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SYNTHESIS OF PALLADIUM(II) DIIMINE COMPLEXES AND THE HYDROLYSIS OF α-DIIMINE LIGAND

(Sintesis Kompleks Diimina Palladium(II) dan Hidrolisis Ligan α-Diimina)

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Abstract

The reactions of dichlorobis(acetonitrile)palladium(II) precursors with 1,4-diaza-1,3-butadienes (α-diimine) give rise to the products (1,4-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene)dichloropalladium(II) (**2a)** and (1,4-bis(4-methylphenyl)-1,4-diaza-1,3-butadiene)dichloropalladium(II) (**2b**), as deduced from elemental analysis, FTIR, and UV-Vis. Both complexes are soluble in dimethylformamide and single crystals were collected for an X-ray crystallographic study. Based on the crystallographic data, complex **2a** is crystalized in a monoclinic system with $P2_1/c$ space group. The Pd-N bond lengths for Pd001-N004 and Pd001-N005 are 2.045(2) and 2.033(2) Å, respectively. Surprisingly, when complex **2b** dissolved in dimethylformamide, 4-methylaniline was produced from the hydrolysis of the α-diimine ligand **1b,** therefore *trans*-dichloridobis(4-methylaniline-κN)-palladium(II) (**2c**) was formed as confirmed, by crystallographic data. Complex **2c** is crystallized in a triclinic system with $P\ 2_1/b\ 2_1/c\ 2_1/a$ (Pbca) space group. The bond lengths of Pd-N are 2.050(3) Å and Pd-Cl is 2.318(8) Å. There are weak intermolecular N-H···Cl hydrogen bonds, that are responsible for the packing of the molecules in formation.

Keywords: 1,4-diaza-1,3-butadienes, palladium diimine complex, X-ray crystal, hydrolysis, hydrogen bonds

Abstrak

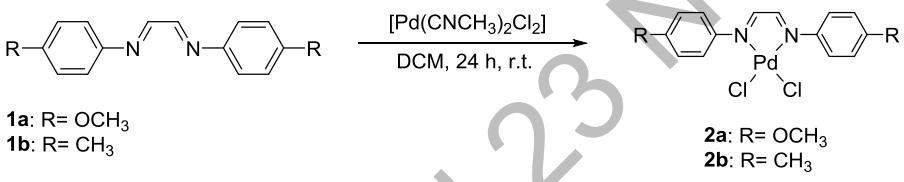
Tindak balas diklorobis(asetonitril)palladium(II) prakursor dengan 1,4-diaza-1,3-butadiena menghasilkan produk sebagai (1,4-bis(4-metoksifenil)-1,4-diaza-1,3-butadiena)dikloropalladium(II) atau 4-bis(4-metilfenil)-1,4-diaza-1,3-butadiena)dikloro palladium(II) yang disimpulkan daripada analisis unsur, FTIR, dan UV-Vis. Kedua-dua kompleks ini larut dalam dimetilformamida dan hablur tunggal telah dikumpulkan untuk kajian kristalografi sinar-X. Berdasarkan data kristalografi, kompleks **2a** menghablur dalam sistem monoklinik dengan kumpulan ruang P21/c. Panjang ikatan Pd-N ialah 2.045 (2) untuk Pd01-N004 dan 2.033 (2) Å untuk Pd01-N005. Walau bagaimanapun, apabila kompleks **2b** larut dalam dimetilformamida, 4-metilanilina telah dihasilkan dari hidrolisis ligan α-diimine **1b**, oleh itu, *trans*-dikloroidobis(4-metilanilina-κN)-palladium(II) **(2c**) telah terbentuk seperti yang dibuktikan oleh data hablur. Kompleks **2c** menghablur dalam sistem triklinik dengan kumpulan ruang P 21/b 21/c 21/a (Pbca). Panjang ikatan Pd-N ialah 2.050 (3) Å dan Pd-Cl ialah 2.318 (8) Å. Terdapat ikatan intermolekul yang lemah N-H···Cl yang bertanggungjawab untuk pemadatan molekul.

