of the C≡O bonds with the maxima at 1884, 1909, 1928, and 2010 cm^{-1} in the IR spectrum of complex **5** also confirmed the presence of the $W(CO)_4$ fragments.[20] The ^1H NMR spectra of complexes **3**—**5** exhibited signals for all the groups of protons of the ligand, that indicated that its skeleton remained intact, but most signals became strongly broadened and partially collapsed, in particular, the signals for the methyl groups in the menthyl substituents and the methylene protons in the diazadiphosphacyclooctane fragments. Such a phenomenon has been observed earlier for metal complexes of 3,7-di(*l*-menthyl)-1,5-di-*p*-tolyl-1,5-diaza-3,7-diphosphacyclooctane because of the interconversion between two nonequivalent *chair*—*boat* conformations of the ligand, the rate of which is the intermediate in the NMR time-scale.[16,21] A similar character of the spectra indicates that analogous slowed down interconversions between two *chair*—*boat* conformations are also in place for diazadiphosphacyclooctane fragments in complexes **3**—**5**. In these conformations, the transition metal ions should be outside of the macrocycle cavity, likewise in the earlier described complex of platinum dichloride with 38-membered cage macrocycle [1^3,1^7,7^3,7^7-tetra(*l*-menthyl)-3,3,5,5,9,9,11,11-octamethyl)-1,7(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctane]-2,4,6,8,10,12(1,4)-hexabenzenacyclododecaphane, the structure of which was confirmed by X-ray diffraction.[14] The data obtained indicate that all the complexes have a binuclear bis-*P*,*P*-chelate structure and are {[1^3,1^7,8^3,8^7-tetra(*l*-menthyl)-3,6,10,13-tetraoxa-1,8(1,5)-di(1,5-diaza-3,7-diphosphacyclooctane]-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane}-bis(dichloroplatinum) (**3**), -bis(dichloropalladium) (**4**), and -bis(tetracarbonyltungsten) (**5**), in which the metal-containing fragments most likely are placed outside the macrocycle cavity.

In conclusion, the results of our work demonstrate a possibility to use an approach based on a covalent self-assembly in the condensation of bis(hydroxymethyl)-organylphosphines with diamines for the synthesis of P,N-containing cyclophanes with large internal cavities, the bridging fragments of which include four phenylene groups, in the case when the central fragment of the spacer is conformationally rigid, in particular, a biphenyl one. The introduction of an additional bridge between the central phenylene groups leads to the loss of selectivity of the reaction. The 46-membered cage macrocyclic tetraphosphines 3,6,10,13-tetraoxa-1,8(1,5)-di(1,5-diaza-3,7-diphosphacyclo-octane)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphanes react with platinum(II), palladium(II), and tungsten(0) derivatives as tetradentate ligands with the formation of bis-*P*,*P*-chelated complexes.

Experimental

All the experiments were carried out at 303 K. ^1H and ^{31}P NMR spectra were recorded on a BrukerAvance-DRX 400 spectrometer (400.13 and 161.98 MHz, respectively). Chemical shifts are given in δ scale (ppm) relative to the signal of $SiMe_4$ (δ_H 0.0) and relative to the signal of H_3PO_4 (δ_P 0.0). The atom numbering system is given in Schemes 1 and 2. Mass spectra FAB_{pos} were obtained on a ZAB-HSQ-VG Analytical Manchester spectrometer. Mass spectra ESI_{pos} were recorded on a Esquire3000 plus spectrometer. The starting phenyl-[22] and menthylphosphine,[23] (cyclooctadiene)dichloroplatinum(II)[24] and -palladium(II),[24] a solution of (tetrahydrofuran)pentacarbonyltungsten(0) in THF[25] were synthesized according to the known procedures. All the manipulations with phosphines were carried out under inert atmosphere. Solvents were purified and degassed by standard methods.

1^3,1^7,8^3,8^7-Tetraphenyl-3,6,10,13-tetraoxa-1,8(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane (1). A mixture of phenylphosphine (0.48 g, 4.36 mmol) and paraformaldehyde (0.26 g, 8.67 mmol) was heated at 100—110 °C until homogenization.

