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Cyclometallation of anthracen-9-ylmethylene-phenyl-amine by palladium(II) compounds

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Abstract

The cyclometallation of anthracen-9-ylmethylene-phenyl-amine with palladium(II) acetate and with the system $PdCl_2$, NaCl and $NaOAc{\cdot}3H_2O$ is studied. In both cases, the C1–H bond activation of the anthracen-9-yl group takes place, affording an entry to a new type of endocyclic six-membered cyclopalladated organic imine that contains a metallated aromatic carbon atom.

Keywords: Cyclometallation; Palladium

1. Introduction

Since Onoue and Moritani reported the first examples of cyclometallated organic imines [1], there has been unbroken interest in the synthesis and applications of compounds of this type, and Refs. [2–4] describe some recent advances in this subject.

It is well known [5–10] that cyclo*ortho* palladation of benzyl-benzylidene-amines yields endocyclic cyclo*ortho*-palladated compounds in which the nitrogen–carbon double bond is included in the metallacycle. Five- and six-membered exocyclic cyclo*ortho* palladated benzylidene-amines can be obtained if the hydrogens in the *ortho* positions, which give rise to the endocyclic compounds, are replaced by chloro, fluoro or methoxy substituents [11–14]. Alternatively, exocyclic cyclo*ortho* palladated imines have been prepared by treating bis[2-(benzyl-imino-methyl)-phenolato-(*N*,*O*)]-palladium(II) complexes with acetic acid [15,16] or by oxidative addition of benzylidene-(2-bromobenzyl)-amines to palladium(0) compounds [9,17]. Furthermore, 2,4,6-trimethylbenzylidene-amines allow the preparation of endocyclic six-membered cyclopalladated compounds with a metallated benzylic carbon atom [5,6,18–20]. Thus, Fig. 1 shows the five fundamental structures (**A**–**E**) found for the metallacycle of cyclopalladated organic imines. It should be noted that the cyclometallated organic imines containing metal centres other than palladium(II) described to date present the **A** structure [21–32], except for one ruthenium(III) complex [33] and a few platinum(IV) complexes [34], which contain the **B** metallacycle.

In this paper, we present the cyclometallation of anthracen-9-ylmethylene-phenyl-amine with palladium-(II) acetate and with the system $PdCl_2$, NaCl and $NaOAc{\cdot}3H_2O$. In both cases, the C1–H bond activation of the anthracen-9-yl group takes place, affording an entry to a new type of endocyclic six-membered cyclopalladated organic imine that contains a metallated aromatic carbon atom.

2. Results and discussion

Scheme 1 shows the new compounds prepared and the numbering of the hydrogen and carbon atoms for the following discussion.

Anthracen-9-ylmethylene-phenyl-amine (**1**) was prepared in a condensation reaction between anthracen-9-carbaldehyde and phenylamine in refluxing ethanol, as described elsewhere [35]. This condensation reaction and its work-up were straightforward and produced, in good yield, imine **1** as yellow needles that gave satisfactory elemental analyses, FAB^+, IR and ^1H-NMR spec-

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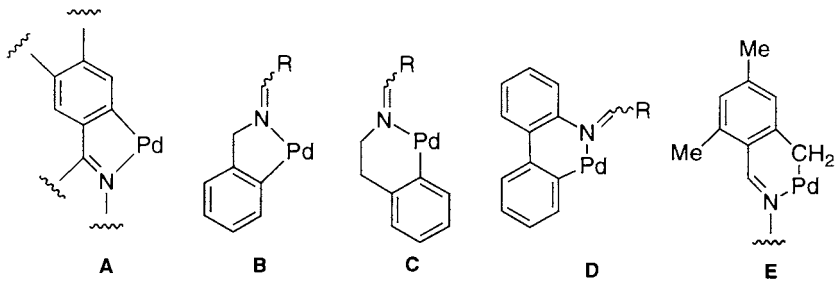


