Cyclometalation *vs.* Werner-type coordination of sterically enforced palladium(II)-1,3-bis(pyridyl-2-imino)isoindolines (Pd-BPIs)†‡

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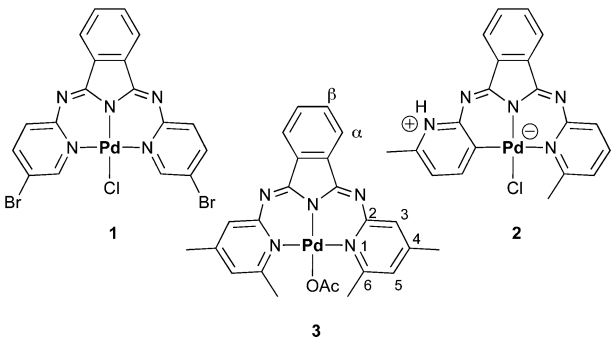
Received 10th January 2007, Accepted 1st February 2007
First published as an Advance Article on the web 14th February 2007
DOI: 10.1039/b700400a

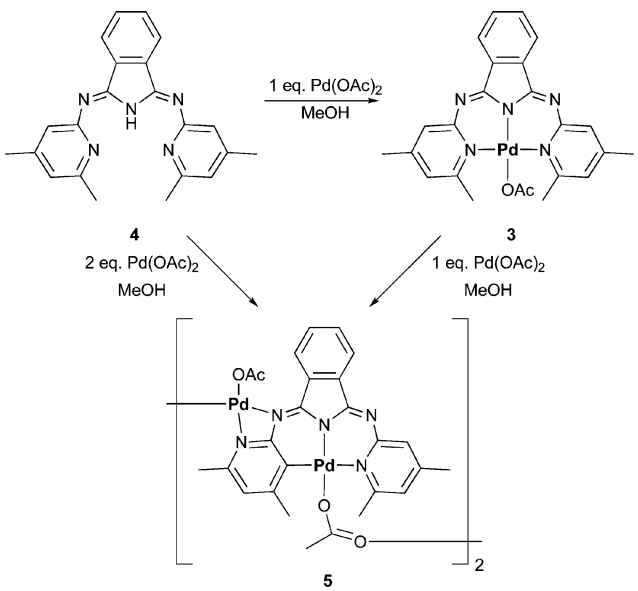
The reaction of 1,3-bis(4,6-dimethylpyridyl-2-imino)isoindoline and palladium acetate in methanol selectively yields the expected acetato palladium *N*,*N*,*N*-chelate or a cyclometalated tetranuclear dimer depending on the stoichiometry of the reactants.

Palladacycles[1] are compounds which typically constitute from one palladium(II) ion bound to a *C*,*X*- or *X*,*C*,*X*-chelate ligand. After their initial isolation from a complexation study on azobenzene derivatives in the 1960s[2] cyclopalladated compounds have received much attention, and numerous reviews have been dedicated to their synthesis and structure. In recent years many potential applications in organic synthesis, organometallic catalysis and in the construction of molecule-based materials have been found,[3] and in several instances palladacycles have been proposed as intermediates in palladium induced reactions.[4]

Very recently a cyclopalladation reaction was reported to occur yielding the 1,3-bis(6-methylpyridyl-2-imino)isoindoline (6-MeBPI) species **2**.[5] The driving force for the CH activation was proposed to be the strain that a classical Werner-type *N*,*N*,*N* binding would suffer from. Well-studied non-hindered examples of this class of palladium complex like **1** and others are known as classical coordination compounds.[6] Since we had studied the influence of intramolecular strain on the reactivity and structure of palladium(II) chelates of related meridonal-tridentate *N*,*N*,*N* ligands[7] before we were interested to see how the BPI system reacts if no unstrained alternative is provided. For the study we sought the tetramethyl derivative **3** as an ideal candidate, and we will show here, that under these circumstances a rearrangement and cyclopalladation can be induced by the coordination of a second palladium(II) ion.

