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PEPPSI-Type Pd(II)—NHC Complexes on the Base of *p-tert*-Butylthiacalix[4]arene: Synthesis and Catalytic Activities

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Abstract: The creation of effective catalytic systems for cross-coupling reactions, reduction, etc., capable of working in water-organic or pure aqueous media is in great demand. The article presents the synthesis of NHC-palladium complexes of the PEPPSI type based on monoimidazolium derivatives of thiacalix[4]arene. The structure of the imidazolium precursors, obtained in 81–88% yields and the complexes themselves, obtained in 40–50% yields, is established using modern methods, including X-ray structural analysis and high-resolution mass spectrometry. It is shown that the obtained complex with bulk substituents near the palladium atom is not inferior to the well-known PEPPSI-type Organ's catalyst in the catalysis of Suzuki-Miyaura coupling and is four times superior to the latter in the *p*-nitrophenol reduction reaction. Given the presence of free phenolic hydroxyl groups in the macrocycle, the obtained complexes are of interest for further post-modification or for immobilization on a carrier.

Keywords: thiacalix[4]arene; NHC; palladium; cross-coupling; PEPPSI complex

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1. Introduction

Palladium-catalyzed cross-coupling reactions allow the creation of new carbon-carbon or carbon-heteroatom bonds under mild conditions [1]. The reliability and reproducibility of these reactions are particularly attractive in fine organic synthesis [2], pharmaceuticals [3] or materials chemistry [4]. Palladium(II) complexes based on N-heterocyclic carbene [NHC] ligands used as catalysts have several advantages, the most important of which are their resistance to moisture and air oxygen [5–7] and the pronounced σ-donating ability of NHC. NHCs increase the electron density at the metal center by attaching an unshared electron pair to the d-orbital of the metal via a σ-bond [8]. The steric factor also has a significant effect. There is a tendency to increase the selectivity of the catalyst action in the presence of bulk substituents, while the availability of the active center decreases [9]. Modern NHC complexes of transition metals, in particular palladium, have great catalytic activity and potential for the further adjustment of properties [10]. The so-called PEPPSI (Pyridine-Enhanced Precatalyst: Preparation, Stabilization and Initiation) complexes of palladium (II), introduced into practice by an Organ's group, have recently become popular among catalysts of NHC type [11–13]. The latter Pd-PEPPSI complexes show high catalytic activity, with no need for an inert atmosphere and require a low catalyst load [14,15].

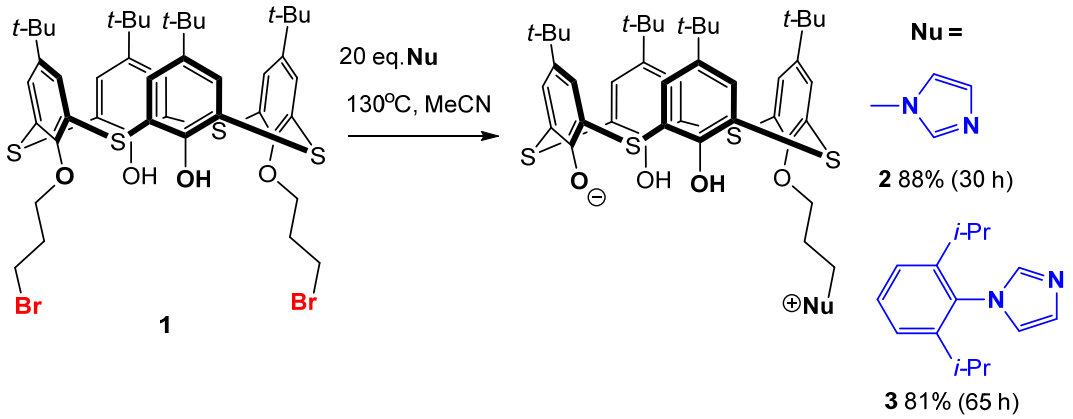
Combining Pd(II) NHC complexes and calix[4]arene platforms can significantly expand the application of catalysts [16]. Large macrocycles can act as bulky ligands, which

facilitate the formation of monoligated intermediates [17] and can promote the final reductive elimination step in coupling reactions [18]. A number of successfully obtained NHC complexes based on the classical calixarene are presented in the literature [19], including PEPPSI-type complexes [20–23]. However, all presented structures require a non-convenient multistage step-by-step modification of the upper rim to introduce imidazolium fragments. We proposed the use of the thiacalix[4]arene platform for the construction of bis-NHC palladium complexes in a different way. In this case, the desired NHC complexes were obtained in only four reaction steps by modifying the lower rim of the macrocycle to give final complexes in the *1,3-alternate* stereoisomeric form [24]. Recently [25], we discovered the unique ability of thiacalix[4]arenes to form monoimidzolium derivatives when distally disubstituted bromopropyl macrocycle is introduced into reaction with imidazoles. In the present work, the synthesis and catalytic activities of thiacalix[4]arene PEPPSI-type palladium complexes are discussed. The resulting complexes are characterized by ease of synthesis and can also be post-modified or immobilized onto cationic carriers for heterogeneous catalysis

2. Results and Discussion

2.1. Synthesis

To obtain precursors of NHC complexes based on thiacalix[4]arene in the cone stereosomeric form, the reaction between bromo derivative **1** and N-methylimidazole was performed (Scheme 1). The spectral characteristics of compound **2** correspond to the literature data [25]. The derivative **3** with bulky 2′,6′ di-isopropylphenyl fragment was obtained by a similar technique. Due to steric hindrance of N-2′,6′ di-isopropylphenyl imidazole, it took 65 h of heating to fully complete the reaction.



