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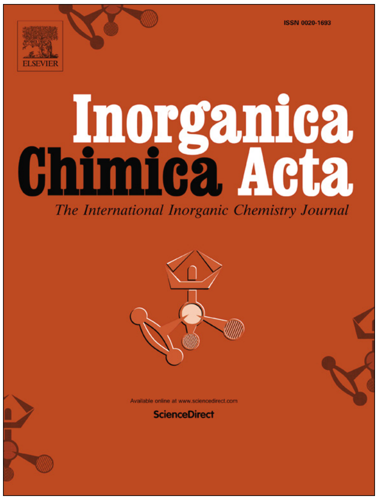

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TITLE: Synthesis and characterization of a palladium(0) complex with cyclophosphazene bearing two diphenylphosphine ligands and application in Suzuki-Miyaura cross-coupling

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Abstract

This paper describes the synthesis of a cyclophosphazene-based diphenylphosphine ligand and a new Pd(0) complex. Infrared spectroscopy (ATR-IR), ESI+-MS, ^{31}P, ^{1}H and ^{13}C NMR, Raman, WD-XRF, ICP-OES and TGA analysis show the coordination of two palladium atoms per unit of cyclophosphazene. A semiempirical calculation method was employed to find the lowest energy structure among the possible ones and Density Functional Theory (DFT) was used to optimize the found structure and obtain its bond angles, dihedral angles, bond lengths, atomic distances, and to calculate the vibrational spectrum (PBE/def2-TZVP(-f)). The new Pd complex showed activity in Suzuki-Miyaura cross-coupling reactions with halobenzenes and phenylboronic acid, tolerating different functional groups.

KEYWORDS: Pd(0) complexes; cyclophosphazene-based ligands; Suzuki-Miyaura cross-coupling.

1. Introduction

Palladium-catalyzed cross-coupling reactions are among the most important synthetic tools for organic chemistry, providing facile access to carbon-carbon (C-C) bond construction. In particular, the Suzuki-Miyaura C-C coupling experienced a notorious growth in both publications and patents over the past decades when compared to other classes of C-C coupling [1,2]. This approach became the most attractive due to several advantages such as mild reaction conditions and tolerance to many functional groups. The improvement of

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methods allowed its application in several areas such as natural product synthesis, material science, medicinal, biological and supramolecular chemistry, as well as catalysis and coordination chemistry [3,4].

Cyclophosphazene-based ligands have attracted interest due to the versatility presented by these structures: coordination can occur not only by nitrogen and phosphorus atoms of the cycle, but also by exocyclic groups. In the latter case, examples were reported with cyclophosphazenes bearing such side groups as pyrazolyl, hydrazides, pyridyl, amino, and phosphine bonded to several transition metals [5–7]. A more ambitious application of these inorganic rings as scaffolds to more complex structures was proposed by Chandrasekhar et al. who anchored a copper complex in a polymeric matrix and employed it in catalytic hydrolysis of phosphate esters without loss of activity even after catalyst recycling [8].

Since we have been interested in the immobilization of transition metal complexes by the sol-gel method [9–11], we decided to synthesize the ligand $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ **(3)** and its complex with palladium in order to establish a structural characterization, and to evaluate its activity in Suzuki-Miyaura coupling reactions. Therefore, our objective was to determine the feasibility of employing such structures in a future immobilization of palladium complexes.

2. Experimental

All reactions were carried out under a dried argon atmosphere by using standard Schlenk techniques. Solvents were treated according to standard procedures [12] and were degassed prior to use. Potassium carbonate (Nuclear) and cesium carbonate (Aldrich) were oven dried at 140 °C for 24 h. Ammonium chloride (Vetec) was dried in a desiccator with phosphorus pentoxide. Potassium tert-butoxide was dried under vacuum (^{t}BuOK, Aldrich). Deca-hydronaphthalene (Aldrich) was distilled and stored over molecular sieves. Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, Aldrich), 2,2'-biphenol (Aldrich), 4-bromophenol (Aldrich), *n*-butyllithium (*n*-BuLi, 2.5 mol L^{-1} in hexane, Aldrich), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, Aldrich), chlorodiphenylphosphine (Aldrich), (4-hydroxyphenyl)diphenylphosphine (Aldrich), aryl bromides and chlorides as well as arylboronic acids (Aldrich) were used without further treatment.

Proton-decoupled ^{31}P and ^{13}C NMR spectra, and ^1H NMR spectra were recorded either with a Bruker-Biospin Avance-III 500 MHz or an Avance DPX 250 MHz spectrometer at 25 ºC. Attenuated total reflectance infrared (ATR-IR) spectra were recorded with an Agilent Technologies Cary 630 FTIR spectrometer, in the 4000-400 cm^{-1} range, 64 scans, with a

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resolution of 4 cm^{-1}. The thermogravimetric analyses (TGA) were carried out on a TGA Q600 (TA Instruments) operated with a constant air flow of 100 mL min^{-1}, with a heating rate of 10 ºC min^{-1}. The samples were heated to 100 °C, kept at this temperature for 15 min, and then heated up to 900 °C, with this temperature maintained for 120 min. Electrospray mass spectrometry (ESI+-MS) analysis was performed on a Q-Tof (Waters) mass spectrometer within an *m/z* range of 100-2000, with a capillary voltage of 3 kV and a cone voltage of 50 V. The nebulizer gas flow was 0.5 L h^{-1}. The samples were injected by direct infusion in a flow of 40 μL min^{-1}. Raman spectra were recorded using a confocal Horiba Scientific T64000 spectrometer. The excitation source was a laser of 633 nm, focused with a 100× focal-lens objective with a resolution of 2 cm^{-1}. The recorded spectra were smoothed by using the Savitsky-Golay [13] method, setting a window size of 7 points, and a polynomial fit of second order. The baseline correction was performed by employing the Tan et al [14] method with $\lambda = 10^7$ and p = 0.001. The degradation and decomposition of the ligand and complex, respectively, were recorded on a PF1500 Farma (Gehaka). X-ray fluorescence spectrometry was carried out with a Shimadzu XRF-1800 spectrometer, in which the wavelength dispersion (WD-XRF) was employed using Rh radiation (3 kV and of 95 mA). The palladium percentage in the complex was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), on a Perkin Elmer Optima 8300 spectrograph, with $\lambda = 340.458$ nm. The sample was prepared by digestion in H_2SO_4:H_2O_2 (3:1). After that, the solution was placed on an ultrasound bath, diluted in high purity water (resistance of 18.2 MΩ), filtered and analyzed.

