



## The influence of moisture on deprotonation mode of imidazolinium chlorides with palladacycle acetate dimer

M. Emin Günay<sup>a,\*</sup>, Namık Özdemir<sup>b</sup>, Mahmut Ulusoy<sup>c</sup>, Melih Uçak<sup>a</sup>, Muharrem Dinçer<sup>b</sup>, Bekir Çetinkaya<sup>c</sup>

<sup>a</sup> Department of Chemistry, Adnan Menderes University, 09010 Aydın, Turkey

<sup>b</sup> Department of Physics, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey

<sup>c</sup> Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey

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### ABSTRACT

Deprotonation of 1,3-diorganyl imidazolinium salts, **1**, with N,C-type palladacyclic acetate dimer **2** afforded novel NHC coordinated complexes **3** along with ring opening hydrolysis products **4**, which may coordinate to palladium center via NH group to give **5a**. The hydrolysis necessitates the study of NHC complex formation in anhydrous media. The new compounds were characterized by spectroscopic methods and three of them (**3c**, **4c**, **5a**) by X-ray single-crystal diffraction studies.

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## 1. Introduction

Although the majority of palladacycles reported to date contain phosphines as ancillary ligands to stabilize the palladium center [1–5], the price associated with alkyl phosphines, along with phosphine ligand decomposition byproduct removal difficulties, have led to the use of N-heterocyclic carbenes (NHCs) as a versatile ligand alternative. A number of palladacycles bearing unsaturated NHCs have been found to be efficient catalysts for a variety of C–C coupling reactions [6–9]. However, the studies on palladacycles with saturated NHC ligands are limited [10].

In view of the above information and as part of our long-running project towards saturated NHCs [11–14], we focused our attention on C,N-type cyclopalladated NHCs with 4-dimethylaminobenzyl substituted complexes. We thought it should be interesting to determine the effect produced by NMe<sub>2</sub> substituents, which attached to *p*-position of N-benzyl group has shown a strong influence, despite the isolated methylene groups between Pd and phenyl ring [15]. In this study we sought to synthesize more  $\sigma$ -donating NHC complexes of palladium(II) via direct interaction of imidazolinium salts (**1**) with N,C-type palladacyclic acetate (**2**) and discovered that hydrolysis of the ligand to afford N-formyl compounds is facile.

## 2. Results and discussion

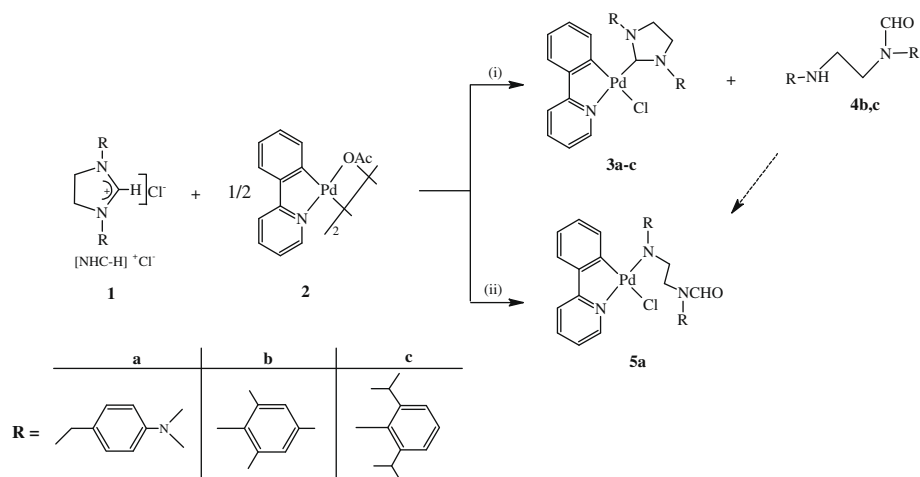
### 2.1. Synthesis and characterization

Complexes with imidazolin-2-ylidenes and imidazolidin-2-ylidenes can be prepared by various methods [16]. Among them *in situ*, deprotonation reactions involving basic metal salts, such as Pd(OAc)<sub>2</sub>, has attracted continuous interest since NHC complexes can be obtained in high yields, under mild conditions, avoiding the free NHC ligands which are difficult to handle, due to highly reactive nature of the species [17–20].

The reaction of **1a** with **2** in 2:1 ratio did not proceed as we expected in THF, but rather gave **5a** via the bridge cleavage by the *in situ* formed formamide derivative **4**. Because of the appearance of the CHO and NH group in the product **4a**, the conversions could only have been facilitated by **2** in the presence of water. Consistent with these when the reaction was repeated in carefully dried and distilled toluene the formation of **3a** was favored (Scheme 1). Although the possible mechanism would be speculative, it seems obvious that free NHC or the corresponding carbene dimer must be generated initially followed by insertion into H–OH bond, then cleavage of the ring and coordination of the hydrolysis product to palladium center through NH group. Previous studies on the reactivity of NHC showed that the saturated ring react instantly with water to give formamide derivatives [21,22].

Upon these results, we examined additional imidazolinium salts **1b** and **1c** to determine the scope of the reaction in the dried

\* Corresponding author. Tel.: +90 256 212 8498; fax: +90 256 213 5379.  
E-mail address: [megunay@adu.edu.tr](mailto:megunay@adu.edu.tr) (M. Emin Günay).



