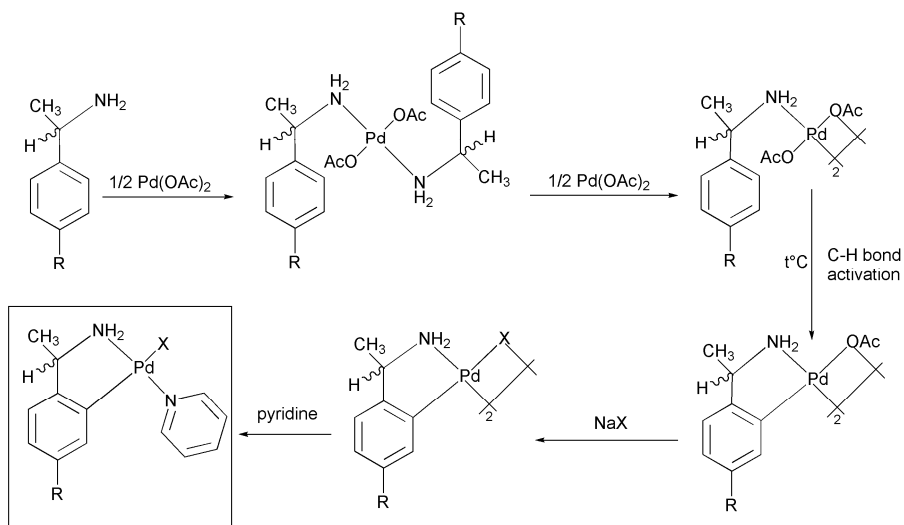


Electronic Supplementary Information (ESI)

- Reaction pathway for cyclopalladation of primary amines
- Simulated and experimental powder patterns for **1**
- Conformations of minimum and maximum energy according to force field calculations
- Molecular conformations for all independent molecules in **1**, **1**·0.5 MeCN and **2**·0.5 MeCN
- Classical hydrogen bonds in **1**
- Enantiomer distribution in the unit cell of **1**
- Structure solution and refinement for **1**
- List of references for structures with $Z' \geq 16$
- Spectroscopic and analytical characterisation of **1** and **2**

- Reaction pathway for cyclopalladation of primary amines



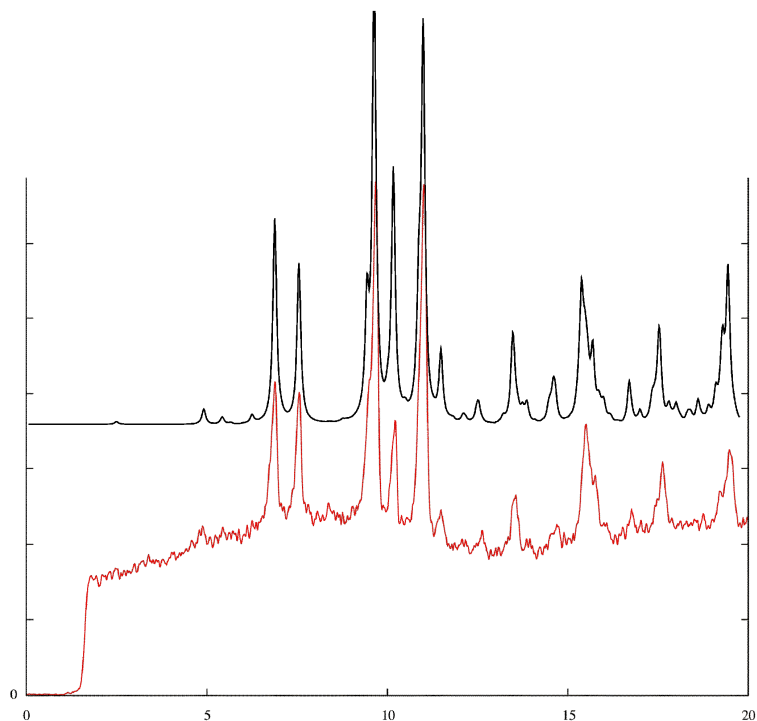
R = CH₃, OCH₃, F, Cl, Br

X = Cl, Br, I

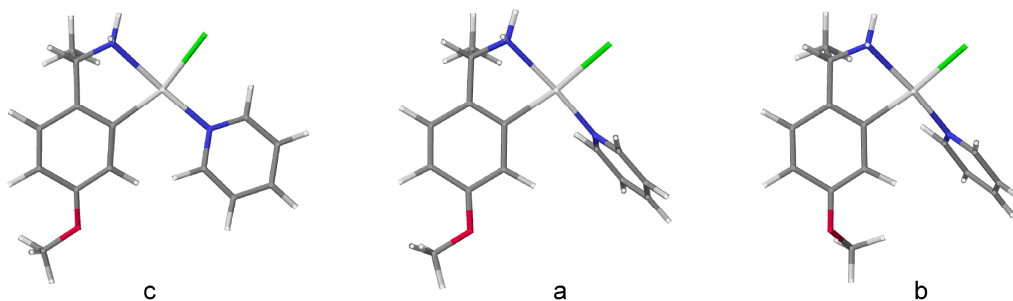
For the mononuclear complex: R = OCH₃, X = Cl (**complex 1**)