The catalytic experiments were monitored by gas phase chromatography using an Agilent 7890 gas chromatograph equipped with an HP 5 capillary column and a flame ionization detector (FID). Conversions of halobenzenes with different functional groups were determined using calibration curves obtained with standard solutions. Mass spectra were obtained on a gas chromatograph-mass spectrometer (GC-MS) Agilent 7890A using an HP-5 capillary column.

2.1. Synthesis of the ligand

$[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ **(1)** and $[N_3P_3(OC_6H_4Br)_2(O_2C_{12}H_8)_2]$ **(2)** were prepared as described by Carriedo et al. [15]. For details, see Supporting Information (Figs. S1-S8 and Scheme S1).

2.1.1. $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ (3) – by lithiation

In an attempt to form **(3),** a procedure adapted from the literature [16] was carried out. Several experiments were performed aiming to optimize the reaction conditions for the attack

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on the electrophile by n-butyllithium, and for further reaction with chlorodiphenylphosphine, see Supporting Information (Table S1 and Figs. S9-S12).

^{31}P NMR ($CDCl_3$, δ ppm): 25 (m), 9.6 (m), -6.4 (s). **ESI+-MS:** *m/z* calcd for $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4)_2]^+$ 690.1113, found 690.0945; *m/z* calcd for $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)(OC_6H_5)] + O_2$ 890.1504 $[M^+ + O_2]$, found 890.1368; *m/z* calcd for $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2] + O_2$ 1090.1895 $[M^+ + O_2]$, found 1090.1940.

2.1.2. $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ (3) – conventional route

The synthesis of **(3)** was based on the methodology proposed by Carriedo et al. [17]. **(1)** (1.0 g, 1.74 mmol), (4-hydroxyphenyl)diphenylphosphine (0.96 g, 3.48 mmol) and Cs_2CO_3 (2.27 g, 6.96 mmol) were dissolved in acetone (80 mL) and the solution was refluxed for 1.5 h. The solvent was removed under vacuum and the resulting product was then extracted with CH_2Cl_2 (8 × 20 mL). Yield: 1.43 g, 77.8%.

The degradation of the ligand **(3)** was carried out in the temperature range 86-92 °C in oxidizing (air) atmosphere. **^{31}P NMR ($CDCl_3$, δ ppm):** 9.6 [dd, *P*$(OC_6H_4\text{-}PPh_2)_2$], 25.6 [d, *P*$(O_2C_{12}H_8)$, AB_2 system, J_{AB} = 93 Hz], -6.4 (s, *P*Ph_2). **^{13}C NMR ($CDCl_3$, δ ppm):** 121.4, 121.9, 128.7, 129.6, 130.7, 148.0 ($C_{12}H_8$), 116.7, 128.6, 128.8, 133.6, 133.9, 135.2, 137.1, 151.4 ($OC_6H_4PPh_2$). **^{1}H NMR ($CDCl_3$, δ ppm):** 7.1-7.5 (m). For details, see Supporting Information (Figs. S13 and S14). **ATR-IR (cm^{-1}):** 3060 $\nu_{C\text{-}H(ar.)}$, 1585 and 1497 $\nu_{C=C(ar.)}$, 1227 and 1165 $\nu_{P=N}$, 971 $\nu_{P\text{-}O\text{-}C.}$ **TGA:** -2.7% (100 °C), -97.3% (100-890 °C). Residue at 900 °C: 0%. **ESI+-MS:** *m/z* calcd for $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2] + O_2$ 1090.1895 $[M^+ + O_2]$, found 1090.1730. **Raman (cm^{-1}):** 1612, 1586 and 1501 $\nu_{C=C(ar.)}$, 1310 and 1274 $\nu_{C\text{-}OP}$, 1251 and 1157 $\nu_{P=N}$, 1094 and 1039 $\nu_{C\text{-}H(ar.)}$, 754 $\nu_{P\text{-}N\text{-}P}$.

2.2. Pd complex (4): $Pd_2[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2(dba)_2]$

Ligand **(3)** (0.49 g, 0.04 mmol) and $Pd_2(dba)_3$ (0.21 g, 0.02 mmol) were dissolved in 4 mL of dry THF and the solution was stirred for 1 h at room temperature. After the reaction, the solvent was evaporated under vacuum, followed by the addition of 5 mL of benzene. The resulting red/brown solution was filtered, the solid dried under vacuum and washed with ether/hexane (50% v/v).

The decomposition of the Pd complex **(4)** was carried out in the temperature range 76-78 °C in oxidizing (air) atmosphere. **^{31}P NMR (C_6D_6, δ ppm):** 10.2 [dd, *P*$(OC_6H_4\text{-}PPh_2)_2$], 25.5 [d, *P*$(O_2C_{12}H_8)$, AB_2 system, J_{AB} = 94 Hz], 24.7 (s, Pd-*P*Ph_2). **^{1}H (C_6D_6, δ ppm):** 6.8-7.7 (m). **ATR-IR (cm^{-1}):** 3060 $\nu_{C\text{-}H(ar.)}$, 1590 and 1475 $\nu_{C=C(ar.)}$, 1230 and 1164 $\nu_{P=N}$, 970 $\nu_{P\text{-}O\text{-}C.}$

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Raman (cm^{-1}): 190 ν_{Pd-P}. **WD-XRF:** P, Pd, and Si. **TGA:** -86.8% (100-895 °C). Residue at 900 °C: 13.2%. **ICP-OES:** 11.6%.

2.3. Theoretical calculations of the ligand (3) and Pd complex (4)

As the complex contains two metal centers with one dibenzylideneacetone (dba) ligand coordinated to each Pd(0), it is expected to find up to four possible conformations by changing the way both dba ligands are coordinated to Pd(0). Since the lowest conformation energy is of great interest due to its higher stability, we computationally employed a low level of theory to investigate the energy of all possible conformations. Hence, our energy analysis of all conformations was done using the semiempirical Geometry, Frequency, Non-covalent Tight Binding method (GFN-xTB) [18] by Grimme's XTB software, which was set to perform its highest level of optimization (optlv 2). Once the conformation with the lowest energy was found, it was submitted to further computation using DFT.

