



## COORDINATION CHEMISTRY OF A (N<sup>^</sup>N<sup>^</sup>C) PALLADACYCLE

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### INTRODUCTION

Cyclometallated Pd(II) complexes or palladacycles are used as catalysts in cross coupling reactions and, their optical and biomedical applications are being investigated by many scientists (Zhang and Lei, 2011) (Bruneau *et al.*, 2015). Katlenok and Balashev (2012) reported optical properties of an acetate-bridged binuclear cyclometallated Pd(II) complex derived from 2-phenylbenzotiazole. Cyclometallated Pd(II) complexes of the type [(N<sup>^</sup>N<sup>^</sup>S)PdCl] based on thiosemicarbazones have shown high anti-proliferative effect against A431 cells and are potential chemotherapeutic drug candidates (Ferraz *et al.*, 2011). The complexes of the type [(N<sup>^</sup>N<sup>^</sup>C)Pd(acetylide)] exhibit phosphorescence in the solid state and in solution at room temperature. They could act as a photosensitizer in light-induced aerobic oxidative C-H functionalization of amines and for light-induced hydrogen production (Chow *et al.*, 2014). Thus, it is of interest to explore the coordination chemistry of the (N<sup>^</sup>N<sup>^</sup>C) palladacycle (1) and to develop synthetic routes to its tosylates, acetylides and binuclear bridging complexes. The use of tosylate ion as a coordinating and non-coordinating ligand was investigated.

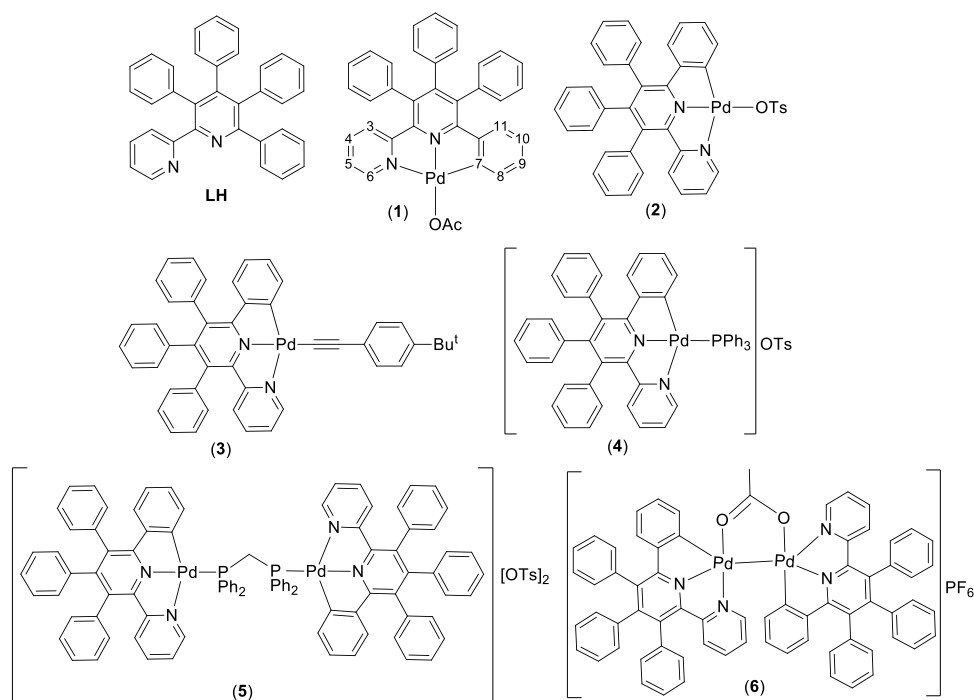


Figure 1: Molecular structures and atom labelling used for the assignment of NMR data.



## METHODOLOGY

All the experiments were carried out in an inert atmosphere (nitrogen or argon). Elemental analyses were carried out on a Carlo Erba 1006 automatic analyser. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. NMR spectra were recorded on a Bruker DPX 400 spectrometer (operating frequencies for  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  are 400, 161 and 101 MHz, respectively) or Bruker Avance<sup>II</sup> 600 spectrometer (operating frequencies for  $^1\text{H}$  and  $^{13}\text{C}$  are 600 and 151 MHz).  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts ( $\delta$ ) are in ppm with respect to TMS and coupling constants (J) are in Hz. 3,4,5,6-Tetraphenyl-2,2'-bipyridine (LH) and [(L)PdOAc] (**1**) were prepared according to literature procedures (Ollangnier *et al.*, 2008).

