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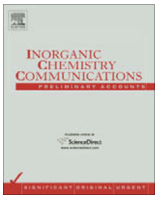

New (κ^2-*C*,*N*)-palladacyclic complexes with benzimidazol-2-ylidene ligand: Synthesis, crystal structures and characterization

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ABSTRACT

Reaction of unsymmetrical benzimidazolium bromides (**1**) with Ag_2O and subsequent transmetallation with chloro-bridged dinuclear palladacycle, $[Pd(dmba)(\mu\text{-}Cl)]_2$ (dmba: *N*,*N*-dimethylbenzylamine) afforded benzannulated monocarbene complexes [Pd(dmba)(NHC)Cl], **2**. The palladacycles (**2a–c**) were characterized by elemental analysis; NMR spectroscopy and the molecular structure of **2a** and **2c** were determined by X-ray crystallography.

Palladacycles have been known for over 30 years [1–4]. They are intensively studied classes of organopalladium derivatives, primarily due to their easy synthetic accessibility, structural versatility and intriguing applications in organic synthesis, organometallic catalysis, and new molecular materials. In particular, most of carbon–carbon bond forming reactions such as Heck reaction, Stille reaction, Suzuki reaction and other C–C couplings are palladium catalyzed [5–7]. In the C–C bond formation reactions, the role of palladacycle moiety has been proposed to release Pd(0), through a slow process which helps to suppress the nucleation and growth of inactive palladium metal particles [3].

On the other hand, in recent years, the uses of N-heterocyclic carbene (NHC) ligands over various metals have been applied in organometallic chemistry and catalysis [8–10]. In addition, the combination of a palladacycle framework with an NHC was reported by Herrmann [11–13], and others [14,15]. However, to the best of our knowledge, there have been only a few examples of spectroscopically characterized cyclometalated NHC–Pd(II) complexes reported [16,17].

For the present study, we selected the unsymmetrical alkyl substituted benzimidazol-2-ylidene precursor as N-heterocyclic carbene ligand. This choice was guided by several conditions. An important characteristic of the carbene ligands in active complexes is their strong electron donating effect. As a matter of fact, benzimidazol-2-ylidenes have structures reminiscent of imidazole-2-ylidenes, but spectroscopic properties and reactivity which are close to saturated imidazole-2-ylidenes [18–20]. However, modifications and overall synthesis of benzimidazol-2-ylidenes are more facile than imidazol(in)-2-ylidenes. Furthermore, methoxyethyl and methylated benzyl substituents have been reported to display enhanced activity [18].

In this work, we describe a practical approach to NHC-ligated palladacycles by carbene transfer from a silver N-heterocyclic carbene precursor to $[Pd(dmba)(\mu\text{-}Cl)]_2$ in room temperature in dichloromethane.

The general route to the target NHC ligand precursors and palladacyclic complexes is shown in Scheme 1. The methylated benzyl bromides were synthesized according to the methods previously known [21]. The introduction of the 2-chloroethyl methyl ether substituent into the benzimidazole was achieved by direct alkylation in DMSO. The resulting 1-alkylbenzimidazole can be alkylated to give **1a–c**. These salts were purified by recrystallization from $EtOH/Et_2O$. The IR data for unsymmetrical benzimidazolium salts clearly indicate the presence of the –C=N– group with a $\nu_{C=N}$ stretching vibration between 1553 and 1563 cm^{-1}.

These benzimidazolium salts have been characterized by ^1H and ^{13}C NMR spectroscopy. ^1H NMR chemical shifts were consistent with the proposed structures; the resonances for C2-hydrogens were observed as sharp singlet between 9.88 and 10.46 ppm. ^{13}C NMR of these salts showed the C2 carbon at 141.9–142.8 ppm. The benzylic protons appeared as singlet between 5.78 and 6.91 ppm.

The *in situ* reaction of the Ag–NHC complexes with the $[Pd(dmba)(\mu\text{-}Cl)]_2$ in dichloromethane resulted in the NHC-ligated palladacyclic compound as a crystalline solid [22,23]. The pallada-

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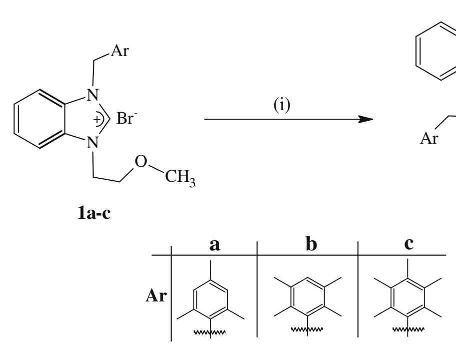

Scheme 1. *Reagents and conditions:* (i) DCM, Ag_2O, 3 h, RT, then $[Pd(dmba)(\mu\text{-}Cl)]_2$, 24 h, RT.

cyclic complexes, which are very stable in the solid state, were characterized by analytical and spectroscopic techniques [24]. The C2 carbons were found to be shifted downfield in the ^{13}C NMR spectra of the complexes. The chemical shifts for the carbene carbon atom (**2a–c**) fall in the range δ 185.8–186.1 ppm.

