ELSEVIER

Journal of Organometallic Chemistry 522 (1996) 97–103

Journal of Organometallic Chemistry

A way to obtain cyclopalladation of unsubstituted 2-phenylimidazole derivatives

Félix Zamora [a,*,1], Santiago Luna [a], Pilar Amo-Ochoa [a], Luis Alfonso Martínez-Cruz [b], Angel Vegas [b]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[b] *Departamento de Cristalografía, Instituto Rocasolano-CSIC, Serrano 119, 28006 Madrid, Spain*

Received 23 November 1995; in revised form 21 December 1995

Abstract

This work shows the difficulties of obtaining cyclopalladated complexes with 2-phenylimidazole and 2-phenylbenzimidazole as ligands. The protection of the NH group in the heterocycle with an acetyl group allows the formation of several cyclopalladated complexes of both ligands. The X-ray structure of the dimeric acetate-bridge complex of *N*-acetyl-2-phenyl-benzimidazole is described. The subsequent displacement of the protective group affords a monomeric cyclopalladated complex of 2-phenylbenzimidazole, as well as a coordination complex of this ligand.

Keywords: Palladium; Cyclopalladation; Imidazoles

1. Introduction

The study of cyclometalation complexes containing at least three planar fused rings, with capacity to induce intercalation on DNA, have been a focus of our interest [1,2]. Thus, 2-phenylbenzimidazole and 2-phenylimidazole are suitable ligands to give four and three fused rings respectively. These ligands are also interesting because they have an NH group at position 1 of the imidazole ring which could induce DNA interaction by H-bonding [3].

We have observed that the presence of this NH group seems to be problematic for obtaining cyclometalated complexes by direct reaction between these ligands and palladium(II) reactives. Our previous results on cyclometalation of 2-phenylimidazoline [1], substituted benz-imidazole, -oxazole and -thiazole [2], as well as some work with *N*-alkylimidazole ligands [4,5], thiazole and oxazole derivatives [6] and some oxazolines [7] in which the pyrrolic nitrogen of the imidazole ring was blocked or substituted, induce us to think that the reactivity of the NH group could affect the usual cyclopalladation of these ligands. Therefore, the purpose was to obtain cyclopalladation of 2-phenylbenzimidazole and 2-phenylimidazole with the NH group free.

This work presents the results obtained by using an acetyl protective group in 2-phenylbenzimidazole and 2-phenylimidazole and the subsequent reactions as a means of obtaining cyclopalladation complexes with the NH group free.

2. Results and discussion

The reactions of $Pd(OAc)_2$ with 2-phenylbenzimidazole (1) and 2-phenylimidazole (2) were carried out under several time and temperature conditions in acetic acid, chloroform and toluene, always with identical results and the formation of two very insoluble solids. An NMR study of these solids was not possible owing to the low solubility (even in DMSO, DMF and DMA). Both MS FAB spectra do not give additional information. Their IR spectra show the corresponding stretching vibrations ca. 1570 and 1415 cm^{-1} of the acetate bridge group [8]. Although, these data suggest the possible cyclometalation of these ligands, they do not allow their full structural characterization.

* Corresponding author.
[1] Present address: Fachbereich Chemie (Anorganisch), Universität Dortmund, Otto Hahn Straße 6, D-44221 Dortmund, Germany.

PII S0022-328X(96)06148-7

As cyclopalladation of several imidazole derivatives ligands in which the NH group is substituted for *N*-alkyl or other isoelectronic atoms (such as O or S) are possible [1,2,4–7], we suggest blocking of the nitrogen as a first step to get the cyclopalladation of **1** and **2** ligands (with the N-blocked, **3** and **4** respectively), and in a second step the posterior displacement of this protective group to regenerate the NH group. The protective group has been selected taking into account the usual cyclopalladation conditions (solvents, temperature, ...) as well as the subsequent reaction in which the protective group should easily be removed from the cyclopalladate complex. In this way, acetyl and several silyl groups were selected. However, silyl groups [9] do not undergo reactions with ligands **1** and **2** under several conditions.

Fig. 1 shows the scheme of the cyclopalladation reactions carried out with **3**.

