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An New Type of Oxidative Addition of an Iodoarene to a Pd(II) Complex

Inmaculada Vicente-Hernández,[a] Maria-Teresa Chicote,[a] José Vicente,*[,a] and Delia Bautista[b]

[a]Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain.

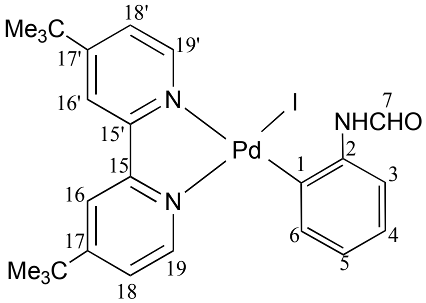
[b]SAI, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain.

1. Experimental Section

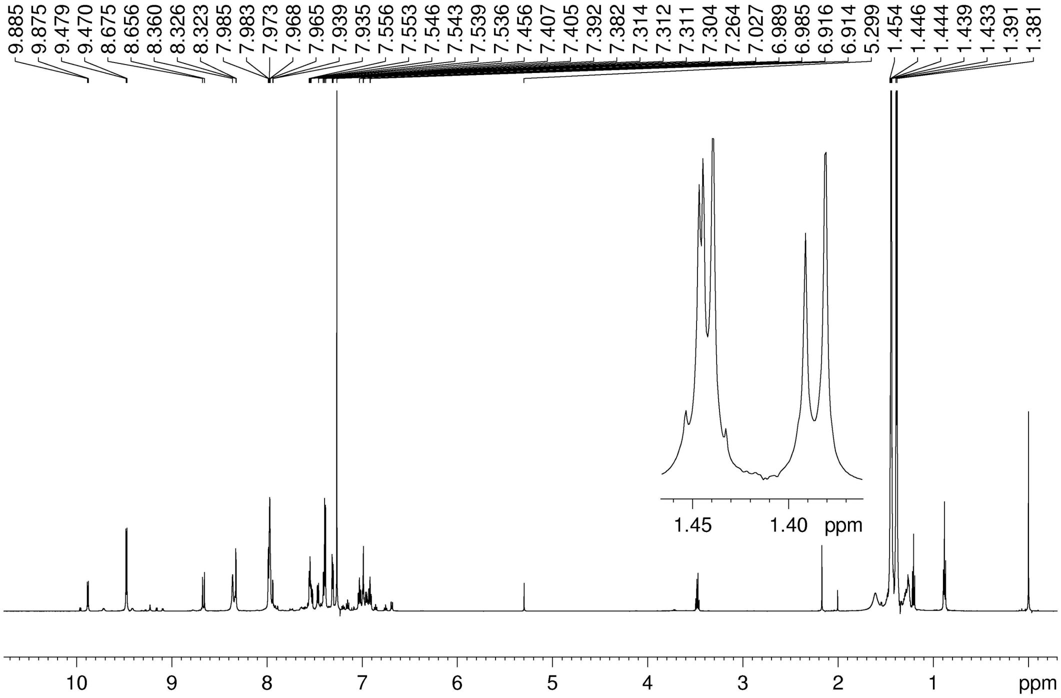
Unless otherwise stated the reactions were carried out at room temperature without special precautions against moisture. The 1H and 13C{1H} NMR spectra were recorded with Varian Unity-300, 400 and 600 spectrometers in CDCl3 solution and chemical shifts are referred to TMS [1H, $^{13}C\{^1H\}$]. The amide C_6H_4\{NHC(O)H\}I-2 [T. Kesharwani, A. K. Verma, D. Emrich, J. A. Ward and R. C. Larock, *Org. Lett.* 2009, **11**, 2591] and the isocyanide C_6H_4(NC)I-2 [A. Lygin, A *Org. Lett.* 2009, **11**, 389] were prepared as reported in the literature.

C_6H_4\{NHC(O)H\}I-2: 1H NMR (300 MHz, d6-dmso): Major isomer, δ 6.93 (t, 1 H, H4 or H5, $3J_{HH}$ = 7.5 Hz), 7.37 (t, 1 H, H4 or H5, $3J_{HH}$ = 8.1 Hz), 7.77 (d, 1 H, H3 or H6, $3J_{HH}$ = 8.1 Hz), 7.89 (d, 1 H, H3 or H6,$3J_{HH}$ = 7.5 Hz), 8.33 (s, 1 H, CHO), 9.52 (s, br, 1 N, NH). Minor isomer: 7.01 (t, 1 H, $3J_{HH}$ = 7.2 Hz), 7.34 (t, 1 H, $3J_{HH}$ = 7.8 Hz), 7.89 (d, 1 H, $3J_{HH}$ = 7.8 Hz), 9.63 (s, br, 1 N, NH). The resonances at 7.77 and 8.33 ppm are coincident for both isomers which are in 1:0.32 molar ratio. IR(cm-1): ν(NH), 3221; ν(CO), 1659.

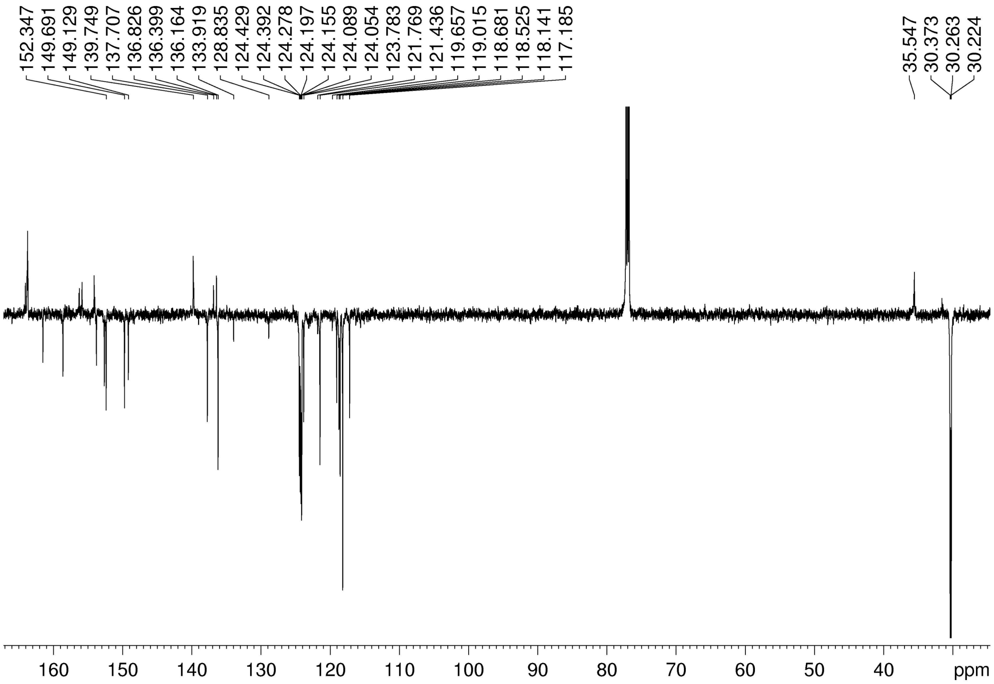
C_6H_4(NC)I-2: 1H NMR (400 MHz,CDCl3): δ 7.11 (ddd, 1 H, H4 or H5,$^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.39 (dd, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.40 (m, H4 or H5), 7.90 (dd, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz). IR(cm^{-1}): ν(CN), 2117.



