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Palladium complexes of *N*-aryl-2-pyridylamines

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Abstract

Palladium complexes of *N*-phenyl-2-pyridylamine (**4**) and dipyridylamine substrates (**7**, **11**) have been studied. Due to the coordination ability of the pyridine-nitrogen atoms, the pyridyl substrates, **4**, **7**, **11** were subjected to $Pd(OAc)_2$ complexations and a number of *N*-aryl-2-pyridylamine Pd complexes (**13**–**17**) were isolated and characterised, in particular by NMR and ESI-MS. A new method for the preparation of the acetato-bridged six-membered ring palladacycle complex (**13**) of **4** is reported. The dipyridyl amines **7**, **11** formed *cis*/*trans* bis-dentate acetato-bridged dimeric $Pd_2Lig_2(OAc)_2$ (**14a**,**b**/**16a**,**b**) and $Pd_3Lig_2(OAc)_4$ complexes (**15a**,**b**/**17a**,**b**). The *N*-aryl-2-pyridylamine substrates (**4**, **7**, **11**) were prepared by oxidative nucleophilic substitution, by 1,3-cycloaddition reaction or by Buchwald amination.

Keywords: *N*-aryl-2-pyridylamines; Preparation; Pd^{II} dimeric complexes; NMR; ESI-MS

1. Introduction

We wanted to study the palladium promoted reactions of electron-deficient *N*-aryl-2-pyridylamino substrates (**1b**,**c**, Scheme 1). Oxidative cyclisations of diphenylamine compounds (**1a**), being ring closure reactions involving two consecutive C–H activation processes are well known to provide important biologically active carbazoles (**2a**) [1–6] (Scheme 1). However, due to the coordination ability of the pyridine-nitrogen atom(s) of *N*-arylpyridylamines (**1b**,**c**), potential oxidative cyclisation to afford the heterotricyclic compounds (**2b**,**c**, Scheme 1) were unlikely to take place. Such $Pd(OAc)_2$ activation reactions of substrates **1b**,**c** would thus afford *N*-aryl-2-pyridylamine–palladium complexes. Consequently, the formation of the tricyclic products **2b**,**c** (Scheme 1) and the new α-carboline (**5**) [7–12] and pyridoazaindol (**9**, **12**) products from the *N*-aryl-2-pyridylamino substrates **4**, **7**, **11** (Scheme 2a–d) were not expected.

Our results for the preparation of the appropriate *N*-aryl-2-pyridylamine substrates (**4**, **7**, **11**) and the subsequent palladium promoted reactions are discussed below.

2. Results and discussion

2.1. Preparation of N-aryl-2-aminopyridine intermediates

The *N*-arylaminopyridyl substrates were prepared by (i) oxidative nucleophilic substitution (**4**), (ii) 1,3-dipolar cycloaddition (**7**) and (iii) Buchwald amination (**7**, **11**) from appropriate substrates:

(i) Sodioformanilide has been reported to give diphenylamines by nucleophilic aromatic substitution of halonitrobenzene substrates followed by spontaneous decarbonylation (Scheme 3a) [13]. Direct amination of pyridines has been carried out on pyridine *N*-oxides; regiospecific amination in the 6-position followed by hydrolysis afforded phenylaminopyridines (Scheme 3b) [14]. Sodioformanilide has also been used to prepare 5-anilino-2-pyridinecarboxylate by nucleophilic aromatic substitution (NAS) of the nitro

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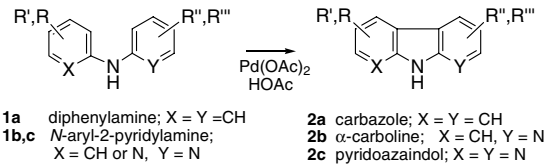
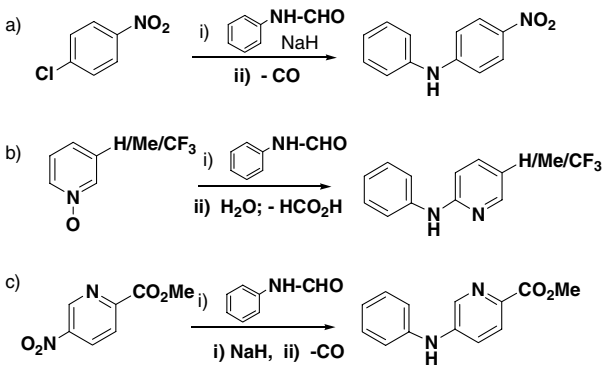


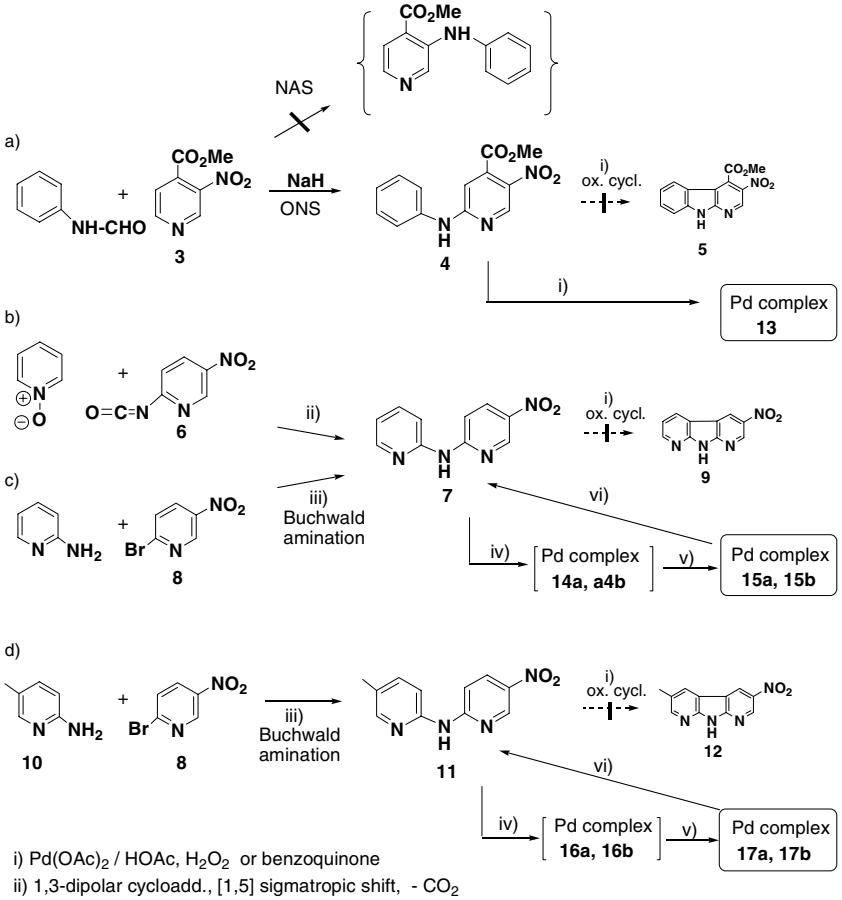
Scheme 1.

group in methyl 5-nitro-2-pyridinecarboxylate (Scheme 3c) [15]. 3-Nitropyridines are now readily available through an improved nitration method [16,17]. The electron-withdrawing effect of the substituents in 3-nitro-4-pyridinecarboxylate (**3**, Scheme 2a) would activate for NAS of the nitro group to give the substitution product, or alternatively activate for direct oxidative nucleophilic substitution (ONS) to afford the anilinopyridine product **4**. When sodioformanilide was applied on methyl 3-nitro-4-pyridinecarboxylate (**3**) the nitro group was retained but, instead ONS had taken place in the *para* position relative to the nitro position (Scheme 2a). The anilinopyridine product, methyl 5-nitro-2-(phenylamino)-4-pyridinecarboxylate (**4**), was thus formed after formanilide attack and subsequent decarbonylation by hydrolysis. It has previously been discussed whether the spontaneous oxidation and re-aromatisation of the ONS adduct intermediates may be caused by air oxygen present in the reaction mixture [18].

