

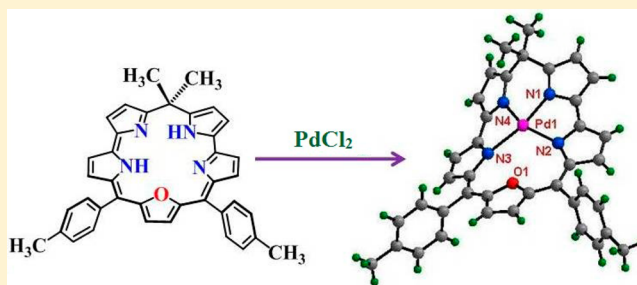
# Synthesis, Structure, and Catalytic Activity of Pd(II) Complex of Calixoxasmaragdyrin

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## Supporting Information

**ABSTRACT:** The palladium(II) complex of calixoxasmaragdyrin was prepared in 80% yield by treating the free base calixoxasmaragdyrin with PdCl<sub>2</sub> in CH<sub>3</sub>CN at reflux temperature. The crystal structure solved for Pd(II) calixoxasmaragdyrin indicates that the calixoxasmaragdyrin macrocycle is highly distorted and attained a boat shaped structure. The Pd(II) ion is coordinated to four pyrrolic nitrogens in square planar fashion, and it is placed at ~0.138 Å above from the four coordinating pyrrole nitrogens plane (N1N2N3N4). The Pd–N bond lengths are inequivalent, and the Pd(II) ion is positioned more toward the dipyrromethane moiety of calixoxasmaragdyrin. The complex shows one broad absorption band at 477 nm and is not very stable under redox conditions. The Pd(II) calixoxasmaragdyrin showed good catalytic activity in the Suzuki–Miyaura cross coupling reactions.



## INTRODUCTION

Expanded porphyrins are macrocyclic compounds containing more than four heterocyclic rings such as pyrrole, thiophene, furan, etc. linked together either directly or through spacers and containing a larger internal cavity as compared to the cavity present in tetrapyrrolic macrocycles.<sup>1</sup> The expanded porphyrins are expected to show porphyrin like coordination chemistry because of their large internal cavity and greater number of coordinating atoms.<sup>2</sup> However, the investigations carried out over the years revealed that the expanded macrocycles cannot form metal complexes easily like porphyrins. Thus, metal coordination chemistry of expanded porphyrins and their derivatives is still an unexplored area. The immediate congeners of tetrapyrrolic porphyrins are pentapyrrolic macrocycles. Among all pentapyrrolic systems, sapphyrins<sup>3</sup> (having only one direct pyrrole–pyrrole linkage) and smaragdyrins<sup>4</sup> (having two direct pyrrole–pyrrole linkages) are of special interest because of novel electronic and cation/anion sensing properties. Seesler and Tomat,<sup>5</sup> Chandrashekar et al.,<sup>6</sup> and other research groups<sup>7</sup> have developed several methods for preparing core modified sapphyrins and their metal complexes (Chart 1), but the reports on metallo-smaragdyrins (Chart 1) are very few, which is attributed mainly because of their inherent instability.<sup>4a</sup> Chandrashekar and co-workers<sup>8</sup> isolated the rhodium(I) complex of oxasmaragdyrin where the Rh(I) is coordinated in an  $\eta^2$  fashion with two nitrogen atoms of the dipyrromethane moiety of smaragdyrin, and this is the only metallo-smaragdyrin structure reported in the literature. We recently reported the synthesis of calixoxasmaragdyrins<sup>9</sup> **3**, which are stable macrocycles containing four pyrrole rings and one furan ring connected via two  $sp^2$  and one  $sp^3$  *meso*-carbons (Chart 1). Our studies revealed that the calixoxasmaragdyrin **3** can be used as specific

sensors for the HSO<sub>4</sub><sup>−</sup> ion.<sup>9</sup> Since the macrocycle is flexible and contains four donor nitrogens with two ionizable protons like porphyrins, we anticipated that the calixoxasmaragdyrin can be used to form transition metal complexes readily. We tested the metal coordination chemistry of the calixoxasmaragdyrin **3** with various transition metal salts, but our efforts remained unsuccessful for a long period. In this paper, we report our successful synthesis of the Pd(II) complex of calixoxasmaragdyrin **Pd3** by treating the macrocycle with PdCl<sub>2</sub> in CH<sub>3</sub>CN at reflux temperature. Under same reaction conditions, the other transition metal salts including Ni(II) and Pt(II) salts did not form a metal complex with calixoxasmaragdyrin. The **Pd3** is stable and freely soluble in common organic solvents. The crystal structure of **Pd3** revealed that Pd(II) is coordinated with four pyrrolic nitrogens in square planar fashion, and the overall complex is significantly distorted compared to free base calixoxasmaragdyrin **3**. Furthermore, **Pd3** shows efficient catalytic behavior in Suzuki–Miyura coupling of aryl bromides with aryl boronic acids.

