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Synthesis and characterization of new heterocyclic Schiff base palladacycles: Ring activation through *N*-oxide formation

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Reaction of the Schiff base ligand derived from 4-pyridinecarboxaldehyde $NC_5H_4C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]$, (**1**), with palladium(II) acetate in toluene at 60 °C for 24 h gave $[Pd\{NC_5H_4C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}_2(OCOCH_3)_2]$, (**2**), with two ligands coordinated through the pyridine nitrogen. Treatment of the Schiff base ligand derived from 4-pyridinecarboxaldehyde *N*-oxide, $4\text{-}(O)NC_5H_4C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]$, (**4**), with palladium(II) acetate in toluene at 75 °C gave the dinuclear acetato-bridged complex $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(OCOCH_3)]_2$, (**5**) with metallation of an aromatic phenyl carbon. Reaction of complex **5** with sodium chloride or lithium bromide gave the dinuclear halogen-bridged complexes $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(Cl)]_2$, (**6**) and $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(Br)]_2$, (**7**), after the metathesis reaction. Reaction of **6** and **7** with triphenylphosphine gave the mononuclear species $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(Cl)(PPh_3)]$, (**8**) and $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}\text{-}(Br)(PPh_3)]$, (**9**), as air stable solids. Treatment of **6** and **7** with $Ph_2P(CH_2)_2PPh_2$ (dppe) in a complex/diphosphine 1:2 molar ratio gave the mononuclear complexes $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(PPh_2(CH_2)_2PPh_2)][Cl]$, (**10**), and $[Pd\{4\text{-}(O)NC_5H_3C(H){=}N[2',4',6'\text{-}(CH_3)C_6H_2]\}(PPh_2(CH_2)_2PPh_2)][PF_6]$, (**11**), with a chelating diphosphine. The molecular structure of complex **9** was determined by X-ray single crystal diffraction analysis.

1. Introduction

The chemistry of cyclometallated transition metal complexes has been of interest to the organometallic chemist [1,2] not only due to their synthetic and structural characteristics but also to their growing applications such as the use in catalytic and synthetic processes [3], as chiral auxiliaries [4] or as building blocks for complex molecular architectures [5]. They also show interesting mesogenic [6], luminescent, electronic properties [7] and potential applications in medicine and biology [8].

This has prompted our interest in the synthesis of new cyclometallated metalloligands bearing uncoordinated pyridine rings. Ligands with pyridine rings have been extensively studied as building blocks in the construction of supramolecular assemblies [9–17]; yet, few examples in which the heterocyclic ring is part of a cyclometallated ligand have been reported [18–20]. This is probably due to the ease with which the pyridine nitrogen coordinates to the metal center, precluding the access of the C–H bond to the palladium atom [21], in which case the use of indirect methods may be necessary to metallate the ligand [19]. In our quest for new types of metalloligands bearing cyclometallated units we studied the reaction between the Schiff base **1**, bearing a pyridine ring, and palladium(II) acetate that only gave a complex with the ligand coordinated to the palladium atom through the pyridine nitrogen, and no palladium–carbon bond formation. We reasoned that by protecting the pyridine nitrogen we could preclude *N*-coordination and favour *C*-metallation; consequently, reaction of **1** with MeI gave the *N*-methylated Schiff base **3** that, however, did not in turn produce the expected cyclometallated complex; nevertheless, the analogous *N*-oxide Schiff base was readily metallated, bringing forth a new family of potentially oxygen coordinating metalloligands.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterized by elemental analysis (C, H, N), and IR and ^1H, $^{13}C\{1H\}$ and $^{31}P\{1H\}$ spectroscopy (see Section 3) and, in part, by mass spectrometry and X-ray single crystal diffraction

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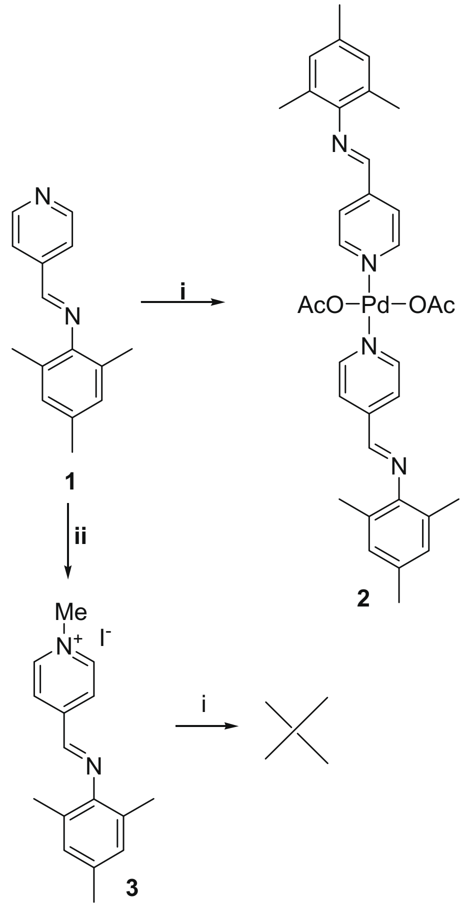

Scheme 1. (i) $Pd(OAc)_2$, toluene, 60 °C; (ii) MeI, toluene, 90 °C.

