

Structure of a C,N,N-Cyclometallated Palladium(II) Complex of 2-Amino-4-phenylamino-6-(2-pyridyl)-1,3,5-triazine, an α -Diimine Ligand with Donor–Acceptor–Donor Hydrogen-bonding Capability

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A new class of (2,4-diamino-1,3,5-triazinyl)pyridine ligand has been made and its cyclopalladation reaction with palladium(II) studied; the crystal structure of the C,N,N-cyclometallated complex reveals a rigid planar structure with a donor–acceptor–donor hydrogen-bonding function on its surface.

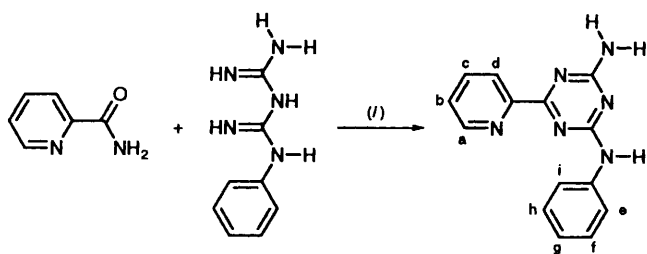
2,4,6-Triamino-1,3,5-triazine and its derivatives have attracted great interest as substrates for molecular self-assembly processes¹ and crystal engineering,² particularly by Lehn, Whitesides and their co-workers. We have sought to develop bifunctional ligands which combine good ligating properties and hydrogen-bonding sites on their surface that can complement those on pyrimidine bases such as uracil [(1*H*,3*H*)pyrimidine-2,4-dione] and can also control crystal packing. We have achieved these aims with nickel dithiobiuret complexes.³ Herein, we report the synthesis of 2-amino-4-phenylamino-6-(2-pyridyl)-1,3,5-triazine (HL), which is analogous to 2,2'-bipyridine and 2,2':6',2''-terpyridine,⁴ and its complexation to palladium(II) under mild conditions.

The triazine ligand HL was prepared in 50% yield by the one-step condensation of 1-phenylbiguanide and pyridine-2-carboxamide (Scheme 1).[†] Its subsequent reaction with Na₂[PdCl₄] in acetone–water (1.5:1, v/v) afforded [PdCl(L)] in 80% yield.[†] However only an isomeric mixture of [PdCl₂(*syn*-/*anti*-HL)] was isolated when the reaction was conducted with less water in the solvent mixture (acetone–water

7.5:1).[†] The bidentate ligand in [PdCl₂(HL)] can be cyclometallated quantitatively by heating in acetone–water (1.5:1). (The solvent effect on ruthenium cyclometallation reactions has been studied.⁵) The relevant sequence of reactions leading to the cyclometallated product are shown in Scheme 2.

The molecular and crystal structures of [PdCl(L)]Me₂CO·H₂O are shown in Fig. 1. They confirm that the C,N,N-terdentate cyclometallated ligand is arranged in a slightly distorted square-planar geometry about the palladium atom.[‡] The metallated phenyl ring is co-ordinated to palladium with bond angles C(16)–C(15)–Pd and C(20)–C(15)–Pd equal to 122.5(2) and 122.3(2)° respectively, and the metal–carbon bond distance is comparable to related C,N,N palladium complexes.⁶ The two Pd–N bond distances are significantly different, that *trans* to C(phenyl) being about 0.12 Å longer than the other, consistent with the stronger *trans* influence exerted by the phenyl carbon.^{6b} The bite angle involving the α -diimine [79.95(9)°] and the Pd–N bond length for the triazine nitrogen [2.003(2) Å] are close to those described in other polypyridyl–palladium complexes and this supports the ‘pseudo-bipyridine’ nature of HL.

This is the first example of a C,N,N-cyclometallated palladium(II) complex with a planar six-membered cyclometallated ring. Other C,N,N-cyclometallated complexes consisting of five- and six-membered chelate rings have the bridging atoms in a puckered conformation.⁷ *Ab initio* molecular-orbital calculations performed on 2,4-diamino-1,3,5-triazine