All computations including hessian calculations were performed using DFT in the Orca software package (version 4.0.1) [19] with tight criteria set to both optimization and self-consistent field (SCF). The employed functional was PBE [20] with basis set def2-TZVP(-f) [21] and auxiliary basis def2/J [22] with resolution of identity (RI) [23–29] approximation to speed up calculations. Also, dispersion correction was computed by using D3BJ [30,31]. The guess method used to predict the starting orbitals was PModel. Finally, in order to overcome instabilities found in SCF the approximate second order in the SCF [32,33] was chosen, and it was set to start with an orbital gradient value below 0.001.

2.4. General procedure for Suzuki-Miyaura coupling reactions

In a typical experiment, a mixture of aryl bromide (0.175 mmol), phenylboronic acid (0.28 mmol), potassium tert-butoxide (0.42 mmol), a solution of the catalyst in THF (200 µL; 0.5 mol% with respect to palladium), 14 µL of deca-hydronaphthalene (as an internal standard for gas chromatography) and dry toluene (4 mL) were placed in a Schlenk tube, which was then sealed under argon and warmed at 110 °C for 4 h. Duplicate experiments were carried out for each catalytic run in order to ensure reproducibility.

3. Results and discussion

Synthesis and characterization of species **(1)** and **(2)** are described in Supporting Information. An attempt to synthesize **(3)** *via* lithiation of **(2)** followed by a nucleophilic attack of a chlorodiphenylphosphine aimed to check its feasibility, and open access to a variety of cyclophosphazene-based phosphines, as shown in Supporting Information (Scheme S1). Such a route had already been described for total substitution of chlorine in

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hexachlorocyclophosphazene [16], even by one of us [34][1]. To our surprise, the ^{31}P NMR spectrum of a solution of the obtained solid shows peak splitting (Fig. S9), suggesting the presence of more than one configuration in solution: a racemic mixture of (*R,R*) and (*S,S*) enantiomers, as well as the meso (*R,S)* form [35]. Such results imply that the desired bisphosphine was not obtained.

The ^{31}P NMR spectra obtained in experiment 7 (after lithiation and without reaction with chlorodiphenylphosphine) do not show peak splitting, depicting a homogeneous chemical environment (Fig. S10), while no signal is observed around 118 ppm (Fig. S11) in the ^{13}C NMR region where a peak assigned to the carbon bonded to the halide would be expected [15,36]. These results indicate the complete replacement of bromine.

According to Díaz et al. [36], the difficulty in achieving the desired product could be due to the lack of reaction of the second phosphine group (Fig. S15). Despite *n*-butyllithium excess and dilithiation completion, the bulkiness of the phosphine ligand would hamper its access to the phenoxide carbon. Thus, even if **(3)** was formed in minor amounts, the reaction with diphenylphosphine also favored the formation of an inseparable and undesirable mixture of products as $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_5)_2]$ and $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)(OC_6H_5)]$. Therefore, this route to ligand **(3)** and eventual analogues appeared to be unsatisfactory.

Although the procedure is described in the literature by Allcock et al. [16,37], it is important to mention that this experimental approach seems to have been set aside. Thus, the subsequent experimental procedures were carried out according to the conventional route, available only for the diphenylphosphine derivative.

When **(1)** was allowed to react with (4-hydroxyphenyl)diphenylphosphine, the ^{31}P NMR spectrum of the resulting product (Fig. 1) exhibits an AB_2 spin pattern with three resonance signals: a doublet at 25.6 ppm; a doublet of doublets at 9.6 ppm, corresponding to the phosphorus atom of phosphazene-bearing two $(O_2C_{12}H_8)$ and $(OC_6H_4\text{-}PPh_2)_2$ groups, respectively; and a singlet at -6.4 ppm, relative to the phosphorus atom of *P*Ph$_2$ groups. This spectrum clearly shows that the synthesis of **(3)** was successful.

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[1] Although peak integration in ^{31}P NMR always suggested six phosphine groups per cyclophosphazene unit, a misinterpretation of the experimental results and the presence of more than one species cannot be ruled out.

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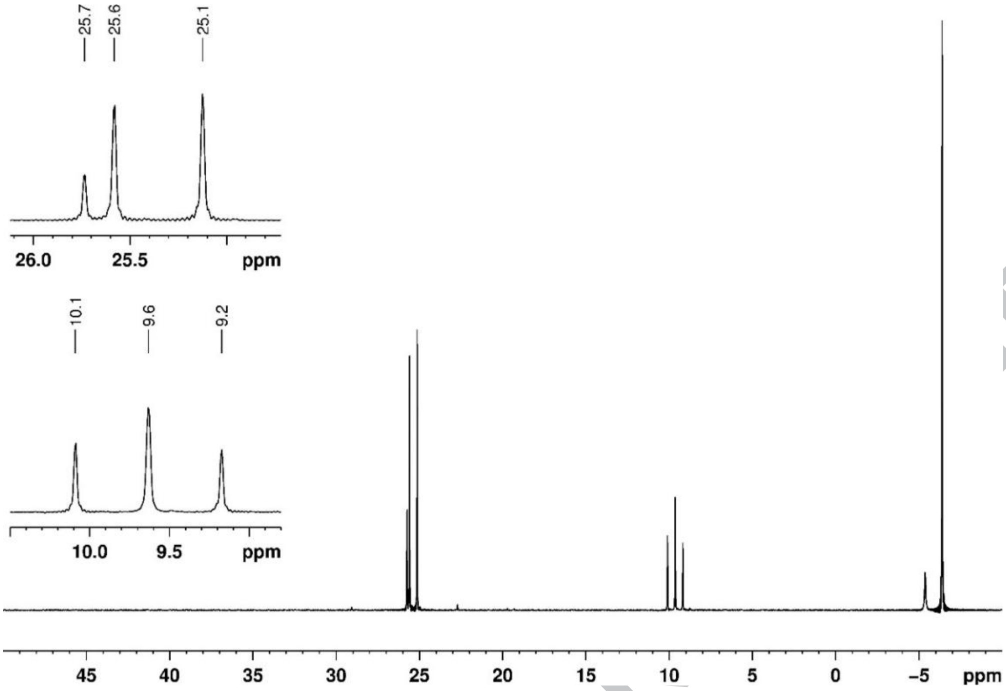

Fig. 1. ^{31}P NMR spectrum ($CDCl_3$, 500 MHz) of **(3)**.

In addition, the spectrum shows a singlet at 25.7 ppm, corresponding to the replacement of all chlorine atoms by 2,2'-dioxybiphenyl groups, $[N_3P_3(O_2C_{12}H_8)_3]$. Nevertheless, this impurity does not affect the synthesis of **(3)** nor the synthesis of the palladium complex **(4)**, since it is not reactive during the process [15].

