CHEMISTRY LETTERS, pp. 1607-1610, 1986.

Transition Metal Ketene Complexes as Active Intermediate for Catalytic Carbonylation of Geminal Dibromoalkanes

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$MX_2(PPh_3)_2$ (M= Ni, Pd, Pt; X= Cl, Br) and $Co_2(CO)_8$ catalyze alkoxy- and aminocarbonylation of geminal dibromoalkanes, $R^1R^2CBr_2$ (R^1, R^2= H and CH_3). In the course of the catalysis, initial formation of the transition metal ketene complexes, $M(CH_2{=}C{=}O)L_2$, was followed by the reaction with alcohols to yield carbalkoxymethyl metal intermediate leading to esters.

Carbonylation of organic halides using transition metal catalysts has drawn considerable attention because of their importance of various industrial process.[1)] In particular, recent development on Pd-catalyzed double-carbonylation of organic halides are current topics in homogeneous transition metal catalysis.[2)] On relevance of CO activation under mild conditions, we report catalytic carbonylation of geminal dibromoalkanes with transition metal complexes and describe its reaction mechanism involving η^2-(C,C) ketene complex of transition metal which is thought to be a CO-derived C_2-template for leading to C_2-organic products.

$$R^1R^2CX_2 \;+\; CO \;+\; HY \;+\; Zn \xrightarrow[\text{[M]}]{} R^1R^2CHCOY \;+\; ZnX_2$$

1a, R^1, R^2= H; **1b**, R^1= H, R^2= CH_3; **1c**, R^1, R^2= CH_3 Y= OCH_3, $N(C_2H_5)_2$

Alkoxycarbonylation of CH_2Br_2 was typically carried out in a pressure bottle (270 ml) containing $NiBr_2(PPh_3)_2$ (0.45 mmol), PPh_3 (0.3 mmol) and Zn powder (9.0 mmol), into which freshly distilled THF (5 ml) was added at 18 °C under N_2 to stir vigorously for 2 h. Then, addition of CH_2Br_2 (9.0 mmol) and CH_3OH (6.0 mmol) was followed by introduction of carbon monoxide (4 atm). The mixture was allowed to react at the specified temperature for the prescribed time. The reaction products were, then, determined by GLC using an internal standard and identified by NMR, Mass, and IR spectroscopies after isolation with preparative GLC.

$MX_2(PPh_3)_2$ (M= Ni, Pd, Pt; X= Cl, Br) and $Co_2(CO)_8$ were found to facilitate catalytic alkoxycarbonylation of geminal dibromoalkanes to yield the corresponding carboxylates under mild conditions as summarized in Table 1. $Co_2(CO)_8$ was found to be most effective for these catalysis. Low product yields for the reaction of CH_3CHBr_2 using Pd or Pt complex can be taken into account by generating ethylene as a major product during the reactions. In Table 2, aminocarbonylation of CH_2Br_2 with $Co_2(CO)_8$ and $MX_2(PPh_3)_2$ (M= Ni, Pd, Pt) was summarized. In benzene, the yield of acetamide was improved by increasing CO pressure and reaction temperature using $Co_2(CO)_8$ catalyst.

Table 1. Methoxycarbonylation of geminal dibromoalkanes a)

Catalyst	Yield of $R^1R^2CHCO_2CH_3$ b)		
	1a	1b	1c
$NiBr_2(PPh_3)_2$	16%	23	37
$PdCl_2(PPh_3)_2$	26	2	26
$PtCl_2(PPh_3)_2$	42	4	33
$Co_2(CO)_8$	68	46	54

a) Reaction conditions: $R^1R^2CBr_2$/Zn/cat. ≃ 1/1/0.05 (molar ratio), at 18 °C, for 25 h. p(CO)= 4 atm. b) Based on $R^1R^2CBr_2$.

Table 2. Aminocarbonylation of CH_2Br_2 a)

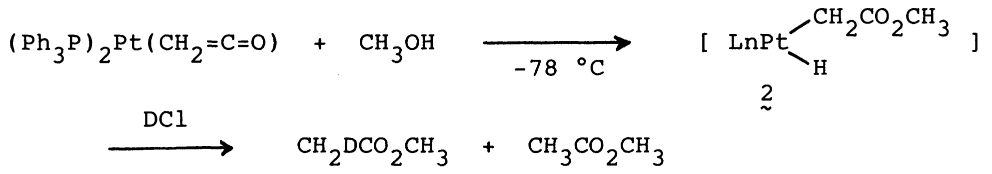
Catalyst	Solvent	CH_3CONEt_2 b)
$NiBr_2(PPh_3)_2$	THF	3%
$PdCl_2(PPh_3)_2$	THF	4
$PtCl_2(PPh_3)_2$	THF	6
$Co_2(CO)_8$	THF c)	1
	THF	9
	$HNEt_2$	2
	C_6H_6	9
	C_6H_6 d)	14
	C_6H_6 e)	31

a) Reaction conditions: CH_2Br_2/Zn/cat. ≃ 1/1/0.03 (molar ratio), for 24 h, at 18 °C. b) Based on CH_2Br_2. c) In the absence of Zn. d) At 50 °C. e) At 50 °C and p(CO)= 20 atm.

