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First Tetradentate Diamidophosphite Based on [5,10,15,20−Tetrakis(4−hydroxyphenyl)porphyrinato]zinc: Synthesis, Spectral Features, Coordination, and Application in Asymmetric Pd−Catalyzed Reactions

Igor S. Mikhel,[a] Konstantin N. Gavrilov,[b@] Sergey V. Zheglov,[b] Ivan M. Novikov,[b] Kirill P. Birin,[a] Andrey Yu. Chernyadyev,[a] and Vladimir S. Tyurin[a]

[a]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia*
[b]*S.A. Esenin Ryazan State University, 390000 Ryazan, Russia*
[@]*Corresponding author E-mail: k.gavrilov@365.rsu.edu.ru*

*The synthesis of the tetradentate diamidophosphite (**L**) containing four 1,3,2-diazaphospholidine rings and a porphyrin moiety, its characterization and application in asymmetric Pd-catalyzed reactions are reported. The best results (up to 63 % ee) were obtained for the Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate with dimethylmalonate. The complex **L**[Ru(p-cymene)Cl$_2$]$_4$ was synthesized in situ and characterized by spectroscopic data. The structure of the compounds obtained is discussed based on ^{1}H, ^{13}C, ^{13}C DEPT, ^{31}P, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY NMR spectroscopy, as well as UV-Vis and fluorescence spectroscopy.*

Keywords: Asymmetric allylic substitution, palladium, diamidophosphites, ruthenium complexes, porphyrins.

Первый тетрадентатный диамидофосфит на основе 5,10,15,20−тетракис(4−гидроксифенил)порфирината цинка: синтез, спектральные особенности, координация и применение в асимметрических Pd−катализируемых реакциях

И. С. Михель,[a] К. Н. Гаврилов,[b@] С. В. Жеглов,[b] И. М. Новиков,[b] К. П. Бирин,[a] А. Ю. Чернядьев,[a] В. С. Тюрин[a]

[a]*Институт физической химии и электрохимии им. А.Н. Фрумкина РАН, 119071 Москва, Российская Федерация*
[b]*Рязанский государственный университет им. С.А. Есенина, 390000 Рязань, Российская Федерация*
[@]*E-mail: k.gavrilov@365.rsu.edu.ru*

*В данной работе сообщается о синтезе, характеристиках и применении в асимметрических Pd-катализируемых реакциях тетрадентатного диамидофосфита (**L**), содержащего четыре 1,3,2-диазафосфолидиновых кольца и порфириновую часть. Наилучшие результаты (до 63 % энантиомерного избытка) были достигнуты для Pd-катализируемого аллильного алкилирования (E)-1,3-дифенилаллилацетата диметилмалонатом. Комплекс **L**[Ru(p-cymene)Cl$_2$]$_4$ был синтезирован in situ и охарактеризован спектральными данными. Структура полученных соединений обсуждается с привлечением данных ^{1}H, ^{13}C, ^{13}C DEPT, ^{31}P, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY ЯМР спектроскопии, а также УФ и флуоресцентной спектроскопии.*

Ключевые слова: Асимметрическое аллильное замещение, палладий, диамидофосфиты, рутения комплексы, порфирины.

Introduction

The current stage of the development of organic synthesis is characterized by the extensive use of chiral transition metal complexes as catalysts for the preparation of the organic and organoelement compounds with high enantiomeric purity. Such compounds are used as components of pharmaceuticals, agricultural crop protection products, food additives and fragrances.[1–7] In turn, the current progress in the field of asymmetric catalysis is mainly determined by recent advances in the design and synthesis of chiral ligands, primarily phosphorus-containing ones, thousands of which were used in various asymmetric transformations.[1–12] However, the vast majority of known chiral phosphorus ligands in the corresponding metal complexes are able to catalyze efficiently only a certain type of the asymmetric reaction. Only few ligands, the so-called "privileged" ones, can be successfully applied in diverse asymmetric transformations. Phosphoramidites are an excellent example of this type of ligands.[11] Indeed, the binaphthol(biphenol)-based phosphoramidites are widely universal, readily accessible and very efficient stereoselectors. Therefore, the design and synthesis of new promising phosphorous-containing stereoselectors are ongoing and represent a serious challenge to researchers.

In general, phosphorous acid derivatives are a promising class of ligands due to their stability to oxidation, pronounced π-acceptor ability, ease of preparation and low cost. They can be obtained from readily available precursors by simple condensation, including parallel and solid-state syntheses.[5,7,11–17] In addition, the presence of a chiral phosphorus atom as a donor center in the structure of such ligands often significantly increases the asymmetric induction in the catalytic reaction.[2,18–21] Recently, chiral supramolecular derivatives of phosphorous acid based on porphyrins have attracted increasing attention.[22–37]

We have previously reported the preparation of a series of chiral ligands – phosphorous acid derivatives, which were successfully applied in Pd-catalyzed allyl substitution reactions.[38–43] In those cases, porphyrins were used both as achiral additives[38–41] to increase enantioselectivity, and as starting substrates for phosphorylation.[42–44] In a preliminary communication,[44] we reported the synthesis of the first tetradentate diamidophosphite **1** (Figure 1) and its application in asymmetric Pd-catalyzed alkylation of cinnamyl acetate. This work is devoted to the synthesis of zinc-containing tetradentate diamidophosphite **2**, its complexation with $[Ru(p\text{-cymene})Cl_2]_2$, as well as the study of the photophysical properties of ligands **1** and **2** and their application in a number of asymmetric Pd-catalyzed processes.

