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C_{sp^2}–Br bond activation of Br-pyridine by neophylpalladacycle: formation of binuclear seven-membered palladacycle and bipyridine species†

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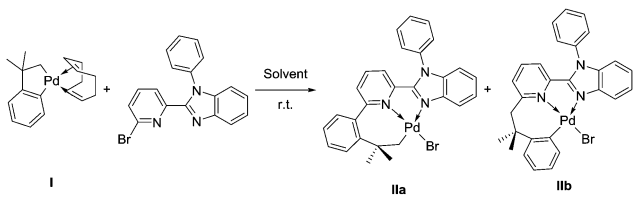
In this work, the synthesis and reactivity of seven-membered palladacycles are described, and a novel bi-pyridine synthesis in a catalytic pathway is reported. Neophyl-palladacycle(I) reacts with an excess of 2-Br-pyridine, giving the desired new binuclear seven-membered palladacycle (1) and unexpectedly, a bipyridine complex, [Pd(BiPy)Br$_2$]. ESI-HRMS experiments show that fragmentation of the Pd–Br bond in 1 can take place producing unusual two coordinated Pd(II) molecular ions, [Pd(NeoPyR)]$^+$.

Palladacycles are useful tools in organic synthesis and versatile precursors in materials science.[1] In 2001, Carmona *et al.* reported the synthesis and characterization of the five-membered neophyl-palladacycle complex **I** (Chart 1),[2a] and an elegant work about synthetically useful transformations of this molecule, especially the migratory insertion chemistry towards unsaturated inorganic and organic molecules (CO, CS_2, SO_2 or alkynes).[2b] Furthermore, compound **I** has been used as a precursor of cationic κ^2-hydrotrispirazolylborate palladacycles that have been proved to be an excellent starting material for the synthesis of Pd(IV) complexes either through electrochemical or aliphatic C–X bond activation.[2] Interestingly, in the latter case, it has been reported that the reaction of CH_2X_2 (X = Br or I) with the cationic palladacycle gives rise to relatively stable six-membered metallacycles as a result of the insertion of CH_2 into the Pd–C_{sp^2} bond. In recent works by the Sanford and Mirica groups, the synthesis and reactivity of Pd(IV) complexes containing a neophyl fragment and N-donor ligands were reported.[3] Shi *et al.* demonstrated that palladacycle **I** is a useful catalytic precursor in the synthesis of indolines through a coupling reaction of α-methylstyrene and di-*tert*-butyldiaziridinone.[4] However, the synthesis of palladacycles larger than six members has proven to be difficult since these types of derivatives undergo facile reductive elimination. Thus examples of well-characterized compounds of this kind are rare.[5] A few years ago, we reported the synthesis and characterization of unusual seven-membered palladacycles (**IIa** and **b**) through selective room temperature C–Br bond activation of a Br-pyridine-benzimidazole (PyBn) derivative, prompted by a stoichiometric amount of **I** (Chart 1).[6]

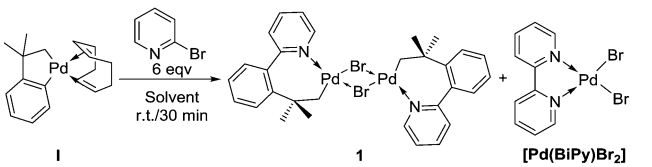
The important role of 1,5-cyclooctadiene (COD) as a non-innocent auxiliary ligand in the formation of Pd(IV) intermediates was demonstrated by theoretical DFT studies. Compounds **II** are part of a small library of fully structurally characterized seven- or eight-membered palladacycles.[5,6] In view of the above findings, the present study is focused on answering the following queries: will the imidazole fragment, in PyBn, be a necessary condition to stabilize the seven-membered ring? What complexes will be formed if 2-Br-pyridine (BrPy) is used as a reactant instead of PyBn; would these complexes be a five or seven-membered palladacycle?

As an extension of our earlier report, we carried out a study of the reactivity of palladacycle **I** toward non-substituted BrPy; C_6D_6 or $CDCl_3$ was used a solvent incapable of replacing COD in **I** (Scheme 1). Thus, **I** reacts immediately with an excess of BrPy; the workup gives a moderate yield of the new seven-membered



I IIa IIb

Chart 1



I 1 [Pd(BiPy)Br$_2$]