Scheme 1. Synthesis of imidazolium salts **2** and **3**.

Crystals suitable for X-ray diffraction analysis were obtained for compound **2**. In the resulting crystal, compound **2** is presented in zwitter-ionic form as a dimer (Figure 1) formed due to electrostatic interactions between the phenolate anion of one macrocycle and the imidazolium fragment of another macrocycle. The phenolate ion is stabilized by strong hydrogen bonding with neighboring phenolic hydroxyl groups (Figure S1). The asymmetric unit comprises two thiacalixarene molecules. The thiacalix[4]arene molecules themselves are in a pinched cone configuration; the distance between the opposing carbon atoms in the para-position (C43 and C86) is 5.756 Å and for (C46 and C60)—10.171 Å for one molecule and 5.762 (C13 and C122)/10.407 Å (C6 and C116)—for another. The cavity distortion occurs because the substituted phenolic hydroxyl group does not participate in hydrogen bonding and is directed outside the lower rim of thiacalix[4]arene. This structural motif is typical of the crystal structures of monosubstituted thiacalix[4]arene derivatives [26,27], including the only example in the literature of a zwitter-ion salt [28], which, unlike compound **2**, is an internal zwitter-ion in the solid phase.

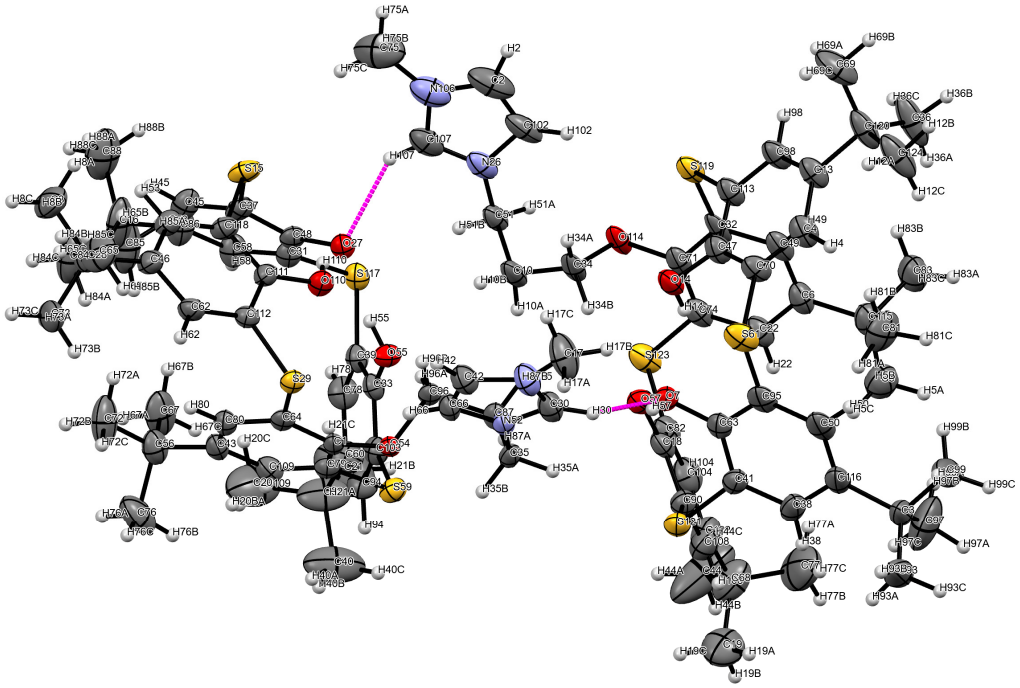
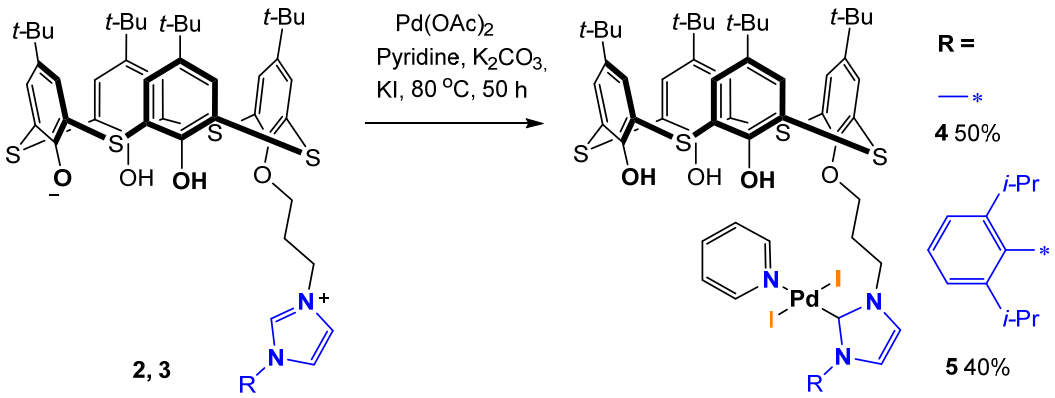


Figure 1. ORTEP representation of **2** showing 50% probability thermal ellipsoids. C atoms—grey, N atoms—blue, O atoms—red, S atoms—yellow.

The structure of compound **3** was also proved by a complex of physical methods. Thus, in the NMR ^{1}H spectrum (Figure S2), after quaternization, an acidic proton signal appears at 10.01 ppm, as well as an imidazole proton signal as a broad singlet at 8.66 ppm. According to the two-dimensional Nuclear Overhauser Effect Spectroscopy (NOESY) ^{1}H-^{1}H spectrum, a series of cross-peaks of protons of the imidazolium fragment with methylene protons of the propyl linker are presented (Figure S2). Proton signals of phenolic hydroxyl groups do not appear in the NMR ^{1}H spectrum due to rapid exchange, as previously shown for compound **2** [25], but in the IR spectrum, there is a broad band at 3388 cm^{-1} corresponding to the valent vibrations of hydrogen-bonded OH groups. The $[M+H]^{+}$ quasimolecular ion with m/z 989.4551 (calculated for $[C_{58}H_{73}N_2O_4S_4]^{+}$ 989.4448) was found in the high-resolution electrospray ionization mass spectrometry (HR ESIMS) spectrum (Figure S2).

