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THE EXCHANGE OF CYCLOMETALLATED LIGANDS

II *. ATTEMPTS TO PREPARE SIX-MEMBERED PALLADOCYCLES VIA THE LIGAND EXCHANGE REACTION

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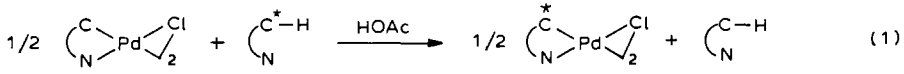
Summary

Reactions of the cyclopalladated *N,N*-dimethylbenzylamine chloro-bridged dimer with 2-benzylpyridine (bpH), 2-benzoylpyridine (bopH), and acetanilide have been studied in acetic acid/chloroform at 50°C. 2-Benzylpyridine readily undergoes ligand exchange to afford the six-membered cyclopalladated complex $[PdCl(bp)]_2$ in a high yield. In contrast to bpH, 2-benzoylpyridine reacts in two time-resolved steps. A bis-adduct, *trans*-$[PdCl_2(bopH)_2]$, having no palladium–carbon bond, is formed first, followed by precipitation of the cyclopalladated species. Acetanilide does not react with the *N,N*-dimethylbenzylamine complex at all. The reasons for such different behaviour of these three ligands are discussed taking into account some of the ^1H NMR spectral data.

Introduction

The increasing number of applications of cyclopalladated complexes in organic syntheses [1] provides further impetus in the preparation of these compounds. We recently put forward a novel procedure via the ligand exchange reaction [2]. This involves the interaction of a soluble cyclopalladated chloro-bridged dimer and a *N*-donor organic ligand, which is able to form the chelate with the palladium–carbon bond, to afford a new palladocycle (eq. 1).



(1)

The ligand exchange reaction occurs at 25–50°C, but only in the presence of acetic

* For Part 1 see ref. 2.

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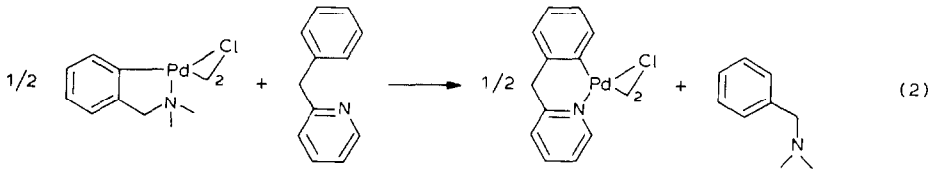
acid as co-solvent. A number of complexes have been prepared by this procedure, including cyclopalladated derivatives of azobenzene, benzylidene aniline, 8-methylquinoline, as well as *N*,*N*-diethyl-4-nitrobenzylamine which is not available by other methods [3]. In this paper we describe the attempts to apply this approach in the preparation of six-membered cyclopalladated complexes, starting from 2-benzylpyridine (bpH), 2-benzoylpyridine (bopH), and acetanilide. Our study has revealed that the procedure can only be used successfully for the preparation of the cyclopalladated 2-benzylpyridine derivative. 2-Benzoylpyridine reacts to produce predominantly *trans*-$[PdCl_2(bopH)_2]$, while acetanilide is completely unreactive under identical conditions.

Results

The preparation and characterization of six-membered chloro-bridged cyclopalladated derivatives of 2-benzyl- [4], 2-benzoylpyridine [5], and acetanilide [6] have been recently reported. The syntheses involved palladation of the ligands by Pd^{II} acetate followed by metathetical replacement of bridging acetates for chlorides. We have tried to obtain these complexes in one step via the reaction using di-μ-chlorobis(*N*,*N*-dimethylbenzylamine-2*C*,*N*)dipalladium(II) ($[PdCl(dmba)]_2$) and the corresponding ligand. Treatment of bpH with $[PdCl(dmba)]_2$ in acetic acid/chloroform (1 : 1, v/v) at 50°C for 20–24 h affords the desired cyclopalladated complex $[PdCl(bp)]_2$ in 84.5% yield according to reaction 2:



(2)