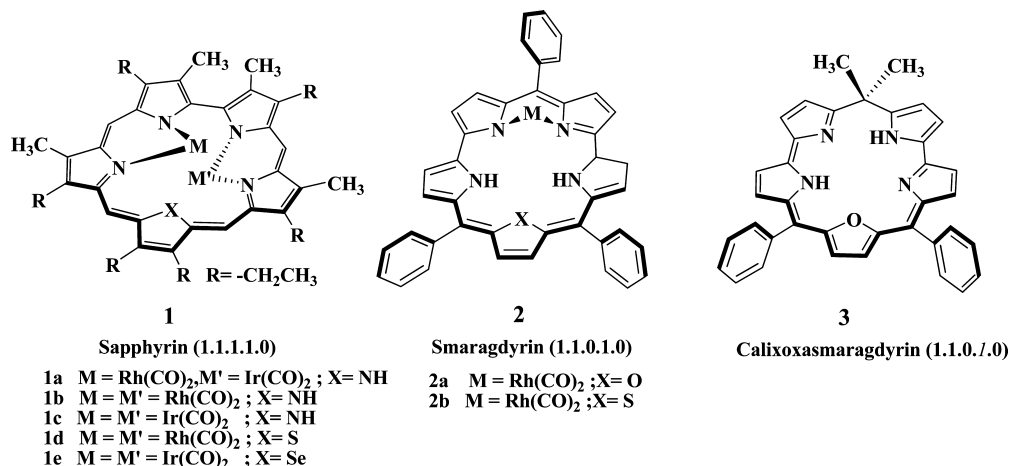
## RESULT AND DISCUSSION

The required calixoxasmaragdyrin **3** was synthesized by condensing one equivalent of dipyrromethane<sup>10</sup> **4** with one equivalent of 16-oxatripyrrane<sup>11</sup> **5** under mild acid catalyzed conditions as reported earlier<sup>9</sup> (Scheme 1). The Pd(II) insertion into the calixoxasmaragdyrin **3** was carried out by reacting **3** with 1.5 equiv of PdCl<sub>2</sub> in CH<sub>3</sub>CN in the presence of excess K<sub>2</sub>CO<sub>3</sub> at reflux temperature (Scheme 1). The progress of the reaction was indicated by a clear color change of the reaction mixture from

Received: July 4, 2014

Published: September 17, 2014

Chart 1. Molecular Structures of Reported Metallosapphyrins, Metallosmaragdyrins, and Calixoxasmaragdyrin



Scheme 1. Synthesis of Pd(II) Calixoxasmaragdyrin Pd3

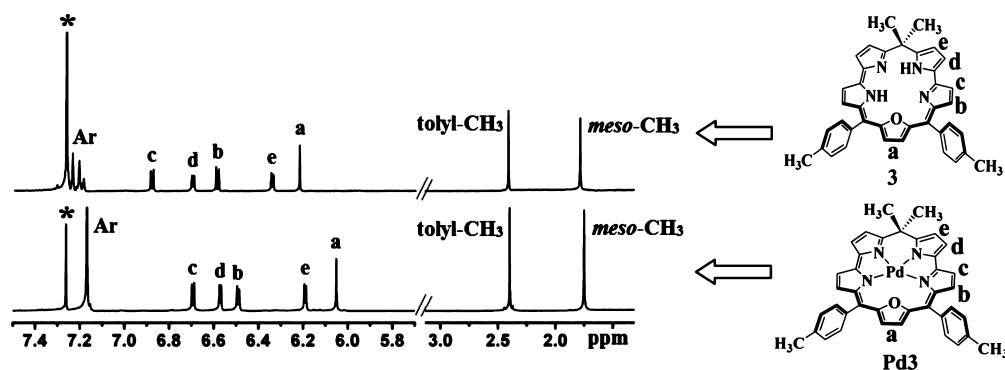
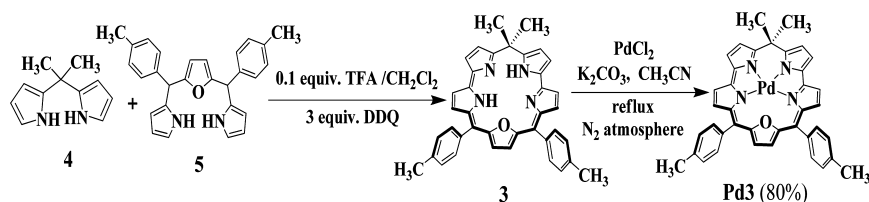