Nucleophhilic Aromatic Substitution [13-15]:



Scheme 3.



Scheme 2.

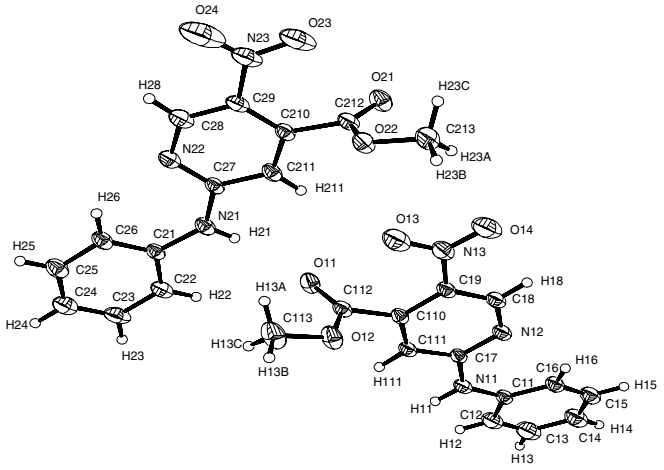


Fig. 1. Molecular structure of anilinopyridine product **4**, (X-ray [19]; crystals with two molecules in the asymmetric unit).

The sodioformanilide was generated by sodium hydride in DMF. Heating for 2 h in DMF followed by acetic acid hydrolysis afforded the anilinopyridine product **4** in 33% yield. The identity of the product was confirmed by X-ray [19] (Fig. 1) as well as by spectroscopy.

We have previous experience with the general good leaving group ability of the nitro group in carboxylate **3** in NAS, using N-, O-, S-, F- and C-nucleophiles [20–22]. The NAS product was likely to be formed and the ONS product **4** was thus unexpected. The results illustrate that due to the electron deficient nature of 3-nitro-4-pyridinecarboxylate (**3**), atypical oxidative reactions may take place.

The corresponding sodioformamide method was not successful for the preparation of products **7** or **11** from nitropyridines **6** or **8**, demonstrating the more electron-deficient character of the pyridylformamides and that more activated pyridine substrates would be required to give dipyridylamines by oxidative nucleophilic substitution.

(ii) The dipyridylamine intermediate **7** was prepared by a 1,3-cycloaddition reaction of nitropyridyl isocyanate **6** and pyridine *N*-oxide followed by a [1,5] sigmatropic shift and decarboxylation, as previously reported by us (Scheme 2b) [23].

(iii) Both dipyridylamine intermediates (**7**, **11**) were prepared by Buchwald amination from 2-bromo-5-nitropyridine (**8**) and 2-aminopyridine and its 5-methyl derivative (**10**) in 62–64% yield (Scheme 2c and d).

The nitropyridylcompound **7** has previously been prepared by nitration of dipyridylamine [24–26], while compound **11** is hereby prepared for the first time.

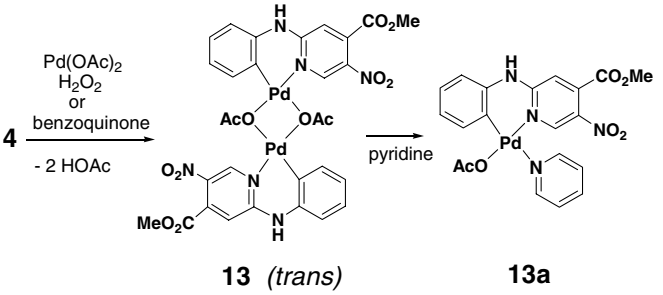
The palladium promoted reactions of the *N*-phenylaminopyridine **4** and the dipyridylamino substrates **7** and **11** afford the Pd^{II} complexes **13**–**17** (Scheme 2).

2.2. Palladium promoted reactions of *N*-phenylaminopyridine

The coordination ability of the pyridine-nitrogen in the *N*-phenylaminopyridine substrate **4** would activate for palladium complexation. However, for the anilinopyridine substrate **4**, no reaction took place at all by applying $Pd(OAc)_2$/acetic acid [1–6] or TFA [3] conditions. The low reactivity may be due to the total electron-withdrawing nature of the 3-nitro- and the 4-carboxylate groups of **4**. However, by introducing a new modified method, including an additional oxidant, such as H_2O_2 or benzoquinone, orthopalladation took place and a palladacyclic complex (**13**, Scheme 4) could be isolated (42%) and characterised. Excess of H_2O_2 or, alternatively, 1.2 equiv. of benzoquinone was used. Both palladium and the oxidant were thus necessary for complexation. In contrast to the heterocyclic 3-anilinoquinoline (see Scheme 1b) which previously has been reported to undergo oxidative cyclisation [3], our substrate **4** is a 2-aminosubstituted pyridine. The position of the pyridyl N-atom therefore allows for complexation to palladium to form a 6-membered palladacycle.

^1H and ^{13}C NMR studies of Pd complex **13**, including HSQC, HMBC and COSY experiments as well as electrospray (ESI) MS data, indicated that a 6-membered palladacycle was formed [27]. The deprotonated substrate **4** functions as a ligand (Lig = **4**-H^+) and is chelated through the pyridine-N and the phenyl-*ortho*-C-atom. Both the presence of one acetyl group per anilinopyridine unit and the loss of one phenyl-proton relative to substrate **4**, as shown by NMR, support the palladacyclic $Pd_2Lig_2(OAc)_2$ structure **13** shown in Scheme 4.

Electrospray (ESI)-MS data also confirmed the dimeric structure of the Pd^{II} complex **13**. In general, molecular ions or fragments containing palladium give rise to a number of peaks showing the characteristic natural isotope per cent distributions of palladium in compounds containing for example Pd, Pd_2 and Pd_3. Observed isotope patterns in ESI-MS can be compared with the corresponding calculated theoretical patterns. Standard cone voltage for ESI-MS is often 50 V. The cone voltage may be altered to vary the energy of the ions formed in the electrospray. Important differences were observed by studying the ESI-MS spectra using cone voltage 10, 30, 40 and 50 V.



Scheme 4.

Table 1
ESI-MS data for Pd^{II} complexes **13**–**17**

Pd complex	ESI-MS *m/z*[a] mol ion+H^+ (fragment)	Corresponds to formula[b]	Fits calculated theoretical spectrum and Pd_{1-3} isotope distribution of
13	877; (419[c])	$Pd_2Lig_2(OAc)_2+H^+$ PdLig(MeCN)	$C_{30}H_{26}N_6O_{12}Pd_2+H^+$ $C_{15}H_{13}N_4O_4Pd$
14a,**b**	763; (381[c])	$Pd_2Lig_2(OAc)_2+H^+$ PdLigOAc	$C_{24}H_{20}N_8O_8Pd_2+H^+$ $C_{12}H_{11}N_4O_4Pd$
15a,**b**	927[c];	$Pd_3Lig_2(OAc)_3^d+H^+$	$C_{26}H_{22}N_8O_{10}Pd_3+H^+$
16a,**b**	791; (395[c])	$Pd_2Lig_2(OAc)_2+H^+$ PdLigOAc	$C_{26}H_{24}N_8O_8Pd_2+H^+$ $C_{13}H_{13}N_4O_4Pd$
17a,**b**	955[c]	$Pd_3Lig_2(OAc)_3^dd+H^+$	$C_{28}H_{26}N_8O_{10}Pd_3+H^+$

