ELSEVIER

Journal of Organometallic Chemistry 522 (1996) 87–95

Journal of Organometallic Chemistry

Cyclometallation of 2-phenylaniline and (*R*)-α-methylbenzylamine by palladium(II) acetate. X-ray molecular structure of $[Pd\{2\text{-}(2'\text{-}NH_2C_6H_4)C_6H_4\}Br(PPh_3)]$

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Received 13 November 1995

Abstract

The action of palladium(II) acetate on the primary amines 2-phenylaniline and (*R*)-α-methylbenzylamine and subsequent treatment with LiBr allows the preparation of the corresponding cyclopalladated dimers $[Pd(C\text{–}N)Br]_2$ (**1a** and **1b** respectively). Mononuclear compounds $[Pd(C\text{–}N)Br(L)]$, **3** (L = py-d_5) and **2** (L = PPh_3), have been obtained by reaction of **1** with py-d_5 and PPh_3. Addition of PPh_3 to chloroform solutions of **2** produces a rapid exchange between coordinated and free PPh_3. $^{31}P\{^1H\}$ NMR at variable temperature suggests that this exchange proceeds for **2a** through the fast equilibrium $[Pd(C\text{–}N)Br(PPh_3)_2] \Leftrightarrow [Pd(C\text{–}N)Br(PPh_3)] + PPh_3$, while the usual mechanism in substitution reactions in d^8 planar square complexes is involved in the case of **2b**. The X-ray crystal structure of **2a** has been determined. **2a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.182(3)$, $b = 10.502(2)$, $c = 9.998(2)$ Å, $\alpha = 99.24(2)$, $\beta = 94.69(2)$ and $\gamma = 99.13(2)°$.

Keywords: Palladium; Cyclometallation; Amines; X-ray structure

1. Introduction

Since Kleiman, Cope and coworkers [1] described the first examples of cyclometallation reactions, there has been continuous interest in the study of these processes, not only for their contribution to the elucidation of the mechanisms of C–H activation by metal centres [2], but also for their applications, among these their use in organic synthesis [3] and in the design of new metallomesogens [4], photoactive compounds [5], molecular receptors [6], antitumoral drugs [7] and organometallic polymers [8] are remarkable.

Although many suitable organic molecules undergo cyclopalladation with the tetrachloropalladate(II) anion [9], there are some that fail to undergo this reaction with this metallating agent, among them the primary and secondary benzylamines. The reaction of an excess of these amines with $[PdCl_4]^{2-}$ generally gives only the coordination compounds $[PdCl_2(L)_2]$ [10]. Ryabov [2] has justified this result by their unfavourable equilibrium constant to form the coordinately unsaturated complex $[PdCl_2(L)]$ (the necessary intermediate to produce cyclopalladation) from the starting coordination compounds $[PdCl_2(L)_2]$. Nevertheless, Cockburn et al. [11] and Dunina and coworkers [12,13] have achieved cyclometallation with $[PdCl_4]^{2-}$ of the following hindered primary and secondary benzylamines: α,α-diphenylbenzylamine, N-methyl-α-methylbenzylamine, N-methyl-α,α-diphenylbenzylamine, N-isopropyl-α-methylbenzylamine and N-isopropyl-α-(2-naphthyl)ethylamine. Ryabov et al. [14] have found that, for cyclopalladation of N,N-dimethylbenzylamines with palladium(II) acetate in chloroform solution, the C–H activation is the rate determining step. The activation parameters ($\Delta H^{\ddagger} = 11$ kJ mol^{-1} and $\Delta S^{\ddagger} = -254$ J K^{-1} mol^{-1}) are consistent with an early highly ordered transition state in which the formation of the metal–carbon bond dominates and the leaving proton is accepted by the acetato ligand (Fig. 1). Thereafter, the results obtained by Cockburn, Dunina and coworkers [11–13], if they denote a kinetic effect, should be explained by a more favorable $\Delta S^{\ddagger}$ for hindered primary and secondary benzylamines, as a consequence of

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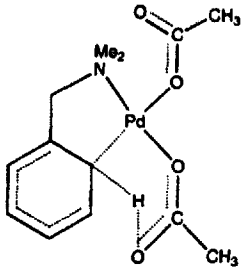


Fig. 1.

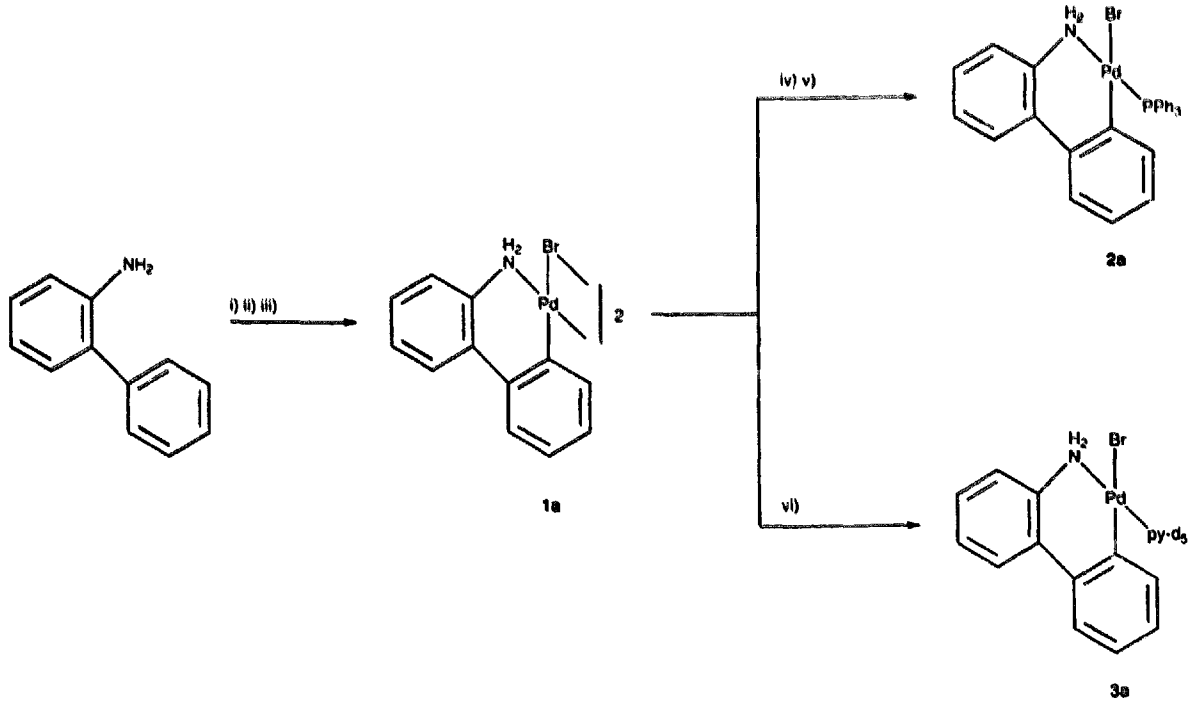
the loss of rotational entropy once they are coordinated to the metal.