A brief inspection of literature indicates that in the square-planar complexes, [PdCl(dmba)(NHC)] formed between a NHC and $[Pd(dmba)(\mu\text{-}Cl)]_2$, the NHC ligand might be bonded to Pd atom either trans to *ortho*-carbon or NMe_2 of the dmba moiety [25]. The spectroscopic information obtained above did not allow us to distinguish these possibilities. Therefore, X-ray structure determination was required [26] and the structure of the complexes **2a** and **2c** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in the caption of figures. These complexes contain a benzimidazole ligand with a Pd^{II} metal centre, an *N*,*N*-dimethyl-1-phenylmethanamine ligand and one chlorine ligand. The coordination around the Pd^{II} ion is distorted *cis*-square-planar, and the Pd^{II} ion is coordinated by one amine N atom and one aryl C atom from the bidentate ligand, one carbenic C atom from the monodentate ligand, and one Cl atom.

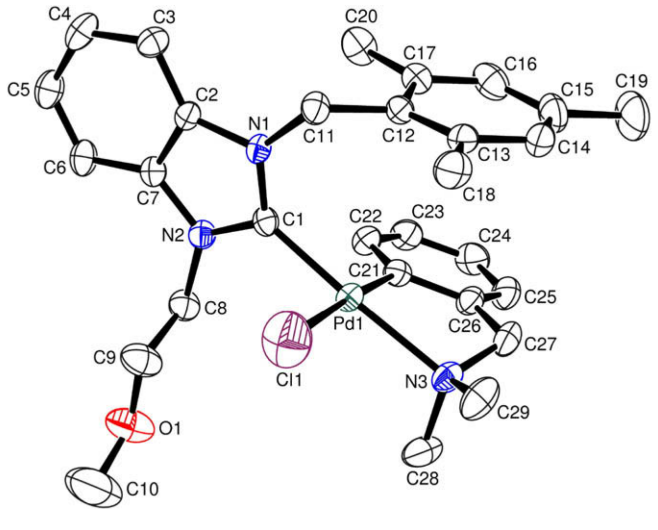

Fig. 1. A view of the complex (**2a**), showing 40% probability displacement ellipsoids and the atom-numbering scheme. Pd1–C1 1.968 (4), Pd1–C21 1.979 (4), Pd1–N3 2.136 (3), Pd1–Cl1 2.4417 (9), O1–C9 1.385 (6), O1–C10 1.422 (8), N1–C1 1.352 (4), N1–C2 1.395 (4), N1–C11 1.470 (4), N2–C1 1.359 (4), N2–C7 1.389 (5), N2–C8 1.459 (5), N3–C28 1.470 (6), N3–C29 1.477 (5), N3–C27 1.489 (6), C8–C9 1.526 (7), C11–C12 1.516 (5) Å, C1–Pd1–C21 92.74 (15), C1–Pd1–N3 175.59 (13), C21–Pd1–N3 82.87 (15), C1–Pd1–Cl1 89.60 (10), C21–Pd1–Cl1 177.02 (11), N3–Pd1–Cl1 94.81 (10), C9–O1–C10 112.0 (6), C1–N1–C2 110.5 (3), C1–N1–C11 125.8 (3), C2–N1–C11 123.3 (3), C10–O1–C9–C8 175.0 (5), C1–N2–C7 110.5 (3), C1–N2–C8 124.0 (3), C7–N2–C8 125.0 (3), C28–N3–C29 108.0 (4), C28–N3–C27 109.4 (4), C29–N3–C27 109.6 (4), N1–C1–N2 106.4 (3), N2–C8–C9 109.1 (3), O1–C9–C8 107.3 (4), N1–C11–C12 114.8 (3), N2–C8–C9–O1 −177.4 (4)°.