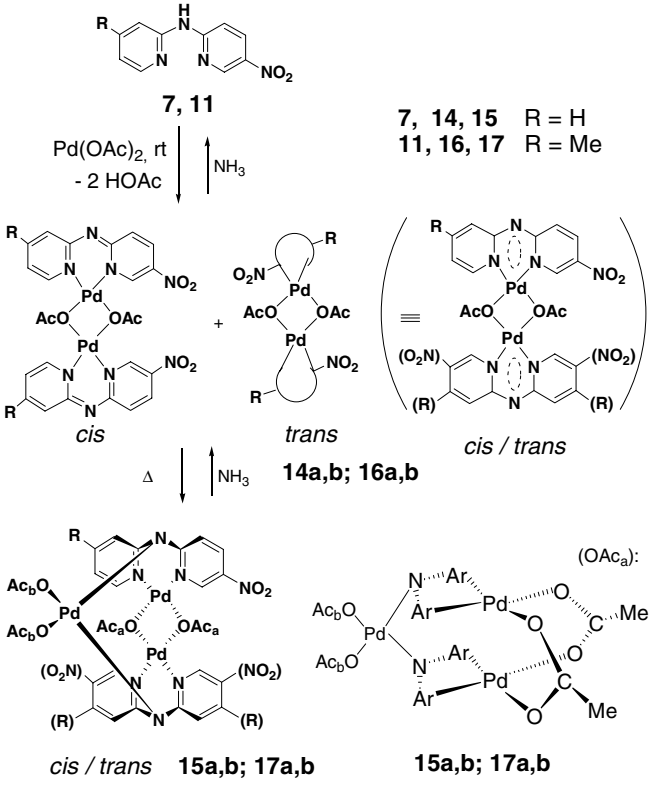
[a] ESI-MS data are obtained by cone energy 10 V. The reported *m/z* values represent the major peak in the group of peaks caused by the Pd isotope distribution as shown in Fig. 2.
[b] **13**: Lig = **4**-H^+; **14**, **15**; Lig = **7**-H^+;**16**, **17**; Lig = **11**-H^+.
[c] Base peak.
[d] One of the four OAc groups, shown by ^1H NMR, is lost in ESI-MS of **15a**,**b** and **17a**,**b**.

The 10 V ESI-MS of complex **13** dissolved in acetonitrile showed the expected molecular ion of $Lig_2Pd_2(OAc)_2+H^+$ (**13**+H^+ = *m/z* 877) and fitted exactly with the theoretically calculated spectrum, see Table 1. The base peak represented the ion of the monomer, $M_w/2$, after exchange of an acetate ligand with acetonitrile (LigPd(MeCN); *m/z* 419). The exchange of ligands with solvent molecules such as the observed acetate/acetonitrile exchange, is common and is often observed in ESI-MS. We have made similar observations in other ESI-MS spectra, as discussed below. The molecular ion is not observed in the higher voltage (30–50 V) ESI-MS spectra of the Pd complex **13** in acetonitrile or methanol, since splitting into the monomer, fragmentation and solvent/ligand exchange mostly were observed and thus dominate these spectra.

Both ESI-MS (50 V) and EI-MS, including HRMS, confirmed the presence of the protonated molecular ion (*m/z* 271+H^+) of the oxidative cyclisation product **5**. The product (**5**) is probably formed as an MS oxidation product from the palladium complex **13**, as shown by a major ion in MS. Redox reactions are well known electrospray processes. The oxidative cyclisation product **5** could, however, not be obtained by further heating in dichlorobenzene or acetic acid or by microwave promoted reaction conditions.

Such cyclopalladation complexes are normally quite unreactive, but CO, alkene and alkyne [28] insertion has been carried out. Acetato-bridged complexes may also give the pyridine-ligand derivative by pyridine treatment [27]. We readily obtained the pyridine mononuclear complex (**13a**) in 70% yield by pyridine treatment (Scheme 4).

Acetato-bridged dimers of five-membered ring palladacycles are well known [29], but six-membered palladacycles are in general much less common [27]. Acetato ligands are not so often reported as the chloro ligands. Acetato-bridged 5-ring palladacyclic dimers are reported to exhibit a "boat" form to permit greater electron delocalization. [29] Such dimeric 5-ring acetato-bridged [30–32] and 6-ring chloro-bridged [32] palladacycles are known to be formed as single *trans* isomers, often by an indirect C–H activation route, using a precursor $(PdAr–CH_2NMe_2Cl)_2$ palladacycle as the Pd source [27,28] It has, however, been shown that 5-ring palladacyclic dimeric complexes also may adopt both *cis* and/or *trans* geometry depending on intermolecular interactions [33]. The H_2O_2/benzoquinone protocol represents a simple and new preparation method for the dimeric acetato-bridged 6-membered ring palladacycle **13**.



Scheme 5.

2.3. Palladium promoted reactions of dipyridylamines

Based on the experience with the one-pyridyl compound **4**, the two pyridyl-nitrogen atoms in the dipyridylamino substrates **7** and **11** were expected to be more reactive towards intramolecular coordination with $Pd(OAc)_2$ [34]. Crystalline mixtures of palladium complexes **14a**,**b** and **16a**,**b**, respectively, were readily obtained by stirring **7** or **11** with $Pd(OAc)_2$ in dichloromethane at room temperature overnight (Scheme 5). By more vigorous conditions, by heating **7** or **11** with $Pd(OAc)_2$ in acetic acid for 1 h, different sets of isomer complexes, **15a**,**b** and **17a**,**b**, were formed. The products **15**, **17** were also simply formed directly by heating **7**, **11** with $Pd(OAc)_2$ in toluene for 5 min or in dichloromethane for 3 h. Based on NMR studies, the products **14**–**17** appeared as approximately 1:2 mixtures of similar compounds; **14a**,**b**–**17a**,**b**, respectively, proposed to be *cis*/*trans* isomers, as discussed below. The Pd complexes **14a**,**b** or **16a**,**b** could readily be transformed into **15a**,**b** or **17a**,**b** by heating in dichloromethane for 3 h.

The amines **7** and **11** were recovered when the respective Pd complexes **14a**,**b**, **15a**,**b**, **16a**,**b** or **17a**,**b** were treated with aqueous NH_3.

2.4. ESI-MS

Similar ESI-MS observations were made for Pd^{II} complexes **14a**,**b**–**17a**,**b** as for **13**. By using high cone voltage of 50 V the molecular ions were not observed and fragmentation, solvent/ligand exchange and splitting into the monomers always represented the dominating peaks in the 50 V spectra, due to the high-energetic molecular ions. The 10 V spectra, however, clearly showed the molecular ions of **14**–**17** as shown in Table 1. The obtained spectra of compounds **14**–**17** were in full agreement with the corresponding calculated theoretical spectra, matching completely the molecular peak per cent distribution caused by the Pd isotopes, as shown in Table 1 and illustrated for complex **16a**,**b** in Fig. 2. It is evident from ESI-MS, including the number of observed Pd atoms, that dimer complexes are formed. The total number of present hydrogen