Avshu et al. [15] and Vicente et al. [16] have also found that upon reaction of the coordination compounds $[PdI_2(benzylamine)_2]$ and $[PdCl_2(\alpha\text{-methylbenzylamine})_2]$ with $AgBF_4$ in ethylacetate or $AgClO_4$ in acetone respectively, the corresponding solvated species $[Pd(L)_2(S)_2]^{2+}$ undergo cyclopalladation. These results have been explained by the increase of the electrophilic character of palladium(II) in the solvated species and the lability of their solvent molecules, which gives an entry to coordinately unsaturated intermediate complexes. Furthermore, Fuchita and coworkers [17] and Vicente et al. [18] have recently reported the cyclopalladation by palladium(II) acetate of the primary and secondary benzylamines $C_6H_5CH_2NHR$ (R = hydrogen, methyl, isopropyl, phenyl and neopenthyl) and (*S*)-α-methyl-4-nitrobenzylamine. Surprisingly, these cyclopalladation reactions proceed with good yields (50–90%). These results are explained by the better electrophilic character of palladium(II) acetate in relation to $[PdCl_4]^{2-}$ and the easier generation of coordinately unsaturated species from the coordination compounds $[Pd(O_2CMe)_2(L)_2]$ in relation to $[PdCl_2(L)_2]$, owing to the larger effective volume of the acetato ligand than the chloro ligand. In this work we present, as an extension of these latter findings, the cyclometallation by palladium(II) acetate of the primary amines 2-phenylaniline and (*R*)-α-methylbenzylamine.

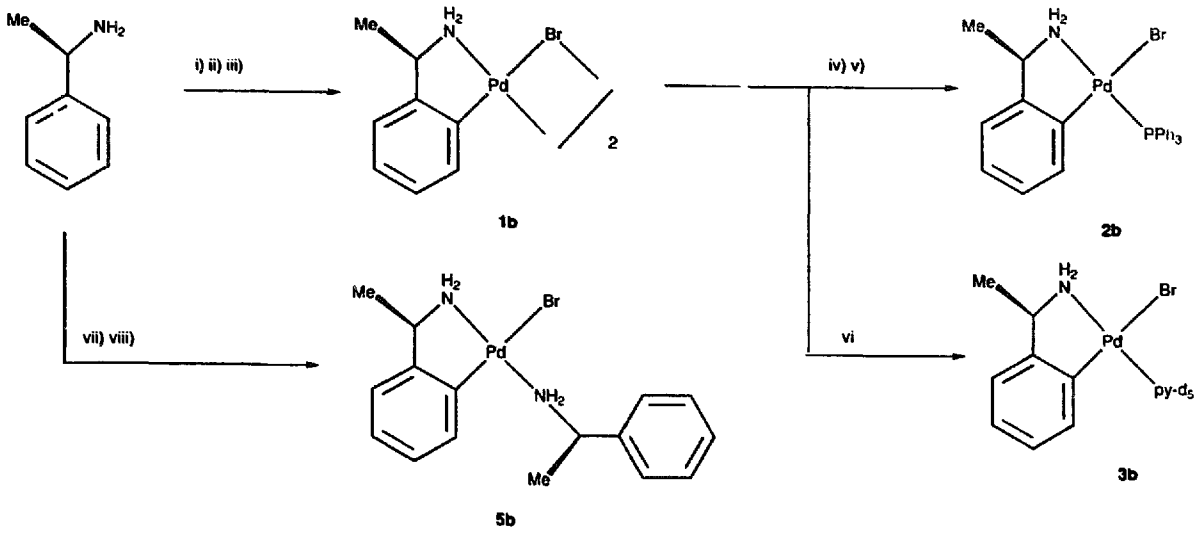
2. Results and discussion

2.1. Cyclopalladation reactions

Cyclopalladation of the primary amines 2-phenylaniline and (*R*)-α-methylbenzylamine with palladium(II) acetate is best performed under mild conditions. Thus, when palladium(II) acetate was treated in toluene with 2-phenylaniline or (*R*)-α-methylbenzylamine, in molar ratio 1 : 1, at room temperature with continuous stirring for 1 day, a deep red suspension or solution was obtained respectively. In both cases the solvent was removed and the residues were treated with an excess of LiBr in ethanol with vigorous stirring at room temperature for 30 min. This latter treatment results in the formation of deep red solutions which contained the cyclopalladated dimers **1** (Schemes 1 and 2). It is remarkable that compound **1a** is the first six-membered palladacycle of a primary amine obtained by C–H activation.



Scheme 1. (i) $Pd(O_2CMe)_2$ (amine/$Pd(O_2CMe)_2$ 2 : 1), toluene, room temperature, 1 day; (ii) LiBr, EtOH, room temperature, 30 min; (iii) $SiO_2/CHCl_3/MeOH$ (100 : 2), second coloured band; (iv) PPh_3 (PPh_3/**1a** 2 : 1), acetone, room temperature, 15 min; (v) $SiO_2/CHCl_3/MeOH$ (100 : 1), yellow band; (vi) py-d_5, $CDCl_3$.