Then, the reaction mixture was dissolved in anhydrous degassed DMF (3 mL), followed by the addition of a solution of 4,4′-bis-(4′-aminophenoxy)biphenyl (0.82 g, 2.22 mmol) in anhydrous degassed DMF (13 mL). The reaction mixture was stirred for 1.5 days at 110 °C. A precipitate formed was filtered, washed once with DMF and three times with acetonitrile, and dried for 4 h at 0.1 Torr. The filtrate of the reaction mixture was concentrated *in vacuo* approximately to 1/4 of the initial volume. A precipitate formed subsequently was allowed to stand for 1 day at −20 °C, filtered, washed thrice with acetonitrile, recrystallized from DMF, and washed with acetonitrile. After drying, the powder obtained was combined with the first portion. The yield of compound **1** was 0.21 g (15%), m.p. 231 °C. Found (%): C, 75.13; H, 5.68; N, 4.51; P, 9.46. $C_{80}H_{68}N_4O_4P_4$. M = 1273.32. Calculated (%): C, 75.46; H, 5.38; N, 4.40; P, 9.73. MS FAB_{pos}, *m/z* (I_{rel} (%)): 1273 $[M + H]^+$ (96), 1289 $[M + O + H]^+$ (100), 1305 $[M + 2 O + H]^+$ (76), 1321 $[M + 3 O + H]^+$ (38). ^1H NMR (DMSO-d_6), δ: 4.19 (dd, 8 H, $H(1,1')_{eq}$, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ = = 11.2 Hz); 4.59 (br.d, 8 H, $H(1,1')_{ax}$, $^2J_{HH}$ = 13.7 Hz); 6.71 (d, 8 H, H(3), $^3J_{HH}$ = 7.8 Hz); 6.96 (d, 4 H, H(7), $^3J_{HH}$ = 7.8 Hz); 6.98 (d, 4 H, H(7′), $^3J_{HH}$ = 7.8 Hz); 7.04 (d, 8 H, H(4), $^3J_{HH}$ = = 7.8 Hz); 7.40—7.55 (m, 12 H, H(11,13)); 7.57 (d, 8 H, H(8,8′), $^3J_{HH}$ = 7.8 Hz); 7.61—7.70 (m, 8 H, H(12)). $^{31}P\{^1H\}$ NMR (DMSO-d_6), δ: −51.20 (s). $^{31}P\{^1H\}$ NMR (DMF), δ: −50.18 (s).