R = OCH₃, X = I (**complex 2**)

b) Simulated (black) and experimental (red, Stoe image plate detector IP-PDS) powder pattern for **1**

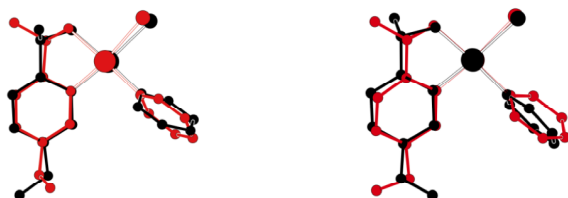


c) Conformations of minimum and maximum energy according to force field calculations



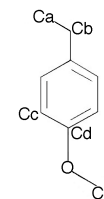
Conformations corresponding to the force field minimum (a) and in the energy maximum obtained by rotation around the aryl-OMe bond (b) and the Pd-N(pyridine) bond (c). CACheVersion 4.9 for PowerMacintosh, Fujitsu, 2003.

Independent molecules in **1** cover a wide range with respect to both soft degrees of freedom: The figure shows overlap plots [PLATON, A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148] of the independent molecule 4 and 11 (left) and 9 and 14 (right). Molecules 4 and 9 are shown in black, 11 and 14 in red.



d) Torsion and dihedral angles characterising the soft degrees of freedom in **1**, **1**·0.5 MeCN and **2**·0.5 MeCN

complex	Indep. mol.	Torsion angle	Torsion angle θ	Dihedral angle ϕ
		C _a -C _b -O-C _e (°)	C _c -C _d -O-C _e (°)	Pd coordination vs. plane through py (°) ^a
1	1	-73.8(8)	16.5(12)	59.0(3)
1	2	152.6(10)	169.5(8)	68.8(3)
1	3	-83.1(8)	3.5(12)	63.5(4)
1	4	-87.3(10)	2.7(15)	57.6(4)
1	5	-89.3(9)	5.2(13)	49.7(4)
1	6	85.6(9)	173.8(9)	72.4(3)
1	7	-72.8(9)	12.6(13)	72.8(3)
1	8	97.4(11)	177.8(11)	84.4(4)
1	9	99.7(10)	178.0(10)	71.9(4)
1	10	115.7(8)	-168.8(8)	73.3(3)
1	11	105.7(10)	136.9(11)	53.3(6)
1	12	129.8(12)	-173.7(12)	56.7(4)
1	13	-23.4(11)	9.5(18)	62.7(4)
1	14	5.0(13)	28.7(19)	55.4(5)
1	15	-86.6(13)	-19.6(19)	73.4(5)
1	16	168.8(16)	-174.5(16)	100.6(5)
1 ·0.5 MeCN	1	101.6(3)	-167.7(3)	80.85(13)
1 ·0.5 MeCN	2	-84.7(3)	7.1(5)	73.98(14)
2 ·0.5 MeCN	1	104.1(3)	-167.4(3)	79.59(12)
2 ·0.5 MeCN	2	-84.3(3)	6.2(5)	77.49(13)



All values are given for *S* configuration.

^a Dihedral angle subtended by the Pd coordination plane (amine N, pyridine N, Pd-bonded C, Cl) and the least squares plane through all non-hydrogen atoms of the pyridine ring; the angle is taken as opposite to the side of the chiral C atom.

