Efficiently Catalytic C-H Activation. Direct and Mild Carbonylation of Benzene and Cyclohexane by RhCl(CO)(PMe<sub>3</sub>)<sub>2</sub> under Irradiation

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A high turnover number was achieved in the photo-assisted carbonylation of C-H bonds of benzene catalyzed by  $RhCl(CO)(PMe_3)_2$ under mild conditions (1 atm, 37 °C) to give mainly benzaldehyde. Cyclohexane could also be carbonylated under the same conditions.

Although great efforts have been made to activate and to functionalize C-H bonds of alkanes or arenes under mild conditions assisted by transition metal complexes,<sup>1)</sup> there have been few catalytic reactions attained. Several groups reported the intermolecular oxidative addition of C-H bonds to iridium or rhodium complexes under irradiation,<sup>2-4)</sup> but the reactions were not catalytic. Although catalytic carboxylations of benzene under oxidative conditions to produce benzoic acid by  $Pd(OAc)_2$ -t-BuOOH system was reported, the turnover numbers were not so high.<sup>5)</sup> Photo-assisted carbonylation of benzene to afford benzaldehyde by  $IrH_3(CO)(Ph_2PCH_2CH_2PPh_2)$  was reported by Eisenberg et al.<sup>6)</sup> The reactivity, however, was low and it is not clear whether the reaction proceeds catalytically. Very recently, they reported another system using RhCl(CO)(PPh\_3)<sub>2</sub>, but the yields were still very poor.<sup>7)</sup> They ascribed this to the equilibrium between benzene and benzaldehyde (Eq. 1).<sup>8)</sup>

 $PhH + CO \longrightarrow PhCHO$  (1)

In search for efficient complex catalysts, we have also examined the carbonylation of benzene using rhodium carbonyl complexes under irradiation. The mixture (Rh 0.21 mg-atom, benzene 30  $\text{cm}^3$ ) in a Pyrex flask was irradiated by a 100 W high pressure mercury lamp under an atmospheric pressure of CO (balloon)

at 37 °C. Among several complexes investigated, a Vaska type complex  $RhCl(CO)(PPh_3)_2$  was found to afford benzaldehyde and benzoic acid<sup>9)</sup> (Eq. 2),

PhH + CO 
$$\xrightarrow{h \cup, 37 \ ^{\circ}C, 16.5 \ h}$$
 PhCHO + PhCO<sub>2</sub>H (2)  
(1 atm)  $\xrightarrow{RhCl(CO)(PPh_3)_2 \ (7 \ mM)}$  20%/Rh 11%/Rh

although the yield was low.<sup>10)</sup> The complex remained almost unchanged after the reaction as judged from IR.  $RhCl(CO)[P(p-tolyl)_3]_2$  also gave benzaldehyde (45%/Rh after 16.5 h) proving that the aldehyde came from benzene rather than the ligand cleavage.<sup>11)</sup> The complexes such as  $RhCl(CO)_2[P(p-tolyl)_3]$ , [RhCl(CO)<sub>2</sub>]<sub>2</sub>,  $Rh_4(CO)_{12}$  were ineffective.

Since higher electron density on the central metal is favorable for the oxidative addition reaction,<sup>12)</sup> the poor reactivity observed with  $RhCl(CO)(PPh_3)_2$  seems to be due to the low electron-donating power of the ligand. In fact, the use of an even weaker electron donor,  $P(OMe)_3$ , instead of  $PPh_3$  resulted in a poorer yield (PhCHO 8%/Rh after 16.5 h), whereas a highly electron donating trialkylphosphine,  $PEt_3$ , improved the yield markedly (172%/Rh). Another factor which controls the reactivity in this system might be "tail biting" (the oxidative addition of ligand C-H bonds). As a matter of fact, a further improvement of the yield (811%/Rh) was achieved by RhCl(CO)(PMe\_3)<sub>2</sub> in place of RhCl(CO)(PEt\_3)<sub>2</sub>. A substantial amount of PhCH<sub>2</sub>OH, PhCOPh, and Ph-Ph was also formed in these reactions.<sup>13</sup>)