Experimental

^{31}P, ^{13}C and ^{1}H NMR spectra were recorded on a Bruker Avance III 600 (242.9 MHz for ^{31}P, 150.9 MHz for ^{13}C and 600.13 MHz for ^{1}H) spectrometer. The assignment of the resonances in the ^{1}H and ^{13}C NMR spectra was achieved by the use of DEPT, COSY, ROESY, HSQC and HMBC techniques. Chemical shifts (ppm) were given relative to Me_4Si (^{1}H and ^{13}C) and 85 % H_3PO_4 (^{31}P NMR). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet); coupling constants ^{n}J in Hertz (Hz) integration, "n" values are reported in the case of their unambiguous determination. HPLC analyses were performed on Agilent 1100 and Stayer instruments using Chiralcel® and Kromasil® columns. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O. Electronic absorption spectra (EAS) were measured on Perkin Elmer Lambda 35 spectrophotometer, using quarts cuvettes of 1 cm pathlength. Luminescence spectra were measured on Fluorolog 3 instrument of Horiba Jobin Yvon, fitted with Hamamatsu R928 photomultiplier tube. Fluorescence quantum yield was measured by absolute method for the solutions in moisture free and non-degassed CH_2Cl_2 (optical density of the solution was not more

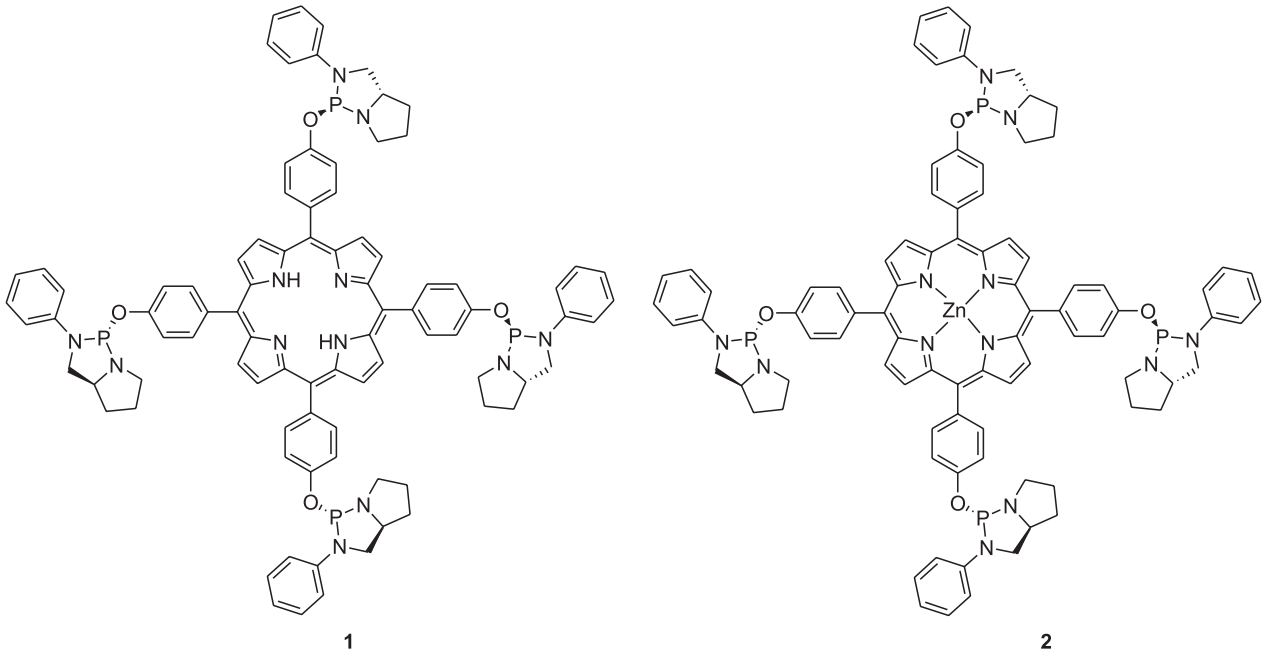


Figure 1. Structures of compounds **1** and **2**.

than 0.1 for the maximum of the most intensive Q band in quarts cuvette of 1 cm pathlength in order to avoid self-absorption effect). Light of fluorescence was collected by Quanta-φ F-3029- sphere linked with Fluorolog 3 by Fiber-Optics adaptor FL-3000 produced by Horiba Jobin Yvon. Fluorescence quantum yields were calculated by FluoroEssence™ software of Horiba.