Scheme 2. (i) $Pd(O_2CMe)_2$ (amine/$Pd(O_2CMe)_2$ 1:1), toluene, room temperature, 3 days; (ii) LiBr, EtOH, room temperature, 30 min; (iii) $SiO_2/CHCl_3$/MeOH (100:2), second coloured band; (iv) PPh_3 (PPh_3/**1b** 2:1), acetone, room temperature, 15 min; (v) $SiO_2/CHCl_3$/MeOH (100:1), yellow band; (vi) py-d_5, $CDCl_3$; (vii) $Pd(O_2CMe)_2$ (amine/$PdO_2CMe)_2$ 2:1), toluene, reflux, 3 h; (viii) $SiO_2/CHCl_3$/MeOH (100:2), yellow band.

Compounds **1** were isolated in pure form, after removal of the ethanol of the latter red solutions and elution of the residues through an SiO_2 column with $CHCl_3$/MeOH (100:2). Compounds **1a** and **1b** were eluted in the second coloured band (the first coloured band contains coordination compounds) and were obtained as pale brown and pale yellow powders respectively after removal of the solvents and addition of diethylether to the residues. These samples of **1a** and **1b** retain large amounts of diethylether. Attempts to remove the diethylether by prolonged drying in vacuum only succeeded for **1b**, while **1a** gave a powder of composition **1a** · 0.58 diethylether. (The amount of diethylether retained by **1a** was determined by integration of the signals corresponding to the NH_2 protons of **3a** and the CH_2 protons of the diethylether (see reactions with py-d_5.)

1a · 0.58 diethylether and **1b** gave satisfactory elemental analyses and infrared spectra. As common features for analogous $[Pd(C,N)Br]_2$ dinuclear cyclopalladated compounds [19], the positive FAB mass spectra of **1** show intense peaks corresponding to $[M]^+$, $[M-Br]^+$ and $[M/2+Pd]^+$. Although compounds **1** were only slightly soluble in $CDCl_3$, it was possible to perform the ^1H NMR spectra in this solvent (Fig. 2 shows the hydrogen numbering scheme for ^1H NMR discussion).

The ^1H NMR spectrum of **1a** shows only one set of signals, which indicates that in solution the cyclometallated dimer **1a** consists of only a geometrical isomer which we propose, according to the literature [20], to be the *trans* isomer. Moreover, the NH_2 protons appear as a broad singlet centred at 3.74 ppm, which indicates that at room temperature the rate of conformational inversion of the six-membered palladacycles, which are not planar (see X-ray molecular structure of **2a**), lies in the fast range. Although the H^3–H^{10} aromatic protons give sharp doublets and triplets, their assignation is quite difficult because they appear in a narrow interval (7.60–6.80 ppm) and some of them overlap. The ^1H NMR spectrum of **1b** also shows only one set of signals, but in this case the signals are broad. This finding indicates a dynamic behaviour in solution which could be related to an exchange of cyclopalladated units between cyclopalladated dimers, as we have recently described for related cyclopalladated dimers of N-benzylidene-(*R*)-α-methylbenzylamines [21], but a dynamic process in-

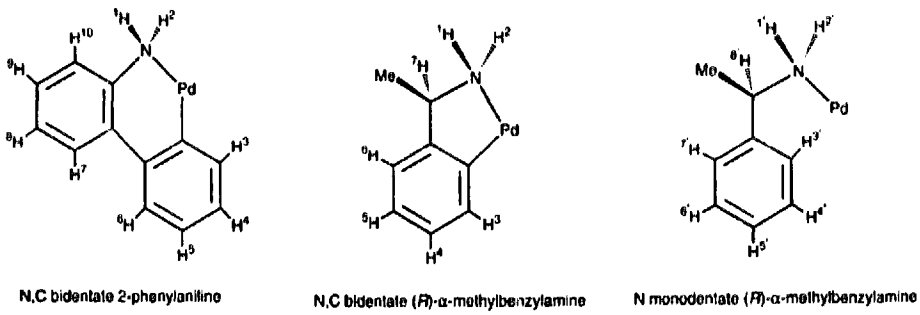


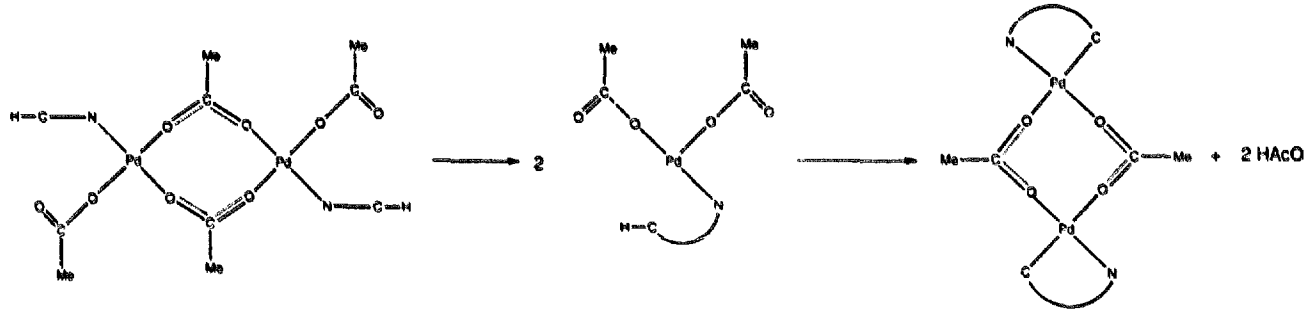
Fig. 2. Hydrogen numbering for ^1H NMR assignments.

volving conformational inversion of the five-membered metallacycles, which are not planar [21], cannot be ruled out. Under the reaction conditions discussed above, **1a** and **1b** were obtained in 35% and 17% yield respectively. Longer reaction times between (*R*)-α-methylbenzylamine and palladium(II) acetate led to an increase in the **1b** yield. Thus, when palladium(II) acetate was treated with (*R*)-α-methylbenzylamine, in molar ratio 1:1, for 3 days at room temperature, the **1b** yield increased to 44%. A longer reaction time or more drastic reaction conditions (toluene, 60°C, 1 day) did not improve the **1b** yield substantially.

