

SYNTHESIS AND STRUCTURE OF TWO PALLADIUM(II) COMPLEXES BEARING ACETONITRILE AND *N*-HETEROCYCLIC CARBENE DERIVED FROM IMIDAZOLE

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Abstract. The reaction of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (**1**) with either 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) or 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) in the presence of Ag_2O afforded two mixed monocarbene- CH_3CN complexes, namely *trans*- $[\text{PdCl}_2(\text{CH}_3\text{CN})(\text{IMes})]$ (**2**) and *trans*- $[\text{PdCl}_2(\text{CH}_3\text{CN})(\text{IPr})]$ (**3**), with the high yield (85-90 %). The structure of **2** and **3** were elucidated by ESI mass, IR, ^1H NMR and ^{13}C NMR spectra. For **2**, single-crystal X-ray diffraction study was also carried out. The results show that the CH_3CN in **2** and **3** coordinates with Pd(II) via the N atom, the deprotonated imidazolium salts are bound up with Pd(II) via the C atom (NCHN) and occupy *trans*-position in comparison with the CH_3CN .

Keywords: *N*-heterocyclic carbenes, Pd(II) complexes, acetonitrile, NMR spectra, single-crystal X-ray diffraction.

Classification numbers: 2.6.1, 2.10.2, 2.10.3.

1. INTRODUCTION

Since Arduengo *et al.* reported the first isolation of stable *N*-heterocyclic carbenes (NHCs), this kind of ligand has attracted a great interest and tremendous success has been achieved in carbene chemistry [1]. In particular, their transition-metal complexes have been the focus of intense research in organometallic chemistry, homogeneous catalysis and medicinal [1-7]. Example, palladium-carbene complexes derived from imidazolium precursors have been successfully developed as highly active precatalysts for C-C coupling reactions such as Mizoroki-Heck, Sonogashira and Suzuki-Miyaura couplings as well as C-H bond activation processes, etc. [1, 3-9].

Many nitrile complexes have been synthesized and found valuable applications [10], since nitrile ligand is a rather weak ligand that can be readily replaced by other ligands. Thus, they are also suitable as starting materials for synthesis of other complexes, inorganic materials, and catalysts [10, 11]. Recently, some palladium(II) complexes bearing acetonitrile and NHCs have been synthesized and studied via their structures as well as catalytic activities [2, 6, 7]. However,

the palladium(II) complexes bearing acetonitrile and N-heterocyclic carbene derived from imidazole have not been studied. In the present work, the synthesis, structure of two new palladium(II) complex bearing acetonitrile and either 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene were described.

2. MATERIALS AND METHODS

2.1. Synthesis of the compounds

1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) were synthesized according to the reference [12] with the following procedure:

A mixture of 1,4-diaryl-1,4-diaza-butadiene (10 mmol) and paraformaldehyde (315 mg, 10.5 mmol) was suspended in ethyl acetate (20 mL) and stirred at ambient temperature. A solution of chlorotrimethylsilane (1.3 mL, 10.5 mmol) in ethyl acetate (10 mL) was added dropwise over 20 min with vigorous stirring and the resulting yellow suspension was stirred for 2 h at 70 °C. After cooling to 10 °C, the suspension was filtered and washed with ethyl acetate (3 × 5 mL), then dried to constant weight at 100 °C, obtained the product as a white powder. This yielded: 70 % (2.83 g, 7 mmol) for IMes·HCl and 72 % (3.05 g; 7.2 mmol) for IPr·HCl.

2.1.1. Synthesis of $[PdCl_2(CH_3CN)_2]$ (**1**)

$PdCl_2$ (708 mg, 4 mmol) was stirred under reflux in the excess of CH_3CN (15 mL) for 1 hour. The resulting solution was filtered through Celite to give a clear solution. Then the solvent was removed under vacuum to give a crystalline solid, which was washed with diethyl ether (2 × 5 mL) then dried under vacuum for 2 h afforded the product as a yellow need. Yielded: 98 % (414 mg, 9.8 mmol).