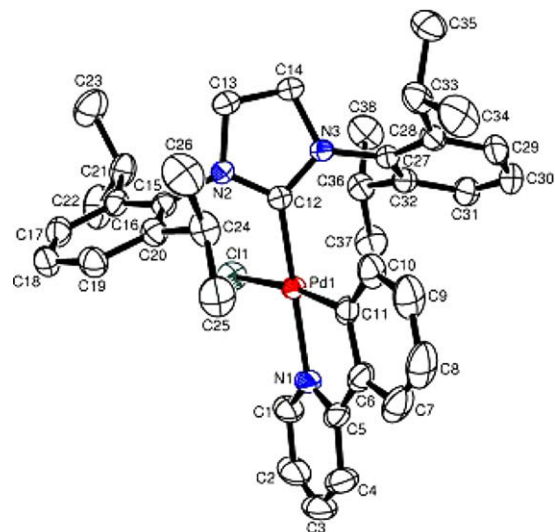
**Scheme 1.** Synthesis of carbene adducts, **3a–c**. Reagent and Conditions: (i) PhMe, 8 h, 110 °C; (ii) THF, 6 h, 65 °C.

toluene. We found that steric hindrance of the imidazolium salts do not diminish the generality of hydrolysis reaction with the basic palladacyclic dimer **2**. Thus, attempted deprotonation gave mixtures of desired NHC complexes **3b,c** along with hydrolysis products **4b,c**, indicating that H<sub>2</sub>O might also originate from the crystals of imidazolium salts. Therefore, the salts **1** were subjected to TGA and observed to contain ca. 1 mol H<sub>2</sub>O. The difference in coordination ability of hydrolysis products **4** were attributed to the nature of alkylic R group and the steric congestion of **5b** and **5c**; however the basicity of NMe<sub>2</sub> group in **1a** might play important role here. These results suggest that the synthetic chemist must be aware of the well-received deprotonation protocol involving imidazolium salts with basic transition metal precursors might fail due to water content of the solvents or salts of any reaction [23]. Clearly, the imidazolium salt has a higher propensity for the ring opening reaction than the imidazolium counterpart. In this connection we also noticed that for the preparation of Ag–NHC complexes from Ag<sub>2</sub>O and saturated NHC–salts, use of molecular sieve is necessary to improve the yield and purity [24,25].

All new compounds were characterized by NMR spectroscopy and compounds **3c**, **4c** and **5a** were further analyzed by X-ray crystallography. In the <sup>1</sup>H NMR spectra, the methylene protons show multiplets rather than AB patterns in CDCl<sub>3</sub>. In the <sup>13</sup>C NMR spectra, the formation of **3a–c** can readily be verified by the carbene carbon atoms resonating in the range of δ 201.1–207.2, which are slightly more deshielded than those *cis*-PdX<sub>2</sub>(NHC) complexes derived from saturated NHCs [26,27]. The complexes show only one carbene signals in the <sup>13</sup>C NMR spectra, suggesting that only one isomer was obtained.

## 2.2. Structural description of **3c**, **4c** and **5a**

The structure of complex **3c** is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The complex contains a phenylpyridine ligand, (I), with a Pd<sup>II</sup> metal center, a 1,3-bis(2,6-diisopropylphenyl)imidazolidine ligand, (II), and one chloride ligand. The coordination around the Pd<sup>II</sup> ion is distorted *cis*-square-planar, and the Pd<sup>II</sup> ion is coordinated by one pyridine N atom and one aryl C atom from the bidentate ligand (I), one carbene C atom from the monodentate ligand (II), and one Cl atom. In the square-planar coordination, atoms Pd1, C11, C11, C11 and C12 deviate by 0.026(1), –0.017(1), 0.007(1), –0.021(1) and 0.005(1) Å, respectively, from the mean plane through these five atoms. The Cl-atom occupies the *trans* site with respect to the metallated aryl C-atom. A carbene C-atom satisfies the fourth coordination site in the

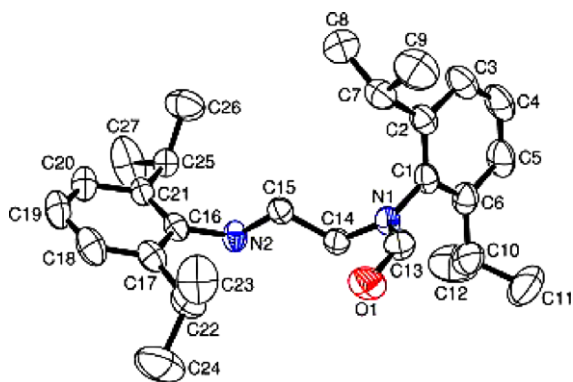


**Fig. 1.** A view of complex **3c**, showing 40% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry codes: (i)  $-x+1, y-1/2, -z+1/2$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $-x+1, y+1/2, -z+1/2$ .

**Table 1**  
Selected bond lengths (Å) and angles (°) for **3c**.

Bond lengths			
Pd1–C12	1.9897(18)	Pd1–C11	2.3868(6)
Pd1–C11	1.990(2)	N2–C12	1.341(2)
Pd1–N1	2.0807(17)	N3–C12	1.352(2)
Bond angles			
C12–Pd1–C11	97.52(8)	C12–Pd1–C11	89.36(5)
C12–Pd1–N1	178.25(8)	C11–Pd1–C11	172.70(7)
C11–Pd1–N1	81.13(9)	N1–Pd1–C11	91.94(7)

complex. The pyridine N- and aryl C-donor atoms form a five-membered metallacycle (containing atoms N1/C5/C6/C11/Pd1) with a maximum deviation from planarity being 0.056(2) Å for atom N1. The angle sum about the divalent Pd atom is 359.9°, the greatest deviation from orthogonality being 81.13(9)° for N1–Pd1–C11. The bond angles at the Pd atom involving *trans* pairs of substituents deviate from the expected value of 180°, being 178.25(8)° for the N1–Pd1–C12 angle and 172.70(7)° for the C11–



