

# Palladium complexes of unsaturated secondary aziridines. Crystal structure of *trans*dichlorobis(2,2-dimethyl-3-phenyl-3allylaziridine)palladium(II)

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Abstract—Six secondary aziridines (Az) bearing unsaturated vinylic or allylic groups on one of the carbon atoms of the ring have been reacted with palladium compounds. Complexes of general formula  $PdCl_2(Az)_2$  have been isolated and spectroscopically characterized for fully substituted aziridines. The crystal structure of the complex of allylaziridine has been determined, showing the *trans*-arrangement of the ligands around the palladium center. © 1997 Elsevier Science Ltd

Keywords: complex; palladium; aziridine; allyl; vinyl; X-ray structure.

Hybrid ligands exhibiting two different coordination sites have been widely studied and have found numerous applications in coordination chemistry and in homogeneous catalysis, as proved by the industrial SHOP process of oligomerization of ethylene to linear  $\alpha$ -olefins [1]. We continue to be interested in the chemistry of hybrid ligands containing one nitrogen site and either phosphorus or carbon–carbon double bond as second coordination site. The first case is illustrated by synthesis of transition-metal complexes of cyclic aminophosphonites arising from the P-N bond cleavage of bicyclic phosphoranes [2] and their applications in homogeneous hydroformylation, oligomerization and teleomerization of alkenes and dienes. The second series of hybrid ligands is confined to secondary aziridines (abbreviated Az) bearing an unsaturated substituent on one of the carbon atoms of the ring. We have recently described the synthesis of rhodium complexes with 2,2-dimethyl-3-phenyl-3allylaziridine 1. The X-ray crystal structure of the carbonyl complex Rh(CO)(Az)Cl (Az = 1) has proved that 1 is simultaneously bound to the metal by the double bond of the allyl substituent and by the nitrogen atom in a chelating mode [3]. This species is active for the hydroformylation of styrene and is recovered unchanged after reaction. The complex is very stable and the double bond of the allyl group is not activated by coordination to rhodium. Then, it should be interesting to change the metal in order to make the double bond reactive and to transform the starting aziridine. Thus, we have devoted the present paper to a study of the reactions between some palladium complexes with the unsaturated aziridines described in Scheme 1.

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azide and have obtained a trans-PdCl<sub>2</sub>(Az)<sub>2</sub> species. Bertani et al. [6] proved the formation of carbene complexes from ethylenimine and isocyanide palladium complexes. Tanner [7] described the use of chelating bis-aziridines in palladium complexes and their use in various catalytic reactions. Very recently, Beck et al. [8] studied the chelating behavior of Laziridine-2-carboxylate with various transition metals. Most of the catalytic reactions described in the literature are devoted to the ring expansion of the aziridine by insertion in the C-N bond of either carbon monoxide [9], heteroallenes [10], or C-C double bond [11] giving rise to four and five-membered heterocycles. Other reactions are represented by isomerization [12], formation of unsaturated amines by aziridine ring opening [13] and catalytic hydrogenation [14].

## **RESULTS AND DISCUSSION**

The allyl and vinylaziridines 1-4 have already been described and were prepared according to the published methods [15]. The hitherto unknown spiro aziridines 5 and 6 have been synthesised by the action of respectively allyl and vinyl magnesium bromide on cyclohexyl-2-spiro-3-phenyl azirine [16] following the method described by Chaabouni *et al.* [15] and have been fully characterized.

Reaction of aziridines 1–6 does not give any defined product with Pd(dibenzylideneacetone)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub> or PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Two equivalents of 1–6 react with 1 equiv. of PdCl<sub>2</sub>(PhCN)<sub>2</sub> or PdCl<sub>2</sub>(cod), but only the tetrasubstituted compounds 1, 2, 5 and 6 give a well defined complex of formula PdCl<sub>2</sub>(Az)<sub>2</sub> in good yields (Scheme 2).

The non-fully substituted aziridines 3 and 4 are not stable enough in the presence of the palladium salt. Indeed, the aziridine 3 gives the corresponding complex 9, but in only moderate yield (55%), while the aziridine 4 undergoes decomposition and polymerization under the reaction conditions. Therefore, the degree of substitution of the starting aziridine strongly influences its coordinating properties.