Monosubstituted thiacalix[4]arenes **2** and **3** were used to create PEPPSI-type NHC complexes. The reaction was performed in pyridine at 80 °C using palladium acetate as a metal source and potassium carbonate as a base with the addition of KI as a source of halogen ligands (Scheme 2). The reaction was carried out for 50 h of heating in an inert atmosphere, and the target complexes were isolated by column chromatography.



Scheme 2. Synthesis of PEPPSI complexes **4** and **5**.

The disappearance of the signal of the acidic C-N-C proton in the NMR spectra, as well as the appearance of a series of signals of the pyridine ring protons in the downfield region, testify to the successful formation of complexes **4** and **5**. In the ^{13}C NMR spectra, signals corresponding to the carbene carbon atom appear at 157.8 ppm (for **3**) and 155.5 ppm (for **4**). In the 2D (^{1}H-^{1}H) NMR NOESY spectrum of compound 4 (Figure S3), the cross-peaks between signals of pyridine protons ($_{\delta}$H = 9.11 ppm) and N-methyl protons ($_{\delta}$H = 4.04 ppm) unequivocally prove the structure of compound **4**. The composition of complexes **4** and **5** was confirmed by HR ESIMS. Thus, the quasimolecular ion $[M\text{-}I\text{-}Py]^+$ with m/z 1075.1354 (calculated for $[C_{47}H_{58}IN_2O_4PdS_4]^+$ 1075.1354) is present in the mass spectrum of compound **4**, and the quasimolecular ion $[M\text{-}I\text{-}Py]^+$ with m/z 1221.2458 (calculated for $[C_{58}H_{72}IN_2O_4PdS_4]^+$ 1221.2449) is present in the spectrum of compound **5** (Figures S3 and S4).

The structure of **4** was also established by X-ray diffraction analysis (Figure 2). According to the data obtained, the carbene and pyridine ligands are coordinated at the palladium atom in the trans position. The bond lengths between the palladium and the NHC fragment/pyridine are 1.963 Å and 2.102 Å, respectively, which closely correspond to the values of the PEPPSI-type complex obtained by Organ [29] (1.969 Å and 2.137 Å). The small N46-C47-N43 angle (106.16°) is typical of singlet carbenes. The angle between the NHC-Pd-Py bonds (177.99°) is also consistent with the literature data on PEPPSI complexes [30,31]. It is noteworthy that the macrocyclic platform does not undergo severe distortions—the distances between the opposing oxygen atoms are 4.481 (O23–O39) and 3.707 (O31–O55) Å. The reason for this is the cyclic hydrogen bond with the incorporation of all four oxygen atoms, which fixes the cone configuration.

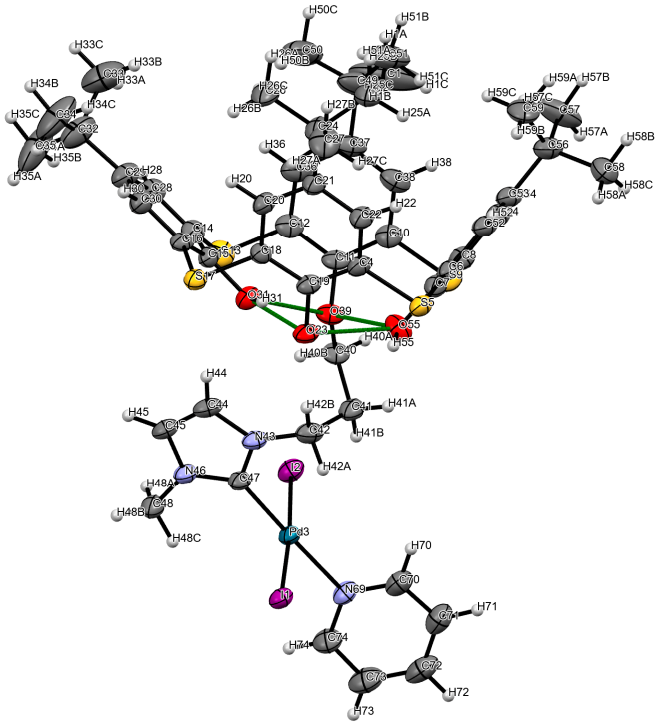
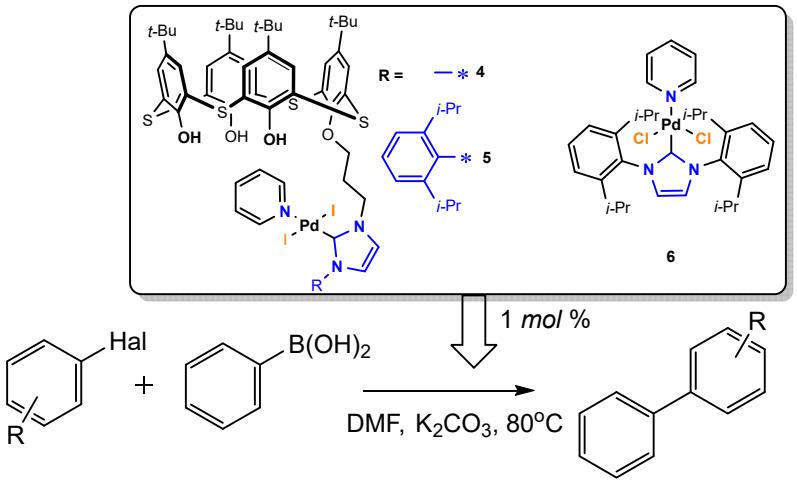


Figure 2. ORTEP representation of **4** showing 50% probability thermal ellipsoids. C atoms—grey, N atoms—blue, O atoms—red, S atoms—yellow, Pd atoms—emerald, I atoms—purple.