Ligand **(3)** was also characterized by infrared spectroscopy. Its ATR-IR spectrum is shown in Fig. 2 and can be compared to the spectra of **(1)** and **(2),** shown in Supporting Information, Figs. S4 and S8.

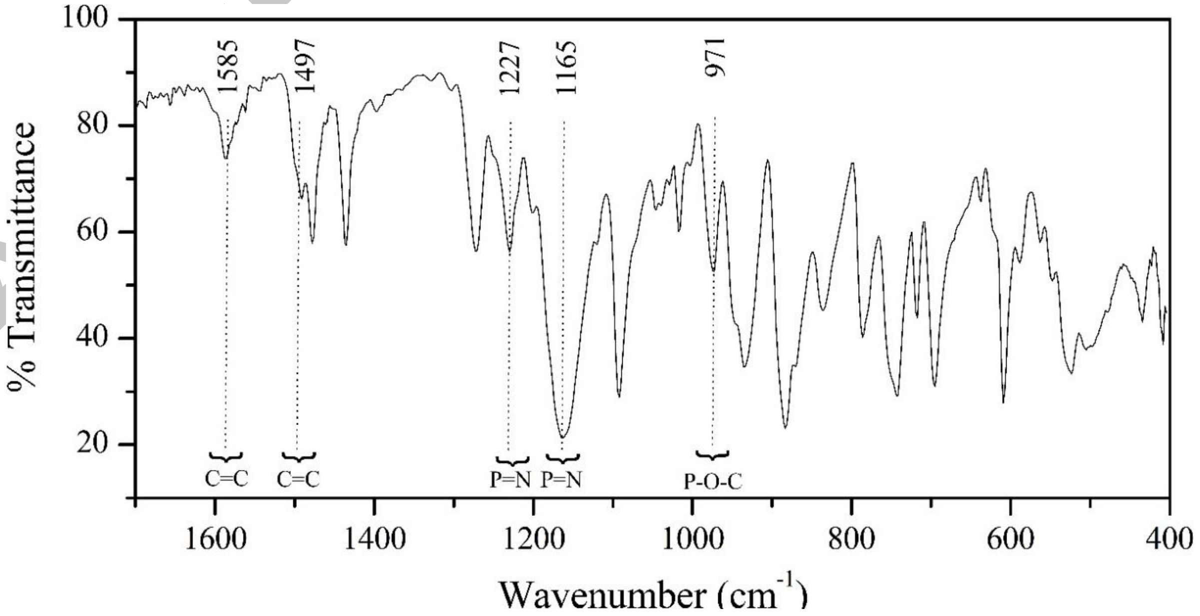

Fig. 2. ATR-IR spectrum of **(3)**.

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The ATR-IR spectrum of **(3)** confirms the formation of the ligand as the characteristic stretching peaks in the spectra of the phosphazenes $\nu_{P=N}$ are clearly present. The band at 3060 cm^{-1} (see Supporting Information, Fig. S16) can be assigned to stretching vibrations of the C-H bond while the aromatic ring $\nu_{C=C(ar.)}$ has symmetrical stretching frequencies at 1585 and 1497 cm^{-1} [38–40]. The spectrum also shows bands corresponding to the phosphazene moiety, $\nu_{P=N}$ stretching vibrations between 1227 and 1165 cm^{-1}, and a vibration band around 971 cm^{-1}, ascribed to $\nu_{P\text{-}OC}$ [35,38,41].

ESI+-MS analysis of a methanol solution of the ligand **(3)** showed a main peak at *m/z* = 1090.1730, which presents the isotopic patterns corresponding to the oxidized species, Fig. 3.

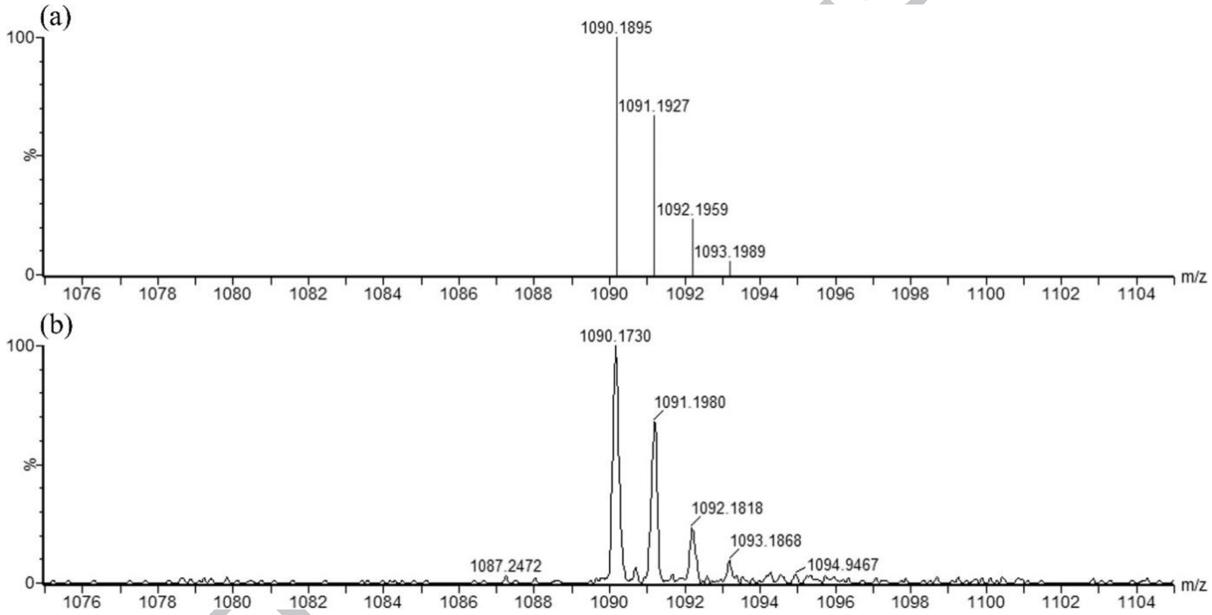

Fig. 3. ESI+-MS of **(3)** (a) simulated isotopic pattern and (b) experimental isotopic pattern for $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4(P=O)Ph_2)_2]$.

