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Inner C-arylation of a doubly N-confused porphyrin–Pd complex in toluene—the possibility of a Pd^{3+} intermediate†

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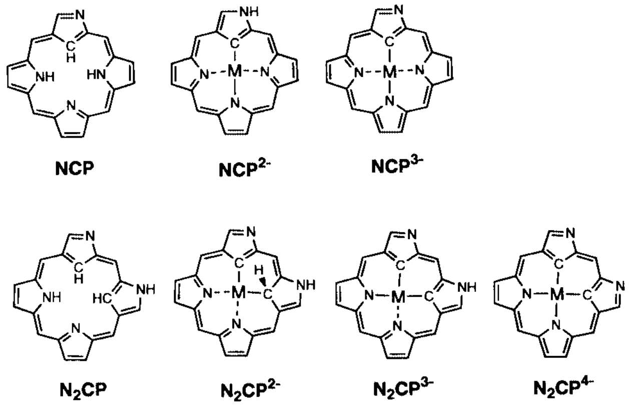
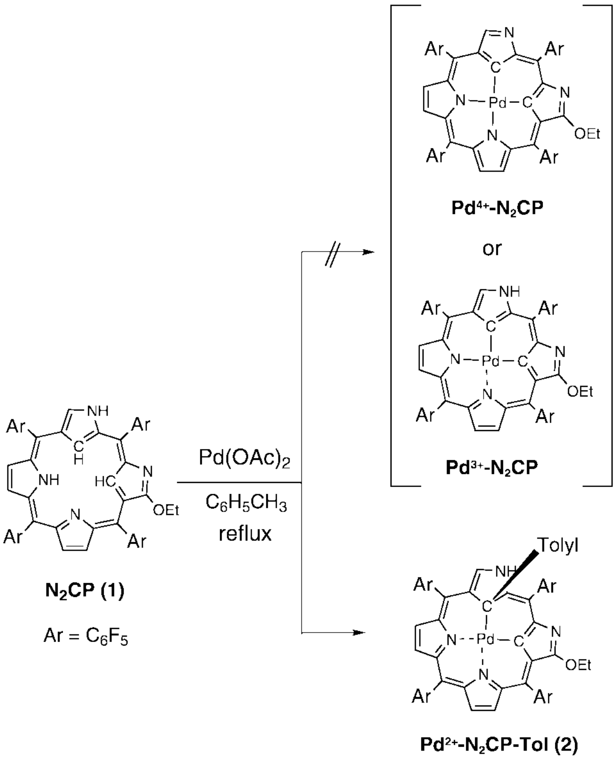
An inner C-tolyl substituted Pd^{2+} complex of a doubly N-confused porphyrin (N$_2$CP) was obtained from the reaction of N$_2$CP and Pd(OAc)$_2$ in toluene and the structure was revealed by a single crystal X-ray analysis.

'N-Confused porphyrin' (NCP) or 'inverted porphyrin' is a porphyrin isomer wherein one of the pyrrolic rings is inverted.[1,2] Owing to the inner core carbon and outward pointing nitrogen, NCP coordination chemistry differs greatly from that of normal porphyrins.[3–5] For example, NCP can serve as both a divalent (NCP^{2-}) and a trivalent (NCP^{3-}) ligand with d^8 metals such as Ni^{2+} and Ag^{3+}.[2,5] Recently, we have succeeded in synthesizing 'doubly N-confused porphyrin (N$_2$CP)' and disclosed its trivalent (N$_2$CP^{3-}) ligand nature in the complexation of Cu^{3+} and Ag^{3+}.[6] If the multi-valence property observed in NCP was common in all NCP families,[7] other valences, such as N$_2$CP^{2-} or N$_2$CP^{4-}, could be expected for divalent (M^{2+}) or tetravalent (M^{4+}) metal coordination. By keeping this point in mind, we have examined Pd complexation with N$_2$CP because square planar coordination of Pd^{2+} and/or Pd^{4+} is well known.[8] Interestingly, the synthesized complex was Pd^{2+}–N$_2$CP bearing a solvent molecule at an inner core carbon. In this communication, the X-ray structure and absorption spectrum of a novel Pd complex, Pd^{2+}–N$_2$CP–Tol (**2**), are reported.