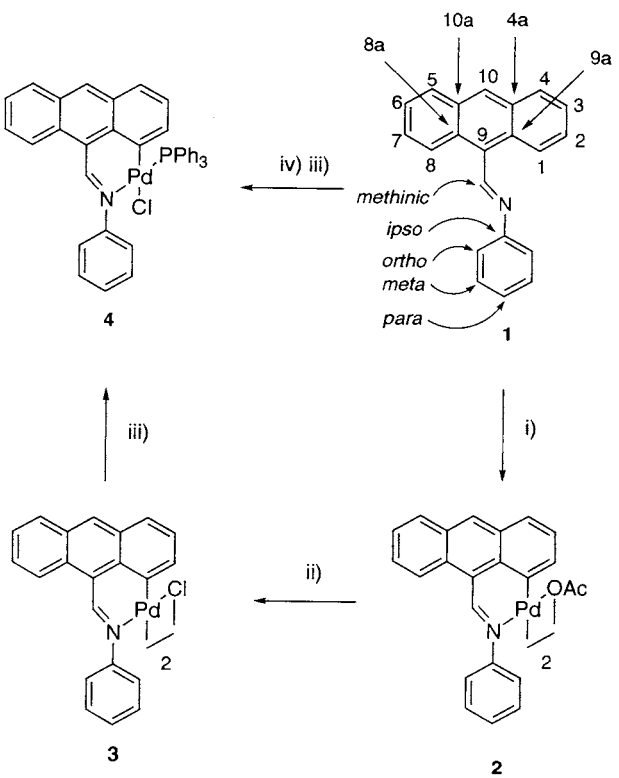
Fig. 1. General structures for the metallacycle of cyclopalladated organic imines.

tra. In the infrared, the C=N stretching appears at 1622 cm^{-1} and in the FAB^+, the base peak corresponds to $[M+H]^+$. The ^{1}H-NMR spectrum of **1** shows only one set of signals. This result indicates that imine **1** adopts only one configuration around the C=N bond which, according to the literature [35], we assume to be the *E* configuration. A NOESY experiment for **1** was consistent with this assumption since the methinic hydrogen showed NOE with the hydrogens in an *ortho* position to the iminic nitrogen.

The cyclometallation reactions of **1** with palladium(II) acetate in acetic acid at 60°C for 4 h and in $CHCl_3$ at −10°C for 3 days were studied. In both cases, deep red solutions were formed from which the new acetato-bridged six-membered cyclopalladated dimer **2** was isolated in 60 and 40% yield, respectively, after purification of the crude reactions by column chromatography.

Compound **2** gives satisfactory elemental analyses, FAB^+, IR and ^{1}H-NMR spectra. In the IR the asymmetric and symmetric stretchings of the carboxylate groups appear at 1576 and 1410 cm^{-1}, respectively, indicating that the acetato ligands present a bidentate bridging coordination mode [36]. Also in the FAB^+, the base peak corresponds to $[M/2-OAc-Pd]^+$, which is not the usual base peak for cyclopalladated dimers [37] and we assign it to the radical organic cation shown in Fig. 2. The ^{1}H-NMR spectrum of **2** in $CDCl_3$ at room temperature (r.t.) shows only one set of signals, and the acetato bridging ligands give a singlet at 1.38 ppm. These results indicate that the cyclopalladated dimer **2** adopts a *trans* configuration [38]. A combination of ^{1}H–^{1}H COSY and NOESY experiments allowed the assignation of the H2 hydrogen and this hydrogen resonates as a doublet of doublets with coupling constants of 7 and 1 Hz, which is consistent with the absence of the H1 hydrogen in compound **2**. Moreover, the high-field shift of the methinic hydrogen in relation to the free imine (1.57 ppm) was also consistent with the endocyclic structure of **2** [13].

Compound **2** reacted with LiCl in acetone, yielding the chloro-bridged cyclopalladated dimer **3**, which was insoluble in $CDCl_3$, but gave satisfactory elemental analyses, FAB^+ and IR. Moreover, **3** reacted with PPh_3 affording the mononuclear compound **4**, which was fully characterised by elemental analyses, FAB^+, IR and NMR spectroscopy. The NMR data of **4** show that the PPh_3 ligand is in the *trans* position to the iminic nitrogen atom, which was inferred from the chemical



Scheme 1. (i) $Pd(OAc)_2$, HOAc, 60°C, 4 h or $Pd(OAc)_2$, $CHCl_3$, −10°C, 3 days; (ii) LiCl, acetone, (iii) PPh_3, acetone, (iv) $PdCl_2$, NaCl, $NaOAc{\cdot}3H_2O$, MeOH, r.t., 3 days.

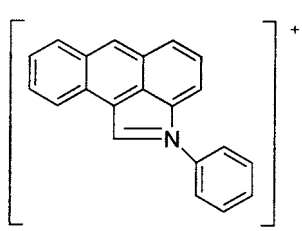


Fig. 2. Proposed structural formula for the base peak of **2** in the FAB^+.

shift of the phosphorus atom (37.23 ppm) and the coupling constant between the methinic hydrogen and the phosphorus atom (10 Hz) [12,19]. Furthermore, a combination of $^1H-^1H$ COSY and NOESY experiments for **4** allowed the unambiguous assignation of the H3 hydrogen, and its chemical shift (6.42 ppm) was a diagnostic for both the *trans* arrangement of the PPh_3 ligand in relation to the iminic nitrogen and the bonding of the palladium atom to the carbon 1 of the imine ligand [39].