In contrast, in the cyclopalladation of 2-phenylaniline with palladium(II) acetate, in molar ratio 1:1, no increase in the **1a** yield was observed, either when reaction times were longer than 1 day or when more drastic reaction conditions than stirring at room temperature were used. However, when 2-phenylaniline and palladium(II) acetate were treated in a molar ratio of 2:1 at room temperature for 1 day, the **1a** yield increased to 49%.

Interestingly, when the reaction between (*R*)-α-methylbenzylamine and palladium(II) acetate was performed in molar ratio 2:1, *ortho*-palladation was not observed. In this case, after treatment with LiBr, the coordination compound $[PdBr_2\{(R)$-α-methylbenzylamine$)_2\}]$ (**4b**) was isolated. This compound was also the major reaction product when (*R*)-α-methylbenzylamine and palladium(II) acetate, in molar ratio 2:1, were treated in toluene at 60°C for 1 day. However, when this reaction was performed in refluxing toluene, together with the coordination compound **4b**, the cyclopalladated monomer **5b** was obtained in 39% yield. Interestingly, **5b** presents two molecules of (*R*)-α-methylbenzylamine coordinated to palladium(II); one acts as an N,C bidentate ligand and the other acts as an N monodentate ligand (see Scheme 2).

4b and **5b** give satisfactory elemental analyses and infrared spectra. As common features with analogous $[PdCl_2(L)_2]$ coordination compounds [19], the positive FAB mass spectrum of **4b** shows intense peaks corresponding to $[M-Br]^+$ and $[M-Br-HBr]^+$. The latter is the base peak in the positive FAB mass spectrum of **5b**, which indicates that under the FAB conditions the coordination compound **4b** undergoes cyclopalladation. Cyclopalladation under FAB conditions has been reported in coordination [19] and organometallic [22] palladium(II) complexes. The positive FAB mass spectrum of **5b**, together with the base peak $[M-Br]^+$, shows another intense peak corresponding to the loss of the bromo ligand and the N-coordinated amine ($[M-Br-amine]^+$). The ^1H NMR spectrum of **4b** shows only one set of signals, which indicates that it consist of only a geometrical isomer which we propose, according to the literature [10], to be the *trans* isomer. The ^1H NMR spectrum of **5b** shows well separated sets of signals for the N,C- and N-coordinated amines. The H^3–H^6 aromatic protons of the *ortho*-metallated ring appear high-field shifted, owing to the magnetic anisotropy of the aromatic ring of the N-coordinated amine, which confirms the *cis* arrangement between the N-coordinated amine and the metallated carbon atom. The moderate yield in which compounds **1** are obtained suggests that cyclopalladation of these amines is not very favourable thermodynamically. Thus, the increase in the yield of cyclopalladated 2-phenylaniline when an excess of this amine is used in its cyclopalladation reaction could reflect a thermodynamic effect. However, a change in the reaction path cannot be ruled out, because in molar ratios 2:1 and 1:1 the major starting coordination compounds should be $[Pd(O_2CMe)_2(L)_2]$ (**A**) and $[(L)(MeCO_2)Pd(\mu\text{-}O_2CMe)_2Pd(O_2CMe)(L)]$ (**B**) respectively. The fact that *ortho*-palladation is not observed when (*R*)-α-methylbenzylamine and palladium(II) acetate react in molar ratio 2:1 at room temperature, suggests that the coordination compounds of class **B** are the species which evolve to undergo cyclopalladation, probably by cleavage of the acetato bridges and subsequent activation of the C–H bond at the unsaturated palladium(II) complex generated:



(1)

The faster rate of cyclopalladation of 2-phenylaniline in relation to (*R*)-α-methylbenzylamine is consistent with its lesser σ-N-donor character and its larger effective volume, which renders the starting coordination compounds more prone to undergo dissociation of the ligands and their palladium(II) centre more electrophilic.

In order to characterize the new cyclopalladated

dimers **1** more fully we have studied their reactivity towards py-d_5 and PPh_3.

2.2. Reactions with py-d_5

These reactions were performed in an NMR tube and studied by ^1H NMR. The action of an excess of py-d_5 on $CDCl_3$ suspensions of dimers **1** produces a nearly instantaneous dissolution of the precipitates. ^1H NMR of the resulting solutions reveals the formation of the cyclopalladated monomers **3** (Schemes 1 and 2). Furthermore, the lack of signals corresponding to compounds **1** indicates that these splitting reactions are quantitative. The large down-field shift of the protons of the amino group relative to the free amine confirms its coordination to the palladium atom. In the literature [23], cleavage of the Pd–N bond and formation of a monomer of formula $[Pd(C-N)X(py)_2]$ has been observed only for a very labile eight-membered metallacycle. The high-field shift of the H^3 and H^4 aromatic protons, due to the pyridine ring [17], confirms the *cis* arrangement between the py-d_5 and the metallated carbon atom. In a recent kinetic study [24], it has been shown that this arrangement of the ligands, in most cases, corresponds to the reaction product of thermodynamic control. Analysis of the aromatic region of the ^1H NMR spectra confirms the metallation. Thus, monomer **3b** shows well separated signals for all the aromatic hydrogens and gives the characteristic pattern of two doublets and two triplets for a 1,2-disubstituted aromatic ring, according to its *ortho*-palladated character. In the case of **3a**, although H^3–H^5 aromatic protons give well separated signals with the appropriate multiplicity and shifted to high-field, which renders their assignation straightforward (see Experimental part), unambiguous assignation of the H^6 aromatic proton is only possible after a COSY experiment, because one of the doublets of H^7 and H^{10} aromatic protons appears in the same region (7.40–7.80 ppm). Finally, it should be noted that the NH_2 protons of compound **3a** appear as a broad singlet, which indicates that at room temperature conformational inversion of the six-membered palladacycle lies in the fast range, as is also the case for the cyclopalladated dimer **1a**.