2.1.2. Synthesis of $[PdCl_2(CH_3CN)(NHC)]$ (**2-3**)

A mixture of $[PdCl_2(CH_3CN)_2]$ (259 mg, 1.0 mmol), imidazolium chloride (1.0 mmol) and Ag_2O (140 mg, 0.6 mmol) were suspended in CH_3CN (5 mL), stirred and shielded from light at ambient temperature for 10 h. The reaction mixture was then filtered through Celite, and the residue was repeatedly washed with CH_3CN until the filtrate was colorless. The solvent of the filtrate was removed under vacuum to give a light yellow powder, which was subsequently washed with water (3 × 3 mL) and diethyl ether (1 × 5 mL). This yielded: 90 % (470 mg; 0.9 mmol) for *trans*- $[PdCl_2(CH_3CN)(IMes)]$ (**2**) and 85 % (514 mg; 0.85 mmol) for *trans*- $[PdCl_2(CH_3CN)(IPr)]$ (**3**).

Single crystals of **2** suitable for XRD determination were obtained by slow evaporation over 10 h from a concentrated acetonitrile solution at ambient temperature.

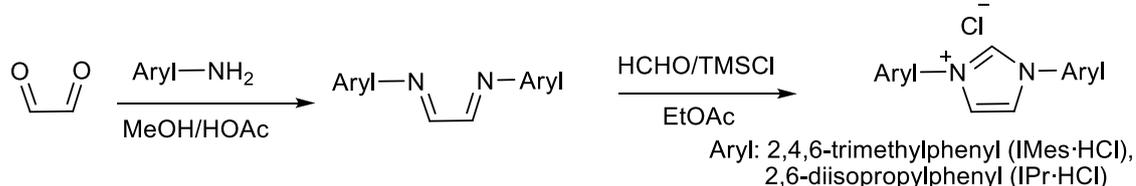
2.2. Equipment

Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (Merck, Kieselgel 60 F254). The studied compounds were visualized under UV-light at 254 nm. The EDX spectrum was recorded on a JED-2300 instrument at Institute of Materials Science, Vietnam Academy of Science and Technology (VAST). The ESI

mass spectra were recorded on a 1100 Series LC-MSD-Trap-SL; The IR spectra were recorded on IMPACK-410 NICOLET spectrometer in KBr discs in the range 400 - 4000 cm^{-1} ; The NMR spectra were recorded on Bruker AVANCE 500 MHz (all at 298-300 K with TMS as internal standard in suitable solvent) at Institute of Chemistry, VAST. Single crystal X-ray diffraction was carried out on a Bruker AXS SMART APEX diffractometer using graphite monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at Department of Chemistry, National University of Singapore.

3. RESULTS AND DISCUSSION

One of the most straightforward to prepare symmetrically N,N' -substituted imidazolium salts with various aryls is condensation of Schiff base with formaldehyde. The reaction undergoes two distinct steps: (1) in acidic environment the reaction proceeds through a coupling between the amine and the glyoxal to form the corresponding Schiff base; (2) condensation between the Schiff base and the formaldehyde leads to the imidazolium salt [13]. According to [12], this condensation can be done in the presence of hydrochloric acid, chloromethylethylether or chlorotrimethylsilane (TMSCl), however, using TMSCl for the highest efficiency.



Scheme 1. Reaction equation for preparation of imidazolium chloride.

In this research, we synthesized 1,4-bis-(2,4,6-trimethylphenyl)-1,4-diaza-butadiene and 1,4-bis-(2,6-diisopropylphenyl)-1,4-diaza-butadiene (DAD) from aniline derivatives and glyoxal, then condensed DAD with HCHO in the presence of TMSCl to form IMes·HCl and IPr·HCl. The general reaction equation is described in Scheme 1.