The calculated IR spectrum of the optimized structure of the Pd complex **(4)** shows good agreement with the experimental spectrum (see Supporting Information, Fig. S17), and it was in accordance with the obtained results for the previously proposed structure, as the vibrations bands of the spectra of Pd complex **(4)** and ligand **(3)** were similar.

Raman spectra of ligand **(3)** and of the corresponding Pd complex **(4)** are shown in Fig. 4 and Fig. S18. The vibrational bands observed at 1612, 1586 and 1501 cm^{-1} are attributed to the $\nu_{C=C(ar.)}$ stretching. The medium intense bands near 1310 and 1274 cm^{-1} correspond to the $\nu_{C\text{-}OP}$. In addition, the bands near 1251 and 1157 cm^{-1} can be assigned to $\nu_{P=N}$. The medium intense bands near 1094 and 1039 cm^{-1}, and 754 cm^{-1} can be assigned to $\nu_{C\text{-}}$

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$_{H(ar.)}$ and $\nu_{P\text{-}N\text{-}P}$ stretching modes, respectively. The strong band near 1000 cm^{-1} corresponds to the interaction between the aromatic ring vibration, and the stretching of the P-C bonds [42,43]. The Raman spectrum of **(4)** shows bands of medium intensity because the laser power was regulated by a filter to prevent sample heating and degradation, a new band at 190 cm^{-1}, assigned to the Pd-P stretching, confirms the coordination of the phosphine ligand to the palladium center [44].

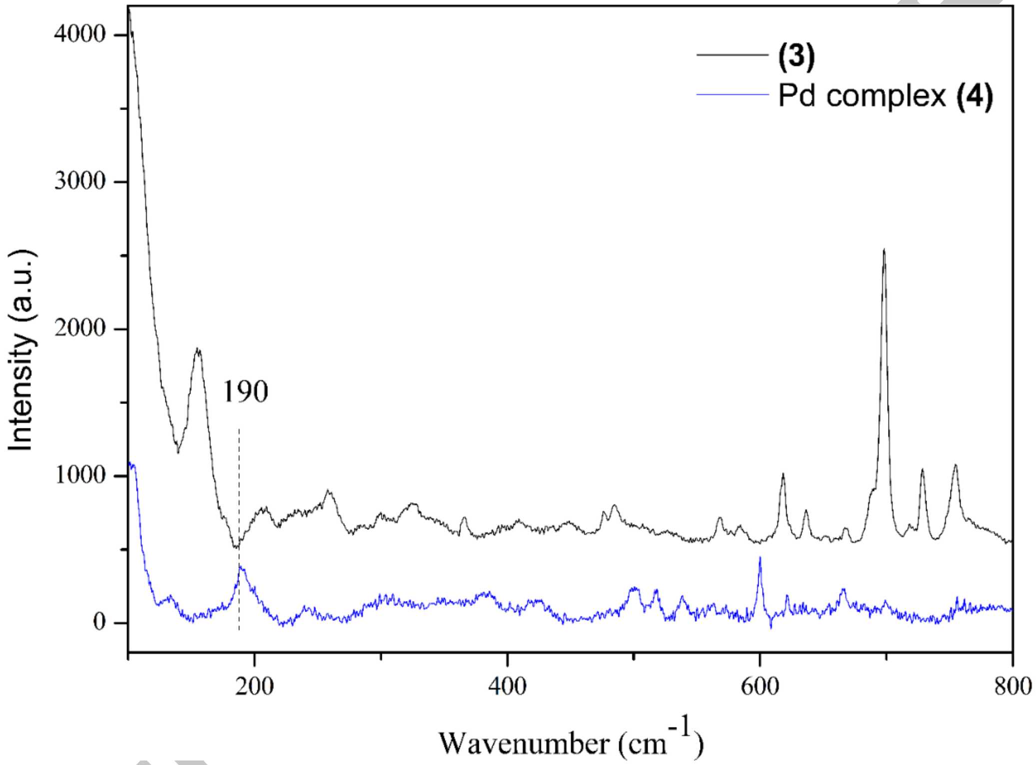

Fig. 4. Raman spectra of the Pd complex **(4)** and of ligand **(3)**.

The ^{31}P NMR spectrum of **(4)** is shown in Fig. 5. The signal assigned to the coordinated phosphine is shifted downfield (24.7 ppm) compared to the free ligand (-6.4 ppm) [45].

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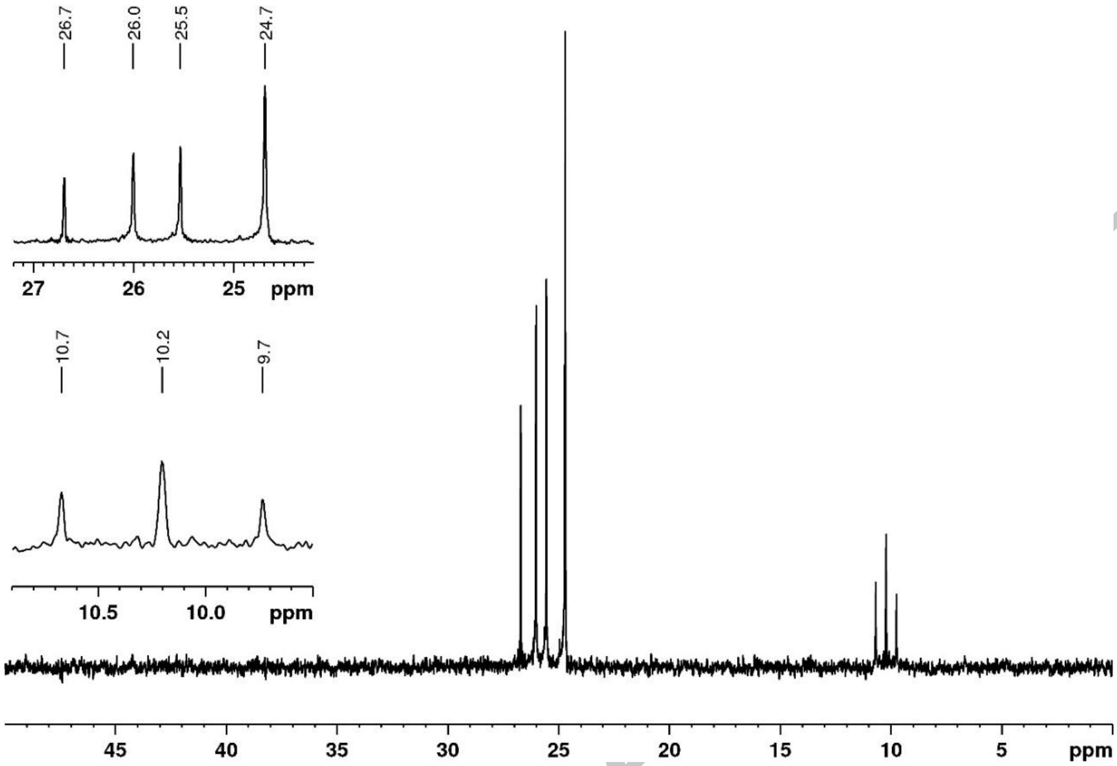

Fig. 5. ^{31}P NMR spectrum (C_6D_6, 500 MHz) of the Pd complex **(4)**.