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. For example, toluene and tetrahydrofuran were freshly distilled from sodium benzophenone ketyl before use; dichloromethane was distilled from CaH_2. *N*,*N*-Diisopropylethylamine and pyrrolidine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. Thin-layer chromatography was performed on E. Merck pre-coated silica gel 60 F254 and Macherey-Nagel Alugram Alox N/UV_{254} plates. Column chromatography was performed using silica gel MN Kieselgel 60 (230 – 400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. 5,10,15,20-Tetrakis(4-hydroxyphenyl)porphine (**3**) was purchased from Aldrich and dried over P_2O_5 at 55 °C for 2 h before use. Phosphorylating reagent (5S)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4**) was prepared as published and freshly distilled.[45] 5,10,15,20-Tetrakis(4-{(2R,5S)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy}phenyl)porphine (**1**), (2R,5S)-2-(4-(zinc(II)-10,15,20-triphenylporphyrin-5-yl) phenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**5**), (Sa)-4-(4-(10,15,20-triphenylporphyrin-5-yl)phenoxy) dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (**6**) and (2R,5S)-2-((5,10,15,20-tetraphenylporphyrin-2-yl)methoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**7**) were synthesized according to literature procedures.[44,42] The $[Pd(allyl)Cl]_2$ and (*E*)-1,3-diphenylallyl acetate (**8**) were obtained as published.[46] $[Ru(p\text{-cymene})Cl_2]_2$, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl) acetamide), cinnamyl acetate (**9**) and ethyl 2-oxocyclohexane-1-carboxylate (**10**) were purchased from Aldrich and Acros Organics and used without further purification.

[5,10,15,20-Tetrakis(4-{(2R,5S)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octyloxy}phenyl)porphyrinato]zinc(II) (2). Compound **3** (0.371 g, 0.5 mmol) was added in one portion to a vigorously stirred solution of phosphorylating reagent **4** (0.555 g, 2.3 mmol, 15 % of excess) and *i*-Pr_2NEt (1.1 mL, 6.3 mmol) in toluene (10 mL). The mixture was heated to the boiling point, stirred for 10 min, and then cooled to 20 °C. The resulting suspension was filtered through a short plug of Al_2O_3/SiO_2, the column was washed twice with toluene (5 mL), and the solvent was evaporated under reduced pressure (40 Torr). The crude ligand was then purified by flash chromatography on silica gel (benzene) under pressure of argon and the product obtained as a violet powder (0.413 g, 53 %). Found: C 68.09, H 5.41, N 10.52 %. $C_{88}H_{80}N_{12}O_4P_4Zn$ requires C 67.80, H 5.17, N 10.78.

*Procedure for the NMR investigations of the reaction of **2** with $[Ru(p\text{-cymene})Cl_2]_2$ at 1:2 molar ratio.* An argon-flushed Schlenk tube equipped with magnetic stirring bar and septum was charged with 1 equiv. of **2** (0.0125 g, 0.008 mmol) and 2 equivs. of $[Ru(p\text{-cymene})Cl_2]_2$ (0.0098 g, 0.016 mmol), freshly distilled solvent CD_2Cl_2 (1 mL) was added, and the mixture was stirred for 30 min at room temperature. Subsequently the sample was transferred to an argon-flushed NMR tube and spectroscopic experiments were carried out.

Catalytic Reactions

*Pd-Catalyzed allylic alkylation of substrate **8** with dimethyl malonate*. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.005 mmol or 0.0025 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. Substrate **8** (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 mL, 0.44 mmol), BSA (0.11 mL, 0.44 mmol) and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-dimethyl-2-(1,3-diphenyl-allyl)malonate (**11**).[47,48] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Daicel Chiralcel OD-H column, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).

*Pd-Catalyzed allylic amination of substrate **8** with pyrrolidine*. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.005 mmol or 0.0025 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. Substrate **8** (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**12**).[49,50] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Daicel Chiralcel OD-H column, C_6H_{14}/*i*-PrOH/$HN(Et)_2$ = 200/1/0.1, 0.9 mL/min, 254 nm, *t*(*R*) = 5.0 min, *t*(*S*) = 6.1 min).