IMes·HCl and IPr·HCl are well soluble in halogenated solvents and alcohols as well as in CH_3CN , DMSO, water, and DMF. They are white powders which are air-stable and can be stored for a prolonged period without apparent decomposition. The downfield signals at 10.94 and 10.04 ppm for the NCHN protons of IMes·HCl and IPr·HCl (Table 1) indicate the formation of the imidazolium salts.

Table 1. ^1H signals of IMes·HCl and IPr·HCl, δ (ppm), J (Hz)^{a)}.

<p>IMes·HCl</p>	<p>NCHN: 10.94 s; H_{imy}: 7.58 s; Ar-H: 7.05 s; CH_3: 2.36/2.20 s</p>	<p>IPr·HCl</p>	<p>NCHN: 10.04 s; H_{imy}: 8.15 s; Ar-H: 7.57 t 3J 8, 7.34 d 3J 8; CH: 2.44 m; CH_3: 1.28/1.24 d 3J 6</p>
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a) solvent: CDCl_3

The interaction of IMes·HCl with PdCl_2 or $\text{Pd}(\text{OAc})_2$ in the presence of cesium carbonate at 80 °C in dioxane has been studied [14]. The result shows that the product is biscarbene complex,

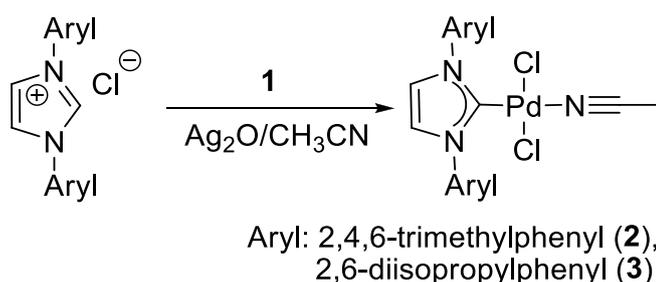
trans-[PdX₂(IMes)₂] (X: Cl or OAc), but not monocarbene. With expectation of monocarbene Pd(II) complexes product, we implemented the interaction of [PdCl₂(CH₃CN)₂] (**1**) with either IMes·HCl or IPr·HCl. Complex **1** was easily synthesized by the reaction between PdCl₂ and CH₃CN at 75 ÷ 80 °C with the high yield of 98 %.

The reactions of **1** with IMes·HCl/IPr·HCl were conducted by changing the reaction conditions such as temperature and reaction time. The solvent and base were fixed on CH₃CN, Ag₂O, respectively. As imidazolium salts are stable in the reaction conditions, the molar ratio of Pd^{II} : salt was fixed on 1 : 1, this also avoided the formation of dichloro-biscarbene complex, *trans*-[PdCl₂(NHC)₂]. The results of some selected experiments are summarized in Table 2.

The products *trans*-[PdCl₂(CH₃CN)(IMes)] (**2**) and *trans*-[PdCl₂(CH₃CN)(IPr)] (**3**) obtained after the filtration of AgCl precipitate and drying under vacuo are light yellow powders. In addition, the yield tends to decrease when the temperature increases from 25 ÷ 30 to 45 ÷ 50 °C (Table 2). This may be due to that at higher temperature Ag₂O is decomposed partially. The optimized reaction condition for synthesizing of **2** is N^o. 4 in Table 2 that was applied for producing complex **3** with the yield of 85 % (N^o. 7). The general reaction equation is described in Scheme 2.

Table 2. Experiments for the interaction between **1** and imidazolium salts.

N ^o .	Molar ratio of 1 : salt : Ag ₂ O	Time (h)	Temp. (°C)	Feature of the product	Product	Yield
1	1 : 1 : 0.5	2	25 ÷ 30	Light yellow powder	2	50 %
2	1 : 1 : 0.5	5	25 ÷ 30	Light yellow powder	2	65 %
3	1 : 1 : 0.6	8	25 ÷ 30	Light yellow powder	2	85 %
4	1 : 1 : 0.6	10	25 ÷ 30	Light yellow powder	2	90 %
5	1 : 1 : 0.6	12	25 ÷ 30	Light yellow powder	2	90 %
6	1 : 1 : 0.6	6	45 ÷ 50	Light yellow powder	2	40 %
7	1 : 1 : 0.6	10	25 ÷ 30	Light yellow powder	3	85 %



Scheme 2. Reaction equation for preparation of *trans*-[PdCl₂(CH₃CN)(NHC)] (**2**, **3**).