Taking into account that η^2-(C,C) ketene complexes of Ni, Pd and Pt, $M(CH_2{=}C{=}O)L_2$, have been cleanly isolated from the reaction of MX_2L_2 with CH_2Br_2 and CO in the presence of Zn,3) it should be noted that these ketene complexes are presumed to play key roles in these catalyses.4) As the matter of fact, the isolated ketene complexes readily reacted stoichiometrically with alcohols, or primary and secondary amines to give the corresponding alkyl carboxylate or amides in quantitative yield.

$$MX_2L_2 + CH_2Br_2 + CO \xrightarrow[THF]{Zn} L_2M(CH_2{=}C{=}O) + ZnBr_2$$

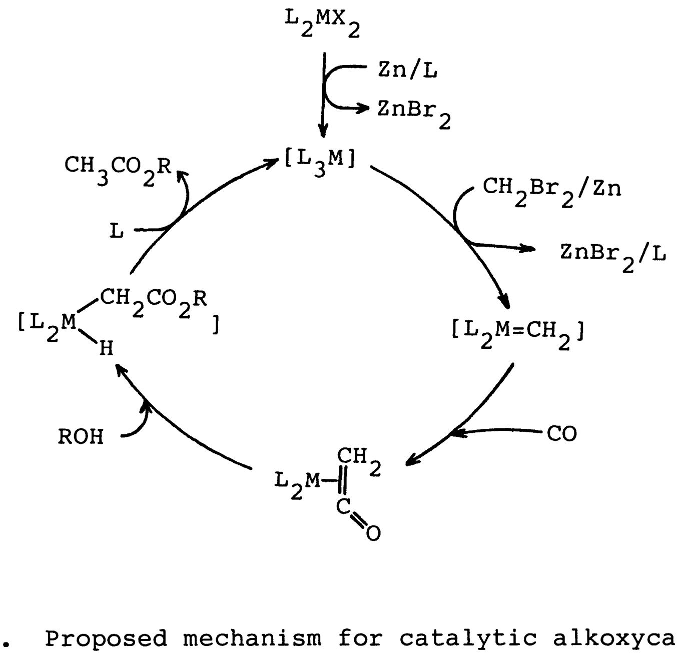
A question about how alcohol as a nucleophile attacks the ketene moiety so as to form the reaction intermediate leading to alkyl carboxylate, was investigated by the treatment of $Pt(CH_2{=}C{=}O)(PPh_3)_2$ with equimolar of CH_3OH below -78 °C. It was found that the resulting yellow solution afforded $CH_2DCO_2CH_3$ (55%/Pt) and $CH_3CO_2CH_3$ (37%/Pt) after quenching with dry deuterium chliride.



$$(Ph_3P)_2Pt(CH_2{=}C{=}O) + CH_3OH \xrightarrow[-78\ °C]{} \underset{\mathbf{2}}{\left[\ LnPt\begin{matrix}\diagup CH_2CO_2CH_3\\ \diagdown H\end{matrix}\ \right]}$$

$$\xrightarrow{DCl} CH_2DCO_2CH_3 + CH_3CO_2CH_3$$

These results are substantially in accordance with the formation of carbomethoxymethyl platinum complex **2** in the course of the reaction,5) although attempted isolation of the reaction intermediate **2** has been so far unsuccessful.



Scheme 1. Proposed mechanism for catalytic alkoxycarbonylation via transition metal ketene complexes.

Based on these results of stoichiometric model reactions, we propose main features of the catalytic alkoxycarbonylation processes, depicted in Scheme 1,[6)] which could be composed of the elementary process of (a) initial reduction of MX_2L_2 with Zn to give M(0)Ln complexes, (b) formation of transition metal carbene intermediates from the reaction of $M(0)L_3$ with CH_2Br_2/Zn, (c) CO-coupling reaction with carbene species resulting transition metal ketene complexes, (d) attack of alcohol on the $CH_2=C=O$ ligand to give a carbalkoxymethyl-hydride metal intermediate and (e) reductive elimination of acetate to regenerate the M(0) species as a carrier of the subsequent catalytic cycle. Aminocarbonylation of $R^1R^2CBr_2$ could proceed as well.

It should be noted that transition metal ketene complexes, which were believed to be one of active intermediate as C_2-template for CO reduction chemistry, played key role for catalytic carbonylation of organic halides.

References

1) M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, and Y. Uchida, Bull. Chem. Soc. Jpn., 48, 2075 (1975); J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes," Springer-Verlag, West Berlin (1975).

2) F. Ozawa, H. Soyama, T. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto, and A. Yamamoto, J. Am. Chem. Soc., 107, 3235 (1985); T. Kobayashi and M. Tanaka, J. Organomet. Chem., 233, C64 (1982).

3) A. Miyashita, H. Shitara, and H. Nohira, J. Chem. Soc., Chem. Commun., 1985, 850; Organometallics, 4, 1463 (1985).

4) $Co_2(CH_2=C=O)(CO)_7$, isolated from the reaction of $Co_2(CO)_8$ with CH_2Br_2 in the presence of Zn, may not be actual intermediate for these catalysis. Detailed studies on its structure and chemical behavior will be reported elswhere.

5) A recent report on the formation of carbalkoxymethyl complex of Fe by the treatment of $[Fp(CH_2=C=O)]^+$ complex with alcohol has been made. E. J. Crawford, C. Lamberd, K. P. Menard, and A. R. Cutler, J. Am. Chem. Soc., 107, 3130 (1985).

6) An alternative route involving methoxycarbonyl-methylene metal species seems to be conceivable for heterogeneous surface chemistry. J. Hackenbruch, W. Keim, M. Röper, and H. Strutz, J. Mol. Cat., 26, 129 (1984).

(Received June 28, 1986)