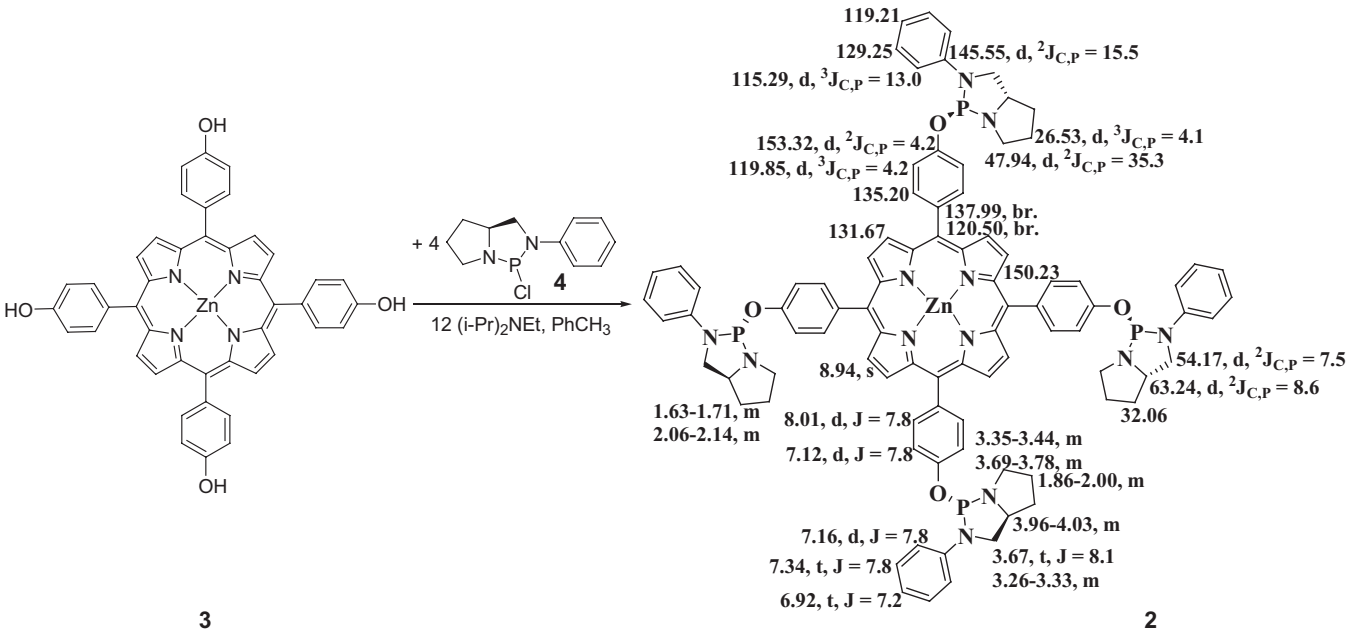
*Pd-Catalyzed allylic alkylation of substrate **9** with reagent **10**.* A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand ((0.0025 mmol or 0.005 mmol or 0.01 mmol or 0.02 mmol) in toluene (1.5 mL) was stirred for 40 min. Substrate **9** (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. Compound **10** (0.06 mL, 0.375 mmol), BSA (0.25 mL, 1 mmol) and zinc acetate (0.005 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or toluene (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexanecarboxylate (**13**).[51] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 95/5, 0.4 mL/min, 254 nm, *t*(*R*) = 14.3 min, *t*(*S*) = 16.4 min).

Results and Discussion

Ligand Synthesis

The new porphyrin-functionalized tetradiamidophosphite **2** was synthesized in one step through the reaction of the corresponding 5,10,15,20-tetrakis(4-hydroxyphenyl) porphine **3** with four equivalents of the phosphorylating reagent **4** in the presence of *i*-Pr_2NEt as HCl scavenger in toluene (Scheme 1). The crude ligand was then purified by flash chromatography and have been fully characterized by a combination of NMR spectroscopic methods (^1H, ^{13}C, ^{13}C DEPT, ^{31}P, ^{13}C-^1H HSQC, ^{13}C-^1H HMBC, ^1H-^1H COSY and ^1H-^1H ROESY) as well as by elemental analysis. It gave us an opportunity to make a complete assignment of all ^1H and ^{13}C resonances (Scheme 1).

The ^{31}P NMR spectrum of **2** in CD_2Cl_2 showed one singlet at δ 124.3 ppm, corresponding to the diamidophosphite phosphorus centers. According to the ^{31}P and ^{13}C NMR spectroscopy data, the exclusive formation of the stereodefined tetradiamidophosphite **2** with an (R)-configuration at the P*-stereocenters occurred. In particular, the ^{13}C spectrum of **2** is characterized by a large spin-spin coupling



Scheme 1. Synthesis of **2** and full assignment of all ^{13}C and ^{1}H resonances for the ligand.

constant $^{2}J_{C,P}$ = 35.3 Hz at δ 47.94 ppm, which is indicative of the *syn*-orientation of the phosphorus lone pair with respect to the PN***C***H_2 carbon atom. Correspondingly, the pseudoequatorial exocyclic substituent at the phosphorus atom and the -$(CH_2)_3$- of the pyrrolidine fragment of the phosphabicyclic skeleton are in the *anti*-arrangement (Figure 2).[52–58]

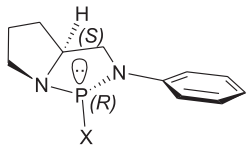


Figure 2. Stereochemistry of the phosphabicyclic part in ligand **2** (X = exocyclic substituent).