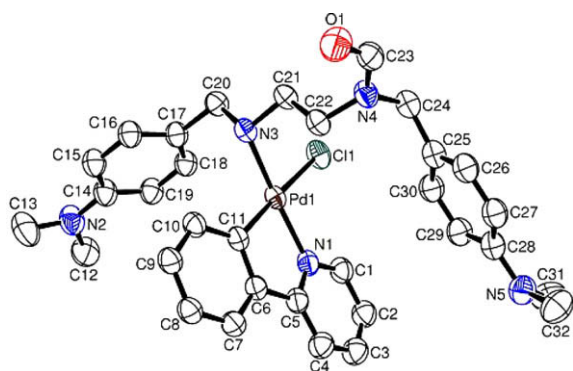
**Fig. 2.** A view of compound **4c**, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry codes: (i)  $x + 1/2, y, -z + 1/2$ .

Pd1–C11 angle. The plane of the phenylpyridine ligand is quasi-coplanar with the coordination plane [interplanar dihedral =  $8.32(11)^\circ$ ], perhaps in consequence of the “protonic” H atom at C1 forming an in-plane hydrogen bond to the adjacent Cl<sup>−</sup> ligand.

As can be seen, the molecule is highly crowded with both the carbene and phenylpyridine ligands presenting considerable steric encumbrance around the periphery of the approximately square planar complex. The plane of the carbene is approximately orthogonal to the square plane [ $70.39(7)^\circ$ ]. The bonding within the N-heterocyclic carbene (NHC) ring indicates a pattern of delocalization that extends from atom N2 to atom N3 through atom C12, the N2–C12 [ $1.341(2) \text{ \AA}$ ] and N3–C12 [ $1.352(2) \text{ \AA}$ ] distances being significantly shorter than the N2–C13 [ $1.469(2) \text{ \AA}$ ] and N3–C14 [ $1.473(2)^\circ$ ] distances, in accordance with a previous study [28]. This observation is possibly indicative of a greater partial double-

**Table 2**  
Selected bond lengths (Å) and Angles (°) for **4c**.

Bond lengths			
O1–C13	1.220(3)	N2–C16	1.422(4)
N1–C13	1.333(4)	N2–C15	1.461(3)
N1–C1	1.450(3)	C14–C15	1.505(4)
N1–C14	1.466(3)		
Bond angles			
C13–N1–C1	120.8(3)	O1–C13–N1	124.6(3)
C13–N1–C14	118.9(2)	N2–C15–C14	109.2(2)
C1–N1–C13–O1	−179.4(3)	C14–N1–C13–O1	−2.6(5)



**Fig. 3.** A view of complex **5a**, showing 40% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry codes: (i)  $-x + 1/2, -y + 1/2, -z + 1$ ; (ii)  $-x, y, -z + 1/2$ .

bond character due to partial electron donation by nitrogen to the carbene C-atom donor [29]. Theoretical studies also indicate that the stability of these carbenes is due to electron donation from the N-atom lone pairs into the formally empty  $p(\pi)$  orbital on the carbene C atom [30].

The molecular structure of compound **4c** is shown in Fig. 2 and selected geometric parameters are listed in Table 2. In the compound, the C13–N1 bond length of  $1.333(4) \text{ \AA}$ , which is intermedi-

**Table 3**  
Selected bond lengths (Å) and angles (°) for **5a**.

Bond lengths			
Pd1–C11	1.983(4)		
Pd1–N1	2.032(4)	N4–C23	1.334(7)
Pd1–N3	2.079(4)		
Pd1–C11	2.4239(13)		
O1–C23	1.193(7)		
Bond angles			
C11–Pd1–N1	80.92(18)	N3–Pd1–C11	89.66(11)
C11–Pd1–N3	93.52(17)	C21–N3–C20	109.4(4)
N1–Pd1–N3	169.71(16)	C23–N4–C22	120.7(5)
C11–Pd1–C11	176.64(15)	O1–C23–N4	125.6(6)
N1–Pd1–C11	96.10(12)		
C21–N3–C20–C17	−179.0(4)		
C20–N3–C21–C22	178.3(4)	C22–N4–C23–O1	4.8(10)
C24–N4–C22–C21	−83.0(6)	C24–N4–C23–O1	−179.8(6)
N3–C21–C22–N4	166.1(4)	C22–N4–C24–C25	−72.1(6)