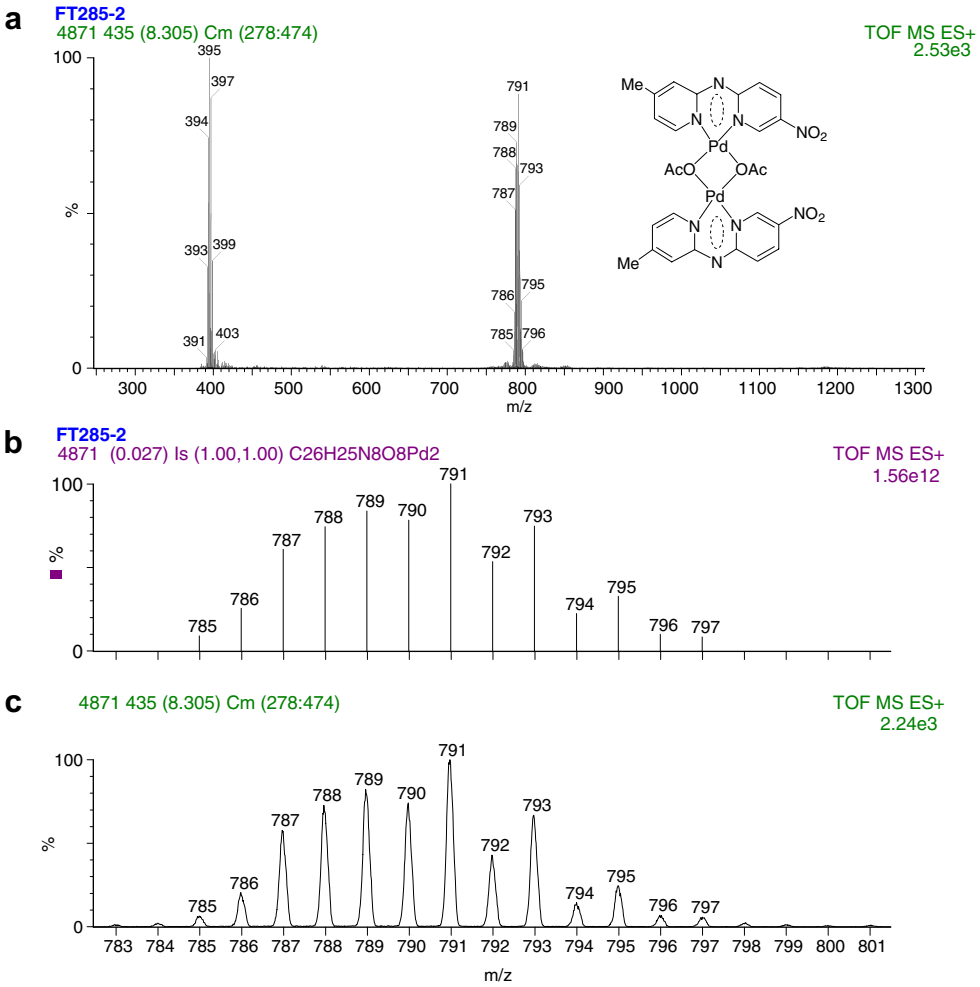


Fig. 2. (a) ESI-MS of complex **16a**,**b**; (b) theoretically calculated and (c) observed ESI-MS peak/isotope distribution of the molecular ions of complex **16a**,**b**; *m*/*z* 791 = $C_{26}H_{24}N_8O_8Pd_2+H^+$.

atoms indicates that the complexations involve the loss of one hydrogen atom from each ligand. In complexes **14/15** and **16/17** the ligands are therefore deprotonated **7** or **11** (Lig = **7**-H^+ or **11**-H^+), respectively. Complexes **14** and **16** are dimers of the PdLigOAc monomers. By the conversion of **14/16**, $(PdLigOAc)_2$, into **15/17** an additional $Pd(OAc)_2$ unit is introduced into the complex to give $(Pd_3Lig)_2(OAc)_4$. However, the ESI-MS spectra of **15a**,**b** and **17a**,**b** correspond to $(OAc)_3$ complexes, since the base peaks represent loss of one unstable acetato ligand. The complex composition was, however, confirmed by the presence of four acetate (2:2) groups in the ^1H NMR spectra, as shown by the correct integrals.

The ESI-MS spectra confirmed the experimental observations that the Pd_3 complexes **15a**,**b** and **17a**,**b** were significantly more stable than the Pd_2 complexes **14a**,**b** and **16a**,**b**, since the molecular ions represented the base peaks as the single and only ion in the former spectra of the Pd_3 complexes, while the latter spectra were dominated by the splitting of the $Pd_2Lig_2(OAc)_2$ complexes into the PdLigOAc monomers. This is shown for complex **16a**,**b** in Fig. 2a.

2.5. NMR

^1H NMR spectra for compounds **7**, **14a**,**b** and **15a**,**b** (Scheme 5) are shown in Fig. 3 and illustrate the formation of two isomers (1:2) by Pd complexation, represented by two sets of signals for complexes **14a**,**b** and **15a**,**b**. Because of the unsymmetrical nature of substrates **7**,**11**, it is suggested that the bis-ligand Pd complexes **14**–**17** assemble as mixtures of *cis* and *trans* structures, as shown in Scheme 5. Individual *cis* and *trans* isomers were characterised by ^1H and ^{13}C NMR.

The spectra also demonstrate some characteristic shielding and deshielding effects observed by Pd complexation and complex transformation. The Pd^{II} complexation of **7** to give **14a**,**b** caused a strong shielding effect and characteristic high field shift values of all protons, as compared with the precursor ligands **7**. This effect was most pronounced for H3, demonstrating a shift to $\Delta\delta$ 1.4 ppm lower frequency (Fig. 3). Since the number of aromatic proton signals from the precursors **7** are retained, the deprotonation observed by ESI-MS takes place at the amino position. Therefore, in structure **14a**,**b**, the bridging N-atom of **7** is deprotonated and the complexes can be represented by the resonance structures as shown in Scheme 5 and discussed other places [34]. The deprotonation gives rise to shielding of all protons; in particular for H3 next to the new potential C=N double bond, as shown in Fig. 3. In contrast, the transformation of **14a**,**b** into **15a**,**b** caused a general deshielding of all protons relative to **14a**,**b**. However, in particular for H3 and H3′ a pronounced down-field

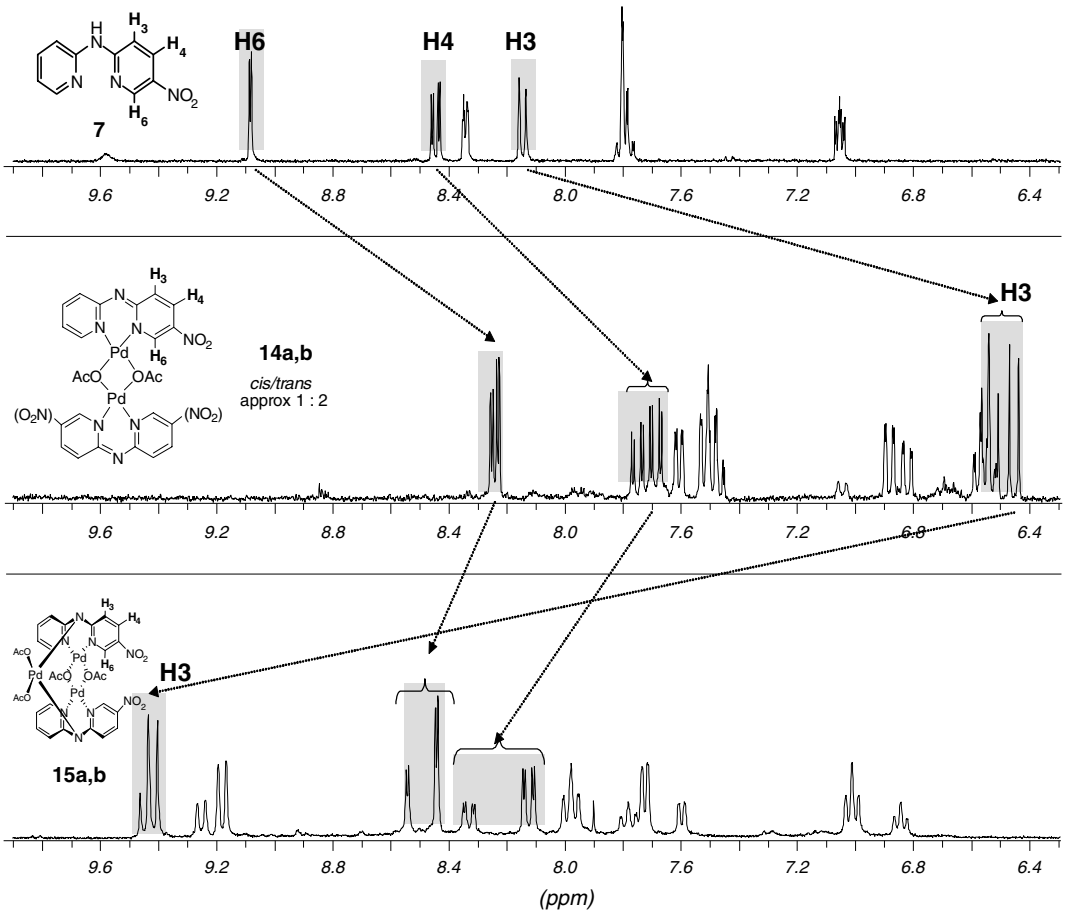


Fig. 3. ^1H NMR spectra of substrate **7** and Pd complexes **14a**,**b** and **15a**,**b**.