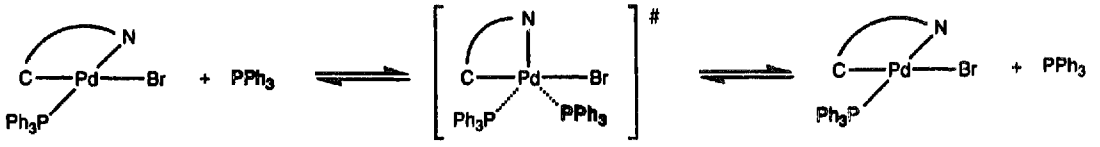
2.3. Reactions with PPh_3

The action of PPh_3 on cyclopalladated dimers **1** in molar ratio 2:1 produces the corresponding cyclopalladated monomers **2** (Schemes 1 and 2). Compounds **2** give satisfactory elemental analyses and the infrared spectra show the bands of the coordinated amine and phosphine. As common features for analogous $[Pd(C-N)Br(PPh_3)]$ mononuclear compounds [19], the positive FAB mass spectra of **2** do not present a molecular peak and the maximum m/z peak, which is the most abundant, corresponds to the loss of the bromo ligand ($[M-Br]^+$). ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** are consistent with the proposed structures. Thus the high-field shift of the H^3 and H^4 aromatic protons relative to the free amines and the chemical shift of the phosphorus atom (35.89 ppm for **2a** and 41.63 ppm for **2b**) confirm the *cis* arrangement between phosphorus and metallated carbon atoms [21].

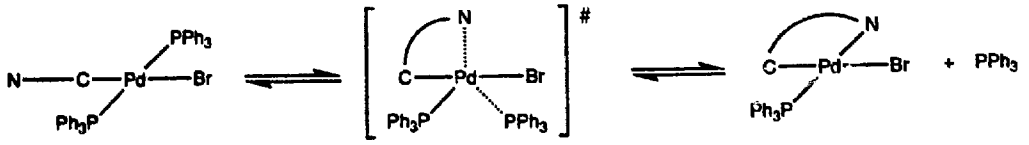
In contrast with the situation found for **1a** and **3a**, the NH_2 protons of **2a** are not isochronous, giving two broad signals centred at 5.18 and 4.92 ppm, which indicates that the rate of conformational inversion of the six-membered metallacycle lies in the slow range at room temperature. These results are consistent with those found with mononuclear derivatives of cyclopalladated 2-benzylpyridine of formula $[Pd\{2-(C_6H_4CH_2)-C_5H_4N\}Cl(L)]$, for which $\Delta G^{\ddagger}$ of the conformational inversion of the six-membered palladacycle depends only on the steric effects of the L ligand and increases with its effective volume [25].

To check the stability of the Pd–N bond of **2**, an excess of PPh_3 (1.5 mol of PPh_3 per mol of **2**) was added to chloroform solutions of these compounds. These experiments were performed in an NMR tube and studied by $^{31}P\{^1H\}$ NMR. The action of an excess of PPh_3 on the chloroform solution of **2b** does not cleave the Pd–N bond since the $^{31}P\{^1H\}$ NMR at 240 K shows two sharp signals corresponding to **2b** and PPh_3 at 43.28 and −6.29 ppm respectively. In contrast, in the experiment with **2a** at 220 K together with PPh_3 a sharp signal at 22.18 ppm was observed. This signal corresponds to the mononuclear compound *trans*-$[Pd(C-N)Br(PPh_3)_2]$ (**4a**) without the Pd–N bond [26]. The different behaviour of **2** towards PPh_3 agrees with the lower stability of the six-membered metallacycle and the presence of a less basic nitrogen atom in **2a**.

When the spectrum of **2b** in the presence of PPh_3 was recorded at higher temperatures, the signals became broader and at 310 K no signal was observed. These results indicate a fast exchange between coordinated and free PPh_3, which proceeds through the usual mechanism in substitution reactions in square planar d^8 metal complexes [27]:



When the spectrum of **4a** in the presence of PPh_3 was recorded at higher temperatures, the signals became broader and at 260 K the coalescense temperature was reached. At higher temperatures (298 K) two broad signals centred at 30.66 and 0.96 ppm appear. From these results it seems likely that **4a** exchanges PPh_3 through the fast equilibrium shown in Eq. (3), since the broad signal centred at 30.6 ppm is placed between the signals corresponding to **4a** (22.18 ppm) and **2a** (35.89 ppm):



(3)

This equilibrium is present in the solutions of many other analogous compounds of formula $[M(C-N)X(PR_3)_2]$ (M = Pd or Pt, X = Cl, Br or I and R = phenyl or alkyl) and explains some of their chemical properties, such as the reactions depicted in Eq. (4) [28]:

$$2[M(C-N)X(PR_3)_2] + [\overline{M(C-N)}X]_2 \longrightarrow 4[\overline{M(C-N)}X(PR_3)]$$

$$2[M(C-N)X(PR_3)_2] + MX_2 \longrightarrow 2[\overline{M(C-N)}X(PR_3)] + [MX_2(PR_3)_2] \quad (4)$$

2.4. X-ray crystal structure of 2a

Fig. 3 shows the molecular structure of **2a**, together with the numbering scheme, and Tables 1 and 2 give selected bond distances and angles as well as the final atomic coordinates. Selected angles between normals to planes are listed in Table 3. The crystal structure consists of discrete molecules separated by van der Waals distances. The Pd atom is in a square planar environment, coordinated to P, Br, N and C(12) atoms. The deviations from the coordination plane are as follows: Pd −0.005 Å; Br 0.013 Å; P −0.011 Å; N −0.014 Å and C(12) 0.017 Å. The distances and angles around the palladium atom are in the normal intervals [29]. The six-membered metallacycle is not planar and presents the Pd and C(12) atoms out of the plane defined by the remaining four atoms of the metallacycle: −1.683 and −0.707 Å respectively.