The purity of **2** and **3** was preliminarily examined by thin layer chromatography. The results showed that **2** and **3** had adequate purity for further characterization with spectroscopic methods.

Several physical properties of **1** - **3** are listed in Table 3. The data reveal that **2** and **3** have good solubility in chloroform, CH₃CN and DMSO, whereas **1** is only soluble in DMSO.

Table 3. Ions detected by ESI mass spectroscopy of **2**, **3** and solubility of **1** – **3**.

Comp.	+MS (<i>m/z</i> (au)/intensity)	Form	Color	Solubility in some solvents (30 °C)			
				acetone	CHCl ₃	CH ₃ CN	DMSO
1	-	Need	Yellow	insoluble	insoluble	insoluble	soluble
2	[M - Cl - CH ₃ CN + IMes] ⁺ : 751/25 [IMes + H] ⁺ : 305/100	Cubic	light-yellow	insoluble	soluble	soluble	soluble
3	[M - Cl - CH ₃ CN + IPr] ⁺ : 917/100 [IPr + H] ⁺ : 389/65	Cubic	light-yellow	insoluble	soluble	soluble	soluble

The composition of complex **1** was determined by EDX spectrum. The result shows that atomic ratio of Pd : Cl is 1 : 2.1, which is in good agreement with the theoretical value of 1:2.

The data in Table 3 show that pseudomolecular cations [**M** - Cl - CH₃CN + NHC]⁺, *i.e.* [PdCl(NHC)₂]⁺, and [NHC + H]⁺ with different relative intensity were detected in the both positive ESI mass spectra of **2** and **3**. Moreover, the isotopic envelopes of the assigned peaks are comparable to the calculated patterns. This indicates that complexes **2** and **3** have formula as expected, *i.e.* [PdCl₂(CH₃CN)(NHC)].

In the IR spectra of **1** - **3**, characteristic bands for the functional groups in the compounds can be observed clearly (Table 4). For instance, the presence of CH₃CN in **1** - **3** as well as of IMes in **2**, IPr in **3** is confirmed by strong bands for ν_{CH} aliphatic at approximately 2986 ÷ 2879 cm⁻¹. The weak band for ν_{CN} in **1** at 2203 cm⁻¹ decreases in comparison with that in free CH₃CN (*cf.* 2293 ÷ 2253 cm⁻¹) [8] showing that CH₃CN has coordinated with Pd(II) in **1**. The bands characteristic for ν_{CN} in **2** and **3** are beyond observation due to their too weak intensities. Unlike **1**, there are some absorption bands characteristic for aromatic ring of the NHC ligand in the IR spectra of **2** and **3**. This indicates that the deprotonated imidazolium salts have replaced one of the two acetonitrile ligands in **1** to coordinate with Pd(II) via the carbon atom of the NHCs.

Table 4. Main bands in the IR spectra of **1** - **3** (cm⁻¹).