### [(L)PdOTs] (**2**)

A solution of *p*-toluenesulfonic acid (TsOH) monohydrate (46 mg, 0.24 mmol) in methanol (1 mL) was added to a solution of [(L)PdOAc] (30 mg, 0.048 mmol) in dichloromethane (1.5 mL). After 1 h, the resulting yellow solution was concentrated to yield yellow crystals, which were filtered and washed with cold methanol, (31 mg, 88%). Found: C, 64.79; H, 3.97; N, 3.59, calcd. (%) for  $\text{C}_{41}\text{H}_{30}\text{N}_2\text{O}_3\text{PdS}\cdot 0.4\text{CH}_2\text{Cl}_2$ : C, 64.55; H, 4.03; N, 3.64. IR (neat,  $\text{cm}^{-1}$ ): 3054, 1627, 1598, 1544, 1470, 1442, 1403, 1163, 1268, 1160, 1102, 982, 816, 756 and 700. ESI-MS (MeCN, *m/z*): Found: 606.1149, Calcd. 606.1161 for  $\text{C}_{36}\text{H}_{26}\text{N}_3\text{Pd}$ ,  $[\text{M-OTs}+\text{MeCN}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 9.12 (dd, 1H,  $^3\text{J}(\text{HH})$  5.5,  $^4\text{J}(\text{HH})$  1.5 Hz,  $\text{H}^6$ ), 7.98 (d, 2H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^{\text{Ar}}$ ), 7.43-7.32 (m, 2H,  $\text{H}^4$  &  $\text{H}^5$ ), 7.26-7.17 (m, 8H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^{\text{Ar}}$ ), 7.08-6.99 (m, 6H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^8$ ), 6.92-6.86 (m, 2H,  $\text{H}^{\text{Ph}}$ ), 6.80 (td, 1H,  $^4\text{J}(\text{HH})$  1.5 and  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^9$ ), 6.71-6.64 (m, 2H,  $\text{H}^{\text{Ph}}$ ), 6.58 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^3$ ), 6.51 (dt, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^{10}$ ), 5.84 (dd, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $^4\text{J}(\text{HH})$  1.0,  $\text{H}^{11}$ ) and 2.37 (s, 3H, Me).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 162.8, 155.5, 155.1, 154.7, 151.7, 151.4, 147.9 ( $\text{C}^6$ ), 141.1, 140.6, 138.2 ( $\text{C}^4$ ), 135.83, 135.8, 135.5, 134.8, 133.8 ( $\text{C}^8$ ), 129.9 ( $\text{C}^{\text{Ph}}$ ), 129.7 ( $\text{C}^{\text{Ph}}$ ), 129.6 ( $\text{C}^9$ ), 129.5 ( $\text{C}^{\text{Ph}}$ ), 129.2 ( $\text{C}^{\text{Ph}}$ ), 128.8 ( $\text{C}^{\text{Ph}}$ ), 128.7 ( $\text{C}^{\text{Ph}}$ ), 128.5, 128.3 ( $\text{C}^{11}$ ), 128.1, 127.1 ( $\text{C}^{\text{Ph}}$ ), 126.9, 126.7 ( $\text{C}^{\text{Ar}}$ ), 126.3 ( $\text{C}^5$ ), 126.2 ( $\text{C}^3$ ) 124.5 ( $\text{C}^{10}$ ) and 21.4 (Me).