2.2. Catalytic Activities

The obtained complexes were used in the catalysis of the Suzuki-Miyaura cross-coupling reaction [32]. To compare the catalytic activity of the synthesized NHC palladium complexes of the PEPPSI type, a well-known Organ's PEPPSI palladium, complex **6**, was obtained according to the known literature procedure [29] (Scheme 3).



Scheme 3. Model Suzuki-Miyaura cross-coupling reaction and studied catalytic systems.

The catalytic activity of palladium NHC complexes **4**–**6** was studied in Suzuki-Miyaura cross-coupling reactions between phenylboronic acid and various aryl halide derivatives (p-iodoanisole, p-bromoanisole, p-iodonitrobenzene, p-bromotoluene, 2-bromomesitylene, p-bromoacetophenone) in degassed, dry DMF (Table 1) in the presence of 1 mol % pre-catalyst. Conversion in the reaction was determined by halogenarene intake using gas chromatography-mass spectrometry (GCMS) with the absolute calibration method; selectivity was determined by the ratio of the target product to the homo-coupling products. In some cases (entries 1, 5, 9, 13, 15, 17, 19, 21 and 23 in Table 1), the product was preparatively isolated to estimate the isolated yield.

According to the data obtained, donor substituents decrease the halogen mobility at the stage of oxidative addition, which is observed when using p-iodoanisole (positive mesomeric (+M) effect) as a reagent in the cross-coupling reaction (entries 1, 5 and 9 in Table 1). On the contrary, the acceptor nitro group (negative mesomeric (-M) and inductive (-I) effects) activates the halogen mobility (entries 13, 15 and 18 in Table 1) [33,34]. Halogens directly bonded to an aromatic ring have low reaction activity through conjugation of their electron pair with the benzene ring. Therefore, the transition to less active bromine in comparison with iodine results in a decrease in conversion (entries 19, 21 and 23 in Table 1). A slight change in the structure of the organic NHC-ligand leads to the different activity of the NHC complexes, which is clearly demonstrated by the reaction with the less active p-bromoanisole. The difference in catalytic activity is associated with different rates of formation of active catalytic particles. The bulkier ligand (in the case of **5**) stabilizes the formed particles more efficiently [35,36]. The cross-coupling reaction was also carried out in an aqueous-organic medium DMF-water with different water contents (20, 50 and 80% of water). When water is added to the reaction mixture with p-iodoanisole, the conversion reaches 99%, with a slight decrease in selectivity, as shown when using **4** and **5** as catalytic systems (entries 2–4, 6–8 and 10–12 in Table 1). This change is due to the better solubility of the K_2CO_3 in the water-organic system. At the same time, the addition of water leads to a decrease in selectivity due to the transition of phenylboronic acid to the more reactive form of phenylborate anion, which leads to an increase in the yield of the homocoupling product [37]. An increase in conversion is also observed when water is added to the reaction mixture with p-bromoanisole (entries 20, 22 and 24 in Table 1). A slight decrease in selectivity is observed when the reaction is carried out with the addition of water and in the case of p-iodonitrobenzene (entries 14, 16 and 18 in Table 1). The influence of substituents is well observed in the series of bromo derivatives (entries 25–27 in Table 1). Thus, when the reaction is carried out with p-bromotoluene (+I effect), the conversion only reaches 56%, significantly increasing when the reaction is carried out with bromacetophenone with an acceptor (-M and -I effects) acetyl substituent. In the case of the reaction with 2-bromomesitylene, both conversion and selectivity are drastically reduced

(biphenyl-product of phenylbonic acid coupling is mainly observed), which is due to the essential steric hindrances of this substrate.

Table 1. Conversion and selectivity of different Pd-containing catalytic systems in Suzuki-Miyaura cross-coupling [1].

Entry	Complex	Hal	R	Conversion, %	Isolated yield, %	Selectivity, %
1	**6**	-I	*p*-OCH_3	66	53	85
2	**6** *			99		71
3	**6** **			99		65
4	**6** ***			99		69
5	**5**			75	61	91
6	**5** *			99		82
7	**5** **			99		85
8	**5** ***			99		84
9	**4**			27	14	96
10	**4** *			99		91
11	**4** **			99		88
12	**4** ***			99		78
13	**6**	-I	*p*-NO_2	99	65	99
14	**6** *			99		72
15	**5**			93	35	99
16	**5** *			99		95
17	**4**			75	35	99
18	**4** *			95		80
19	**6**	-Br	*p*-OCH_3	70	48	71
20	**6** *			94	56	71
21	**5**			54	37	75
22	**5** *			62	42	76
23	**4**			6	3	99
24	**4** *			18	12	99
25	**5** *	-Br	*p*-CH_3	56		71
26	**5** *		-Mesityl	23		30
27	**5** *		*p*-$COCH_3$	99		98

[1] Conversion and selectivity were determined by GCMS. C(haloarene) = 100 mM, C(phenylboronic acid) = 120 mM, C(K_2CO_3) = 200 mM, V = 0.5 mL, DMF, 85 °C, 21 h. * 20% H_2O, ** 50% H_2O, *** 80% H_2O.