The ^{1}H NMR and ^{13}C NMR spectra corroborate these results and suggest the presence of coordinated dba in the metal complex, see Supporting Information (Figs. S19 and S20).

In addition, the Raman spectrum of $Pd_2(dba)_3$ was also recorded, (see Supporting Information, Fig. S21). It shows that the commercial complex is fluorescence active, most probably due to its structural characteristics, presenting conjugated double bonds, quite different from Pd complex **(4)**. X-Ray fluorescence analysis detected P, Pd, and Si. The presence of Si is associated with the starch impurity used in the analysis.

A thermal decomposition analysis was performed, and the TGA curves of **(3)** and **(4)** are shown in Figs. S22 and S23, respectively. The curve for the complex shows a series of weight loss events, the first loss (5.4 wt %) around 100 °C, corresponding to the volatiles. The Pd complex **(4)** also exhibits losses between 100 and 895 °C, corresponding to the decomposition of the ligands (86.8% observed weight loss, 87.7% calculated). It was not possible to attribute those weight losses of the ligands, since they have high molar mass and complex structures, with many possibilities of bond-breaking and consequent formation of several decomposition products. The Pd complex **(4)** was completely degraded to metal Pd with a mass loss of 13.2% (calcd: 12.3%), even after a period of 2 h at 900 °C. The ICP-OES analysis was used to quantify the amount of palladium present in solution. The obtained value of 11.6% is in agreement with the proposed structure with two palladium atoms per unit of

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Entry	Molecular modelling	X-ray average

cyclophosphazene, $Pd_2[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2(dba)_2]$ (Fig. 6). The difference between the experimental and the calculated value can be attributed to the presence of the $[N_3P_3(O_2C_{12}H_8)_3]$. Therefore, two geminal phosphines are not involved in coordination to only one palladium center. It is worthwhile to mention that by using a cyclophosphazene bearing five phosphine groups, Chandrasekhar et al. [45] concluded that there was only one Pd atom per cyclophosphazene unit, and the metal was bonded to two nongeminal phosphines.

The unusual 14-electron structure $[PdL_2]$ of complex **(4)** can be rationalized in terms of the sterical demands of bulky ligands [46–49], which play an essential role in geometry and coordination of the proposed structure.

As the structure determination was not possible by XRD of single crystals, theoretical calculations for both the ligand **(3)** and the Pd complex **(4)** were performed. Since transition metal complexes bearing more than 180 atoms, with possible non-covalent interactions and with different possible conformations, highly increases the computational cost, the GFN-xTB [18] semiempirical method was employed to screen among the four possible molecular structures of Pd complexes. The lowest energy conformation among the four starting structures was chosen as the first guess for the most stable compound (see Supporting Information, Figs. S24-S27). Subsequently, the molecular structures of both the ligand **(3)** and the chosen Pd complex **(4)** were optimized using DFT with the functional PBE/def2-TZVP(-f) [20,21].

The structure of the ligand **(3)** before and after coordination to the metal center is depicted in Fig. 6. They were studied by observing the following structural descriptors: bond angles, dihedral angles, atomic distances and bond lengths, which were compared to transition metal complexes containing cyclophosphazene-based ligands, as well as for Pd complexes with dibenzylideneacetone (dba) and phosphines ligands. The structures to which we compared our calculated structural descriptors are reported in the Cambridge Crystallographic Database CSD (Table 1). Although the number of structures is restricted, the geometry optimization at DFT level showed a good agreement with the average values of experimental structural descriptors observed herein.

Table 1.

Ligand **(3)** and Pd complex **(4)** - bond lengths, bond angles, dihedral angles and atomic distances calculated using DFT with the functional PBE/def2-TZVP(-f) compared to values found from crystal structures from the CSD

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		Pd complex (4)	Ligand (3)	
	Bond lengths (Å)			
1	Pd117-C159	2.172		2.176 [a], 2.172 [b]
2	Pd117-C158	2.176		2.149 [a], 2.154 [b]
3	P0-Pd117	2.269		2.343 [b]
4	Pd118-C130	2.168		2.154 [b]
5	Pd118-C131	2.194		2.172 [b]
6	P85-Pd118	2.259		2.331 [b]
7	C158-C159	1.409		1.411 [a], 1.395 [b]
8	C162-C163	1.350		1.292 [b]
9	C131-C130	1.404		-
10	C126-C127	1.350		-
11	P33-N42	1.594	1.595	1.581 [c], 1.581 [d]
12	P33-N45	1.604	1.601	1.585 [c], 1.583 [d]
13	P36-N42	1.596	1.596	1.581 [c], 1.579 [d]
14	P36-N39	1.598	1.596	1.573 [c], 1.589 [d]
15	P37-N39	1.591	1.592	1.576 [c], 1.574 [d]
16	P37-N45	1.591	1.590	1.573 [c], 1.578 [d]
17	P33-O34	1.632	1.631	-
18	P33-O35	1.618	1.622	-
19	P36-O46	1.623	1.628	1.593 [c]
20	P36-O49	1.621	1.617	1.587 [c]
21	P37-O40	1.626	1.624	1.591 [c]
22	P37-O43	1.624	1.624	1.586 [c]
	Bond angles (°)			
23	N45-P33-N42	118.624	118.641	117.044 [c], 117.719 [d]
24	N39-P36-N42	120.060	120.401	118.088 [c], 118.189 [d]
25	N39-P37-N45	119.589	119.277	118.328 [c], 117.571 [d]
26	O34-P33-O35	98.757	98.371	-
27	O46-P36-O49	102.326	102.588	102.762 [c]
28	O40-P37-O43	101.945	102.157	103.121 [c]
29	P36-O46-C57	120.901	121.542	119.997 [c]
30	P36-O49-C63	118.276	119.112	120.295 [c]
31	P37-O43-C38	121.598	120.982	119.473 [c]
32	P37-O40-C51	119.809	119.457	120.704 [c]
	Dihedral angles (°)			
33	C51-C56-C50-C38	-42.215	-42.187	-42.833 [c]
34	C57-C62-C64-C63	-42.292	-43.006	-43.105 [c]
	Atomic distances (Å)			
35	P0-P85	11.062	9.751	-
36	P0-P33	6.495	6.411	-
37	P85-P33	6.880	6.768	-