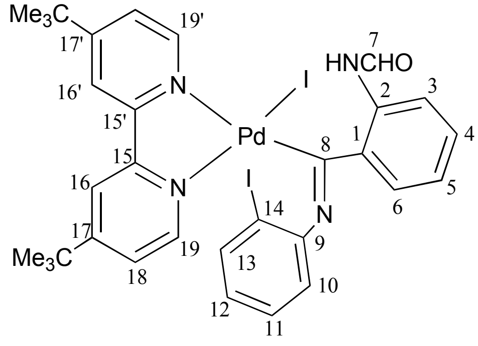
Synthesis of [Pd\{C_6H_4\{NHC(O)H\}-2\}I(^{t}Bubpy)] (1). A suspension containing Pd(dba)$_2$ (1.69 g, 2.94 mmol), ^{t}Bubpy (788 mg, 2.94 mmol) and C_6H_4\{NHC(O)H\}I-2 (725 mg, 2.94 mmol) in dry toluene (20 mL) was stirred under nitrogen atmosphere for 5 h or heated at 60 °C for 1.5 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (30 mL) and filtered through Celite. The filtrate was concentrated under vacuum to 5 mL and n-hexane was added. The sticky solid obtained was washed with hot n-hexane (10 x 20 mL) and then was stirred for 15 min with n-hexane (30 mL, in an ice/water bath). The suspension was filtered and the solid collected was dried under vacuum to give **1** as an orange solid. Yield: 1.47 g, 2.36 mmol. 80 %. Mp: 155 °C. ^1H NMR (600.1 MHz, $CDCl_3$): δ 1.38 (s, Me), 1.39 (s, Me), 1.433 (s, Me), 1.439 (s, Me), 1.44 (s, Me), 1.45 (s, Me), 6.69 (d, H3 or H6, $^3J_{HH}$ = 7 Hz), 6.75 (t, H4 or H5, $^3J_{HH}$ = 7.2 Hz), 6.86 (t, H4 or H5, $^3J_{HH}$ = 7.2 Hz), 6.92 (td, H4 or H5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1 Hz), 6.99-6.94 (overlapped signals, H3 and/or H6), 7.03 (td, H4 or H5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz), 7.15 (td, H4 or H5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz), 7.20 (t, H4 or H5, $^3J_{HH}$ = 7.2 Hz), 7.31 (dd, H18 or H18', $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.38-7.41 (overlapped signals, H19 or H19' and H3 or H6), 7.46 (d, H3 or H6, $^3J_{HH}$ = 7 Hz), 7.52 (d, H16 or H16', $^4J_{HH}$ = 2 Hz), 7.53 (d, H16 or H16', $^4J_{HH}$ = 2 Hz), 7.54 (d, 16 or H16', $^4J_{HH}$ = 2 Hz), 7.56 (d, H16 or H16', $^4J_{HH}$ = 2 Hz), 7.93 (d, 16 or H16', $^4J_{HH}$ = 2 Hz), 7.97-7.97 (several signals, H18 or H18'), 8.32-8.36 (several signals, ^{t}Bubpy), 8.67 (d, H7, $^3J_{HH}$ = 11 Hz), 9.47 (d, H19 or H19', $^3J_{HH}$ = 6 Hz), 9.88 (d, H19 or H19', $^3J_{HH}$ = 6 Hz), NH not observed. $^{13}C\{^1H\}$ APT NMR (150.9 MHz, $CDCl_3$): δ 30.2 (Me), 30.4 (Me), 35.5 (Me), 117.2 (C3 or C6), 118.1 (C16 or C16'), 118.5 (C16 or C16'), 118.7 (C16 or C16'), 119.0 (C16 or C16'), 121.4 (C3 or C6), 123.8-124.4 (several signals, C18 or C18' and C4 or C5), 136.2 (C3 or C6), 136.4 (C1 or C2), 136.8 (C1 or C2), 137.7 (C3 or C6), 139.6 (C1 or C2), 139.7 (C1 or C2), 149.1 (C19 or C19'), 149.7 (C19 or C19'), 152.3 (C19 or C19'), 152.6 (C19 or C19'), 153.7 (C15 or C15'), 153.9 (C15 or C15'), 154.1 (C15 or C15'), 155.8 (C15 or C15'), 156.2 (C15 or C15'), 158.6 (C7), 161.5 (C7), 163.7 (C17 or C17'), 164.0 (C17 or C17'), 163.8 (C17 or C17'). IR (cm^{-1}): ν(NH) 3341, 3320; ν(CO) 1698, 1683. Anal. Calcd for $C_{25}H_{30}IN_3OPd$: C, 48.29; H, 4.86; N, 6.76. Found: C, 48.04; H, 4.76; N, 6.72.



