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LITHIUM CHLORIDE-INDUCED DISSOCIATION OF CYCLOPALLADATED LIGANDS FROM CHLORO(LIGAND-*C,N*)TRIPHENYLPHOSPHINE-PALLADIUM(II) COMPLEXES IN ACETIC ACID SOLVENT

ALEXANDER D. RYABOV

Department of Chemistry, Moscow State University, 117234, Moscow (U.S.S.R.)

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Summary

The chloro(ligand-*C,N*)triphenylphosphinepalladium(II) complexes with cyclopalladated *N,N*-dialkylbenzylamines (alkyl = methyl, ethyl and n-propyl), azobenzene, 8-methylquinoline, dimethylaminomethylferrocene and 2-benzylpyridine undergo lithium chloride-induced solvolysis in acetic acid solvent usually at 80°C to afford the corresponding non-palladated ligands and the poorly soluble, dinuclear complex $[PdCl_2(PPh_3)]_2$. The reactivity pattern for *N,N*-diethylbenzylamine derivative II provides evidence that the reaction proceeds in two steps. The first step is palladium–nitrogen bond cleavage to afford the dechelated, σ-bonded zwitterionic complex *cis*-$[PdCl_2(C_6H_4CH_2NHEt_2)(PPh_3)]$, and the second step is protonolysis of the palladium–carbon bond by acetic acid to yield the final products.

Introduction

Because of the increasing number of applications of cyclopalladated compounds in organic syntheses [1], the preparation and dissociation of these compounds remain a topic of current interest. Among the latter processes, which result in cleavage of the palladium–carbon bonds, are reductions by lithium aluminium hydride [2], sodium borohydride [3], and dihydrogen [4]; cyanide-induced dissociation in methanol solvent [5]; "reductive carbonylation" under basic conditions [6]; and protonolysis by hydrochloric acid [7]. These reactions afford the corresponding organic ligands together with palladium metal or the palladium(II) salt. In this paper a novel procedure for the dissociation of palladocycles is described, namely the lithium chloride-mediated departure of cyclopalladated ligands from complexes I–VII of general formula $[PdCl(L)(PPh_3)]$ (where L stands for a cyclopalladated ligand) in acetic acid solvent leading to free ligands, LH, and the insoluble complex $[PdCl_2(PPh_3)]_2$. Evidence suggesting a possible mechanism of the reaction is also presented. A preliminary note has been published [8].

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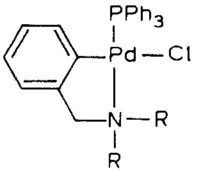
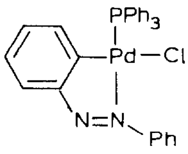
Results and discussion

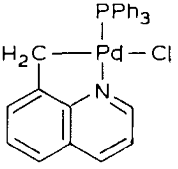
The cyclopalladated chloro-bridged dimers are stable enough in acetic acid solvent [9]. On the contrary, the corresponding monomeric derivatives, obtained from the former by cleaving the bridging chlorides with triphenylphosphine, do not withstand heating in this solvent and readily decompose. Incubation of I for ca. 30 min at 80°C results in the formation of a brown-black precipitate, which was not analysed further. The reaction course changes dramatically in the presence of a stoichiometric amount or an excess of lithium chloride. In the case of I, the reaction is completed within 10 min, yielding a poorly soluble, orange-red compound which is formulated as the dinuclear complex $[PdCl_2(PPh_3)]_2$ [10] on the basis of analytical and spectral data. GLC analysis of the soluble products revealed the presence of free *N,N*-dimethylbenzylamine. Thus the reaction proceeds according to 1:



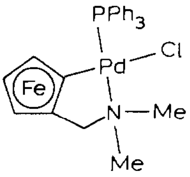
(I, R = Me,
II, R = Et,
III, R = n-Pr)



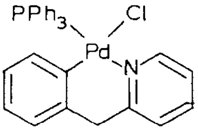
(IV)



(V)



(VI)



(VII)

$$I + LiCl + HOAc \rightarrow C_6H_5CH_2NMe_2 + 1/2[PdCl_2(PPh_3)]_2 + LiOAc \qquad (1)$$

TABLE 1

LITHIUM CHLORIDE-INDUCED DISSOCIATION OF CYCLOPALLADATED COMPLEXES IN ACETIC ACID SOLVENT AT 80°C

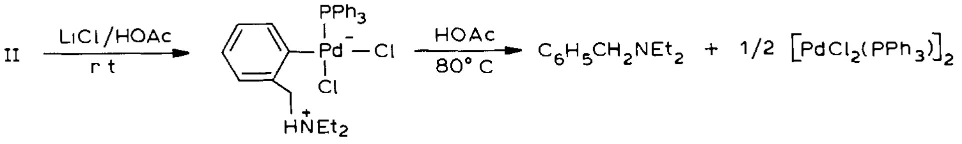
Entry	Complex	Reaction time (h)	Yield based on $[PdCl_2(PPh_3)]_2$ (%)
1	I	10 min	86
2	II	40 min	40
3	III	3	81
4	IV	24	58
5	V	24	46
6	VI	10[a]	62
7	VII	21	58

[a] Ambient temperature.