**Table 4**  
Summary of crystallographic data for **3c**, **4c** and **5a**.

Parameter	<b>3c</b>	<b>4c</b>	<b>5a</b>
Empirical formula	C <sub>38</sub> H <sub>46</sub> ClN <sub>3</sub> Pd	C <sub>27</sub> H <sub>40</sub> N <sub>2</sub> O	C <sub>32</sub> H <sub>38</sub> ClN <sub>5</sub> OPd
Crystal size (mm)	0.72 × 0.63 × 0.56	0.72 × 0.37 × 0.13	0.38 × 0.32 × 0.26
<i>M<sub>r</sub></i>	686.63	408.61	650.52
<i>T</i> (K)	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> (Å)	12.1913(5)	11.8990(6)	36.227(2)
<i>b</i> (Å)	15.0091(4)	22.2188(12)	9.8879(3)
<i>c</i> (Å)	21.0279(10)	19.6748(14)	19.3348(10)
$\alpha$ (°)	90	90	90
$\beta$ (°)	115.210(3)	90	116.270(4)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	3481.2(3)	5201.7(5)	6210.5(5)
<i>Z</i>	4	8	8
$\rho_{\text{calcd}}$ (Mg/m <sup>3</sup> )	1.310	1.044	1.391
$\mu$ (mm <sup>−1</sup> )	0.64	0.72	0.72
$\theta$ Range (°)	1.73–27.94	1.83–26	2.12–27.89
Index ranges	−15 ≤ <i>h</i> ≤ 15, −19 ≤ <i>k</i> ≤ 19, −27 ≤ <i>l</i> ≤ 27	−14 ≤ <i>h</i> ≤ 14, −27 ≤ <i>k</i> ≤ 27, −24 ≤ <i>l</i> ≤ 24	−47 ≤ <i>h</i> ≤ 47, −13 ≤ <i>k</i> ≤ 12, −25 ≤ <i>l</i> ≤ 24
Number of observed reflections	49933	35771	31523
Number of independent reflections	8261	5102	7390
Number of parameters	388	271	362
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.005	0.942	1.053
Maximum/minimum $\Delta\rho$ (e Å <sup>−3</sup> )	0.43, −0.47	0.24, −0.22	0.47, −0.83
<i>R</i> , <i>wR</i> (observed data) <sup>a</sup>	0.0286, 0.0683	0.0655, 0.1575	0.0513, 0.1344
<i>R</i> , <i>wR</i> (all data) <sup>a</sup>	0.0435, 0.0715	0.1524, 0.1947	0.0798, 0.1451

<sup>a</sup> Refinement method, full-matrix least-squares on *F*<sup>2</sup>.

ate between a single and a double bond, and the bond angles around atom N1 suggest that the lone pair of electrons on N1 undergoes delocalization, affording double-bond character to the C13–N1 bond and forcing the O1/C13/N1/C1(C14) atoms into an almost planar conformation. The difference between the N2–C15 and N2–C16 [1.461(3) and 1.422(4) Å, respectively] can be attributed to the different hybridization of the  $C_{sp3}$  and  $C_{sp2}$  atoms.

The structure of complex **5a** is shown in Fig. 3 and selected geometric parameters are listed in Table 3. The complex contains a phenylpyridine (ppy) ligand, (I), with a Pd<sup>II</sup> metal center, an N-[4-(dimethylamino)benzyl]-N-[2-[4-(dimethylamino)benzylamino]ethyl] formamide ligand, (II), and one chloride ligand. The coordination around the Pd<sup>II</sup> ion is distorted *trans*-square-planar, and the Pd<sup>II</sup> ion is coordinated by one pyridine N atom and one aryl C atom from the bidentate ligand (I), one amine N atom from the monodentate ligand (II), and one Cl atom. In the square-planar coordination, atoms Pd1, Cl1, N1, N3 and C11 deviate by 0.052(2), 0.063(2), –0.105(2), –0.098(2) and 0.088(2) Å, respectively, from the mean plane through these five atoms. The Cl-atom occupies the *trans* site with respect to the metallated C-atom. An amine N-atom satisfies the fourth coordination site in the complex. The pyridine N- and aryl C-donor atoms form a five-membered metallacycle (containing atoms N1/C5/C6/C11/Pd1) with a maximum deviation from planarity being 0.062(3) Å for atom N1. The plane of the phenylpyridine ligand is quasi-coplanar with the coordination plane [interplanar dihedral = 10.94(8)°], perhaps in consequence of the “protonic” H atom at C1 forming an in-plane hydrogen bond to the adjacent Cl<sup>–</sup> ligand.

The C23–N4 bond length of 1.334(7) Å, which is intermediate between a single and a double bond, and the bond angles around atom N4 suggest that the lone pair of electrons on N4 undergoes delocalization, affording double-bond character to the C23–N4 bond and forcing the O1/C23/N4/C22(C24) atoms into an almost planar conformation.

The single-crystal data and X-ray collection parameters are given in Table 4.

### 3. Conclusion

This study, involving deprotonation of imidazolium salts (**1**) with **2** revealed that the nature of products can be influenced by the presence of water either in the solvent or as hydrate and N-substituents on the ring [23,31]. Thus, N-benzyl substituted salt **1a** in THF reacts only to give **5a** as a result of hydrolysis of the expected NHC. The same reaction in dried toluene affords the expected Pd–NHC complex in 85% yield. Whereas N-aryl substituted bulkier **1b** and **1c** with **2** yields both the Pd–NHC complex (**3b,c**) and the formamides **4b** and **4c**. Such reactions might account for low yields obtained in deprotonation procedures. Further studies on the catalytic properties of NHC complexes **3a–c** are currently in progress.

### 4. Experiment

#### 4.1. General comments

All reactions and manipulations of air-sensitive materials were carried out under nitrogen and using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. The precursors (**1b,c**) were prepared according to the literature [32]. Palladium dimer (**2**) was also prepared according to the literature [33]. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR instrument at 400 MHz (<sup>1</sup>H), 100.56 MHz (<sup>13</sup>C). NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; sept., septet; m,

multiplet; br., broad; signal. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the analytical service of TUBITAK with a LECO CHNS 932 instrument. The thermogravimetry (TG) curves were obtained by using TG-DTA Perkin–Elmer Diamond system apparatus. The measurements were performed under a dynamic nitrogen atmosphere at a flow rate of 200 mL min<sup>–1</sup> up to 800 °C. Melting points were determined using an Electrothermal 9100 melting point detection apparatus.