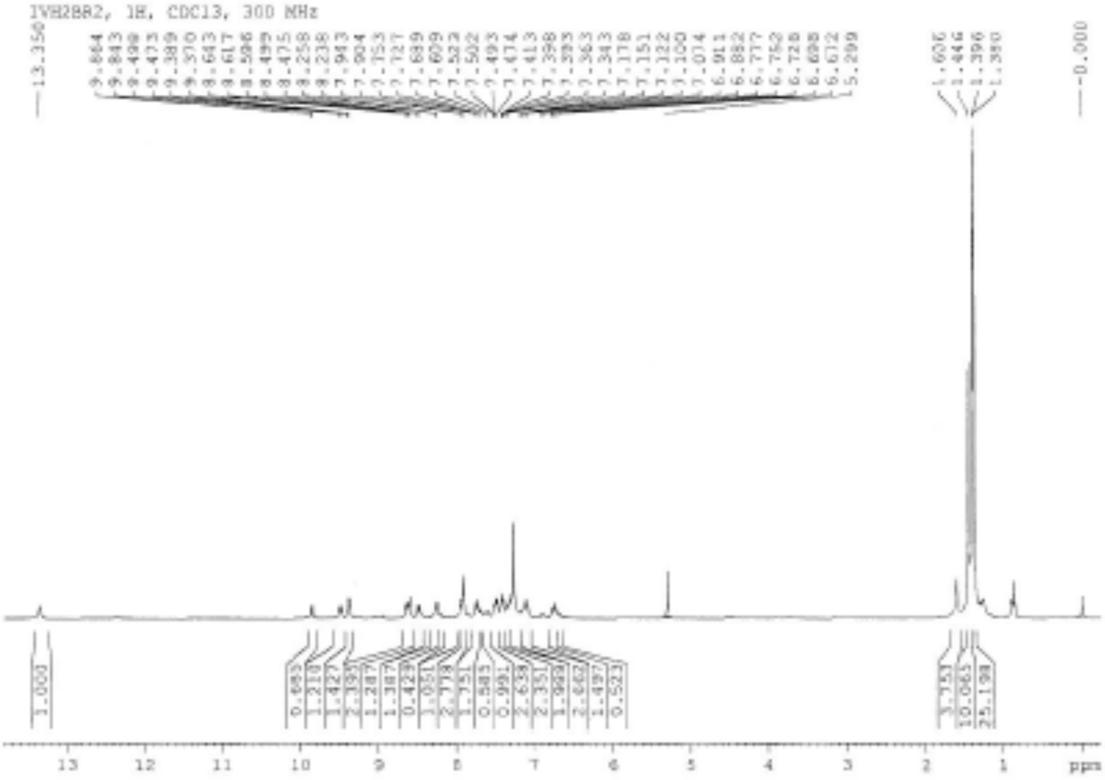
^{1}H NMR spectrum of **1** in $CDCl_3$.



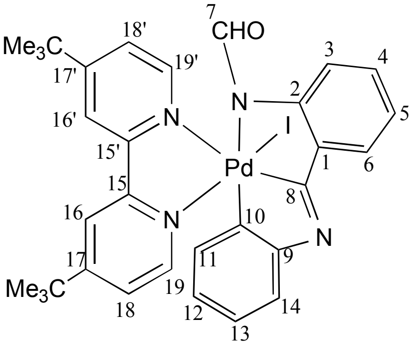
^{13}C{^{1}H}-APT NMR spectrum of **1** in $CDCl_3$.



Synthesis of [Pd{C(=NC_6H_4I-2)C_6H_4{NHCHO}-2}I(^{t}Bubpy)] (2). To a solution of 1 (203.6 mg, 0.33 mmol) in CH_2Cl_2 (20 mL) was added 2-iodophenyl isocyanide (75 mg, 0.33 mmol). The solution was stirred for 20 min, filtered through a short pad of Celite and concentrated under vacuum to 1 mL. Upon the addition of pentane (15 mL) a suspension formed which was filtered and the solid collected was dried by suction to give 2 as a yellow-orange solid. Yield 185 mg, 0.22 mmol, 66%. Mp: 157 ºC (decomp). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.38 (s, Me), 1.40 (s, Me), 1.45 (s, Me), 6.67-7.75 (various overlapped multiplets of different intensities), 7.90 (s, NH), 7.94 (d, H16 or H16', $^4J_{HH}$ = 1 Hz), 8.25 (d, $^3J_{HH}$ = 6 Hz), 8.49 (d,$^3J_{HH}$ = 7 Hz), 8.60 (d, H16 or H16', $^4J_{HH}$ = 2 Hz), 8.63 (d, $^3J_{HH}$ = 8 Hz), 9.38 (d, $^3J_{HH}$ = 6 Hz), 9.48 (d, $^3J_{HH}$ = 8 Hz), 9.85 (d, $^3J_{HH}$ = 6 Hz), 13. 35 (s, br, NH). **2** is not enough stable in solution as to allow its ^{13}C NMR spectrum to be measured. In the absence of HMQC and HMBC experiments, the ^{1}H NMR could not be assigned. IR (cm^{-1}): ν(NH) not observed; ν(C=O), ν(C=N) 1687, 1576. Anal. Calcd for $C_{32}H_{34}I_2N_4OPd$: C, 45.17; H, 4.03; N, 6.58. Found: C, 44.97; H, 4.11; N, 6.32.