The reaction of the *N*-acetyl-2-phenylbenzimidazole ligand with $Pd(OAc)_2$ in acetic acid, under nitrogen, at 60 °C, afford the dimeric bridged-acetate orthopalladated complex **3a**. The IR spectrum of **3a**, shows two strong bands at 1569 cm^{-1} and 1415 cm^{-1} corresponding to the ν_{as}(COO) and ν_s(COO) stretching vibrations of the acetate bridge respectively [8]. Moreover, one strong band at 1746 cm^{-1} is indicative of the presence of the acetyl group. The ^{1}H NMR spectrum (Table 1) shows a singlet at 2.80 ppm corresponding to the methyl

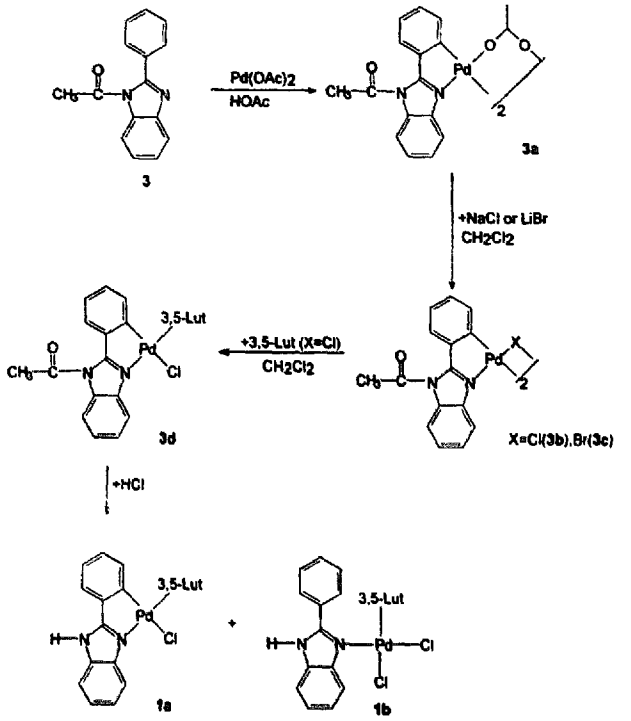
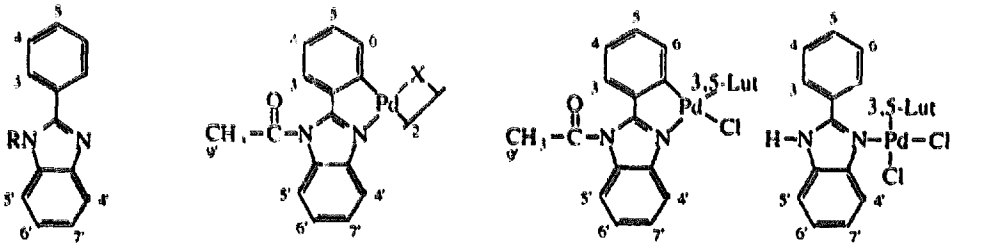


Fig. 1. Scheme of the synthetic routes used with ligand **3**.

group of the acetyl, as well as a sharp singlet at 2.32 ppm together with two weak singlets at 2.39 and 2.30 ppm corresponding to the methyl groups of the acetate

Table 1
^{1}H NMR parameters for **1**, **1a**, **1b**, **3**, **3a**, **3c** and **3d** (δ ppm)



	1 [a]	1a [a]	1b [a]	3 [a]	3 [b]	3a [a]	3c [b]	3d [a]
H3	7.27 m	7.44 m	8.75 m	7.66 m 2H	7.74 m 2H	7.15 dd (7.8, 1.4) 1H	7.52 dd (7.6, 1.6) 1H	7.43 m
H4	7.49 m	6.99 dt (7.8, 1.2) 1H	7.55 m	7.53 m	7.55 m	6.43 dt (7.8, 1.2) 1H	7.06 m	7.09 dt (7.7, 1.1) 1H
H5	7.49 m	6.85 dt (7.4, 1.4) 1H	7.55 m	7.53 m	7.55 m	6.13 dt (7.8, 1.4) 1H	7.06 m	6.97 dt (7.4, 1.5) 1H)
H6		6.05 dd (7.8, 1.2) 1H				6.53 dd (7.8, 1.2) 1H	7.86 m 1H	6.17 dd (7.7, 1.1) 1H
H4'	8.05 m 2H	9.17 m 1H	8.75 m	7.79 m 1H	8.10 m 1H	7.60 m 1H	8.05 dd (7.8, 1.2) 1H	9.15 m 1H
H5'	7.27 m 2H	7.44 m	7.40 m	7.41 m	7.40 m	7.23 m	7.43 m	7.43 m
H6'	7.27 m 2H	7.44 m	7.20 m	7.41 m	7.40 m	7.23 m	7.43 m	7.43 m
H7'	8.05 m 2H	7.67 m 1H	7.20 m	8.16 m 1H	8.17 m 1H	7.23 m	8.17 s.b 1H	7.63 m 1H
H8'	7.65 s.a 1H		10.04 s					
H9'				2.20 s 3H	2.23 s 3H	2.80 s 3H	2.96 s 3H	2.87 s 3H
H10'		8.63 s 2H	8.51 s 2H					8.63 s 2H
H11'		2.35 s 6H	2.32 s 6H			2.32 s 3H		2.35 s 6H
H12'		7.47 s 1H	7.40 m					7.47 s 1H

[a] $CDCl_3$; [b] DMSO-d_6; s-singlet; d-doublet; t-triplet; m-multiplet; b-broad; (J) in Hz.