The identity of the complex $[PdCl(bp)]_2$ obtained in this study with that reported previously has been established as follows. Poorly soluble greenish crystals of $[PdCl(bp)]_2$ can be converted into soluble monomeric pyridine or the triphenylphosphine derivatives [PdCl(bp)(py)] or $[PdCl(bp)(PPh_3)]$ by reacting $[PdCl(bp)]_2$ with the corresponding ligand in chloroform. These species show dynamic behaviour in $CDCl_3$ solvent as shown by ^1H NMR spectroscopy at various temperatures. Because the inversion of the six-membered palladocycle in [PdCl(bp)(py)] is slowed down, a singlet for the methylene protons at δ 4.46 ppm (50°C) splits into an AB quartet at −30°C, the doublets being centred at δ 4.00 and 4.96 ppm. This is in complete agreement with the data of Hiraki et al. [4] obtained for the 3,5-dimethylpyridine analogue of [PdCl(bp)(py)]. In the case of the triphenylphosphine monomer $[PdCl(bp)(PPh_3)]$, the inversion is retarded by the more bulky phosphine ligand, leading to an increase in coalescence temperature up to ca. 110°C in chloroform/iodobenzene. We are currently investigating the kinetics of the inversion and the results will be presented elsewhere [7]. $[PdCl(bp)(PPh_3)]$ undergoes lithium chloride-induced acidolysis in acetic acid solvent to give $[PdCl_2(PPh_3)]_2$ and the free ligand likewise related cyclopalladated complexes [8].

The reaction of 2-benzoylpyridine with a stoichiometric amount of $[PdCl(dmba)]_2$ under the same conditions proceeds in two steps. The first, which is completed in 12–14 h, gives fine, orange crystals in a moderate yield. Initially we assumed these to

be a cyclopalladated derivative of bopH, but efforts to prepare the soluble monomeric complex by treating the product with triphenylphosphine in chloroform at 50–60°C gave *trans*-$[PdCl_2(PPh_3)_2]$ instead. This, together with the analytical data, suggests that the product is *trans*-$[PdCl_2(bopH)_2]$. The *trans* arrangement of the chloro-ligands is supported by strong ν(Pd–Cl) absorption at 345 cm^{-1} (cf. ν(Pd–Cl) 343 cm^{-1} for *trans*-$[PdCl_2(bpH)_2]$ [4]). The bopH ligands are bound to the metal through the pyridine nitrogen rather than the carbonyl oxygen, since the carbonyl stretching frequency (1670 cm^{-1}) remains unchanged in the free and complexed bopH ligands.

Further heating of the reaction mixture for 50–60 h, after the removal of *trans*-$[PdCl_2(bopH)_2]$, leads to the formation of a pale green precipitate. The ^1H NMR spectrum of this material in $CDCl_3$ in the presence of pyridine-d_5 was consistent with the cyclopalladated nature of 2-benzoylpyridine; however, the product was contaminated with non-palladated bopH. The addition of hexane to this solution precipitated a homogeneously pure, light yellow compound, [PdCl(bop){py-d_5}], whose ^1H NMR spectrum was very close to that reported for its 3,5-dimethylpyridine analogue [5]. In particular, the compound had two characteristic resonances appearing as doublets at δ 9.55 and 6.67 ppm ascribed to the protons "*ortho*" to the pyridine nitrogen and the palladium–carbon bond, respectively [5].

Formal stoichiometry of the formation of *trans*-$[PdCl_2(bopH)_2]$ given by eq. 3

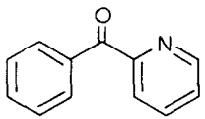
$$[PdCl(dmba)]_2 + 2bopH + 2\ HOAc \rightarrow [PdCl_2(bopH)_2] + 2C_6H_5CH_2NMe_2 + \text{“}Pd(OAc)_2\text{”} \quad (3)$$

necessitates an accumulation of Pd^{II} acetate. This accounts for the existence of the second reaction step leading to cyclopalladated 2-benzoylpyridine. As mentioned above, bopH undergoes *ortho*-palladation readily in the presence of Pd^{II} acetate in refluxing acetic acid solution [5]. Under the conditions used in the present study (50°C), this reaction proceeds more slowly and it takes many hours for palladation to occur. As a result, a poorly soluble product, $[PdCl(bop)]_2$, precipitates in the presence of chloro-ligands, the material being contaminated with non-palladated bopH.

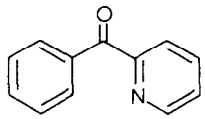
Attempts to carry out the reaction between $[PdCl(dmba)]_2$ and acetanilide under the same conditions failed. We did not observe the formation of any product. Moreover, the starting *N*,*N*-dimethylbenzylamine complex was not consumed after thermostating the reaction mixture at 50°C for 8 h, as shown by UV-visible spectrophotometry. We detected only traces of free *N*,*N*-dimethylbenzylamine after 10 h by GLC.