When N$_2$CP, 2-ethoxy-5,10,15,20-tetrakis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (**1**),[6] was treated with 2 equiv. of Pd(OAc)$_2$ in refluxing toluene for 5 h, a yellow-greenish product was obtained in 18% yield. A FABMS peak at *m/z* 1217.8 indicated the attachment of a tolyl group to the Pd–N$_2$CP complex. The ^{1}H NMR signals of the complex showed distinctly in the range from 11 to 1 ppm in CD$_2$Cl$_2$, which suggested that the Pd oxidation state of the complex was diamagnetic, either Pd^{2+} (d^8) or Pd^{4+} (d^6). The tolyl signals derived from the solvent were observed in the high field region (5.61–6.36 ppm), which indicated that the tolyl group was located on the porphyrin core, presumably at an inner carbon or nitrogen. The methyl groups on the tolyl substituent were found to occur at the *para* and *meta* positions in a 1 : 2 ratio. Moreover, an outer NH signal was observed at 10.37 ppm, which suggested N$_2$CP^{2-} type ligand formation, that is, Pd^{2+} coordination. Pd^{2+}–N$_2$CP–Tol (**2**) was isolated as a single product and the formation of neither Pd^{3+}–N$_2$CP nor Pd^{4+}–N$_2$CP was observed (Scheme 1). By using CHCl$_3$ or C$_6$H$_6$ as the solvent, the complexation reaction did not proceed and N$_2$CP (**1**) was recovered. However, in the presence of C$_6$H$_6$ and toluene (1/1 v/v), both C-phenyl and C-tolyl Pd–N$_2$CP complexes were formed. Furthermore, the formation of a C-arylated complex was observed in *m*-xylene but not in *p*-xylene in which the steric hindrance was significant.

The explicit structural details of the Pd^{2+}–N$_2$CP–Tol (**2**) complex was derived from a single crystal X-ray diffraction analysis (Fig. 1).[9] Surprisingly, a solvent tolyl group is bound to the inner carbon of a confused pyrrole ring which does not have an ethoxy group. The tolyl-substituted confused pyrrole ring is bent at 56.3° and the tolyl group stands almost vertically (88.6°) at the opposite side of a mean N$_2$C$_2$ plane consisting of core



Scheme 1 Reaction of N$_2$CP (**1**) and Pd(OAc)$_2$.

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† Electronic supplementary information (ESI) available: synthesis details, ^{1}H and ^{13}C NMR spectra, thermal ellipsoid plot showing all atoms, unit cell packing diagram for **2**. See http://www/rsc.org/suppdata/cc/b0/b003022h/

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nitrogens and carbons. The Pd–C bond distances are 1.97(1) and 2.202(9) Å, and the Pd–N distances are 2.09(1) and 2.056(8) Å.[10] Reflecting the tilting of the confused pyrrole ring and the different carbon atom types, sp^2 and sp^3, the two Pd–C bond distances differ greatly (0.23 Å). On the other hand, the Pd–N bond distances are slightly longer than in Pd^{2+}–tetraphenylporphyrin, 2.009 Å.[11] In the single crystal, the tolyl group was disordered and refinement of the structure was well performed with the assumption of a *para*:*meta* ratio of 2:3, in agreement with the ^1H NMR data. Similar structures, such as a perpendicular orientation of the C-substituted group and/or the strong tilting of the coordinating 5-membered ring, have been observed in N-alkylporphyrin and Pd–thiaporphyrin complexes.[4,12] The absorption spectrum of **2** displays three broad bands with peak maxima at 318.0, 410.0 and 662.0 nm indicating the distortion of the porphyrin ring (Fig. 2).

