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The cyclopalladation reaction of benzylamine revisited

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Abstract

The reaction of benzylamine and palladium(II) acetate in a one-to-one molar ratio in toluene or in glacial acetic acid at 60 °C for 24 h produced the acetato bridged cyclopalladated dimer of benzylamine $(\mu\text{-OAc})_2[Pd(C_6H_4CH_2NH_2)]_2$ (**1**) in yields of 40–75% and of 20–40%, respectively. In addition, mixtures of compounds **1**, **1d1** of formula $[(3\text{-}DC_6H_3CH_2NH_2)Pd](\mu\text{-OAc})_2[Pd(C_6H_4CH_2NH_2)]$ and **1d2** of formula $(\mu\text{-OAc})_2[Pd(3\text{-}DC_6H_3CH_2NH_2)]_2$ were obtained when benzylamine and palladium(II) acetate in a one-to-one molar were treated in monodeuterated acetic acid (DOAc) at 60 °C for 24 h. These mixtures were isolated in yields of 10–30% and deuterium contents in the range between 0.7 and 0.9. Furthermore, the treatment of benzylamine and palladium(II) acetate in a one-to-one molar ratio under reflux of glacial acetic acid for 45 min produced the acetato bridged *endo*-cyclopalladated dimer of benzyl-benzylidene-amine $(\mu\text{-OAc})_2[Pd(C_6H_4CH{=}NCH_2C_6H_5)]$ (compound **4**), which was isolated in 14% yield relative to the initial palladium(II) acetate, together with other unidentified compounds.

Keywords: Cyclometallation; Benzylamine; Palladium(II) acetate

1. Introduction

Despite the fact that benzylamine is one of the least elaborated N-donor ligands that can undergo the cyclopalladation reaction [1], not until quite recently have methods for its cyclopalladation been reported. The first attempt to cyclopalladate benzylamine was described by Cope and Friedrich in 1968 [2]. In this paper, and with the aim of preparing the chloro bridged cyclopalladated dimer of benzylamine $(\mu\text{-Cl})_2[Pd(C_6H_4CH_2NH_2)]_2$, benzylamine and $Li_2[PdCl_4]$ in a two-to-one molar ratio were treated in methanol at room temperature for 4 h. However, the coordination compound $[PdCl_2(benzylamine)_2]$ was formed in these reaction conditions. Avshu et al. [3] later found that treating the coordination compound $[PdI_2(benzylamine)_2]$ with $Ag[BF_4]$ in ethyl acetate and a posterior reaction with $[Bu_4N]I$ allowed the isolation of the iodo bridged cyclopalladated dimer of benzylamine $(\mu\text{-I})_2[Pd(C_6H_4CH_2NH_2)]_2$ in 73% yield. Recently, Fuchita et al. [4,5] showed that the treatment of benzylamine and palladium(II) acetate in a one-to-one molar ratio in benzene at 60 °C for 24 h gave place to the acetato bridged cyclopalladated dimer of benzylamine $(\mu\text{-OAc})_2[Pd(C_6H_4CH_2NH_2)]_2$ (compound **1**) in 53% yield. Additionally, Vicente et al. [6] reported that both the treatment of benzylamine and palladium(II) acetate in a one-to-one molar ratio under reflux of acetonitrile and the treatment of the coordination compound $(\mu\text{-OAc})_2[Pd(OAc)(benzylamine)]_2$ under reflux of acetonitrile, produced **1** in yields of 40–50%. It should also be noted that in 1985 Dyke et al. [7] published the synthesis of the bromo bridged cyclopalladated dimer of benzylamine $(\mu\text{-Br})_2[Pd(C_6H_4CH_2NH_2)]_2$ by reacting 2-bromobenzylamine with bis(dibenzylideneacetone)palladium(0).

In view of these precedents and the interest in the organic and bioorganic chemistry applications of cyclopalladated primary and secondary amines [8–23], we decided to undertake a detailed study on the reaction between benzylamine and palladium(II) acetate in a one-to-one molar ratio in different solvents and under different reaction conditions. The results of this study are reported below.