$1^3,1^7,8^3,8^7$-Tetra(*l*-menthyl)-3,6,10,13-tetraoxa-1,8(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctane)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane (2). A mixture of menthylphosphine (1.01 g, 5.87 mmol) and paraformaldehyde (0.35 g, 11.66 mmol) was heated at 110—115 °C until homogenization. Then, the dense liquid obtained was dissolved in anhydrous degassed toluene (5 mL). 4,4′-Bis(4′-aminophenoxy)biphenyl (1.08 g, 2.93 mmol) in toluene (28 mL) was added to the warmed-up suspension, the reaction mixture was stirred for 2.5 days at 100 °C. A precipitate formed was filtered, washed once with toluene, then thrice with acetonitrile, and dried for 4 h at 0.1 Torr. The yield of compound **2** was 0.57 g (24%), m.p. 200—204 °C. Found (%): C, 75.41; H, 8.37; N, 3.81; P, 8.25. $C_{96}H_{124}N_4O_4P_4$. M = 1521.93. Calculated (%): C, 75.76; H, 8.21; N, 3.68; P, 8.14. MS ESI_{pos}, *m/z* ($I_{rel.}$ (%)): 1521 $[M + H]^+$ (100). ^1H NMR ($CDCl_3$), δ: 0.75 (d, 12 H, H(18), $^3J_{HH}$ = 5.9 Hz); 0.86—1.08 (m, 32 H, $\underline{H}_{ment}$ + H(17,19)); 1.09—1.20 (m, 4 H, $\underline{H}_{ment}$); 1.32—1.48 (m, 8 H, $\underline{H}_{ment}$); 1.58—1.88 (m, 16 H, $\underline{H}_{ment}$); 2.66—2.79 (m, 4 H, H(16)); 3.62 (d, 4 H, $H(1)_{ax}$, $^2J_{HH}$ = 15.6 Hz); 3.77 (d, 4 H, $H(1')_{ax}$, $^2J_{HH}$ = 15.7 Hz); 4.30 (br.d, 4 H, $H(1)_{eq}$, $^2J_{HH}$ = 15.6 Hz); 4.47 (dd, 4 H, $H(1')_{eq}$, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH}$ = 4.1 Hz); 6.55 (d, 8 H, H(3), $^3J_{HH}$ = 8.3 Hz); 6.96 (d, 8 H, H(4), $^3J_{HH}$ = 8.3 Hz); 7.02 (d, 8 H, H(7,7′), $^3J_{HH}$ = 8.3 Hz); 7.52 (d, 8 H, H(8,8′), $^3J_{HH}$ = 8.3 Hz). ^1H NMR ($CDCl_3$—DMSO-d_6, 9 : 1), δ: 0.76 (d, 12 H, H(18), $^3J_{HH}$ = 6.8 Hz); 0.90—0.99 (m, 8 H, H_{ment}); 0.92 (d, 12 H, H(19), $^3J_{HH}$ = 6.3 Hz); 0.94 (d, 12 H, H(17), $^3J_{HH}$ = 6.8 Hz); 1.00—1.08 (m, 4 H, H_{ment}); 1.10—1.20 (m, 4 H, H_{ment}); 1.35—1.46 (m, 8 H, H_{ment}); 1.67—1.75 (m, 4 H, H_{ment}); 1.75—1.84 (m, 8 H, H_{ment}); 2.66—2.74 (m, 4 H, H(16)); 3.66 (dd, 4 H, $H(1)_{ax}$, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH}$ = = 3.2 Hz); 3.82 (br.d, 4 H, $H(1')_{ax}$, $^2J_{HH}$ = 15.3 Hz); 4.27 (dd, 4 H, $H(1')_{eq}$, $^2J_{HH}$ = 15.3 Hz, $^2J_{PH}$ = 5.9 Hz); 4.44 (dd, 4 H, $H(1)_{eq}$, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH}$ = 6.8 Hz); 6.53 (d, 8 H, H(3), $^3J_{HH}$ = 9.0 Hz); 6.93 (d, 8 H, H(4), $^3J_{HH}$ = 9.0 Hz); 7.01 (d, 8 H, H(7,7′), $^3J_{HH}$ = 8.6 Hz); 7.52 (d, 8 H, H(8,8′), $^3J_{HH}$ = 8.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −46.54 (s). $^{31}P\{^1H\}$ NMR (toluene), δ: −50.48 (s). $[\alpha]_D^{20}$ −63 (*c* 0.3677, $CHCl_3$).

{$1^3,1^7,8^3,8^7$-Tetra(*l*-menthyl)-3,6,10,13-tetraoxa-1,8(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane}bis(dichloroplatinum)(II) (3). A solution of (cyclooctadiene)dichloroplatinum(II) (0.0507 g, 0.135 mmol) in anhydrous degassed chloroform (4 mL) was added to a solution of compound **2** (0.1032 g, 0.067 mmol) in anhydrous degassed chloroform (5 mL). The reaction mixture was stirred for 2.5 h at ~20 °C, then concentrated *in vacuo* virtually to dryness. The crystals formed were filtered, thoroughly washed with acetonitrile and dried for 4 h at 0.1 Torr. The yield of compound **3** was 0.1012 g (84%), m.p. > 300 °C. Found (%): C, 55.81; H, 5.88; N, 2.61; P, 6.23; Cl, 6.75. $C_{96}H_{124}N_4O_4P_4Pt_2Cl_4$. M = 2053.90. Calculated (%): C, 56.14; H, 6.09; N, 2.73; P, 6.03; Cl, 6.90. ^1H NMR ($CDCl_3$, δ: 0.70—1.05 (m, H_{ment}, H(18,19)); 0.92 (d, H(17), $^3J_{HH}$ = 6.2 Hz) (a total intensity 52 H); 1.40—1.59 (m, 12 H, H_{ment}); 1.70—1.81 (m, 8 H, H_{ment}); 1.97—2.10 (m, 4 H, H(16)); 3.60—3.88 (m, 16 H, H(1,1′)); 7.00—7.06 (m, 24 H, H(3,4,7)); 7.49 (d, 8 H, H(8), $^3J_{HH}$ = 8.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −5.72 (s, $^1J_{PtP}$ = 3178.8 Hz). $[\alpha]_D^{20}$ −44 (*c* 0.3243, CH_2Cl_2).

