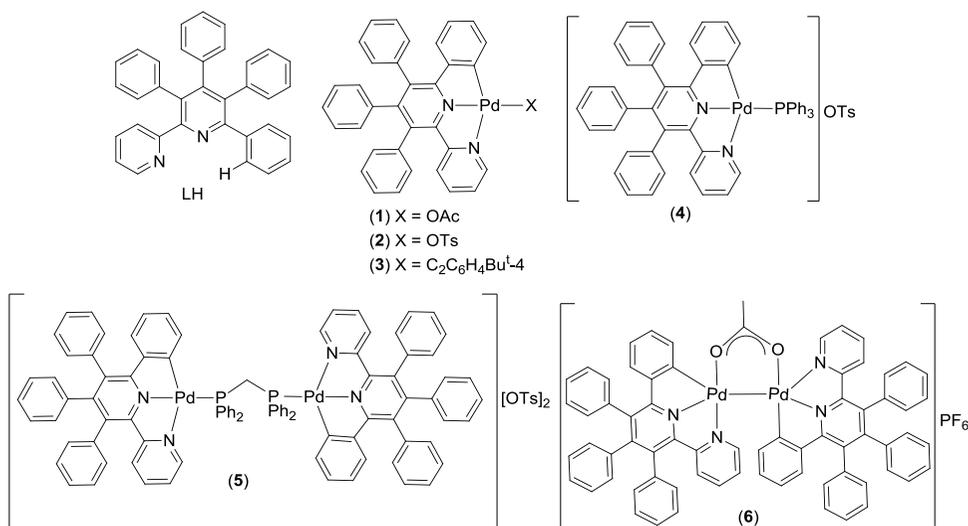


COORDINATION CHEMISTRY OF A (N[^]N[^]C) PALLADACYCLE

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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[^]N[^]C)Pd(acetylide)] could act as a photosensitizer in light-induced aerobic oxidative C-H functionalization of amines and for light-induced hydrogen production. [(N[^]N[^]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[^]N[^]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)₂] in CH₂Cl₂ yielded the (N[^]N[^]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≡CC₆H₄Bu^t-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 ³J(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 PPh₃ to a solution of complex (**2**) in CH₂Cl₂ 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.

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