The results obtained in the reactions between **1** and palladium(II) acetate show that this imine is quite prone to cyclopalladation. This prompted us to verify its cyclopalladation by the system $PdCl_2$, NaCl and $NaOAc{\cdot}3H_2O$, which is known to be a less active metallating agent than palladium(II) acetate [40].

Thus, imine **1** was treated with $PdCl_2$, NaCl and $NaOAc{\cdot}3H_2O$ in a molar ratio of 1:1:2:1 in methanol at r.t. for 3 days and the suspension formed was concentrated in vacuum, but attempts to purify the crude reaction by recrystallization or chromatography were unsuccessful due to its poor solubility in organic solvents. Nevertheless, treatment of the crude reaction with PPh_3 and subsequent purification by column chromatography allowed the isolation of compound **4** in 25% yield, showing that the system $PdCl_2$, NaCl and $NaOAc{\cdot}3H_2O$ is also active in promoting the C1–H bond activation of **1**.

3. Experimental

3.1. Instruments and reagents

Elemental analyses of C, H and N were performed with an Eager 1108 microanalyser. IR spectra were recorded on a Nicolet 520-FTIR spectrophotometer using KBr pellets. ^1H-NMR at 500 MHz (mono- and bi-dimensional experiments) were recorded on Varian Unity Inova 500 or Bruker Avance DMX 500 instrument. The $^{31}P\{^1H\}$-NMR at 101.2 MHz was recorded on a Bruker DRX-250 instrument. Chemical shifts (ppm) were measured relative to $SiMe_4$ for ^1H and to trimethylphosphite for ^{31}P. 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: chloroform over CaO; acetone, ethanol and methanol over $CaCl_2$ and diethyl ether over sodium and benzophenone.

3.2. Preparation of *1*

A 2×10^{-2} mol (4.125 g) sample of anthracene-9-carbaldehyde was treated with 2×10^{-2} mol (1.862 g) of phenylamine in ethanol (30 cm^3) at reflux for 4 h. The boiling solution was filtered and allowed to cool, whereupon most of imine **1** separated as yellow needles, which were filtered and dried under vacuum. Yield: 80% (4.501 g).

3.3. Preparation of *2* in acetic acid

A suspension formed by 2.22×10^{-3} mol (0.500 g) of $Pd(OAc)_2$, 2.22×10^{-3} mol (0.626 g) of **1** and 30 cm^3 of acetic acid was stirred at 60°C for 4 h. The resulting red solution was concentrated in vacuum and the residue was eluted through a column of SiO_2 with $CHCl_3$–methanol (100:4). The intense red band was collected and concentrated under vacuum. Addition of diethyl ether (10 cm^3) to the residue produced the precipitation of **2** as an intense red powder, which was filtered and dried under vacuum. Yield: 60% (0.594 g).

3.4. Preparation of *2* in chloroform

A 2.22×10^{-3} mol (0.500 g) sample of $Pd(OAc)_2$ was added at -10°C to a solution of 2.22×10^{-3} mol (0.626 g) of **1** and 30 cm^3 of chloroform and the suspension was stirred for 3 days at -10°C. The resulting red solution was concentrated under vacuum at -10°C and the residue was eluted through a SiO_2 column with $CHCl_3$–methanol (100:4). The intense red band was collected and concentrated under vacuum. Addition of diethyl ether (10 cm^3) to the residue produced the precipitation of **2** as an intense red powder, which was filtered and dried under vacuum. Yield: 40% (0.396 g).

3.5. Preparation of *3*

A solution formed by 5.60×10^{-4} mol (0.500 g) of **2** and 20 cm^3 of acetone was treated with 1.12×10^{-3} mol (0.047 g) of LiCl and the resulting suspension was stirred at r.t. for 30 min. After that, 100 cm^3 of water was added to the suspension and the stirring was continued for 30 min. The precipitate was filtered and dried under vacuum. Yield: 89% (0.378 g).

3.6. Preparation of *4*

A suspension formed by 1.18×10^{-4} mol (0.100 g) of **3**, 2.36×10^{-4} mol (0.062 g) of PPh_3 and 20 cm^3 of acetone was stirred at r.t. for 30 min. The resulting suspension was concentrated in vacuum and the residue was eluted through a column of SiO_2 with $CHCl_3$–methanol (100:2). The orange band was collected and concentrated in vacuum. Addition of diethyl ether (6 cm^3) to the residue produces the precipitation of **4** as a red powder, which was filtered and dried under vacuum. Yield: 67% (0.108 g).

