

CATALYSIS OF RHODIUM CLUSTERS.

P-C BOND CLEAVAGE REACTION OF TRIPHENYLPHOSPHINE

Kiyotomi KANEDA, Kotaro SANO, and Shiichiro TERANISHI

Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

$\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ cluster complexes catalyze the P-C bond cleavage reaction of triphenylphosphine to give benzaldehyde and benzyl alcohol. Formaldehyde is necessary for attaining high yield of benzaldehyde.

Much attention has been paid to metal clusters because the metal clusters catalyze many new kinds of chemical reactions and form models for studying the heterogeneous metal catalysis.¹⁾

In the course of studies of rhodium carbonyl cluster catalysis, we have found that the rhodium clusters catalyzed the P-C bond cleavage reaction of triphenylphosphine accompanying the carbonylation to give benzaldehyde and benzyl alcohol under mild conditions. Previously, we have reported the palladium-assisted P-C bond cleavage reaction which was stoichiometric with respect to palladium.²⁾ In contrast to the palladium reaction, this rhodium reaction is catalytic and characteristic to the rhodium cluster complexes.

Representative examples are shown in Table. Rhodium carbonyl clusters containing metal-metal bond catalyze the P-C bond cleavage reaction. $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ gave a quantitative yield of benzaldehyde, respectively.³⁾ On the contrary, RhCl_3 , $\text{RhCl}(\text{PPh}_3)_3$, and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ had no activity. $\text{Pd}(\text{OAc})_2$ which had assisted the P-C bond cleavage reaction to give stilbene, did not give benzaldehyde or benzyl alcohol under present reaction conditions.

Formaldehyde is necessary for attaining high yield of benzaldehyde. For example, in the absence of formaldehyde, the yield of benzaldehyde decreased to 27%. It is remarkably dependent on CO pressure; the optimum CO pressure is 5 atm. Under high pressure of CO, triphenylphosphine can not coordinate to rhodium because CO molecules occupy all coordinating sites. Furthermore, the presence of H_2 depressed the yield. In the absence of CO, the yield fell to 40%. It seems that CO might play an important role of retaining cluster frame. Detailed roles of formaldehyde are not clear yet. Probably, the aldehyde might act as a main source of supply of CO and hydrogen.

Other phosphorous compounds were applied to this reaction. However, alkylphosphine, phosphine oxides, and phosphites gave no P-C, P-O, or C-O bond cleavage products. Triphenylphosphine only reacts. Furthermore, other triphenyl-compounds of the group V elements were tried but the yields of benzaldehyde were low (10% for $\text{Sb}(\text{C}_6\text{H}_5)_3$, 8% for $\text{As}(\text{C}_6\text{H}_5)_3$, and 1% for $\text{Bi}(\text{C}_6\text{H}_5)_3$). Triphenylamine gave no products. Conclusively, this rhodium-catalyzed cleavage reaction shows a high reactivity for phenyl-phosphorous compound.

Recently, Hong et. al., reported that rhodium clusters catalyzed addition of aromatic C-H bond in benzene to unsaturated compounds to give phenyl substituted ones.⁴⁾ Under present conditions,

Table. Effect of Various Rhodium Compounds and Reaction Conditions on Carbonylation^a

Catalyst	Pressure		Product Yield(%) ^b	
	CO(atm)	H ₂ (atm)	Benzaldehyde	Benzyl alcohol
Rh ₂ (CO) ₄ Cl ₂	5	0	0	0
Rh ₄ (CO) ₁₂	5	0	98	trace
Rh ₆ (CO) ₁₆	5	0	99	trace
Rh ₁₂ (CO) ₃₀ ²⁻	5	0	98	trace
Rh ₆ (CO) ₁₆ ^c	1	0	4	5
Rh ₆ (CO) ₁₆	0	10	16	4
Rh ₆ (CO) ₁₆	1	9	64	11
Rh ₆ (CO) ₁₆ ^d	20	30	16	4
Rh ₆ (CO) ₁₆	5	0	27	0
Rh ₆ (CO) ₁₆	argon(10 atm)		40	5
Rh ₆ (CO) ₁₆ ^e	2	8	72	22

a. Using catalyst, 5×10^{-2} mmol; paraformaldehyde, 2.5 mmol; PPh₃, 1 mmol; H₂O, 0.1 ml at 80°C for 24 hr in 10 ml of dioxane. b. Based on PPh₃ mol. c. Refluxed in dioxane. d. Without adding formaldehyde. e. Using formalin, 50 mmol.

however, benzene was not activated to give C-H bond cleavage products, e. g., benzaldehyde, benzyl alcohol or biphenyl.

In the case of tri-*p*-tolylphosphine, *p*-tolualdehyde was exclusively formed. It can be said that this reaction does not involve the ortho-metalation process.⁵⁾ Considering that only cluster complexes have a catalytic activity and high reactivity for phenyl group,^{4,6,7)} we can imagine that two metal centers might assist the P-C bond cleavage reaction, which is demonstrated for heterogeneous catalysts (Fig).

References and Notes

- 1) For an excellent review see, E.L.Muetterties, *Science*, **196**, 839 (1977).
- 2) R.Asano, I.Moritani, Y.Fujiwara, and S.Teranishi, *Bull.Chem.Soc.Japan*, **46**, 2610 (1973).
- 3) After 24 hr reaction using Rh₆(CO)₁₆, triphenylphosphine, triphenylphosphine oxide, and biphenyl could not be detected. It was reported that Rh₄(CO)₁₂ and Rh₆(CO)₁₆ reacted with triphenylphosphine in the presence of CO to give rhodium dimer complexes: a) R.Whyman, *J.Chem.Soc., Dalton Trans.*, 1375 (1972). b) B.L.Booth, M.J.Else, R.Fields, and R.N.Haszeldine, *J.Organomet.Chem.*, **27**, 119 (1971). Details of reaction mechanism are under investigation by using IR spectroscopy; the resulting solution showed absorptions at 1820 and 1985 cm⁻¹ due to bridging and terminal CO, respectively.
- 4) a) P.Hong, H.Yamazaki, K.Sonogashira, and N.Hagiwara, *Chem. Lett.*, 535 (1978). b) P.Hong, B.Cho, and H.Yamazaki, *ibid.*, 339 (1979).
- 5) R.F.Heck, "Organotransition Metal Chemistry, Mechanistic Approach" Academic Press, New York and London, p.38 (1974).
- 6) M.S.Jarrel and B.S.Gates, *J.Catal.*, **54**, 81 (1978).
- 7) C.W.Bradford, R.C.Nyholm, G.J.Gainsford, J.M.Guss, P.R.Ireland, and R.Mason, *J.Chem.Soc., Chem. Commun.*, 87 (1972).

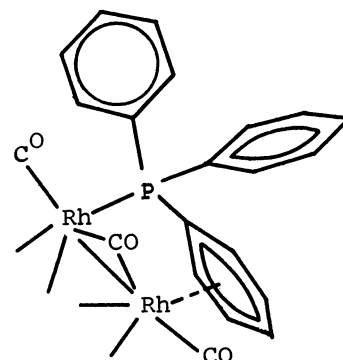


Fig. Interaction between Rh-Cluster and Triphenylphosphine

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