As for the isolated yield, it mainly corresponds to the observed conversion taking into account the selectivity. In the case of p-iodonitrobenzene, the isolated yield is rather strongly reduced (entries 13, 15 and 17 in Table 1), which is probably due to losses during the extraction of the reaction mixture.

The obtained complexes dissolved in THF were used in the catalysis of the model reduction reaction of p-nitrophenol and more hydrophobic p-ethylnitrobenzene [38]. The reaction is easily controlled by UV-visible spectroscopy and carried out at an excess of sodium borohydride in aqueous medium at 21 °C in the presence of 5 nmol (2 mol% to p-nitrophenol) complexes (Table 2, Figure 3). This reaction does not proceed in the absence of the catalyst.

Table 2. Catalytic activity of 4-6 for the reduction of *p*-nitrophenol and *p*-ethylnitrobenzene [1].

System	*p*-Nitrophenol		*p*-Ethylnitrobenzene	
	Apparent Rate Constant, k, s^{-1}	Specific Catalytic Activity, K_a, $\times 10^5$ $mol^1 s^{-1}$	Apparent Rate Constant, k, s^{-1}	Specific Catalytic Activity, K_a, $\times 10^5$ $mol^1 s^{-1}$
6	2.1×10^{-3}	4.2	2.2×10^{-3}	4.4
5	4.2×10^{-3}	8.4	2.4×10^{-3}	4.8
4	1.2×10^{-3}	2.4	2.7×10^{-3}	5.4

[1] C (*p*-nitrophenol) = C (*p*-ethylnitrobenzene) = 0.1 mM, C ($NaBH_4$) = 5 mM, C (4–6) = 0.02 mM, 0.1% THF-H_2O, 21 °C, V = 2.5 mL, l = 10 mm.

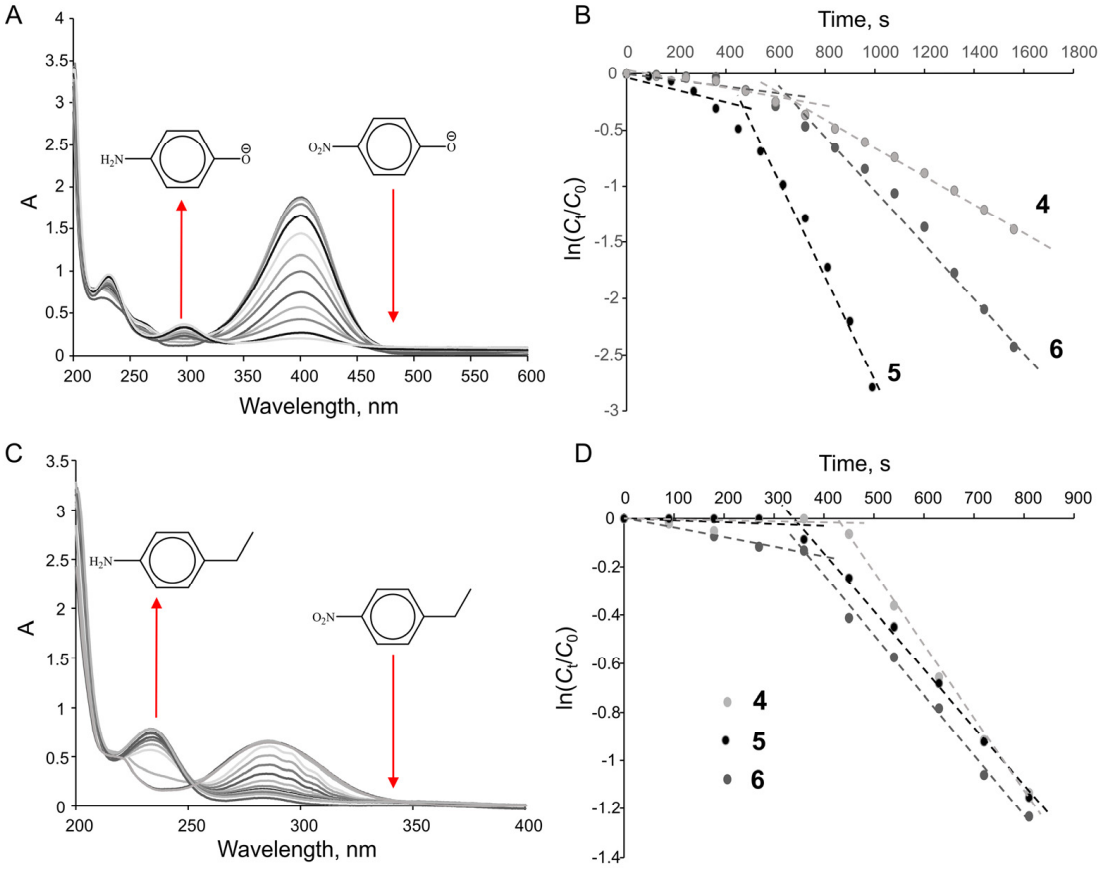


Figure 3. Changes in the UV–VIS spectrum during the reduction of (**A**) *p*-nitrophenol and (**C**) *p*-ethylnitrobenzene in the presence of 5; dependence of $\ln(C_t/C_0)$ *vs* t in the presence of different complexes: (**B**) for *p*-nitrophenol and (**D**) *p*-ethylnitrobenzene. C (*p*-nitrophenol) = C (*p*-ethylnitrobenzene) = 0.1 mM, C ($NaBH_4$) = 5 mM, C (4–6) = 0.002 mM, 0.1% THF-H_2O, 21 °C, V = 2.5 mL, l = 10 mm.