The infrared NH stretching band of aziridine in the complexes  $PdCl_2(Az)_2$  are slightly shifted towards low frequencies as expected for a coordinated NH group (Table 1). On the contrary, the C=C stretching bands are practically unchanged, in accordance with a free double bond.

NMR spectra of the complexes are described in the Experimental section and the discussion will be focused on complex 7 with the aziridine 1. The main feature of the <sup>1</sup>H NMR spectrum is a significant deshielding of most of the peaks, compared to those of the corresponding free aziridine. Simultaneously, the protons of the methyl groups give rise to two singlets of unequal intensity. All the signals in the  $^{13}C{^{1}H}$  NMR spectrum, but those of the methylene group of the allylic substituent are split. Such a splitting may originate from several reasons. First, both aziridine ligands are not strictly symmetrical around palladium. However, in this case, the magnitude of the splitting would be much smaller than that observed, particularly for the most shielded methyl group  $(\Delta \delta = 0.08 \text{ ppm for aziridine 1})$ . A second possibility is the presence of both cis- and trans-isomers, but that would give rise to two distinct peaks for the NH signal. Finally, the existence of two asymmetric centres for the aziridine ligands in the complex can induce the formation of a mixture of two diastereomeric complexes (R,R) and (R,S). This last hypothesis has been confirmed for complex 7  $PdCl_2(Az)_2$  with Az = 1 by means of an X-ray crystal structure analysis. Single crystals of 7 were grown by slow evaporation of 0.5 g of the complex dissolved in a hot mixture of 25% THF/75% petroleum ether v/v and contained 5% THF. The diastereomeric species isolated in the crystalline form has the (R,R) configuration. The structure consists of two slightly different molecules ligated by hydrogen bonds between hydrogen atom of the

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Table 1. Infrared data of aziridines 1-6 and their complexes in CHCl<sub>3</sub> (cm<sup>-1</sup>)

Aziridine	Band	Free	Pd-bound
1	N—H	3250	3185
	C=C	1645	1645
2	N—H	3290	3160
	C=C	1630	1625
3	N—H	3300	3130
	C=C	1650	1610
4	N—H	3300	
	C=C	1640	
5	N-H	3270	3200
	C=C	1640	1640
6	N—H	3280	3200
	C=C	1620	1625

NH groups of 1 in the molecule A and chlorine atoms of the other molecule **B**, as shown in Table 2 and Fig. 1. The N(A)  $\cdots$  Cl(B) and N(B)  $\cdots$  Cl(A) distances (3.36 Å) between two adjacent molecules indicate the existence of weak hydrogen bonding, ensuring the crystalline cohesion.

Figure 2 shows a perspective view of one molecule of complex 7 and clearly indicates that the aziridine ligands are bound to palladium in a monodentate mode, by their nitrogen atom and that they are located in *trans* position. This structure is very close of that observed by Hassner *et al.* [17] for a *trans*-PdCl<sub>2</sub>(2-

p-tolyl-azirine)<sub>2</sub>. Some selected distances and bond angles are gathered in Table 3.

The coordination polyhedron around palladium is roughly square planar, as proved by Cl—Pd—N angles ranging from 88.0(1) to 92.6(1)° and a mean value of N—Pd—N equal to 169.7° and of Cl—Pd—Cl to 176°. The mean Pd—Cl (2.305 Å) and Pd—N bonds (2.034 Å) fall in the range generally observed [18], 2.326(43) Å and 2.04(36) Å, respectively. The projection of the molecule clearly demonstrates that the absolute configuration of C(1) and C(14) atoms is (R\*,R\*).

The bond lengths inside the aziridine ring (C(1)-N = 1.498 Å; C(2)-N = 1.495 Å; C(1)-C(2) = 1.501 Å) are very similar to those observed in Rh(Az)(CO)Cl (C(1)-N = C(2)-N = 1.499 \text{ Å}; C(1)-C(2) = 1.498 \text{ Å}). In contrast, the C=C bond length of the allylic substituent (C(19)-C(20) = 1.256 Å) is shorter than in the rhodium complex in which the double bond is coordinated (1.388 Å), and close to the value generally found for a free C=C double bond (1.299 Å) [18].