Kata kunci: 1,4-diaza-1,3-butadiena, kompleks diimina palladium, hablur sinar-X, hidrolisis, ikatan hidrogen

Introduction

The coordination chemistry of α-diimines, also known as 1,4-diaza-1,3-butadiene (R-DAB) compounds has been of substantial interest, over the past few decades due to the compounds displaying both flexibilities in their coordination mode to a metal centre, and their interesting electronic properties [1]. From the aspect of coordination chemistry, α-diimines are bidentate nitrogen donor ligands which have been widely used as ancillary ligands in metal complex formation, giving complexes with five-membered chelate rings [1, 2]. In addition, the double bond in the C=N bonds and the lone pair electrons on the nitrogen atoms allow the diimine molecule to act both as σ-donor and π-acceptor ligand in a coordination complex. Therefore, the versatility of this class of compounds has given rise to a number of applications in the fields of organic and organometallic synthesis and catalysis [3-7]. However, diimine compounds with an electron acceptor, are difficult to synthesize because of the insufficient basicity of amine attack to the carbonyl group to form imine bond. In addition, these types of compounds were often unstable and easily hydrolysed back to the amine. In this research, we observed that hydrolysis happened to palladium(II) diimine complexes, despite the diimine ligand being with an electron donor group substituent.

Hence, we report the synthesis of two palladium diimine complexes, through the reaction of R-DAB ligands with dichlorobis(acetonitrile)palladium(II), $[PdCl_2(CNMe)_2]$ precursors as shown in Scheme 1. Apart from showing the molecular structure of palladium diimine complex **2a**, the molecular structure of hydrolysed complex **2c** is also discussed in this paper.



Scheme 1. Synthesis of palladium diimine complexes

Materials and Methods

All of the synthetic reactions were conducted at room temperature. Palladium(II) chloride ($PdCl_2$) was purchased from Precious Metal Online, as the starting materials for the synthesis of $[PdCl_2(CNMe)_2]$ precursors. All chemicals used for the reaction were purchased from Fluka, Aldrich and Acros-organic. Unless otherwise stated, the chemicals and solvents were used without further purification. All NMR spectra were recorded on a JEOL 500 MHz FT-NMR spectrometer with appropriate deuterated solvent (DMSO-d_6: 2.50 ppm) and tetramethylsilane was used as the internal standard. The absorption spectra of the synthesized compounds were recorded on a Jasco V-630 Ultraviolet spectrophotometer in the range of 200–800 nm. Elemental analyses for carbon, hydrogen, nitrogen percentages in the synthesized compounds and complexes were carried out with Flashea 1112 Series CHN Elemental Analyzer.

Fourier-transform infrared spectroscopy (FT-IR) was recorded, in a KBr disc, using Thermo Scientific Nicolet iS10 Fourier-Transform Infrared Spectrophotometer, with the wavelength range from 400 to 4000 cm^{-1}. X-ray measurements for palladium(II) diimine complexes were performed on a Bruker D8 Venture diffractometer equipped with PHOTON II CPAD detector and IμS 3.0 Microfocus source of Cu Kα radiation source. The frame integration was performed using the program SAINT [8]. The structure was solved by a direct method provided by the program package SHELXTL-97 and refined a full matrix least square against F2 for all data [9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically.

Preparation of R-DAB compounds

The R-DAB compounds, 1,4-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene, **1a** and 1,4-bis(4-methylphenyl)-1,4-diaza-1,3-butadiene, **1b** were synthesized according to the procedure mentioned in previous paper [10].

Preparation of palladium complexes: Preparation of [1,4-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene] dichloropalladium(II) (2a)

$[PdCl_2(CNMe)_2]$ precursor (0.19 mmol, 0.050 g) was transferred to a conical flask followed by addition of compound **1a** (0.19 mmol, 0.052 g) and 20 mL of dichloromethane. The mixture was stirred at room temperature for 24 hours yielding the product as a red precipitate, isolated by filtration, washed several times with cold dichloromethane and dried *in vacuo*. X-ray quality crystal was grown by slow evaporation of a DMF solution. Yield: 0.075 g, 88%. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.46 (s, 2H, HC=N), 7.42 (d, 4H, J = 9 Hz, H_{Ar}), 7.00 (d, 4H, J = 9 Hz, H_{Ar}), 3.80 (s, 6H, OCH_3). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 159.3, 157.6, 142.5, 123.2, 114.6, 55.6. IR (KBr, cm^{-1}): 2986(w), 2929(w), 1601(s), 1499(s), 1303(m), 1252(s), 540(m). UV-VIS (CH_2Cl_2 λmax /nm): 271, 319, 467, 499 and 534 nm. Anal. Calcd for $C_{16}H_{16}O_2N_2PdCl_2$: C, 43.12; H, 3.62; N, 6.29; Found: C, 43.06; H, 3.82; N, 6.21%.