Solvent= Benzene, C_6D_6 or $CDCl_3$

Scheme 1

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palladacycle **1** as an orange-pale solid. According to the proton NMR experiments, after 30 min, a complete consumption of **I** takes place with a concomitant formation of compound **1** (see ESI,† Fig. S1). The structure of binuclear complex **1** is confirmed by 1D and 2D NMR spectroscopic data and their further reactivity (see below). The ^{1}H NMR spectrum of **1** (in DMSO-d_6) shows eight signals from 8.85 to 7.32 ppm, attributed to the aromatic protons of phenyl and pyridine rings. Additionally, two broad signals appear at 2.45 and 2.24 ppm, attributed to the non-equivalent methylene protons. Up-field two signals are observed at 1.44 and 0.61 ppm, corresponding to the methyl groups. The Pd–CH_2 peak appears at *ca.* 52.41 ppm in the ^{13}C NMR spectra. In the aromatic region, eleven signals appear in the range of 160.81–124.11 ppm attributed to the neophyl-pyridine fragment. It is noteworthy that when the reaction is carried out using strong coordinating solvents like DMSO-d_6 or CD_3CN, the formation of **1** does not take place, which further confirms the non-innocent role of the COD as an auxiliary ligand.[6,7]

Unexpectedly, when the liquor solution containing the remaining BrPy excess was left at room temperature, a deep orange crystal was obtained, which corresponds to the well-known bipyridine (BiPy) palladium complex [Pd(BiPy)Br_2] (**9**) reported by Van Koten *et al.* (see ESI†).[8] This result was obtained from at least three independent experiments, which suggests a competitive reaction path between the formations of **1** and **9**.

According of the high-resolution mass spectrum acquired for the binuclear palladacycle **1**, an unusual excision on the Pd–Br bond occurs in the ESI source, with a concomitant formation of two-coordinate Pd(II) complex ions. Two ionic species are detected in the HRMS spectrum (see ESI,† Fig. S2); *m*/*z* 316.0302 corresponds to $[C_{15}H_{16}NPd]^{+}$ and *m*/*z* 357.0562 to the adduct of this ion with acetonitrile which was used as a diluent (**1^{+}-nitrile**). To obtain further experimental evidence that would allow us to propose the reaction mechanism, we obtained ESI-HRMS spectra for the liquor crude solution. The identity of compound **1a** (Fig. 1) is evident based on the consistency between the experimental exact mass and isotopic pattern and those calculated *in silico* (see ESI,† Fig. S3).

Once compound **1a** was found as the reaction intermediate, a plausible mechanism is proposed as shown in Fig. 1. The first step involves an oxidative C_{sp^2}–Br bond activation reaction, yielding a tentative Pd(IV) intermediate, [Pd(Br)(C-κ^1-Py)(κ^2-neophyl)(COD)] (**Pd-Int1**), where the COD plays a key role as a non-innocent auxiliary ligand. The role of COD was demonstrated by examining the effect of different solvents (the first section of Results and Discussion); it is also supported by our previous theoretical

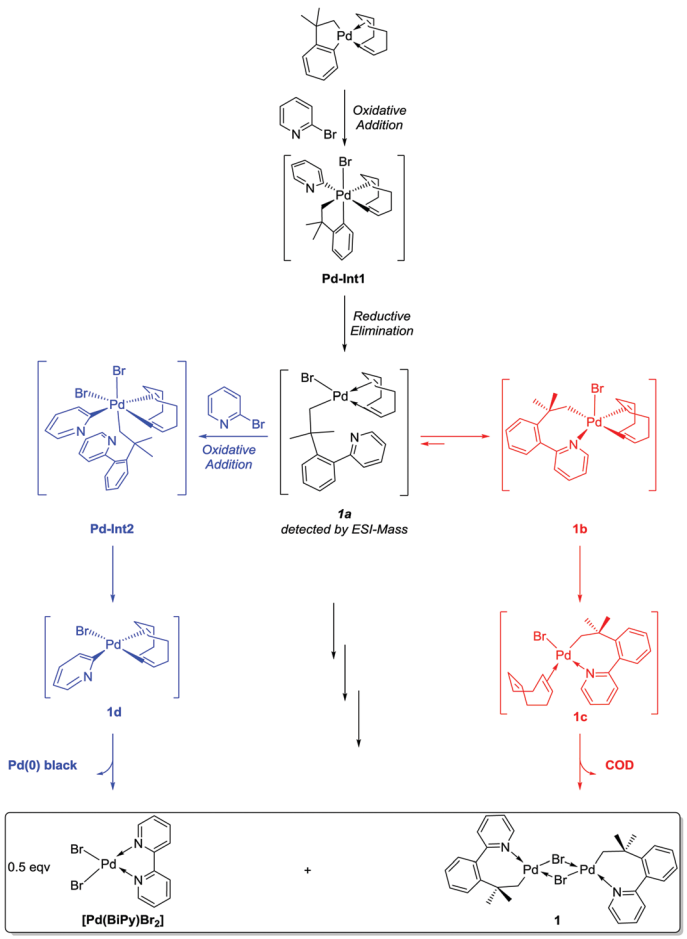


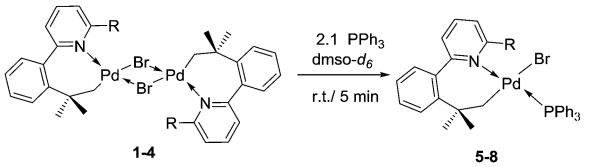
Fig. 1 A plausible mechanism for the formation of binuclear seven-membered palladacycle **1** and [Pd(BiPy)Br_2] complexes.