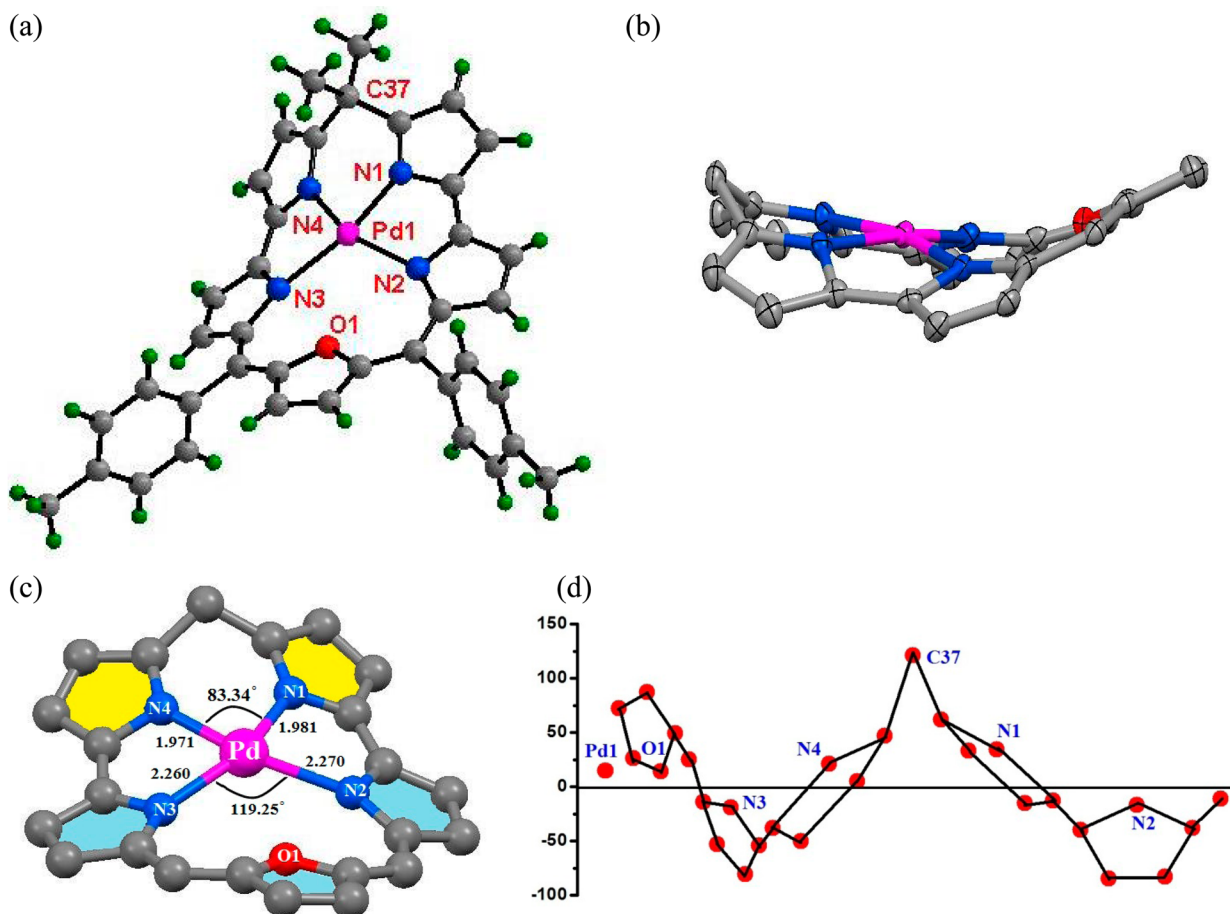
Figure 1. Comparison of partial <sup>1</sup>H NMR spectra of Pd(II) calixoxasmaragdyrin (Pd3) and calixoxasmaragdyrin (3) recorded in CDCl<sub>3</sub> (\* residual solvent peak) at room temperature.

green to orange. TLC analysis also showed the disappearance of the spot corresponding to 3 with an appearance of a new polar spot corresponding to the desired Pd3. Column chromatography on basic alumina afforded the pure Pd3 as a brownish solid in 80% yield.

The formation of Pd3 was confirmed by HR-MS (Supporting Information S1) and detailed 1D and 2D NMR. The comparison of <sup>1</sup>H NMR spectra of Pd3 with free base calixoxasmaragdyrin 3 is shown in Figure 1. The resonances of 3 were identified and assigned using 1D and 2D NMR spectroscopy as described earlier.<sup>9</sup> Compound 3 exhibits four sets of doublets for eight β-pyrrole protons in the 6.32–6.86 ppm region and one singlet for two β-furan protons at 6.22 ppm. The signals for inner pyrrole NH protons of 3 were not observed at room temperature due to rapid tautomerism. However, when we recorded the <sup>1</sup>H NMR spectra of compound 3 at –20 °C, we observed a sharp signal at 5.14 ppm due to inner pyrrole NH protons.<sup>9</sup> The <sup>1</sup>H NMR spectrum of Pd3 showed similar features like 3 with slight upfield shifts, as evident from Figure 1. The eight β-pyrrole protons