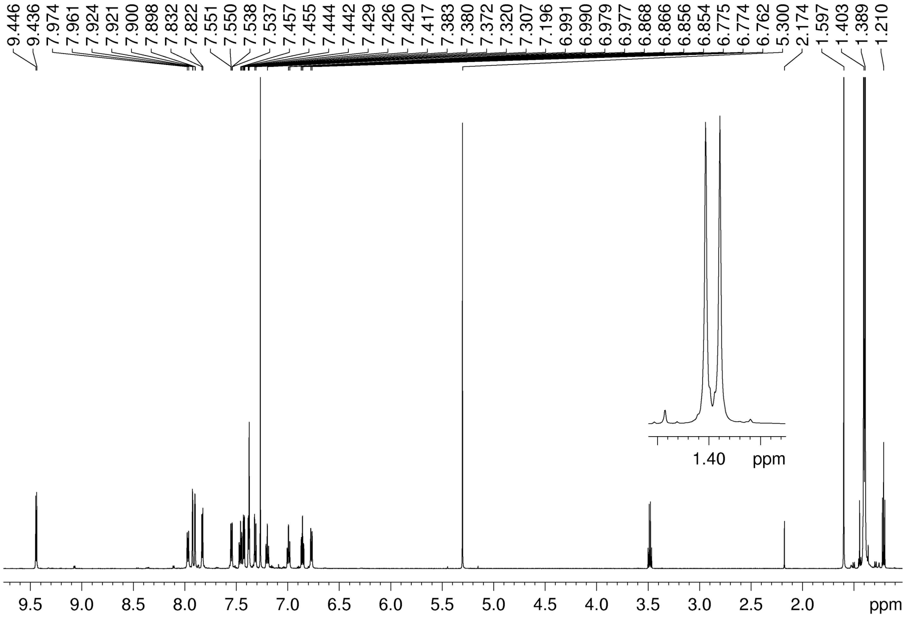


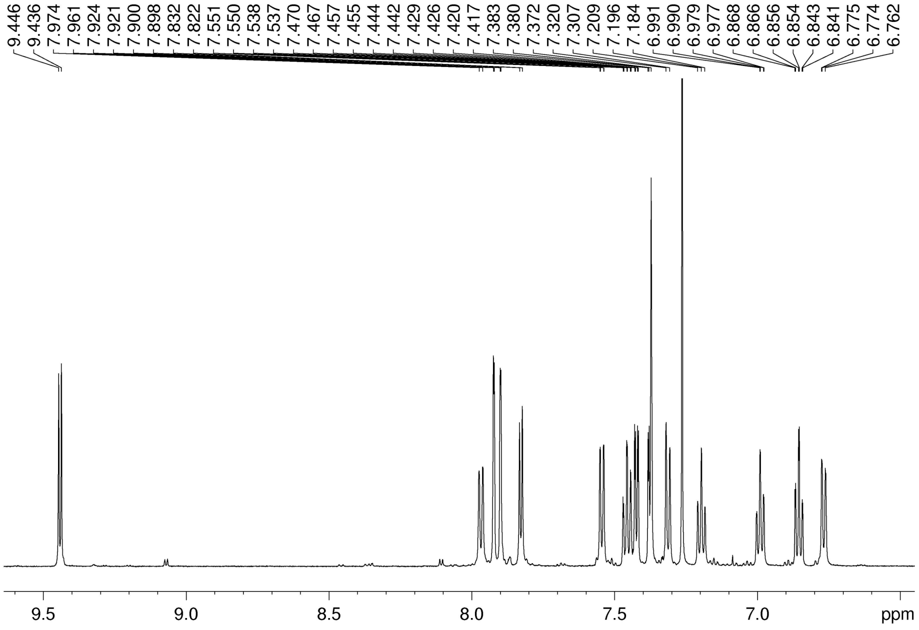
^{1}H NMR spectrum of **2** in CDCl$_3$.



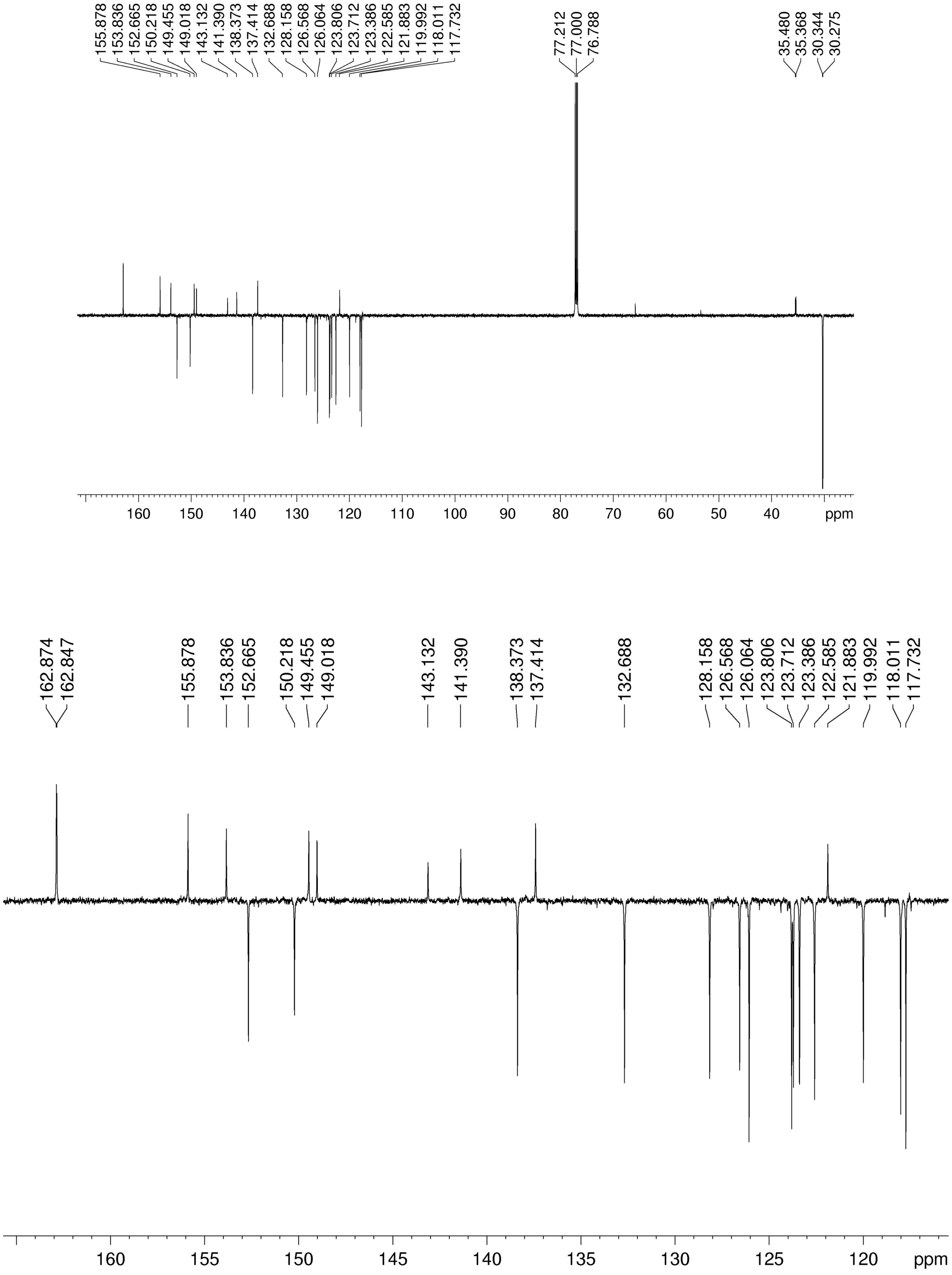
Synthesis of OC-6-35-[Pd{C,C,N-C(=NC$_6$H$_4$-2)C$_6$H$_4${NCHO}-2}I(^{t}Bubpy)] (4). To a solution of **2** (250 mg, 0.29 mmol) in acetone (15 mL) was added Tl(acac) (acacH = acetylacetone, 89.2 mg, 0.29 mmol). A yellow suspension immediately formed which was stirred for 1 h and concentrated under vacuum to dryness. The residue was stirred with CH$_2$Cl$_2$ (20 mL) and the suspension was filtered through a short pad of Celite. The solution was concentrated (1 mL), pentane (20 mL) was added and the suspension was filtered. A CHCl$_3$ solution of the dark orange solid collected was heated at 50 ºC for 5 h or, alternatively, stirred at room temperature for two days. The solution was concentrated under vacuum (1 mL), pentane (15 mL) was added, the suspension was filtered, and the red solid collected was dried, first by suction and then in an oven at at 40 ºC overnight. Yield: 157 mg, 0.22 mmol, 75% . Mp: 202 ºC (decomp). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.39 (s, 9 H, Me), 1.40 (s, 9 H, Me), 6.77 (dd, 1 H, H11 or H14, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.85 (td, 1 H, H12 or H13, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.99 (ddd, 1 H, H5, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.20 (td, 1 H, H12 or H13, $^3J_{HH}$= 8 Hz, $^4J_{HH}$ = 1 Hz), 7.31 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.37 (dd, 1 H, H18 or H18', $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.38 (s, 1 H, H7), 7.42 (dd, 1 H, H18 or H18', $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.46 (td, 1 H, H4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.54 (dd, 1 H, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.83 (d, 1 H, H19 or H19',$^3J_{HH}$ = 6 Hz), 7.90 (d, 1 H, H16 or H16', $^4J_{HH}$ = 2 Hz), 7.92 (d, 1 H, H16 or H16', $^4J_{HH}$ = 2 Hz), 7.97 (dd, 1 H, H11 or H14, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 9.45 (d, 1 H, H19 or H19', $^3J_{HH}$ = 6 Hz). 13C{1H} APT NMR (150.9 MHz, CDCl$_3$): δ 30.28 (Me), 30.34 (Me,), 35.4 (CMe$_3$), 35.5 (CMe$_3$), 117.7 (C16 or C16'), 118,0 (C16 or C16'), 120.0 (C11 or C14), 122.6 (C12 or C13), 123.4 (C18 or C18'), 123.7 (C5), 123.8 (C18 or C18'), 126.1 (C3), 126.6 (C11 or C14), 128.2 (C12 or C13), 132.7 (C4), 137.4 (C9 or C10), 138.4 (C6), 141.4 (C2), 143.1 (C1), 149.0 (C7), 149.5 (C8), 150.2 (C19 or C19'), 152.7 (C19 or C19'), 153.8 (C15 or