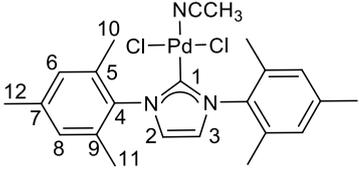
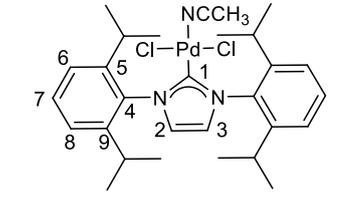
Complexes	ν _{CH} aromatic	ν _{CH} aliphatic	ν _{CN}	ν _{C=C} , ν _{C=N}	ν _{C-C}
[PdCl ₂ (CH ₃ CN) ₂] (1)	-	2984; 2927	2203	-	1410; 1350
<i>trans</i> -[PdCl ₂ (CH ₃ CN)(IMes)] (2)	3090	2981; 2888	-	1553; 1470	1417; 1313
<i>trans</i> -[PdCl ₂ (CH ₃ CN)(IPr)] (3)	3095	2986; 2879	-	1555; 1470	1385; 1312

To clarify the coordination of the ligands in **2** and **3**, we measured their ¹H and ¹³C NMR spectra in CD₃CN. The proton and carbon signals are assigned based on their chemical shift (δ), intensity, shape, spin-spin splitting pattern. The result is listed in Table 5.

Table 5 shows the resonances for all protons and carbons of the CH₃CN and NHC in **2** and **3**. The absence of the NCHN proton of IMes·HCl and IPr·HCl in the ¹H NMR spectra of **2** and **3** suggests the successful formation of the metal NHC moieties. Besides, all chemical shift of

protons and carbons of the CH₃CN in **2** and **3** changed unconsiderably in comparison with the CH₃CN free, this indicates the weak bond of the CH₃CN with Pd(II). This also makes the resonance of the C_{carbene} in **2** and **3** (C1: 139.5-138.5 ppm) shifts upfield in comparison to that in the series of complexes *trans*-[PdX₂(NHC)₂] (152-176 ppm) with NHC derived from imidazole [5, 14].

Table 5. ¹H and ¹³C NMR signals of **2** and **3**, δ (ppm), J (Hz).

	¹ H NMR: H2/H3: 7.27 s; H6/H8: 7.12 s; H12: 2.42 s; H10/H11: 2.27 s, CH ₃ CN: 1.97 overlap with the solvent ¹³ C NMR: C1: 139.5; C2/C3: 136.5; C4: 135.1; C6/C8: 129; C10/C11: 18.2; C12: 20.2; C5/C9: 128.6; C7: 125.0; CH ₃ CN: 117.8; CH ₃ CN: 1.3
	¹ H NMR: H2/H3: 7.93 s; H6/H8: 7.70 t ³ J 8; H7: 7.52 d ³ J 8; CH: 2.46 m, CH ₃ : 1.31/1.24, d ³ J 6 Hz; CH ₃ CN: 1.97 overlap with the solvent ¹³ C NMR: C1: 138.5; C2/C3: 146.0; C4: 132.8; C5/C9: 130.4; C6/C8: 125.4; C7: 132.8; CH: 29.5; CH ₃ : 24.1/23.5; CH ₃ CN: 117.9; CH ₃ CN: 1.3

In order to confirm the configuration of **2** and **3**, concretely to determine the position of acetonitrile and NHC in the coordination sphere of Pd(II), single crystal X-ray diffraction is still the most effective method. After numerous efforts, we have just obtained suitable single crystals of **2** for XRD measurements. The molecular structure of **2**, depicted in Figure 1, shows the expected square planar arrangement with two Cl atoms, the carbon of IMes ligand and the N atom of the acetonitrile ligand coordinate to the Pd^{II} atom. The IMes ligand occupies *trans*-position in comparison with the CH₃CN. Although it was not possible to obtain good quality crystals for **3**, its *trans* configuration is persuaded by following evidences: the two Aryl groups of IPr presenting in the ¹H NMR spectrum of **3** are equivalent; the structure of **3** is similar to that of **2** and some other complexes, [PtBr₂(CH₃CN)(NHC)] [5, 7], which were elucidated *trans* configuration by XRD method.