### [(L)Pd(C $\equiv$ CC $_6$ H $_4$ -Bu $^t$ -4)] (**3**)

To a degassed solution containing [(L)PdOTs] (30 mg, 0.04 mmol), 4-*tert*-butylphenyl acetylene (26 mg, 0.17 mmol) and triethylamine (0.5 mL) in dichloromethane (3 mL) was added CuI (2.0 mg, 0.01 mmol). The reaction mixture was stirred under argon for 20 h. It was filtered and concentrated to a low volume and methanol was added to give the required product as a yellow solid (27 mg, 93%). IR (neat,  $\text{cm}^{-1}$ ): 2959, 2094, 1592, 1499, 1465, 1442, 1401, 1268, 1014, 836, 806, 759 and 698. Maldi (DCM, *m/z*): Found: 722.1934; Calcd. 722.1913 for  $\text{C}_{46}\text{H}_{36}\text{N}_2\text{Pd}$ ,  $[\text{M}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 9.15 (d, 1H,  $^3\text{J}(\text{HH})$  4.0 Hz,  $\text{H}^6$ ), 8.11 (d, 1H,  $^3\text{J}(\text{HH})$  6.7 Hz,  $\text{H}^8$ ), 7.57 (d, 2H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $\text{H}^{\text{Ar}}$ ), 7.45 (m, 1H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $^4\text{J}(\text{HH})$  1.7 Hz  $\text{H}^4$ ), 7.36 (m, 1H,  $^3\text{J}(\text{HH})$  8.6 Hz,  $\text{H}^5$ ), 7.33 (d, 2H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $\text{H}^{\text{Ar}}$ ), 7.31-7.21 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 7.14-7.06 (m, 4H,  $\text{H}^{\text{Ph}}$ ), 6.99 (t, 1H,  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^9$ ), 6.96-6.89 (m, 3H,  $\text{H}^{\text{Ph}}$ ), 6.73 (m, 2H,  $\text{H}^{\text{Ph}}$ ), 6.63 (d, 1H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $\text{H}^3$ ), 6.58 (t, 1H,  $^3\text{J}(\text{HH})$  7.1 Hz,  $\text{H}^{10}$ ), 6.14 (d, 1H,  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^{11}$ ) and 1.34 (s, 9H,  $\text{CMe}_3$ ).

### [(L)Pd(PPh $_3$ )]OTs (**4**)

[PdL(OTs)] (20 mg, 0.027 mmol) and triphenyl phosphine (7.3 mg, 0.0278 mmol) were dissolved in degassed dichloromethane (2 mL) to give a pale yellow solution. After 1 h, the solvent was removed, and the residue triturated with diethyl ether to give the required product as a pale yellow solid, (26 mg, 96%). IR (neat,  $\text{cm}^{-1}$ ): 3054, 1578, 1481, 1436, 1406, 1228, 1097, 836, 770, 745 and 699. Maldi (DCM, *m/z*): Found: 827.1820; calcd. 827.1807 for  $\text{C}_{52}\text{H}_{38}\text{N}_2\text{PPd}$ ,  $[\text{M-OTs}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.89-7.77 (m, 8H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^{\text{Ar}}$ ), 7.71 (t, 1H,  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^4$ ), 7.67-7.59 (m, 3H,  $\text{H}^{\text{Ph}}$ ), 7.58-7.49 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 7.34-7.23 (m, 8H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^{\text{Ar}}$ ), 7.21-7.09 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 7.07 (d, 2H,  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^5$ ), 7.01-6.93 (m, 3H,  $\text{H}^{\text{Ph}}$ ),



6.85 (d, 1H,  $^3J(\text{HH})$  5.0 Hz, H<sup>6</sup>), 6.60-6.54 (m, 1H, H<sup>10</sup>), 6.52-6.46 (m, 2H, H<sup>8</sup> & H<sup>9</sup>), 6.33 (d, 1H,  $^3J(\text{HH})$  7.5 Hz, H<sup>11</sup>) and 2.29 (s, 3H, Me).  $^{31}\text{P}$  NMR (161 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 42.1 (s).