analysis. Reaction of the Schiff base ligand **1** with palladium(II) acetate in toluene at 60 °C for 24 h gave the non-cyclometallated complex **2** with two ligands coordinated to the palladium atom through the pyridine nitrogen. The doublet signals assignable to the H2/H6 protons, in the ^1H NMR spectrum, was in agreement with absence of Pd–C bond formation in **1**. The values shown by the $\nu(C{=}N)$ stretch, 1610 cm^{-1}, in the IR spectrum and by the the *H*C=N resonance in the ^1H NMR spectrum, 8.22 ppm, were similar to those for the free ligand, in accordance with the absence of bonding between the palladium and the non-aromatic iminic nitrogen [22,23]. Two strong bands at 1300 and 1555 cm^{-1} were assigned to the symmetric and asymmetric $\nu(COO)$ vibrations, respectively, in agreement with those expected for mono-coordinate acetato ligands [24,25]. The ^1H NMR spectrum showed a singlet signal for the acetate CH_3COO^- protons at 2.29 ppm and the $^{13}C\{1H\}$ NMR two signals assigned to the CH_3COO and the CH_3COO acetate carbons at 178.36 and 23.23 ppm, respectively. Regardless of the reaction conditions used (dichloromethane, room temperature; acetic acid, reflux) the reaction between ligand **1** and palladium(II) acetate gave in all cases the coordination complex **2** and not the expected cyclometallated compound.

The pyridine nitrogen of ligand **1** could be *N*-methylated with MeI in toluene at 90 °C in order to hinder its coordination through the pyridine nitrogen and, consequently, favour the cyclometallation reaction. However, reaction of the methylated Schiff base **3** with palladium(II) acetate under analogous reaction conditions as used in the synthesis of **2** (toluene, 60 °C) did not yield the desired product; instead of this a large amount of black palladium appeared in the reaction tube and an untreatable reaction mixture was isolated from the solution. Other reaction conditions ($Pd(OAc)_2$, CH_2Cl_2, r.t.; K_2PdCl_4, H_2O, r.t.; Li_2PdCl_4, MeOH, r.t.) failed to produce the expected complexes.

However, treatment of the *N*-oxide of the Schiff base, **4**, with $Pd(OAC)_2$ in toluene at 75 °C for 48 h gave the dimer **5**, metallated at the aromatic C6 carbon atom. The IR spectrum of **5** showed the $\nu(C{=}N)$ stretching band (see Section 3) shifted to lower frequency (compared to the free imine) in agreement with nitrogen coordination to metal center [22]. This was supported by the characteristic upfield shift (0.43 ppm) of the NMR signal for the imine proton, observed in the cyclometallated complexes as a consequence of *N*-coordination [23,26–28]. The IR spectrum showed to strong bands $\nu_{as}(COO)$ and $\nu_s(COO)$ at 1577 and 1420 cm^{-1}, respectively, in accordance with bridging acetate groups [24,26,28]. The *trans* geometry of the cyclometallated moieties was determined by the presence at 2.44 ppm of a singlet signal in the ^1H NMR spectrum, assigned to the two equivalent methyl acetate protons [29]. Complex **5** was also characterized by $^{13}C\{1H\}$ NMR spectroscopy, being the most noticeable feature the shift to higher frequency of the C6, C=N, and C1 resonances (as compared to the uncoordinated ligand or the non cyclometallated complex **2**), confirming the formation of the cyclometallated ring [25,30,31]. The FAB-mass spectrum showed at 809 amu the cluster of peaks assigned to $[\{(L\text{-}H)(OAc)Pd\}_2]^+$ (L-H = cyclometallated ligand), thereby confirming the dinuclear nature of the complex [32].

Complex **5** readily experimented metathesis reactions with sodium chloride or lithium bromide in acetone/water or methanol/water, respectively, to give the corresponding complexes with bridging halide ligands **6** and **7**. The mass spectra showed peaks assigned to $[\{(L\text{-}H)XPd\}_2H]^+$ (X = Cl, 763 amu; X = Br, 853 amu), consequent with the dinuclear formulation of the complexes. The IR and ^1H NMR spectra were similar to those for complex **5**, being the most noticeable differences the absence of the characteristic acetate bridging ligand signals.

Reaction of the halide-bridged complexes **6** and **7** with triphenylphosphine in chloroform gave the mononuclear complexes **8** and **9**, respectively, which were fully characterized (see Section 3). The IR spectra of these complexes showed the typical low-frequency shift of the $\nu(C{=}N)$ band (*vide supra*). In the ^1H NMR spectra the *H*C=N and H5 protons were coupled to the ^{31}P nucleus [δ *ca.* 8.08 ppm ($J(PH) = 7.8$ Hz) and δ *ca.* 7.0 ppm ($J(PH) = 3.9$ Hz), respectively], and the $^{31}P\{1H\}$ NMR spectra showed singlet resonances at *ca.* 39.5 ppm. In the $^{13}C\{1H\}$ spectra the low-field shift observed for the C6, C=N, and C1 resonances was similar to those found in the spectrum of **5** (*vide supra*) and the C5, resonance showed the coupling to the ^{31}P nucleus [$J(C5P)$ *ca.* 11]. The mass spectra of **8** and **9** showed peaks centred at 607 amu corresponding to the loss of the halide ligand and, for complex **8** at 643 amu assigned to the molecular ion.

2.1. Molecular structure of complex 9

Suitable crystals were grown by slowly evaporating a chloroform solution of **9**. The molecular structure is illustrated in Fig. 1.

The asymmetric unit comprises two solvent molecules of chloroform and a molecule of complex **9**; molecules of **9** are aligned along the *a*-axis and packed in layers parallel to *a* and *c*, between which the chloroform solvent molecules are located. The palladium atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the pyridine ring, the imine N(1) atom, the Br(1) atom and to the P(1) phosphorus atom of the triphenylphosphine ligand. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90° with the most noticeable distortions corresponding to the bite angle C(1)–Pd(1)–N(1) of 81.06(9)°. The sum of the angles about palladium is approximately 360°.