[$1^3,1^7,8^3,8^7$-Tetra(*l*-menthyl)-3,6,10,13-tetraoxa-1,8(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane]bis(dichloropalladium)(II) (4) was obtained similarly to compound **3** from compound **2** (0.1057 g, 0.069 mmol) and (cyclooctadiene)dichloropalladium(II). After completion of the reaction, the mixture was concentrated to dryness, the residue was crystallized from acetonitrile, the crystals formed were filtered, thoroughly washed with acetonitrile, and dried for 4 h at 0.1 Torr. The yield of compound **4** was 0.0929 g (78 %), m.p. > 300 °C. Found (%): C, 60.97; H, 6.34; N, 2.72; P, 6.86; Cl, 7.22. $C_{96}H_{124}N_4O_4P_4Pd_2Cl_4$. M = 1876.58. Calculated (%): C, 61.44; H, 6.66; N, 2.99; P, 6.60; Cl, 7.56. ^1H NMR ($CDCl_3$), δ: 0.70—1.00 (m, H_{ment}); 0.97 (d, H(17), $^3J_{HH}$ = 6.2 Hz) (a total intensity 56 H); 1.02—1.25 (m, 4 H, H_{ment}); 1.45—1.60 (m, 4 H, H_{ment}); 1.61—1.79 (m, 8 H, H_{ment}); 1.90—2.05 (m, 4 H, H(16)); 3.39—3.82 (m, 16 H, H (1,1′)); 6.97—7.10 (m, 24 H, H (3,4,7)); 7.50 (d, 8 H, H(8), $^3J_{HH}$ = 8.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 16.51 (s). $[\alpha]_D^{20}$ −55 (*c* 0.3629, CH_2Cl_2).

[$1^3,1^7,8^3,8^7$-Tetra(*l*-menthyl)-3,6,10,13-tetraoxa-1,8(1,5)-di-(1,5-diaza-3,7-diphosphacyclooctana)-2,4,5,7,9,11,12,14(1,4)-octabenzenacyclotetradecaphane]bis(tetracarbonyltungsten)(0) (5). A 0.0426 *M* solution of $(THF)W(CO)_5$ in THF (0.289 mmol, 6.8 mL) was added to a solution of compound **2** (0.1002 g, 0.066 mmol) in anhydrous degassed THF (20 mL). The reaction mixture was stirred for 56 h at 50 °C, then another portion of 0.0426 *M* solution of $(THF)W(CO)_5$ in THF (0.119 mmol, 2.8 mL) was added, and the stirring was continued for another 44 h at 50 °C. A dark precipitate formed was filtered, the filtrate of the reaction mixture was concentrated *in vacuo* to dryness, the residue was crystallized from acetonitrile. A powdered precipitate formed was filtered, twice thoroughly washed with acetonitrile, and dried for 4 h at 0.1 Torr. The yield of compound **5** was 0.049 g (35 %), m.p. > 300 °C. Found (%): C, 58.86; H, 6.04; N, 2.53; P, 5.64. $C_{104}H_{124}N_4O_{12}P_4W_2$. M = 2113.69. Calculated (%): C, 59.10; H, 5.91; N, 2.65; P, 5.86. ^1H NMR (C_6D_6), δ: 0.61 (d, 12 H, H(18), $^3J_{HH}$ = 6.4 Hz); 0.78—0.90 (m, H_{ment}); 0.82 (d, H(19), $^3J_{HH}$ = 5.9 Hz) (a total intensity 16 H); 1.12 (d, 12 H, H(17), $^3J_{HH}$ = 5.9 Hz); 1.17—1.29 (m, 4 H, H_{ment}); 1.31—1.41 (m, 4 H, H_{ment}); 1.42—1.51 (m, 4 H, H_{ment}); 1.58—1.75 (m, 16 H, H_{ment}); 2.01—2.13 (m, 8 H, H_{ment}, H(16)); 3.44—3.58 (m, 12 H, $H(1)_B$, H(1′)); 3.64 (br.d, 4 H, $H(1)_A$, $^2J_{HH}$ = 11.2 Hz); 6.99 (d,

8 H, H(3), $^3J_{HH}$ = 8.8 Hz); 7.06 (d, 8 H, H(4), $^3J_{HH}$ = 8.8 Hz); 7.10 (d, 8 H, H(7), $^3J_{HH}$ = 8.8 Hz); 7.34 (d, 8 H, H(8), $^3J_{HH}$ = = 8.8 Hz). ^{31}P NMR (C_6D_6), δ: 6.95 ($^1J_{WP}$ = 204.4 Hz). $[\alpha]_D^{20}$ –41 (*c* 0.2854, C_6H_6).

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