appeared as four sets of doublets at 6.68, 6.56, 6.48, and 6.18 ppm, which were identified based on the NMR spectrum of 3, coupling constants, and proton-to-proton correlation in the COSY NMR (Supporting Information S3). The β-pyrrole protons were slightly upfield shifted in Pd3 compared to 3, indicating that the Pd(II) complexation of calixoxasmaragdyrin alters the electronic properties of the macrocycle. The two β-furan protons in Pd3 appeared as a singlet at 6.05 ppm, which was slightly upfield shifted compared to 3. Furthermore, the meso-aryl protons in Pd3 appeared as a broad signal at 7.16 ppm, and the six meso-methyl protons appeared as a singlet at 1.75 ppm. Thus, the Pd(II) complexation of calixoxasmaragdyrin did not influence significantly the chemical shifts of various protons of the calixoxasmaragdyrin macrocycle.

**Crystallographic Characterization of Compound Pd3.** Further conclusive proof of the structural identity of the palladium(II) complex of calixoxasmaragdyrin Pd3 was obtained from the X-ray crystal structure. The orange crystals of compound Pd3 were grown via slow evaporation of *n*-hexane into a chloroform solution of Pd3 at room temperature over a period of 2 days. The crystal



**Figure 2.** (a) Perspective view of compound **Pd3**. Thermal ellipsoids are drawn in 50% probability. (b) Side view of compound **Pd3** (*meso*-tolyl groups and hydrogen atoms are omitted for clarity) and (c) representing the coordination features of the central Pd(II) ion in compound **Pd3**. (d) Diagram showing out-of-plane displacements (in units of 0.01 Å) of the Pd(II) calixoxasmaragdyrin core atoms from the mean plane consisted of C<sub>23</sub>N<sub>4</sub>OPd atoms.

structure of **Pd3** is shown in Figure 2 (CCDC No. 987564). Compound **Pd3** crystallized in the monoclinic crystal system with space group *P*<sub>21</sub>/*n*. The crystallographic data and data collection parameters are given in Table 1, while the relevant bond lengths and bond angles of **Pd3** are summarized in Table 2. The solid state structure of the Pd(II) complex of calixoxasmaragdyrin revealed that the Pd(II) metal ion is approximately in square planar geometry and coordinated to the four pyrrole nitrogens and the furan oxygen is not involved in bonding (Figure 2a). The mode of metal complexation is new for the smaragdyrins family, and to best of our knowledge, this is the first crystal structure of metallo-oxasmaragdyrin where the metal is forming a square planar complex with an NNNN coordination environment. Furthermore, the Pd(II) ion in **Pd3** is placed at ~0.161 Å slightly above from the mean plane of the macrocycle (28 atoms) defined by the five heterocyclic rings and three *meso*-carbons, whereas it is placed at ~0.138 Å above from the four coordinating pyrrole nitrogens plane (N1N2N3N4). The Pd–N bond lengths are inequivalent. The distances between the two pyrrole nitrogen atoms of the dipyrromethane moiety and Pd(II) (Pd1–N1 = 1.981 Å; Pd1–N4 = 1.971 Å) are shorter than the distances between the Pd(II) ion with other two pyrrole nitrogen atoms of the tripyrrane moiety (Pd1–N2 = 2.270 Å; Pd1–N3 = 2.260 Å). The average Pd–N bond distances observed for **Pd3** are similar to those of other reported Pd(II) expanded porphyrin complexes<sup>12</sup> (~2.002 Å).

**Table 1. Crystal Data and Data Collection Parameters for Compound Pd3**

parameters	Pd3
mol formula	C <sub>30</sub> H <sub>30</sub> N <sub>4</sub> OPd
formula weight	677.07
crystal system	monoclinic
space group	<i>P</i> <sub>21</sub> / <i>n</i>
temp (K)	100(2)
<i>a</i> (Å)	11.352(4)
<i>b</i> (Å)	10.914(4)
<i>c</i> (Å)	24.893(9)
$\alpha$ (deg)	90
$\beta$ (deg)	90.047(5)
$\gamma$ (deg)	90
<i>V</i> (Å <sup>3</sup> )	3084.1(19)
<i>Z</i>	4
$\mu$ (mm <sup>-1</sup> )	0.640
<i>d</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.458
F(000)	1384
2 $\theta$ range (deg)	3.0–29.1
independent reflection	8280
R1, WR2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0705, 0.1171
R1, WR2 (all data)	0.0831, 0.1227
GOF	1.157
largest diff. peak/hole, (e/ Å <sup>3</sup> )	0.83, –1.24

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compound Pd3

parameters	bond length [Å]	parameters	bond angle [deg]
Pd1–N1	1.981	N1–Pd1–N4	83.34
Pd1–N2	2.270	N1–Pd1–N2	78.31
Pd1–N3	2.260	N1–Pd1–N3	161.05
Pd1–N4	1.971	N2–Pd1–N3	119.25
		N2–Pd1–N4	159.77
		N3–Pd1–N4	78.16