#### [(L)Pd( $\square$ -dppm)Pd(L)](OTs)<sub>2</sub> (5)

To a degassed solution containing [(L)PdOTs] (20 mg, 0.027 mmol) in dichloromethane (1.5 mL) was added bis(diphenylphosphino)methane (dppm) (5.2 mg, 0.0135 mmol) and the reaction mixture was left at room temperature for 24 h. The resulting yellow solution was concentrated, and diethyl ether was added to give the required product as a pale yellow solid, (14 mg, 56%). Found: C, 65.71; H, 4.56; N 2.81, calcd. (%) for  $\text{C}_{107}\text{H}_{82}\text{N}_4\text{O}_6\text{P}_2\text{S}_2\text{Pd}_2 \cdot 1.5\text{CH}_2\text{Cl}_2$ : C, 65.61; H, 4.31; N 2.82. IR (neat,  $\text{cm}^{-1}$ ): 3054, 1628, 1598, 1545, 1471, 1436, 1404, 1163, 1012, 817 and 758. ESI-MS (MeCN,  $m/z$ ): Found: 949.2086; Calcd. 949.2093 for  $\text{C}_{59}\text{H}_{45}\text{N}_2\text{P}_2\text{Pd}$ ,  $[\text{Pd}(\text{L})(\text{dppm})]^+$ .  $^{31}\text{P}$  NMR (161 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 24.3 ppm.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.11 (m, br, 8H, H<sup>Ph</sup>), 7.81 (d, 4H,  $^3J(\text{HH})$  8.0 Hz, H<sup>Ar</sup>), 7.63 (d, br, 2H,  $^3J(\text{HH})$  4.0 Hz, H<sup>6</sup>), 7.56-7.43 (m, 4H, H<sup>4</sup> & H<sup>5</sup>), 7.36 (s, br, 2H, H<sup>8</sup>), 7.33-7.19 (m, 24H, H<sup>Ph</sup> & H<sup>Ar</sup>), 7.18-7.04 (m, 12H, H<sup>Ph</sup>), 7.01-6.91 (m, 6H, H<sup>Ph</sup>), 6.88-6.76 (m, 4H, H<sup>Ph</sup>), 6.73-6.64 (m, 4H, H<sup>3</sup> & H<sup>10</sup>), 6.58 (t, br, 2H,  $^3J(\text{HH})$  6.5 Hz, H<sup>9</sup>), 6.28 (d, 2H,  $^3J(\text{HH})$  8.0 Hz, H<sup>11</sup>), 4.76 (t, 2H,  $^2J(\text{PH})$  11 Hz, CH<sub>2</sub>) and 2.33 (s, 6H, Me).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 152.8 (C<sup>6</sup>), 139.6 (C<sup>4</sup>), 138.8 (C<sup>8</sup>), 130.4 (C<sup>11</sup>), 129.7 (C<sup>9</sup>), 128.2 (C<sup>5</sup>), 127.2 (C<sup>3</sup>) and 125.4 (C<sup>10</sup>).

#### [(L)Pd( $\square$ -OAc)Pd(L)]PF<sub>6</sub> (6)

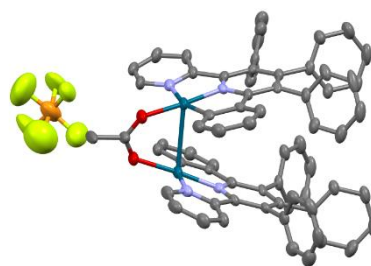
A solution of  $\text{NH}_4\text{PF}_6$  (12 mg, 0.074 mmol) in methanol (1 mL) was added to a solution containing [(L)PdOAc] (1) (20 mg, 0.032 mmol) in dichloromethane (1.5 mL) to give a pale-yellow solution. Upon standing at room temperature, yellow needles were formed, which were filtered off and washed with cold methanol (21 mg, 98%). IR (neat,  $\text{cm}^{-1}$ ): 3353, 3287, 1596, 1573, 1542, 1468, 1443, 1403, 830, 756 and 701.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$ ): 8.53 (br, s, 2H, H<sup>6</sup>), 7.68 (br, t, 2H,  $^3J(\text{HH})$  7.0 Hz, H<sup>4/5</sup>), 7.57 (br, t, 2H,  $^3J(\text{HH})$  6.0 Hz, H<sup>4/5</sup>), 7.39-7.26 (m, 12H, H<sup>Ph</sup>), 7.23-7.13 (m, 8H, H<sup>Ph</sup>), 7.13-7.01 (m, 4H, H<sup>Ph</sup>), 6.99-6.91 (m, 6H, H<sup>Ph</sup>), 6.90-6.84 (m, 4H, H<sup>Ph</sup>), 6.76-6.64 (m, 4H, H<sup>Ph</sup>), 6.03 (d, 2H,  $^3J(\text{HH})$  7.5 Hz, H<sup>11</sup>) and 3.20 (s, br, 3H, Me).  $^{31}\text{P}$  NMR (161 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$ ): -143.4 (septet,  $^1J(\text{PF})$  715 Hz,  $\text{PF}_6^-$ ). The complex (6) is quite insoluble in  $\text{CDCl}_3$  and it is slightly soluble in  $\text{CD}_3\text{CN}$ .

