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Synthesis and characterization of cationic cyclopalladated complexes derived from *p*-*tert*-butyl-calix[4]arene bisphosphite with nitrogen donors

Pathik Maji

Dept. of Inorganic and Physical Chemistry, IISc, Bangalore, India

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Dedicated to Professor. S.S. Krishnamurthy on his 70th birthday

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ABSTRACT

A series of new cationic cyclopalladated complexes **2–6** have been synthesized from neutral cyclopalladated complex **1** of *p-tert*-butyl-calix[4]arene bisphosphite with various nitrogen donor ligands (acetonitrile, pyridine, aniline, (R)-(+)-1-phenylethylamine and 4,4'-bipyridine) in presence of Ag(OSO₂CF₃) as a chloride scavenger. These cationic cyclopalladated complexes have been characterized by NMR spectroscopy. Single crystal X-ray diffraction studies performed on cationic cyclopalladated complexes **3** and **6** in solid state reveal nearly square planar geometry around the metal and distorted cone conformation of the calix[4]arene framework. These cationic cyclopalladated complexes based on hetero ligands having variable steric and electronic properties could be efficient catalysts for important organic transformation reactions.

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1. Introduction

Calixarenes are phenolic macrocycles which display significant features such as structural versatility, conformational flexibility, tunable molecular shape in both upper and lower rims and presence of well-defined cavities [1,2]. The chemistry of calixarene has been grown up along several directions during last two decades. Particularly the transition metal chemistry of phosphorus functionalized calixarenes and their use in catalysis are significantly interesting and have been studied from a variety of perspectives by many research groups [3-13]. Previous studies in our laboratory have shown that transition metals (Pd, Pt) dichloride complexes of *p-tert*-butyl calix[4]arene bisphosphites readily undergo cyclometalation by C-C, C-H bond activation to give metallacycle at higher temperature [14,15]. In continuation with our ongoing studies on phosphorus functionalized calixarenes and their coordination chemistry [16], in this paper the synthesis of a series of new cationic cyclopalladated complexes derived from *p*-*tert*-butyl calix[4]arene bisphosphite with various nitrogen donor ligands such as acetonitrile, pyridine, aniline, (R)-(+)-1-phenylethylamine and 4,4'-bipyridine in presence of Ag(OSO₂CF₃) as a chloride scavenger is reported. The characterization of these cationic cyclopalladated complexes 2-6 by NMR spectroscopy and X-ray crystallography is also discussed here.

2. Experimental

2.1. General

All the reactions were carried out under an atmosphere of dry nitrogen or argon by using Schlenk tube techniques. The solvents were dried and distilled by conventional methods and deoxy-genated before use. The starting neutral cyclopalladated complex **1** was prepared from *p-tert*-butyl calix[4]arene bisphosphite as reported [14]. Specific rotation of complex **5** was measured on a JASCO DIP-370 digital polarimeter. The NMR spectra were recorded in CDCl₃ using a Bruker Avance-400 spectrometer with Me₄Si as an internal standard for ¹H NMR measurements and 85% H₃PO₄ as an external standard for ³¹P NMR measurements. Elemental analysis was carried out using a Perkin–Elmer 2400 CHN analyzer.

2.2. Synthesis

Complex **2**: The neutral cyclopalladated complex **1** (30 mg, 2.44×10^{-5} mol) was dissolved in chloroform (15 ml) with Ag (OSO₂CF₃) (6 mg, 2.44×10^{-5} mol) and treated with few drops of acetonitrile. The reaction mixture was stirred at 25 °C for 2 h. The precipitate of AgCl was filtered off and the filtrate was evaporated to dryness. Pure complex **2** was obtained by precipitation of using chloroform and petroleum ether (1:2). Yield: 21 mg (64%); *Anal.* Calc. for C₇₃H₉₂O₉P₂F₃N₁S₁Pd₁ (mol. wt.: 1384.94): C, 63.31; H, 6.70; N, 1.01. Found: C, 63.36; H, 6.68; N, 0.98%; ³¹P NMR (162 MHz, CDCl₃), AX spectra $\delta = 114.4$ ppm (d), 103.7 ppm (d),



