Journal of Organometallic Chemistry, 334 (1987) C9–C13
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The preparation and reductive elimination behavior of *trans*-Pd(COPh)($CONMe_2$)(PMe_3)$_2$: a model intermediate in the catalytic double carbonylation of aryl halides with amines to give α-keto amides

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(Received February 16th, 1986)

Abstract

The cationic benzoylcarbonylpalladium(II) complex, *trans*-[Pd(COPh)(CO)(PMe_3)$_2$]$^+BF_4^-$ (**1**), reacts with Me_2NH under CO to give *trans*-Pd(COPh)($CONMe_2$)(PMe_3)$_2$ (**3**). Complex **3** is stable in neat solvent, whereas rapid decomposition of **3** to give $PhCOCONMe_2$ takes place in the presence of $Me_2NH_2BF_4$ and Me_2NH under CO.

The palladium-catalyzed double carbonylation reactions of organic halides provide a convenient synthetic route to α-keto acid derivatives as potentially useful starting materials in organic synthesis [1,2].

$$R'X + 2CO + 2HNR_2 \xrightarrow{[Pd]} R'COCONR_2 + R_2NH_2X \quad (1)$$

(R′ = aryl, alkenyl; X = Br, I; R = alkyl)

$$R'X + 2CO + ROH + Et_3N \xrightarrow{[Pd]} R'COCOOR + Et_3NHX \quad (2)$$

(R′ = aryl; X = I, (Br); R = alkyl, H)

From previous studies we have proposed the following mechanism for the catalytic conversion of aryl halides and amines into α-keto amides (eq. 1) [3,4 *]. α-Keto ester formation (eq. 2) has been shown to proceed through essentially the same process as that in Scheme 1 [5,6]. In this scheme the intermediacy of **A**, **B**, and **C** has been evidenced by studies on reactions of isolated phenyl- and benzoyl-palladium complexes with amines and CO. On the other hand, the aroylcarbamoylpal-

* Reference number with asterisk indicates a note in the list of references.

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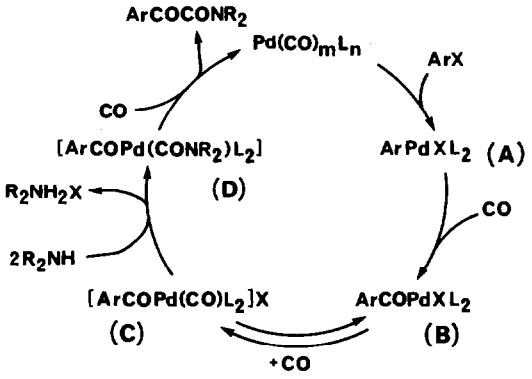


Scheme 1. L = t-phosphine.

ladium intermediate (**D**), presumably formed by nucleophilic attack of amine on the aroylcarbonylpalladium species (**C**), has yet to be characterized. Since the process which occurs after the rate-determining step, that of attack of amine on **C**, is rapid in the actual catalytic systems, identification of **D** in these is not feasible.