C15'), 155.9 (C15 or C15), 162.8 (C17 or C17'), 162.9 (C17 or C17'). IR (cm-1): νC=O, νC=N, ν(CC+CN)arom,1611, 1593, 1581, 1563 1683. Anal. Calcd for $C_{32}H_{33}IN_4OPd$: C, 53.16; H, 4.60; N, 7.75. Found: C, 52.98; H, 4.63; N, 7.70.





1H NMR spectrum of **4**·CH_2Cl_2 in $CDCl_3$.



$^{13}C\{1H\}$-APT NMR spectrum of **4**·CH_2Cl_2 in $CDCl_3$.

2. X-ray Crystallographic Data of $\mathbf{4 \cdot CH_2Cl_2}$

A crystal of $4 \cdot CH_2Cl_2$ suitable for X-ray diffraction studies were obtained by the liquid-liquid diffusion method from CH_2Cl_2 and Et_2O. Numerical details are presented in Table 1. The data were collected on Bruker D8 QUEST diffractometers using monochromated Mo-$K\alpha$ radiation in ω-scan mode. The structure was solved by direct methods and refined anisotropically on *F*2 using the program SHELXL-97 (G. M. Sheldrick, *SHELX* -97, University of Göttingen, Göttingen, Germany, 1997)

The hydrogens of the methyl groups were refined using rigid groups and the other hydrogens were refined using a riding mode.

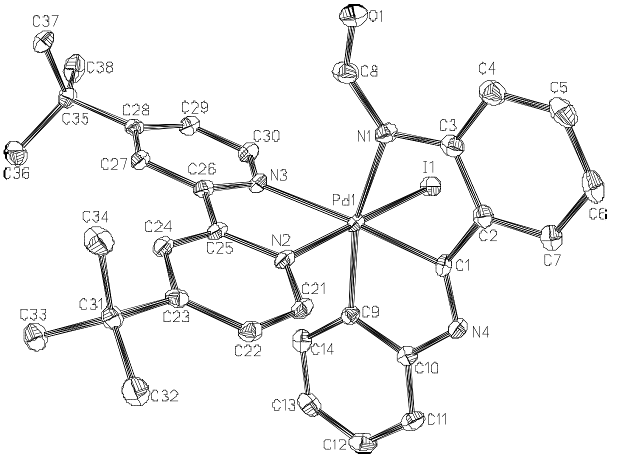


Figure 1. Ortep drawing (50% probability ellipsoids) of complex $\mathbf{4 \cdot CH_2Cl_2}$.

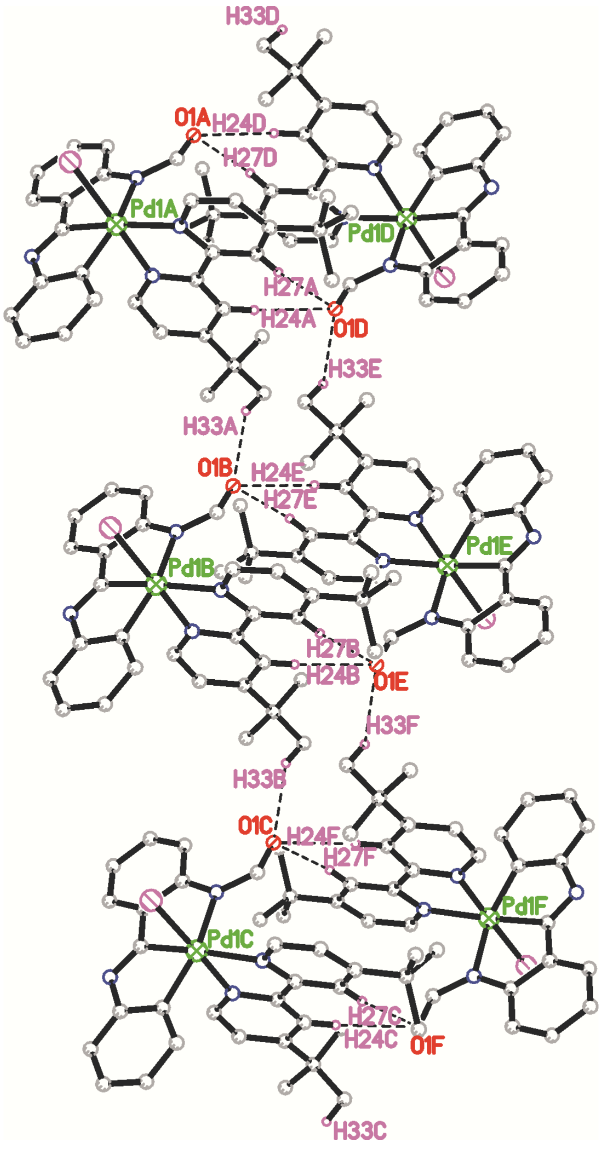


Figure 2. Chain of dimers staked along the a axis in **4·CH$_2$Cl$_2$**.