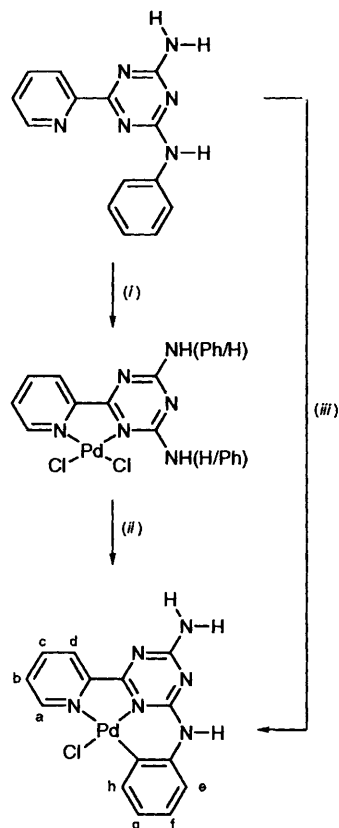
Scheme 1 (i) KOBu⁺, MeOH, reflux

[†] Characterization of HL (Found: C, 62.80; H, 4.70; N, 31.45. Calc. for C₁₄H₁₂N₆: C, 63.65; H, 4.60; N, 31.80%), m.p. 225 °C. ¹H NMR [(CD₃)₂SO]; δ 9.70 (NH), 7.30 (NH₂), 8.70 (d, H^a), 7.54 (dd, H^b), 7.96 (t, H^c), 8.27 (d, H^d), 7.86 (dd, H^e and H^f), 7.30 (t, H^g and H^h), 7.00 (t, Hⁱ).

[PdCl(L)] (Found: C, 41.35; H, 2.65; N, 20.45. Calc. for C₁₄H₁₁ClN₆Pd: C, 41.50; H, 2.75; N, 20.75%). ¹H NMR [(CD₃)₂SO]; δ 10.59 (NH), 8.04 and 7.80 (NH₂), 9.21 (dd, H^a), 7.94 (td, H^b), 8.30 (td, H^c), 8.39 (dd, H^d), 7.09 (dd, H^e), 6.98 (td, H^f), 6.68 (td, H^g), 8.28 (dd, H^h).

[PdCl₂(*syn*-/*anti*-HL)] (Found: C, 40.35; H, 3.10; N, 16.95. Calc. for C₁₄H₁₂Cl₂N₆Pd·Me₂CO: C, 40.85; H, 3.65; N, 16.80%). Analysis of the *syn*-/*anti*-isomer ratio using NMR spectroscopy was difficult because of the extensive overlap of aromatic and NH signals.

[‡] Single crystals suitable for crystallographic analysis were obtained by slow evaporation of an acetone solution of the complex. Crystal data for C₁₄H₁₁ClN₆Pd·Me₂CO·H₂O: *M* = 481.23, monoclinic, space group *P*2₁/*n*, *a* = 9.3040(10), *b* = 7.8120(10), *c* = 26.154(2) Å, β = 93.728(3)°, *U* = 1896.9(3) Å³, *Z* = 4, *D*_c = 1.69 g cm⁻³, μ (Mo-K α) = 11.5 cm⁻¹, λ = 0.710 73 Å, *F*(000) = 968. A yellow prism of crystal dimensions 0.50 × 0.17 × 0.13 mm was used. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-K α radiation (ω scans). 3337 Independent reflections were measured ($2\theta \leq 50^\circ$) of which 2842 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by the heavy-atom method and the non-hydrogen atoms were refined anisotropically by full-matrix least squares using absorption corrected data to give *R* = 0.028, *wR* = 0.070 [$wR^2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]$]. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 2 (i) Acetone–water (7.5:1), Na₂[PdCl₄]; (ii) acetone–water (1.5:1); (iii) acetone–water (1.5:1), Na₂[PdCl₄]

suggest that delocalization of the lone-pair of electrons on the amino groups into the electron-deficient triazine may lead to coplanarity of the diamino–triazine moiety.⁸ The results presented here not only provide structural proof, but also suggest that the co-ordinating power of HL may be enhanced by the electron donation from the amino group and the presence of the adjacent 2-pyridyl group. The C–N bond lengths between the amino groups and the triazine ring are close to the calculated value (1.338 Å) for 2,4-diamino-1,3,5-triazine⁸ and shorter than that between the NH and the phenyl groups which is comparable to the C–N bond length in aniline (1.402 Å *via* microwave spectroscopy⁹) and that in *N,N'*-diphenylmelamine, 2-amino-4,6-bisphenylamino-1,3,5-triazine, (1.424 Å).¹⁰