study and by studies from other research groups.[6,7] Next, the reaction follows by a reductive C_{sp^2}–C_{sp^2} bond coupling between the neophyl and pyridyl fragments proceeded *via* a crucial intermediate formation of the Pd(II) complex [Pd(Br)(C-κ^1-NeoPy)(COD)] (**1a**), which was observed *via* mass spectrometry. At this point, compound **1a** might react in two competitive ways: (i) irreversible COD substitution with a concomitant formation of **1**, *via* **1b** and **1c** species; and (ii) a second BrPy reacts *via* C_{sp^2}–Br bond activation to give the intermediate [Pd(C-κ^1-Py)(C-κ^1-NeoPy)(COD)Br$_2$] (**Pd-Int2**) which after reductive elimination and disproportion reactions produces the bipyridine palladium complex and a Pd(0) black precipitate.

Having in hand these favourable conditions, we decided to carry out the reaction of complex **I** with an excess of 6-Br,2-R-pyridine (R = $CH(OCH_2)_2$, COH, and CN). Unexpectedly, the formation of the desired compounds did not take place under these conditions. Nevertheless, if the reaction mixture is gently warmed to *ca.* 40 °C, new palladacycles **2–4** are obtained. Compounds **2–4** are isolated as orange-pale solids in moderate yields, showing that the introduction of donor- or electron withdrawing groups into the pyridine ring does not affect the C_{sp^2}–Br bond activation reaction. All compounds were characterized by 1D and 2D NMR (see ESI,† Fig. S4–S31). Each of the obtained compounds can be stored in the solid state for a year under a laboratory atmosphere; however, when **1–4** are left in a DMSO-d_6 solution at room temperature, a slow decomposition initiates after two weeks with a concomitant black palladium formation.

A comparative analysis of proton spectra for **1–4** reveals that CH_2 signals are clearly affected by the pyridine ring substituent. Additionally, small changes are observed for the diastereotopic CH_3 groups (see ESI,† Fig. S32; 3.50–0.00 ppm). Specifically, compound **1** shows two broad signals at 2.45 and 2.24 ppm, with a 0.21 ppm splitting delta. The nitrile group for compound **4** gives rise to well-defined doublet signals at 2.47 and 2.41 ppm, with a splitting of 0.09 ppm. In addition, the $CH(OCH_2)_2$ substituent on **2** has a similar behaviour, showing two doublets at 2.47 and 2.41 ppm, with a delta of 0.08 ppm. Unexpectedly, the carbonyl group in **3** generates a broad signal at 2.54 ppm which is attributed to the CH_2 protons. Finally, the aromatic region shows the expected typical signals.

Our next goal was to synthesize the mononuclear species [Pd(*N*,C-κ^2-NeoPyR)(Br)(PPh_3)], **5–8**, through the reaction of **1–4** with a slight excess of PPh_3 at room temperature in DMSO-d_6, respectively. According to the analysis of the proton NMR spectra, a spontaneous reaction took place with concomitant formation of **5–8**, after *ca.* 5 min (Scheme 2).[9] Two main significant changes in the aliphatic region were observed (against **1–4**): (i) the methylene proton signals appeared as two well-resolved doublet of doublets, which are attributed to the coupling with the phosphorus nucleus in the *trans*-position, at 2.32 and 1.42; 2.34 and 1.59; and 2.08 and 1.45 ppm, for **6** and **7**, respectively (Fig. S33 (ESI†), right side); and (ii) the phosphorus nucleus increased the splitting value from the methylene protons to *ca.* 0.47, 0.63, 0.75 and 0.90 ppm, for **5**, **8**, **7** and **6**, respectively.