Other monomeric complexes (II–VII) behave in a similar way and the results obtained are summarized in Table 1. The reaction of azobenzene complex IV was used to confirm the stoichiometry of the process by GLC. Under the conditions of entry 4, Table 1, the yield of free azobenzene was found to be 60.5%; this value might be compared with that of 58% obtained by measuring the weight of precipitated $[PdCl_2(PPh_3)]_2$.

The reaction appears to be rather general for various cyclopalladated complexes with aliphatic and aromatic carbon–palladium bonds, as well as five- and six-membered palladocycles (Table 1). Complexes with a dialkylaminomethyl fragment in the chelate ring possess enhanced reactivity in comparison with azo- or pyridine-type compounds.

Apparently, two general mechanisms of the dissociation may be operative. The reaction may start with cleavage of the palladium–nitrogen bond, followed by protonolysis of the palladium–carbon bond with acetic acid, or vice versa. Discrimination between the two became possible owing to the reactivity pattern for *N,N*-diethylbenzylamine complex II. The acidolysis of II at ambient temperature did not lead to $[PdCl_2(PPh_3)]_2$, but instead a white crystalline precipitate was formed within ca. 45 min. GLC measurements have shown that the formation of this new complex is not accompanied with the dissociation of *N,N*-diethylbenzylamine in the bulk solvent. At the same time, heating its suspension in acetic acid either in the presence or absence of LiCl at 80°C caused such dissociation with a concomitant colour change from white to orange-red, indicating conversion of the white solid into $[PdCl_2(PPh_3)]_2$. The white complex unfortunately possesses a low solubility in common solvents, thus excluding the possibility of an NMR study. As a result, the structure of this compound has been assigned on the basis of analytical, IR and mass spectral data. The former indicates that incorporation of one chloro-ligand by II has occurred during the reaction course. In the far-IR region, the compound has two ν(Pd–Cl) vibrations at 310 and 275 cm^{-1}, the latter being more intense, confirming a *cis* arrangement of the chloro-ligands [11]. A group of bands at 2730, 2660 and 2610 cm^{-1}, which is absent in the starting complex II, indicates the presence of a tertiary ammonium salt fragment of the $R_3\overset{+}{N}–H$ type [12]. In accordance with this assumption, when the reaction is performed in DOAc, the group shifts to lower frequencies and appears at 2190, 2130 and 2100 cm^{-1}, as expected for the $R_3\overset{+}{N}–D$ analogue [12]. These findings suggest that the white complex is the *N*-protonated, dechelated compound VIII. The existence of the palladium–carbon bond in VIII was confirmed by its protonolysis in DOAc at 80°C and the subsequent chromatographic and mass spectral analysis of the dissociated *N,N*-diethylbenzylamine (eq. 2). The most intense peak in the electron-impact mass spectra of the related compounds is at *m/z* 91 ($C_6H_5CH_2$) [13] and this appears to be very useful since



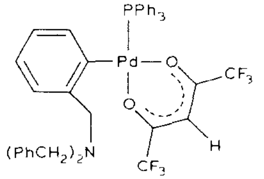
(VIII)

SCHEME 1

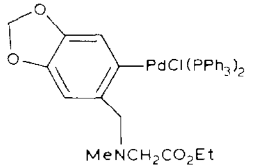
$$VIII + DOAc \rightarrow o\text{-}DC_6H_4CH_2NEt_2 + 1/2[PdCl_2(PPh_3)]_2 + HOAc \qquad (2)$$

the observation of this particular peak eliminates all the complications which, in principle, may arise due to protonation of the ligand nitrogen in acetic acid. To this end, it was found that deuterium incorporation into the aromatic ring was not less than 78% (*m/z* 92). Obviously, the utilization of DOAc as solvent for carrying out reactions of type (1) provides a route to *ortho*-deuteriated compounds.

Of late, zwitterionic complexes analogous to VIII have not been reported in the literature. Only very recently Crociani et al. have isolated *cis*-$[PdX_2(2\text{-}pyH)(PPh_3)]$ (where X = Cl or Br), a compound with a *N*-protonated 2*C*-bonded pyridine ligand [11]. The IR characteristics of this complex are quite similar to those of VIII. On the other hand, VIII is a rare example of a dechelated benzylamine derivative with a palladium–carbon bond. Among related compounds are IX prepared by Okeya et al. [14], and X obtained by an Australian group of workers [15].