shift of $\Delta\delta$ 3 ppm was observed. The shift for H3 from δ 6.5 (**14a**,**b**) to δ 9.5 (**15a**,**b**) can be seen in Fig. 3. This exceptional effect may be accounted for by the proposed structures for **15a**,**b** (Scheme 5). In complexes **15a**,**b** the ligands have changed electronically back to pyridine ligands and the pyridine aromatic character is regained. This would cause a general deshielding of all protons. The additional Pd is thus introducing a new di-amido-palladium bridge. The additional low field shift of H3, H3′ may be due to anisotropy effect of the neighbouring aromatic ligand kept in proximity by the additional coordination and the bridging mode of the third Pd, as shown by the three-dimensional **15a**,**b** structure in Scheme 5. Relative to the precursor molecule **7**, the other protons H4, H6, H4′–6′ are almost unaffected by the transformation into the Pd_3 complexes **15a**,**b**. Similar and supportive observations were made by comparing the ^{13}C NMR spectra of the precursor **7** and complexes **15a**,**b**, since only C3 and C3′ are affected by complexation to the Pd_3 complex. The specific deshielding of these atoms is shown by the low field shift ($\Delta\delta$ 12–13 ppm) from 111/113 ppm (**7**) to 124/125 ppm (**15a**,**b**) for C3/C3′.

The two different acetate/acetato groups in each of the trinuclear complexes **15a** and **15b** gave rise to two individual sets of ^1H NMR ($2\times CH_3$, Ac_a and Ac_b) and ^{13}C NMR ($2\times CH_3$ and $2\times O–C–O$, Ac_a and Ac_b) signals for each isomer. The assignments of corresponding Ac_a, Ac_b signals (see Section 4) were based on HMBC NMR experiments. Since all the corresponding Ac_b ^1H and ^{13}C NMR signals are identical for the two **15a**,**b** isomers, we suggest that Ac_b may be assigned to the $Pd(OAc)_2$ moiety (as indicated in Scheme 5), not being diastereotopic or influenced by the *cis*/*trans* stereochemistry. In contrast, all the Ac_a ^1H and ^{13}C NMR **15a**,**b** signals were non-identical and may represent the acetato bridges, being diastereotopic due to the *cis*–*trans* stereochemistry. Multiple ^1H and ^{13}C NMR signals caused by diastereotopic acetato bridges in other *cis*/*trans* dimeric Pd complexes have previously been observed [35–37].

All the ^1H and ^{13}C NMR effects discussed above were similarly noticed for the transformations of methyl compound **11** into Pd complexes **16a**,**b** and **17a**,**b**.

Since the ESI-MS spectra of **15a**,**b** and **17a**,**b** corresponded to $Pd_3(OAc)_3$ complexes, it was important to notice that the corresponding ^1H NMR spectra clearly showed the presence of four acetate groups. In contrast, only two acetate groups were shown in the ^1H NMR spectra of **14a**,**b** and **16a**,**b**.

2.6. Structures

The MS and NMR data discussed above are in accordance with the proposed structures for **14a**,**b**–**17a**,**b**, as shown in Scheme 5. The bidentate ligands coordinate to the palladium atoms via their two nitrogen donor atoms. Based on ESI-MS data, the complexes are dimers, formed through acetato-bridging. Thus two six-membered chelating rings with the palladium atoms are formed (**14/16**) after deprotonation of the amino-bridge by Pd complexation at room temperature.

As shown by ESI-MS and ^1H NMR, an additional $Pd(OAc)_2$ unit is introduced by the transformation of Pd_2 complexes **14/16** to Pd_3 complexes **15/17** by heating.

The formation of linear trinuclear cyclopalladated complexes has previously been studied [35–38]. Such structures have been shown to consist of three palladium, four acetato bridges and two chelate units. Their structures have been determined to be as shown in Fig. 4.

However, such linear Pd_3 structures would not be consistent with the NMR data for our trinuclear bidentate palladium complexes **15/17**. In particular, the exceptional down-field shift of H3/H3′ by the formation of **15/17** from **14/16**, as discussed in Section 2.5, would not be expected by the formation of such linear Pd_3 complexes. Additionally, for the *cis*/*trans* dinuclear complexes (**14a**,**b**, **16a**,**b**) only small differences in ^1H NMR chemical shifts ($\Delta\delta$ 0.02–0.06) are reported for the diastereotopic sets of acetate signals [37], indicating a similar nature of all the acetato bridges. In contrast, for our Pd_3 complexes **15/17**, ^1H and ^{13}C NMR data indicates two principal different characters of the acetate groups. This is demonstrated by the large differences in ^1H NMR chemical shifts between the two kinds of acetate/acetato bridge groups in **15a** (1.79 and 2.08 ppm; $\Delta\delta$ 0.29 ppm) and **15b** (1.80 and 2.08 ppm; $\Delta\delta$ 0.28 ppm), respectively. ^{13}C NMR data show similar effects due to the different character of the acetate/acetato groups in each trinuclear complex (CH_3; $\Delta\delta_H$ Ac_b–Ac_a = 1.3–1.6 ppm) (O–*C*–O; $\Delta\delta_C$ Ac_b–Ac_a = 3–14 ppm).

Acetato-bridged Pd dipyridylamine dimers, closely related to **14** and **16**, have been determined to have a "boat" form as shown below in Fig. 5 [39].

Based on this fact, the additional Pd-bridge between the two amino-bridges, as shown for the proposed structures **15** and **17**, would not be expected to add further strain in the complex structure. Tentatively, for complexes **15/17** we therefore propose coordination of the third Pd to each of the deprotonated nitrogen atoms. To the best of our knowledge, similar trinuclear Pd dimeric complexes (**15a**,**b** and **17a**,**b**) with both acetate ligands, acetato bridges, and unsymmetrical ligands have not previously been studied. However, since the complexes **14–17** appeared as *cis*/*trans* mixtures, no crystals suitable for X-ray have been obtained.

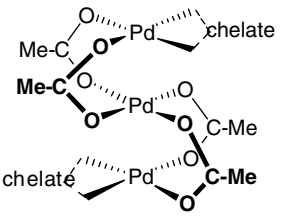


Fig. 4. Structure of linear trinuclear cyclopalladated complexes [37,38].

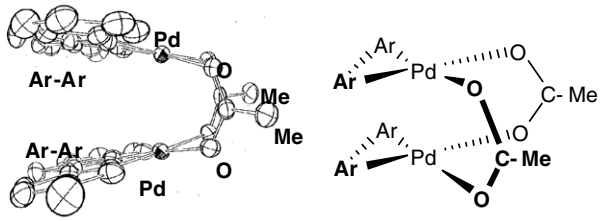


Fig. 5. "Boat" form of acetato-bridged Pd dipyridylamine dimers [39].

3. Conclusion

Due to the Pd coordination ability of the pyridine-nitrogens, the *N*-aryl-2-pyridylamine substrates **4**, **7**, **11** were subjected to $Pd(OAc)_2$ complexations and a number of *N*-aryl-2-pyridylamine Pd complexes (**13**–**17**) were isolated and characterised. The suggested structures for the palladium complexes are in particular based on ESI-MS and a series of NMR experiments.

$Pd(OAc)_2$ and an additional oxidant, such as H_2O_2 or benzoquinone afforded a dimeric acetato-bridged 6-membered palladacycle **13** from phenylpyridylamine **4**. This protocol represents a simple and new preparation method for the formation of the dimeric Pd^{II} complex **13**.

Pd complexes, **14a**,**b** or **15a**,**b** were formed by stirring **7** with $Pd(OAc)_2$ at low or high temperature, respectively. Complexes **16a**,**b** or **17a**,**b** were correspondingly formed from substrate **11**. The dipyridylamines **7**, **11** formed acetato-bridged dimeric $Pd_2Lig_2OAc_2$ complexes **14a**,**b**/**16a**,**b** at room temperature, while an additional $Pd(OAc)_2$ was introduced at higher temperature to give $Pd_3Lig_2OAc_4$ complexes **15a**,**b**/**17a**,**b**. Due to the unsymmetrical nature of the substrates, suggested structures for **14a**,**b**–**17a**,**b** would be *cis*/*trans* Pd complexes where the deprotonated dipyridylamine coordinates to Pd^{II} in a bidentate manner through the two pyridine-nitrogen atoms (**14a**,**b**/**16a**,**b**) and additionally through the amino-nitrogens (**15a**,**b**/**17a**,**b**). The amines **7** and **11** were recovered when the respective complexes **14a**,**b**, **15a**,**b**, **16a**,**b** or **17a**,**b** were treated with NH_3.