Figure 1 shows the time dependence of the reaction catalyzed by  $RhCl(CO)(PMe_3)_2$ . The total turnover number for Ph group reached 47.8 after 94 h (Eq. 3). The low reaction rate after 60 h is not due to the limitation of the

DI U	+ (1	00	hv, 37 °C					_					
рпн		atm)	$RhCl(CO)(PMe_3)_2$ (7 mM)										
				PhCHO	+	${\tt PhCH}_2{\tt OH}$	+	$^{\rm PhCO}2^{\rm H}$	+	Ph-Ph	+	PhCOPh	(3)
		16.5	h	811%/	Rh	103		6		21		49	
		94.0	h	2519		931		109		77		533	

equilibrium (Eq. 1), because, when the catalyst concentration was increased from 7 mM to 35 mM, the benzaldehyde formation doubled.<sup>14)</sup> PhCH<sub>2</sub>OH, PhCOPh, and PhCO<sub>2</sub>H are presumably secondary products from PhCHO, since the ratio of these products to PhCHO increased clearly as the reaction proceeded (Eq. 3).



Fig. 1. Time dependence of the reaction catalyzed by  $RhCl(CO)(PMe_3)_2$ . Reaction conditions; Rh 0.21 mg-atom, benzene 30 cm<sup>3</sup>, CO 1 atm, 37 °C.





Scheme 1 represents a tentative mechanism which includes well documented elementary steps, namely, photo-assisted CO dissociation, oxidative addition of benzene, CO insertion, and followed by reductive elimination of the aldehyde.

It is noteworthy that the system reported herein is applicable to the carbonylation of alkanes. Thus, cyclohexane gave cyclohexanecarboxaldehyde and cyclohexanecarboxylic acid (Eq. 4).<sup>13)</sup> This is the first example of carbonylation of alkane C-H bonds assisted by transition metal complexes. Since the rhodium complex remained almost unchanged after the reaction, the reaction is essentially catalytic, though it is sluggish.

 $\begin{array}{c} cyclo-C_{6}H_{12} + CO & \xrightarrow{h\nu, 37 \ ^{\circ}C, 16.5 \ h} \\ (1 \ atm) & \xrightarrow{RhCl(CO)(PMe_{3})_{2}} \\ (6.4 \ \text{mM}) & \xrightarrow{cyclo-C_{6}H_{11}CHO} + cyclo-C_{6}H_{11}CO_{2}H \ (4) \\ 3\%/Rh & \xrightarrow{3\%/Rh} \end{array}$ 

Regioselective carbonylation of substituted benzenes and non-cyclic alkanes as well as the improvement of catalytic activity is now under investigation.

References

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- 8) In spite of this statement, the yields obtained in their experiments were by far lower than the value expected from the equilibrium constant caluculated by themselves  $(K = 5.9 \times 10^{-2} \text{ atm}^{-1}).^{6)}$
- 9) Benzoic acid seems to be an oxidation product of benzaldehyde by O<sub>2</sub>. Gas phase analysis revealed that air had come in through the balloon during the reaction.
- 10) The yield of benzaldehyde was comparable to that reported by Eisenberg et al. (CO 615 mmHg, 20 h, PhCHO 24%/Rh; see Ref. 7.).
- Aldehyde formation via the cleavage of phosphine ligands is well documented. See for example T. Sakakura, T. Kobayashi, T. Hayashi, Y. Kawabata, M. Tanaka, and I. Ogata, J. Organomet. Chem., <u>267</u>, 171 (1984).
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- 13) All the products were characterized by the comparison of the retention time of GC and MS fragmentation pattern with authentic samples.
- 14) The thermodynamic limitation may allow about 100 turnovers for benzaldehyde formation under the conditions of this paper (Rh 7 mM, CO 1 atm). $^{6,8)}$

(Received October 6, 1986)

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