The N–Pd–N bond angles are also not equal and ranging from 78° to 161° (Table 2). This feature clearly reflects that the Pd(II) ion is not positioned at the middle of the macrocycle cavity but positioned slightly more toward the dipyrromethane side, and the Pd(II) ion is at the middle of all coordinated pyrrole nitrogen atoms (Figure 2c). The calixoxasmaragdyrin ring of the Pd3 is highly distorted as depicted in Figure 2d, where the out of plane displacements in units of 0.01 Å of calixoxasmaragdyrin core atoms are compared. The Pd(II) ion, furan ring, and sp<sup>3</sup> meso-carbon (C37) are deviated above from the least-squares plane of the 28 smaragdyrin core atoms. The two pyrrole rings are completely moved below the least-squares plane, while four nitrogen atoms and two sp<sup>2</sup> meso-carbons are placed near the mean plane.

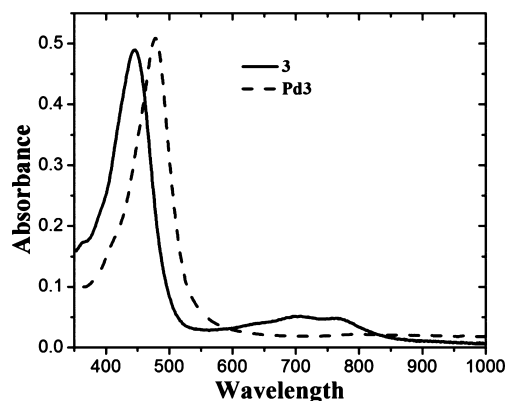
Furthermore, for a better understanding of the effect of metalation on the macrocyclic core of calixoxasmaragdyrin, we compared the crystal structure of compound Pd3 with the structure of its free base 3 (Table 3). Both macrocycles were distorted to a different magnitude. However, the macrocycle in Pd3 is less planar compared to its free base 3. In Pd3, since the Pd(II) ion is coordinated to the four pyrrole nitrogen atoms in almost square planar fashion, the metal ion is located at one end of the macrocyclic cavity, which forces all four pyrrole nitrogen atoms to remain in the same plane and impose extra strain in the macrocyclic skeleton. As a result, the furan ring along with two sp<sup>2</sup> meso-carbons of the macrocycle becomes far bent compared to its free base 3 (the distance of furan oxygen from the mean plane: (3: ~0.094 Å); (Pd3: ~0.146 Å)). The furan oxygen atom also experiences more deviation after metalation from the four coordinating pyrrole nitrogen plane (N1N2N3N4). It is placed at ~0.717 Å far from the four atom mean plane (N1N2N3N4) in Pd3, whereas it is deviated to an extent of ~0.338 Å in the case of 3. Furthermore, the flexible sp<sup>3</sup> meso-carbon center belonging to the dipyrromethane moiety in Pd3 also significantly deviated to 1.223 Å (only 0.833 Å in case of compound 3) to the same side of furan ring. The dihedral angles observed between the two meso-tolyl groups and the mean planes of the macrocycle are 73° and 80°. This indicates that the meso-tolyl groups are almost perpendicular to the plane of the macrocycle. Thus, on complexation with the Pd(II) ion, the overall smaragdyrin macrocycle becomes more distorted compared to its free base and attains a boat shaped structure (Figure 2b).

**Absorption and Electrochemical Properties.** The absorption properties of the Pd(II) complex of calixoxasmaragdyrin Pd3 is studied and compared with its free base 3. The comparison of absorption spectra of Pd3 and 3 is presented in Figure 3. Compound 3 exhibits two ill-defined Q-bands at 698 and 766 nm and a broad Soret band at 443 nm. However, after complexation with the Pd(II) ion, the calixoxasmaragdyrin showed a clear change from green to orange and exhibited only one band at 477 nm. The electrochemical properties of Pd3 were investigated by cyclic voltammetry and differential pulse voltammetry using tetrabutyl ammonium perchlorate as a

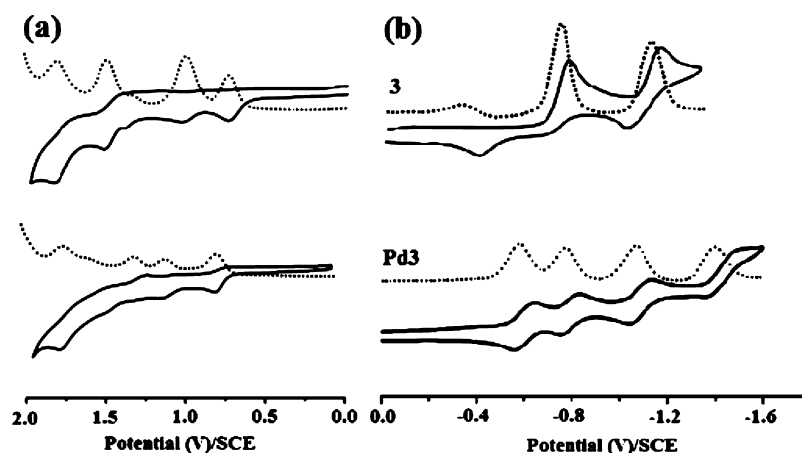
**Table 3.** Some Selected Crystal Structure Parameters for 3 and Pd3