Mechanistically, it is not clear which Pd oxidation state, either Pd^{2+}, Pd^{3+} or Pd^{4+}, is formed before the tolyl group is incorporated at the inner carbon. One of the possible mechanisms is the initial formation of the unstable Pd^{3+}–N_2CP complex, like Ag^{3+} and Cu^{3+}, which is then attacked successively by a toluene molecule at either Pd or the Pd-connected carbon. As the Pd^{3+} (d^7) species is paramagnetic, a radical mechanism could be involved in the formation of **2** (Scheme 2).[13] Supporting this, the ratio of the obtained tolyl complex shows the statistical distribution, p:m = 1:2.[14] The H-radical derived from toluene would change to H^+ eventually, because palladium black (Pd^0) is always associated with this reaction. It is reported that $Pd(OAc)_2$ causes the facile palladation of aromatic compounds to afford biaryls.[15,16] Although we have not detected bitolyl in this reaction, the other mechanism involving a tolyl–Pd complex before the formation of a Pd–carbon bond with the confused pyrrole can not be excluded. As this reaction implies the possibility of aromatic C–H activation, detailed study of the mechanism in addition to investigations with other group 10 metals is currently underway.[17]

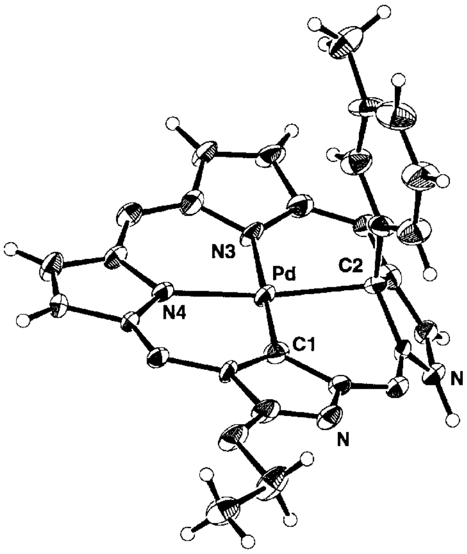


Fig. 1 X-Ray structure of Pd–N_2CP–Tol (**2**). Solvents and pentafluorophenyl groups are omitted for clarity. Selective bond lengths (Å) and angles (°): Pd–C1, 1.97(1); Pd–C2, 2.202(9); Pd–N3, 2.09(1); Pd–N4, 2.056(8); C1–Pd–C2, 90.1(5); C2–Pd–N3, 90.6(4); N3–Pd–N4, 90.1(4); N4–Pd–C1, 89.2(4); C1–Pd–N3, 179.1(3); C2–Pd–N4, 170.5(3).

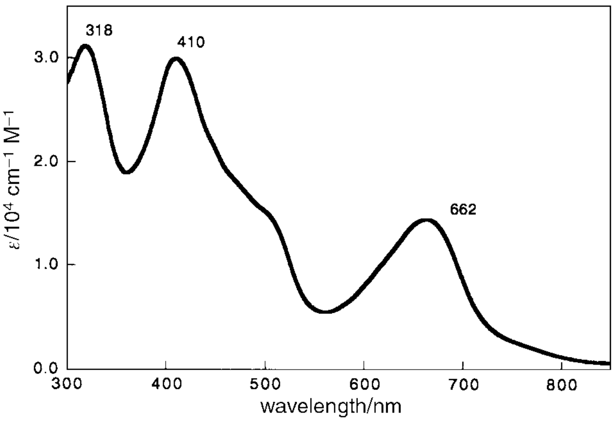
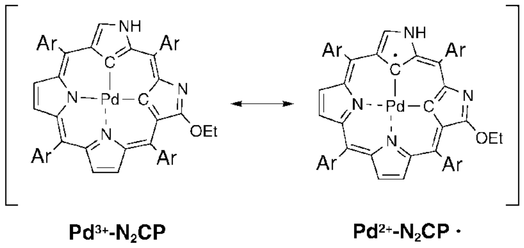


Fig. 2 Absorption spectrum of Pd–N_2CP–Tol (**2**) in $CHCl_3$.



Scheme 2 A possible intermediate Pd^{3+}–N_2CP.

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