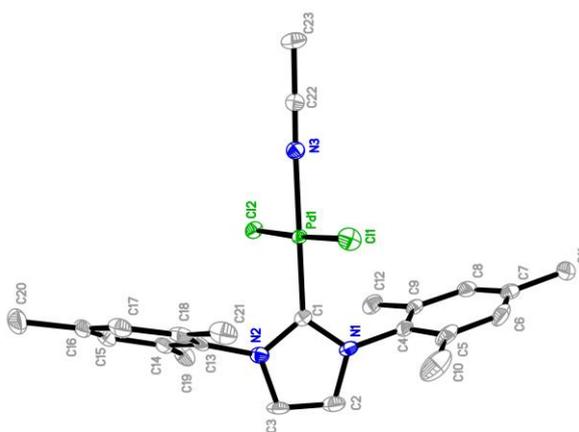


Figure 1. Molecular structure of the complex *trans*-[PdCl₂(CH₃CN)(IMes)] (**2**) with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity.

Table 6. Selected crystallographic data of **2**.

Empirical formula	C ₂₃ H ₂₇ Cl ₂ N ₃ Pd
Formula weight	522.77
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
a = 8.274(2) Å	90.00(3)°
b = 28.107(6) Å	100.33(3)°
c = 19.975(4) Å	90.00(3)°
Volume	4570.1(18) Å ³
Z	8
Density (calculated)	1.520 Mg/m ³
Absorption coefficient	1.060 mm ⁻¹
Crystal size	0.26 × 0.24 × 0.15 mm ³
Reflections collected	62269
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0620

Some selected crystallographic data, bond lengths and angles of **2** are shown in Table 6, 7. The Pd1–C1 (1.948(4) Å) and Pd1–N3 (2.050(2) Å) bond lengths are comparable to the corresponding bond parameters of analogue *trans*-[PdBr₂(CH₃CN)(Pr₂-bimy)] [6].

Table 7. Selected bond lengths [Å] and angles [°] of **2**.

Bond	[Å]
Pd(1)-C(1)	1.948(3)
Pd(1)-N(3)	2.050(2)
Pd(1)-Cl(1)	2.2861(11)
Pd(1)-Cl(2)	2.2934(11)
Angle	[°]
C(1)-Pd(1)-N(3)	179.50(10)
C(1)-Pd(1)-Cl(1)	92.14(8)
N(3)-Pd(1)-Cl(1)	88.29(7)
C(1)-Pd(1)-Cl(2)	90.60(8)
N(3)-Pd(1)-Cl(2)	88.97(7)
Cl(1)-Pd(1)-Cl(2)	177.26(3)
C(2)-N(1)-C(1)-Pd(1)	-176.8(2)
C(4)-N(1)-C(1)-Pd(1)	0.5(4)

The C1-Pd1-N3 angle (179.5(4)) in **2** is bigger than that in the analogue (175.35(18)). In addition, the two chloro ligands *cis* to the NHC lie almost perpendicular to the NHC plane and are bent toward CH₃CN ligand (N3-Pd1-Cl1 88.29(7)° and N3-Pd1-Cl2 88.97(7)°) rather than toward the NHC ligand. This is different from the observation in the analogue complexes [5, 7].

4. CONCLUSION

The interaction of [PdCl₂(CH₃CN)₂] (**1**) with either 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) or 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) in the presence of base Ag₂O has been studied. The result showed that the deprotonated imidazolium salts easily replaces one of the two CH₃CN molecules in **1** to form two new complexes *trans*-[PdCl₂(CH₃CN)(IMes)] (**2**) and *trans*-[PdCl₂(CH₃CN)(IPr)] (**3**) with very high yields (85-90 %). The structure of **2** and **3** were elucidated by ESI mass, IR, ¹H NMR, ¹³C NMR spectra and single-crystal X-ray diffraction. Complexes **2** and **3** possess *trans* configuration, in which the deprotonated imidazolium salts coordinate with Pd(II) via the carbon atom of the NHCs and the CH₃CN coordinates with Pd(II) via the N atom. Complexes **2** and **3** will be favorable precursors to synthesize other Pd(II) complexes bearing NHC. And attempts will be made to explore potential applications of such complexes.

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