Preparation of [1,4-bis(4-methylphenyl)-1,4-diaza-1,3-butadiene]dichloropalladium(II) (2b)

A similar procedure to the synthesis of **2a** was adopted. Yellow solid was obtained by reacting $[PdCl_2(CNMe)_2]$ precursor (0.23 mmol, 0.060 g) with compound **1b** (0.23 mmol, 0.055 g). Yield: 0.088 g, 92%.^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.44 (s, 2H, HC=N), 7.30 (d, 4H, J = 8 Hz, H_{Ar}), 7.26 (d, 4H, J = 8 Hz, H_{Ar}), 2.34 (s, 6H, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 159.1, 147.2, 137.6, 129.9, 121.5, 20.7. IR (KBr, cm^{-1}): 3046(w), 2982(w), 1603(s), 1499(s), 1301(m), 530(m). UV-VIS (CH_2Cl_2 λmax /nm): 294, 371, 400 and 506 nm. Anal. Calcd for $C_{16}H_{16}N_2PdCl_2$: C, 46.46; H, 3.90; N, 6.77; Found: C, 46.16; H, 3.95; N, 6.72%.

Preparation of *trans*-dichloridobis(4-methylaniline-κN)-palladium(II) (2c)

Complex **2c** was obtained accidently from the recrystallization of complex **2b** *via* slow evaporation of DMF solution. The light orange crystal obtained was suitable for X-ray crystallography and discovered the formation of complex **2c**. In order to fully characterize complex **2c**, this complex was prepared accordingly to literature procedure [11] with slightly modification. $[PdCl_2(CNMe)_2]$ precursor (0.078 g, 0.30 mmol) was transferred to a conical flask followed by addition of 4-methylaniline (0.064 g, 0.60 mmol) and 15 mL of dichloromethane. The solution was stirred at room temperature and rapid formation of an orange yellow precipitate corresponding to **2c** was observed. The stirring was continued for 24 hours and then the orange yellow solid was isolated by filtration, washed with cold dichloromethane (3 × 2 mL) and dried *in vacuo*. X-ray quality crystal was grown by slow evaporation of a THF solution. Yield: 0.105 g, 89%. IR (KBr, cm^{-1}): 3281 (s), 3205 (s), 3120 (m), 3035 (w), 2915(w), 2859 (w), 1593(w), 1570 (m), 1511 (s), 1379 (w), 1217 (m), 1117 (s), 814 (s), 742 (m), 559 (w). Anal. Calcd for $C_{14}H_{18}Cl_2N_2Pd$: C, 42.94; H, 4.63; N, 7.15; Found: C, 42.82; H, 4.56; N, 7.12%.

Results and Discussion

The palladium precursor, $[PdCl_2(CNMe)_2]$ was synthesized according to the literature procedure for the corresponding benzonitrile complexes [12]. The synthesis of palladium complexes **2a** and **2b** was conducted by reacting R-DAB ligands with the precursor complex, in DCM for 24 h (Scheme 1). The palladium diimine complexes were fully characterized using spectroscopic techniques and the molecular structures were determined using X-ray diffraction analysis.

The palladium(II) diimine complexes **2a** and **2b** were stable at room temperature in solid state, without observing any significant changes after being left in the air for a long period of time. However, the complex is unstable in the solution state, especially in DMSO. When a small amount of complex **2a** was dissolved in deuterated DMSO, the colour of the sample changed from red to orange in a few minutes. It was suspected that complex **2a,** underwent dissociation in DMSO solution, whereby the Pd-N bond was broken and the diimine compound **1a** was reformed. This was observed when we attempted to perform the NMR analysis for complexes **2a** and **2b** in DMSO-d_6, whereby a residual precipitate of $PdCl_2$ was found at the bottom of NMR tube. Consequently, no chemical shift was observed in the NMR spectra of complexes **2a-2b** as compared to the free ligands. Meanwhile, the NMR spectrum of complex **2c** displays a mixture of complex **2c** and 4-methylaniline, which was then hydrolysed from the diimine ligand **1b**. This can be supported by a literature study, whereby the successful formation of complex **2c** can only be characterized by solid state NMR spectroscopy, that produced spectra showing hydrogen and carbon peaks compatible with the proposed structure [11]. Despite the NMR spectroscopy not providing ~~strong and~~ convincing

evidence for the formation of palladium complexes, the spectroscopic data from IR and UV have provided evidence for the changes, after the complexation reactions. In addition, further evidence for the successful formation of palladium diimine complexes was shown in the CHN analysis (Table 1) whereby the differences in percentages of carbon, hydrogen and nitrogen were less than ±0.4% indicating that the complexes **2a-2c** were pure.