The chemistry of such complexes has been detailed for the allylaziridine complex, with the main objective being to synthesize a complex in which both nitrogen atom and C=C double bond are bound to the palladium in a chelating or bridging mode. Such a  $\pi$ coordinated double bond might be activated and manifest enhanced reactivity. The reaction of only one equivalent of aziridine per PdL<sub>2</sub>Cl<sub>2</sub> [L<sub>2</sub> = cod, (PhCN)<sub>2</sub>] might give the expected Pd[ $\kappa^2$ -

 Table 2. Hydrogen bonds (Å) and angles (°) in complex 7: cis-dichlorobis(2,2-dimethyl-3-phenyl-3-allylaziridine)

 palladium(II)

$N(1A)\cdots C(1B)$	3 370(4)	$N(1B)\cdots C(1A)$	3.317(4)
N(1A) - H(N1A)	0.90(6)	N(1B) - H(N1B)	0.89(4)
$H(N1A)\cdots Cl(1B)$	2.49(5)	$H(N1B)\cdots Cl(1A)$	2.52(6)
$N(1A) - H(N1A) \cdots Cl(1B)$	165(6)	N(1B)— $H(N1B)$ ····Cl(1A)	149(5)
$N(2A) \cdots Cl(2B)$	3.421(4)	$N(2B) \cdots Cl(2A)$	3.327(4)
N(2A) - H(N2A)	0.89(5)	N(2B)—H(N2B)	0.89(6)
$H(N2A) \cdots Cl(2B)$	2.63(6)	$H(N2B)\cdots Cl(2A)$	2.44(5)
$N(2A) - H(N2A) \cdots Cl(2B)$	147(6)	N(2B)— $H(N2B)$ ····Cl(2A)	170(6)



Fig. 1. Perspective view of two molecules of complex 7 illustrating the intermolecular hydrogen bond interactions.



Fig. 2. ORTEP representation of molecule of complex 7.

N,C=C)Az]Cl<sub>2</sub> species, but actually gives only an equimolar mixture of the starting material and the disubstituted complex  $PdAz_2Cl_2$ . Another possibility lies in the methatetical exchange of chloro ligands of the pre-formed  $Pd(Az_2Cl_2)$  by non-coordinating

anions, like tetrafluoroborate or hexafluorophosphate by means of the silver or thallium salt, giving rise to a cationic complex **12** (Scheme 3).

A third way going through the preliminary formation of a cationic complex and further addition of

Table 3. Selected bond lengths (Å) and angles (°) in molecules A and B of complex 7

	Molecule A	Molecule B
Palladium environment		
Pd-Cl(1)	2.301(1)	2.302(2)
Pd—Cl(2)	2.303(1)	2.313(2)
Pd—N(1)	2.037(4)	2.039(4)
Pd—N(2)	2.028(4)	2.033(3)
Cl(1)—Pd—Cl(2)	169.19(4)	170.73(4)
Cl(1)—Pd—N(1)	88.6(1)	92.6(1)
Cl(1) - Pd - N(2)	88.0(1)	89.7(1)
Cl(2)PdN(1)	93.0(1)	88.1(1)
Cl(2)—Pd—N(2)	90.1(1)	89.0(1)
N(1)—Pd— $N(2)$	176.6(2)	175.5(2)
Ligand		
N(1) - C(1)	1.494(6)	1.502(6)
C(1) - C(2)	1.506(7)	1.497(8)
C(2) - N(1)	1.502(6)	1.487(7)
C(1)C(5)	1.524(7)	1.505(8)
C(1) - C(8)	1.505(8)	1.500(8)
C(5)-C(6)	1.474(9)	1.490(10)
C(6) - C(7)	1.269(11)	1.201(16)
C(14) - C(15)	1.508(6)	1.507(7)
C(15) - N(2)	1.499(6)	1.482(6)
C(14) - C(18)	1.521(7)	1.512(8)
C(14) - C(21)	1.494(7)	1.501(7)
C(18)—C(19)	1.507(9)	1.516(8)
C(19)—C(20)	1.263(12)	1.252(12)
Pd-N(1)-C(1)	127.0(3)	127.6(3)
Pd - N(1) - C(2)	132.2(3)	133.5(3)
C(1) - N(1) - C(2)	60.4(3)	60.1(3)
Pd-N(2)-C(14)	131.6(3)	134.0(3)
Pd-N(2)-C(15)	128.1(3)	129.1(3)
C(14) - N(2) - C(15)	60.4(3)	60.7(3)
N(1) - C(1) - C(2)	60.1(3)	59.4(3)
N(1) - C(2) - C(1)	59.5(3)	60.4(3)
C(1) - C(5) - C(6)	113.7(5)	114.0(5)
C(5) - C(6) - C(7)	126.2(8)	132.4(9)
N(2) - C(14) - C(15)	59.8(3)	59.1(3)
N(2) - C(15) - C(14)	59.7(3)	60.3(3)
C(14) - C(18) - C(19)	112.3(4)	112.5(5)
C(18) - C(19) - C(20)	125.8(7)	128.0(8)
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Estimated standard deviations in the least significant digit are given in parentheses.