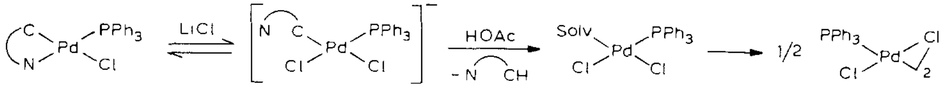


(IX)



(X)

Attempts to isolate complexes of type VIII starting from I or III were not successful. The white solid was formed in the case of I at ambient temperature, but the yield was very poor and the product changed its colour very rapidly indicating the formation of $[PdCl_2(PPh_3)]_2$. The same situation was observed for III, but the appearance of the white solid became noticeable only after several days at room temperature. The yield was small, and attempts to decrease the reaction time by increasing the temperature resulted in a change in colour. Nevertheless, these qualitative observations demonstrate that the reaction sequence depicted in Scheme 1 may be general for all the complexes listed in Table 1, and the mechanism of lithium chloride-induced protonolysis of cyclopalladated compounds by acetic acid may be as follows:



Solv = solvent molecule, N C = cyclopalladated ligand

We have recently presented quantitative evidence [1] that alkali metal perchlorates undergo acidolysis in acetic acid:

$$MClO_4 + HOAc \rightleftharpoons HClO_4 + MOAc$$

A similar process is likely valid in the case of lithium chloride. Thus the dechelation of starting complexes may be stabilized by protonation of the amine nitrogens with the hydrochloric acid formed. Obviously, palladium–nitrogen bond scission is also favoured by the remarkable *trans* influence of the phosphine ligand, previously noted in other cyclopalladated complexes [16].

In conclusion, it should be pointed out that the structure of VIII is analogous to that of the postulated intermediate [17] of acid cleavage of the Pd–C bond in *trans*-$[PdBr(Ph)(PPh_3)_2]$ on the basis of kinetic data. These authors assumed the rate-determining step to be proton attack on the intermediate *cis*-$[PdBr_2(Ph)(PPh_3)]^-$. Thus the results presented here indirectly support the mechanism put forward by Tiomkin and co-workers [17].

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. UV-visible spectra were obtained on a Hitachi-356 spectrophotometer. GLC analyses were performed on a Chrom-5 gas chromatograph. Chromatographic mass and spectral data were obtained on a JEOL JMS D300 instrument.

N,N-Diethylbenzylamine, azobenzene, 8-methylquinoline and 2-benzylpyridine were obtained from Reakhim. *N,N*-Dimethylbenzylamine and dimethylaminomethylferrocene were purchased from Koch-Light. *N,N*-Di(n-propyl)benzylamine was prepared as described in ref. 7. The dinuclear chloro-bridged derivatives of the benzylamines [7], azobenzene [18], dimethylaminomethylferrocene [19], 8-methylquinoline [9] and 2-benzylpyridine [20], the precursors of I–VII, were prepared by published methods. Corresponding monomeric triphenylphosphine complexes were synthesized by standard procedures [21,22]. Special attention has been drawn to the preparation of IV, since IV can react with additional PPh_3 ligand to afford the X-type complex.

Preparation of chloro(azobenzene-2C,N)triphenylphosphinepalladium(II) (IV)

To a suspension of di-μ-chlorobis(azobenzene-2*C*,*N*)dipalladium(II) (0.090 g, 0.14 mmol) in 5 ml CH_2Cl_2 was added 0.073 g (0.28 mmol) triphenylphosphine. Hexane (5 ml) was added to the solution and the mixture was cooled to −78°C and kept for 24 h. The resulting crystals were filtered off, washed with hexane, and air-dried to yield 0.096 g of the product (58%). Traces of the unreacted starting complex were removed by column chromatography (SiO_2/MeOH). M.p. 205–206°C. Found: C, 60.7; H, 4.1; P, 5.1. $C_{30}H_{24}N_2PClPd$ calcd.: C, 61.6; H, 4.1; P, 5.3%. UV λ_{max}^{EtOH} (ϵ, 1 mol^{-1} cm^{-1}) 430(3750), 355(10650), and 305(10650) nm.

General procedure for lithium chloride-induced acidolysis in acetic acid solvent

One of the complexes I–VII (0.1–0.2 mmol) was dissolved in 6 ml solvent (HOAc, C_6H_6 or CH_2Cl_2 depending on solubility) and a solution of LiCl (0.1–0.6 mmol) in 6 ml acetic acid was added. The solution was thermostated at 80°C (ambient temperature in the case of VI) for an appropriate time. The precipitated orange-red crystals of $[PdCl_2(PPh_3)]_2$ were filtered, washed with acetic acid and hexane, and dried over NaOH. M.p. 240–255°C dec., lit. 250°C dec. [23]. Found: C, 48.0; H, 3.5; P, 7.1; N, 0.0. $C_{36}H_{30}P_2Cl_4Pd_2$ calcd.: C, 49.2; H, 3.4; P, 7.1%. UV-visible and IR characteristics of the compound were identical to those of the independently prepared complex [23].

cis-Dichloro(N,N,N-hydrogendiethylbenzyamine-2C)triphenylphosphinepalladium(II) (VIII)

To a solution of II (0.113 g, 0.2 mmol) in 6 ml acetic acid was added a solution of LiCl (0.026 g, 0.6 mmol) in the same solvent. The mixture was kept at ambient temperature. After ca. 5 min precipitation of the white crystals of VIII began and was complete after 45 min. The crystals were filtered, washed with HOAc, and dried over NaOH. Yield 69% (0.083 g). M.p. 164–168°C dec. Found: C, 57.3; H, 5.5, $C_{29}H_{32}NPCl_2Pd$ calcd.: C, 57.8; H, 5.4%.

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