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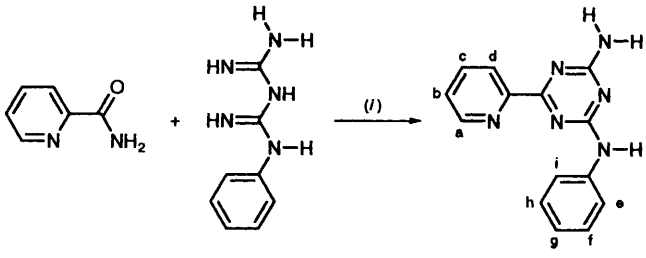
A new class of (2,4-diamino-1,3,5-triazinyl)pyridine ligand has been made and its cyclopalladation reaction with palladium(II) studied; the crystal structure of the C,N,N-cyclometallated complex reveals a rigid planar structure with a donor–acceptor–donor hydrogen-bonding function on its surface.

2,4,6-Triamino-1,3,5-triazine and its derivatives have attracted great interest as substrates for molecular self-assembly processes[1] 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 $Na_2[PdCl_4]$ in acetone–water (1.5:1, v/v) afforded [PdCl(L)] in 80% yield.† However only an isomeric mixture of [$PdCl_2$(*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 [$PdCl_2$(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.



Scheme 1 (*i*) KOBu^t, MeOH, reflux

The molecular and crystal structures of [PdCl(L)]Me_2CO·H_2O 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.

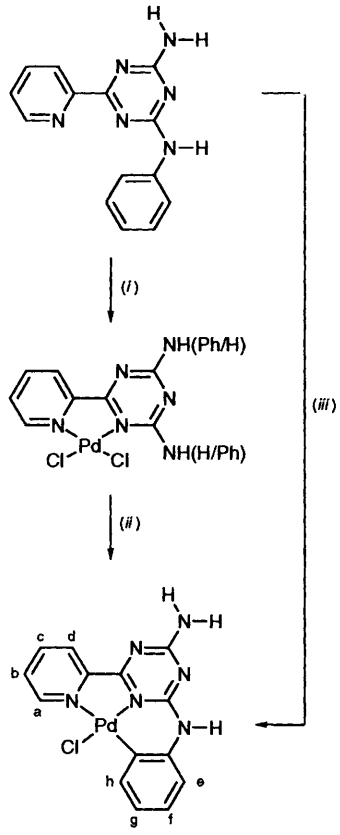
This is the first example of a C,N,N-cyclometallated palladium(II) complex with a planar six-membered cyclometallated ring. Other C,N,N-cyclometallated complexes consisting of five- and six-membered chelate rings have the bridging atoms in a puckered conformation.[7] *Ab initio* molecular-orbital calculations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

† Characterization of HL (Found: C, 62.80; H, 4.70; N, 31.45. Calc. for $C_{14}H_{12}N_6$: C, 63.65; H, 4.60; N, 31.80%), m.p. 225 °C. ^{1}H NMR [$(CD_3)_2SO$]; δ 9.70 (NH), 7.30 (NH_2), 8.70 (d, H^a), 7.54 (dd, H^b), 7.96 (t, H^c), 8.27 (d, H^d), 7.86 (d, H^e and H^i), 7.30 (t, H^f and H^h), 7.00 (t, H^g).

[PdCl(L)] (Found: C, 41.35; H, 2.65; N, 20.45. Calc. for $C_{14}H_{11}ClN_6Pd$: C, 41.50; H, 2.75; N, 20.75%). ^{1}H NMR [$(CD_3)_2SO$]; δ 10.59 (NH), 8.04 and 7.80 (NH_2), 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).

