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The First *trans*-Configured Cyclopalladated Amine

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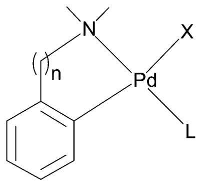
Summary: More than 100 ortho-palladated neutral arylamines with two additional monodentate ligands, namely, a N- or P-bonded Lewis base L and a mononegative ligand X, correspond to the cis configuration with respect to their Pd−C and Pd−L bonds. In contrast, (S)-[2-(1-aminoethyl)phenyl-κ^{2}C^1,N]chloro(3,4,5-trichloropyridine-κN)palladium(II) represents the first structurally characterized trans-configured complex of this class.

Orthometalation of an arylamine with suitable palladium precursors[1] will usually result in *cis*-configured complexes[2−5] (Chart 1). The CSD[6] database contains 95 examples of these *cis* complexes. Our recently published results on 11 pyridine derivatives of primary amines[7−9] as well as several yet unpublished compounds[10] confirm this rule. In agreement with this experimental evidence, theoretical calculations on tertiary cyclopalladated amines predict a stabilization of 6 kcal·mol^{-1} in favor of the *cis* isomers.[11]

In addition to the complexes matching Chart 1, the database contains (i) another two examples of cationic rather than neutral *cis* cyclopalladated complexes carrying an aqua ligand instead of X; (ii) three more examples in which the monodentate ligand L is bonded via an As or a S atom.

Although to the best of our knowledge no *trans*-configured complex of an *ortho*-palladated amine has been described, we should mention a small number of reports concerning chemically related compounds in this configuration: (i) three cyclopalladated imines in *trans* geometry[12−14] have been published; (ii) the *trans* configuration was also found for a platinum complex of a tertiary amine and monodentate Cl and pyridine ligands;[5] (iii) the study of palladium complexes obtained via insertion of an alkyne into a Pd−C bond revealed a singular case in which the product adopts a *trans* configuration.[15]

Chart 1



n = 1, 2
L = N, P-bonded ligand
X = (pseudo)halogen, O-bonded anionic ligand

In addition, the coexistence of both *cis* and *trans* isomers of a cyclopalladated imine in solution has been deduced from NMR studies.[16]

Following the initial work of Cope and Friedrich[17] on cyclopalladation, Lewis[18] and Dunina[19] have been able to extend the range of substrates considerably. In the context of our synthetic efforts aiming at the synthesis of molecular building blocks for crystal engineering we have prepared (*S*)-[PdCl($C_6H_4CHMeNH_2$)(3,4,5-trichloropyridine)] (**1**) by using well-established methods.[20,21]

Single-crystal X-ray diffraction[22] showed that **1** exists in the solid state as an essentially planar *trans* isomer.[23]

For steric reasons an alternative *cis* isomer would be restricted to a nonplanar geometry. The conformational degree of freedom for rotation around the palladium−pyridine bond in such a hypothetical *cis* complex was explored[25] with an augmented MM2[26] force field: an essentially planar geometry would necessarily result in

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(22) Crystallographic data: $C_{13}H_{12}Cl_4N_2Pd$, fw = 444.45, triclinic space group $P1$, $a = 6.6982(19)$ Å, $b = 8.581(3)$ Å, $c = 13.423(4)$ Å, $\alpha = 76.702(5)°$, $\beta = 84.661(6)°$, $\gamma = 88.959(6)°$, $V = 747.6(4)$ Å^3, $Z = 2$, $T = 110$ K, $\rho_{calcd} = 1.974$ g/cm^3, μ(Mo Kα) = 1.944 cm^{-1}, 14 365 reflections, $R_{int} = 0.0581$, 6784 unique reflections, $R_1 = 0.0683$, $wR_2 = 0.1674$, Goof = 1.013, Flack parameter = −0.11(7).