E-mail addresses: pathikm.iisc@gmail.com, pathik.maji@ucd.ie

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 ${}^{2}J_{P-P}$ = 82.1 Hz; ¹H NMR δ = 1.13 (s, 9H, Bu^t), 1.14 (s, 18H, Bu^t), 1.16 (s, 18H, Bu^t), 1.40 (s, 18H, Bu^t of aryl substituent), 2.29 (s, 3H, Me), 2.37 (s, 3H, Me), 3.12 (bs, 3H, Me of acetonitrile), 3.66 (d, H, Hb₂, *J* = 13.2 Hz), 3.73 (d, 2H, Hb₃, *J* = 14.8 Hz), 3.85 (d, H, Hb₁, *J* = 15.6 Hz), 4.78 (d, H, Ha₂, *J* = 15.2 Hz), 4.83 (d, 2H, Ha₃, *J* = 15.6 Hz), 5.11 (d, H, Ha₁, *J* = 15.2 Hz), 6.66(s), 6.78(s), 6.82(s), 6.94(s), 7.08(s), 7.17(s), 7.19(s), 7.20(s) (12H, aromatic protons from phenyl and calixarene).

The complexes **3**, **4**, 5 and **6** were synthesized from neutral complex **1** on employing a procedure similar to that for complex **2** (for details see the Supplementary information).

Complex **3:** Yield: 24 mg (66%); *Anal.* Calc. for $C_{76}H_{94}O_9P_2F_3N_1S_1Pd_1(3H_2O)$ (mol. wt.: 1477.03): C, 61.80; H, 6.82; N, 0.95. Found: C, 61.83; H, 6.79; N, 0.94%; ³¹P NMR (162 MHz, CDCl₃), AX spectra $\delta = 117.7$ ppm (d), 104.1 ppm (d), $^2J_{P-P} = 83.7$ Hz; ¹H NMR $\delta = 1.08$ (s, 9H, Bu^t), 1.16 (s, 18H, Bu^t), 1.19 (s, 18H, Bu^t), 1.32 (s, 18H, Bu^t of aryl substituent), 2.21(s, 3H, Me), 2.28 (s, 3H, Me), 3.50(d, H, Hb₂, J = 12.2 Hz), 3.55 (d, 2H, Hb₃, J = 12.4 Hz), 3.64 (d, H, Hb₁, J = 13.0 Hz), 4.72 (d, H, Ha₂, J = 13.6 Hz), 4.76(d, 2H, Ha₃, J = 14.0 Hz), 5.09 (d, H, Ha₁, J = 14.2 Hz), 6.81(s), 6.82(s), 6.91(s), 6.93(s), 6.96(s), 7.01(s), 7.16(s), 7.24(s) (12H, aromatic protons of phenyl and calixarene), 7.42(bs), 8.14(bs), 8.81(bs), (5H, aromatic protons of pyridine).

Complex **4**: Yield: 22 mg (62%); *Anal.* Calc. for $C_{77}H_{96}O_9P_2F_3N_1S_1Pd_1$ (mol. wt.: 1437.02): C, 64.36; H, 6.73, N, 0.97. Found: C, 64.38; H, 6.69; N, 0.96%; ³¹P NMR (162 MHz, CDCl₃), AX spectra δ = 119.3 ppm (d), 107.5 ppm (d), ² J_{P-P} = 90.2 Hz; ¹H NMR δ = 1.11 (s, 9H, Bu^t), 1.12 (s, 18H, Bu^t), 1.14 (s, 18H, Bu^t), 1.38 (s, 18H, Bu^t of aryl substituent), 2.26 (s, 3H, Me), 2.34 (s, 3H, Me), 3.37 (bs, 2H, $-NH_2$), 3.67 (d, H, Hb₂, J = 11.6 Hz), 3.76 (d, 2H, Hb₃, J = 11.8 Hz), 3.82 (d, H, Hb₁, J = 13.6 Hz), 4.88 (d, H, Ha₂, J = 14.4 Hz), 4.91 (d, 2H, Ha₃, J = 12.8 Hz), 5.32 (d, H, Ha₁, J = 13.4 Hz), 6.76(s), 6.80(d), 6.83(s), 6.92 (s), 7.12(s), 7.13(s), 7.17(s), 7.18(s), 7.21(d), 7.22(d), 7.25(s) (17H, aromatic protons of phenyl, calixarene and aniline).