Table 1. Analytical data for complexes **2a-2c**

Complex	Formula	Physical Appearance	Yield (%)	Observed (Calculated) C%	H%	N%
2a	$C_{16}H_{16}Cl_2N_2O_2Pd$	Red crystal	88	43.06 (43.12)	3.82 (3.62)	6.21 (6.29)
2b	$C_{16}H_{16}Cl_2N_2Pd$	Yellow solid	92	46.16 (46.46)	3.95 (3.90)	6.72 (6.77)
2c	$C_{14}H_{18}Cl_2N_2Pd$	Light orange crystal	89	42.82 (42.94)	4.56 (4.63)	7.12 (7.15)

Spectroscopy analysis of palladium complexes: FTIR analysis

The formation of the palladium diimine complexes **2a** and **2b** were supported by IR spectra as shown in Figures 1 and 2, respectively. In the IR spectra of the free R-DAB compounds, the C=N stretching vibration of imine group is located at 1607 cm^{-1} [10]. After complexation, the ν(C=N) stretching band was shifted to lower frequencies at 1600 cm^{-1} proving the presence of back bonding from the Pd metal centre to the π*orbitals of the diazadiene moiety. This shifting reveals the binding of imine nitrogen to the palladium metal centre was successfully formed. In addition, the ν(C-N) stretching vibration was also shifted to lower frequency at 1303 cm^{-1} which further support the participation of nitrogen atom in the complex formation. Besides, a new IR band is also observed at 540 cm^{-1} in the fingerprint region which is assigned to Pd-N bond [13].

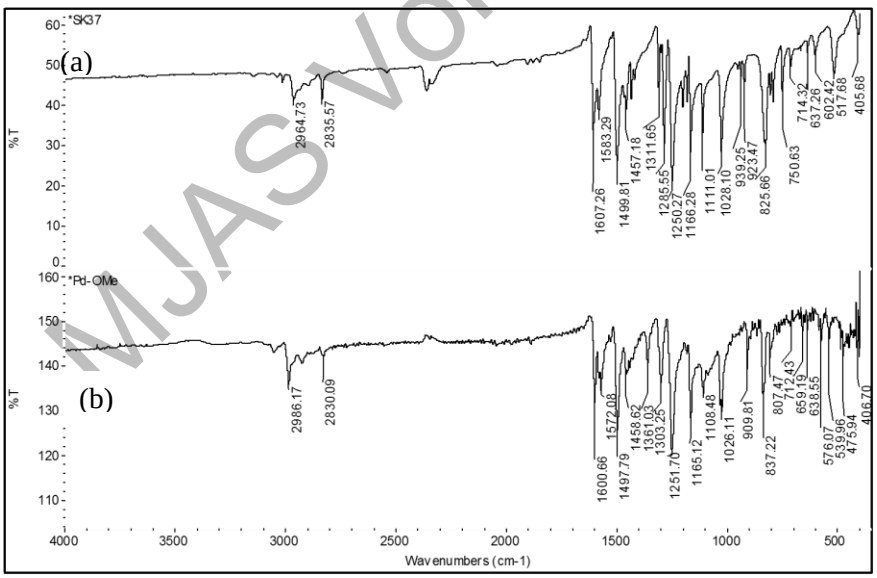


Figure 1. IR spectra of (a) R-DAB compound **1a** and (b) palladium diimine complex **2a**

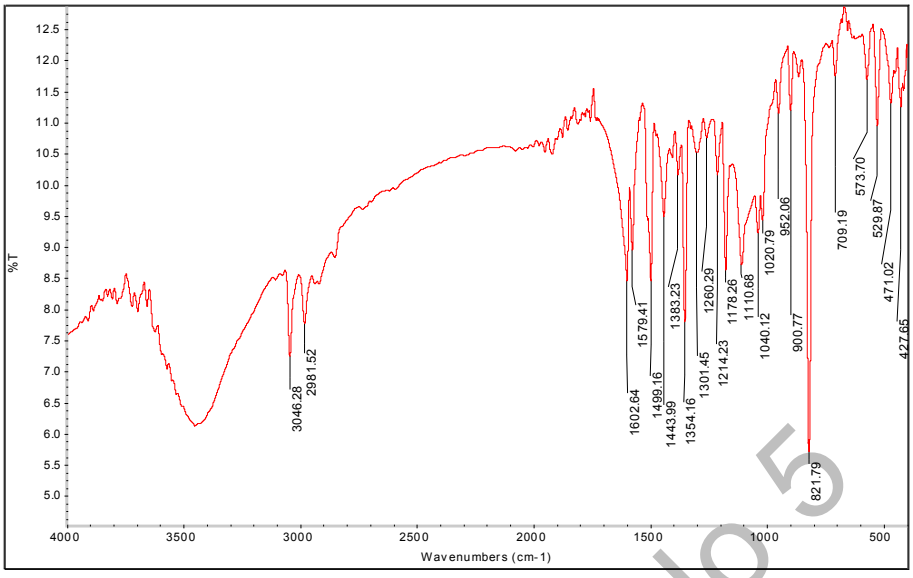


Figure 2. IR spectrum of palladium diimine complex **2b**

Based on the IR spectrum of complex **2c** (Figure 3), there is no sharp band observed in the range of 1630 cm^{-1} to 1600 cm^{-1} which corresponds to the -C=N- stretching vibration [14]. The absence of this signal proves that complex **2b** might undergo dissociation during recrystallization to form the diimine compound **1b**, and subsequently change the parent amine. The presence of amine can be indicated by the occurrence of two N-H absorption bands at 3280 cm^{-1} and 3204 cm^{-1}. Moreover, a new band was also observed at 559 cm^{-1} in the fingerprint region which is assigned to Pd-N bond [13].