Photophysical Properties

In order to clarify the photophysical properties of the new tetradentate diamidophosphite **2** and the previously reported[44,42] **1** and **5**–**7** (Figure 3), electronic absorption (EAS) and fluorescence spectra were recorded. EAS of free base porphyrins contain four Q absorption bands corresponding to the split electronic transitions S0-S1 (Table 1). As for **6**, absorption maxima of the Q bands are located at 515, 550, 591, and 648 nm. Q bands of **1**, **7** are similar, with slight (no more than 2–3 nm) blue (**7**) and red (**1**) shifts. Zinc complexes **2**, **5** possessing higher symmetry of the chromophore relative to the free base porphyrins exhibit only two Q bands with maxima at 548 and 586 nm for **5** and 550, 590 nm for **2**. Soret bands corresponding to the electronic transition S0-S2, are observed at 418–422 nm for the studied compounds. The similarity of the spectra is determined by the common chromophore of *meso*-tetraarylporphine and by a weak influence of the peripheral substituents at benzene ring. Comparing the porphyrins **1**, **7** and the zinc complexes **2**, **5** it can be noted that an increase in the number of electron-donating diamidophosphite substituents at the benzene rings of the porphyrin from one to four leads to a small bathochromic shift (3 nm) of the Soret band and slightly larger (from 3 to 5 nm) bathochromic

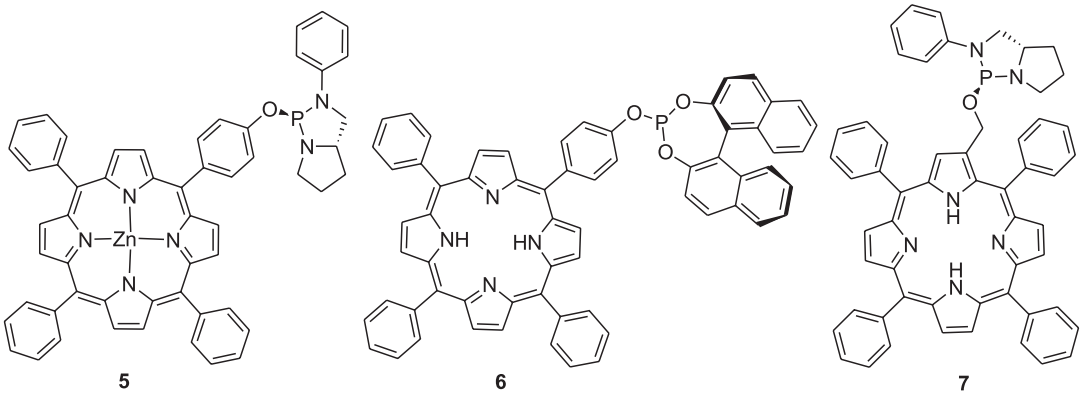


Figure 3. Structures of compounds **5**–**7**.

Table 1. Data of electronic absorption spectra, fluorescence spectra and quantum yields of fluorescence for compounds **1**, **2** and **5**–**7** in CH_2Cl_2.

Compound	Soret band maximum of EAS, nm	Q band maxima of EAS, nm	Fluorescence maxima, nm	Fluorescence quantum yield at 298 K
1	421	517, 554, 593, 649	656, 721	11.7 %
2	422	550, 590	600, 649	3.1 %
5	419	548, 586	597, 646	2.5 %
6	418	515, 550, 591, 648	654, 717	10.3 %
7	418	514, 549, 589, 645	652, 716	8.0 %

shifts of the Q bands. The effect of changing the type of the substituent from the triarylphosphite in **6** to diamidophosphite in **7** on their electronic spectra is even less appreciable. The weak impact of the substituents at benzene ring of tetraarylporphyrins on the chromophore properties is due to the low degree of π-electronic conjugation of the benzene rings with the tetrapyrrolic macrocycle being a result of their almost perpendicular orientation relative to the plane of the macrocycle.

Compounds **1**, **2** and **5**–**7** manifest luminescence in the red visible region (Figure 4). Emission spectra of the free base porphyrins **1**, **6**, **7** contain two maxima at 650 and 720 nm. Zinc(II) porphyrins **2**, **5** exhibit two maxima of fluorescence as well, however they are significantly blue shifted to 600 and 650 nm, as well as the Q absorption bands, due to the influence of metal cation on the electronic structure of the porphyrin core (Table 1). Quantum yields of fluorescence of free base porphyrins **1**, **6**, **7** are high enough (8–12 %) resembling that of *meso*-tetraphenylporphyrin.[59] It confirms electron donating character of diamidophosphite groups covalently linked to the benzene rings of the free base porphyrins **1**, **6**, **7** as electron withdrawing substituents at benzene ring of tetraarylporphyrins are known to enhance non-radiative deactivation of electronic excited states of the porphyrin core.[60] Fluorescence quantum yields of zinc(II) porphyrins **2**, **5** are typically lower (2.5–3.1 %) than that of the free base porphyrins **1**, **6**, **7**. It can be explained by the increase of the intersystem crossing rate due to the effect of zinc cation leading to a decrease of the population of S1 level in favour of the triplet level T1. Such effect was described earlier for the analogous zinc(II) porphyrinates.[61]