As an example, Figure 3A,C shows changes in the UV-VIS spectra of a mixture of sodium borohydride and nitrobenzene derivatives after the addition of complex **5**. The absorption band of p-nitrophenol at 400 nm decreases and the absorption band of p-aminophenol at 300 nm appears. In the case of p-ethylnitrobenzene, the absorption band disappears at 290 nm and appears at 240 nm, which indicates the progress of the reaction. Due to the use of a 50-fold excess of $NaBH_4$, the reduction process is a pseudo-first-order reaction and is described by the equation $-k_t = \ln(C_t/C_0)$, where C_0 and C_t are the initial concentration of nitroarene and its concentration at time t, respectively. A linear time dependence of $\ln(C_t/C_0)$ is observed starting from ~400 s after the initial induction period of the reaction (Figure 3B,D). The rate constants and specific catalytic activity of the synthesized complexes are shown in Table 2. As in the cross-coupling reaction, the most effective

catalyst is **5**, where the bulkier ligand is more effective in stabilizing the resulting palladium particles. However, upon switching to the more hydrophobic p-ethylnitrobenzene, the difference between the complexes is erased and the activity decreases. This difference can be explained by the different orientations of the reagents: more hydrophobic p-ethylnitrobenzene can be absorbed by the hydrophobic cavity of the macrocycle, and thereby separated from the active palladium center. This conclusion can also be made by considering the rate constants of the reduction reactions of nitrobenzene derivatives in the presence of **6**, where its activity does not change when switching to a more hydrophobic substrate.

To demonstrate the preparative use of complex 5 in the reduction reaction of nitroarenes, the reduction products were isolated after the reaction was complete. The isolated yields of *p*-aminophenol and *p*-ethylaniline were found to be 81 and 83%, respectively.

3. Materials and Methods

Chemicals were purchased from commercial suppliers and used as received. The synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-dibromopropyloxy-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene **1** and N-(2′,6′-diisopropylphenyl)imidazole was performed according to the literature procedures [39,40].

5,11,17,23-Tetra-*tert*-butyl-25, 27-dihydroxy-26-oxido-28-(3-(3-N-methylimidazolium) propoxy)-2,8,14,20-tetrathiacalix[4]arene (**2**) was synthesized according to the previously published method [25].

^{1}H and ^{13}C NMR spectra, as well as 2D ^{1}H-^{1}H NOESY, were recorded on a Bruker Avance 400 Nanobay (Bruker Corporation, Billerica, MA, USA) with signals from residual protons of $CDCl_3$ as the internal standard.

The melting points were measured using an OIptimelt MPA100 melting point apparatus (Stanford Research Systems, Sunnyvale, CA, USA).

IR spectra in KBr pellets were recorded on a Bruker Vector-22 spectrometer (Bruker Corporation, MA, USA).

High-resolution mass spectra with electrospray ionization (HRESI MS) were obtained on an Agilent iFunnel 6550 Q-TOF LC/MS (Agilent Technologies, Santa Clara, CA, USA) in positive mode: carrier gas Cnitrogen, temperature 300 °C, carrier flow rate 12 L·min^{-1}, nebulizer pressure 275 kPa, funnel voltage 3500 V, capillary voltage 500 V, total ion current recording mode, 100–3000 m/z mass range, scanning speed 7 spectra·s^{-1}.

Data sets for single crystals **2** and **4** were collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocus X-ray tube using Cu Kα (1.54184 Å) radiation at a low temperature. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module was used for the analysis of systematic absences and space group determination. The structure was solved by direct methods using SHELXT [41] and refined using the full-matrix least-squares on F2 using SHELXL [42]. Non-hydrogen atoms were anisotropically refined. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The figures were generated using the Mercury 4.1 [43] program. Crystals were obtained using the slow evaporation method.

GCMS was performed on a GCMS-QP2010 Ultra gas chromatography-mass spectrometer (Shimadzu, Kyoto, Japan) equipped with an HP-5MS column (the internal diameter was 0.32 mm and the length was 30 m). The parameters were as follows: helium 99.995% purity was the carrier gas; the temperature of an injector was 250 °C; the flow rate through the column was 2 mL/min; the thermostat temperature program was a gradient temperature increase from 70 to 250 °C with a step of 10 °C/min. The range of scanned masses was m/z

35–400. The absolute calibration method using known quantities of haloarene was used for the quantitative analysis.

UV-vis spectra were recorded in a 1-cm quartz cuvette using a Shimadzu UV-2600 spectrophotometer equipped with a Shimadzu TCC-100 thermostat (Shimadzu Corporation, Kyoto, Japan).

Crystal data for **2**: $C_{94}H_{116}N_4O_8S_8$ (M = 1686.38 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 19.1157(2) Å, b = 14.1120(3) Å, c = 40.4978(6) Å, β = 96.7749(14)°, V = 10,848.4(3) Å^3, Z = 4, T = 100.00(10) K, μ(Cu Kα) = 1.896 mm^{-1}, *Dcalc* = 1.033 g/cm^3, 82183 reflections measured (4.394° ≤ 2Θ ≤ 152.436°), 21919 unique (R_{int} = 0.0644, R_{sigma} = 0.0569), which were used in all calculations. The final R_1 was 0.1015 (I > 2σ(I)) and wR_2 was 0.2886 (all data). CCDC refcode: 2276991.