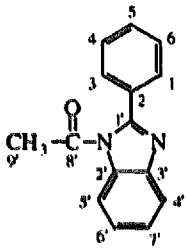
bridge. The resonances are ascribed [4,7] to the two geometrical isomers, anti and syn (the isomer ratio is 7:1). Crystallization of the mixture allowed the isolation of the anti isomer to be studied by X-ray diffraction (see below). However, the syn isomer could not be isolated. The downfield shifts of all protons, in comparison with the free ligand, are due to anisotropic effects produce by the 'open-book' configuration of the complex in which the cyclometalated ligands are nearly face-to-face [10].

The ^{13}C NMR spectrum (Table 2) shows the signals corresponding to the acetyl protective group at 26.9 (C9′) and 169.6 (C8′) ppm. Cyclopalladation is confirmed by a strong deshielding in the C1 atom, probably due to Pd–C back-bonding [11], as well as a significant shift to downfield in the signals corresponding to C1 and C2, attributed to orthopalladation.

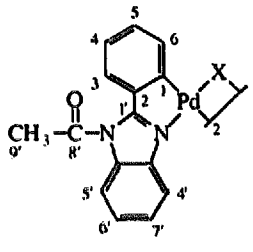
The MS FAB spectrum of **3a** shows peaks at m/z 802.0 and 743.0 assigned to $[M^+]$ and $[M^+ - OAc]$ ions respectively, when the distribution of palladium isotopes is taken into account.

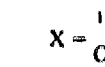
The reaction between **4** and $Pd(OAc)_2$ in HOAc under nitrogen, leads to the formation of a brown solid together with a yellow solution. The brown solid shows low solubility and a similar IR spectrum and elemental analysis to the solid obtained by reaction of **2** and $Pd(OAc)_2$. However, the yellow solution affords the dimeric bridged-acetate complex **4a**. The IR spectrum of **4a** shows two strong bands at 1572 and 1409 cm^{-1}, corresponding to $\nu(COO)$ of acetate, as well as a band at 1759 cm^{-1} of the acetyl group. The ^1H NMR spectrum of **4a** (Table 3) shows a singlet at 2.51 ppm corresponding to the methyl group of acetyl. The presence of only one singlet at 2.22 ppm for the acetate group indicates the formation of the anti isomer. The ^{13}C NMR spectrum (Table 2) shows peaks at 24.4 and 181.4 ppm corresponding to the acetyl protective group. The ^1H and ^{13}C NMR of **4a** undergo analogous effects to that described for **3a** as consequence of the cyclopalladation. Thus, these data suggest a typical 'open-book' disposition of complex **4**. The results obtained indicate

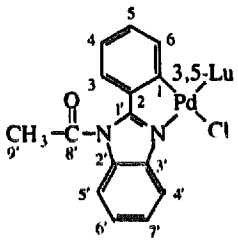
Table 2
^{13}C NMR parameters (δ, ppm)

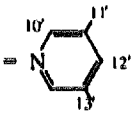


(3,4[a])



X =  (3a,4a[a]), Br(3c)



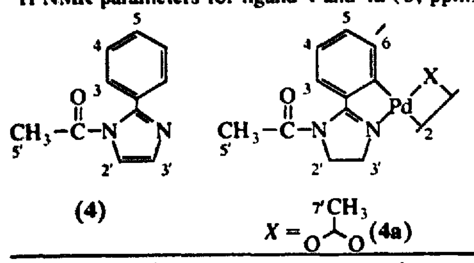
3,5-Lut = 
(3d)

[a] compounds without 5–7′ carbons

	3 [a]	4 [a]	3a [a]	3c [b]	3d [a]	4a [a]
C1	128.9	128.2	150.3	n.o.	153.1	149.2
C2	131.9	131.6	132.5	139.1	135.0	134.1
C3	128.9	128.2	125.2	125.2	125.5	125.4
C4	129.3	129.3	122.5	125.0	124.5	123.2
C5	130.5	129.6	127.7	129.5	130.0	128.1
C6	129.3	129.3	131.4	134.6	132.8	131.7
C1′	153.0	148.7	158.1	n.o.	159.4	154.5
C2′	133.9	118.8	130.3	131.4	132.3	116.2
C3′	142.4	129.1	139.4	n.o.	139.2	127.2
C4′	120.0		118.4	117.8	120.7	
C5′	125.5		124.7	123.0	126.1	
C6′	125.0		124.5	123.0	125.7	
C7′	115.2		112.2	112.2	111.9	
C8′	170.1	167.9	169.6	171.2	170.2	167.1
C9′	27.3	25.1	26.9	27.3	27.5	24.6
C10′			181.2		150.2	181.4
C11′			24.8		18.1	24.4
C12′					139.5	
C13′					135.5	

[a] $CDCl_3$; [b] DMSO-d_6.