aziridine does not work either. Finally, addition of triphenylphosphine on the  $Pd(Az)_2Cl_2$  species with various PPh<sub>3</sub>/Pd ratios only induces the substitution of the aziridine ligand by the phosphorus ligand without any formation of mixed complexes containing both types of ligand. Only Pd(PPh\_3)\_2Cl\_2 is detected in the reaction mixture beside the starting complex. This observation is in agreement with the fact that neither Pd(PPh\_3)\_4 nor Pd(PPh\_3)\_2Cl\_2 reacts with aziridine. Such behavior is very similar to that observed with cyclic aminophosphonite ligands, for which rhodium complexes always exhibit bidentate  $\kappa^2$ -P, N chelation, whereas palladium prefers the monodentate  $\kappa^1$ -P mode in most of the characterized complexes [2].

# **EXPERIMENTAL**

All manipulations were performed under argon atmosphere. All solvents were dried by standard methods and distilled before use. The starting allyl and vinylaziridines 1-4, palladium complexes PdCl<sub>2</sub>(PhCN)<sub>2</sub> and PdCl<sub>2</sub>(cod) were prepared according to literature methods [15,16].

Spectroscopic measurements were performed with the following equipment. IR: Perkin–Elmer 597 and FT-IR 1725 X (Nujol mull or film between KBr plates or in solution). NMR: Bruker AC 200 (<sup>1</sup>H, 200.13 MHz; <sup>13</sup>C, 50.32 MHz, TMS as external standard; <sup>31</sup>P, 81.01 MHz, H<sub>3</sub>PO<sub>4</sub> 85% in D<sub>2</sub>O as external/ internal standard, in a coaxial capillary tube).

Elemental analyses were obtained from the Service d'Analyse du Laboratoire de Chimie de Coordination du CNRS in Toulouse and the Service Central d'Analyse du CNRS in Solaize.

#### Syntheses of new aziridines 5 and 6

The cyclohexyl-2-spiro-3-phenyl-3-allyl aziridine **5** was prepared by the action of 30 mmol of magnesium allyl bromide in THF with 15 mmol of cyclohexyl-2-spiro-3-phenyl azirine according to the method described by the literature [15]. The crude was distilled *in vacuo* leading to **5** with 85% yield. Anal.  $C_{16}H_{21}N$ 



Scheme 3.

(277) Calc.: C, 84.54; H, 9.30; N, 6.16 Found: C, 84.95; H, 9.34; N, 5.93 NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H): 1.40– 2.10 (m, 11H); 2.29–2.95 (m, 2H); 4.83–4.92 (m, 2H); 5.55–5.71 (m, 1H); 7.2–7.9 (m, 5H Ph).

 $\delta$  (<sup>13</sup>C): 24.23 (t); 25.13 (t); 25.52 (t); 31.74 (t); 33.76 (t); 40.06 (t); 46.18 (s); 51.05 (s); 116.61 (t); 126.07 (d, Ph); 127.46 (d, Ph); 127.88 (d, Ph); 128.63 (d, Ph); 134.19 (d); 141.29 (s, Ph).