Complex **5**: Yield: 23 mg (64%); $[\alpha]_D^{25} = 38.5$ (1.0, CHCl₃); *Anal.* Calc. for C₇₉H₁₀₀O₉P₂F₃N₁S₁Pd₁(mol. wt.: 1465.07): C, 64.76; H, 6.88; N, 0.96. Found: C, 64.78; H, 6.85; N, 0.94%; ³¹P NMR (162 MHz, CDCl₃), AX spectra $\delta = 117.3$ ppm (d), 110.2 ppm (d), $^2J_{P-P} = 77.3$ Hz; ¹H NMR $\delta = 0.95$ (d, Me, phenylethylamine), 1.03 (s, 9H, Bu^t), 1.10 (s, 18H, Bu^t), 1.12 (s, 18H, Bu^t), 1.18 (s, 9H, Bu^t of aryl substituent), 1.20 (s, 9H, Bu^t of aryl substituent), 2.06 (s, 3H, Me), 2.24 (s, 3H, Me), 2.84 (bs, H, phenylethyl-amine), 3.37(d, H, Hb₄, *J* = 13.6 Hz), 3.46 (d, H, Hb₂, *J* = 14.0 Hz), 3.61 (d, H, Hb₃, *J* = 14.4 Hz), 3.66 (d, H, Hb₁, *J* = 14.6 Hz), 4.10 (bs, 2H, -NH₂ of phenylethylamine), 4.46 (d, H, Ha₄, *J* = 14.2 Hz), 4.60 (d, H, Ha₂, *J* = 13.6 Hz), 4.65 (d, H, Ha₃, *J* = 15.6 Hz), 5.16 (d, H, Ha₁, *J* = 13.8 Hz), 6.89(s), 6.96(s), 6.98(s), 7.01(s), 7.05(s), 7.11(s), 7.25(s), 7.28(s), 7.37(s), 7.38(s) (17H, aromatic protons of phenyl, calixarene and (*R*)-(+)-1-phenylethyl).

Complex **6**: Yield: 44 mg (63%); *Anal.* Calc. for $C_{152}H_{186}O_{18}P_4F_6N_2S_2Pd_2$ (mol. wt.: 2843.96): C, 64.19; H, 6.59; N, 0.99. Found: C, 64.21; H, 6.58; N, 0.97%; ³¹P NMR (162 MHz, CDCl₃), AX spectra δ = 118.1 ppm (d), 104.4 ppm (d), ²J_{P-P} = 85.3 Hz; ¹H NMR δ = 1.15 (s, 9H, Bu^t), 1.17 (s, 18H, Bu^t), 1.20 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t of aryl substituent), 2.09 (s, 3H, Me), 2.16 (s, 3H, Me), 3.52 (d, H, Hb₂, *J* = 12.4 Hz), 3.58 (d, H, Hb₃, *J* = 12.8 Hz), 3.66 (d, H, Hb₁, *J* = 13.2 Hz), 4.72 (d, H, Ha₂, *J* = 13.8 Hz), 4.78(d, 2H, Ha₃, *J* = 14.2 Hz), 5.08 (d, H, Ha₁, *J* = 14.4 Hz), 6.81(s), 6.92(s), 6.94(s), 6.97(s), 6.99(s), 7.04(s), 7.11(d), 7.25(s) (12H, aromatic protons), 8.57(bs), 8.30(bs), (8H, aromatic protons of 4,4'-bipyridine).