#### 4.2. Preparation of 1,3-bis(4-dimethylaminobenzyl)imidazolium chloride (**1a**)

A mixture of 1,2-bis(4-dimethylaminobenzylamino)ethane [34] (3.26 g, 10.0 mmol), NH<sub>4</sub>Cl (0.53 g, 10.0 mmol) in triethyl orthoformate (20 mL) was heated in a distillation apparatus until the distillation of ethanol ceased. The temperature of the reaction mixture reached 110 °C. Upon cooling to room temperature, diethyl ether (20 mL) was added giving a colorless solid precipitate, which was collected by filtration, and dried in vacuum. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O at 25 °C, gave colorless needles crystals of **1a** which was manually separated giving 82% yield (306 mg), m.p.: 222–223 °C.

<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 2.87 [s, 12H, C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 3.67 [s, 4H, NCH<sub>2</sub>CH<sub>2</sub>N]; 4.68 [s, 4H, NCH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 6.58 [d, 4H, *J* = 8.4 Hz, Ar-CH]; 7.19 [d, 4H, *J* = 8.4 Hz, Ar-CH]; 10.02 [s, 1H, NCHN]. <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): 40.5 [N(CH<sub>3</sub>)<sub>2</sub>]; 48.1 [NCH<sub>2</sub>CH<sub>2</sub>N]; 51.2 [NCH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 113.0, 121.2, 130.3, 151.1 [Ar-C]; 157.4 [NCHN].

#### 4.3. Preparation of chloro[1,3-bis(4-dimethylaminobenzyl)imidazolium-2-ylidene][2-(2-pyridyl)phenyl]palladium(II) (**3a**)

A mixture of 1,3-bis(4-dimethylaminobenzyl)imidazolium chloride (**2a**), (0.233 g, 0.626 mmol) and complex **1** (0.200 g, 0.313 mmol) was heated in PhMe (5 mL) at 110 °C for 8 h. The solvent was removed *in vacuo*, cold ether (5 mL) was added to induce crystallization and the solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: 0.167 g, (85%), m.p.: 165–166 °C. Anal. Calc. for C<sub>32</sub>H<sub>36</sub>ClN<sub>5</sub>Pd: C, 60.76; H, 5.74; N, 11.07. Found: C, 60.54; H, 5.88; N, 10.48%.

<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 2.89 [s, 12H, C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 3.43–3.50 [m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N]; 5.08 [d, 2H, *J* = 14.4 Hz, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 5.13 [d, 2H, *J* = 14.4 Hz, NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 6.63 [d, 4H, *J* = 8.8 Hz, Ar-CH]; 7.08–7.20 [m, 4H, Ar-CH]; 7.28 [d, 4H, *J* = 8.8 Hz, Ar-CH]; 7.58 [d, 1H, *J* = 8.4 Hz, Ar-CH]; 7.70 [d, 1H, *J* = 8.4 Hz, Ar-CH]; 7.77 [t, 1H, *J* = 8.0 Hz, Ar-CH]; 9.35 [d, 1H, *J* = 5.6 Hz, Ar-CH]. <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): 40.8 [N(CH<sub>3</sub>)<sub>2</sub>]; 48.2 [NCH<sub>2</sub>CH<sub>2</sub>N]; 55.2 [NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 112.7, 118.1, 122.2, 123.8, 123.9, 124.2, 129.9, 130.1, 137.5, 138.5, 146.8, 149.9, 150.4, 155.4, 164.3, [Ar-C], 201.1 [Pd-C<sub>carbene</sub>].

#### 4.4. Preparation of chloro[4-dimethylaminobenzyl{2-(4-dimethylaminobenzyl(formyl)amino)ethyl}ammonio][2-(2-pyridyl)phenyl]palladium(II) (**5a**)

A mixture of *N,N'*-bis(4-dimethylaminobenzyl)imidazolium chloride (**1a**) (0.175 g, 0.47 mmol) and complex **2** (0.150 g, 0.234 mmol) was heated in THF (5 mL) at 65 °C for 6 h. The solvent was removed *in vacuo*, cold ether (5 mL) was added to induce crystallization and the white solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: 0.100 g, (65%), m.p.: 178–180 °C. Anal. Calc. for C<sub>32</sub>H<sub>38</sub>ClN<sub>5</sub>OPd: C, 59.08; H, 5.89; N, 10.77. Found: C, 59.34; H, 5.57; N, 10.56%.

<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 2.86–2.94 [m, 12H, C<sub>6</sub>H<sub>4</sub>-*p*-N(CH<sub>3</sub>)<sub>2</sub>]; 3.38–3.85 [m, 4H, NHCH<sub>2</sub>CH<sub>2</sub>NCHO]; 4.27–4.36 [m, 2H, HNCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-



$N(CH_3)_2$ ]; 4.53–4.62 [m, 2H,  $NCHOCH_2C_6H_4-p-N(CH_3)_2$ ]; 6.21 [d, 4H,  $J = 8.0$  Hz, Ar-CH]; 6.38 [d, 2H,  $J = 8.0$  Hz, Ar-CH]; 6.62–6.69 [m, 3H, Ar-CH]; 6.99–7.15 [m, 2H, Ar-CH]; 7.21–7.27 [m, 1H, Ar-CH]; 7.42–7.46 [m, 1H, Ar-CH]; 7.59–7.63 [t, 1H,  $J = 8.2$  Hz, Ar-CH]; 7.75–7.80 [q, 1H, Ar-CH]; 8.26 [s, 1H, CHO]; 9.45 [d, 1H,  $J = 8.0$  Hz, Ar-CH].  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ): 40.6, 40.7, 40.8 [ $N(CH_3)_2$ ]; 43.1 [ $CH_2C_6H_4-p-N(CH_3)_2$ ]; 45.3 [ $NHCH_2CH_2NCHO$ ]; 52.1 [ $NHCH_2CH_2NCHO$ ]; 111.0, 112.3, 112.6, 118.3, 118.5, 119.0, 123.1, 124.1, 129.0, 129.3, 130.1, 138.6, 138.8, 146.3, 150.0, 152.5, 165.5 [Ar-C]; 163.0 [NCHO].