## RESULTS AND DISCUSSION

Treatment of 3,4,5,6-tetraphenyl-2,2'-bipyridine (LH) with  $[\text{Pd}(\text{OAc})_2]$  in boiling dichloromethane gave the cyclometallated Pd(II) complex [(L)PdOAc] (1) (Ollangnier *et al.*, 2008). Substitution of the acetate group was achieved by reacting this (N<sup>^</sup>N<sup>^</sup>C) palladacycle (1) with an excess of *p*-toluenesulfonic acid (TsOH) to give the Pd(II) tosylate [(L)PdOTs] (2) as a yellow solid in 88% yield. This complex and other complexes were characterized by IR, Mass and NMR spectroscopy. In the proton NMR spectrum of (2), aryl protons of the OTs group appeared as an AB pattern at 7.98 and *ca.* 7.23 ppm with  $^3J(\text{HH}) = 8.0$  Hz and the methyl resonance appeared as a singlet at 2.37 ppm. Treatment of (2) with 4-*tert*-butylphenyl acetylene in the presence of the base triethylamine and catalytic amount of CuI resulted in the formation of the yellow Pd(II) acetylide [(L)PdC $\equiv$ CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4] (4) in 93% yield. In the  $^1\text{H}$  NMR spectrum, the resonances of the alkynyl group appeared as an AB pattern at 7.57 (d) and 7.33 (d) ppm with  $^3J(\text{HH}) = 8.3$  Hz for aryl protons and a singlet at 1.34 ppm for the nine *tert*-butyl protons. The IR spectrum of (4) showed an IR band at 2094  $\text{cm}^{-1}$  for the acetylide ligand. Addition of one equivalent of  $\text{PPh}_3$  to a solution of complex (3) in dichloromethane yielded the monocationic salt [(L)Pd( $\text{PPh}_3$ )]OTs (4), in which OTs ion is a non-coordinating ligand. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of (4) showed a singlet at 27.6 ppm. Replacement of two OTs groups from two palladacycles (2) by one dppm ligand gave the dppm-bridged binuclear dicationic salt [(L)Pd( $\square$ -dppm)Pd(L)](OTs)<sub>2</sub> (5). The phosphorus resonance of (5) was 24.3 ppm. Addition of a methanol solution of  $\text{NH}_4\text{PF}_6$  to a solution of (2) in dichloromethane forced two palladacycles to form an acetate-bridged binuclear salt [(L)Pd( $\square$ -OAc)Pd(L)]PF<sub>6</sub> (6) as yellow needles in 98% yield. The complex (6) was characterised by X-ray crystallography and its Pd-Pd bond



distance is 311.88 pm.



**Figure 2:** Molecular structure of complex (6)

## CONCLUSION

Synthetic routes to neutral (N<sup>^</sup>N<sup>^</sup>C) palladacycles with tosylate and alkynyl groups and salts such as [(L)Pd(PPh<sub>3</sub>)]OTs were developed. The tosylate ion can act as a coordinating or non-coordinating ligand. Binuclear (N<sup>^</sup>N<sup>^</sup>C) palladacycles such as [(L)Pd(□-dppm)Pd(L)](OTs)<sub>2</sub> and [(L)Pd(□-OAc)Pd(L)]PF<sub>6</sub> with bridging ligands were also prepared.