[$PdCl_2$(*syn*-/*anti*-HL)] (Found: C, 40.35; H, 3.10; N, 16.95. Calc. for $C_{14}H_{12}Cl_2N_6Pd$·Me_2CO: 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 $C_{14}H_{11}ClN_6Pd$·Me_2CO·H_2O: M = 481.23, monoclinic, space group $P2_1/n$, a = 9.3040(10), b = 7.8120(10), c = 26.154(2) Å, β = 93.728(3)°, U = 1896.9(3) Å^3, Z = 4, D_c = 1.69 g cm^{-3}, μ(Mo-Kα) = 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-Kα radiation (ω scans). 3337 Independent reflections were measured (2θ ≤ 50°) 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 anisitropically by full-matrix least squares using absorption corrected data to give R = 0.028, $wR2$ = 0.070 $\{wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}\}$. 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), $Na_2[PdCl_4]$; (*ii*) acetone–water (1.5:1); (*iii*) acetone–water (1.5:1), $Na_2[PdCl_4]$

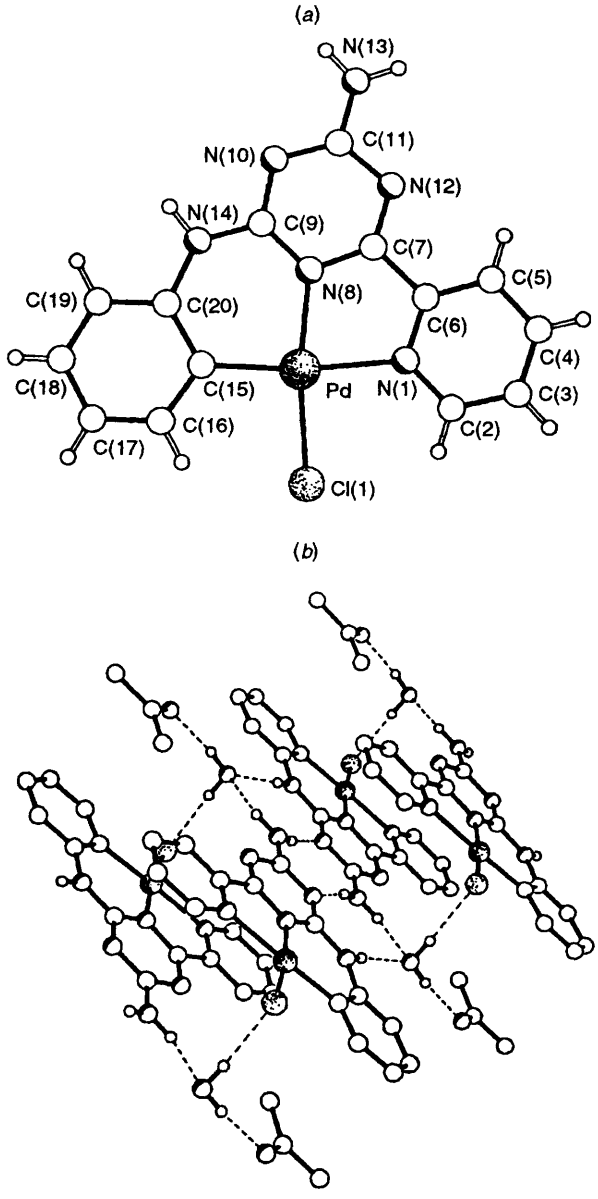


Fig. 1 (*a*) Molecular structure of [PdCl(L)] showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Pd–C(15) 1.990(3), Pd–N(1) 2.121(3), Pd–N(8) 2.003(2), Pd–Cl(1) 2.3292(8); C(15)–Pd–N(8) 92.64(11), N(8)–Pd–N(1) 79.95(9), N(1)–Pd–Cl(1) 91.53(7), Cl(1)–Pd–C(15) 95.91(9), N(8)–Pd–Cl(1) 171.43(7), C(15)–Pd–N(1) 172.5(1), C(9)–N(14)–C(20) 131.5(3). (*b*) Crystal packing of $[PdCl(L)]\cdot Me_2CO\cdot H_2O$ showing both graphitic interactions and hydrogen-bonding interactions

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-triazine[8] 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 spectroscopy[9]) 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 NH_2 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 hemihydrate[11]] with their respective hydrogen-bond acceptor and donor on neighbouring molecules related by a crystallographic centre of inversion. The remaining proton on the NH_2 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 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-workers'[12] 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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