2.3. X-Ray crystallography

X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer. The SMART [17] software was used for cell refinement and data acquisition and the SAINT [18] software was used for data reduction. An absorption correction was made on the intensity data using SADABS [19] program. The structures were solved using SHELXS [20] and the WinGX graphical user interface. Least square refinements were performed by the full-matrix method with SHELXL [21]. The PLATON/SQUEEZE routine was used to remove the contributions of any disordered solvent molecules. The CIF format output from PLATON is appended to the CIF. Some of the tert-butyl groups were disordered and hydrogen atoms of these disordered groups were neither located nor fixed during the refinement.

3. Results and discussion

3.1. Synthesis of cationic cyclopalladated complexes and their NMR spectra

A series of cationic cyclopalladated complexes **2–6** have been synthesized from neutral cyclopalladated complex **1** of *p-tert*-butyl-calix[4]arene bisphosphite with various nitrogen donor ligands (acetonitrile, aniline, (R)-(+)-1-phenylethylamine, pyridine and 4,4'-bipyridine) in presence of Ag(OSO₂CF₃) as a chloride scavenger. These reactions are shown in Scheme 1. Ligand such as 4,4'-bipyridine plays an important role for the synthesis of cationic dinuclear palladium complex **6** due to its length which renders less steric strain between the two metal centre.

The ³¹P NMR spectra of the cationic cyclopalladated complexes **2–6** show an AX pattern as it is in the neutral cyclopalladated complex **1** (see the ESI, Figs. S1–S3). The chemical shifts and coupling constants are in the same range as those observed for neutral cyclopalladated complex **1** and are listed in Table 1. The chemical shift value of the phosphorus atom P_x moves to an upfield region for all the cationic complexes **2–6** in comparison with the neutral cyclopalladated complex **1**. The chemical shift value of the phosphorus atom P_x moves to an upfield region for all the cationic complexes **2–6** in comparison with the neutral cyclopalladated complex **1**. The chemical shift value of the phosphorus atom P_A is almost unchanged for all cationic cyclopalladated complexes except for complexes **4** and **5**. For cationic complex **5** the chemical shift value of P_A moves down field to a significant extent. The chemical shift value of the phosphorus atom P_x in cyclopalladated complex **2** is in more upfield region (114.4 ppm) with respect to other cationic cyclopalladated complexes **3–6**.

The ¹H NMR spectrum of cationic cyclopalladated complexes **2–4**, **6** show six doublets (three doublets are in the downfield region and three doublets are in the upfield region) with a coupling constant typical of geminal protons. The intensity ratio of the three doublets in both upfield and downfield region is 1:1:2 which is same in neutral cyclopalladated complex **1**. For cationic cyclopalladated complex **5** which contains a chiral CH(Me)(Ph) group, all the methylene protons are magnetically nonequivalent and the intensity ratio of the four doublets in both upfield and downfield region is 1:1:1.

3.2. X-ray crystallographic studies

The solid-state structures of complexes **3** and **6** have been determined by single crystal X-ray diffraction analysis. Details pertinent to data collection, structure solution and refinement are summarized in Table 2. Selected bond lengths and angles are given respectively in Tables 3 and 4. The data are comparable with neutral cyclopalladated calix[4]arene bisphosphite complex **1** reported by Mahalakshmi et al. [14].

The ORTEP plots of the molecular structures of cationic cyclopalladated complexes **3** and **6** are presented in Figs. 1 and 2, respectively. The cyclopalladated complex **3** crystallizes in the monoclinic system of P2/c space group with three water molecules. The geometry around the palladium is nearly square planar and that around the two phosphorus atoms is nearly tetrahedral. The



Scheme 1. (i) CHCl₃, AgOSO₂CF₃, CH₃CN, 25 °C, 2 h; (ii) CHCl₃, AgOSO₂CF₃, pyridine, 25 °C, 2 h; (iii) CHCl₃, AgOSO₂CF₃, aniline, 25 °C, 2 h; (iv) CHCl₃, AgOSO₂CF₃, (*R*)-(+)-1-phenylethylamine, 25 °C, 2 h; (v) CHCl₃, AgOSO₂CF₃, 4,4'-bipyridine, 25 °C, 2 h.