#### 4.5. Preparation of chloro[1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene][2-(2-pyridyl)phenyl]palladium(II), **3b** and *N,N'*-bis(2,4,6-trimethylphenyl)-*N*-formylethylenediamine (**4b**)

A mixture of *N,N'*-bis(2,4,6-trimethylphenyl)imidazolium chloride (**1b**) (0.157 g, 0.46 mmol) and complex **2** (0.150 g, 0.23 mmol) was heated in PhMe (5 mL) at 110 °C for 8 h. The solvent was removed *in vacuo*, cold ether (5 mL) was added to induce crystallization and the solid was recrystallized from  $CH_2Cl_2$ /hexane. Yield: 0.103 g (75%), m.p.: 212–213 °C. Anal. Calc. for  $C_{32}H_{34}ClN_3Pd$ : C, 63.79; H, 5.69; N, 6.97. Found: C, 63.28; H, 5.61; N, 6.97%.

$^1H$  NMR ( $\delta$ ,  $CDCl_3$ ): 2.16 [s, 6H,  $C_6H_2(CH_3)_3$ ]; 2.32 [s, 6H,  $C_6H_2(CH_3)_3$ ]; 2.70 [s, 6H,  $C_6H_2(CH_3)_3$ ]; 4.03–4.05 [m, 2H,  $NCH_2CH_2N$ ]; 4.11–4.14 [m, 2H,  $NCH_2CH_2N$ ]; 6.71 [s, 2H, Ar-CH]; 6.87 [td, 1H,  $J = 8.0$  Hz, Ar-CH]; 6.91 [s, 2H, Ar-CH]; 6.98 [td, 2H,  $J = 8.0$  Hz, Ar-CH]; 7.27 [dd, 1H,  $J = 8.0$  Hz, Ar-CH]; 7.36 [d, 1H,  $J = 8.0$  Hz, Ar-CH]; 7.40 [dd, 1H,  $J = 8.0$  Hz, Ar-CH]; 7.48 [td, 1H,  $J = 8.0$  Hz, Ar-CH]; 9.23 [dd, 1H,  $J = 8.0$  Hz, Ar-CH].  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ): 20.1 [ $C_6H_2(CH_3)_3$ ]; 20.4 [ $C_6H_2(CH_3)_3$ ]; 20.9 [ $C_6H_2(CH_3)_3$ ]; 52.0 [ $NCH_2CH_2N$ ]; 117.4, 121.4, 122.9, 123.6, 127.6, 129.1, 129.9, 135.2, 136.2, 137.7, 140.3, 146.3, 150.0, 154.1, 164.0 [Ar-C]; 205.6 [Pd- $C_{carbene}$ ]. The crude mixture was purified using flash chromatography (90% Hexane– $CH_2Cl_2$ , 9:1; 10% ethyl acetate). Compound **4b** was obtained as a white solid. Yield: 0.010 g (7%), m.p.: 151–152 °C. Anal. Calc. for  $C_{21}H_{28}N_2O$ : C, 77.74; H, 8.70; N, 8.63. Found: C, 77.62; H, 8.55; N, 8.68%.

$^1H$  NMR ( $\delta$ ,  $CDCl_3$ ): 2.15–2.25 [m, 18H,  $C_6H_2(CH_3)_3$ ]; 3.16 [t, 2H,  $NCH_2CH_2NH$ ]; 3.80 [t, 2H,  $NCH_2CH_2NH$ ]; 4.73 [br, 1H, NH]; 6.78 [s, 2H, Ar-CH]; 6.94 [s, 2H, Ar-CH]; 8.03 [s, 1H, NCHO].  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ): 20.3 [ $C_6H_2(CH_3)_3$ ]; 21.1 [ $C_6H_2(CH_3)_3$ ]; 21.6 [ $C_6H_2(CH_3)_3$ ]; 21.7 [ $C_6H_2(CH_3)_3$ ]; 47.2 [ $NCH_2CH_2NH$ ], 52.1 [ $NCH_2CH_2NH$ ], 129.2, 129.5, 129.6, 129.7, 129.8, 135.9, 138.4, 143.2 [Ar-C]; 164.2 [NCHO].

#### 4.6. Preparation of chloro[1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene][2-(2-pyridyl)phenyl]palladium(II) (**3c**) and *N,N'*-bis(2,6-diisopropylphenyl)-*N*-formylethylenediamine (**4c**)

A mixture of *N,N'*-bis(2,6-isopropylphenyl)imidazolium chloride (**1c**) (0.197 g, 0.46 mmol) and complex **2** (0.150 g, 0.23 mmol) was heated in PhMe (5 mL) at 110 °C for 8 h. The solvent was removed *in vacuo*, cold ether (5 mL) was added to induce crystallization and the solid was recrystallized from  $CH_2Cl_2$ /hexane. The yellow crystals (**3c**) were manually separated from the reaction mixture. Yield: 0.110 g (70%), m.p.: 229–230 °C. Anal. Calc. for  $C_{38}H_{46}ClN_3Pd$ : C, 66.47; H, 6.75; N, 6.12. Found: C, 66.54; H, 7.01; N, 6.22%.