e) Classical hydrogen bonds in **1**

Nr	Typ	Res	Donor ---H....Acceptor	Equiv. Pos. Code	D - H	H...A	D...A	D - H...A
1	1		N(11) --H(11A) ..Cl(3)	<i>i</i>		0.92	2.49	3.407(6) 174
2	1		N(11) --H(11B) ..Cl(14)			0.92	2.47	3.312(7) 151
3	2		N(21) --H(21A) ..Cl(10)			0.92	2.55	3.458(8) 169
4	2		N(21) --H(21B) ..Cl(11)			0.92	2.53	3.378(8) 154
5	3		N(31) --H(31A) ..Cl(1)	<i>v</i>		0.92	2.42	3.338(7) 172
6	3		N(31) --H(31B) ..Cl(13)			0.92	2.50	3.309(7) 147
7	4		N(41) --H(41A) ..Cl(7)	<i>vii</i>		0.92	2.51	3.349(7) 152
8	4		N(41) --H(41B) ..Cl(5)	<i>v</i>		0.92	2.37	3.283(7) 174
9	5		N(51) --H(51A) ..Cl(6)	<i>ii</i>		0.92	2.51	3.337(7) 150
10	5		N(51) --H(51B) ..Cl(4)	<i>i</i>		0.92	2.41	3.329(7) 176
11	6		N(61) --H(61A) ..Cl(7)	<i>iii</i>		0.92	2.37	3.267(7) 163
12	6		N(61) --H(61B) ..Cl(5)	<i>viii</i>		0.92	2.54	3.374(7) 152
13	7		N(71) --H(71A) ..Cl(6)	<i>vi</i>		0.92	2.39	3.284(7) 164
14	7		N(71) --H(71B) ..Cl(4)	<i>iv</i>		0.92	2.46	3.302(7) 152
15	8		N(81) --H(81A) ..Cl(9)	<i>iii</i>		0.92	2.71	3.609(11) 167
16	8		N(81) --H(81B) ..Cl(16)			0.92	2.76	3.575(8) 148
17	9		N(91) --H(91A) ..Cl(8)	<i>vi</i>		0.92	2.47	3.376(9) 167
18	9		N(91) --H(91B) ..Cl(15)	<i>vi</i>		0.92	2.69	3.489(8) 146
19	10		N(101) --H(10G) ..Cl(2)			0.92	2.48	3.366(8) 162
20	10		N(101) --H(10H) ..Cl(12)			0.92	2.50	3.365(7) 158
21	11		N(111) --H(11C) ..Cl(12)			0.92	2.47	3.388(8) 175
22	11		N(111) --H(11D) ..Cl(2)			0.92	2.50	3.330(7) 150
23	12		N(121) --H(12A) ..Cl(11)			0.92	2.56	3.414(10) 155
24	12		N(121) --H(12B) ..Cl(10)			0.92	2.56	3.395(8) 152
25	13		N(131) --H(13A) ..Cl(14)	<i>v</i>		0.92	2.46	3.374(8) 172
26	13		N(131) --H(13B) ..Cl(3)			0.92	2.49	3.321(8) 149
27	14		N(141) --H(14G) ..Cl(13)	<i>i</i>		0.92	2.43	3.343(7) 172
28	14		N(141) --H(14H) ..Cl(1)			0.92	2.49	3.330(8) 151
29	15		N(151) --H(15A) ..Cl(8)			0.92	2.51	3.317(8) 146
30	15		N(151) --H(15B) ..Cl(16)			0.92	2.59	3.483(12) 162
31	16		N(161) --H(16G) ..Cl(9)	<i>iii</i>		0.92	2.61	3.420(11) 147
32	16		N(161) --H(16H) ..Cl(15)			0.92	2.50	3.402(11) 169

Equivalent Position Code

$i = x, y, 1+z$

$ii = x, -y, 1/2+z$

$iii = -1+x, y, z$

$iv = 1+x, -y, 1/2+z$

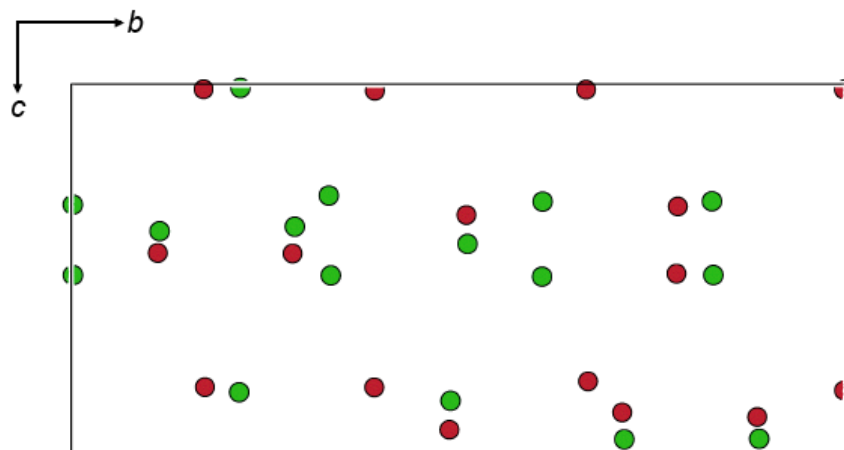
$v = x, y, -1+z$

$vi = 1+x, y, z$

$vii = -1+x, -y, -1/2+z$

$viii = x, -y, -1/2+z$

f) Enantiomer distribution in the unit cell of **1**



Distribution of *R*-configured (brown) and *S*-configured (green) molecules in the unit cell of **1**; each complex molecule is represented by the position of its central Pd atom.