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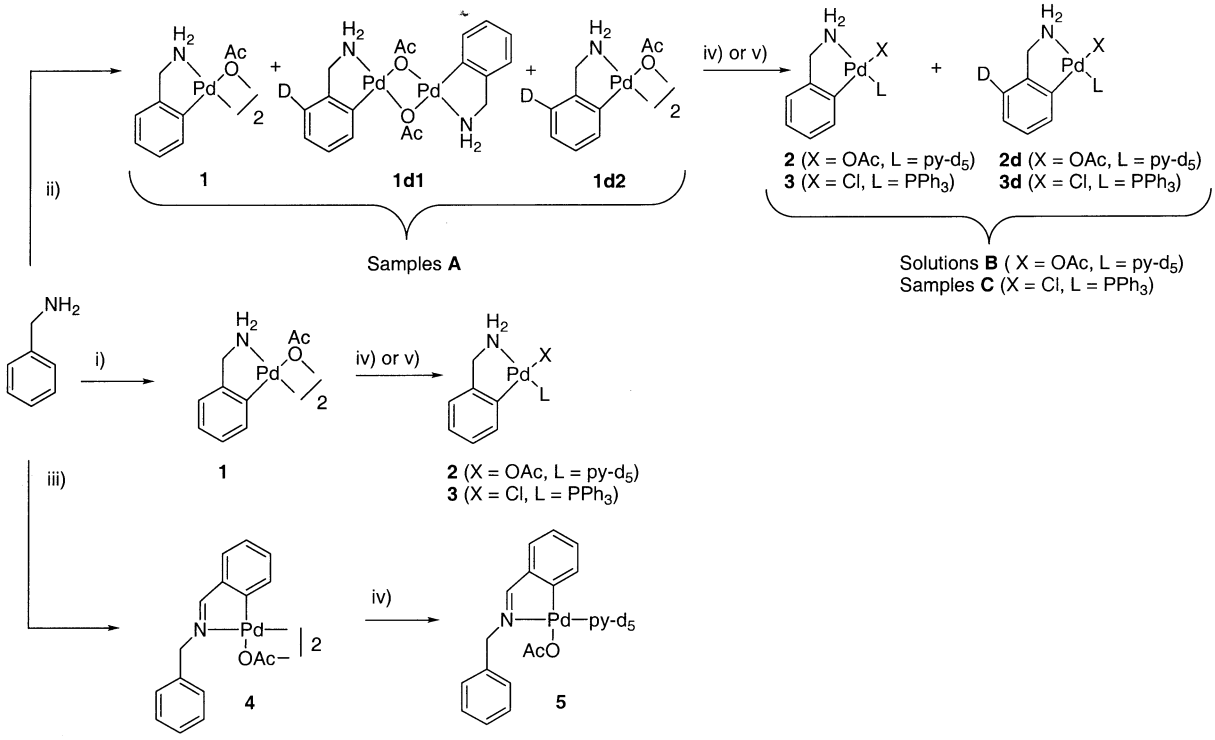

Scheme 1. (i) $Pd(OAc)_2$ (molar ratio benzylamine/$Pd(OAc)_2 = 1$), toluene or acetic acid, 60 °C, 24 h; (ii) $Pd(OAc)_2$ (molar ratio benzylamine/$Pd(OAc)_2 = 1$), monodeuterated acetic acid, 60 °C, 24 h; (iii) $Pd(OAc)_2$ (molar ratio benzylamine/$Pd(OAc)_2 = 1$), acetic acid, reflux, 45 min; (iv) py-d_5, $CDCl_3$, room temperature; (v) LiCl and PPh_3, acetone, room temperature.

2. Results and discussion

Scheme 1 shows the compounds prepared in this work and Fig. 1 gives the numbering of the hydrogen and carbon atoms of the palladated phenyl ring for the discussion that follows.