Table 1. Crystal data and structure refinement.

Identification code	ivh4d1_0m	
Empirical formula	C33 H35 Cl2 I N4 O Pd	
Formula weight	807.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7622(11) Å	α= 114.432(3)°
	b = 12.8238(12) Å	β= 100.558(3)°
	c = 13.4282(12) Å	γ = 93.044(3)°
Volume	1641.4(3) Å^3	
Z	2	
Density (calculated)	1.634 Mg/m^3	
Absorption coefficient	1.701 mm^{-1}	
F(000)	804	
Crystal size	0.13 x 0.09 x 0.07 mm^3	
Theta range for data collection	2.28 to 28.28°	
Index ranges	-14<=h<=14, -16<=k<=17, -17<=l<=17	
Reflections collected	59143	
Independent reflections	8138 [R(int) = 0.0406]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9281 and 0.8478	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8138 / 0 / 385	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0519	
R indices (all data)	R1 = 0.0369, wR2 = 0.0552	
Largest diff. peak and hole	0.851 and -0.566 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	4185.5(2)	5988.4(1)	2912.6(1)	12.2(1)
I(1)	2595.1(1)	4494.0(1)	3067.2(1)	17.7(1)
N(1)	2741.6(18)	7016.8(16)	2772.8(16)	17.0(4)
C(1)	3498(2)	5119.1(19)	1265.6(18)	14.0(4)
N(4)	4052.4(18)	4281.9(16)	721.7(15)	15.4(4)
C(2)	2454(2)	5626.8(19)	855.6(19)	15.4(4)
C(3)	2064(2)	6605.3(19)	1653(2)	16.6(5)
C(4)	1046(2)	7085(2)	1269(2)	22.2(5)
C(5)	469(2)	6610(2)	140(2)	24.4(5)
C(6)	874(2)	5665(2)	-643(2)	23.8(5)
C(7)	1869(2)	5169(2)	-284(2)	19.1(5)
C(8)	2586(2)	7994(2)	3632(2)	21.0(5)
O(1)	1882.6(17)	8712.8(15)	3632.9(15)	25.8(4)
C(9)	5393(2)	4808.8(18)	2566.6(18)	13.7(4)
C(10)	5084(2)	4076.2(19)	1407.7(19)	14.9(4)
C(11)	5820(2)	3210(2)	962(2)	20.3(5)
C(12)	6861(2)	3091(2)	1666(2)	23.0(5)
C(13)	7183(2)	3827(2)	2796(2)	21.3(5)
C(14)	6450(2)	4701(2)	3259(2)	17.3(5)
N(2)	5558.4(18)	7144.9(16)	2847.4(15)	13.9(4)
N(3)	5072.7(18)	7057.7(16)	4673.9(15)	14.4(4)
C(21)	5859(2)	7060.2(19)	1898.2(18)	15.4(4)
C(22)	6700(2)	7891(2)	1872.6(18)	15.4(4)
C(23)	7248(2)	8878.1(19)	2853.1(18)	13.4(4)
C(24)	6948(2)	8936.3(19)	3843.6(18)	14.5(4)
C(25)	6136(2)	8060.2(19)	3834.2(18)	13.7(4)
C(26)	5870(2)	8002.0(19)	4863.3(18)	13.4(4)
C(27)	6419(2)	8829.2(19)	5940.3(18)	14.0(4)
C(28)	6160(2)	8688.0(19)	6868.0(18)	13.9(4)
C(29)	5358(2)	7700.1(19)	6651.9(19)	15.7(4)
C(30)	4831(2)	6916(2)	5551.8(19)	16.6(5)
C(31)	8119(2)	9864(2)	2860.3(18)	14.1(4)
C(32)	8481(2)	9530(2)	1728(2)	21.4(5)
C(33)	9343(2)	10193(2)	3779.9(19)	18.7(5)

C(34)	7395(2)	10913(2)	3100(2)	22.2(5)
C(35)	6764(2)	9601(2)	8056.7(18)	16.6(5)
C(36)	8226(2)	9701(2)	8223(2)	27.7(6)
C(37)	6341(2)	10767(2)	8200.8(19)	20.1(5)
C(38)	6367(3)	9284(2)	8948(2)	25.8(6)
C(99)	10071(3)	6480(3)	4323(3)	40.6(7)
Cl(1)	9445.4(7)	6541.3(7)	5462.3(7)	41.8(2)
Cl(2)	9053.0(7)	6878.8(7)	3414.4(7)	39.4(2)

Table 3. Bond lengths [Å] and angles [°].

Pd(1)-C(1)	1.989(2)
Pd(1)-C(9)	2.010(2)
Pd(1)-N(2)	2.0767(19)
Pd(1)-N(1)	2.1224(19)
Pd(1)-N(3)	2.1763(18)
Pd(1)-I(1)	2.5992(3)
N(1)-C(8)	1.351(3)
N(1)-C(3)	1.404(3)
C(1)-N(4)	1.273(3)
C(1)-C(2)	1.462(3)
N(4)-C(10)	1.417(3)
C(2)-C(7)	1.395(3)
C(2)-C(3)	1.417(3)
C(3)-C(4)	1.405(3)
C(4)-C(5)	1.381(4)
C(5)-C(6)	1.391(4)
C(6)-C(7)	1.387(3)
C(8)-O(1)	1.223(3)
C(9)-C(14)	1.383(3)
C(9)-C(10)	1.408(3)
C(10)-C(11)	1.391(3)
C(11)-C(12)	1.387(3)
C(12)-C(13)	1.378(4)
C(13)-C(14)	1.401(3)
N(2)-C(21)	1.335(3)
N(2)-C(25)	1.362(3)
N(3)-C(30)	1.332(3)
N(3)-C(26)	1.350(3)
C(21)-C(22)	1.376(3)
C(22)-C(23)	1.393(3)
C(23)-C(24)	1.399(3)
C(23)-C(31)	1.529(3)
C(24)-C(25)	1.381(3)
C(25)-C(26)	1.492(3)
C(26)-C(27)	1.385(3)
C(27)-C(28)	1.404(3)
C(28)-C(29)	1.386(3)
C(28)-C(35)	1.528(3)
C(29)-C(30)	1.385(3)
C(31)-C(32)	1.530(3)
C(31)-C(33)	1.533(3)
C(31)-C(34)	1.538(3)
C(35)-C(37)	1.532(3)
C(35)-C(38)	1.534(3)
C(35)-C(36)	1.539(3)
C(99)-Cl(2)	1.742(3)
C(99)-Cl(1)	1.756(3)