parameters	Pd3	3
$\Delta_{28}^{Pd a}$	0.161	
$\Delta_{28}^{O b}$	0.146	0.094
$\Delta_{28}^{N1 c}$	0.355	0.415
$\Delta_{28}^{N2 d}$	0.170	0.009
$\Delta_{28}^{N3 e}$	0.189	0.029
$\Delta_{28}^{N4 f}$	0.226	0.316
$\Delta_4^{Pd g}$	0.138	
$\Delta_4^{N1 h}$	0.040	0.038
$\Delta_4^{N2 i}$	0.027	0.024
$\Delta_4^{N3 j}$	0.027	0.024
$\Delta_4^{N4 k}$	0.040	0.039
$\Delta_4^{O l}$	0.717	0.338
$\Delta_{28}^{C37 m}$	1.222	0.833

<sup>a</sup>Displacement (Å) of palladium from the 28-atom mean plane of the smaragdyrin core. <sup>b</sup>Displacement (Å) of heteroatom (O) from the 28-atom mean plane of the smaragdyrin core. <sup>c</sup>Displacement (Å) of N1 from the 28-atom mean plane of the smaragdyrin core. <sup>d</sup>Displacement (Å) of N2 from the 28-atom mean plane of the smaragdyrin core. <sup>e</sup>Displacement (Å) of N3 from the 28-atom mean plane of the smaragdyrin core. <sup>f</sup>Displacement (Å) of N4 from the 28-atom mean plane of the smaragdyrin core. <sup>g</sup>Displacement (Å) of palladium from the mean plane of four coordinated atoms of smaragdyrin core. <sup>h</sup>Displacement (Å) of N1 from the mean plane of four coordinated atoms of smaragdyrin core. <sup>i</sup>Displacement (Å) of N2 from the mean plane of four coordinated atoms of smaragdyrin core. <sup>j</sup>Displacement (Å) of N3 from the mean plane of four coordinated atoms of smaragdyrin core. <sup>k</sup>Displacement (Å) of N4 from the mean plane of four coordinated atoms of smaragdyrin core. <sup>l</sup>Displacement (Å) of O from the mean plane of four coordinated atoms of smaragdyrin core. <sup>m</sup>Displacement (Å) of C37 from the 28-atom mean plane of the smaragdyrin core.

**Figure 3.** Comparison of absorption spectra of compound Pd3 ( $1 \times 10^{-6}$  M) (dotted line) and 3 ( $1 \times 10^{-6}$  M) (solid line) recorded in CHCl<sub>3</sub> solvent at room temperature.

supporting electrolyte (0.1 M) and saturated calomel electrode (SCE) as a supporting electrode in dichloromethane as the solvent. The comparison of reduction waves of Pd3 with 3 is shown in Figure 4. The free base calixoxasmaragdyrin 3 shows three macrocycle based irreversible reductions at –0.24 V, –0.69 V, and –1.12 V and four irreversible oxidations at 0.66 V, 0.89 V, 1.36 V, and 1.61 V. The Pd(II) complex Pd3 also showed four macrocycle based irreversible reductions at –0.57 V, –0.76 V, –1.06 V, and –1.39 V and four irreversible oxidations at 0.76 V, 1.08 V, 1.28 V, and 1.74 V. However, compared to 3, the Pd3



**Figure 4.** Comparison of (a) oxidation waves and (b) reduction waves of cyclic voltammogram along with differential pulse voltammograms (dotted line) of compounds **3** and **Pd3** recorded in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP as a supporting electrolyte and saturated calomel electrode (SCE) as a reference electrode at scan rates of  $50 \text{ mVs}^{-1}$ .

**Table 4.** Suzuki–Miyaura Reactions of Phenylboronic Acid with Various Aryl Bromides<sup>a</sup>, Reaction Yields, and TONs

$\text{Ar-Br} + \text{C}_6\text{H}_5\text{-B(OH)}_2 \xrightarrow[\text{K}_2\text{CO}_3, \text{Toluene}, 80^\circ\text{C}, 3 \text{ h}]{\text{Cat. Pd3 (0.05 mol\%)}} \text{C}_6\text{H}_5\text{-Ar}$				
Entry	Aryl halide	Product	GC yield%	TON <sup>b</sup>
1			83%	1660
2			82%	1640
3			85%	1700
4			82%	1640
5			71%	1420
6			81%	1620
7			83%	1660
8			80%	1600
9			81%	1620
10			75%	1500

<sup>a</sup>Reactions are carried out in a sealed tube, using 0.05 mmol of aryl bromide, 0.06 mmol of phenyl boronic acid, 0.075 mmol of  $\text{K}_2\text{CO}_3$ , 0.05 mol % **Pd3** in 2 mL of solvent. <sup>b</sup>Yield are calculated by GC using *n*-decane as standard and TON are calculated from GC yield.

appears to be difficult to oxidize and reduce and not very stable under redox conditions.