The reaction of benzylamine and palladium(II) acetate in a one-to-one molar ratio in toluene or in glacial acetic acid at 60 °C for 24 h produced a yellow suspension or a red solution, respectively. In both cases, the reaction mixture was concentrated under vacuum and the residue was eluted through a SiO_2 column with a solution of methanol in chloroform in a 6-to-100 volume ratio. Compound **1** eluted in the most polar band, which was concentrated under vacuum. Addition of a minimum volume of acetone to the resulting residue produced the precipitation of **1** as a pale yellow powder, which was isolated in yields of 40–75% in the reaction in toluene and in yields of 20–40% in the reaction in acetic acid. Compound **1** produced satisfactory elemental analyses, FAB^+ and IR spectrum, but it was only slightly soluble in $CDCl_3$. However, when a suspension of **1** in $CDCl_3$ was treated with py-d_5, a pale yellow solution was formed, whose ^1H NMR at 300 MHz showed the signals corresponding to compound **2**.

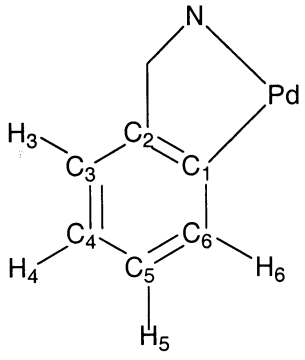

Fig. 1. Numbering of the hydrogen and carbon atoms of the palladated phenyl ring of the compounds under discussion.

In order to characterize **1** fully, it was converted into the mononuclear compound **3**. Compound **3** afforded satisfactory elemental analyses, IR, FAB^+ and NMR data. The ^1H NMR at 500 MHz and ^1H–^1H COSY and NOESY experiments at 500 MHz were consistent with the proposed structure for **3** [24] and allowed the unambiguous assignation of the signals of the H3–H6 aromatic protons. The signals of the H3 and H4 protons were quite well separated and other aromatic protons did not interfere with them. Thus, the ratio of the integrals of these two signals should give insight into the composition of samples **C** (see below).

When benzylamine and palladium(II) acetate in a one-to-one molar ratio were treated in monodeuterated acetic acid (DOAc) at 60 °C for 24 h, samples **A** were isolated in yields of 10–20%. Samples **A** were a mixture of compounds **1**, **1d1** of formula [(3-

$DC_6H_3CH_2NH_2)Pd](\mu\text{-}OAc)_2[Pd(C_6H_4CH_2NH_2)]$ and **1d2** of formula $(\mu\text{-}OAc)_2[Pd(3\text{-}DC_6H_3CH_2NH_2)]_2$. This was inferred from the ^1H NMR at 300 MHz of solutions **B**, which presented the signals corresponding to compounds **2** and **2d** of formula *trans-N,N*-[Pd(3-$DC_6H_3CH_2NH_2)(OAc)(py\text{-}d_5)$]. Solutions **B** were obtained by treating suspensions of samples **A** in $CDCl_3$ with py-d_5. The ^1H NMR in perdeuterated acetic acid of benzylamine demonstrated that benzylamine was in the $C_6H_5CH_2ND_2$ form in this solvent, but the ^1H NMR of solutions **B** showed that the amino groups of samples **A** did not present deuterium. This latter result suggested that the amino groups of the samples **A** exchanged D by H with water or methanol molecules, which were present in the eluant used for their isolation by chromatography.

In order to characterize samples **A** fully, they were converted into samples **C**. The ^1H NMR spectra at 500 MHz of samples **C** proved that they were a mixture of compounds **3** and **3d** of formula *trans-N,P*-[Pd(3-$DC_6H_3CH_2NH_2)Cl(PPh_3)$]. This was inferred from the decrease of the integral of the signal of the H3 proton in relation to the integrals of the signals of the H4–H6 protons. In addition, the ^2H NMR at 76.77 MHz of solutions in $CHCl_3$ of samples **C** presented a broad signal centred at 6.96 ppm, which was coincident with the chemical shift of the H3 proton of compound **3**, showing that deuterium was selectively located at the 3 position of the palladated phenyl ring. The ^1H NMR at 500 MHz of mixtures **C** allowed the determination of their molar composition by means of Eq. (1), where $\chi_{\mathbf{3d}}$ and r were, respectively, the mole fraction of **3d** and the ratio between the integrals of the H3 and H4 protons of the sample **C** under study.