Table 1										
The ³¹ P	NMR	chemical	shifts	for	cationic	cyclopalladated	complexes	2-6	and	the
neutral	cyclop	alladated	comple	ex 1	.a					

Complex	³¹ P NMR (ppm)	$^{2}J_{P-P}$ (Hz)	
	P _x	P _A	
2	114.4(d)	103.7(d)	82.1
3	117.7(d)	104.1(d)	83.7
4	119.3(d)	107.5(d)	90.2
5	117.3(d)	110.2(d)	77.3
6	118.1(d)	104.4(d)	85.3
1	120.6(d)	103.4(d)	77.3

^a Recorded in CDCl₃ at 25 °C and at 161.9 MHz, δ in ppm.

cationic cyclopalladated dinuclear complex **6** crystallizes in the triclinic system of $P\bar{1}$ space group. The pyridine ring in complex **3** is almost parallel with the 2,6-*di-tert*-butyl-4-Me-phenyl ring to minimize steric strain. Similarly, the 4,4'-bipyridine ring in complex **6** is also parallel with the 2,6-*di-tert*-butyl-4-Me-phenyl ring which is not bonded with the palladium. In comparison with the bond angle $[C(36)-Pd(1)-Cl(1) = 92.5(3)^{\circ}]$ of the neutral cyclopalladated palladium complex **1** [14], the bond angle [C(36)-Pd(1)-N(1)] of the cationic cyclopalladated complexes **3** and **6** is slightly lower. This result suggests that the distortion towards the cone conformation is more in the cationic cyclopalladated complex **6** and **3** as compared with the neutral complex **1**. The average P–O bond distance in the cationic cyclopalladated complexes **3** and **6** is close to the average P–O distance in the neutral cyclopalladated complex **1**. The distance between palladium metal and the carbon atom of the phenyl ring [Pd(1)-C(36)] in cationic cyclopalladated complexes **3** [2.078(6) Å] and **6** [2.086(5) Å] is slightly higher than

Table 2

Details of X-ray data collection and refinement for cationic cycloplladated complexes 3 and 6.

Empirical formula	C ₇₆ H ₁₀₀ F ₃ N O ₁₂ P ₂ Pd S (3)	$C_{152} \; H_{186} \; F_6 \; N_2 \; O_{18} \; P_4 \; Pd_2 \; S_2 \; (6)$
Formula weight	1477.03	2843.96
Temperature	293(2) K	293(2) K
Wavelength	0.7107	0.7107
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	ΡĪ
Unit cell dimensions	$a = 16.041(5)$ Å, $\alpha = 90^{\circ}$	$a = 16.970(2)$ Å, $\alpha = 112.068(2)^{\circ}$
	$b = 30.972(9)$ Å, $\beta = 114.346(4)^{\circ}$	$b = 17.643(2)$ Å, $\beta = 108.452(2)^{\circ}$
	$c = 18.857(5)$ Å, $\gamma = 90^{\circ}$	$c = 17.727(2)$ Å, $\gamma = 98.874(2)^{\circ}$
Volume	8535(4) Å ³	4435(8) Å ³
Ζ	4	1
Density (calculated)	1.149 Mg/m ³	1.052 Mg/m ³
Absorption coefficient	0.338 mm^{-1}	0.320 mm^{-1}
F(0 0 0)	3112	1460
Crystal size	$0.42 \times 0.34 \times 0.24 \text{ mm}$	$0.48\times0.38\times0.32~mm$
Theta range for data collection	1.36–25.00°	1.33–27.85°
Index ranges	$-21 \le h \le 19, -33 \le k \le 36,$	$-21 \leq h \leq 21$, $-23 \leq k \leq 22$,
	$-22 \le l \le 22$	$-22 \leq l \leq 23$
Reflections collected	60,107	42,057
Independent reflections	14,994 [R(int) = 0.0936]	15,522 [<i>R</i> (int) = 0.0599]
Completeness to theta	99.8%	90.1%
Absorption correction	Empirical	Empirical
Maximum and minimum transmission	0.911 and 0.877	0.905 and 0.862
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F ²
Data/restraints/parameters	4994/0/883	15522/0/859
Goodness-of-fit on F^2	0.904	0.974
Final R indices $[I > 2 \text{sigma}(I)]$	$R_1 = 0.0936, wR_2 = 0.2520$	$R_1 = 0.0802, wR_2 = 0.2423$
R indices (all data)	$R_1 = 0.1484, wR_2 = 0.2823$	$R_1 = 0.1113, \ wR_2 = 0.2636$
Largest diff. peak and hole	1.347 and -0.410 e A ⁻³	1.390 and -0.501 e Å ⁻³