$^1H$  NMR ( $\delta$ ,  $CDCl_3$ ): 0.75 [d, 6H,  $J = 6.8$  Hz,  $HC(CH_3)_2$ ]; 1.23 [dd, 12H,  $J = 6.8$  Hz,  $HC(CH_3)_2$ ]; 1.60 [d, 6H,  $J = 6.8$  Hz,  $HC(CH_3)_2$ ]; 3.59–3.62 [m, 2H,  $HC(CH_3)_2$ ]; 3.75–3.77 [m, 2H,  $HC(CH_3)_2$ ]; 4.19 [s, 4H,  $NCH_2CH_2N$ ]; 6.88 [t, 1H,  $J = 6.8$  Hz, Ar-CH]; 7.00–7.03 [m, 2H, Ar-CH]; 7.09 [dd, 2H,  $J = 6.8$  Hz, Ar-CH]; 7.27 [dd, 4H,  $J = 4.8$  Hz, Ar-CH]; 7.32 [dd, 1H,  $J = 6.4$  Hz, Ar-CH]; 7.41 [d, 1H,  $J = 8.0$  Hz, Ar-CH]; 7.50 [td, 2H,  $J = 6.8$  Hz, Ar-CH]; 9.23 [dd, 1H,

$J = 6.0$  Hz, Ar-CH].  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ): 23.7 [ $HC(CH_3)_2$ ]; 24.6 [ $HC(CH_3)_2$ ]; 26.5 [ $HC(CH_3)_2$ ]; 27.3 [ $HC(CH_3)_2$ ]; 28.7 [ $HC(CH_3)_2$ ]; 29.2 [ $HC(CH_3)_2$ ]; 54.6 [ $NCH_2CH_2N$ ]; 117.6, 121.5, 123.1, 123.4, 124.5, 124.9, 129.0, 129.3, 136.8, 137.7, 137.9, 146.7, 146.8, 148.4, 150.1, 156.1, 164.4, [Ar-C]; 207.2 [Pd- $C_{carbene}$ ].

The remaining colorless crystals were recrystallized from  $CH_2Cl_2$ /hexane to give **4c**. Yield: 0.016 g (10%), m.p.: 140–141 °C. Anal. Calc. for  $C_{27}H_{40}N_2O$ : C, 79.36; H, 9.87; N, 6.86. Found: C, 79.53; H, 9.34; N, 6.18%.

$^1H$  NMR ( $\delta$ ,  $CDCl_3$ ): 1.14–1.15 [d, 6H,  $J = 7.0$  Hz,  $CH(CH_3)_2$ ]; 1.17–1.18 [d, 12H,  $J = 7.0$  Hz,  $CH(CH_3)_2$ ]; 1.22–1.24 [d, 6H,  $J = 6.7$  Hz,  $CH(CH_3)_2$ ]; 3.01–3.05 [m, 2H,  $CH(CH_3)_2$ ]; 3.11–3.15 [m, 2H,  $CH(CH_3)_2$ ]; 3.17–3.21 [m, 2H,  $NCH_2CH_2NH$ ]; 3.87 [t, 2H,  $NCH_2CH_2NH$ ]; 7.02–7.07 [m, 3H, Ar-CH]; 7.21–7.23 [d, 1H,  $J = 7.8$  Hz, Ar-CH]; 7.35–7.37 [d, 2H,  $J = 7.8$  Hz, Ar-CH]; 8.09 [s, 1H, NCHO].  $^{13}C$  NMR ( $\delta$ ,  $CDCl_3$ ): 23.7 [ $NHC_6H_3CH(CH_3)_2$ ]; 24.4 [ $NHC_6H_3CH(CH_3)_2$ ],  $NC_6H_3CH(CH_3)_2$ ]; 25.6 [ $NC_6H_3CH(CH_3)_2$ ]; 28.5 [ $NC_6H_3CH(CH_3)_2$ ]; 48.9 [ $NHCH_2CH_2N$ ]; 49.1 [ $NHCH_2CH_2N$ ]; 123.7, 123.9, 124.7, 129.7, 135.7, 142.5, 143.1, 147.9 [Ar-C]; 164.1 [NCHO].

#### 4.6.1. Crystal structure determinations

Diffraction data for **3c**, **4c** and **5a** were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296 K. The structures were solved by direct-methods using program SHELXS-97 [35]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods using program SHELXL-97 [36]. All hydrogen atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97, 0.98, 0.93 and 0.91 Å for  $CH_3$ ,  $CH_2$ , CH, aromatic CH and NH, respectively. The displacement parameters of the H atoms were constrained as  $U_{iso}(H) = 1.2U_{eq}$  (1.5 $U_{eq}$  for methyl) of the carrier atom. Data collection: X-AREA [37]; cell refinement: X-AREA; data reduction: X-RED32 [37]; molecular graphics: ORTEP-3 for Windows [38]; software used to prepare material for publication: WINGX [39] and PLATON [40].

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#### Appendix A. Supplementary material

CCDC 693272, 693273 and 693274 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.02.023](https://doi.org/10.1016/j.jorganchem.2009.02.023).