**Catalytic Activity of Pd3.** The palladium catalyzed Suzuki–Miyaura cross coupling reaction is one of the best and versatile

ways to make aryl–aryl bond formation involving aryl halides with aryl boronic acids. This coupling reaction has been widely used in the synthesis of pharmaceuticals, conducting polymers, medicine, optical materials, and ligands for catalysis.<sup>13</sup> It is well

Table 5. Suzuki–Miyaura Reactions of Bromobenzene with Various Arylboronic Acid Derivatives<sup>a</sup>, Reaction Yields, and TONs

Entry	Aryl boronic acid	Product	GC yield%	TON <sup>b</sup>
1			83%	1660
2			82%	1640
3			85%	1700
4			82%	1640
5			71%	1420

<sup>a</sup>Reactions are carried out in a sealed tube, using 0.05 mmol of aryl bromide, 0.06 mmol of phenyl boronic acid, 0.075 mmol of K<sub>2</sub>CO<sub>3</sub>, 0.05 mol % Pd3 in 2 mL of solvent. <sup>b</sup>Yield are calculated by GC using *n*-decane as standard and TON are calculated from GC yield.

established that metalloporphyrins<sup>14</sup> and metallocorroles<sup>15</sup> can be used as catalysts for various organic transformations. Recently, some Pd(II) complexes of porphyrins and related macrocycles have been used for catalysts for various coupling reactions.<sup>16</sup> As we have synthesized the first stable Pd(II) complex of calixoxasmaragdyrin, we investigated the catalytic activity of the Pd3 and employed it in the Suzuki–Miyaura cross-coupling reactions. To best of our knowledge, this is first report where we attempt to examine the catalytic activity of a metalloexpanded calixphyrin.

The coupling reactions were performed in toluene by coupling 1 equiv of different substituted bromoarels with 1.2 equiv of phenyl boronic acid in the presence of 0.05 mol % of Pd3 and 1.5 equiv of K<sub>2</sub>CO<sub>3</sub> at 90 °C for 3 h. We observed moderate yields of coupled products ranging from 70 to 85% for different substituted bromoarels with phenyl boronic acid (Table 4). Our studies indicate that the Pd3 could catalyze the range of substituted bromoarels that includes heteroaromatics, electron donating, electron withdrawing, and sterically crowded bromoarels efficiently (Table 4). Furthermore, in order to establish the versatility of the Pd3, different aryl boronic acids were coupled with 4-bromobenzene (Table 5) and our results clearly indicate that Pd3 is a promising catalyst for Suzuki–Miyaura coupling reaction. Although the mechanism is unclear at the present, we tested the stability of Pd3 in coupling reactions by recording the absorption and ESI-MS mass spectrum of Pd3 before and after the coupling reaction (Supporting Information, S5 and S6). We noted some amount of degradation (~15–20%) of Pd3 in coupling reactions, but compound Pd3 is largely intact in the reaction supporting the participation of Pd3 in the coupling reactions. Thus, our preliminary studies are promising, but detailed studies are required to establish the catalytic activity of Pd3 for various coupling reactions.

## CONCLUSIONS

In summary, we successfully prepared the stable Pd(II) complex of calixoxasmaragdyrin Pd3 in decent yield by treating the calixoxasmaragdyrin with PdCl<sub>2</sub> in acetonitrile under reflux conditions. The X-ray structure revealed that the Pd(II) ion is located at one end of the macrocyclic cavity and coordinated with four pyrrole nitrogens in square planar fashion. Upon metalation, the calixoxasmaragdyrin macrocycle becomes further distorted and

thereby attains a boat shaped structure. The absorption spectrum of Pd3 showed only one broad band at 477 nm unlike its free base, which showed two ill-defined Q-type bands and one broad Soret-type band. The Pd3 is not very stable under redox conditions like its free base calixoxasmaragdyrin. Our preliminary studies indicate that Pd3 is a promising catalyst for the Suzuki–Miyaura coupling reaction between bromoarels and aryl boronic acids.

