CHEMISTRY LETTERS, pp. 865-868, 1982.

DOUBLE CARBONYLATION REACTIONS OF METHYL- AND PHENYLPALLADIUM(II) COMPLEXES IN THE PRESENCE OF SECONDARY AMINES AFFORDING α-KETO AMIDES

Fumiyuki OZAWA and Akio YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

The reactions of trans-$PdR(X)(PMePh_2)_2$ (R = Me, X = I and R = Ph, X = Br) with carbon monoxide in the presence of secondary amines, R'_2NH, were found to give α-keto amides, $RCOCONR'_2$, as double carbonylation products under mild conditions in good yields and selectivities.

Carbonylation reactions of organic compounds such as alkenes, and alkyl and aryl halides constitute a very important process used in industry as well as in academic laboratories.[1)] In general, these types of reactions give mono carbonylation products; for example, alkoxycarbonylation[2)] and amidation[3)] of aryl and vinyl halides catalyzed by $Pd\text{-}PPh_3$ complexes afford esters and amides, respectively. On the other hand, precedents of double carbonylation reactions are extremely limited.[4,5)] We now report that the reactions of trans-$PdR(X)(PMePh_2)_2$ (R = Me and X = I (**1**); R = Ph and X = Br (**2**))[6)] and carbon monoxide in the presence of secondary amines, R'_2NH (Et_2NH, piperidine, and morpholine), give α-keto amides as double carbonylation products in good yields and selectivities under mild conditions.

$$\begin{array}{llll} \underline{\text{trans}}\text{-}PdR(X)(PMePh_2)_2 + R'_2NH + CO \longrightarrow & RCOCONR'_2 & + \ RCONR'_2 & (1) \\ \mathbf{1}\text{: } R = Me,\ X = I & \text{(I)} & \text{(II)} & \\ \mathbf{2}\text{: } R = Ph,\ X = Br & \text{(major)} & \text{(minor)} & \end{array}$$

In a typical procedure, THF (1 ml) and Et_2NH (0.97 mmol) were added to a 50 ml stainless-steel autoclave containing trans-$PdMe(I)(PMePh_2)_2$ (0.074 mmol) under an atmosphere of nitrogen. After evacuation, CO gas (10 atm) was introduced and the mixture was magnetically stirred at room temperature. After 1 day, N,N-diethylpyruvamide (0.88) and N,N-diethylacetamide (0.07 mol/mol of complex) were obtained as identified by means of GLC and GC-mass spectrometry comparing with authentic samples. Typical results are given in the table. The following several characteristic features of the carbonylation reactions emerge from these experiments. (1) More basic amines such as Et$_2$NH and piperidine are favorable for obtaining double carbonylation products (runs 1-4). (2) The reaction carried out under pressured CO gives double carbonylation products in higher yields than the reaction under atmospheric pressure (runs 1 and 2). (3) Nonpolar solvents such as toluene give higher yields of the double carbonylation products than polar solvents (runs 4-7).

Table. Carbonylation of Methyl- and Phenylpalladium Complexes in the Presence of Amines a)

Run	Complex	Amine	CO (atm)	Solvent	Products ratio		Total yield(%)
					I	II	
1	**1**	Et$_2$NH	10	THF	93	7	95
2	**1**	Et$_2$NH	1	THF	79	21	51 b)
3	**1**	Piperidine	10	THF	82	18	77
4	**1**	Morpholine	10	THF	56	44	93
5	**1**	Morpholine	10	Toluene	94	6	80
6	**1**	Morpholine	10	DMF	46	54	91
7	**1**	Morpholine	10	CH$_2$Cl$_2$	41	59	67
8	**2**	Et$_2$NH	10	THF	96	4	74

a) Reactions have been carried out using complex(~0.1 mmol), amine(~1 mmol), and solvent(1 ml) in a stainless-steel autoclave(50 ml) at room temperature for 1 day. b) Formation of *trans*-Pd(COMe)I(PMePh$_2$)$_2$ in the system was confirmed.

The first stage of the present carbonylation reaction must be the single insertion of carbon monoxide into the Pd-C bond to give acetyl- and benzoylpalladium complexes as supported by isolation of *trans*-Pd(COMe)I(PMePh$_2$)$_2$ (run 2). 7) Attack on the acetyl- or benzoylpalladium complex by amine gives acetamide or benzamide. The second CO insertion into the acyl-palladium intermediate yielding RCOCO-Pd species followed by attack of the amine would give the α-keto amide:

$$\begin{tikzcd} \mathrm{R\text{-}Pd(X)L_2} + \mathrm{CO} \arrow[r] & \mathrm{RCO\text{-}Pd(X)L_2} \arrow[r, "\mathrm{R'_2NH}"] \arrow[d, "+\mathrm{CO}"] & \mathrm{RCONR'_2}\ (+\ \mathrm{PdH(X)L_2}) \\ (\mathrm{L} = \mathrm{PMePh_2}) & \mathrm{RCOCO\text{-}Pd(X)L_2} \arrow[r, "\mathrm{R'_2NH}"] & \mathrm{RCOCONR'_2}\ (+\ \mathrm{PdH(X)L_2}) \end{tikzcd} \tag{2}$$