To throw some light on the mechanisms of the processes investigated, we have undertaken a ^1H NMR study of the interaction between $[PdCl(dmba)]_2$ and bpH or bopH in $CDCl_3$ solvent. The addition of a small excess of bpH to $[PdCl(dmba)]_2$ solution results in monomerization of the dimer (eq. 4), as shown by the upfield shift of the H^a proton [9] appearing as a doublet at δ 5.79 ppm. At 30°C, the singlet resonances for the $N–CH_2$ and $N–CH_3$ groups of dmba are observed at δ 3.90 and 2.90 ppm, respectively. At −50°C, splitting of the $N–CH_2$ protons into an AB quartet and a pronounced broadening of the $N–CH_3$ signal take place due to the lack of rapid rotation of the perpendicularly coordinated bpH ligand around the pyridine nitrogen–palladium bond [9]. A similar study using bopH has revealed a

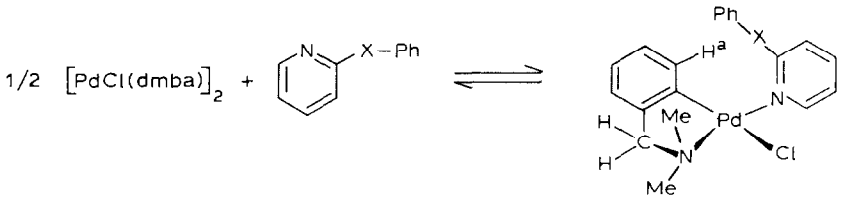
more complicated picture. At 0°C, monomerization also occurs as suggested by the observation of two doublets at δ 5.99 and 5.76 ppm. At the same time, the dmba N–CH_2 and N–CH_3 protons split into two sets of signals of approximately equal intensity, each consisting of an AB quartet and two singlets. The broader "upfield" set is located at δ 3.30 (N–CH_2), 2.55 and 2.35 ppm (two N–CH_3), while the "downfield" one is observed at δ 3.90 (N–CH_2), 2.88 and 2.78 ppm (two N–CH_3). Since it is known that rotation around the carbonyl carbon–phenyl bond is char-



syn



anti



(4)

acterized by a substantial activation barrier [10], both *syn* and *anti* forms of bopH can exist. If the *syn–anti* interconversions are slow on the NMR time-scale, the splitting of the dmba N–CH_2 and N–CH_3 protons in the presence of bopH may reflect the interaction of $[PdCl(dmba)]_2$ with its *syn*- and *anti*-isomers. An increase in temperature leads to coalescence of the signals of the "upfield" set first, the coalescence temperature for both N–CH_2 and N–CH_3 groups being ca. 25°C, and then to that of the "downfield" set (T_c ca. 45°C). At the same time, broadening of the H^a doublets becomes apparent. At higher temperatures, two broad singlets for the N–CH_2 protons, as well as for the N–CH_3 protons, coalescence at ca. 50°C appearing now at δ 3.95 and 2.85 ppm, respectively, while the signals for the H^a proton disappear. The latter can be the consequence of two processes which are: (i) the incorporation of bopH into the palladium plane [9] via substitution of chloride by carbonyl oxygen (eq. 5); and (ii) isomerization of the monomer to produce the

$$[PdCl(dmba)(bopH)] \rightleftharpoons [Pd(dmba)(bopH)]Cl \quad (5)$$

complex in which both nitrogens are *cis*. However, this isomerization might involve [Pd(dmba)(bopH)]Cl as a possible intermediate. In any case, processes (i) and (ii) can only occur for *syn*-2-benzoylpyridine, and the data presented above suggest that palladium is coordinated to the *syn* form of bopH at 40–60°C in $CDCl_3$ solvent.

Discussion

The difference in the reactivity of the three ligands studied can be rationalized assuming monomeric complex I to be a key intermediate. Its further possible transformations are shown in Scheme 1. Cleavage of the palladium–carbon bond leads to complex II, where X represents a solvent molecule or a vacant coordination site [11]. If the incoming ligand has a conformation suitable for subsequent *ortho*-palladation, II transforms into III as in the case of 2-benzylpyridine. If such a

conformation is not realized, palladation does not occur and instead II abstracts chloride from the starting complex to afford IV, which then transforms into the final bis-adduct. The latter path is observed in the case of 2-benzoylpyridine in which, under the reaction conditions, the predominant *syn*-form is completely unfavourable for the subsequent *ortho*-palladation.