The proton donor–acceptor–donor hydrogen-bonding function on the surface of the ligand is not self complementary, but examination of the packing of the cyclometallated complex [Fig. 1(b)] reveals the formation of hydrogen-bonded dimers which utilize donor and acceptor groups to form an eight-membered ring. One of the NH₂ protons and N(10) on the triazine ring form two linear hydrogen bonds N–H...N 171°, N...N distance 3.08 Å [the NH...N distances 3.060 and 3.045 Å were reported for 6-(β-D-ribofuranosyl)-1,3,5-triazine-2,4-diamine hemihydrate¹¹] with their respective hydrogen-bond acceptor and donor on neighbouring molecules related by a crystallographic centre of inversion. The remaining proton on the NH₂ and that on N(14) are hydrogen bonded to the lone pair of a water molecule (N...O 2.86 and 3.04 Å respectively). The OH protons are weakly hydrogen bonded to the chlorine atom on the adjacent stack (O...Cl 3.13 Å) and the carbonyl oxygen of acetone within the same plane (O...O 2.77 Å), respectively. The N(12) triazine-ring nitrogen is not involved in hydrogen bonding probably due to its inaccessible location.

The cyclometallated complex provides the first example of a

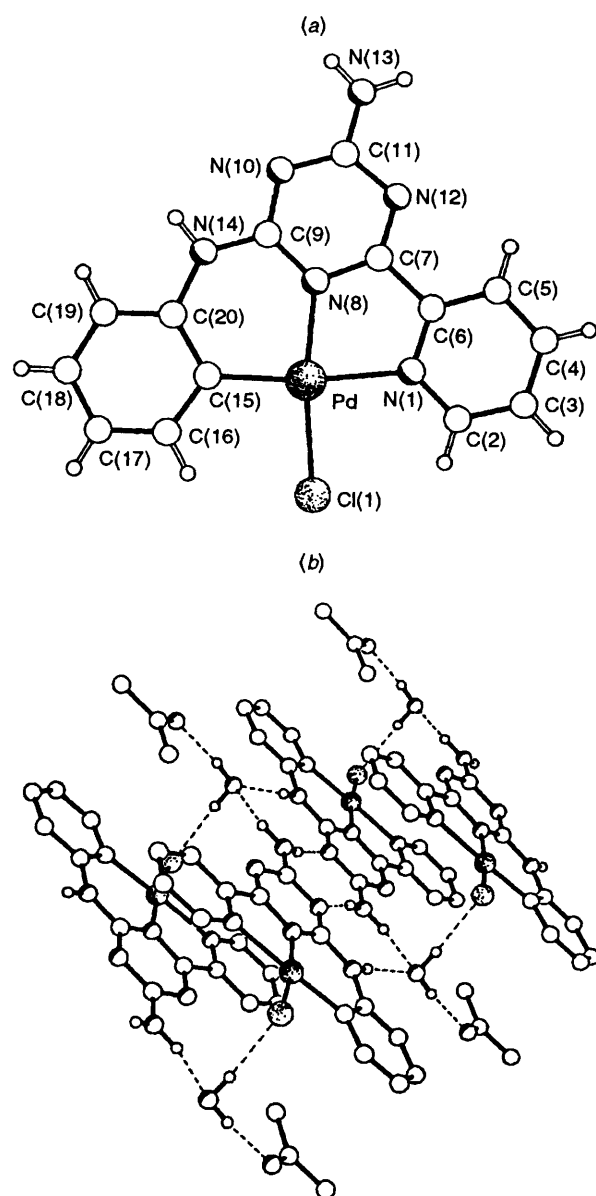


Fig. 1 (a) Molecular structure of [PdCl(L)] showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Pd–C(15) 1.990(3), Pd–N(1) 2.121(3), Pd–N(8) 2.003(2), Pd–Cl(1) 2.3292(8); C(15)–Pd–N(8) 92.64(11), N(8)–Pd–N(1) 79.95(9), N(1)–Pd–Cl(1) 91.53(7), Cl(1)–Pd–C(15) 95.91(9), N(8)–Pd–Cl(1) 171.43(7), C(15)–Pd–N(1) 172.5(1), C(9)–N(14)–C(20) 131.5(3). (b) Crystal packing of [PdCl(L)]·Me₂CO·H₂O showing both graphitic interactions and hydrogen-bonding interactions

planar organometallic complex with triple hydrogen bonding sites which complement those in uracil, barbituric acid and cyanuric acid [(1*H*,3*H*,5*H*)-1,3,5-triazine-2,4,6-trione], therefore it has great potential as a building block for crystal engineering involving transition-metal compounds and it may also exhibit interesting biological recognition properties. The results demonstrate how Whitesides and co-workers¹² elegant supramolecular studies on 2,4,6-triamino-1,3,5-triazine derivatives may be developed to incorporate transition-metal ions.

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