The bond lengths, atomic distance, bond angles and dihedral angles represented are for the crystal structures reported in the October 2017 version of CSD. [a] Averages calculated including all structures containing Pd complexes with dba and phosphines ligands. [b] [Pd(η^2-dba)(PPh$_3$)$_2$] [50]. [c] Averages calculated including structures containing cyclophosphazene backbone blocked by the biphenoxide groups. [d] Averages calculated including all structures containing a cyclophosphazene backbone.

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For the Pd complex **(4)** only one of the double bonds (C158-C159 with 1.409 Å and C131-C130 with 1.404 Å) of each dba-ligand is coordinated to Pd centers (Table 1, entries 7 and 9). As described by Majchrzak et al. [50], this causes a decrease in the bond lengths of the double bonds (C162-C163 and C126-C127 with 1.350 Å) that are not involved with the metal interaction (Table 1, entries 8 and 10).

Looking at Table 1 it is clear that besides a slight variation found in both bond lengths and angles, for the cyclophosphazene backbone of the Pd complex **(4)**, and the ligand **(3)** (Table 1, entries 11-34) those values remained almost unchanged even after coordination to the metal center, showing that the cyclophosphazene backbone does not have a significant interaction with Pd. Comparing entries 35-37, however, we observe an increase in the atomic distances P0-P85 (from 9.751 Å to 11.062 Å), P0-P33 (from 6.411 Å to 6.495 Å) and P85-P33 (from 6.768 Å to 6.880 Å), which is attributed to the hindrance caused after coordination to the Pd center.

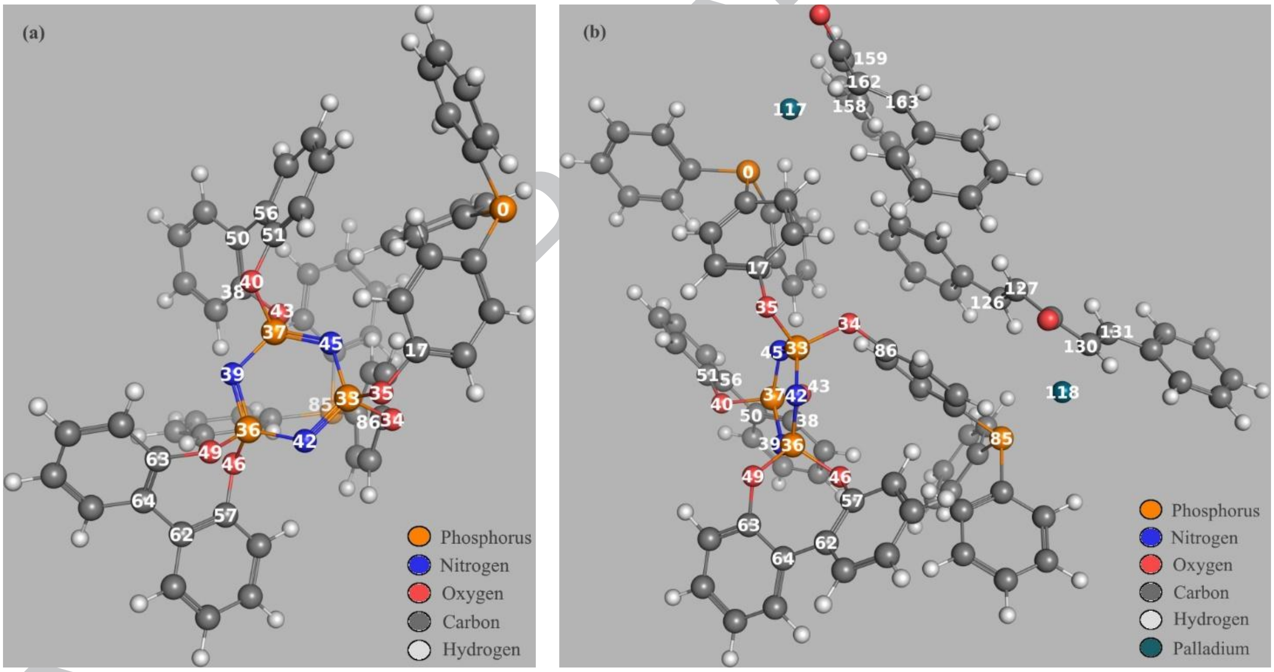

Fig. 6. Theoretical structure for both (a) ligand **(3)** and (b) Pd complex **(4)**.

The Pd complex **(4)** was tested in Suzuki-Miyaura coupling reactions since this is the most studied method for the C-C bond formation from simple molecules [51,52]. The catalyst was inactive for aryl chlorides with neutral or electron-donating groups due to the binding strength of Ar-Cl bonds (Table 2, entries 1-3), which could be potentially retarding the oxidative addition, the first step of the catalytic cycle, hampering the formation of ArPd(II)X [53]. Moreover, homocoupling products of the phenylboronic acid and/or the halide were observed and identified by GC-MS.

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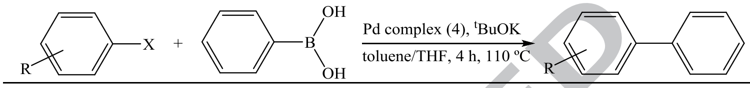
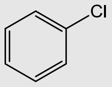
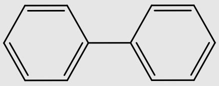
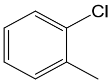
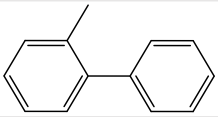
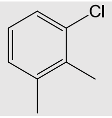
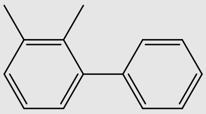
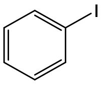
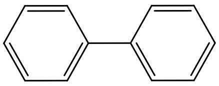
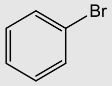
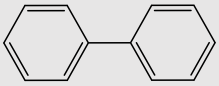
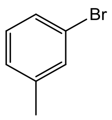
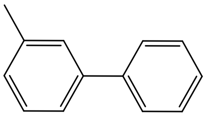
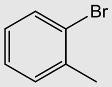
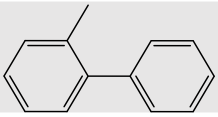
When different halobenzenes, Ar-I (Table 2, entry 4) or Ar-Br (Table 2, entry 5) were employed, the expected product was obtained, with yields following the order of Ar-I > Ar-Br > Ar-Cl. However, in the presence of non-activated aromatic rings and/or sterically hindered substrates, lower yields (Table 2, entries 6-8) were obtained. An *ortho* methoxy group (moderate electron-donating group) also led to lower yield, probably due to steric problems [54].