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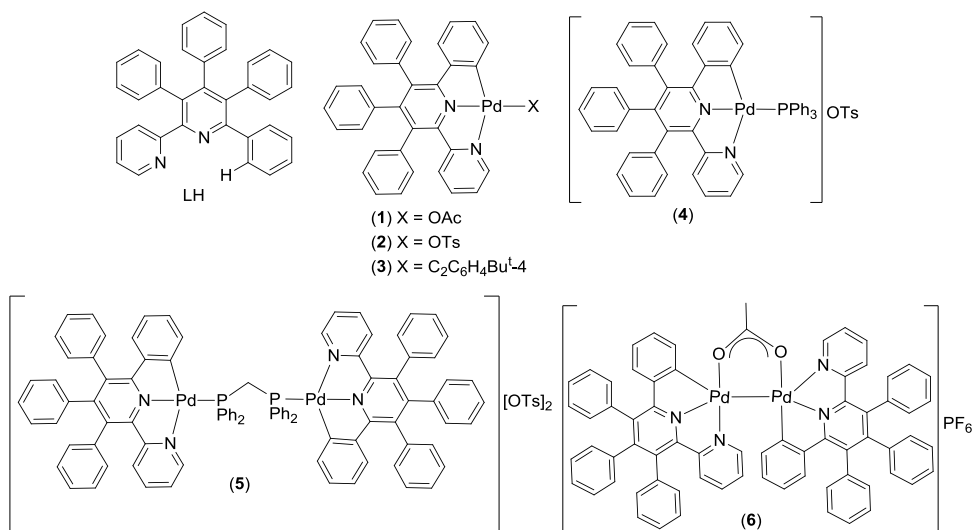
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## COORDINATION CHEMISTRY OF A (N<sup>^</sup>N<sup>^</sup>C) PALLADACYCLE

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Cyclometallated Pd(II) complexes or palladacycles are used as catalysts in cross coupling reactions, and their optical and biomedical applications are being investigated by many scientists. Katlenok and Balashev reported optical properties of an acetate-bridged binuclear cyclometallated Pd(II) complex derived from 2-phenylbenzotiazole. Luminescent [(N<sup>^</sup>N<sup>^</sup>C)Pd(acetylidy)] could act as a photosensitizer in light-induced aerobic oxidative C-H functionalization of amines and for light-induced hydrogen production. [(N<sup>^</sup>N<sup>^</sup>S)PdCl] complexes based on thiosemicarbazones have shown high anti-proliferative effect against A431 cells and are potential candidates for chemotherapeutic drugs. Thus, it is of interest to explore the coordination chemistry of the (N<sup>^</sup>N<sup>^</sup>C)palladacycle (**1**) and to develop synthetic routes to its tosylates, acetylides and binuclear bridging complexes.



Treatment of 3,4,5,6-tetraphenyl-2,2'-bipyridine (LH) with [Pd(OAc)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> yielded the (N<sup>^</sup>N<sup>^</sup>C)palladacycle [(L)PdOAc] (**1**). Complex (**1**) when treated with an excess of *p*-toluenesulfonic acid (TsOH) gave the Pd(II) tosylate [(L)PdOTs] (**2**) as a yellow solid in 88% yield. The methyl proton resonance of the OTs group appeared as a singlet at 2.37 ppm. Treatment of (**2**) with 4-*tert*-butylphenyl acetylene afforded the yellow Pd(II) acetylide [(L)PdC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4] (**3**) in 93% yield. The proton resonances of the alkynyl group appeared as an AB pattern at 7.57 (d) and 7.33 (d) ppm with <sup>3</sup>J(HH) = 8.3 Hz for aryl protons and a singlet at 1.34 ppm for the nine *tert*-butyl protons. Addition of one equivalent of PPh<sub>3</sub> to a solution of complex (**2**) in CH<sub>2</sub>Cl<sub>2</sub> yielded the monocationic salt

$[(L)Pd(PPh_3)]OTs$  (**4**), in which OTs ion is a non-coordinating ligand. The phosphorus resonance of (**4**) showed a singlet at 27.6 ppm. Replacement of two OTs groups from two palladacycles (**2**) by one bis(diphenylphosphino) methane (dppm) ligand gave the dppm-bridged binuclear dicationic salt  $[(L)Pd(\mu-dppm)Pd(L)](OTs)_2$  (**5**), with a phosphorus resonance of 24.3 ppm. Addition of  $NH_4PF_6$  to a solution of (**2**) in  $CH_2Cl_2$  forced two palladacycles to form an acetate-bridged binuclear salt  $[(L)Pd(\mu-OAc)Pd(L)]PF_6$  (**6**) as yellow needles in 98% yield. The complex (**6**) was characterised by X-ray crystallography and its Pd-Pd bond distance is 311.88 pm.

*Author wishes to thank the Trinity College Dublin for a Research Fellowship and Professor S. M. Draper for laboratory facilities and other support.*

Keywords: coordination chemistry, palladacycles, cyclometallation, Palladium complexes

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