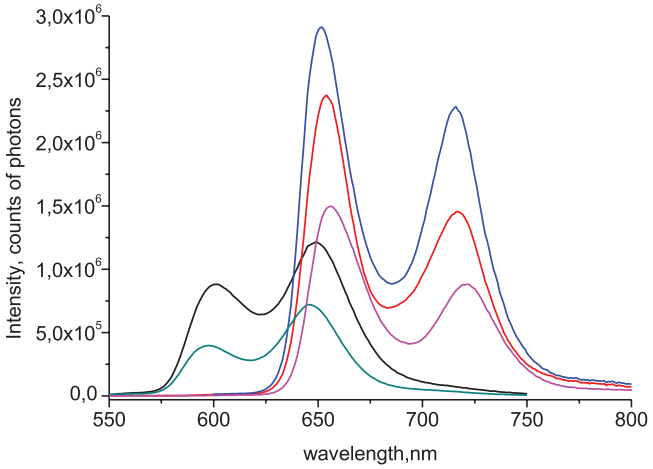


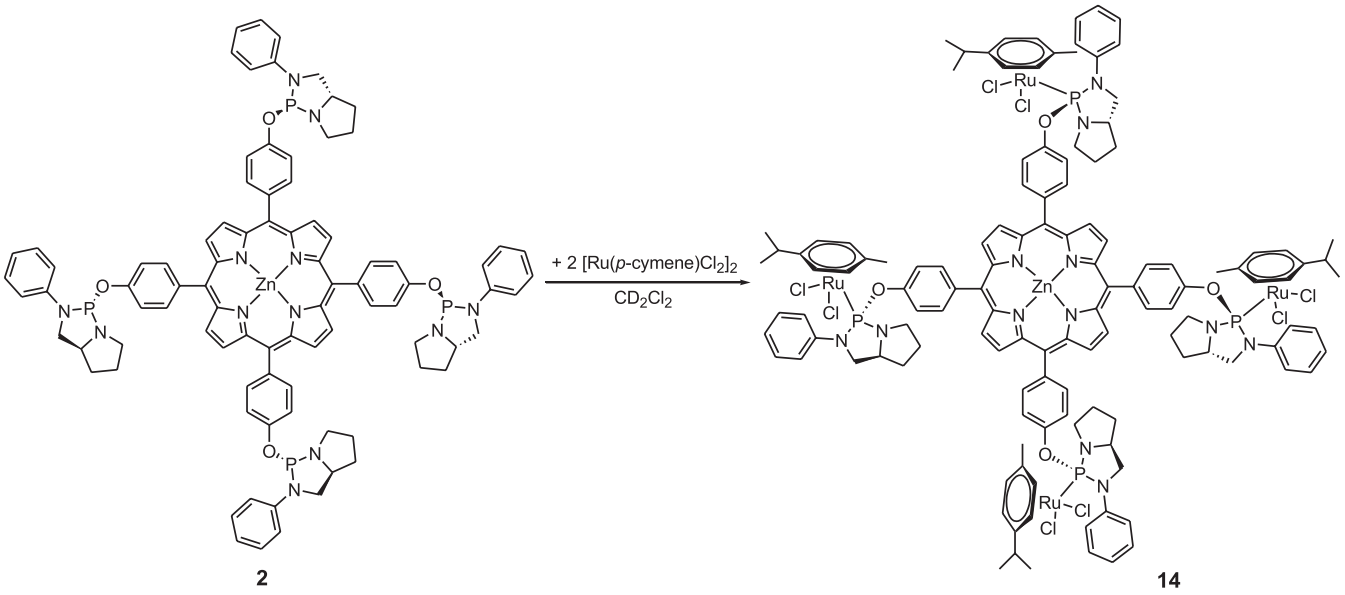
Figure 4. Fluorescence spectra of **1**, **2** and **5**–**7** in CH_2Cl_2 (purple – **1**, black – **2**, green – **5**, orange – **6**, blue – **7**).