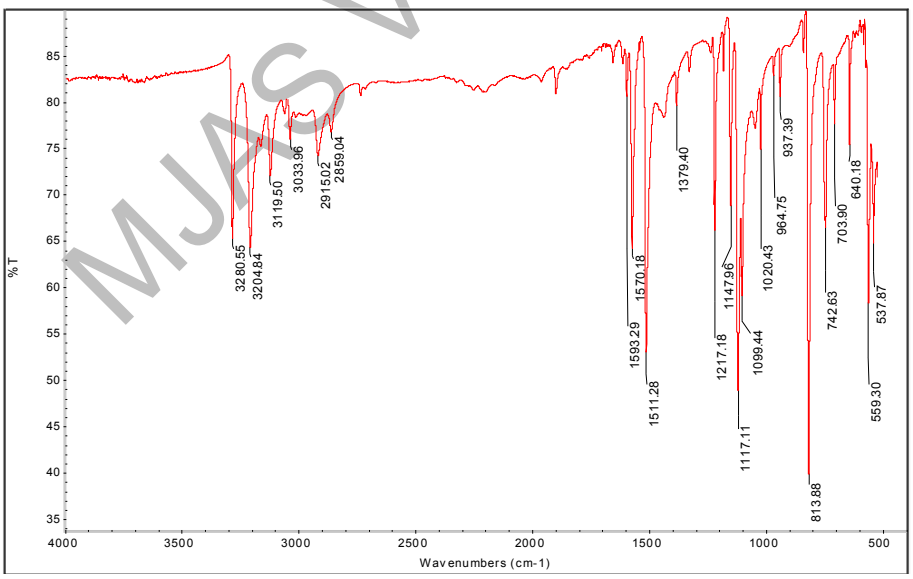


Figure 3. IR spectrum of complex **2c**

UV-Vis

The UV-Visible spectra of palladium(II) complexes **2a-2b**, were recorded in DCM solution at room temperature, at the wavelength of 240–800 nm. The important absorption peaks of compounds **1a-1b** and complexes **2a-2c** are

summarized in Table 2. In the UV-Visible spectrum of complex **2a** (Figure 4), five absorption peaks are observed at 271, 319, 467, 499 and 534 nm. The bands that appear at 271 nm are assigned to intra-ligand transition in the complex, indicating the π to π* transitions, due to the presence of benzene ring. In addition, the transition appeared at 319 nm, which is assigned to n to π* transition due to the presence of imine C=N bond [15]. In the visible region of the square planar palladium complexes, three spin-allowed d-d transitions were considered [16]. These transitions are corresponding to the transitions $^1A_{1g}\rightarrow{}^1A_{2g}$ at 467 nm, $^1A_{1g}\rightarrow{}^1B_{1g}$ at 499 nm and $^1A_{1g}\rightarrow 1E_g$ at 534 nm [17]. The UV-Visible spectrum of complex **2b** is similar to complex **2a**, except that there is lack of one band observed in the visible region due to the presence of very intense charge transfer band covering this band. Hence, only the band $^1A_{1g}\rightarrow{}^1B_{1g}$ at 400 nm, and $^1A_{1g}\rightarrow{}^1E_g$ at 506 nm are clearly observed.

Table 2. The UV-Vis data of compounds **1a-1b** and **2a-c**

Compounds	**Type of Transitions**				
	π→π*	**n→π***	***d-d***		
			$^1A_{1g}\rightarrow{}^1A_{2g}$	$^1A_{1g}\rightarrow{}^1B_{1g}$	$^1A_{1g}\rightarrow 1E_g$
1a	241, 294	373			
2a	217	319	467	499	534
1b	285	349			
2b	294	371		400	506