The cyclohexyl-2-spiro-3-phenyl-3-vinyl aziridine **6** was prepared in the same manner as **5** and purified by silica gel column chromatography using a mixture of 50% ether-50% petroleum ether as eluent and leading to 6H with 50% yield. NMR (CDCl<sub>3</sub>) :  $\delta$  (<sup>1</sup>H) : 1.01–1.70 (m, 11H) ; 4.94 (dd, 1H, J = 20 Hz, J' = 2 Hz) ; 5.15 (dd, 1H, J = 12 Hz, J' = 2 Hz) ; 6.16 (dd, 1H, J = 18 Hz, J' = 7 Hz) ; 7.2–7.4 (m, 5H Ph).

 $\delta$  (1<sup>3</sup>C): 24.37 (t); 25.42 (t); 25.66 (t); 31.83 (t); 33.24 (t); 48.45 (s); 53.11 (s); 116.55 (t); 126.52 (d, Ph); 127.90 (d, Ph); 128.42 (d, Ph); 138.89 (d); 139.79 (s, Ph).

# Syntheses of palladium complexes 7-11

The dichlorobis(2,2-dimethyl-3-phenyl-3-allylaziridine)<sub>2</sub>palladium(II) 7 was prepared by dropwise addition of a solution of 385 mg of aziridine 1 (2.06 mmol) in  $CH_2Cl_2$  (5 cm<sup>3</sup>) to a solution of 500 mg of PdCl<sub>2</sub>(PhCN)<sub>2</sub> (1.03 mmol)] in the same solvent (10 cm<sup>3</sup>). After stirring for 15 min and having removed 75% of the solvent in vacuo, the addition of  $5 \text{ cm}^3$  of petroleum ether caused the immediate precipitation of a yellow solid. The precipitate was filtered off, washed with petroleum ether and crystallised from a mixture of 50% ether and 50% petroleum ether leading to 540 mg (95% yield) of complex 7. The same complex 7 was also obtained from PdCl<sub>2</sub>(cod) : a solution of 419 mg of 1 (2.24 mmol)] in toluene (15 cm<sup>3</sup>) was added dropwise to a solution of 320 mg of PdCl<sub>2</sub>(cod) (1.12 mmol)] in the same solvent  $(5 \text{ cm}^3)$ . The colour turned yellow. After 4 h of stirring, the solution was evacuated to dryness and the crude was then dissolved in 5 cm<sup>3</sup> of hexane and maintained for a night in the freezer. A precipitate appeared which was filtered off, leading to 605 mg (97% yield) of 7. Anal. C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>PdCl<sub>2</sub> (551.30) Calc. : C, 56.59; H, 6.21; N, 5.1 Found : C, 56.88; H, 6.33; N, 5.9. NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H): 1.20 and 1.33 (s, 3H); 1.86 (s, 3H); 3.18 (m, 2H); 3.92 (s broad, NH); 4.75-5.16 (m, 2H); 5.5-6.06 (m, 1H); 7.1-7.6 (m, 5H Ph).

 $\delta$  (<sup>13</sup>C): 21.70 and 21.95 (q); 25.18 and 25.41 (q); 42.71 and 43.16 (t); 46.12 and 46.41 (s); 54.17 and 54.43 (s); 118.43 (t); 127.35 and 127.70 (d, Ph); 127.85 (d, Ph); 128.17 and 128.39 (d, Ph); 129.11 and 129.39 (d, Ph); 133.25 and 133.35 (d); 137.72 and 138.07 (s, Ph).

Complexes 8-11 were synthesized by the first method used for complex 7.

Dichlorobis(2,2-dimethyl-3-phenyl-3-vinylaziridine)<sub>2</sub> palladium(II), **8** (yield: 98%). Anal. C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>PdCl<sub>2</sub> (527.30) Calc.: C, 55.06; H, 5.77; N, 5.35; Cl, 13.55; Pd, 20.33 Found: C, 55.09; H, 6.03; N, 5.23; Cl, 13.87; Pd, 20.27. NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H): 1.25 and 1.33 (s, 3H); 1.84 and 1.86 (s, 3H); 4.06 and 4.39 (s broad, NH); 4.78 and 4.84 (2d, 1H, J = 16 Hz, J' = 17 Hz); 5.35 and 5.39 (2d, 1H, J = 10.3 Hz, J' = 10.5 Hz); 6.77 (dd, 1H,  $^{3}J = 18$  Hz,  $^{3}J' = 11$  Hz); 7.22–7.59 (m, 5H, Ph).