Table 3

Selected bond lengths (Å) for the cationic cyclopalladated complexes ${\bf 3}$ and ${\bf 6}.$

Bond distance Complex 3 Complex 6 Bond distance Complex 3 Complex 6 Complex 3 Complex	omplex 6
P(1)-Pd(1) 2.371(2) 2.394(2) P(1)-O(2) 1.593(5) 1.	.598(4)
P(2)-Pd(1) 2.194(2) 2.197(3) P(1)-O(3) 1.595(5) 1.	.602(4)
N(1)-Pd(1) 2.101(8) 2.165(4) $P(2)-O(4)$ 1.584(5) 1.	.576(4)
C(36)-Pd(1) 2.078(8) 2.086(5) P(2)-O(5) 1.577(5) 1.	.587(4)
P(1)-O(1) 1.603(5) 1.596(4) P(2)-O(6) 1.607(5) 1.	.595(4)

 Table 4

 Selected bond angles (°) for the cationic cyclopalladated complexes 3 and 6.

Bond angle	Complex 3	Complex 6	Bond angle	Complex 3	Complex 6
P(2) - Pd(1) - P(1)	91.5(7)	88.8(5)	O(3) - P(1) - Pd(1)	124.1(2)	125.2(2)
P(2)-Pd(1)-N(1)	168.5(2)	169.8(1)	O(1) - P(1) - Pd(1)	110.5(2)	108.3(1)
P(1)-Pd(1)-N(1)	99.6(2)	101.4(1)	O(2) - P(1) - Pd(1)	107.9(2)	110.9(2)
P(2)-Pd(1)-C(36)	79.5(2)	79.3(2)	O(6)-P(2)-O(5)	105.2(3)	105.7(2)
P(1)-Pd(1)-C(36)	167.4(2)	164.9(2)	O(6)-P(2)-O(4)	104.9(3)	103.5(2)
C(36)-Pd(1)-N(1)	89.0(3)	90.8(2)	O(5)-P(2)-O(4)	103.7(3)	103.8(2)
O(3) - P(1) - O(1)	102.8(3)	104.8(2)	O(6) - P(2) - Pd(1)	107.8(2)	108.0(1)
O(3)-P(1)-O(2)	106.5(3)	103.1(2)	O(5)-P(2)-Pd(1)	114.9(2)	117.1(1)
O(1)-P(1)-O(2)	103.0(2)	102.1(2)	O(4) - P(2) - Pd(1)	119.1(2)	117.3(1)

the distance in neutral cyclopalladated complex 1 [2.064(8) Å] [14] because of the electronic property of pyridine and 4,4'-bipyridine.

3 and **6** is higher than that of the neutral cyclopalladated complex **1**.