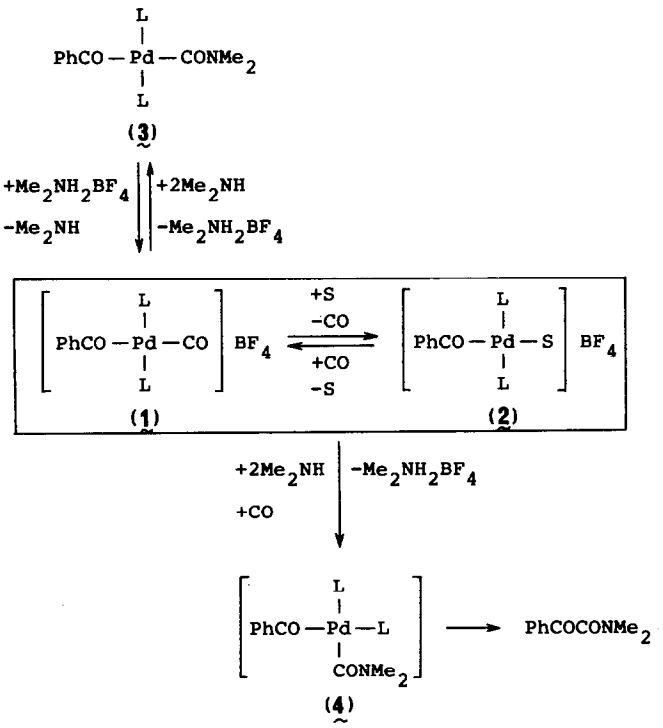
In previous studies the steric repulsion between the tertiary phosphine ligands in **C** and secondary amine has been suggested to be the main factor controlling the rate of reaction of **C** with amine [3], and a bulky and less basic tertiary phosphine ligand has been suggested to favor the dissociation of ligand with subsequent promotion of the reductive elimination of the aroyl and carbamoyl groups. Thus we reasoned that utilization of a small and basic tertiary phosphine ligand such as trimethylphosphine and a compact secondary amine such as dimethylamine would make the attack of the amine on the CO-coordinated complex more facile and would render the resultant PMe_3-coordinated aroylcarbamoyl species sufficiently resistant to reductive elimination to permit its isolation.

Treatment of *trans*-Pd(COPh)Cl$(PMe_3)_2$ with an equimolar amount of $AgBF_4$ in acetone under CO gave a homogeneous yellow solution containing an equilibrium mixture of *trans*-[Pd(COPh)(CO)$(PMe_3)_2$]BF_4 (**1**) * and *trans*-[Pd(COPh)(acetone)-$(PMe_3)_2$]BF_4 (**2**) formed in the system, after the white precipitate of AgCl had been removed. Upon addition of Me_2NH (10 equiv./Pd) to the system at $-20\,^{\circ}C$ the color of the solution quickly changed into bright red, and after a few minutes, red crystals of *trans*-Pd(COPh)$(CONMe_2)(PMe_3)_2$ (**3**) gradually separated (60% yield). Complex **3** was characterized by IR and NMR spectroscopy, and elemental analysis **.

Complex **3** is stable in neat solvent. Furthermore, no decomposition was observed when the complex was allowed to stand for 1 d in acetone containing an excess

* Complex **1** is very unstable in solution as well as in solid state and easily loses its CO ligand on isolation. Formation of **1** in solution under CO atmosphere was confirmed by IR spectroscopy: ν(CO) = 2132 (terminal) and 1638 cm^{-1} (benzoyl).

** Anal. Found: C, 44.37; H, 7.10; N, 3.07. $C_{16}H_{29}NO_2P_2Pd$ calc: C, 44.10; H, 6.71; N, 3.21%. ^1H NMR (in δ ppm, in CD_3COCD_3 at room temp.): 1.12 (t, J(HP) 3.7 Hz, 18H, P*Me*$_3$), 2.74 (s, 3H, N*Me*), 3.32 (s, 3H, N*Me'*). $^{31}P\{^1H\}$ NMR (in ppm) referred to external PPh_3, downfield positive): −14.4 (s). IR (KBr disk): 1564 ($\nu(CO)_{benzoyl}$), 1526 cm^{-1} ($\nu(CO)_{carbamoyl}$).