## EXPERIMENTAL SECTION

**General.** The known compounds such as dipyrromethane<sup>10</sup> 4, 16-oxatripyrrane<sup>11</sup> 5, and calixoxasmaragdyrin<sup>9</sup> 3 were synthesized by following the literature methods. The <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using tetramethylsilane (Si(CH<sub>3</sub>)<sub>4</sub>) as an internal standard. The HR-MS spectra were recorded with a Q-ToF micromass spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were carried out with a BAS electrochemical system by utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. GC analyses were performed using an Agilent Gas Chromatograph 7890 series, equipped with a Hewlett-Packard HP5-MS capillary column (30 m × 0.25 mm × 0.25 μm) and an FID detector.

**X-ray Crystal Structure Analysis.** Single-crystal X-ray structure analysis was performed on a Rigaku Saturn724 diffractometer that was equipped with a low-temperature attachment. Data were collected at 100 K using graphite-monochromated Mo Kα radiation (λ<sub>a</sub> = 0.71073 Å) with the ω-scan technique. The data were reduced by using CrystalClear-SM Expert 2.1 b24 software. The structures were solved by direct methods and refined by least-squares against F<sup>2</sup> utilizing the software packages SHELXL-97,<sup>17</sup> SIR-92,<sup>18</sup> and WINGX.<sup>19</sup> All non-hydrogen atoms were refined anisotropically.

**Synthesis of Compounds Pd3.** Samples of PdCl<sub>2</sub> (10 mg, 0.056 mmol) and K<sub>2</sub>CO<sub>3</sub> (25 mg, 0.181 mmol) were added to a solution of calixoxasmaragdyrin 3 (20 mg, 0.034 mmol) in 20 mL of acetonitrile in one portion, and the resulting mixture was refluxed for 2 h. The green color of the solution gradually changed to an orange color as the reaction progressed. The progress of the reaction was monitored by TLC analysis and absorption spectroscopy. After completion of the reaction as judged by the disappearance of the spot corresponding to free base calixoxasmaragdyrin and the appearance of a new spot corresponding to metalated calixoxasmaragdyrin on TLC, the solvent was removed completely under reduced pressure. The crude solid was subjected to

flash basic alumina column chromatography, and the fast moving orange-brownish color band of the desired compound **Pd3** was collected by using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:1) solvent mixture as an eluent. The solvent was removed on a rotary evaporator and afforded a dark brownish solid. The compound was recrystallized from the CHCl<sub>3</sub>/*n*-hexane mixture and afforded pure compound **Pd3** as brownish solid in 80% yield (~19 mg, 0.028 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.16 (br, 8H, Ar), 6.68 (d, 2H, *J* (H,H) = 4.9 Hz, β-pyrrole H, type c), 6.56 (d, 2H, *J* (H,H) = 4.0 Hz, β-pyrrole H, type d), 6.48 (d, 2H, *J* (H,H) = 4.9 Hz, β-pyrrole H, type b), 6.18 (d, 2H, *J* (H,H) = 4.0 Hz, β-pyrrole H, type e), 6.05 (s, 2H, β-furan H, type a), 2.39 (s, 6H, CH<sub>3</sub> tolyl), 1.79 (s, 6H, CH<sub>3</sub>), ppm. <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 168.56, 158.41, 153.48, 152.14, 140.71, 138.67, 136.18, 136.07, 131.69, 128.71, 124.73, 122.87, 121.67, 116.43, 110.25, 39.87, 31.39, 21.49 ppm. UV-vis (λ<sub>max</sub> nm (log ε), CH<sub>2</sub>Cl<sub>2</sub>): 477 (5.70), HR-MS calcd for C<sub>39</sub>H<sub>30</sub>N<sub>4</sub>OPdNa (M+Na)<sup>+</sup>: *m/z* 699.1361. Observed: 699.1361. Calcd for C<sub>39</sub>H<sub>30</sub>N<sub>4</sub>OPd: C, 69.18; H, 4.47; N, 8.27. Found: C, 69.20; H, 4.48; N, 8.31.

CCDC 987564 (for **Pd3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**General Procedure for the Cross-Coupling Reaction.** A clean, oven-dried screw-cap reaction tube with a previously placed magnetic stir-bar was charged with phenyl boronic acid (7.26 mg, 0.06 mmol), bromobenzene (7.85 mg, 0.05 mmol), K<sub>2</sub>CO<sub>3</sub> (10.35 mg, 0.075 mmol), and an appropriate amount of **Pd3** solution (0.05 mol %) in 2 mL of toluene. The correct amount of catalyst was added as a toluene solution made up by multiple volumetric dilutions of the stock solution of **Pd3**. The reaction mixture was heated at 90 °C for 3 h to obtain bi-aryl cross-coupled products. The substrate scope with different aryl bromides and different boronic acids was also tested using the same procedure as above. The GC yields based on products were determined by GC using *n*-decane as an internal standard, and products were confirmed by GC-MS.

## ■ ASSOCIATED CONTENT

### Supporting Information

Characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

M.R. thanks Department of Science and Technology, Govt. of India for funding, and T.C. thanks CSIR for a fellowship.

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