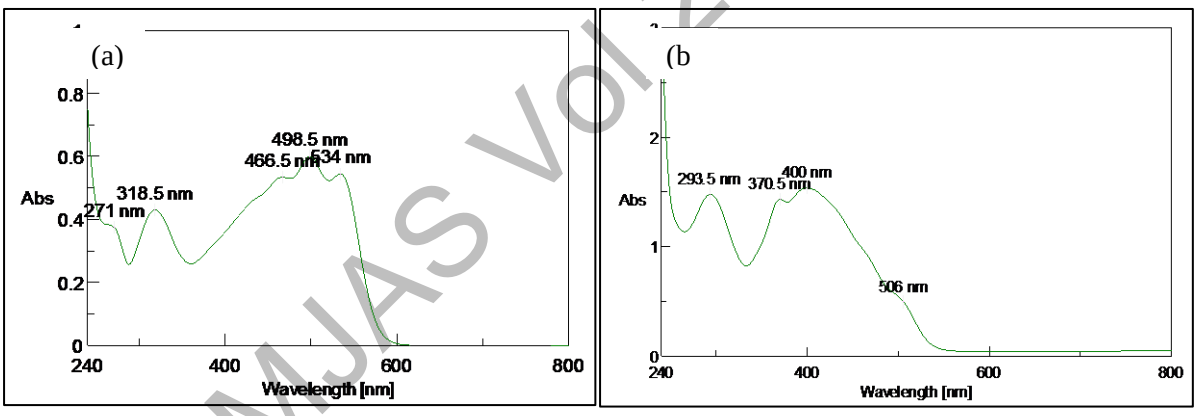


Figure 4. UV-visible spectra of (a) complex **2a** and (b) complex **2b**

Molecular structures of palladium complexes

Red crystal of complex **2a** and light orange crystal of complex **2c** were obtained, *via* slow evaporation of a DMF solution at ambient conditions. Both complexes have been structurally characterized by X-ray crystallography and the ORTEP diagram of both complexes, are shown in Figures 5 and 6. The main crystallographic parameters are tabulated in Table 3 and the selected bond lengths as well as bond angles are tabulated in Tables 4 and 5, respectively.

The X-ray crystallographic analysis of complex **2a**, reveals that the palladium metal centre coordinates with two azomethine nitrogen atoms of the DAB ligand in a *cis* configuration, forming a stable five-membered ring complex. Meanwhile, two chlorine atoms occupy the *trans* site of the azomethine nitrogen atoms. The Pd-N bond lengths are 2.045(2) and 2.033(2) Å, respectively, which is in the typical range for palladium α-diimine complexes [18]. The C00D-C00C bond length is 1.447(4) Å, which is slightly shorter than a standard C-C single bond length (1.54 Å) [19] due to the electron delocalization in the Pd five-membered ring. Complex **2a**, crystallized in a monoclinic

system with $P2_1/c$ space group. The bond angles of N004-Pd01-Cl02 and Cl03-Pd01-N005 were found to be 95.01(6)° and 94.27(6)° and revealed complex **2a** is in a distorted square planar geometry. The sum of internal angles of the chelating ring with the value of 539.31° indicates all of the five atoms of the chelating ring are in one plane [20].

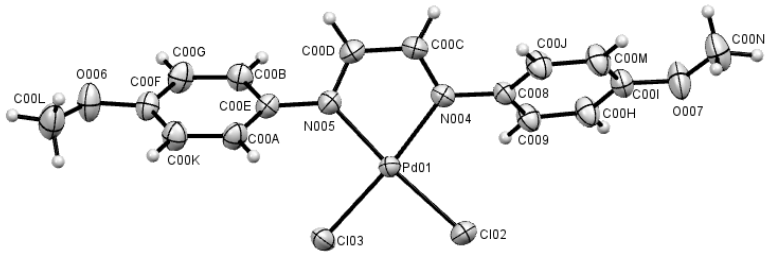


Figure 5. Molecular structure of complex **2a** with the thermal ellipsoids plotted at 50% probability

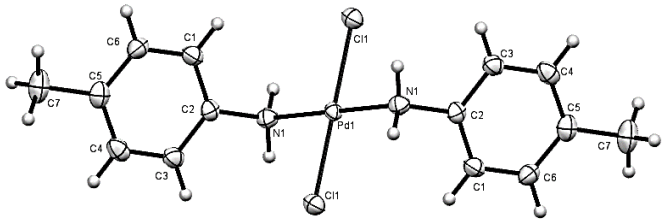


Figure 6. Molecular structure of complex **2c** with the thermal ellipsoids plotted at 50% probability

Table 3. Summary of crystal data and structure refinement parameters of complex **2a** and **2c**