In this reaction the attack of the amine on the acylpalladium species must be a slow process since trans-$\mathrm{Pd(COMe)I(PMePh_2)_2}$ could be isolated in run 2 carried out in the presence of 10 molar excess of diethylamine. Attack on the RCOCO-Pd species by amine, on the other hand, should be a rapid process. This assumption is reasonable in view of the more acidic nature of the doubly carbonylated species than the acylpalladium complex.

However, in view of the scarcity of precedents of double CO insertion into M-C bond the following alternative mechanism which involves the intermediate RCO-Pd(CO)-$\mathrm{(X)L_n}$ attacked by amine should be also considered, since the attack on the coordinated CO ligand by amine to give a carbamoyl species is a known process.[8)]

$$\begin{tikzcd} \mathrm{RCO\text{-}Pd(X)L_2} \arrow[r, "\mathrm{CO}"] & \mathrm{RCO\text{-}Pd(CO)(X)L_n} \arrow[r, "+\mathrm{R'_2NH}", "-\mathrm{HX}"'] & \mathrm{RCO\text{-}Pd\text{-}CONR'_2(L)_n} \arrow[d, "\text{reductive elimination}"] \\ & & \mathrm{RCOCONR'_2} \end{tikzcd} \tag{3}$$

From the presently available data neither mechanism can be excluded. Further study of the reaction mechanism is in progress.

It is only a simple extension from the present finding to design a catalytic system involving the double carbonylation and we did find a catalytic system to produce α-keto amides from aryl halides, cabon monoxide and amines using palladium complexes coordinated with appropriate ligands. The details of the new catalytic double carbonylation reaction will be reported separately.

References

1) J. Falbe, "New Syntheses with Carbon Monoxide", Springer-Verlag, Berlin, Heidelberg (1980); J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes",

Springer-Verlag, Berlin, Heidelberg (1975).

2) A. Schoenberg, I. Bartoletti, and R. F. Heck, J. Org. Chem., 39, 3318 (1974); J. K. Stille and P. K. Wong, ibid., 40, 532 (1975); M. Hidai, Y. Uchida, and I. Ogata, "Organotransition-Metal Chemistry", ed by Y. Ishii and M. Tsutsui, Plenum, New York (1975) p.265-271; M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, and Y. Uchida, Bull. Chem. Soc. Jpn., 48, 2075 (1975).

3) A. Schoenberg and R. F. Heck, J. Org. Chem., 39, 3327 (1974).

4) H. des Abbayes and A. Buloup, J. Chem. Soc., Chem. Comm., 1978, 1090, and references cited therein; the reactions of cis-dimethylpalladium complexes with CO in the presence of amines also give pyruvamides, F. Ozawa, M. Santra, and A. Yamamoto, unpublished results.

5) W. J. Evans, A. L. Wayda, W. E. Hunter, and J. L. Atwood, J. Chem. Soc., Chem. Comm., 1981, 706; P. J. Fagan, J. M. Manriquez, T. J. Marks, V. W. Day, S. H. Vollmar, and C. S. Day, J. Am. Chem. Soc., 102, 5393 (1980).

6) Complexes **1** and **2** were prepared by the oxidative addition reaction of MeI or PhBr to Pd(0)-PMePh$_2$ complex. Elemental analysis, (**1**) Found: C, 49.7; H, 4.6; I, 21.0%. Calcd. for $C_{27}H_{29}IP_2Pd$: C, 50.0; H, 4.5; I, 19.6%. (**2**) Found: C, 57.5; H, 4.7; Br, 12.0%. Calcd. for $C_{32}H_{31}BrP_2Pd$: C, 57.9; H, 4.7; Br, 12.0%.

7) It is well known that the reaction of monoalkylpalladium(II) complex with CO readily gives acylpalladium complex; G. Booth and J. Chatt, J. Chem. Soc., A, 1966, 634; P. E. Garrou and R. F. Heck, J. Am. Chem. Soc., 98, 4115 (1976).

8) R. J. Angelici, Acc. Chem. Res., 5, 335 (1972); C. R. Green and R. J. Angelici, Inorg. Chem., 11, 2095 (1972); W. Beck and B. Purucker, J. Organomet. Chem., 112, 361 (1976).

(Received April 7, 1982)