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Catalytic Formation of Biaryls from Arenes through C-H Bond Activation by $RhCl(CO)(PMe_3)_2$ under Irradiation

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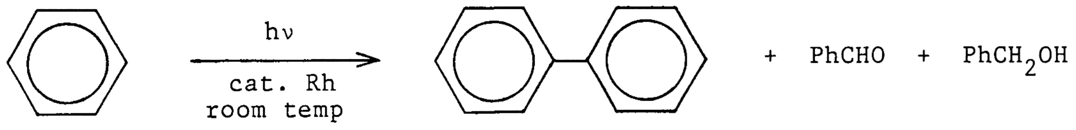
Arenes were dehydrogenatively coupled into biaryls catalyzed by $RhCl(CO)(PMe_3)_2$ at room temperature under irradiation. The regioselectivity obtained in the reaction of toluene suggested the presence of a radical intermediate.

Catalytic functionalization of C-H bonds is one of the most promising and challenging fields in homogeneous catalysis,$^{1)}$ because it hopefully creates an entirely new chemical technology to utilize hydrocarbons directly under mild conditions. An interesting approach to this problem is the palladium-catalyzed reactions of arenes; biaryl synthesis *via* oxidative coupling$^{2)}$ is now an industrial process. However, since the reaction presumably proceeds through electrophilic aromatic substitution by Pd(II), the substrates are restricted to arenes. Hence, new methodologies are highly desired. We have recently reported the carbonylation of alkanes as well as arenes catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation to give aldehydes,$^{3-6)}$ where the catalytic cycle was initiated by the oxidative addition of C-H bonds. Dehydrogenative coupling products were formed in those reactions as by-products. We now report here that the reaction of arenes takes place even under nitrogen yielding biaryls as main products.

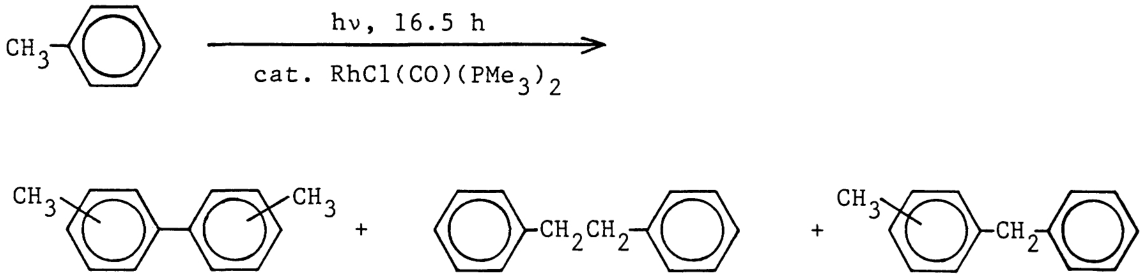
A typical reaction procedure was as follows. A 0.7 mM solution of the catalyst (30 cm^3) placed in a Pyrex flask under nitrogen was irradiated by a immersion-type 100 W high pressure mercury lamp (UVL-100HA, Riko Corp.) at room temperature. The products were characterized by GC retention time and GC-MS spectrometry. The result of benzene reaction is shown in Eq. 1. The reaction



1.0 h	43%/Rh	26%/Rh	2%/Rh
16.5 h	360	3	26
189.0 h	1330	1	45

(1)

mixture appeared homogeneous even after 189 h. The formation of the carbonylated products (benzaldehyde and benzyl alcohol) were ascribed to the carbonyl ligand in the catalyst. Both a triarylphosphine complex, RhCl(CO){P(p-$C_6H_4CH_3)_3\}_2$ and an iridium complex, $IrCl(CO)(PMe_3)_2$ were much less effective catalysts; the yields of biphenyl were 22 and 42%/Rh after 16.5 h, respectively. These trends are similar to those observed in the C-H bond carbonylation reaction.$^{3)}$ The co-existance of the catalyst and the light was essential for the reaction. An attempted thermal reaction after a three hour irradiation to generate coordinatively unsaturated species gave no biphenyl even at 70 °C. The reaction proceeded again by the reirradiation showing that the active species was still alive after the thermal reaction. The reaction of toluene gave a regioisomeric mixture of bitolyls (Eq. 2). 1,2-Diphenylethane and benzyltoluene