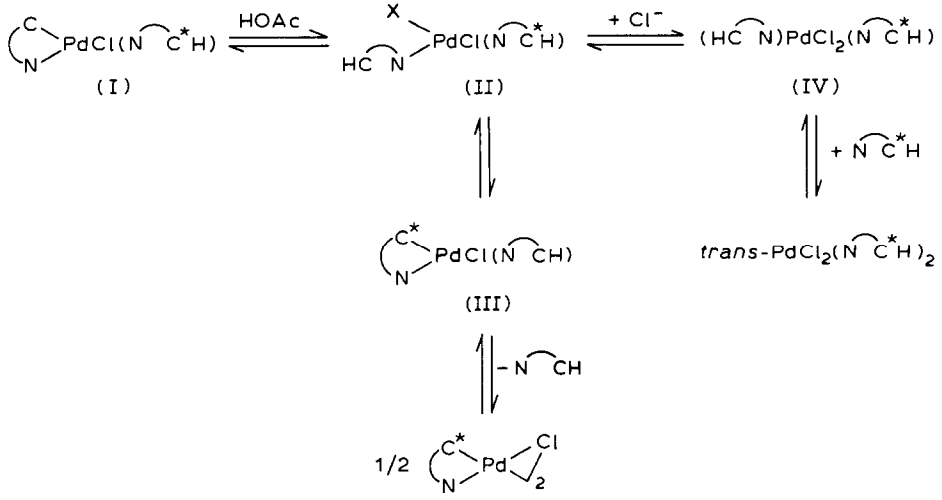
In conclusion we wish to point out that the inability of acetanilide to react provides additional proof of the key role of I-type intermediates in the ligand exchange reaction. Amide oxygen is likely too poor a donor to cleave the bridging chlorides of $[PdCl(dmba)]_2$, and the reactive intermediate is not formed in the case.

Experimental

IR spectra were recorded on a Jasco-200 spectrometer (4000–400 cm^{-1}) in KBr pellets and on a Perkin–Elmer 577 spectrometer (400–200 cm^{-1}) in polyethylene discs. ^1H NMR spectra were obtained on Tesla BS-467 (60 MHz) and BS-497 (100 MHz) spectrometers with hexamethyldisiloxane or tetramethylsilane as internal standard. All chemical shifts are given with respect to TMS. 2-Benzylpyridine was obtained from Reakhim and was distilled before use. 2-Benzoylpyridine and acetanilide (Reakhim) were used as received. Di-μ-chlorobis(*N*,*N*-dimethylbenzylamine-2*C*,*N*)dipalladium(II) was prepared as described in ref. 12. The solvents (acetic acid and chloroform) were purified by standard procedures.

Preparation of di-μ-chlorobis(2-benzylpyridine-2C',N)dipalladium(II), [PdCl(bp)]₂

To a solution of di-μ-chlorobis(*N*,*N*-dimethylbenzylamine-2*C*,*N*)dipalladium(II) (0.117 g, 0.21 mmol) and 2-benzylpyridine (0.071 g, 0.42 mmol) in 3 ml chloroform was added 3 ml acetic acid. The resulting solution was thermostated at 50°C for 24 h. The greenish crystals formed were filtered, washed successively with acetic acid, chloroform, and hexane, and then dried in air. The product yield was 84.5%. The identity of the compound obtained and that previously reported [4] were established on the basis of ^1H NMR measurements in $CDCl_3$ in the temperature range −40 to +50°C in the presence of pyridine-d_5.



SCHEME 1

Chloro(2-benzylpyridine-2C',N)pyridinepalladium(II), [PdCl(bp)(py)], and chloro-(2-benzylpyridine-2C',N)triphenylphosphinepalladium(II), [PdCl(bp)(PPh_3)]

These were synthesized by standard procedures [13] starting from $[PdCl(bp)]_2$, in 94 and 91% yields, and m.p. 225–226 and 163–165°C, respectively.

Reaction of 2-benzoylpyridine with $[PdCl(dmba)]_2$

To a solution of $[PdCl(dmba)]_2$ (0.154 g, 0.279 mmol) and bopH (0.102 g, 0.557 mmol) in 4 ml chloroform was added 4 ml acetic acid. The solution was thermostated at 50°C. The orange crystals which formed after 12–14 h were filtered off (the filtrate was allowed to react further), washed successively as in the case of $[PdCl(bp)]_2$, and air-dried to yield 0.054 g (36%) *trans*-dichlorobis(2-benzoylpyridine-*N*)palladium(II), *trans*-$[PdCl_2(bopH)_2]$. M.p. (dec.) > 235°C. Found: C, 52.55; H, 3.22; N, 4.93. $C_{24}H_{18}N_2O_2Cl_2Pd$ calcd.: C, 52.97; H, 3.39; N, 5.15%. Heating the reaction mixture further resulted in the formation of a pale green crystalline product, which was isolated in the same way as $[PdCl_2(bopH)_2]$ to give 0.035 g (19%) of the cyclopalladated 2-bopH derivative. This was converted into [PdCl(bop){py-d_5}] by the standard procedure [13].

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