Table 3
^1H NMR parameters for ligand 4 and 4a (δ, ppm)



	4	4a
H3	7.44 m 2H	7.81 m 1H
H4	7.53 m	6.90 m
H5	7.53 m	6.90 m
H6		7.05 m 1H
H2′	7.50 d (1.7) 1H	6.42 d (2.1) 1H
H3′	7.10 d (1.7) 1H	6.33 d (2.1) 3H
H5′	2.35 s 3H	2.51 s 3H
H7′		2.22 s 3H

$CDCl_3$, s-singlet; d-doublet; m-multiplet; b-broad; (J) in Hz.

that the reaction between 4 and $Pd(OAc)_2$ induces partial hydrolysis of the N–acetyl bond in HOAc; however, it is possible to isolate the acetate-bridged cyclopalladated complex **4a**. A low stability of the N–acetyl bond is also observed. Even in the presence of air the N–acetyl bond undergoes reaction to afford the insoluble solid. It was not possible to obtain suitable elemental analyses. The solid shows an IR spectrum analogous to that obtained by reaction of $Pd(OAc)_2$ and **2**. These results, together with the elemental analysis [12] obtained, lead us to think that this insoluble solid obtained by direct reaction could be the cyclopalladated complex of **2**. However, with the available data it is not possible to rule out the formation of a palladium adduct.

The hydrolysis reaction of **3a** with HCl 1 mol l^{-1} in CH_2Cl_2 as solvent [13] leads to the metathesis reaction of the acetate bridge affording the chloro-bridged orthopalladated complex **3b**. This complex is also obtained by reaction of **3a** with NaCl (see Experimental section). The IR spectrum of **3b** shows a strong band at 1749 cm^{-1} corresponding to ν(C=O) of the acetyl group, one band at 348 cm^{-1} assignable to ν_{as}(Pd–N), as well as two bands at 327 cm^{-1} and 280 cm^{-1} attributed to the stretching vibrations ν_{as}(Pd–Cl) trans to N and C [14] respectively. ^1H NMR of **3b** is not available owing to its low solubility. When the amount of HCl (ca. 5–10 mol l^{-1}) was increased to get the hydrolysis of **3a** and the suspension obtained was stirred several days, the IR spectrum showed that the intensity of the band at 1749 cm^{-1} decreased, probably due to a partial hydrolysis of the N–acetyl bond of **3a**. However, a complete hydrolysis of this bond was not possible even with a large amount of HCl under reflux, where only decomposition of the complex was observed.

The metathesis reaction of **3a** with LiBr afforded the dimeric μ-bromo complex **3c**. This complex is interesting because of the similar structural characteristics to the μ-chloro complex and usually higher solubility. Therefore, it is possible to get a full structural NMR characterization. The IR spectrum of **3c**, is similar to **3b**. The ^1H NMR spectrum (Table 1) shows a strong deshielding of the signal corresponding to H6 as a consequence of the delocalization in the chelating ring [15] or by the increase of C-substitution [16] observed in previous work [1,2]. The H4 proton undergoes an upfield shift, indicating some Pd–C back-bonding [17]. The H3 and H5 protons appear downfield, probably due to conformational changes after cyclometalation [18]. The ^{13}C NMR spectrum of **3c** (Table 2) shows similar shifts to that observed in the spectrum of complex **3a**.

The MS-FAB spectrum of **3c** shows peaks at m/z 842.8 and 762.9 assigned to [M^+] and [$M^+ -$ Br] ions respectively.

A possible explanation of the problems shown during the hydrolysis of the N–acetyl bond in **3a** could be the formation of the insoluble dimeric chloro **3b** complex. As an alternative, we have proposed the synthesis of a monomeric complex, which is usually more soluble than a dimeric complex and could allow the posterior hydrolysis in an homogeneous solution. Thus, monomeric complex **3d** was obtained from μ-chloro complex **3b** by reaction of this complex with 3,5-lutidine (3,5-Lut). The IR spectrum of **3d** shows a strong band at 1742 cm^{-1} corresponding to the ν(CO) of the acetyl protective group, together with a band at 273 cm^{-1} assignable to the ν_{as}(Pd–Cl) trans to the C atom [14]. The ^1H NMR shows a sharp singlet at 2.87 ppm corresponding to the methyl of the acetyl group. H3,4,5 undergo similar effects to that observed in the dimeric bromo complex **3c**. The signal corresponding to H6 shows an important deshielding due to anisotropic effects of the 3,5-Lut ligand. The ^{13}C NMR does not show significant differences with respect to what is observed for **3a**. The reaction of **3d** with HCl 1 mol l^{-1} in CH_2Cl_2 as solvent (at 20 °C, 48 h) afforded a yellow clear solution where, by ^1H NMR (Table 1), two different complexes and some starting complex **3d** were detected: (i) monomeric cyclometalated complex **1a**, in which the hydrolysis of the N–acetyl bond is observed (showing a new resonance at 11.5 ppm corresponding to the NH group), and (ii) a new coordination complex **1b**, with 3,5-Lut and **1** as ligands coordinated to Pd(II). The posterior precipitation from the mixture with hexane, or the chromatography with acetone as eluent, allows isolation of the complex **1b** by rupture of the Pd–C bond of **1a**.