$$\chi_{\mathbf{3d}} = 1 - r \tag{1}$$

Therefore, mole fractions of **3d** in samples **C** in the range between 0.7 and 0.9 were obtained. The mole fractions of **3d** in samples **C** were thereafter assumed to be the deuterium contents of samples **A**; because the metathesis reactions with LiCl and the splitting reactions with PPh_3, which transform samples **A** into samples **C**, should affect neither the Pd–C σ bonds nor the C–D σ bonds of samples **A**.

The presence of deuterium atoms in the 3 position of the phenyl rings of the molecules which constitute samples **A**, shows that the C–H bond activation in the cyclopalladation reaction of benzylamine is a reversible process in acetic acid. Furthermore, it is consistent with the C–H bond activation taking place in an intramolecular mode, in accordance with the general mechanism accepted for the cyclometallation reaction [25].

In a last reaction, benzylamine and palladium(II) acetate in a one-to-one molar ratio were treated under reflux of glacial acetic acid for 45 min. In these reaction conditions, the formation of palladium(0) was observed. The palladium(0) was separated by filtration and the reaction solution was concentrated under vacuum. Elution of the residue of the reaction solution through a SiO_2 column with a solution of methanol in chloroform in a 6-to-100 volume ratio, allowed the isolation of the acetato bridged *endo*-cyclopalladated dimer of benzyl-benzylidene-amine of formula $(\mu\text{-}OAc)_2$-$[Pd(C_6H_4CH{=}NCH_2C_6H_5)]$ (compound **4**). It should be noted that other compounds formed in this latter reaction could not be identified.

Compound **4** was isolated in a 14% yield in relation to the initial palladium(II) acetate and it was characterized by its ^1H NMR at 200 MHz in $CDCl_3$. This ^1H NMR spectrum was identical to that of a sample of **4** prepared by reacting benzyl-benzylidene-amine with palladium(II) acetate [26]. Furthermore, a $CDCl_3$ solution of **4** reacted with py-d_5 to form quantitatively compound **5**, which was characterized by its ^1H NMR in $CDCl_3$ solution (see Section 3). Experiments for clarifying the mechanism of the transformation of benzylamine in compound **4** when benzylamine is treated in refluxing glacial acetic acid in presence of palladium(II) acetate are currently in progress.

3. Experimental

3.1. General comments and materials

Elemental analyses of C, H and N were performed with an Eager 1108 microanalyzer. IR spectra were recorded on a Nicolet Impact-400 spectrophotometer using pressed discs of diluted samples of compounds **1** and **3** in KBr. ^1H NMR spectra in $CDCl_3$ were recorded at 500 MHz on a Bruker DMX 500 instrument, at 300 MHz on a Varian Unity 300 instrument and at 200 MHz on a Varian Gemini-200 instrument. The $^{31}P\{^1H\}$ NMR spectrum in $CHCl_3$ was recorded at 101.26 MHz on a Bruker DRX 250 instrument. ^2H NMR spectra in $CHCl_3$ at 76.77 MHz were recorded on a Bruker DMX 500 instrument. Chemical shifts are reported in δ values (ppm) relative to $SiMe_4$ for ^1H, 85% H_3PO_4 for ^{31}P and C_3H_6O-d_6 for ^2H. FAB^+ mass spectra were obtained with a VG-Quatro Fisions instrument, using 3-nitrobenzylalcohol as matrix. All chemicals were of commercial grade and used as received. Solvents were distilled before use as follows: $CHCl_3$ over CaO; C_3H_6O and MeOH over $CaCl_2$ and Et_2O over Na and benzophenone.

3.2. Preparation of *1*

3.2.1. Method A

A suspension formed by 2.22×10^{-3} mol (0.500 g) of $Pd(OAc)_2$, 2.22×10^{-3} mol (0.238 g) of benzylamine and 30 cm^3 of $C_6H_5CH_3$ was stirred at 60 °C for 24 h.