C(1)-Pd(1)-C(9)	80.84(9)
C(1)-Pd(1)-N(2)	97.00(8)
C(9)-Pd(1)-N(2)	88.48(8)
C(1)-Pd(1)-N(1)	82.94(8)
C(9)-Pd(1)-N(1)	163.66(8)
N(2)-Pd(1)-N(1)	91.51(7)
C(1)-Pd(1)-N(3)	173.84(8)
C(9)-Pd(1)-N(3)	99.06(8)
N(2)-Pd(1)-N(3)	76.85(7)
N(1)-Pd(1)-N(3)	96.85(7)
C(1)-Pd(1)-I(1)	85.08(6)
C(9)-Pd(1)-I(1)	88.47(6)
N(2)-Pd(1)-I(1)	175.99(5)
N(1)-Pd(1)-I(1)	92.15(5)
N(3)-Pd(1)-I(1)	101.08(5)
C(8)-N(1)-C(3)	125.1(2)
C(8)-N(1)-Pd(1)	123.96(16)
C(3)-N(1)-Pd(1)	110.69(14)
N(4)-C(1)-C(2)	129.7(2)
N(4)-C(1)-Pd(1)	117.99(16)
C(2)-C(1)-Pd(1)	112.09(15)
C(1)-N(4)-C(10)	113.58(19)
C(7)-C(2)-C(3)	121.1(2)
C(7)-C(2)-C(1)	121.1(2)

C(3)-C(2)-C(1)	117.7(2)
N(1)-C(3)-C(4)	125.4(2)
N(1)-C(3)-C(2)	116.5(2)
C(4)-C(3)-C(2)	118.1(2)
C(5)-C(4)-C(3)	119.9(2)
C(4)-C(5)-C(6)	121.8(2)
C(7)-C(6)-C(5)	119.4(2)
C(6)-C(7)-C(2)	119.6(2)
O(1)-C(8)-N(1)	130.0(2)
C(14)-C(9)-C(10)	120.5(2)
C(14)-C(9)-Pd(1)	129.97(17)
C(10)-C(9)-Pd(1)	109.37(15)
C(11)-C(10)-C(9)	119.8(2)
C(11)-C(10)-N(4)	121.9(2)
C(9)-C(10)-N(4)	118.19(19)
C(12)-C(11)-C(10)	119.3(2)
C(13)-C(12)-C(11)	120.8(2)
C(12)-C(13)-C(14)	120.5(2)
C(9)-C(14)-C(13)	118.9(2)
C(21)-N(2)-C(25)	119.20(19)
C(21)-N(2)-Pd(1)	123.76(15)
C(25)-N(2)-Pd(1)	116.99(14)
C(30)-N(3)-C(26)	118.68(19)
C(30)-N(3)-Pd(1)	126.74(15)
C(26)-N(3)-Pd(1)	114.37(14)
N(2)-C(21)-C(22)	122.3(2)
C(21)-C(22)-C(23)	120.3(2)
C(22)-C(23)-C(24)	116.6(2)
C(22)-C(23)-C(31)	122.44(19)
C(24)-C(23)-C(31)	120.99(19)
C(25)-C(24)-C(23)	121.1(2)
N(2)-C(25)-C(24)	120.4(2)
N(2)-C(25)-C(26)	115.30(19)
C(24)-C(25)-C(26)	124.2(2)
N(3)-C(26)-C(27)	121.7(2)
N(3)-C(26)-C(25)	115.00(19)
C(27)-C(26)-C(25)	123.3(2)
C(26)-C(27)-C(28)	119.9(2)
C(29)-C(28)-C(27)	117.4(2)
C(29)-C(28)-C(35)	122.8(2)
C(27)-C(28)-C(35)	119.9(2)
C(30)-C(29)-C(28)	119.6(2)
N(3)-C(30)-C(29)	122.8(2)
C(23)-C(31)-C(32)	111.60(18)
C(23)-C(31)-C(33)	110.20(18)
C(32)-C(31)-C(33)	108.95(18)
C(23)-C(31)-C(34)	108.10(18)
C(32)-C(31)-C(34)	108.62(19)
C(33)-C(31)-C(34)	109.34(19)
C(28)-C(35)-C(37)	109.18(18)
C(28)-C(35)-C(38)	111.79(19)
C(37)-C(35)-C(38)	108.6(2)
C(28)-C(35)-C(36)	108.56(19)
C(37)-C(35)-C(36)	109.5(2)
C(38)-C(35)-C(36)	109.2(2)
Cl(2)-C(99)-Cl(1)	112.95(16))

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	15.7(1)	9.9(1)	9.1(1)	2.3(1)	3.0(1)	2.2(1)
I(1)	18.5(1)	16.0(1)	19.7(1)	8.1(1)	6.1(1)	2.4(1)
N(1)	20.1(10)	14.5(9)	16.5(10)	5.7(8)	5.7(8)	5.8(8)
C(1)	15.9(11)	12.2(10)	11.0(10)	3.6(9)	0.1(8)	-0.9(8)
N(4)	18.4(10)	13.8(9)	11.4(9)	3.5(8)	2.0(7)	3.1(8)
C(2)	15.1(11)	14.9(11)	16.3(11)	7.5(9)	2.6(9)	0.1(9)
C(3)	14.9(11)	15.0(11)	21.6(12)	9.2(10)	5.3(9)	2.0(9)
C(4)	19.6(12)	18.9(12)	28.7(13)	10.6(11)	5.5(10)	5.1(10)