3. Experimental

3.1. General data

Infrared spectra were recorded on a Nicolet 520-FTIR spectrophotometer using KBr pellets. ^1H NMR at 200 MHz and $^{31}P\{^1H\}$ at 32.8 MHz were recorded respectively on Varian Gemini 200 and Bruker WP 80 SY instruments. Chemical shifts (in parts per million) were measured relative to $SiMe_4$ for ^1H and relative to 85% H_3PO_4 for ^{31}P. The solvents used were $CDCl_3$ in ^1H and $CHCl_3$ in ^{31}P. Positive FAB mass spectra were obtained with a VG-Quattro Fisions instrument, using 3-nitrobenzylalcohol as matrix. The microanalyses were performed with Carlo Erba and Eager microanalyzers. 2-phenylaniline, (*R*)-α-methylbenzylamine, palladium(II) acetate, LiBr, PPh_3, silica gel, $CDCl_3$ and py-d_5 were of commercial grade and used as received. Solvents were distilled before use as follows: chloroform and dichloromethane over CaO; acetone, ethanol and methanol over $CaCl_2$; and toluene and diethylether over sodium and benzophenone.

3.2. Preparation of 1a

A suspension formed by 2.23 mmol (0.500 g) of $Pd(O_2CMe)_2$, 4.46 mmol (0.754 g) of 2-phenylaniline and 30 cm^3 of toluene was stirred at room temperature for 1 day. The resulting suspension was concentrated in vacuum and the residue was treated with 4.46 mmol (0.387 g) of LiBr and 25 cm^3 of ethanol at room temperature with vigorous stirring for 30 min. The resulting solution was concentrated in vacuum and the residue was eluted through a column of SiO_2 with chloroform/methanol (100:2). The second coloured band was collected and concentrated in vacuum. Addition of diethylether (10 cm^3) to the residue gave **1a** as a pale brown powder which tenaciously retained diethylether. Overnight drying in vacuum gave 0.409 g (49% yield) of **1a** · 0.58 diethylether. Anal. Found: C, 42.6; H, 3.5; N, 3.7. $C_{24}H_{20}Br_2N_2Pd_2 \cdot 0.58$ diethylether Calc.: C, 42.03; H, 3.46; N, 3.72%. IR (cm^{-1}): 3249s, 3218s (ν NH_2). ^1H NMR: 7.60–6.80 (H^3–H^{10}), 3.74 br s (H^1 and H^2). Positive FAB: 709 ($[M]^+$), 631 ($[M-Br]^+$), 460 ($[M/2 + Pd]^+$).

3.3. Preparation of 1b

A suspension formed by 2.23 mmol (0.500 g) of $Pd(O_2CMe)_2$, 2.23 mmol (0.270 g) of (*R*)-α-methylbenzylamine and 30 cm^3 of toluene was stirred at room temperature for 3 days. The resulting solution was concentrated in vacuum and the residue was treated

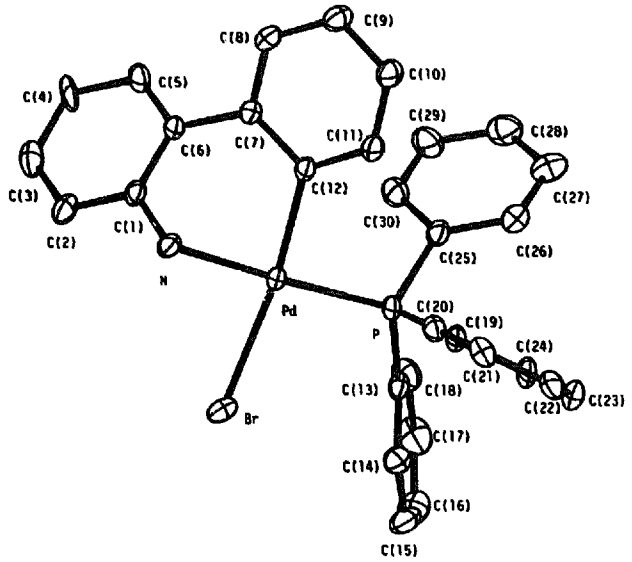


Fig. 3. X-ray molecular structure of **2a**.

with 4.46 mmol (0.387 g) of LiBr and 25 cm^3 of ethanol at room temperature with vigorous stirring for 30 min. The resulting solution was concentrated in vacuum and the residue was eluted through a column of SiO_2 with chloroform/methanol (100:2). The second coloured band was collected and concentrated in vacuum. Addition of diethylether (10 cm^3) to the residue gave 0.300 g (44%) of **1b** as a pale yellow powder. Anal. Found: C, 31.3; H, 3.4; N, 4.4. $C_{16}H_{20}Br_2N_2Pd_2$ Calc.: C, 31.34; H, 3.26; N, 4.57%. IR (cm^{-1}): 3249s, 3218s (ν NH_2). ^1H NMR: 7.40–6.60 (H^3–H^6), 4.30 br m (H^7), 3.30 br signal (H^1 and H^2), 1.56 br signal (Me). Positive FAB: 709 ($[M]^+$), 631 ($[M-Br]^+$), 414 ($[M/2 + Pd]^+$).

3.4. Reactions with py-d_5

A suspension formed by 20 mg of **1a** or **1b** and 0.7 cm^3 of $CDCl_3$ was placed in an NMR tube and treated with an excess of py-d_5 (0.060 cm^3), a nearly instantaneous formation of a solution indicated the transformation of **1** in the monomers **3**.