The conformation of the calix[4]arene backbone can be discussed in terms of either dihedral angles or torsion angles. The dihedral angles of the calix[4]arene aryl rings (A, B, C, and D) with the least square plane X of the four methylene carbons (C2, C8, C14 and C20) for cationic cyclopalladated complexes **3**, 6 are listed in Table 5. These data indicate that the calixarene framework in the cationic cyclopalladated complexes **3** and **6** adopts distorted cone conformation as it is in the neutral cyclopalladated complexes **1** [14]. But the distorsion in the cationic cyclopalladated complexes

The torsion angles involving the bridging methylene carbon atoms and aryl ring carbon atoms for the cationic cyclopalladated complexes **3** and **6** are listed in Table 6. The sequence of signs for the two torsion angles ϕ and χ is found to be + -, + -, + -, + -(or reverse) and confirms the cone conformation for both the complexes. A comparison of the observed torsion angles ϕ and χ for the two cationic complexes **3** and **6** with those expected for an ideal cone conformation [90° and -90°, respectively] shows that there is a larger deviation for two aryl rings (larger torsion angles) and



Fig. 1. ORTEP plot of cationic cyclopalladated complex **3**. Only selected atoms are labelled and hydrogen atoms and solvent atoms are omitted for clarity.

Table 6

Torsion angles ϕ and χ of cationic cyclopalladated complexes **3** and **6**.

Molecular fragment		Complex 3	Complex 6
$\begin{array}{c} C(24)-C(1)-C(2)-C(3)\\ C(1)-C(2)-C(3)-C(4)\\ C(6)-C(7)-C(8)-C(9)\\ C(7)-C(8)-C(9)\\ C(7)-C(8)-C(9)\\ C(12)-C(13)-C(14)-C(15)\\ C(13)-C(14)-C(15)-C(16)\\ C(18)-C(19)-C(20)-C(21)\\ \end{array}$		$\begin{array}{c} 85.8(8) \\ -116.1(7) \\ 93.9(8) \\ -56.0(9) \\ 85.0(8) \\ -125.8(8) \\ 103.6(3) \end{array}$	-118.8(6) 84.2(7) -56.1(8) 106.3(7) -128.0(7) 84.6(2) -55.8(7)
C(19)-C(20)-C(21)-C(22)	[X]	-56.7(1)	96.9(7)

torsion angles are tilted from the mean plane X of the methylene carbon atoms. This type of conformation is known as "flattened cone conformation" [22]. These values indicate that the cone conformation is more flattened in complexes **3** and **6** than in neutral cyclopalladated complex **1** [14].

4. Conclusions

The synthesis of new cationic cyclopalladated mono and dinuclear bisphosphite complexes anchored to *p-tert*-butyl-calix[4]



Fig. 2. ORTEP plot of cationic cyclopalladated dinuclear complex 6. Only selected atoms are labelled and hydrogen atoms are omitted for clarity.

Table 5

Dihedral angles between the different planes of cationic cyclopalladated complexes **3** and **6**.

Dihedral angles (°)		
Plane-Plane	Complex 3	Complex 6
A-X	80.7(1)	40.0(0)
B-X	42.5(0)	83.1(0)
C-X	82.0(0)	31.2(1)
D-X	31.6(1)	83.6(0)

X refers to the least square plane defined by the methylene bridged carbons of the calix[4]arene frame work C2, C8, C14 and C20. A, B, C and D denote to the plane of the aromatic rings bonded to the calix[4]arene oxygens defined by C1-C24-C23-C22-C21-C25, C3-C4-C5-C6-C7-C26, C9-C10-C11-C12-C13-C27, C15-C16-C17-C18-C19-C28, respectively.

smaller deviation for other two aryl rings (smaller torsion angles). The two aryl rings with larger torsion angles are parallel with respect to each other and the other two aryl rings with smaller arene framework was described. Ligand such as 4,4'-bipyridine plays an important role for the synthesis of cationic dinuclear palladium complex because of its length which renders less steric strain between the two metal centre. Single crystal X-ray diffraction studies of cationic cyclopalladated complexes **3** and **6** in solid state reveal nearly square planar geometry around the metal and distorted cone conformation of the calix[4]arene framework. These cationic cyclopalladated complexes based on hetero ligands having variable steric and electronic properties could be efficient catalysts for important organic transformation reactions.

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Appendix A. Supplementary material

CCDC 790438 and 790439 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.085.

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