C(5)	16.9(12)	26.1(13)	34.4(14)	18.8(12)	1.1(10)	5.4(10)
C(6)	17.5(12)	30.4(14)	22.9(13)	14.8(11)	-3.6(10)	-1.3(10)
C(7)	17.4(11)	20.5(12)	18.1(12)	8.3(10)	1.2(9)	0.6(9)
C(8)	19.2(12)	18.4(12)	27.8(13)	10.9(11)	8.2(10)	5.4(10)
O(1)	24.7(9)	20.9(9)	28.3(10)	6.3(8)	6.9(8)	7.6(7)
C(9)	15.8(10)	10.6(10)	13.9(10)	4.3(9)	3.7(8)	1.5(8)
C(10)	16.5(11)	14.1(11)	15.1(11)	6.8(9)	4.4(9)	2.7(9)
C(11)	24.4(12)	17.1(12)	18.3(12)	4.7(10)	8.7(10)	4.8(10)
C(12)	24.9(13)	20.0(12)	30.8(14)	13.7(11)	12.9(11)	10.5(10)
C(13)	16.9(11)	23.6(13)	28.4(13)	17.1(11)	2.7(10)	4.1(10)
C(14)	19.1(11)	16.6(11)	16.7(11)	8.7(10)	1.9(9)	0.1(9)
N(2)	17.8(9)	12.5(9)	9.9(9)	3.1(7)	3.1(7)	3.8(7)
N(3)	18.6(9)	12.4(9)	11.2(9)	3.9(8)	3.7(7)	1.9(7)
C(21)	20.1(11)	14.6(11)	10.0(10)	3.7(9)	3.2(9)	4.4(9)
C(22)	18.1(11)	18.8(11)	10.6(10)	6.6(9)	4.7(9)	5.3(9)
C(23)	12.3(10)	15.7(11)	15.1(11)	8.6(9)	3.8(8)	6.8(8)
C(24)	16.3(11)	12.6(10)	12.1(10)	3.3(9)	1.6(8)	3.3(8)
C(25)	17.6(11)	12.5(10)	10.3(10)	3.3(9)	4.4(8)	5.7(8)
C(26)	15.3(10)	14.2(11)	11.4(10)	5.6(9)	3.2(8)	4.8(8)
C(27)	16.1(11)	12.3(10)	12.5(10)	4.3(9)	3.1(9)	2.8(8)
C(28)	13.1(10)	16.1(11)	11.9(10)	5.3(9)	1.7(8)	6.7(8)
C(29)	20.2(11)	16.0(11)	13.4(11)	8.1(9)	4.5(9)	5.3(9)
C(30)	20.9(12)	15.1(11)	14.1(11)	6.1(9)	4.6(9)	3.1(9)
C(31)	12.4(10)	16.4(11)	13.8(11)	7.9(9)	0.2(8)	2.1(8)
C(32)	20.2(12)	28.1(13)	17.0(12)	11.4(11)	3.6(9)	-0.8(10)
C(33)	16.7(11)	22.3(12)	17.3(11)	10.5(10)	0.1(9)	0.9(9)
C(34)	19.7(12)	19.0(12)	31.5(14)	14.6(11)	5.0(10)	5.2(10)
C(35)	17.6(11)	19.9(12)	8.8(10)	4.0(9)	0.8(9)	1.9(9)
C(36)	17.9(12)	35.6(15)	21.5(13)	6.8(12)	-1.3(10)	3.4(11)
C(37)	24.0(12)	17.5(12)	13.5(11)	1.5(9)	4.1(9)	2.4(10)
C(38)	32.9(14)	28.9(14)	12.1(11)	8.2(11)	-0.1(10)	-1.9(11)
C(99)	31.0(16)	57(2)	44.9(18)	28.7(17)	14.3(14)	21.0(15)
Cl(1)	39.5(4)	49.1(5)	39.0(4)	24.1(4)	5.5(3)	-5.2(3)
Cl(2)	37.4(4)	44.4(4)	43.8(4)	27.0(4)	6.5(3)	7.8(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}).

	x	y	z	U(eq)
H(4)	754	7735	1785	27
H(5)	-224	6938	-109	29
H(6)	472	5362	-1418	29
H(7)	2152	4521	-811	23
H(8)	3101	8145	4345	25
H(11)	5611	2706	183	24
H(12)	7359	2494	1366	28
H(13)	7908	3742	3264	26
H(14)	6675	5212	4037	21
H(21)	5480	6403	1217	18
H(22)	6907	7792	1184	19
H(24)	7309	9589	4534	17
H(27)	6969	9491	6051	17
H(29)	5171	7562	7255	19
H(30)	4274	6248	5418	20
H(32A)	8931	8854	1559	32
H(32B)	9038	10179	1762	32
H(32C)	7705	9344	1139	32
H(33A)	9124	10468	4515	28
H(33B)	9905	10809	3761	28
H(33C)	9782	9514	3651	28
H(34A)	6654	10727	2479	33
H(34B)	7963	11578	3176	33
H(34C)	7107	11104	3799	33
H(36A)	8493	8947	8098	42
H(36B)	8628	10269	8990	42
H(36C)	8490	9953	7686	42
H(37A)	6574	10973	7626	30
H(37B)	6765	11365	8947	30
H(37C)	5413	10710	8121	30
H(38A)	5434	9183	8824	39
H(38B)	6738	9906	9696	39
H(38C)	6677	8562	8895	39
H(99A)	10896	7000	4612	49
H(99B)	10240	5682	3899	49

Table 6. Hydrogen bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(24)-H(24)...O(1)#1	0.95	2.48	3.426(3)	176.3
C(27)-H(27)...O(1)#1	0.95	2.39	3.334(3)	172.5
C(33)-H(33C)...O(1)#2	0.98	2.53	3.399(3)	147.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1 #2 x+1,y,z

3. Discussion on the NMR and IR spectra of complexes.

The ^{1}H NMR spectrum of N-(2-iodophenyl)formamide, measured in d$_6$-dmso solution at room temperature shows the presence of an equilibrium between two isomers in 0.32:1 molar ratio. In complexes **1** and **2** isomers may form not only because of the cis/trans equilibrium for the NH=CHO moiety they contain, but also because of the likely restricted rotation about the bond joining the nitrogen and the aromatic ring caused by the big steric demand of the I- or PdI(tBubpy)-ortho substituents in **1** and **2**, respectively. Additionally, the 2-iodiophenyl fragment in the iminobenzoyl moiety in 2 could adopt two orientations.

The presence of various isomers in the CDCl$_3$ solution of **1** is evidenced by the various Me (tBubpy) resonances. In spite of the fact that we carried out APT, HMQC and HMBC experiments in a Varian 600 spectrometer at room temperature and at - 60 ºC, many of the 1H and 13C resonances can not be distinguished since they are overlapped, which also impeded to get accurate integrals from the ^{1}H NMR spectra. The presence of two ν(NH) and two ν(CO) bands in the IR spectrum of 1, at 3341, 3320 and 1698, 1683 cm^{-1}, respectively, suggests the presence of two isomers in the solid state.

The ^{1}H NMR spectrum of **2** in CDCl$_3$ shows three Me resonances, the central one having an intensity equal to the sum of the two others which is compatible with the presence of two isomers in solution in roughly 2:1 molar ratio. A continuum of multiplets in the 6.6-7.5 ppm region impedes any distinction. When we tried to measure a short-time ^{13}C experiment (APT) abundant decomposition occurred and hence, no 2D spectra could be obtained which made also impossible to assign the ^{1}H NMR spectrum. We could not isolate complex **3**.