Journal of Organometallic Chemistry 694 (2009) 2179–2184

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

M. Emin Günay [a,*], Namık Özdemir [b], Mahmut Ulusoy [c], Melih Uçak [a], Muharrem Dinçer [b], Bekir Çetinkaya [c]

[a] *Department of Chemistry, Adnan Menderes University, 09010 Aydın, Turkey*
[b] *Department of Physics, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey*
[c] *Department of Chemistry, Ege University, 35100 Bornova-Izmir, Turkey*

ARTICLE INFO

Article history:
Received 29 December 2008
Received in revised form 14 February 2009
Accepted 20 February 2009
Available online 5 March 2009

Keywords:
Palladacycles
Imidazolinium salts
N-heterocyclic carbenes
Ring opening
Hydrolysis

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.

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_2 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 σ-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 $Pd(OAc)_2$, 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].

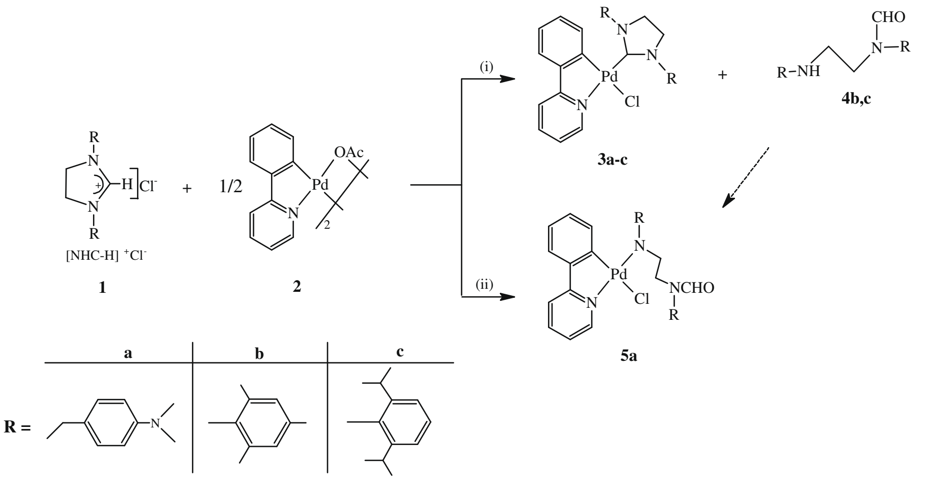
The reaction of **1a** with **2** in 2:1 ratio did not proceed as we expected in THF, but rather gave **5a** via the bridge cleavage by the *in situ* formed formamide derivative **4**. Because of the appearance of the CHO and NH group in the product **4a**, the conversions could only have been facilitated 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 (M. Emin Günay).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.02.023



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 imidazolinium 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_2O might also originate from the crystals of imidazolinium salts. Therefore, the salts **1** were subjected to TGA and observed to contain *ca.* 1 mol H_2O. 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_2 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 imidazolinium salts with basic transition metal precursors might fail due to water content of the solvents or salts of any reaction [23]. Clearly, the imidazolinium salt has a higher propensity for the ring opening reaction than the imidazolinium counterpart. In this connection we also noticed that for the preparation of Ag–NHC complexes from Ag_2O 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 ^1H NMR spectra, the methylene protons show multiplets rather than AB patterns in $CDCl_3$. In the ^{13}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_2(NHC) complexes derived from saturated NHCs [26,27]. The complexes show only one carbene signals in the ^{13}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^{II} metal center, a 1,3-bis(2,6-diisopropylphenyl)imidazolidine ligand, (II), and one chloride ligand. The coordination around the Pd^{II} ion is distorted *cis*-square-planar, and the Pd^{II} 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, N1, Cl1 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 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 Cl1–

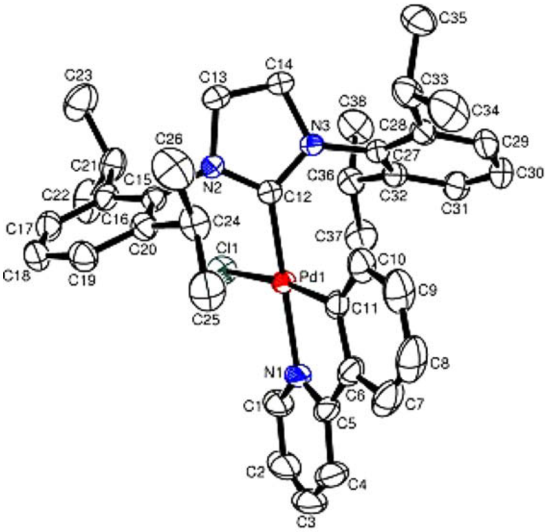


Fig. 1. A view of complex **3c**, showing 40% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry codes: (i) −*x* + 1, *y* − 1/2, −*z* + 1/2; (ii) −*x* + 1, −*y* + 1, −*z*; (iii) −*x* + 1, *y* + 1/2, −*z* + 1/2.

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)