The resulting yellow suspension was concentrated under vacuum and the residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 6-to-100 volume ratio. The most polar band was collected and concentrated under vacuum. Addition of C_3H_6O (4 cm^3) to the residue produced the precipitation of **1** as a yellow powder, which was filtered and dried under vacuum. Yields were in the range between 40 and 75%.

3.2.2. Method B

A suspension formed by 2.22×10^{-3} mol (0.500 g) of $Pd(OAc)_2$, 2.22×10^{-3} mol (0.238 g) of benzylamine and 30 cm^3 of glacial AcOH was stirred at 60 °C for 24 h. The resulting red solution was concentrated under vacuum and the residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 6-to-100 volume ratio. The most polar band was collected and concentrated under vacuum. Addition of C_3H_6O (4 cm^3) to the residue produced the precipitation of **1** as a yellow powder, which was filtered and dried under vacuum. Yields were in the range between 20 and 40%.

3.3. Preparation of *2*

A suspension formed by 0.020 g of **1** and 0.7 cm^3 of $CDCl_3$ was treated with four drops of Py-d_5. The formation of a colourless solution was indicative of the quantitative transformation of compound **1** into **2**.

3.4. Preparation of *3*

A suspension formed by 0.075 g of **1** (1.38×10^{-4} mol), 0.023 g of LiCl (5.52×10^{-4} mol), 0.144 g of PPh_3 (5.52×10^{-4} mol) and 15 cm^3 of C_3H_6O was stirred at room temperature (r.t.) for 15 min. The suspension formed was concentrated under vacuum and the residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 4-to-100 volume ratio. The pale yellow band was collected and concentrated under vacuum. Addition of Et_2O (4 cm^3) to the residue produced the precipitation of **3** as a pale yellow powder, which was filtered and dried under vacuum. Yield: 57% (0.081 g).

3.5. Preparation of samples *A*

A suspension formed by 2.22×10^{-3} mol (0.500 g) of $Pd(OAc)_2$, 2.22×10^{-3} mol (0.238 g) of benzylamine and 5 cm^3 of monodeuterated AcOH (DOAc) was stirred at 60 °C for one day. The resulting red solution was concentrated under vacuum and the residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 6-to-100 volume ratio. The most polar band was collected and concentrated under vacuum. Addition of C_3H_6O (4 cm^3) to the residue produced the precipitation of sample **A** as a yellow powder, which was filtered and dried under vacuum. Yields were in the range between 10 and 30% and deuterium contents in the range between 0.7 and 0.9.

3.6. Preparation of solutions *B*

A suspension formed by 0.020 g of sample **A** and 0.7 cm^3 of $CDCl_3$ was treated with four drops of Py-d_5. The formation of a colourless solution was indicative of the quantitative transformation of the solid sample **A** into solution **B**.

3.7. Preparation of samples *C*

A suspension formed by 0.080 g of sample **A** (1.47×10^{-4} mol), 0.025 g of LiCl (5.89×10^{-4} mol), 0.154 g of PPh_3 (5.89×10^{-4} mol) and 15 cm^3 of C_3H_6O was stirred at r.t. for 15 min. The suspension formed was concentrated under vacuum and the residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 4-to-100 volume ratio. The pale yellow band was collected and concentrated under vacuum. Addition of Et_2O (4 cm^3) to the residue produced the precipitation of sample **C** as a pale yellow powder, which was filtered and dried under vacuum. Yields were in the range between 50 and 65% and the mole fractions of **3d** in the range between 0.7 and 0.9.