Table 1
Selected bond distances (Å) and angles (°) for **2a**

Bond distances		Angles	
Pd–C(12)	2.032(2)	C(12)–Pd–N	84.05(9)
Pd–N	2.101(2)	C(12)–Pd–P	92.69(7)
Pd–P	2.2580(7)	N–Pd–Br	87.48(6)
Pd–Br	2.5399(7)	P–Pd–Br	95.79(3)
N–C(1)	1.436(3)	N–Pd–P	176.71(6)
C(1)–C(6)	1.391(3)	C(12)–Pd–Br	171.46(6)
C(6)–C(7)	1.486(3)	C(1)–N–Pd	107.89(14)
C(7)–C(12)	1.411(3)	C(6)–C(1)–N	119.0(2)
		C(1)–C(6)–C(7)	120.7(2)
		C(12)–C(6)–C(7)	122.5(2)
		C(7)–C(12)–Pd	118.9(2)

Table 2
Atomic coordinates ($\times 10^4$) (Pd Br and P ($\times 10^5$)) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2a**

Atom	x	y	z	U_{eq}
Pd	32939(2)	20063(2)	17308(2)	27(1)
Br	34513(2)	7103(3)	−5986(3)	44(1)
P	19557(5)	30774(5)	10058(6)	29(1)
N	4529(2)	1057(2)	2521(2)	34(1)
C(1)	4024(2)	227(2)	3393(2)	32(1)
C(2)	4068(2)	−1101(3)	3134(3)	43(1)
C(3)	3589(3)	−1903(3)	3973(4)	53(1)
C(4)	3090(2)	−1377(3)	5078(4)	50(1)
C(5)	3063(2)	−47(3)	5336(3)	40(1)
C(6)	3516(2)	779(2)	4487(2)	29(1)
C(7)	3493(2)	2207(2)	4752(2)	29(1)
C(8)	3624(2)	2540(3)	6106(2)	38(1)
C(9)	3622(2)	4171(3)	6447(3)	42(1)
C(10)	3493(2)	4888(3)	5425(3)	41(1)
C(11)	3384(2)	4263(2)	4062(3)	37(1)
C(12)	3367(2)	2929(2)	3692(2)	31(1)
C(13)	1012(2)	2267(2)	−529(2)	33(1)
C(14)	1400(2)	2282(3)	−1798(3)	43(1)
C(15)	710(3)	1724(3)	−2971(3)	53(1)
C(16)	−381(3)	1123(3)	−2898(4)	61(1)
C(17)	−773(3)	1088(4)	−1661(4)	62(1)
C(18)	−67(2)	1654(3)	−465(3)	49(1)
C(19)	2567(2)	4618(2)	531(2)	33(1)
C(20)	3707(2)	5089(2)	864(2)	34(1)
C(21)	4188(2)	6260(3)	502(3)	41(1)
C(22)	3539(3)	6966(3)	−171(3)	46(1)
C(23)	2412(3)	6504(3)	−502(3)	50(1)
C(24)	1917(2)	5332(3)	−162(3)	44(1)
C(25)	966(2)	3446(2)	2212(2)	35(1)
C(26)	543(2)	4599(3)	2412(3)	42(1)
C(27)	−324(3)	4747(4)	3205(3)	55(1)
C(28)	−769(3)	3715(4)	3823(3)	56(1)
C(29)	−338(3)	2577(4)	3657(3)	55(1)
C(30)	537(3)	2458(3)	2886(3)	48(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3a. ^1H NMR: 7.57–7.15 (H^6–H^{10}), 7.06 t $^3J_{H-H}$ = 8.0 Hz (H^5), 6.84 t $^3J_{H-H}$ = 8.0 Hz (H^4), 6.43 d $^3J_{H-H}$ = 8.0 Hz (H^3), 5.90 br s (H^1 and H^2).

3b. ^1H NMR: 7.06 t $^3J_{H-H}$ = 8.0 Hz (H^5), 6.87 d $^3J_{H-H}$ = 8.0 Hz (H^6), 6.82 t $^3J_{H-H}$ = 8.0 Hz (H^4), 6.10 d $^3J_{H-H}$ = 8.0 Hz (H^3), 4.75 br signal (1H, NH_2), 4.47

Table 3
Selected angles (°) between normals to planes for **2a**

Planes	Angle
1 and 2	63.5
1 and 3	62.6
1 and 4	41.4
2 and 3	0.8
2 and 4	36.8
3 and 4	36.1

Plane 1: Pd, Br, P, N, C(12)
Plane 2: N, C(1), C(6), C(7)
Plane 3: C(1)–C(7)
Plane 4: C(7)–C(12)

q $^3J_{H-H}$ = 6.6 Hz (H^7), 3.50 br signal (1H, NH_2), 1.63 d $^3J_{H-H}$ = 6.6 Hz (Me).

3.5. Preparation of 4b

A suspension formed by 2.23 mmol (0.500 g) of $Pd(AcO)_2$, 4.46 mmol (0.540 g) of (*R*)-α-methylbenzylamine and 30 cm^3 of toluene was stirred at room temperature for 3 days. The resulting solution was concentrated in vacuum and the residue was treated with 4.46 mmol (0.387 g) of LiBr and 25 cm^3 of ethanol at room temperature with vigorous stirring for 30 min. The resulting suspension was concentrated in vacuum and the residue was eluted through a column of SiO_2 with chloroform/methanol (100:2). The orange band was collected and concentrated in vacuum. Addition of n-hexane (10 cm^3) to the residue gave 0.462 g (40%) of **4b** as an orange powder. Anal. Found: C, 37.4; H, 4.2; N, 5.3. $C_{16}H_{22}Br_2N_2Pd$ Calc.: C, 37.78; H, 4.36; N, 5.50%. IR (cm^{-1}): 3297s, 3246s, 3221s, 3196s, 3127s (ν NH_2). ^1H NMR: 7.45–7.25 ($H^{3'}$–$H^{7'}$), 4.17 m ($H^{8'}$), 2.95 br s ($H^{1'}$ and $H^{2'}$), 1.76 d $^3J_{H-H}$ = 7 Hz (Me). Positive FAB: 429 ([M–Br]$^+$), 347 ([M–Br–HBr]$^+$).