3.7. Cyclometallation of **1** by the system $PdCl_2$, NaCl and $NaOAc \cdot 3H_2O$

A suspension formed by 1.41×10^{-3} mol (0.397 g) of **1**, 1.41×10^{-3} mol (0.250 g) of $PdCl_2$, 2.42×10^{-3} mol (0.141 g) of NaCl, 1.41×10^{-3} mol (0.191 g) of $NaOAc \cdot 3H_2O$ and 20 cm^3 of methanol was stirred at r.t. for 3 days. After that, the suspension was concentrated under vacuum and 1.41×10^{-3} mol (0.370 g) of PPh_3 and 20 cm^3 of acetone were added to the residue. The resulting suspension was stirred at r.t. for 30 min and then concentrated under vacuum. The residue was eluted through a column of SiO_2 with $CHCl_3$–methanol (100:2) and the orange band was collected and concentrated under vacuum. Addition of diethyl ether (6 cm^3) to the residue produced the precipitation of **4** as a red powder, which was filtered and dried in vacuum. Yield: 25% (0.238 g).

3.8. Characterisation data

1: Anal. Calc. for $C_{21}H_{15}N$: C, 89.65; H, 5.38; N, 4.96. Found: C, 89.6; H, 5.4; N, 4.9%. FAB^+ (selected data): 282 ($[M+H]^+$). IR (cm^{-1}): 1622 st (C=N). ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): 9.67 s (CH=N), 8.74 dd, $^3J_{HH} = 8.5$, $^4J_{HH} = 1.0$ Hz (H1 and H8), 8.54 s (H10), 8.04 dt, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.0$ Hz (H4 and H5), 7.55 m (H2 and H7), 7.52–7.48 m (H3, H6 and *m*-Ph), 7.42 dd, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.0$ Hz (*o*-Ph), 7.32 tt, $^3J_{HH} = 6.0$, $^4J_{HH} = 1.0$ Hz (*p*-Ph).

2: Anal. Calc. for $C_{46}H_{34}N_2O_4Pd_2$: C, 61.97; H, 3.84; N, 3.14. Found: C, 61.5; H, 4.1; N, 3.1%. FAB^+ (selected data): 445 ($[M/2]^+$), 386 ($[M/2-OAc]^+$), 280 ($[M/2-OAc-Pd]^+$). IR (cm^{-1}): 1608 st (C=N), 1576 st as (OAc), 1410 st s (OAc). ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): 8.12 s (CH=N), 8.08 dd, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$ Hz (H2), 7.96 s (H10), 7.79 d, $^3J_{HH} = 8.0$ Hz (H4), 7.55 t, $^3J_{HH} = 7.5$ Hz (H3), 7.42 m (H5), 7.30 t, $^3J_{HH} = 8.0$ Hz (*m*-Ph), 7.24–7.20 m (H6, H7 and *p*-Ph), 7.11 m (H8), 6.94 d, $^3J_{HH} = 7.5$ Hz (*o*-Ph), 1.38 s (OAc).

3: Anal. Calc. for $C_{42}H_{28}N_2Cl_2Pd_2$: C, 59.74; H, 3.34; N, 3.32. Found: C, 60.2; H, 3.3; N, 3.3%. FAB^+ (selected data): 386 ($[M/2-Cl]^+$), 280 ($[M/2-Cl-Pd]^+$). IR (cm^{-1}): 1608 st (C=N).

4: Anal. Calc. for $C_{39}H_{29}NClPPd$: C, 68.43; H, 4.27; N, 2.05. Found: C, 68.2; H, 4.4; N, 2.2%. FAB^+ (selected data): 648 ($[M-Cl]^+$). IR (cm^{-1}): 1617 st (C=N), 1093 *q* X-sensitive mode of the coordinated PPh_3. ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): 9.10 d, $^4J_{PH} = 10$ Hz (CH=N), 8.54 s (H10), 8.39 d, $^3J_{HH} = 8.5$ Hz (H8), 8.06 d, $^3J_{HH} = 8.5$ Hz (H5), 7.73 d, $^3J_{HH} = 8.5$ Hz (*o*-PhN), 7.70 t, $^3J_{HH} = 7.5$ Hz (H7), 7.54 t, $^3J_{HH} = 7.0$ Hz (H6), 7.50–7.43 m (*m*-PhN, *o*-PhP), 7.37 d, $^3J_{HH} = 8.5$ Hz (H4), 7.31 m (*p*-PhP), 7.29 t, $^3J_{HH} = 7.5$ Hz (*p*-PhN), 7.23–7.20 m (*m*-PhP and H2), 6.42 t, $^3J_{HH} = 8.0$ Hz (H3). $^{31}P\{^1H\}$-NMR (101.2 MHz, $CHCl_3$, 298 K): 37.23.

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