The IR spectrum of **1b** shows a band at 336 cm^{-1} corresponding to the ν_{as}(Pd–Cl) of a trans isomer [19,20] and two bands at 364 and 354 cm^{-1} assignable to the ν_{as}(Pd–N) of both ligands [19–21].

The ^{1}H NMR of **1b**, shows a broad singlet at 10.04 ppm corresponding to the NH group. The signals of **1** and H9, H11 of the 3,5-Lut ligand show a significant deshielding, indicative of the coordination to Pd(II) atom [4]. Owing to the low solubility of **1b** it was not possible to obtain the ^{13}C NMR spectrum.

Since **1b** appeared to be a suitable complex to get the cyclometalated complex with the NH group [22], additional activation of the ortho C–H phenyl group is now being studied.

2.1. Crystal structure of 3a

As expected, the related compound is a dimeric form of the anti isomer corresponding to the molecular formula $Pd_2C_{34}H_{28}N_4O_6$. The molecule presents two Pd atoms, tetracoordianted by two oxygens of the acetate groups, and one C and one N in a square-planar environment. The least-square planes for the four atoms coordinating each Pd were calculated as shown in Table 4 [23]. Pd deviates significantly from these planes, which form an angle between them of 21.34°. The Pd–Pd distance is 2.837 (1) Å, indicating metal–metal intramolecular interactions [1,2,10,11,24]. The more significant bond lengths and angles are collected in Table 4. One molecule of solvent ($CHCl_3$) was found to cocrystallize with complex **3a**. The Cl atom is disordered, occupying two different positions with SOF = 0.5 in each case. One of the carbons of the acetyl group directly bonded to N21 is also disordered, and occupies positions C171 and C172 with SOF = 0.5. Fig. 2 shows an ORTEP diagram of complex **3a**.

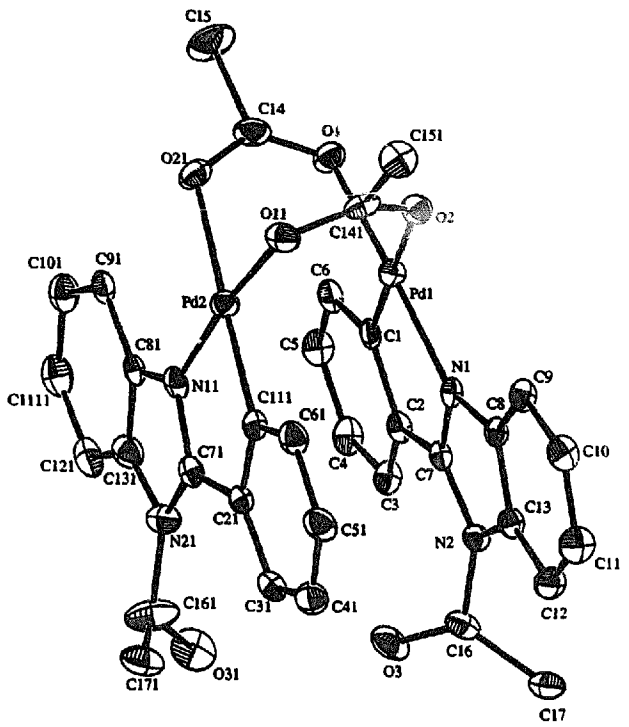


Fig. 2. The molecular structure of **3a** showing the atom numbering scheme.

Table 4
Selected bond distances Å and angles (deg) for **3a**

Distances			
Pd1–Pd2	2.837(1)	N21–C161	1.42(3)
Pd1–O1	2.04(1)	C161–O31	1.18(3)
Pd1–O2	2.140(9)	C161–C171	1.58(3)
Pd1–C1	1.91(1)	C2–C7	1.45(2)
Pd1–N1	2.00(1)	C21–C71	1.48(2)
Pd2–O11	2.012(9)	N1–C7	1.32(1)
Pd2–O21	2.16(1)	N1–C8	1.40(2)
Pd2–N11	1.96(1)	N2–C7	1.38(2)
Pd2–C111	1.98(1)	N2–C13	1.41(2)
N2–C16	1.43(2)	N11–C71	1.32(2)
C16–O3	1.20(2)	N11–C81	1.40(2)
C16–C17	1.51(3)	N21–C71	1.40(2)
C2–C7	1.45(2)	N21–C31	1.42(3)
C21–C71	1.48(2)		
Angles			
O1–Pd1–O2	88.9(4)	O21–Pd2–N11	98.4(4)
O1–Pd1–N1	172.9(4)	O21–Pd2–C111	177.8(5)
O1–Pd1–C1	92.7(5)	N11–Pd2–C111	80.4(5)
O2–Pd1–N1	98.1(5)	O1–C14–O21	128(2)
O2–Pd1–C1	178.3(5)	O11–C141–O2	126(1)
C1–Pd1–N1	80.3(5)	N21–C161–O31	122(2)
O11–Pd2–O21	88.3(4)	N21–C161–C171	109(2)
O11–Pd2–N11	173.2(5)	N2–C16–O3	119(2)
O11–Pd2–C111	92.9(5)	N2–C16–C17	116(1)