Activated aryl iodides (Table 2, entries 9 and 10), and slightly electron-deficient bromophenol (Table 2, entry 11) led to excellent yields. A moderate yield (Table 3, entry 1) was obtained when a deactivated phenylboronic acid was employed. Arylboronic acids with an electron-donating group led to good yields of the coupling reaction products, even in the case of a hindered acid (Table 3, entry 3). Finally, all catalytic results obtained with Pd complex (4) are in agreement with those reported in the literature [51,53,54].

Table 2.

Results for Suzuki-Miyaura coupling reactions of aryl halides and phenylboronic acid in the presence of the Pd complex **(4)**. [a]



Entry	Aryl halide	Product	Yield (%)^{b}
1			0
2			0
3			0
4			49
5			40
6			37
7			30

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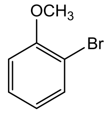
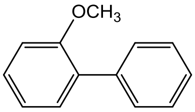
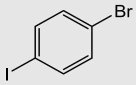
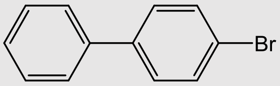
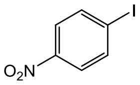
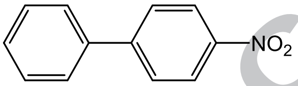
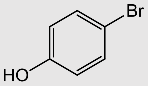
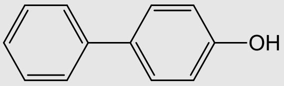
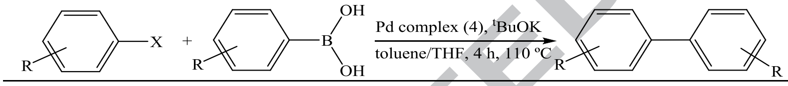
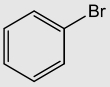
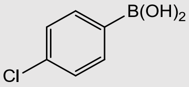
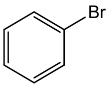
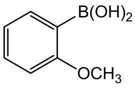
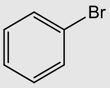
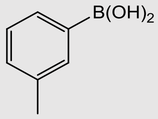
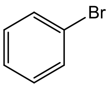
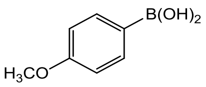
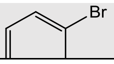
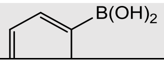
8			31
9			>99
10			>99
11			95

[a] Reaction conditions: aryl halide (0.175 mmol); phenylboronic acid (0.28 mmol); ${}^tBuOK$ (0.42 mmol); Pd Complex **(4)** (0.5 mol%); T = 110 °C; Toluene/THF (v/v = 20:1); 4 h. [b] Yield was determined by GC using deca-hydronaphthalene as an internal standard.

Table 3.

Pd-catalyzed Suzuki-Miyaura reactions of aryl bromides with arylboronic acids. [a]



Entry	Aryl bromides	Arylboronic acid	Yield (%)[b]
1			35
2			56
3			79
4			61
5			65

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[a] Reaction conditions: aryl bromide (0.175 mmol); arylboronic acid (0.28 mmol); ^{t}BuOK (0.42 mmol); Pd Complex **(4)** (0.5 mol%); T = 110 °C; Toluene/THF (v/v = 20:1); 4 h. [b] Yields were determined by GC using deca-hydronaphthalene as an internal standard.

4. Conclusions

The attempted synthesis of a cyclophosphazene-based diphenylphosphine by lithiation of two *para*-bromophenoxy groups was proposed. However, a systematic study showed that this strategy led to a major product containing only one phosphine attached to the cyclophosphazene ring, probably due to steric factors associated with this ligand. Nevertheless, we have successfully prepared a new Pd(0) complex anchored to a cyclophosphazene bearing two phosphine ligands. The Pd complex **(4)** was characterized as $Pd_2[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2(dba)_2]$. The geometry optimization, performed by DFT with the functional PBE/def2-TZVP(-f), for both the ligand **(3)** and the Pd complex **(4)** were successful, showing the best conformation of dba groups in the proposed structure among the four possible structures. Our data are in a very good agreement with those found in the Cambridge Crystallographic Database. This complex showed a good catalytic activity in Suzuki-Miyaura coupling reactions. As expected, aryl halides containing electron-withdrawing groups, and arylboronic acids with electron-donating substituents favored the Suzuki-Miyaura coupling reactions.

Acknowledgments

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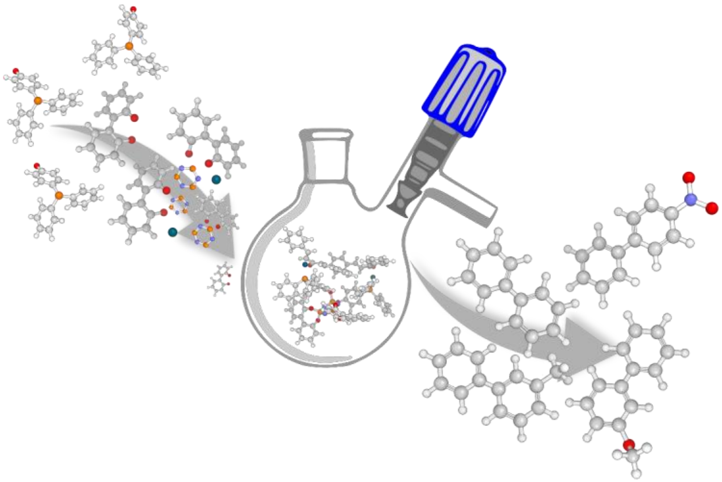

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Synthesis and theoretical studies of a new Pd(0) complex with a cyclophosphazene-based diphenylphosphine ligand. Activity in Suzuki-Miyaura cross-coupling reactions.

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