 $\delta$  (<sup>13</sup>C) : 23.29 (q) ; 25.27 and 25.35 (q) ; 47.96 and 48.08 (s) ; 55.24 and 55.34 (s) ; 118.85 and 119.08 (t) ; 127.64 (d, Ph) ; 127.70 and 127.88 (d, Ph) ; 129.68 (d, Ph) ; 129.94 (d, Ph) ; 135.93 and 136.18 (s, Ph) ; 138.92 and 139.20 (d).

Dichlorobis(2-methyl-3-phenyl-3-vinylaziridine)<sub>2</sub> palladium(II), **9** (yield: 55%). NMR (CDCl<sub>3</sub>):  $\delta$ (<sup>1</sup>H): 1.10 (d, 3H, J = 7 Hz); 1.67 (s, broad 1H, NH); 3.47 (q, 1H, J = 7 Hz); 4.97 (d, 1H, J = 17Hz); 5.5 (d, 1H, J = 11 Hz); 6.76 (dd, 1H, J = 17Hz, J' = 11 Hz); 7.3–7.9 (m, 5H, Ph).

 $\delta$  (<sup>13</sup>C) : 15.47 and 15.50 (q) ; 42.76 and 42.87 (d) ; 53.59 and 53.64 (s) ; 119.38 and 119.46 (t) ; 128.48 and 128.51 (d, Ph) ; 128.57 and 128.76 (d, Ph) ; 129.14 (d, Ph) ; 129.50 (d, Ph) ; 132.12 and 132.82 (d, Ph) ; 137.75 and 137.82 (s, Ph) ; 140.32 and 140.43 (d).

Dichlorobis(cyclohexyl-2-spiro-3-phenyl-3-allylazi ridine)<sub>2</sub>palladium(II), **10** (yield: 97%). Anal.  $C_{32}H_{42}$ N<sub>2</sub>PdCl<sub>2</sub> (632.0) Calc.: C, 60.81; H, 6.70; N, 4.43. Found: C, 60.83; H, 7.26; N, 4.41. NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H): 1.40–1.80 (m, 10H); 2.10–2.50 (m, 2H); 2.80–3.20 (1H, NH); 4.80–5.10 (m, 2H); 5.50– 6.01 (m, 1H); 7.20–7.30 (m, 5H Ph).

 $\delta$  (1<sup>3</sup>C): 24.37 and 24.45 (t); 25.21 and 25.58 (t); 29.41 and 29.55 (t); 33.65 and 34.50 (t); 39.40 and 39.80 (t); 42.46 and 42.91 (t); 51.38 and 51.66 (s); 56.42 and 56.82 (s); 118.14 and 118.25 (t); 126.62 and 126.88 (d, Ph); 127.30 and 127.42 (d, Ph); 127.81 (d, Ph); 128.11 and 128.28 (d, Ph); 133.35 and 133.79 (d); 137.68 and 138.01 (s, Ph).

Dichloro(cyclohexyl-2-spiro-3-phenyl-3-vinylaziridine)<sub>2</sub>palladium(II), **11** (yield: 95%). NMR (CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H): 0.70–2.20 (m, 10H); 2.30–2.60 (m, 1H); 4.90 (dd, 1H, J = 20 Hz, J' = 4 Hz); 5.35 (dd, 1H, J =14 Hz, J' = 2 Hz); 6.05–6.90 (m, 1H); 7.0–7.7 (m, 5H Ph).

 $\delta$  (<sup>13</sup>C): 21.39 and 21.41 (t); 24.07 and 24.31 (t); 29.57 and 29.60 (t); 34.32 and 34.56 (t); 36.92 (t); 41.66 (s); 53.25 (s); 119.52 and 120.08 (t); 127.67 and 127.76 (d, Ph); 127.93 and 128.15 (d, Ph); 128.34 (d, Ph); 128.59 (d, Ph); 132.01 and 132.6 (d, Ph); 136.79 and 136.87 (d); 139.01 (s, Ph)

# X-ray diffraction study of complex 7

Suitable monocrystals of 7 were grown by slow evaporation of a solution of 0.5 g of 7 in a THF 25/petroleum ether 75 mixture and contained 5% of THF:  $[C_{26}H_{34}N_2Cl_2Pd]$  5% THF. X-ray diffraction measurements are summarized in Table 4.