Complexation Results

To examine the complexing capacity of tetradiamidophosphite **2**, two coordination reactions were investigated. In particular, reaction of **2** with $Pd(COD)Cl_2$ (our standard precursor,[39,56,57,62] COD - cycloocta-1,5-diene) proceeded in CD_2Cl_2 and surprisingly resulted in insoluble polymeric residue. In order to shed light on the coordination properties of **2**, we carried out the investigation of the ruthenium(II) complex obtained from the ligand. As a new precursor to study the coordination behavior of **2**, $[Ru(p\text{-cymene})Cl_2]_2$ was selected, which is known to give stable complexes with phosphites, phosphoramidites [63–67] and cyclodiphosphazanes. [68–70] The complexation of the tetradentate diamidophosphite **2** with $[Ru(p\text{-cymene})Cl_2]_2$ in CD_2Cl_2 leads to neutral ruthenium complex **14** with a bridging function of the phosphorus ligand (Scheme 2). ^{31}P NMR analyses confirmed the P-monodentate coordination mode. Indeed, the singlet at δ_P 103.0 ppm and the considerable coordination shift ($\Delta\delta_P$ = –21.3 ppm) are observed in ^{31}P NMR spectrum of *in situ* formed **14** in CD_2Cl_2. At the same time, a typical magnitude of δ_P lies in the range of 152–109 ppm for the complexes $[LRu(p\text{-cymene})Cl_2]$ with coordinated derivatives of phosphorous acid.[63–70] All ^1H and ^{13}C NMR signals were located by the same as for ligand **2** combination of NMR spectroscopic methods (Figure 4). It should be noted that the direct coordination of the phosphorus centers to the Ru atoms was also confirmed by a ^{13}C NMR spectrum of complex **14**, which contained phosphorus-coupled resonances of coordinated *p*-cymene ring. Noteworthy are the pronounced upfield coordination shifts ($\Delta\delta_C$ > –35 ppm) of all *p*-cymene signals compared to the resonances in the spectrum of starting $[Ru(p\text{-cymene})Cl_2]_2$. These results allowed us to conclude that tetradiamidophosphite **4** acts as a *P,P,P,P*-tetradentate ligand with a bridging function of a porphyrin core.

Asymmetric Pd-Catalyzed Allylic Substitution

First of all, the new ligand **2** and the previously described ligand **1** were tested in the asymmetric palladium-catalyzed allylic alkylation of (*E*)-1,3-diphenylacetate (**8**), which is widely used as benchmark substrate (Scheme 3, Table 2). Both ligands showed moderate enantioselectivity.



Scheme 2. Synthesis of complex **14** *in situ* in CD_2Cl_2.

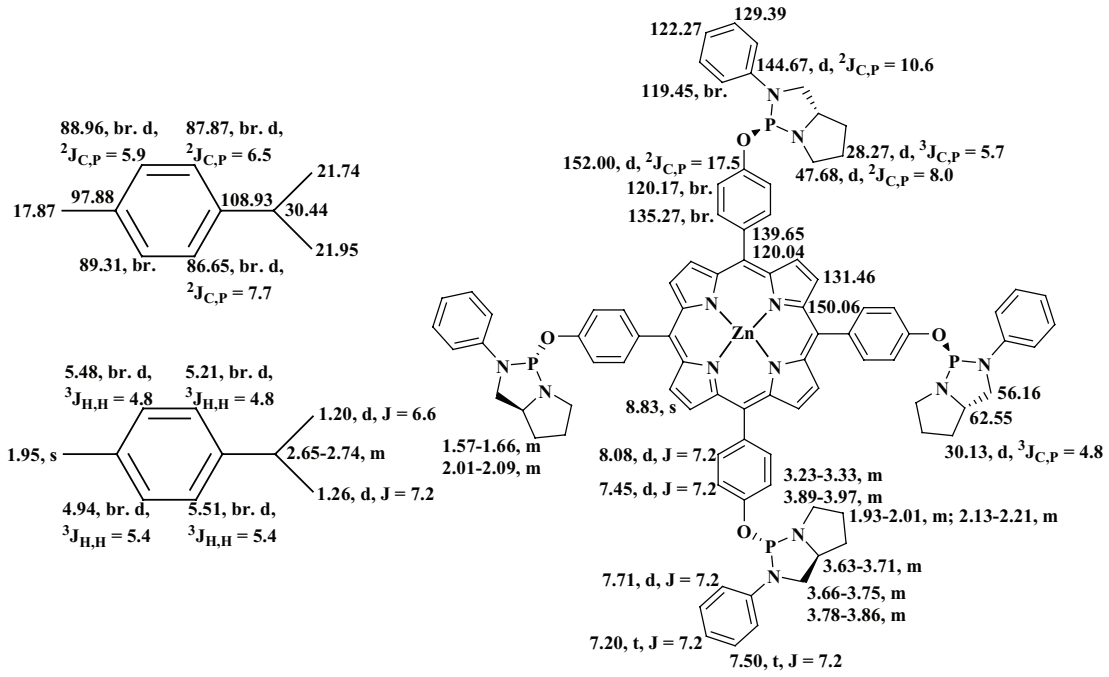
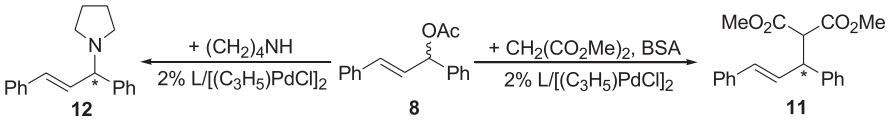


Figure 4. Full assignment of all ^{13}C and ^{1}H resonances for complex **14**.



Scheme 3. Pd-Catalyzed allylic substitution of substrate **8** with dimethyl malonate or pyrrolidine.

The molar ratio L/Pd = ½ and CH_2Cl_2 as the solvent are slightly preferable for both ligands. Undoubtedly, **2** gave better results in any conditions and the combination of **2** at L/Pd = ½ and CH_2Cl_2 as the solvent allowed to obtain *ee* up to 63 % at 100 % conversion (entry 8).