3.6. Preparation of 5b

A suspension formed by 2.23 mmol (0.500 g) of $Pd(AcO)_2$, 4.46 mmol (0.540 g) of (*R*)-α-methylbenzylamine and 30 cm^3 of toluene was stirred in refluxing toluene for 3 h. The resulting solution was concentrated in vacuum and the residue was treated with 4.46 mmol (0.387 g) of LiBr and 25 cm^3 of ethanol at room temperature with vigorous stirring for 30 min. The resulting suspension was concentrated in vacuum and the residue was eluted through a column of SiO_2 with chloroform/methanol (100:2). The yellow band was collected and concentrated in vacuum. Addition of n-hexane (10 cm^3) to the residue gave 0.372 g (39%) of **5b** as a pale yellow powder. Anal. Found: C, 44.6; H, 4.8; N, 6.6. $C_{16}H_{21}BrN_2Pd$ Calc.: C, 44.93; H, 4.95; N, 6.55%. IR (cm^{-1}): 3290s, 3245s, 3221s, 3199s, 3127s (ν NH_2). ^1H NMR: 7.45–7.25 ($H^{3'}$–$H^{7'}$), 6.90–6.50 (H^3–H^6), 5.17 br signal (H^1 or H^2), 4.22 br m and 4.07 br m (H^7 and $H^{8'}$), 3.12 br d (H^1 or H^2), 3.77 br t and 2.10 br signal ($H^{1'}$ and $H^{2'}$), 1.69 d $^3J_{H-H}$ = 7 Hz (Me), 1.49 d $^3J_{H-H}$ = 6 Hz (Me'). Positive FAB: 347 ([M–Br]$^+$), 226 ([M–Br–amine]$^+$).

3.7. Preparation of 2a and 2b

A suspension formed by 0.100 mg of **1a** or **1b**, PPh_3 in molar ratio 2:1, and 25 cm^3 of acetone was stirred at room temperature for 15 min. The resulting solution was concentrated in vacuum and the residue was eluted through a column of SiO_2 with chloroform/methanol (100:1). The yellow band was collected and concentrated in vacuum. Addition of diethylether (10 cm^3) to the residue gave compounds **2** as microcrystals.

2a. Pale yellow, 0.112 g, 64%. Anal. Found: C, 58.0; H, 4.0; N, 2.1. $C_{10}H_{25}BrNPPd$ Calc.: C, 58.42; H, 4.08; N, 2.27%. IR (cm^{-1}): 3305s, 3239s (ν NH_2). ^1H NMR: 7.60–6.90 (H^5–H^{10} and hydrogens of PPh_3), 6.90 (H^5 and H^6), 6.47 (H^3 and H^4), 5.18 br signal (1H, NH_2), 4.92 br signal (1H, NH_2). $^{31}P\{^1H\}$ NMR: 35.89 s. Positive FAB: 536 ([M–Br]$^+$).

2b. White, 0.125 g, 67%. Anal. Found: C, 54.7; H, 4.6; N, 2.5. $C_{26}H_{25}BrNPPd$ Calc.: C, 54.80; H, 4.39; N, 2.46%. IR (cm^{-1}): 3195s, 3126s (ν NH_2). ^1H NMR: 7.80–7.25 (hydrogens of PPh_3), 6.90 br m (H^4 and H^5), 6.40 br m (H^3 and H^6), 4.57 br m (H^7); 4.18 br s (1H, NH_2), 3.56 br s (1H, NH_2), 1.73 d $^3J_{H-H}$ = 6.6 Hz (Me). $^{31}P\{^1H\}$ NMR: 41.68 s. Positive FAB: 488 ([M–Br]$^+$).

Table 4
Crystal data and structure refinement for **2a**

Empirical formula	$C_{30}H_{25}BrNPPd$
Formula weight	616.79
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	$P\bar{1}$
Space group	Triclinic
Unit cell dimensions	a = 12.182(3) Å α = 99.24(2)°
	b = 10.502(2) Å β = 94.69(2)°
	c = 9.998(2) Å γ = 99.13(2)°
Volume (Å^3)	1238.9(5)
Z	2
Density (calc.) (Mg m^{-3})	1.653
Absorption coefficient (mm^{-1})	2.446
F(000)	616
Crystal size (mm^3)	0.1 × 0.1 × 0.2
Theta range for data collection	2.28° to 30.01°
Index ranges	$-17 \leq h \leq 16$, $-14 \leq k \leq 14$, $0 \leq l \leq 14$
Reflections collected	7219
Reflections with $I > 2\sigma(I)$	6085
Independent reflections	7219 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7166/0/366
Goodness-of-fit on F^2	0.560
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320, wR_2 = 0.0856
R indices (all data)	R_1 = 0.0507, wR_2 = 0.1491
Extinction coefficient	0.0000(11)
Largest diff. peak and hole	1.731 and −1.297 e Å^{-3}

3.8. Crystal structure determination

A summary of crystallographic data and details of the refinement are given in Table 4. Crystals of **2a** suitable for the structure determination were grown by slow evaporation of the solvents of a solution of **2a** in CH_2Cl_2/MeOH(1:1). A prismatic crystal (0.1 × 0.1 × 0.2 mm^3) was selected and mounted on a Philips PW-

1100 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8° < \theta < 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromated Mo Kα radiation, using the $\omega/2\theta$ scan technique. 7219 reflections were measured in the range $2.08° \leq \theta \leq 30.01°$. 6085 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made. The structure was solved by Patterson synthesis, using the SHELXS computer program [30] and refined by the full-matrix least-squares method with the SHELX93 computer program [31] using 7166 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w || F_o |^2 - | F_c |^2 |^2$, where $w = [\sigma^2(I) + (0.1377P)^2 + 0.9322P]^{-1}$ and $P = (| F_o |^2 + 2 | F_c |^2)/3$. f, f' and f'' were taken from Ref. [32]. The extinction coefficient was 0.000011. All H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The final R (on F) factor was 0.032, wR (on $| F |^2$) 0.085, and goodness of fit 0.519 for all observed reflections. The number of refined parameters was 366. The max. shift/e.s.d. was 0.3 and the max. and min. peaks in the final difference synthesis were 0.631 and -0.597 e Å^{-3} respectively.

4. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, hydrogen bond lengths and angles, anisotropic displacement parameters, observed and calculated structure factors, remaining bond lengths and angles and least-squares planes and atomic deviations.

Acknowledgements

We are grateful to the Dirección General de Investigación Científica y Técnica (DGICYT) for financial support (Grant No. PB 93-0804) and to the Serveis Científico-Tècnics de la Universtat de Barcelona for many facilities in recording FAB and NMR spectra.

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