#### References

- [1] R.B. Bedford, C.S.J. Cazin, D. Holder, *Coord. Chem. Rev.* 248 (2004) 2283.
- [2] J. Dupont, C.S. Consorti, J. Spencer, *Chem. Rev.* 105 (2005) 2527.
- [3] R.B. Bedford, *Chem. Commun.* (2003) 1787.
- [4] I.P. Beletskaya, A.V. Cheprakov, *J. Organomet. Chem.* 689 (2004) 4055.
- [5] (a) R.B. Bedford, C.S.J. Cazin, M.B. Hursthouse, M.E. Light, V.J.M. Scordia, *Dalton Trans.* (2004) 3864; (b) U. Nettekoven, F. Naud, A. Schnyder, H.U. Blaser, *Synlett* (2004) 2549.
- [6] (a) N.M. Scott, S.P. Nolan, *Eur. J. Inorg. Chem.* (2005) 1815; (b) W.A. Herrmann, *Angew. Chem., Int. Ed.* 41 (2002) 1291.
- [7] M.S. Viciu, R.A. Kelly III, E.D. Stevens, F. Naud, M. Studer, S.P. Nolan, *Org. Lett.* 5 (2003) 1479.
- [8] G.D. Frey, J. Schütz, W.A. Herrmann, *J. Organomet. Chem.* 691 (2006) 2403.
- [9] R.B. Bedford, M. Betham, M.E. Blake, R.M. Frost, P.N. Horton, M.B. Hursthouse, R. Lopez-Nicolas, *J. Chem. Soc., Dalton Trans.* 16 (2005) 2774.

- [10] R.B. Bedford, M. Betham, S.J. Coles, R.M. Frost, M.B. Hursthouse, *Tetrahedron* 61 (2005) 9663.
- [11] A.G. Gürhan, M.E. Günay, M. Aygün, B. Çetinkaya, O. Büyükgüngör, *J. Coord. Chem.* 60 (2007) 805.
- [12] I. Özdemir, M. Yiğit, E. Çetinkaya, B. Çetinkaya, *Appl. Organomet. Chem.* 20 (2006) 187.
- [13] H. Türkmen, B. Çetinkaya, *J. Organomet. Chem.* 691 (2006) 3749.
- [14] B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Semeril, C. Bruneau, P.H. Dixneuf, *Chem. Eur. J.* 9 (2003) 2323.
- [15] T. Seçkin, S. Köytepe, S. Demir, I. Özdemir, B. Çetinkaya, *J. Inorg. Organomet. Polym.* 13 (2003) 223.
- [16] S. Yaşar, I. Özdemir, B. Çetinkaya, J. Renaud, C. Bruneau, *Eur. J. Org. Chem.* (2008) 2142.
- [17] F.E. Hahn, M.C. Jahnke, *Angew. Chem., Int. Ed.* 47 (2008) 3122.
- [18] C.M. Crudden, D.P. Allen, *Coord. Chem. Rev.* 248 (2004) 2247.
- [19] W.A. Herrmann, J. Schutz, G.D. Frey, E. Herdtweck, *Organometallics* 25 (2006) 2437.
- [20] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39.
- [21] M. Iglesias, D.J. Beetstra, A. Stasch, P.N. Horton, M.B. Hursthouse, S.J. Coles, K.J. Cavell, A. Dervisi, I.A. Fallis, *Organometallics* 26 (2007) 4800.
- [22] M.K. Denk, J.M. Rodezno, S. Gupta, A.J. Lough, *J. Organomet. Chem.* 617–618 (2001) 242.
- [23] During the preparation of this manuscript, Kantchev and Ying described one-pot three-component synthesis of NHC ligated C,N-palladacycles derived from *N,N*-dimethylbenzylamine: while the complexation of 1,3-diarylimidazol-2-ylidenes were found to be facile, the saturated analogues required more forcing conditions and the initial addition of 4 Å molecular sieves to suppress the competing carbene precursor hydrolysis, see: E.A.B. Kantchev, J.Y. Ying, *Organometallics* 28 (2009) 289.
- [24] J.C. Garrison, W.J. Youngs, *Chem. Rev.* 105 (2005) 3978.
- [25] A.A.D. Tulloch, A.A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, *J. Chem. Soc., Dalton Trans.* (2000) 4499.
- [26] H. Türkmen, O. Şahin, O. Büyükgüngör, B. Çetinkaya, *Eur. J. Inorg. Chem.* (2006) 4915.
- [27] A.G. Gökce, R. Kılıncarslan, M. Aygün, B. Çetinkaya, S. Garcia-Granda, *Z. Naturforsch.* 62 (2007) 1353.
- [28] D.S. McGuinness, M.J. Green, K.J. Cavell, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 565 (1998) 165.
- [29] (a) W.A. Herrmann, T. Weskamp, V.P.W. Böhm, *Adv. Organomet. Chem.* 48 (2001) 1;  
(b) N. Fröhlich, U. Pidun, M. Stahl, G. Frenking, *Organometallics* 16 (1997) 442.
- [30] (a) C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* 118 (1996) 2023;  
(b) C. Böhme, G. Frenking, *J. Am. Chem. Soc.* 118 (1996) 2039.
- [31] C. Liao, K. Chan, C. Tu, Y. Chang, C. Hu, H.M. Lee, *Chem. A Eur. J.* 15 (2009) 405.
- [32] A.J. Arduengo, R. Krafczyk, R. Schmutzler, *Tetrahedron* 55 (1999) 14523.
- [33] I. Aiello, A. Crispini, M. Ghedini, M. La Deda, F. Barigelletti, *Inorg. Chim. Acta* 308 (2000) 121.
- [34] T. Seckin, E. Çetinkaya, S. Koytepe, B. Yiğit, *Polym. Bull.* 50 (2003) 139.
- [35] G.M. Sheldrick, *SHELXS-97: Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.
- [36] G.M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.
- [37] Stoe & Cie. *X-Area* (Version 1.18) and *X-Red32* (Version 1.04). Stoe & Cie, Darmstadt, Germany, 2002.
- [38] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [39] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [40] A.L. Spek, *J. Appl. Crystallogr.* 36 (2003) 7.