Table 2. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**8**) with dimethyl malonate.

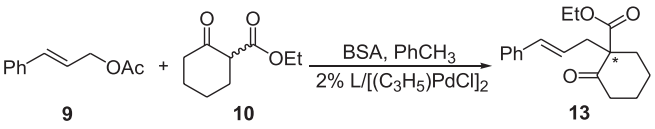
Entry	L	L/Pd	Solvent	Conversion, %	*ee*, %
1	**1**	1/4	THF	59	24 (S)
2	**1**	1/2	THF	57	48 (S)
3	**1**	1/4	CH_2Cl_2	99	28 (S)
4	**1**	1/2	CH_2Cl_2	99	59 (S)
5	**2**	1/4	THF	100	46 (S)
6	**2**	1/2	THF	100	52 (S)
7	**2**	1/4	CH_2Cl_2	100	34 (S)
8	**2**	1/2	CH_2Cl_2	100	63 (S)

In the next step, the chiral tetradentate diamidophosphites **1** and **2** were evaluated in the traditional palladium-catalyzed allylic amination of (*E*)-1,3-diphenylacetate (**8**) with pyrrolidine as the N-nucleophile (Scheme 3, Table 3). As a whole, the catalytic performance in this process followed the same trend as for the allylic alkylation of **8**. In particular, the amination process with participation of ligand **2** resulted in quantitative conversion in all cases (entries 5–8). The best result was obtained in CH_2Cl_2 as reaction medium at L/Pd = ½ (entry 8). However, there is an inverse correlation between the L/Pd molar ratio and enantioselectivity in the amination of **8** with **1** (entries 1–2 and 3–4). The enantioselectivity was low in all cases.

Table 3. Pd-Catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate (**8)** with pyrrolidine.

Entry	L	L/Pd	Solvent	Conversion, %	*ee*, %
1	**1**	1/4	THF	77	36 (R)
2	**1**	1/2	THF	72	27 (R)
3	**1**	1/4	CH_2Cl_2	98	20 (R)
4	**1**	1/2	CH_2Cl_2	99	14 (R)
5	**2**	1/4	THF	100	34 (R)
6	**2**	1/2	THF	100	40 (R)
7	**2**	1/4	CH_2Cl_2	100	38 (R)
8	**2**	1/2	CH_2Cl_2	100	46 (R)

We also screened **2** in the Pd-catalyzed allylic alkylation of cinnamyl acetate (**9**) with ethyl 2-oxocyclohexane-1-carboxylate (**10**) as the C-nucleophile in a toluene solution (Scheme 4, Table 4). In this challenging process, a quaternary C*-stereocenter is generated on a carbon atom belonging to the nucleophile.[51,71] In all experiments almost quantitative conversion (96–98 %) of substrate **9** was observed and the resulting quaternary-substituted β-keto ether **13** had an (S)-configuration. The molar ratio L/Pd = 1 proved to be slightly more efficient with 60 % *ee* and 97 % conversion (entry 7). Surprisingly, in this catalytic reaction ligand **1** demonstrated better enantioselectivity but a lower conversion rate (entries 1–4).[44] Unlike the alkylation reaction with **2** the effect of the L/Pd molar ratio on the asymmetric induction was not unidirectional with ligand **1**. We have no real explanation for these facts. The asymmetric induction of this reaction is difficult to control and a subtle difference in the structure of the diamidophosphite ligands could have a large effect on the enantioselectivity.



Scheme 4. Pd-Catalyzed allylic alkylation of substrate **9** with ethyl 2-oxocyclohexane-1-carboxylate (**10**).

Table 4. Pd-catalyzed allylic alkylation of cinnamyl acetate (**9**) with ethyl 2-oxocyclohexane-1-carboxylate (**10**).

Entry	L	L/Pd	Conversion, %	*ee*, %
1[a]	**1**	1/4	22	75 (S)
2[a]	**1**	1/2	50	62 (S)
3[a]	**1**	1/1	95	56 (S)
4[a]	**1**	2/1	60	76 (S)
5	**2**	1/4	98	54 (S)
6	**2**	1/2	96	46 (S)
7	**2**	1/1	97	60 (S)
8	**2**	2/1	98	48 (S)

[a]Previously published results[44]

Conclusions

Thus, the synthesis of the new chiral tetradentate diamidophosphite ligands on the basis of [5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrinato]zinc was successfully performed for the first time. Complete assignment of ^1H and ^{13}C NMR resonances of the ligand was implemented, and photophysical properties of the compound together with a number of related compounds were studied. Catalytic performance of the synthesized chiral tetradentate diamidophosphites was investigated in asymmetric allyl substitution reactions of a number of model substrates. The catalytic reactions showed moderate enantioselectivity at high conversion. Nevertheless, the new ligands are of great interest from the viewpoints of coordination and supramolecular chemistry, which has successfully been demonstrated by the example of the **L**[Ru(*p*-cymene)Cl_2]$_4$.

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