Compound	**2a**	**2c**
Empirical formula	$C_{16}H_{16}Cl_2N_2O_2Pd$	$C_{14}H_{18}Cl_2N_2Pd$
Formula weight	445.61	391.60
Temperature (K)	298(2)	173(2)
Radiation, λ (Å)	Cu $_{K\alpha}$ 1.54178	Cu $_{K\alpha}$ 1.54184
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pbca
a (Å)	13.1291(3)	6.0261(10)
b (Å)	9.5829(2)	18.7585(4)
c (Å)	13.7811(3)	13.2455(3)
α (°)	90.00	90.00
β (°)	102.7720(10)	90.00
γ (°)	90.00	90.00
Volume (Å^3)	1690.97(6)	1497.28(5)
Z	4	4
ρc_{alcd} (g cm^{-3})	1.750	1.737
Absorption coefficient (mm^{-1})	11.847	13.170

Table 3 (cont'd). Summary of crystal data and structure refinement parameters of complex **2a** and **2c**

Compound	**2a**	**2c**
F(000)	888	784
Theta range for data collection (º)	3.29 to 72.44	5.740 to 76.069
Reflections collected	9901	4280
Independent reflections	3315	1343
Data / Restraints / Parameters	9901/ 0 / 210	4280 / 0 / 89
Goodness-of-fit on F^2	1.289	1.083
Final R indices [I>2σ(I)]	*R*1= 0.0207	*R*1 = 0.0402
	*wR*2= 0.0676	*wR*2 = 0.1103
R indices (all data)	*R*1= 0.0225	*R*1=0.0436
	*wR*2= 0.0699	*wR*2=0.1133
Maximum/minimum residual electron density (e $Å^{-3}$)	0.487/ -0.597	1.446/-0.855

Table 4. Selected bond lengths (Å) and angles (°) of complex **2a**

Bond Lengths (Å)		**Bond Angles (°)**	
Pd01-N004	2.045(2)	Cl03-Pd01-Cl02	90.58(2)
Pd01-N005	2.033(2)	N004-Pd01-Cl02	95.01(6)
Pd01-Cl02	2.2901(6)	N004-Pd01-Cl03	173.99(6)
Pd01-Cl03	2.2726(6)	N005-Pd01-Cl02	175.10(6)
C00C-C00D	1.447(4)	N005-Pd01-Cl03	94.27(6)
C00C-N004	1.283(3)	N005-Pd01-N004	80.18(8)
C00D-N005	1.288(3)		

Table 5. Selected bond lengths (Å) and angles (°) of complex **2c**

Bond Lengths (Å)		**Bond Angles (°)**	
Pd1-Cl1	2.318(8)	Cl1-Pd1-Cl1	180.0
Pd1-Cl1	2.318(8)	N1-Pd1-Cl1	88.64(9)
Pd1-N1	2.050(3)	N1-Pd1-Cl1	91.36(9)
Pd1-N1	2.050(3)	N1-Pd1-Cl1	88.64(9)
N1-C2	1.455(5)	N1-Pd1-Cl1	91.36(9)
		N1-Pd1-N1	180.0

Initially, we expected to obtain a similar structure of complexes **2a** and **2b** from the crystallographic analysis, but surprisingly, the complex **2b** was converted to **2c**, which is another structure, as shown in Figure 6 called *trans*-dichloridobis(4-methylaniline-κN)-palladium(II). This shows the imine (C=N) bond in complex **2b**, underwent hydrolysis and reformed the parent amine (R-NH_2) compound, when it was dissolved in DMF.

The X-ray crystallographic analysis of complex **2c** reveals a square planar geometry (Figure 5). The bond lengths of Pd1-N1 [2.050(3) Å] and Pd1-Cl1 [2.318(8) Å] are comparable with values found in [$PdCl_2(C_6H_5NH_2)_2$] [20]. The longer bond length of Pd-Cl than Pd-N bond indicates that the primary amine ($PhNH_2$) exerts stronger *trans*-effect, than the Cl atom due to its strong σ-donor nature. The crystal structure displays weak intermolecular N-H···Cl hydrogen bonding (Figure 7) [21].