The *N*-aryl-2-pyridylamine substrates (**4**, **7**, **11**) were prepared by oxidative nucleophilic substitution, by 1,3-cycloaddition reaction or by Buchwald amination.

4. Experimental

Solvents: pro analysis quality. $^1H/^{13}C$ NMR: Bruker Avance DPX 300 and 400 MHz spectrometers, chemical shifts are reported in ppm down-field from TMS. *J* values are given in Hz. EI-MS: Finnigan MAT 95 XL (70 eV); ESI-MS: WatersQTOF 2 W (solvent acetonitrile, 10 μL/min; cone voltage 10–50 V). The reported *m*/*z* values represented the major peak in the groups of peaks caused by the respective Pd_{1-3} isotope distribution. IR: Nicolet 20SXC FT-IR spectrophotometer. All melting points are uncorrected, measured by Griffin apparatus. Flash chromatography: Silica (sds, 60 A, 40–63 μm). Methyl 3-nitro-4-pyridine carboxylate (**3**) was prepared according to the literature [16,17].

4.1. Methyl 5-nitro-2-(phenylamino)-4-pyridinecarboxylate (4)

NaH (72.5 mg, 3.02 mmol, 1.1 equiv.) and formanilide (400 mg, 3.29 mmol, 1.2 equiv.) in dry DMF (10 mL) was added methyl 3-nitro-4-pyridinecarboxylate (**3**, 500 mg, 2.74 mmol), dissolved in DMF (3 mL) with stirring [13]. The mixture was heated to 100 °C for 2 h and acetic acid (0.5 mL) was added. The reaction mixture was poured into ice/water (50 mL). A precipitate resulted. Additional material was obtained by diethyl ether extraction. The combined crude product was purified by flash chromatography (ethyl acetate/hexane 4:1) and crystallized from acetone and pentane to give crystalline **4** (244 mg, 33%), pure by NMR. M.p. 160.1–160.6 °C; IR (KBr) 3353m, 2956w, 1720s, 1625m, 1594m, 1548s, 1503s, 1447m, 1325m, 1235m, 1077m, 749w (cm^{-1}); ^1H NMR (300 MHz, DMSO-d_6): δ 3.88 (s, 3H, CO_2CH_3), 6.92 (s, 1H, H-3), 7.12 (t, *J* 7.2, 1H, H-4′), 7.38 (t, *J* 7.9, 2H, H-3′, 5′), 7.67 (d, *J* 7.8, 2H, H-2′], 6′), 8.98 (s, 1H, H-6), 10.34 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 53.8 (CO_2CH_3), 109.1 (C-3), 121.0 (C-2′, 6′), 124.3 (C-4′), 129.5 (C-3′, 5′), 133.4 (C-5), 137.6 (C-4), 139.3 (C-1′), 147.8 (C-6), 159.0 (C-2), 165.6 (CO_2CH_3); EI-MS: *m*/*z* 273 (M^+, 100%), 272 (93), 169 (25), 168 (44), 142 (11), 115 (4); HRMS: calcd for $C_{13}H_{11}N_3O_4$, 273.07495; observed 273.07438. X-ray [14].

4.2. Methyl 3-nitro-9H-pyrido[2,3-b]indole-4-carboxylate (5)

The oxidative cyclisation product **5** was formed from **13** in the MS process (49% of 50 V ESI-MS base peak): ESI-MS: *m*/*z* 271 (M^+, 41%), 241 (7), 226 (7), 195 (7), 181 (4), 167 (23), 140 (5), 60 (70), 43 (100); EI-HRMS: calcd for $C_{13}H_9N_3O_4$, 271.05930; observed 271.05887; ESI-HRMS: calcd for [$C_{13}H_9N_3O_4+H^+$]: 272.0671; observed 272.0664.

4.3. N-(2′-pyridyl)-2-amino-5-nitropyridine (7) [24–26]

To a stirred solution of $Pd_2(dba)_3 \cdot CHCl_3$ (25 mg, 0.025 mmol, 0.02 equiv.) and NaO*t*Bu (165 mg, 1.723 mmol, 1.4 equiv.) in toluene (5 ml) under nitrogen atmosphere was added a solution of 2-aminopyridine (139 mg, 1.477 mmol, 1.2 equiv.), **8** (250 mg, 1.231 mmol, 1 equiv.) and dppp (20 mg, 0.0492 mmol, 0.04 equiv.) in toluene (10 ml) by a syringe. The mixture was stirred for 18 h at room temperature and filtered through celite, eluting with CH_2Cl_2. The filtrate was concentrated under reduced pressure to provide a yellow solid. Compound **7** was isolated by recrystallisation of the crude product from CH_2Cl_2 in 64% yield (169 mg), pure by ^1H NMR. ^1H NMR (400 MHz, DMSO-d_6): δ 7.05 (ddd, *J* 1.6, 4.8, 6.8, 1H,

H5′), 7.75–7.83 (m, 2H, H3′+H4′) 8.15 (d, *J* 9.3, 1H, H3), 8.33 (ddd, *J* 0.8, 1.6, 4.8, 1H, H6′), 8.43 (dd, *J* 2.8, 9.2, 1H, H4), 9.07 (d, *J* 2.8, 1H, H6), 10.70 (br, s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 110.6 (C3), 113.3 (C3′), 118.1 (C5′), 133.1 (C4), 137.1 (C5), 138.1 (C4′), 145.3 (C6), 147.8 (C6′), 152.9 (C2′), 157.9 (C2); NMR assignments are based on HMBC, HSQC and COSY NMR experiments; EI-MS: *m*/*z* 216 (M^+, 26%), 169 (10), 78 (30), 43 (100); HRMS: calcd for $C_{10}H_8N_4O_2$, 216.0673; observed 216.0673. Compound **7** was recovered by treatment of CH_2Cl_2 solutions of **14** or **15** with aqueous NH_3 (25%). Anal. Calc. for $C_{10}H_8N_4O_2$: C, 55.55; H, 3.73; N, 25.91. Found: C, 55.45; H, 3.71; N, 25.85%.

4.4. N-(5′-Methyl-2′-pyridyl)-2-amino-5-nitropyridine (*11*)

The title compound was prepared as described above for **7**, using $Pd_2(dba)_3 \cdot CHCl_3$ (148 mg, 0.025 mmol, 0.02 equiv.) and NaO*t*Bu (961 mg, 9.99 mmol, 1.4 equiv.), toluene (10 ml), **10** (850 mg, 1.48 mmol, 1.2 equiv.), **8** (1450 mg, 7.14 mmol, 1 equiv.) and dppp (118 mg, 0.286 mmol, 0.04 equiv.) in toluene (50 ml). Crystalline **7** was obtained in 62% yield (1014 mg), pure by ^{1}H NMR. M.p. 201.0–201.8 °C; IR (KBr) 3264w, 3188w, 2985m, 1591s, 1552m, 1494s, 1402m, 1335s, 1291s, 1120m, 1033w, 1010w, 824s, 761m (cm^{-1}); ^{1}H NMR (400 MHz, d_6-acetone): δ 2.30, (s, 3 H, CH_3), 7.62 dd, *J* 0.8, 8.4, 1H, (H4′), 7.72 (d, *J* 8.4, 1H, H3′), 8.06 (d, *J* 9.4, 1H, H3), 8.18 (d, *J* 0.8, 1H, H6′), 8.41 (dd, *J* 2.8, 9.4, 1H, H4), 9.06 (d, *J* 2.8, 1H, H6), 9.51 (br, s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8 (Me), 111.3 (C3), 113.8 (C3′), 128.4 (C5′), 133.9 (C4), 138.7 (C2), 139.6 (C4′), 146.2 (C6), 148.5 (C6′), 152.0 (C2), 159.2 (C5); NMR assignments are based on HMBC, HSQC and COSY NMR experiments; EI-MS: *m*/*z* 230 (M^+, 48%), 200 (4), 183 (17), 92 (93), 65 (100); HRMS: calcd for $C_{11}H_{10}N_4O_2$, 230.08038; observed 230.08016. Compound **11** was recovered by treatment of CH_2Cl_2 solutions of **14** or **15** with aqueous NH_3 (25%).