The tetramethyl derivative 4,6-Me_2BPI **4** was prepared by a $CaCl_2$ promoted condensation of 2-amino-4,6-dimethylpyridine with phthalodinitrile according to a literature procedure.[8] Metal insertion proceeds smoothly with one equivalent of palladium acetate at ambient temperature and yields 93% of the Werner-type complex **3** after recrystallization (Scheme 1). **3** was unambigously analyzed by CHN and HRMS methods and further characterized by ^{1}H NMR spectroscopy. The NMR spectrum is indicative of a C_2 symmetric species with singlets for the pyridyl protons at C-3 and C-5 at 7.16 and 6.80 ppm, respectively. Further support for the structural assignment of **3** was obtained by a single crystal X-ray analysis.[9] **3** crystallizes from dichloromethane as a CH_2Cl_2 solvate, space group $P\bar{1}$, with two independant molecules in the asymmetric unit. In molecule A the acetato ligand was refined using a split atom model (66 : 34) for the non-coordinating oxygen atom. Molecule B was free of disorder but displayed a partially occupied position (42%) for a water molecule, hydrogen bonded to the acetato ligand. The metrics of the Pd–BPI complex fragment, however, are only slightly influenced by these differences, so that only the data of molecule A are dicussed further (Fig. 1).





Scheme 1 Formation of Werner-type mononuclear and cyclometallated tetranuclear Pd^{II} chelates **3** and **5** from 4,6-Me_2BPI **4**.

Complex **3** displays a distorted coordination geometry at the Pd^{II} center that could be expected from steric crowding at the terminal methyl positions C1 and C22. As indicated by the

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Full experimental descriptions and spectroscopic data for **3** and **5**. See DOI: 10.1039/b700400a

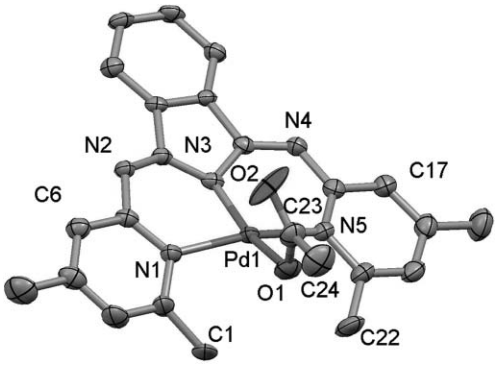

Fig. 1 Molecular structure of **3** (molecule A). Selected bond lengths (Å) and angles (°): Pd1–N1 2.056(4), Pd1–N3 1.960(4), Pd1–N5 2.081(5), Pd1–O1 2.060(4), C1–O1 2.856(7), C22–O1 2.786(9), C1–C22 3.737(10); N1–Pd1–N3 88.64(16), N1–Pd1–N5 166.21(18), N1–Pd1–O1 90.50(16), N3–Pd1–N5 91.27(17), N3–Pd1–O1 161.29(16), N5–Pd1–O1 93.95(16). Ellipsoids are set at 50% probability.

N3–Pd1–O1 angle of 161.29(16)°, the PdN_3O core of **3** deviates markedly from planarity. For **1** and **2** this angle was found to be somewhat relaxed at 167.74 and 165.13°, respectively. The acetato–BPI distances C1···O1 and C22···O1 are as short as 2.856(7) and 2.786(9) Å and therefore 16.0% and 18.1% below the van der Waals limit. A comparison with the data for **1** (Cl···H: 18.1%/20.2%) and **2** (Cl···H: 17.5%; Cl···CH_3: 16.3%) reveals that these percentages are typical lower limits within this class of substances. The data account for a significant amount of intramolecular strain mainly located within the PdN_3O fragment.