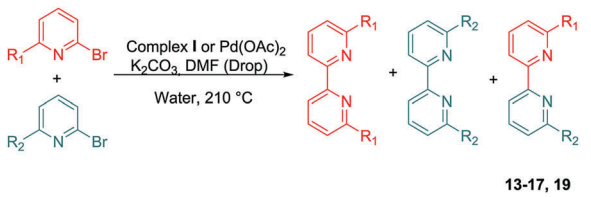


Scheme 2

Surprisingly, when the liquor solution was left at room temperature, the formation of yellow crystals and palladium black metal was observed after one week. The X-ray diffraction study showed that the former complex has the formula [*trans*-$Pd(PPh_3)_2Br_2$] (**10**) reported previously by Whitmire.[10] It should be mentioned at this point that a few binuclear complexes analogous to **5–8** have been described elsewhere;[11] however, all our efforts to isolate microcrystals of **5–8** have been unfruitful. The elucidation of the apparently complex mechanistic pathway of the reactions occurring after PPh_3 addition is currently under investigation and is out of the scope of this work.

Bipyridine derivatives are considered among the most important heterocycle species; these compounds are used as milestone ligands in coordination and organometallic chemistry and have recently been introduced in medicine and materials sciences.[12] So, having in mind their reactivity toward **I**, we carried out different experiments to obtain a BiPy species (see ESI,† Table S3). Once suitable catalytic conditions were achieved, we extended the scope of the reaction into the synthesis of asymmetric 6,6′-di-R2-BiPy species (Scheme 3, see ESI,† Table S4). We found that Pd(II) catalyzes the formation of the asymmetric 6,6′-R-R′-BiPy in low yields, as a consequence of the competitive nature of the potential homocoupling reactions generating the symmetric compounds as a major product.[13] It is important to mention that for each entry, we observed the total consumption of the starting materials (see ESI†).

Firstly, we carried out the reaction between 2-Br-Py and 2-Br-6-COH-Py observing a total consumption and the concomitant formation of bipyridine (**11**), [(2,2′-bipyridine)-6,6′-diyldimethanol] (**12**) and [(2,2′-bipyridine)-6-ylmethanol] (**13**) species. In the second trial, a reaction mixture of 2-Br-6-MeO-Py and 2-Br-Py gives as main compounds [6-methoxy-2,2′-bipyridine] (**14**), **11** and [6,6′-dimethoxy-2,2′-bipyridine] (**15**). Later, the reaction between compounds 2-Br-6-MeO-Py and 2-Br-6-COH-Py gives a new asymmetric species [(6′-methoxy-[2,2′-bipyridine]-6-yl)methanol] (**16**) and the expected symmetric compounds **12** and **15**. The structure of compound **16** is confirmed based on its analysis by NMR spectroscopy. Thus, the proton spectrum of **16** shows characteristic multiple signals from 8.32 to 6.78 ppm, attributed to the



Scheme 3

aromatic protons. The signals observed at 4.81 and 4.04 ppm are in a ratio of 2 : 3, attributed to the methylene and methyl groups, respectively. Finally, the broad signal observed at 4.11 ppm is attributed to the OH group. In the $^{13}C\{^1H\}$ NMR spectrum the resonance signals observed at 64.04 and 53.35 ppm are assigned to the CH_2 and CH_3 groups, respectively. Later, the reaction between 2-BrPy and 2-Br-6-($C_3H_5O_2$)-Py gives the expected coupling product [6-(1,3-dioxolan-2-yl)-2,2′-bipyridine] (**17**) plus **11** and [6,6′-di(1,3-dioxolan-2-yl)-2,2′-bipyridine] (**18**) species (ratio 1 : 3 : 2) (entry 4). The analysis of the ^1H NMR spectrum of **17** shows multiple signals from 8.61 to 7.20 ppm assigned to the aromatic protons of the pyridine ring (7H). Finally, the reaction involving 2-Br-6-COH-Py and 2-Br-6-($C_3H_5O_2$)-Py compounds gives the asymmetric [6-(1,3-dioxolan-2-yl)-6′-methoxy-2,2′-bipyridine] (**19**) and the symmetric species **12** and **18**.

In conclusion, through our experimental results, we have demonstrated that palladacycle **I** reacts with BrPy at room temperature, *via* oxidative addition of the C_{sp^2}–Br bond to get a plausible Pd(IV) complex (**Pd-Int1**), where the COD auxiliary ligand and the solvent play a crucial role in the reaction pathway. The formation of compound **1a** took place after a C_{sp^2}–C_{sp^2} reductive elimination between the neophyl and pyridyl fragments. **1a** evolved in two competitive reaction paths into: (i) the expected seven-membered palladacycle **1** and (ii) the unexpected bipyridine complex [Pd(BiPy)Br_2]. Furthermore, the substitution of a pyridine ring with electron-donating or -withdrawing groups did not affect the pathway of the C_{sp^2}–Br bond activation as demonstrated by the formation of a small library of seven-membered palladacycles (**2–8**). Finally, our efforts to get a catalytic system allowed us to obtain a few asymmetric bipyridine species.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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