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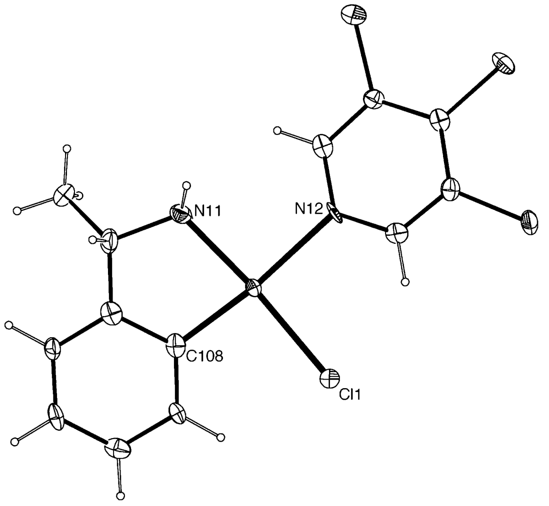

Figure 1. Displacement ellipsoid plot[24] of **1** (50% probability, arbitrary radius for H atoms). Only one of two similar independent molecules is shown.

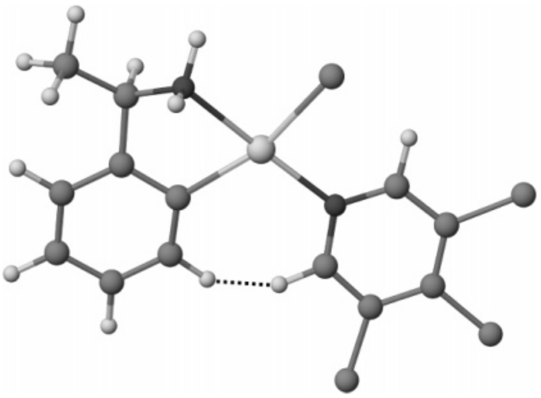

Figure 2. Unfavorable H···H interaction (ca 1.77 Å) in a hypothetical planar *cis* isomer of **1**.

prohibitively short H- -H distances and a distorted square planar environment around the central Pd atom. This obviously unfavorable geometry is shown in Figure 2.

In our example with its electron-withdrawing substituents on the pyridine ring the *trans* planar cyclopalladated complex allows for additional stability in the solid: The crystal structure of **1** contains two independent molecules related by pseudoinversion; translation of this pair in the [100] direction results in stacks of almost equidistant molecules (Figure 3). The Pd···Pd separation within the asymmetric unit shown in Figure 3 amounts to 3.4574(15) Å; that to the next molecule in the *a* direction to 3.4757(15) Å.

The observed packing is stabilized by relatively long hydrogen bonds (NH···ClPd ca. 2.7 Å) between the H atoms of the primary amine and the Pd-bonded Cl

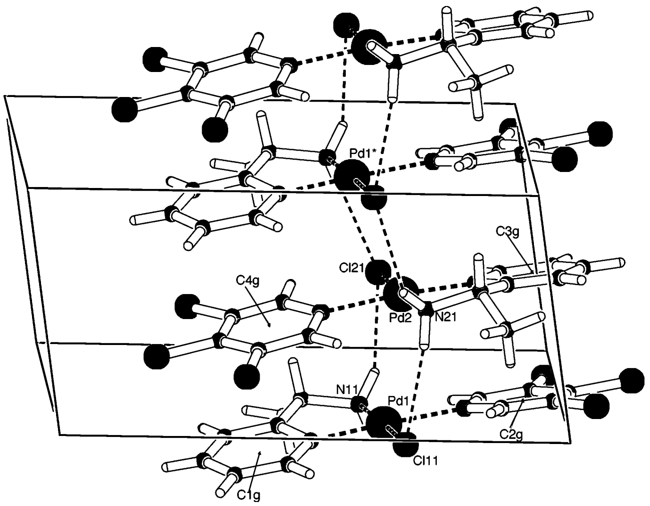

Figure 3. Stacking in the solid-state structure of **1**. The stacking direction is parallel to *a*; the view direction is slightly inclined to [010].