5,11,17,23-Tetra-*tert*-butyl-25, 27-dihydroxy-26-oxido-28-(3-(3-N-(2′,6′ di-isopropyl phenyl)limidazolium)propoxy)-2,8,14,20-tetrathiacalix[4]arene (**3**)

An amount of 0.093 mmol of 5,11,17,23-tetra-*tert*-butyl-25,27-dibromopropyloxy-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene **1**, a 20-fold excess of N-substituted imidazole and 3 mL absolute acetonitrile were added into a glass autoclave. The reaction was carried at 130 °C for 30–50 h. For isolation, the reaction mixture was evaporated to dryness on a rotary evaporator and the final product was isolated by column chromatography on silica gel (eluent- ethanol). The yield was 81%. R_f 0.7 (ethanol). M.p. 170 °C. HR ESIMS: found m/z: 989.4451 $[M+H]^+$; calculated for $C_{58}H_{73}N_2O_4S_4^+$ 989.4448. IR (KBr) ν_{max} cm^{-1}: 1460 (C_{Ar}-O), 1562 (C=N), 2965 (C-H), 3388 (C_{Ar}-H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H, ppm: 1.22–1.48 m (48H, -C(CH_3)$_3$, CH_3), 2.22–2.29 m (2H, CH_2), 3.16–3.28 m (2H, CH), 5.00 br.t (4H, CH_2N+CH_2O), 7.03–7.59 m (11H, H_{Ar}), 8.66 br.s (2H, H_{Imd}), 10.01 s (1H, H_{Imd}). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C, ppm: 24.4, 28.8, 31.5, 32.9, 47.2, 58.6, 74.0, 123.4, 124.1, 124.1, 124.8, 124.8, 129.3, 130.2, 130.6, 131.7, 132.0, 134.0, 136.2, 137.6, 137.7, 139.2, 142.1, 142.5, 145.4, 145.5.

General methodology for the preparation of NHC-palladium complexes of the PEPPSI types **4** and **5**.

Amounts of 0.2 mmol of imidazolium salt **2** or **3** and 6 mL of absolute pyridine were added to a glass autoclave under vigorous stirring in an inert atmosphere. Then, 64 mmol $Pd(AcO)_2$, 78 mmol KI and 81 mmol K_2CO_3 were added. The reaction mixture was stirred at 40 °C for 1 h, and then at 80 °C for 50 h. For isolation, the reaction mixture was evaporated and dissolved in chloroform (20 mL). The resulting solution was passed through Celite® and evaporated to dryness using the rotary evaporator, yielding a dark orange precipitate. The product was reprecipitated from chloroform with hexane and further purified by column chromatography (eluent-ethyl acetate).

Trans-{5,11,17,23-tetra-*tert*-butyl-25, 26, 27-trihydroxy-28-(3-(3-N-methylimidazolin-2-ylidene)propoxy)-2,8,14,20-tetrathiacalix[4]arene }{pyridine} palladium(II) diiodide (**4**).

The yield was 60%. R_f 0.90 (ethyl acetate). M.P.$_{(decomp.)}$ 232 °C. HR ESIMS: found m/z 1075.1354 $[M-I-Py]^+$; calculated for $C_{47}H_{58}IN_2O_4PdS_4^+$ 1075.1354. IR (KBr) ν_{max} cm^{-1}: 2960 (CH_3), 1453 (C_{Ar}=C_{Ar}), 1260 (C_{Ar}-O). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H, ppm: 1.05–1.35 m (36H, -C(CH_3)$_3$), 3.19–3.24 m (2H, CH_2), 4.04 s (3H, CH_3), 4.36 t (2H, NCH_2, J = 5.6 Hz), 5.05 t (2H, NCH_2, J = 6.1 Hz), 6.98 br.t (1H, H_{Imd}), 7.36 t (2H, H_{Py}, J = 5.6 Hz), 7.61 br.t (2H, H_{Ar}), 7.64 br.s (2H, H_{Ar}), 7.65 br.s (2H, H_{Ar}), 7.68 br.d (2H, H_{Ar}), 7.74 t (1H, H_{Py}, J = 5.6 Hz), 7.94 br.d (1H, H_{Imd}), 9.11 d (2H, H_{Py}, J = 5.3 Hz), 9.40–9.43 br.s (3H, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C, ppm: 30.4, 31.2, 31.4, 31.5, 34.3, 34.4, 34.6, 39.59, 48.2, 75.1, 120.3, 120.8, 121.0, 122.8, 124.6, 125.4, 128.6, 136.3, 136.3, 137.2, 137.7, 144.0, 144.33, 144.7, 149.7, 154.0, 156.2, 156.8, 157.8. **Crystal Data** for **4**: $C_{53}H_{63}Cl_3I_2N_3O_4PdS_4$ (M = 1400.85 g/mol): triclinic, space group P-1 (no. 2), a = 13.3095(3) Å, b = 14.0556(3) Å, c = 19.7452(3) Å, α = 81.0478(15)°, β = 78.2544(15)°, γ = 67.9938(18)°, V = 3340.15(12) Å^3, Z = 2, T = 99.98(16) K, μ(Cu Kα) = 12.080 mm^{-1}, *Dcalc* = 1.393 g/cm^3, 44854 reflections measured (4.588° ≤ 2Θ ≤ 152.346°), 13422 unique (R_{int} = 0.0875, R_{sigma} = 0.0566), which were used in all calculations. The final R_1 was 0.0779 (I > 2σ(I)) and wR_2 was 0.2244 (all data). CCDC refcode: 2276992.

Trans-{5,11,17,23-tetra-*tert*-butyl-25, 26, 27-trihydroxy-28-(3-(3-N-(2′,6′ di-isopropylphenyl) imidazolin-2-ylidene)propoxy)-2,8,14,20-tetrathiacalix[4]arene}{pyridine} palladium(II) diiodide (**5**).