Weighted least-square planes. Equation of the plane: $m1X + m2Y + m3Z = d$.
Plane 1 (C1–O1–O2–N1): $m1 = -0.248(3)$; $m2 = -0.9681(8)$; $m3 = -0.033(4)$; $d = -0.97(3)$.
Plane 2 (C61–O21–O11–N11): $m1 = -0.515(3)$; $m2 = -0.816(2)$; $m3 = -0.263(3)$; $d = -0.97(3)$.

3. Experimental section

IR spectra were recorded on Perkin–Elmer 1650 spectrophotometer. The samples were ground with KBr at a concentration of 2 wt.% and pressed into pellets. For the region 600–200 cm^{-1}, the samples were prepared as polyethylene pellets. NMR spectra were recorded with $CDCl_3$ or DMSO-d_6 solutions by using a Bruker AMX-300. NMR spectra were assigned by chemical shift and assisted with ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) [25–27], ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) [28], and COSY when necessary. Elemental analyses were performed on a Perkin–Elmer 240B analyzer. MS spectra were carried out on a WG AutoSpec, on L-SIMS conditions, positive ions (3-nitrobenzyl alcohol as matrix).

Solvents were purified by the standard methods [29]. Palladium(II) acetate and chloride were purchased from Aldrich and Jonhson-Mathey respectively. 2-Phenylbe-

nzimidazole and 2-phenylimidazole were purchased from Aldrich.

3.1. Synthesis of N-acetyl-2-phenylbenzimidazole (3) and N-acetyl-2-phenylimidazole (4)

To a solution of 2-phenylbenzimidazole or 2-phenylimidazole (2 mmol) in 20 ml of $CHCl_3$ under N_2, acetyl chloride (6 mmol) and NEt_3 (8 mmol) at 0 °C, were added respectively. After stirring for 12 h at 20 °C, the residue was extracted with CH_2Cl_2:H_2O 100 ml (1:1), dried over anhydrous Na_2SO_4 and filtered off. Solvent was eliminated on a rotary evaporator and the oil crystallized in CH_2Cl_2:hexane (1:1) and dried in vacuo. Anal. for **3**. Found: C, 75.98; H, 5.05; N, 11.86. Calc.: C, 76.24; H, 5.13; N, 11.52%. M.p. 168–169 °C; yield 95.5%; IR in KBr: ν_{max} 1711 cm^{-1}. ^1H NMR in $CDCl_3$ (δ ppm): 2.20s, 7.41m, 7.53m, 7.66m, 7.79m, 8.16m. ^{13}C NMR in $CDCl_3$ (δ ppm): 27.3, 115.2, 120.0, 125.0, 125.5, 128.9, 129.3, 130.5, 131.9, 133.9, 153.0, 170.1. Anal. for **4**. Found: C, 83.84; H, 5.72; N, 9.57. Calc.: C, 84.48; H, 5.67; N, 9.85%. M.p. 135–136 °C; yield 71.1%; IR in KBr: ν_{max} 1740 cm^{-1}. ^1H NMR in $CDCl_3$ (δ ppm): 2.35s, 7.10d (J = 1.7), 7.44m, 7.50d (J = 1.7), 7.53m. ^{13}C NMR in $CDCl_3$ (δ ppm): 25.1, 118.8, 128.2, 129.1, 129.3, 129.6, 131.6, 148.7, 167.9.

3.2. Synthesis of [{Pd(3)(μ-OAc)}$_2$] (3a)

A mixture of equimolecular amounts of $Pd(OAc)_2$ and ligand in HOAc was heated at 40 °C, under N_2, for 18 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2:H_2O 100 ml (1:1), dried over anhydrous Na_2SO_4 and filtered off. The solvent was eliminated on a rotary evaporator and the residue recrystallized in CH_2Cl_2:hexane. Anal. Found: C, 49.44; H, 3.56; N, 6.78. Calc.: C, 50.95; H, 3.53; N, 6.99%. M.p. 208–216 °C (dec.); yield 60.1%; IR: ν_{max} 1746, 1565, 1415 cm^{-1}.