ligands. Furthermore, distances between 3.43 and 3.47 Å between the centers of gravity of the electron-deficient pyridine ligands (c_{2g}, c_{4g}) and the electron-rich phenyl rings (c_{1g}, c_{3g}) of the next neighbor indicate π-stacking interactions.[27] For our compound this infinite stacking interaction can occur only between planar molecules and is hence limited to the *trans* configuration. Comparable stacking interactions have been observed in other planar Pd complexes, e.g., in dioximato derivatives.[28-31]

To gain insight into the nature of the intermolecular interactions in **1**, we have performed lattice energy minimizations[32] on rigid molecules based on the atom–atom potential approach.[33] When only van der Waals interactions are taken into account, the minimum energy structure is associated with a lattice constant *a* clearly longer than the experimentally established value, whereas the remaining cell parameters are reproduced much closer. The stacking distances between the centers of gravity of electron-rich and electron-deficient rings in the minimized packing expand to ca. 3.72 Å and the closest intermetal distances to ca. 3.79 Å. These qualitative findings corroborate our interpretation that the experimentally observed crystal structure of **1** does not correspond to a simple van der Waals packing. The tentative inclusion of point charges, admittedly a crude approximation, and of an additional attractive interaction to account for the NH···ClPd hydrogen bonds results in good agreement between the minimized and the experimental crystal structure.[34]

In conclusion, we can understand that the *trans* configuration of **1** is compatible with an efficient packing

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[23] The dihedral angle subtended by the pyridine and phenyl rings is 17.8(6)° [18.9(6)°] for the two independent molecules [second molecule in square brackets]. Bond distances (Å) and angles (deg) around Pd: C108–Pd1–N11 82.2(4) [82.1(4)], C108–Pd1–N12 = 172.9(4) [173.4(4)], N11–Pd1–N12 = 91.8(3) [92.1(3)], C108–Pd1–Cl11 = 93.8(3) [93.8(3)], N11–Pd1–Cl11 = 175.4(3) [175.5(3)], N12–Pd1–Cl11 = 92.3(3) [92.1(3)], Pd1–C108 = 1.965(9) [1.969(9)], Pd1–N11 = 2.045(8) [2.047(8)], Pd1–N12 = 2.214(7) [2.202(7)], Pd1–Cl11 = 2.348(4) [2.348(4)].

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in the solid. Our earlier studies on the lability of similar compounds[8] have shown that ligand exchange between different complexes in solution occurs on a time scale of minutes or hours. Our spectrocopic data are in agreement with a single isomer,[35] and the proton *ortho* to the metal−carbon bond does not show the high-field shift expected for a *cis* isomer.[36] We therefore suggest that **1** retains the *trans* configuration in solution.

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Supporting Information Available: Experimental and spectroscopic details, crystallographic data, interatomic distances and angles, details concerning the lattice energy minimizations, comparison of experimental and latttice-minimized structures, CSD refcodes of *cis* cyclopalladated amines; crystallographic data are available also in a CIF file (CCDC 272637). This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) NMR: ^{1}H NMR (500 MHz, DMSO): δ 1.42 (d, 3H, $J = 6.4$ Hz, CH*Me*); 4.12 (q, 1H, $J = 5.8$ Hz, C*H*Me); 5.05 (br, 1H, NH_2); 5.75 (br, 1H, NH_2); 6.84−6.96 (m, 3H, H_3, H_4, H_5, *Ph*); 7.65 (d, 1H, H_2, *Ph*); 8.76(s, H_2, H_6, py) ppm. ^{13}C NMR (125 MHz, DMSO): δ 23.94 (s, C(CH*Me*)); 58.84 (s, C(*C*HMe)); 121.66 (s, C_3, *Ph*); 124.57, 124.92 (s, C_2, C_4, *Ph*); 128.20 (s, C_5, *Ph*); 130.56 (s, C_3, C_5, py); 132.61 (s, C_4, *py*); 148.09 (s, C_2, C_6, *py*); 148.59 (s, C_1, *Ph*); 157.19 (s, C_6, *Ph*) ppm.

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