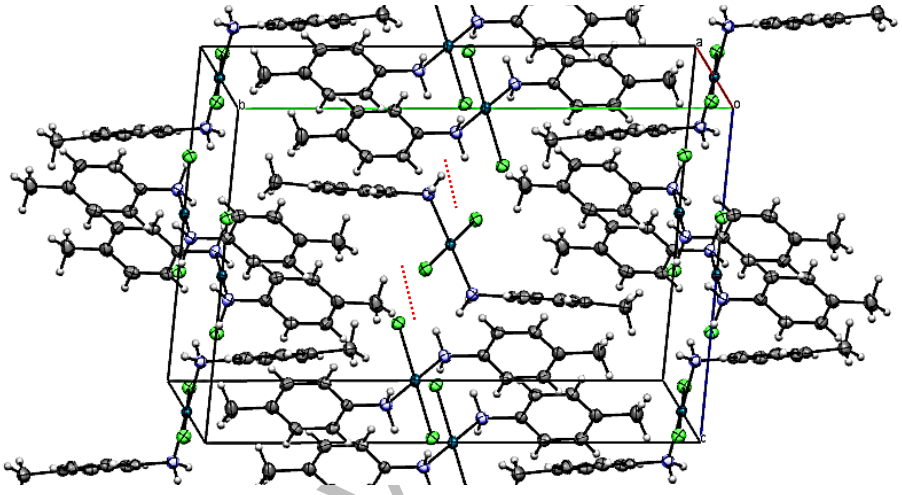
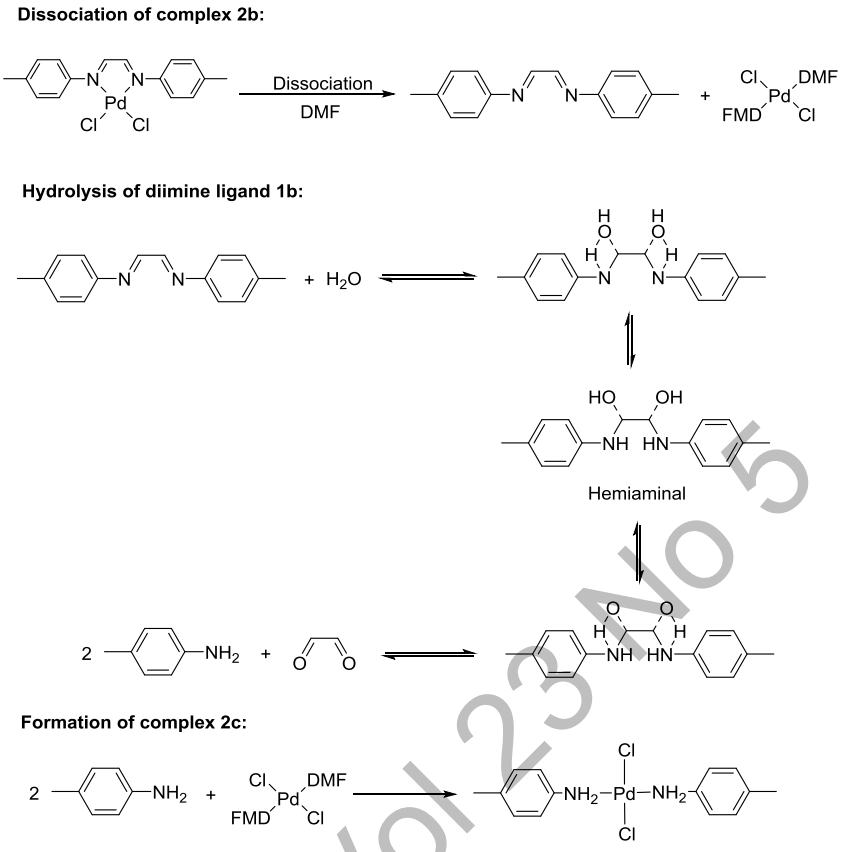


Figure 7. Crystal packing and view of the extensive hydrogen bonding (dashed lines) of complex **2c**

Mechanism of hydrolysis

A general mechanism is postulated (Scheme 2), to explain the formation of complex **2c** from **2b**. During the recrystallization of the palladium(II) diimine complex **2b**, the dissociation of ligand **1b** from the complex **2b** probably occurred, and subsequently led to the hydrolysis of diimine ligand **1b** to its starting materials, 4-methylaniline and glyoxal. In the subsequent step, the amino nitrogen atom of 4-methylaniline binds to the palladium metal to give a molecular complex **2c**. The mechanism for the hydrolysis reaction of diimine ligand **1b** involves three steps, namely: (i) formation of a hemiaminal intermediate; (ii) transferring the hydrogen atom bonded oxygen atom, to a nitrogen atom; and (iii) dissociation of the hemiaminal to give glyoxal and 4-methylaniline.



Scheme 2. Postulated mechanisms for the formation of complex **2c**

Conclusion

In conclusion, two palladium diimine complexes (**2a-2b**) using R-DAB ligands with $[PdCl_2(CNMe)_2]$ precursors were successfully synthesized. Complex **2b** was believed to be dissociated in DMF, to form diimine compound **1b** and subsequently hydrolysed to 4-methylaniline. The coordination of 4-methylaniline with $PdCl_2$ has led to the formation of *trans*-dichloridobis(4-methylaniline-κN)-palladium(II), **2c**. Both complexes were structurally characterized by X-ray crystallography.

Supplementary data

CCDC 1945836 and 1945837 contain the supplementary crystallographic data of complexes **2a** and **2c**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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