When **4** is treated with two equivalents of $Pd(OAc)_2$ the reaction leads to a different product **5**. While HRMS measurements of **5** indicate the presence of a monocationic Pd–BPI fragment the combustion analysis points to a dinuclear BPI species with two additional acetato ligands. The ^{1}H NMR shows a single, non-C_2 symmetric species with only three of the expected four pyridyl-H signals at 7.26, 6.98 and 5.42 ppm and two singlets for different acetato groups at 2.08 and 1.27 ppm. Although ^{13}C NMR data were not obtained due to the low solubility of **5**, the molecular structure could be derived from NOESY and HMBC experiments with the assumption of a dimeric composition [(4,6-Me_2BPI)$Pd_2(OAc)_2$]$_2$. Of particular importance is the finding, that the methyl protons of one of the acetato ligands couple to two different sets of pyridyl methyl group protons, one in the 4′- and the other in the 6-position. This is only possible, if the central palladium ion is bound to one of the pyridyl side chains by a Pd–C bond. Fig. 2 illustrates the NMR structure and indicates the discussed correlations.

Although no single crystals were obtained from **5**, the slow evaporation from a dichloromethane–*n*-hexane solution produced an orange plate of the related compound **5′**, in which the terminal acetates are exchanged against chlorido ligands.[10] The result from the X-ray crystallographic study on **5′** confirms the NMR-derived structure and is given in Fig. 3.[11]

5′ is composed from two crystallographically identical (4,6-Me_2BPI)Pd_2(OAc)Cl units which are located atop of each other and bound in this position by the bridging coordination mode of the acetato ligands. Crystallographically this dimer is situated on an inversion centre. Pd1 is in fact cyclometalated to C17 with a Pd1–C17 distance of 2.046(15) Å. This bond length is

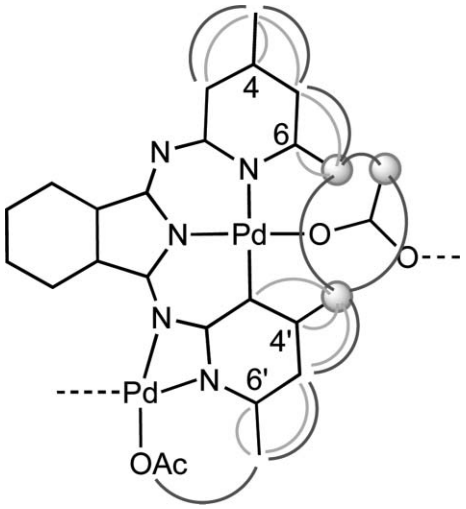

Fig. 2 Selected NOESY (dark) and HMBC (light) correlations for the assignment of the structure of **5** from 2D NMR experiments (400 MHz, CD_2Cl_2, 293 K). The acetato- and pyridyl-methyl groups referred to in the text are drawn as spheres.

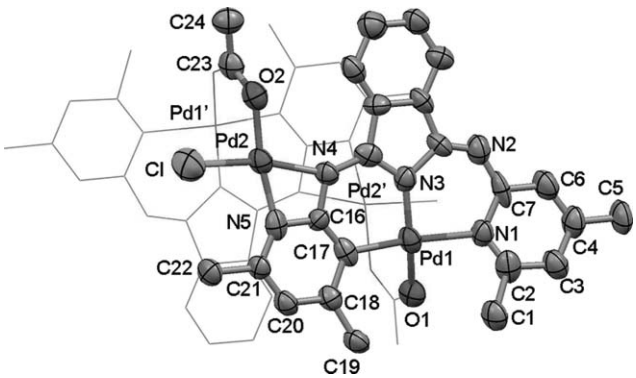

Fig. 3 Molecular structure of **5′**. Selected bond lengths (Å) and angles (°): Pd1–N1 2.161(14), Pd1–N3 1.942(15), Pd1–C17 2.046(15), Pd1–O1 1.998(12), Pd2–N4 2.074(13), Pd2–N5 1.961(15), Pd1–Cl 2.266(8), Pd2–O2 1.978(13), Pd1···Pd2′ 3.1208(18), O1–C1 2.81(2), O1–C19 2.85(2), C1–C19 4.19(3); N1–Pd1–N3 91.7(6), N1–Pd1–C17 166.0(6), N1–Pd1–O1 88.1(6), N3–Pd1–C17 88.3(7), N3–Pd1–O1 163.4(5), C17–Pd1–O1 95.9(6), N4–Pd2–N5 64.2(5), N4–Pd2–Cl 166.7(4), N4–Pd2–O2 108.0(5), N5–Pd2–Cl 103.1(4), N5–Pd2–O2 170.8(5), Cl–Pd2–O2 84.1(4). Pd2′ is at equivalent position (1 − *x*, −*y*, 1 − *z*) to Pd2. Ellipsoids are set at 50% probability.