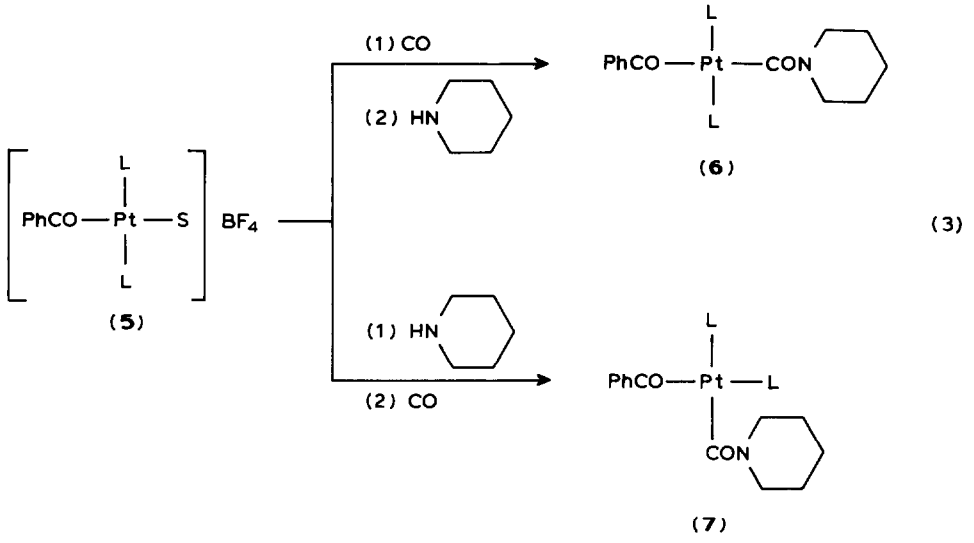
Scheme 2. L = PMe_3, S = acetone, Me_2NH.

amount of Me_2NH under CO at room temperature. On the other hand, treatment of **3** with $Me_2NH_2BF_4$ (1 equiv.) in acetone under CO readily gave an equilibrium mixture of the cationic benzoyl species **1** and **2** along with the formation of Me_2NH (Scheme 2). In this reaction formation of a small amount of $PhCOCONMe_2$ (ca. 20%) was also observed. The yield of α-keto amide was increased by the addition of Me_2NH to the system. For example, **3** gave $PhCOCONMe_2$ in 81% yield upon reaction with $Me_2NH_2BF_4$ (1 equiv.) in acetone containing Me_2NH (10 equiv.) under CO.

The present results show that *trans*-benzoylcarbamoyl complex (**3**) is the kinetic product when *trans*-benzoylcarbonylpalladium (**1**) is treated with Me_2NH. If complex **3** undergoes a *trans-cis* isomerization, the *cis*-benzoylcarbamoyl complex (**4**) produced should afford α-keto amide on reductive alimination *. The isolated benzoylcarbamoyl complex (**3**), however, was fairly inert to *trans-cis* isomerization as well as to reductive elimination in the absence of the $Me_2NH_2BF_4$.

α-Keto amide formation from **3**, on the other hand, proceeded readily in the presence of $Me_2NH_2BF_4$. In this case, the ammonium salt converts **3** into **1**, which forms a rapid equilibrium with **2** in solution. Since complex **1** has *trans* configuration, simple nucleophilic attack of amine on the CO ligand in **1** would generate *trans*-benzoylcarbamoyl complex (**3**), the kinetic product. Thus an alternative pro-

* Since reductive elimination from PdR_2L_2 (R = alkyl group) type complexes takes place only from *cis* isomers [7], the *trans* complex **3** should undergo *trans-cis* isomerization prior to reductive elimination.



cess, which converts **1** or **2** into *cis*-benzoylcarbamoyl complex (**4**), should be operative in the system. Although the process of formation of **4** is presently uncertain, relevant information is available by examining properties of corresponding platinum analogs.

trans-[Pt(COPh)(CO)$(PPh_3)_2$]BF_4, which was prepared by treatment of *trans*-[Pt(COPh)(acetone)$(PPh_3)_2$]BF_5 (**5**) with CO, smoothly reacted with piperidine in acetone to give *trans*-benzoylcarbamoylplatinum (**6**), selectively. In contrast, prior treatment of **5** with piperidine, followed by CO, gave *cis*-benzoylcarbamoylplatinum (**7**) exclusively [8 *]. These results indicate that the configuration of the benzoylcarbamoyl complex varies depending on the order in which CO and amine are added to the cationic benzoyl complex.

The present results together with the previous studies have allowed characterization of all the putative intermediates (**A** to **D**) in the catalytic double carbonylation cycle of aryl halides. Further mechanistic studies are in progress to establish the mechanism of the formation of *cis*-aroylcarbamoylpalladium complexes and subsequent reductive elimination to give α-keto amides.

Acknowledgment. We are grateful for support of this work by a Grant-in-Aid for Special Project Research from Ministry of Education, Science and Culture, Japan (No. 61125005).

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