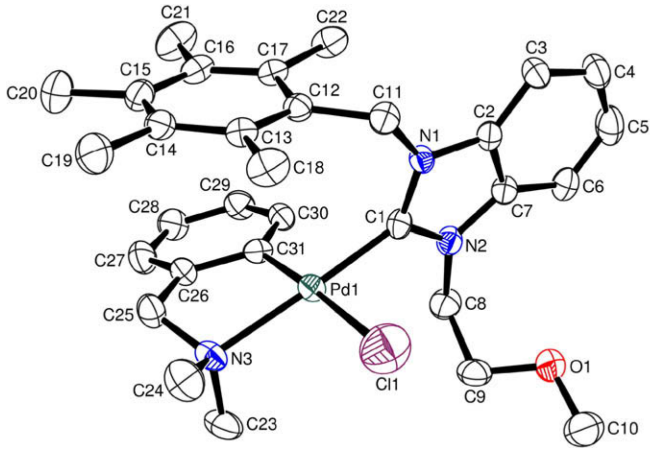

Fig. 2. A view of the complex (**2c**), showing 40% probability displacement ellipsoids and the atom-numbering scheme. Pd1–C1 1.965 (4), Pd1–C31 1.986 (5), Pd1–N3 2.141 (4), Pd1–Cl1 2.4508 (10), O1–C10 1.391 (8), O1–C9 1.404 (7), N1–C1 1.361 (5), N1–C2 1.381 (5), N1–C11 1.478 (5), N2–C1 1.359 (5), N2–C7 1.388 (5), N2–C8 1.460 (6), N3–C24 1.473 (6), N3–C25 1.477 (7), N3–C23 1.485 (6), C8–C9 1.501 (8), C11–C12 1.518 (6) Å, C1–Pd1–C31 92.99 (18), C1–Pd1–N3 175.59 (16), C31–Pd1–N3 82.69 (17), C1–Pd1–Cl1 89.23 (12), C31–Pd1–Cl1 175.75 (12), N3–Pd1–Cl1 95.02 (12), C10–O1–C9 111.8 (5), C1–N1–C2 111.0 (3), C1–N1–C11 124.7 (3), C2–N1–C11 124.0 (3), C10–O1–C9–C8 176.3 (5), C1–N2–C7 110.7 (3), C1–N2–C8 123.8 (4), C7–N2–C8 125.4 (4), C24–N3–C25 109.7 (4), C24–N3–C23 107.9 (4), C25–N3–C23 108.9 (4), N2–C1–N1 105.8 (3), N2–C8–C9 112.9 (4), O1–C9–C8 109.7 (4), N1–C11–C12 114.4 (3), N2–C8–C9–O1 −66.3 (5)°.

The Pd–Cl and Pd–$C_{carbene}$ distances are 2.4417 (9) and 1.968 (4) Å for complex (**2a**) and 2.4508 (10) and 1.965 (4) for complex (**2c**), respectively. When these bonds are compared with those observed in the literature, it is seen that the Pd–$C_{carbene}$ distance is at the lower end of the reported range 1.966–1.996 Å [14,25b,27]. However, the Pd–Cl bond in the complex is somewhat longer than the range observed in the literature (2.379–2.424 Å) [14]. Similar to the complex **2c**, the bonding within the N-heterocyclic carbene (NHC) ring indicates a pattern of delocalization that extends from atom N1 to atom N2 through atom C1, the N1–C1 [1.352 (4) Å] and N2–C1 [1.359 (4) Å] distances being significantly shorter than the N1–C2 [1.395 (4) Å] and N2–C7 [1.389 (5) Å] distances as is in similar NHC transition metal complexes [28–30]. These observations in complex **2a** and **2c** are possibly indicative of a greater partial double-bond character due to partial electron donation by nitrogen to the carbene C-atom donor [31,32]. Theoretical studies also indicate that the stability of these carbenes is due to electron donation from the N-atom lone pairs into the formally empty p(π) orbital on the carbene C atom (herein C1) [33].

The two coordinated C atoms in both complexes are *cis* to each other, which is in agreement with the fact that the donor groups with the largest *trans* influence avoid being mutually *trans* to one another. The change in geometrical parameters due to the difference of the monodentate NHC ligand, does not seem to significantly affect the coordination to the palladium(II) centre.

The single-crystal data and X-ray collection parameters are given in Table 1.

We have synthesized and characterized novel air- and moisture-stable palladacyclic complexes containing unsymmetrical benzimidazol-2-ylidene prepared by *via* Ag–NHC intermediate *in situ*, using the chloro-bridged palladacycle. The structures of **2a** and **2c** were determined by X-ray analysis. These complexes show a characteristic distorted *cis*-square-planar Pd(II) center with the carbene and dimethylamino ligands mutually trans to each other and the plane of the benzimidazole ring and the square-plane involving the palladacycle are close to perpendicular.