4.5. bis(Methyl 5-nitro-2-(phenylamino)-4-pyridinecarboxylate)bis-acetato-Pd_2 palladacycle complex (*13*)

A mixture of **4** (50 mg, 0.183 mmol, 1 equiv.) and palladium(II) acetate (41 mg, 0.183 mmol, 1 equiv.) in acetic acid (1 ml) and H_2O_2 (31 ml, 0.457 mmol, 2.5 equiv.) was heated to 90 °C for 1 h. Alternatively H_2O_2 could be replaced by benzoquinone (1.2 equiv.). The mixture was cooled to room temperature, filtered through silica, eluting with CH_2Cl_2. The filtrate was concentrated under reduced pressure to provide **13** in 42% (67 mg) yield, pure by ^{1}H NMR. IR (KBr) 3444w, 3122w, 1623w, 1602w, 1557s, 1505s, 1456m, 1435s 1336s, 1266s, 1233s, 1150w, 1121s, 1109s, 1022m, 862w, 828w, 770s, 752m (cm^{-1}); ^{1}H NMR (400 MHz, d_6-acetone): δ 2.04 (s, 3H, OAc), 3.90 (s, 3H, ester-CH_3), 6.53 (ddd, *J* 1.2, 6.0, 8.0, 1H, H-4′), 6.61 (dd, *J* 1.2, 8.0, 1H, H6′), 6.80 (ddd, *J* 1.2, 6.0, 8.0, 1H, H-5′), 6.85 (s, 1H, H5), 6.97 (dd, *J* 1.2, 8.0, 1H, H3′), 8.82 (s, 1H, H2), 10.16 (s, br, NH); ^{13}C NMR (100 MHz, d_6-acetone): δ 24.7 (OAc), 53.6 (ester-CH_3), 113.2 (C5), 116.8 (C6′), 118.7 (C2′), 122.8 (C4′), 125.7 (C5′), 133.6 (C1′), 133.8 (C3), 134.2 (C3′), 135.2 (C4), 149.5 (C2), 149.6 (C6), 165.0 (ester C=O), 181.4 (Ac C–O); NMR assignments are based on HMBC, HSQC and COSY NMR experiments; ESI-MS (cone voltage 10 V): 877 ($Pd_2Lig_2(OAc)_2+H^+ = C_{30}H_{26}N_6O_{12}Pd_2+H^+$, 18%), 419 (PdLig(MeCN) = $C_{15}H_{13}N_4O_4Pd$, 100), see Table 1. The data were in full agreement with the corresponding calculated values, matching completely the theoretical isotope distribution pattern. Anal Calc. for $C_{30}H_{26}N_6O_{12}Pd_2$: C, 41.16; H, 2.99; N, 9.60; Pd, 24.31. Found: C, 40.86; H, 3.02; N, 9.54; Pd, 24.07%.

4.6. (Methyl 5-nitro-2-(phenylamino)-4-pyridinecarboxylate)pyridine mononuclear palladacyclic Pd complex (*13a*)

Complex **13** (8 mg, 1 equiv.) in CH_2Cl_2 (2.5 ml) was added pyridine (2 ml, 2 equiv.) and stirred overnight. The crude complex **13a**, obtained by evaporation was dissolved in CH_2Cl_2 and added hexane. Yellow crystal were obtained (6 mg, 70%), pure by NMR. ^{1}H NMR (400 MHz, d_6-acetone): δ 8.83 (s, 1H, H2), 8.57 (d, *J* 4.1, 2H, pyr-H2 and-H6), 7.75 (m, 1H, H4), 7.34 (m, 2H, pyr-H3 and -H5), 7.0 (dd, *J* 8.1, 2.2, 1H, H3′), 6.87 (s, 1H, H5), 6.81 (ddd, *J* 8.4, 6.7, 1.2, 1H, H5′), 6.67 (d, *J* 7.7, 1H, H6), 6.53 (ddd, *J* 8.2, 6.7, 1.2, 1H, H4′), 3.91 (s, 3H, ester-OMe), 2.08 (s, 3H, OAc); The following ^{13}C NMR (100 MHz, d_6-acetone) assignments were observed by HSQC: δ 24.9 (OAc), 53.8 (ester-OMe), 113.1 (C5), 116.8 (C6′), 123.0 (C4′), 125.7 (C5′), 134.3 (C3′), 149.5 (C2).

4.7. bis(N-(2′-Pyridyl)-2-amino-5-nitropyridine)bis-acetato-Pd_2 complexes (*14a,b*)

The title compounds were obtained quantitatively in approximately 1:2 mixture by stirring compound **7** (200 mg, 0.93 mmol) and $Pd(OAc)_2$ (210 mg, 1 equiv.) in dichloromethane (5 ml) at room temperature overnight; IR (KBr) 3431w, 3076w, 2927 m, 1659s, 1636s, 1568s, 1514s, 1482s, 1458s, 1431s 1345s, 1288m, 1236s, 1165m, 1121s, 1029m, 853m, 840m, 778m, 754m, 688m (cm^{-1}); **14a**: ^{1}H NMR (300 MHz, d_6-acetone): δ 2.15 (s, 3H, OAc), 6.45 (d, *J* 9.6, 1H, H-3), 6.55 (m, 1H, H-5′), 6.80 (dd, *J* 1.2, 8.4, 1H, H-6′), 7.48 (m, 1H, H-4′), 7.52 (dd, *J* 1.5, 6.6, 1H, H-3′), 7.69 (dd, *J* 2.7, 9.6, 1H, H-4), 8.23 (d, *J* 2.7, 1H, H-6); **14b**: ^{1}H NMR (300 MHz, d_6-acetone): δ 2.13 (s, 3H, OAc), 6.51 (m, 1H, H-3), 6.55 (m, 1H, H-5′), 6.82 (dd, *J* 1.2, 8.4, 1H, H-6′), 7.48 (m, 1H, H-4′), 7.60 (dd, *J* 1.5, 6.6, 1H, H-3′), 7.75 (dd, *J* 2.7, 9.6, 1H, H-4), 8.25 (d, *J* 2.7, 1H, H-6). NMR assignments are based on COSY NMR experiments; ESI-MS (cone voltage 10 V): 763 ($Pd_2Lig_2(OAc)_2+H^+ = C_{24}H_{20}N_8O_8Pd_2+H^+$, 25%),

381 (PdLig(OAc) = $C_{12}H_{11}N_4O_4Pd$, 100), see Table 1. The data were in full agreement with the corresponding calculated values, matching completely the theoretical isotope distribution pattern. Anal. Calc. for $C_{24}H_{22}N_8O_8Pd_2$: C, 37.76; H, 2.91; N, 14.68; Pd, 27.88. Found: C, 38.31; H, 3.12; N, 16; Pd, 28%.