3.3. Synthesis of [{Pd(4)(μ-OAc)}$_2$] (4a)

To a solution of palladium(II) acetate (1 mmol) in 20 ml of glacial acetic acid under N_2, **2** (1 mmol) in 5 ml of glacial acetic acid was added. The solution was stirred at 40 °C for 45 min. The solution was extracted six times with CH_2Cl_2:H_2O 100 ml (1:1). The yellow organic solution was dried over anhydrous Na_2SO_4, filtered off and the solvent removed under vacuum. The residue was recrystallized in CH_2Cl_2–hexane. Yield 23.8%; IR: ν_{max} 1759, 1572, 1409 cm^{-1}.

3.4. Synthesis of [{Pd(3)(μ-Cl)}$_2$] (3b)

To a solution of **3a** (0.5 mmol) in 10 ml of CH_2Cl_2, a water solution of NaCl (excess) was added. The solid obtained after stirring for 24 h, at 20 °C, was filtered off, washed with water and acetone and dried in vacuo. Anal. Found: C, 47.69; H, 2.84; N, 7.21. Calc: C, 47.78; H, 2.95; N, 7.43%. M.p. 263–267 °C; yield 77.3%; IR: ν_{max} 1749, 348, 327, 280 cm^{-1}.

3.5. Synthesis of [{Pd(3)(μ-Br)}$_2$] (3c)

To a solution of **3a** (0.5 mmol) in 10 ml of CH_2Cl_2, a solution of LiBr (excess) in 1 ml of water, was added. After stirring 12 h at 20 °C, the precipitate obtained was filtered off, washed with water and acetone and dried in vacuo. Anal. Found: C, 42.26; H, 2.49; N, 6.26. Calc: C, 42.73; H, 2.63; N, 6.64%. M.p. 240 °C (dec.); yield 94.1%; IR: ν_{max} 1749, 342 cm^{-1}.

3.6. Synthesis of [Pd(3)Cl(Lut)] (3d)

To a solution of complex **3a** (0.5 mmol) in 10 ml of CH_2Cl_2 a water solution of NaCl (1.5 mmol) was added. After stirring 2 h at 20 °C a precipitate was formed. Then, 3,5-Lut (1 mmol) was added and the suspension obtained was stirred 1 h at 20 °C. To the clear solution obtained, hexane was added dropwise. The precipitate formed was filtered off, washed with water and dried in vacuo. Anal. Found: C, 54.02; H, 3.96; N, 8.50. Calc: C, 54.55; H, 4.17; N, 8.68%. M.p. 100–102 °C (dec.); yield 75.1%; IR: ν_{max} 1742, 273 cm^{-1}.

3.7. Crystal data for complex 3a

$Pd_2C_{34}H_{28}N_4O_6$. M_r = 851.906, triclinic ($P\bar{1}$), a = 13.671(2) Å, b = 12.180(2) Å, c = 12.029(1) Å, α = 82.638(0)°, β = 116.654(0)°, γ = 111.068(0)°, V = 1669.18(3) Å^3, Z = 2, D_{calc} = 1.6950 g cm^{-3}.

Data were collected from a yellow crystal (0.18 × 0.22 × 0.17 mm^3) on a PW-1100 diffractometer, using graphite monochromated Cu Kα radiation. A total of 5229 independent reflections were measured, 4984 of which were considered as observed after the criterion $I \geq 3\sigma(I)$. The structure was solved by heavy atoms methods, and refined with anisotropic parameters for all non-H atoms. The H atoms were geometrically calculated and fixed. Atomic scattering factors for neutral atoms and anomalous dispersion factors for Pd and Cl were taken from the International Tables for X-Ray Crystallography. A total of 451 parameters were varied by using unit weights. The final agreement was R = 0.084, Rw = 0.096. The absorption correction was carried out by using DIFABS [30]. The minimum and maximum absorption corrections were 0.735 and 1.558, (average value: 1.006). No extinction correction was applied. The maximum and minimum residual peaks in the final difference Fourier map were 0.2 e^- Å^{-3} and −0.7 e^- Å^{-3} respectively. The goodness of fit parame-

ter was 1.3754. The max. final shift/esd at the end of the refinement was 0.0500. All calculations were performed by using the XRAY80 [31] and DIRDIF [32].

4. Supplementary material available

Atomic coordinates, listings of anisotropic thermal parameters and tables of observed and calculated structure factors for complex **3a** (24 pages) are available.

Acknowledgements

We wish to thank Professor Dr. C. Navarro-Ranninger and Professor Dr. J.R. Masaguer for their help and useful discussion and Jonhson Mathey Chem-Ltd for their generous gift of $PdCl_2$. Also, thanks to Patrick Fowler for his kind english revision.