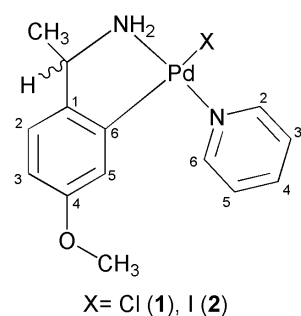
g) Structure solution and refinement for **1**

In view of the unexpected complexity of the structure, we considered potential pitfalls with data collection and intensity integration: Twinning or a small number of $\lambda/2$ reflections might cause an apparently large unit cell. In the present case, however, reciprocal space is not empty: 63 % of the reflections were observed with $I > 2\sigma(I)$, a very acceptable ratio for a structure of this size. We did not find any indication of modulation. The popular space group alternative $P2_1/c$ can be safely ruled out based on 180 reflections $0k0$; they do not match the absence condition $k=2n$. The LePage algorithm [Y. LePage, *J. Appl. Cryst.* 1988, **21**, 983] as implemented in PLATON [A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148] did not indicate any potential higher symmetry which might lead to a smaller Z' . **1** forms inversion twins with variable ratio between the domains. Refinement of the structure model was not straightforward: In the early stages restraints with high weight for the pseudo observations had to be applied, and isotropic displacement parameters were used for all atoms. In subsequent cycles, heavy atoms were assigned anisotropic displacement parameters, and the weight of the restraints could be gradually reduced. In the final refinement stages, anisotropic displacement parameters were assigned to all 304 non-hydrogen atoms in the asymmetric unit, albeit with rigid bond and isotropicity restraints. Similarity restraints for bond distances and angles were imposed, whereas the torsional degrees of freedom were freely refined. Upon convergence, *i.e.* for the minimum of the target function $wR2$, a final unweighted agreement factor $R1$ of 0.1036 for 2769 variables and all 46704 (including weak) observations and a total of 7237 restraints was reached. Residual electron density maxima of ca. $2.2 \text{ e}\text{\AA}^{-3}$ were located in the neighborhood of two metal centers. The metal-peak distances amount to ca 1.2 Å which is too long for termination errors from Fourier syntheses. These maxima probably indicate alternative orientations for molecules 15 and 16 with very small occupancies, visible only for the strongest scattering centers. In agreement with this hypothesis, the Pd atoms in these residues show significantly higher displacement parameters than those in all other 14 molecules.

h) List of references for structures with $Z' \geq 16$

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interpreted as modulated in #pls add lanbos_modulation.pdf reference#
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i) Spectroscopic and analytical characterisation of **1** and **2**



NMR Data for **1**: $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ = 1.57 (d, 3H, CHMe); 3.51 (s, 3H, 4-MeO(Ph)); 3.81 (br, 1H, NH_2); 4.38 (q, 1H, CHMe); 4.82 (br, 1H, NH_2); 5.63 (d, 1H, H_5 , Ph); 6.58 (dd, 1H, H_3 , Ph); 6.81 d, 1H, H_2 , Ph); 7.20 (m, 2H, H_3 , H_5 , py); 7.75 (m, 1H, H_4 , py); 8.54 (m, 2H, H_2 , H_6 , py) ppm. $^{13}\text{C-NMR}$ (500 MHz, DMSO): δ = 24.89 (s, C(CHMe)); 55.21 (s, 4MeO(Ph)); 59.96 (s, C(CHMe)); 109.64 (s, C_3 , Ph); 118.72 (s, C_5 , Ph); 122.53 (s, C_2 , Ph); 125.43, 125.69 (s, C_3 , C_5 , py); 138.02 (s, C_4 , py); 148.73 (s, C_4 , Ph); 150.58 (s, C_5 , Ph); 153.63 (s, C_2 , C_6 , py); 157.19 (s, C_6 , Ph) ppm. Elem. Anal. Data for **1**: MW = 371.18 g/mol. Calc. C: 45.30 %, H: 4.62 %, N: 7.55 %, Experimental: C: 45.27 %, H: 4.40 %, N: 7.44 %.

NMR data for **2**: $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ = 1.57 (d, 3H, CHMe); 3.31 (br, 1H, NH_2); 3.53 (s, 3H, 4-MeO(Ph)); 4.09 (br, 1H, NH_2); 4.42 (q, 1H, CHMe); 5.50 (1H, H_5 , Ph); 6.56 (dd, 1H, H_3 , Ph); 6.82 d, 1H, H_2 , Ph); 7.39 (m, 2H, H_3 , H_5 , py); 7.84 (m, 1H, H_4 , py); 8.89 (m, 2H, H_2 , H_6 , py) ppm. Elem. Anal. Data for **2**: MW = 462.62 g/mol. Calc. C: 36.35 %, H: 3.70 %, N: 6.06 %, Experimental: C: 36.37%, H: 3.94 %, N: 6.31 %.