significantly longer than the one reported for **2** (1.991 Å). The Pd1–N1 bond *trans* to the carbopalladated site, however, appears similarly elongated to 2.161(14) Å (2.152 Å for **2**) by the strong *trans*-influence of the *C* donor. The other palladium ion Pd2 binds to the periphery of the BPI unit at N4 and N5, thus forming a four-membered chelate ring with a N4–Pd2–N5 angle of only 64.2(5)°. This monomer is self-complementary and thus dimerizes to **5′** with a Pd1···Pd2′ distance of 3.1208(18) Å. The strain within the C1, O1, C19 and C1′, O1′, C19′ sections of the compound can be estimated by the short O1···C distances, which are 18.3% and 17.2% below the van der Waals limit and thus about identical to those of the Werner-type complex **3**.

Despite the fact, that the intramolecular strain of **3** and **5** appears about identical, the monomeric **3** reacts readily and

selectively with one equivalent of palladium acetate to yield the rearranged dimeric palladacycle **5**, while a mononuclear CH activated product like **2** has not been found with ligand **4**. This shows that a) intramolecular strain is in fact a sufficient driving force for pyridine ring rotation and CH activation in **2**, while for **4** a chemical trigger, *i.e.* the attack of a second palladium ion, is necessary to promote this process, and that b) the dimerization and formation of tetranuclear **5** as the only product from **4** is presumably a consequence of charge balance and the low solubility of the final product.

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9 Crystal data for $C_{24}H_{23}N_5O_2Pd{\cdot}CH_2Cl_2{\cdot}0.21H_2O$ **3**: red blocks, M = 608.62, triclinic, space group $P\bar{1}$, a = 12.6799(16), b = 14.5846(18), c = 15.753(2) Å, α = 115.166(14), β = 100.800(14), γ = 96.971(15)°, V = 2522.9(5) Å^3, Z = 4, D_c = 1.614 g cm^{-3}, μ = 0.974 mm^{-1}, $F(000)$ = 1281, 22917 reflections collected ($1.92 < \theta < 25.03°$) at 193(2) K, 8379 independent (R_{int} = 0.0488), that are used in the structure refinement, R_1 = 0.0427 [$I > 2\sigma(I)$], wR_2 = 0.1174 (all data), GOF = 1.050 for 677 parameters and 3 restraints, largest difference peak, hole = 0.966, −1.026 e Å^{-3}.

10 The chlorido ligand originatesfrom the decomposition of the solvent, see *e.g.*: D. R. Burfield, E. H. Goh, E. H. Ong and R. H. Smithers, *Gazz. Chim. Ital.*, 1983, **113**, 841.

11 Crystal data for $C_{48}H_{44}Cl_2N_{10}O_4Pd_4$ **5′**: orange plate, M = 1321.44, triclinic, space group $P\bar{1}$, a = 8.5886(16), b = 11.834(3), c = 12.123(3) Å, α = 90.44(3), β = 97.63(2), γ = 104.77(2)°, V = 1179.9(4) Å^3, Z = 1, D_c = 1.860 g cm^{-3}, μ = 1.670 mm^{-1}, $F(000)$ = 652, 11593 reflections collected ($2.41 < \theta < 26.07°$) at 193(2) K, 4296 independent (R_{int} = 0.1183), that are used in the structure refinement, R_1 = 0.0869 [$I > 2\sigma(I)$], wR_2 = 0.2451 (all data), GOF = 0.829 for 313 parameters and 0 restraints, largest difference peak, hole = 1.476, −2.103 e Å^{-3}. CCDC reference numbers 626407 and 626408. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700400a.