3.8. Preparation of *4*

A suspension formed by 2.22×10^{-3} mol (0.500 g) of $Pd(OAc)_2$, 2.22×10^{-3} mol (0.238 g) of benzylamine and 30 cm^3 of glacial AcOH was treated under reflux of AcOH for 45 min. The reaction mixture was filtered thorough a 2 cm path of celite and the red solution was concentrated under vacuum. The resulting residue was eluted through a silica gel column with a solution of MeOH in $CHCl_3$ in a 6-to-100 volume ratio. The orange band was collected and concentrated under vacuum. Addition of Et_2O (5 cm^3) to the residue produced the precipitation of **4** as an orange powder, which was filtered and dried under vacuum. Yield [relative to the initial palladium(II) acetate]: 14% (0.112 g).

3.9. Preparation of *5*

An amount of 0.020 g of **4** was dissolved in 0.7 cm^3 of $CDCl_3$ and the resulting orange solution was treated with four drops of Py-d_5. A change of colour from orange to yellow was indicative of the quantitative transformation of compound **4** into **5**.

3.10. Characterization data

3.10.1. Compound **1**

Anal. Calc. for $C_{18}H_{22}N_2O_4Pd_2$: C, 39.8; H, 4.0; N, 5.2. Found: C, 39.8; H, 4.1; N, 5.0%. FAB$^+$ (most intense peaks): 542 ([M]$^+$), 483 ([M−OAc]$^+$), 212 ([M/2−OAc]$^+$). IR (cm^{-1}): 3293, 3231 st N–H, 1570 st as (carboxylato), 1410 st s (carboxylato).

3.10.2. Compound **2**

^{1}H NMR (300 MHz, $CDCl_3$): 6.97–6.93 (2H, H3 and H4), 6.77 t $^3J_{HH} = 6$ Hz (1H, H5), 6.19 d $^3J_{HH} = 6$ Hz (1H, H6), 5.20 br signal (2H, CH_2), 4.12 t $^3J_{HH} = 6$ Hz (2H, NH_2), 1.90 s (3H, OAc).

3.10.3. Compound **3**

Anal. Calc. for $C_{25}H_{23}ClNPPd$: C, 58.9; H, 4.5; N, 2.7. Found: C, 59.6; H, 4.7; N, 2.6%. FAB$^+$ (most intense peak): 475 ([M−Cl]$^+$). IR (cm^{-1}): 3236, 3180 st N–H, 1094 *q* X-sensitive mode of the coordinated PPh_3. ^{1}H NMR (500 MHz, $CDCl_3$): 7.71–7.30 (15H, PPh_3), 6.96 d $^3J_{HH} = 7$ Hz (1H, H3), 6.81 t $^3J_{HH} = 7$ Hz (1H, H4), 6.39 t $^3J_{HH} = 7$ Hz (1H, H5), 6.34 t $^3J_{HH} = {}^4J_{PH} = 7$ Hz (1H, H6), 4.28 br signal (2H, CH_2), 3.91 br signal (2H, NH_2). ^{31}P{^{1}H} NMR (101.26 MHz, $CHCl_3$): 40.87 s.

3.10.4. Compound **2d**

^{1}H NMR (300 MHz, $CDCl_3$): 6.93 d $^3J_{HH} = 6$ Hz (1H, H4). The rest of the signals are coincident with those of compound **2**.

3.10.5. Compound **3d**

^{1}H NMR (500 MHz, $CDCl_3$) (selected data): 6.81 d $^3J_{HH} = 7$ Hz (1H, H4). The rest of the signals are coincident with those of compound **3**. ^{2}H NMR (76.77 MHz, $CHCl_3$): 6.96 br signal.

3.10.6. Compound **4**

Its ^{1}H NMR is coincident with that previously reported [26].

3.10.7. Compound **5**

^{1}H NMR (300 MHz, $CDCl_3$): 7.70 s (1H, CH=N), 7.40–7.35 (5H, *Ph*CH_2), 7.15 d $^3J_{HH} = 7$ Hz (1H, H3), 6.97 t $^3J_{HH} = 7$ Hz (1H, H4), 6.89 t $^3J_{HH} = 7$ Hz (1H, H5), 6.23 d $^3J_{HH} = 7$ Hz (1H, H6), 4.86 s (2H, CH_2), 1.91 s (3H, OAc).

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