References and notes

[1] C. Navarro-Ranninger, F. Zamora, I. López-Solera, A. Monge and J.R. Masaguer, *J. Organomet. Chem.*, *506* (1996) 149.
[2] C. Navarro-Ranninger, F. Zamora, L.A. Martínez-Cruz, R. Isc and J.R. Masaguer, *J. Organomet. Chem*, in press.
[3] J. Reedijk, *Inorg. Chim. Acta*, *198–200* (1992) 873.
[4] K. Hiraki, Y. Fuchita, H. Nakaya and S. Takakura, *Bull. Chem. Soc. Jpn.*, *52* (9) (1979) 2531.
[5] A. Suárez, J.M. Vila, M.T. Pereira, E. Gayoso and M. Gayoso, *Synth. React. Inorg. Met. Org. Chem.*, *20* (10) (1990) 1425.
[6] M.R. Churchill, H.J. Wasserman and G. Young, *Inorg. Chem.*, *19* (1980) 762.
[7] G. Balavoine, J.C. Clinet, P. Zerbib and K Boubekeur, *J. Organomet. Chem.*, *389* (1990) 259.
[8] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, 4th edn., 1986.
[9] Silyl groups used: Cl-TIPS, Cl-TBDPS, Triflate-TBDMS and Triflate-TMS.
[10] J.L. García-Ruano, I. López-Solera, J.R. Masaguer, C. Navarro-Ranninger, J.H. Rodríguez ans S. Martínez-Carrera, *Organometallics*, *11* (1992) 3013.
[11] J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger and J.H. Rodríguez-Ramos, *J. Organomet. Chem.*, *476* (1994) 111.
[12] Anal. Found: C, 43.2; H, 3.4; N, 9.0. $C_{22}H_{20}N_4O_4Pd_2$. Calc.: C, 42.8; H, 3.3; N, 9.1%.
[13] Under similar conditions hydrolysis of the N-acetyl bond in **3** was observed.
[14] B. Crociani, T. Boshi, R. Pieetropaolo and U. Belluco, *J. Chem. Soc. A*, (1970) 531.
[15] S. Chakladar, P. Paul, K. Venkatsubramanian and K. Nag, *J. Chem. Soc. Dalton Trans.*, (1991) 2669.
[16] G.R. Newkome, K.J. Theriot, F.R. Fronczek and B. Villar, *Organometallics*, *8* (1989) 2513.
[17] M.A. Gutiérrez and G.R. Newkome, *J. Organomet. Chem.*, *202* (1980) 341.
[18] P.J. Steel and G.B. Caygill, *J. Organomet. Chem.*, *327* (1987) 101.
[19] C. Navarro-Ranninger and M. Gayoso, *An. Quim.*, *74* (1978) 717.
[20] C. Navarro-Ranninger and M. Gayoso, *An. Quim.*, *74* (1978) 722.
[21] D. Kovala-Demertzi and S.P. Perlepes, *Trans. Met. Chem.*, *19* (1994) 7.
[22] D.J. Cárdenas, A. Echavarren and A. Vegas, *Organometallics*, *13* (1994) 882.
[23] M. Nardelli, *Comput. Chem.*, *7* (1983) 95.
[24] (a) J. Vicente, M.T. Chicote, J. Martín, M. Artiago, X. Solans, M. Font-Altaba and M. Aguiló, *J. Chem. Soc. Dalton Trans.*, (1988) 141; (b) M.C. Etler and A.R. Siedle, *J. Am. Chem. Soc.*, *105* (1983) 641.
[25] A. Bax, R.H. Griffey and B.L. Hawhins, *J. Magn. Reson.*, *55* (1983) 301.
[26] M.F. Summers, L.G. Marzilli and A. Bax, *J. Am. Chem. Soc.*, *108* (1986) 4285.
[27] A. Bax and S. Subramanian, *J. Magn. Reson.*, *67* (1986) 565.
[28] A. Bax and M.F. Summers, *J. Am. Chem. Soc.*, *108* (1986) 2093.
[29] D.D. Perin, W.L.F. Armarego and D.R. Perin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 2nd edn., 1980.
[30] N. Walker and D. Stuart, DIFABS, *An empirical method for correcting diffractometer data for absorption effects*, Queen Mary College, London, 1983.
[31] J.M. Steewarts (ed.), The XRAY system of crystallographic programs (1980 version), *Technical Rep. TR-446*, 1978 (Computer Science Center, University of Maryland, College Park, MD, USA).
[32] P. Beurskens, W.P. Bosman, H.M. Doesburg, R.O. Gould, T.E.M. Van den Hark, P.A.J. Prick, J.H. Noordij, V. Parthasarati, H.J. Bruins-Slot, R.C. Haltiwanger and J.M.M. Smits, DIRDIF *System*, Crystallography Laboratory, Toernooivel, Nijmegen, Netherlands, 1984.