The treatment of intensity data uses the following

 Table 4. Crystal data, experimental details of the X-ray diffraction study

Crystal	Parameter	s at 2	20°C	from	a	least-squ	ares	fit	of	the
setting a	angles of 2	i refle	ection	is with	n 1	$2.1^{\circ} < \theta$	< 16	6°.6°		

Chem. Formula:	$C_{26.2}OH_{34.40}Cl_2N_2O_{0.05}Pd$
Fw = 555.46	$\lambda = 0.71073 \text{ \AA}$
Crystal habit	red parallelepiped
Crystal dimensions	$0.50 \times 0.45 \times 0.30$ mm
Crystal system	Monoclinic
Absences :	hkl, h+k+l = 2n+1, h0 1
	h, l = 2n + 1
Space Group : I2/a (No. 15)	a = 19.909(2) Å
b = 24.857(3) Å	c = 23.237(3) Å
	$\beta = 102.990(9)^{\circ}$
Z = 16	$V = 11205(2) \text{ Å}^3$
$\rho_{\rm calc} = 1.317 \ {\rm g.cm^{-3}}$	$\mu = 0.868 \text{ mm}^{-1}$
	F(000) = 4576

Measurement of intensity data

Instrument : Enraf-Nonius CAD4	Scan speed : 1.10-8.24°/min
Radiation: Mo-Ka	$(\lambda = 0.71073 \text{ Å})$ graphite monochromated
Max 2θ 47°	(h 0.21 k 0.27 l – 26.26)
Detector window	Height 4.0 nm
Standard	Intensity 3 refl. every 2 h
Width 4.0 mm	Orientation 3 refl. every 400 data refl.
Scan mode $\omega$ -2 $\theta$	Take-off angle $4.0^{\circ}$
Scan range $(0.80 + 0.35 \tan\theta)^{\circ}$	No. of refl. collected 7817

procedure: Reduction to  $F_{\rm O}^2$  and  $\sigma(F_{\rm O}^2)$ , corrections for backgrounds, attenuator and LP in the usual manner [19]. No significant standards variation  $(\pm 0.9\%)$ . Empirical absorption corrections [20]  $(T_{\rm min} = 0.9621, T_{\rm max} = 0.9998)$ . All measured reflections were unique and used. No. of observed data  $[F_{\rm O}^2 > 2\sigma(F_{\rm O}^2)]$ : 5818.

Structure solution and refinement use direct methods using SHELXS-86 [21]. Full-matrix leastsquares refinement using SHELXL-93 [22]. Two independent molecules in the asymmetric unit and one solvent molecule (i.e. THF, O atom in special position refined with an occupancy factor of 0.10 and 2 C atoms with an occupancy factor of 0.20). All non-H atoms anisotropic, except those of phenyl rings and of solvent molecule which were refined isotropically. H atoms bonded to C atoms were introduced in calculations in idealized geometry [d(C-H) = 0.97 Å]. H atoms bonded to N atoms were allowed to vary. All hydrogen thermal parameters were isotropic and kept fixed in final refinement cycles. Scattering factors were taken from 'International Tables for X-ray Crystallography' [23]. Refinement on  $F_{O}^{2}$  for all reflections (7817). Weighted R-factors wR and goodnesses of fit S are based on  $F_{O}^2$ , conventional R-factors R are based on  $F_0$ , with  $F_0$  set to zero for negative  $F_0^2$ . Last refinement cycle: wR(all) = 0.1009, R(all) = 0.0632,

wR(obs) = 0.0866, R(obs) = 0.0364 with 5818 obs.reflections >  $4\sigma(F_0)$ , 461 variable parameters,  $w = [\sigma^2(F_0^2) + (0.0457 P)^2 + 40.5368 P]^{-1}$  where  $P = (F_0^2 + 2F_0^2)/3$ , S(all) = 1.026, S(obs) = 1.031, max. shift/esd = 0.056, mean shift/esd = 0.002, max. and min. residual peaks of 0.502 and 0.519 e/Å<sup>3</sup>.

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