4.8. bis(N-(2′-Pyridyl)-2-amino-5-nitropyridine)tetraacetato-Pd_3 complexes (**15a,b**)

The title compounds were obtained quantitatively in approximately 1:2 mixture by heating compound **7** (200 mg, 0.93 mmol) and $Pd(OAc)_2$ (420 mg, 2 equiv.) in acetic acid for 1 h, in dichloromethane for 3 h or in toluene for 5 min. Alternatively, **14a**,**b** could readily be transformed into **15a**,**b** by heating in dichloromethane for 3 h; IR (KBr) 3444w, 3122w, 1623w, 1602w, 1557s, 1505s, 1456m, 1435s 1336s, 1266s, 1233s, 1150w, 1121s, 1109s, 1022m, 862w, 828w, 770s, 752m (cm^{-1}); ^1H NMR (400 MHz, d_6-acetone): **15a**: δ 1.79 (s, 3H, OAc_a), 2.08 (s, 3H, OAc_b), 7.03 (dt, *J* 1.4, 6.8, 1H, H-5′), 7.79 (dd, *J* 1.2, 6.0, 1 H, H-6′), 8.04 (dt, *J* 1.4, 7.8, 1H, H-4′), 8.12 (dd, *J* 2.8, 9.4, 1H, H-4), 8.43 (d, *J* 2.8, 1H, H-6), 9.31 (d, *J* 8.4, 1H, H-3′), 9.78 (d, *J* 9.4, 1H, H-3); ^{13}C NMR (100 MHz, d_6-acetone): δ 22.3 (OAc_a), 23.9 (OAc_b), 120.5 (C-5′), 124.2 (C-3), 125.1 (C-3′), 132.1 (C-4), 137.5 (C-5), 141.5 (C-4′), 144.9 (C-6), 146.7 (C-6′), 153.5 (C-1′), 157.0 (C-1), 186.36 (Ac_b O–C–O), 189.43 (Ac_a O–C–O); **15b**: δ 1.80 (s, 3H, OAc_a), 2.08 (s, 3H, OAc_b), 6.90 (dt, *J* 1.2, 6.6, 1H, H-5′), 7.68 (dd, *J* 1.4, 6.2, 1H, H-6′), 7.83 (t, *J* 7.7, 1H, H-4′), 8.34 (dd, *J* 2.8, 9.6, 1H, H-4), 8.53 (d, *J* 2.4, 1H, H-6), 9.49 (d, *J* 8.0, 1H, H-3′), 9.75 (d, *J* 9.6, 1H, H-3); ^{13}C NMR (100 MHz, d_6-acetone): δ 22.6 (OAc_a), 23.9 (OAc_b), 119.6 (C-5′), 124.2 (C-3), 125.4 (C-3′), 132.8 (C-4), 138.2 (C-5), 140.9 (C-4′), 145.1 (C-6), 146.5 (C-6′), 153.7 (C-1′), 156.6 (C-1), 186.36 (Ac_b O–C–O), 189.31 (Ac_a O–C–O). NMR assignments are based on COSY, HSQC, HMBC APT NMR experiments; ESI-MS (cone voltage 10 V): 927 (**15a**,**b**-OAc+H^+; $Pd_3Lig_2(OAc)_3+H^+ = C_{26}H_{22}N_8O_{10}Pd_3+H^+$, 100%), see Table 1. The data were in full agreement with the corresponding calculated values, matching completely the theoretical isotope distribution pattern.

4.9. bis(N-(5′-Methyl-2′-pyridyl)-2-amino-5-nitropyridine)bis-acetato-Pd_2 complexes (**16a,b**)

The title compounds were obtained from **11** and $Pd(OAc)_2$ as described above for **14a**,**b**. The complexes **16a**,**b** were, however, more unstable and transformed rapidly into complex mixture **17a**,**b**. Complex **16a**,**b** therefore often appeared in mixture with **17a**,**b**; ^1H NMR (400 MHz, $CDCl_3$): **16a**: δ 2.19 (bs, 3H, CH_3) 6.39 (d, *J* 9.6, 1H, H-3), 6.82 (d, *J* 9.1, 1H, H-6′), 7.22 (m, 1H, H-3′), 7.46 (bs, 1H, H-4′), 7.61 (dd, *J* 2.5, 9.6, 1H, H-4), 8.15 (d, *J* 2.5, 1H, H-6); **16b**: δ 2.12 (bs, 3H, CH_3), 6.47 (d, *J* 9.3, 1H, H-3), 6.77 (d, *J* 8.6, 1H, H-6′), 7.20 (dd, *J* 2.5, 8.6, 1H, H-3′), 7.46 (bs, 1H, H-4′), 7.72 (dd, *J* 2.5, 9.6, 1H, H-4), 8.22 (d, *J* 2.5, 1H, H-6). NMR assignments are based on comparison with complexes **14a**,**b**. ESI-MS (cone voltage 10 V): 791 ($Pd_2Lig_2(OAc)_2+H^+ = C_{26}H_{24}N_8O_8Pd_2+H^+$, 87%), 395 (PdLig(OAc) = $C_{13}H_{13}N_4O_4Pd$, 100), see Table 1 and Fig. 2. The data were in full agreement with the corresponding calculated values, matching completely the theoretical isotope distribution pattern. Anal. Calc. for $C_{26}H_{26}N_8O_8Pd_2$: C, 39.46; H, 3.31; N, 14.16; Pd, 26.90. Found: C, 39.57; H, 3.14; N, 11.55; Pd, 21.89%.

4.10. bis(N-(5′-Methyl-2′-pyridyl)-2-amino-5-nitropyridine)tetraacetato-Pd_3 complexes (**17a,b**)

The title compounds were obtained in a 1:2 mixture from compound **11** (200 mg, 0.87 mmol, 1 equiv.) and $Pd(OAc)_2$ (390 mg, 1.74 mmol, 2 equiv.) as described above for the preparation of **15a**,**b**; IR (KBr) 3444w, 3030w, 2926w, 1614s, 1567s, 1556s, 1497m, 1470s 1423s, 1336s, 1291s, 1272s, 1250m, 1208m, 1226s, 835m, 752m, 736m, 691m (cm^{-1}); ^1H NMR (400 MHz,, $CDCl_3$): **17a**: δ 2.00 (bs, 3H, OAc_a), 2.09 (bs, 3H, OAc_b), 2.25 (bs, 3H, CH_3), 7.45 (bs, 1H, H-6′), 7.76 (dd, *J* 1.6, 8.4, 1H, H-4′), 8.03 (dd, *J* 2.8, 9.6, 1H, H-4), 8.32 (d, *J* 2.8, 1H, H-6), 9.15 (d, *J* 8.4, 1H, H-3′), 9.76 (d, *J* 9.6, 1H, H-3); ^{13}C NMR (100MHz, $CDCl_3$): δ 18.1 (*C*H_3), 23.0 (OAc_a), 24.1 (OAc_b), 123.5 (C-3), 123.9 (C-3′), 130.1 (C-5′), 131.4 (C-4), 136.4 (C-5), 142.2 (C-4′), 143.8 (C-6), 143.9 (C-6′), 151.0 (C-2′), 156.4 (C-2), 179.1 (Ac_a O–C–O), 185.6 (Ac_b O–C–O). Compound **17b**: δ 2.01 (bs, 3H, OAc_a), 2.09 (bs, 3H, OAc_b), 2.15 (bs, 3H, CH_3), 7.31 (bs, 1H, H-6′), 7.56 (dd, *J* 2.0, 8.8, 1H, H-4′), 8.24 (dd, *J* 2.8, 9.6, 1H, H-4), 8.47 (d, *J* 2.8, 1H, H-6), 9.41 (d, *J* 8.8, 1H, H-3′), 9.70 (s, *J* 9.6, 1H, H-3); ^{13}C NMR (100MHz, $CDCl_3$): δ 17.8 (*C*H_3), 23.0 (OAc_a), 24.1 (OAc_b), 123.6 (C-3), 124.4 (C-3′), 128.7 (C-5′), 132.0 (C-4), 137.3 (C-5), 141.7 (C-4′), 143.6 (C-6′), 143.9 (C-6), 151.2 (C-2′), 155.8 (C-2), 179.0 (Ac_a O–C–O), 185.6 (Ac_b O–C–O). NMR assignments are based on COSY, HSQC, HMBC, APT NMR experiments; ESI-MS (cone voltage 10 V): 955 (**17a**,**b**-OAc+H^+; $Pd_3Lig_2(OAc)_3+H^+ = C_{28}H_{26}N_8O_{10}Pd_3+H^+$, 100%), see Table 1. The data were in full agreement with the corresponding calculated values, matching completely the theoretical isotope distribution pattern.

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