The yield was 40%. R_f 0.81 (ethyl acetate). $M.P_{.(decomp.)}$ 202 °C. HR ESIMS: found *m*/*z* 1221.2458 $[M\text{-}I\text{-}Py]^+$; calculated for $C_{58}H_{72}IN_2O_4PdS_4^+$ 1221.2449. IR (KBr) ν_{max} cm^{-1}: 2922 (CH_3), 1445 (C_{Ar}=C_{Ar}), 1268 (C_{Ar}-O). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H, ppm: 0.83–1.62 $_M$ (48H, -C(CH_3)$_3$, CH_3), 3.06–3.24 $_M$ (4H, CH_2+OCH_2), 3.47–3.49 $_M$ (2H, CH), 4.97 br.t (2H, NCH_2), 7.03 br.d (1H, H_{Imd}), 7.21–7.26 m (5H, H_{Ar}), 7.33 br.s (2H, H_{Ar}), 7.35 br.s (4H, H_{Ar}), 7.48 br.d (1H, H_{Imd}), 7.51 br.t (1H, H_{Py}), 7.65 br.t (2H, H_{Py}), 8.77 d (2H, H_{Py}, *J* = 5.3 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C, ppm: 24.0, 26.8, 29.1, 29.8, 29.9, 31.4, 50.8, 77.2, 121.6, 124.0, 124.2, 124.4, 127.2, 128.9, 130.6, 131.0, 134.6, 136.2, 136.4, 136.5, 137.5, 143.1, 143.8, 147.1, 149.7, 153.7, 155.5.

To perform the Suzuki-Miyaura reaction, in a 2 mL vial equipped with a septum and stirrer bar haloarene (C = 100 mM), phenylboronic acid (C = 120 mM) and K_2CO_3 (C = 200 mM) were added into DMF or water-DMF mixture (0.5 mL) followed by 1 mM of the catalyst. The solution was purged with nitrogen through a septum. The reaction was heated on a hot plate at 85 °C for 21 h and then analyzed using GCMS. After cooling to room temperature, the reaction mixture was extracted with hexane (3 × 5 mL) in the presence of brine. The combined organic layer was concentrated in vacuo and the residue was purified using flash chromatography on silica gel with hexane/ethyl acetate (4/1) as eluent to afford target compounds (Table 1).

To perform the model reduction reaction, 0.002 mM of **4**–**6** in THF (2.8 mkL) and nitroarene (C = 0.1 mM, V = 2.5 mL)was added in a quartz cuvette (l = 1 cm). Then, $NaBH_4$ (C = 5 mM) was added and the reaction was monitored using a spectrophotometer. To isolate the aminoarenes after reduction in the presence of **5**, the reactions were carried out in a similar manner with the use of 15 mL of the reaction mixture. The reaction mixture was extracted with hexane (3 × 15 mL) in the presence of brine after the completion of the reaction (UV-vis control). The combined organic layers were concentrated under a vacuum to afford *p*-ethylaniline and *p*-aminophenol as a brine-yellow liquid (0.15 mg, 83%) and solid (0.13 mg, 81%), respectively. Structure conformity was assessed by GCMS from the NIST database (NIST # 228771 for *p*-ethylaniline and # 228504 for *p*-aminophenol).

4. Conclusions

Pd(II) NHC complexes of the PEPPSI type based on imidazolium derivatives of *p*-*tert*-butylthiacalix[4]arene in the cone stereoisomeric form were synthesized for the first time. The catalytic activity of NHC PEPPSI type Pd(II) complexes in model Suzuki-Miyaura cross-coupling and the reduction reactions of nitrobenzene derivatives were studied. As a result, it was found that macrocycle with a bulky 2′,6′ di-isopropylphenyl fragment was not inferior and, in some cases, was superior to the activity of the known Organ's PEPPSI complex and presented 15–20% more selectivity in Suzuki-Miyaura coupling and was four times superior to the latter in *p*-nitrophenol reduction reaction. Given that the structure of the macrocyclic complex contains free phenolic hydroxyl groups that can be used for further functionalization, including covalent attachment of the complex to the carrier, this complex seems very promising for further studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11080326/s1, Figure S1: ORTEP representation of **2** showing 50% probability thermal ellipsoids. C atoms—grey, N atoms—blue, O atoms—red, S atoms—yellow; Figure S2: NMR ^{1}H (**a**), ^{13}C (**b**), FT IR (**c**), HR ESIMS (**d**) and NOESY (^{1}H-^{1}H) NMR spectra (**e**) of 5,11,17,23-tetra-*tert*-butyl-25, 27-dihydroxy-26-oxido-28-(3-(3-N-(2′,6′ di-*iso*propylphenyl)limidazolium)propoxy) -2,8,14,20-tetrathiacalix[4]arene (**3**); Figure S3: NMR ^{1}H (**a**), ^{13}C (**b**), FT IR (**c**), HR ESIMS (**d**) and NOESY (^{1}H-^{1}H) NMR spectra (**e**) of trans-{5,11,17,23-tetra-*tert*-butyl-25, 26, 27-trihydroxy-28-(3-(3-N-methylimidazolin-2-ylidene)propoxy)-2,8,14,20-tetrathiacalix[4]arene}{pyridine} palladium(II) diiodide (**4**); Figure S4: NMR ^{1}H (**a**), ^{13}C (**b**), FT IR (**c**), HR ESIMS (**d**) and HSQC (^{1}H-^{13}C) spectra (**e**) of

trans-{5,11,17,23-tetra-*tert*-butyl-25, 26, 27-trihydroxy-28-(3-(3-N-(2′,6′ di-isopropylphenyl)imidazolin-2-ylidene)propoxy)-2,8,14,20-tetrathiacalix[4]arene}{pyri-dine} palladium(II) diiodide (**5**).

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