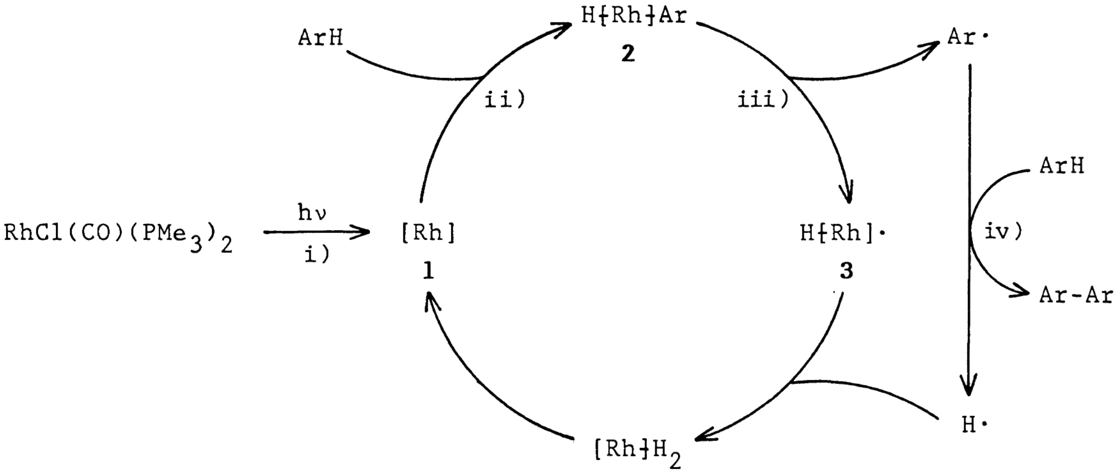


221%/Rh 0%/Rh 0%/Rh (2)

Regioselectivity

o,o'	*o,m'*	*o,p'*	*m,m'*	*m,p'*	*p,p'*
0	43	15	20	19	4

were not detected. The regioisomeric ratio of total tolyl group (ortho : meta : para) was 29 : 50 : 21. If both of the two tolyl groups of the bitolyls have come directly from the tolylrhodium complex formed through the oxidative addition of C-H bonds, the formation of ortho-tolyl group should be very little and m,m'-bitolyl should be the major isomer.7) On the other hand, radical substitution reactions of toluene mainly occurs at the ortho-position.8) A substantial amount of the ortho-isomers formed in the present system possibly suggests the existance of a radical intermediate in the carbon-carbon bond formation.9) But the radical formation via hydrogen abstraction is unlikely, because the benzyl group, which should have been formed very easily by hydrogen abstraction from toluene, was not involved in the products. Taking these results into account, the following mechanism would be acceptable (Scheme 1), although the regeneration process of the active catalyst **1** from **3** is ambiguous at the moment;10) i) formation of a coordinatively unsaturated complex **1** from the initial Vaska-type complex by irradiation, ii) oxidative addition of toluene to the complex affording a tolylrhodium complex **2**, iii) homolytic cleavage of the tolyl-rhodium bond yielding a tolyl radical (presumably effected by the irradiation), iv) substitution reaction of toluene by the tolyl radical to give a bitolyl molecule.11) The regioisomeric ratio of the bitolyls obtained in the reaction was consistent with the expected value calculated from the regioisomeric ratio of the oxidative addition7) and the radical substitution reaction8) of toluene.



Scheme 1.

In conclusion, we have achieved a new application of the C-H activation, a dehydrogenative coupling of arenes, catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation. Further extension of the C-H activation to various homogeneous catalysis is now under investigation.

References

1) R. H. Crabtree, Chem. Rev., 85, 245 (1985).
2) H. Itatani and H. Yoshimoto, J. Org. Chem., 38, 76 (1973); Bull. Chem. Soc. Jpn., 46, 2490 (1973).
3) T. Sakakura and M. Tanaka, Chem. Lett., 1987, 249.
4) T. Sakakura and M. Tanaka, Chem. Lett., 1987, 1113.
5) T. Sakakura and M. Tanaka, J. Chem. Soc., Chem. Commun., 1987, 758.
6) T. Sakakura, T. Hayashi, and M. Tanaka, Chem. Lett., 1987, 859.
7) The carbonylation of toluene catalyzed by $RhCl(CO)(PMe_3)_2$ gave o-, m-, and p-tolualdehyde in the ratio of 2 : 64 : 34, respectively; see Ref. 4.
8) The regioisomeric ratio (o : m : p) obtained in the phenylation of toluene with benzoyl peroxide was 67 : 19 : 14; M. T. Edmison, Chem. Rev., 57, 77 (1957); D. R. Augood and G. H. Williams, ibid., 57, 123 (1957).
9) Addition of radical scavengers (5 equivalent to Rh) such as 2,2-diphenyl-1-picrylhydrazyl, p-benzoquinone, and oxygen markedly suppressed the reaction. However, this doesn't necessarily prove the radical mechanism, because the inhibitory effect is also explainable in terms of the decomposition of the catalyst and the absorption of the light by the radical scavengers rather than the catalyst.
10) The gas phase analysis of the benzene reaction (16.5 h) revealed the existance of hydrogen (about 50%/Rh) and carbon monoxide (24%/Rh). Although the amount of hydrogen is by far smaller than the calculated value for the biphenyl formation, cyclohexane was not detected, which should have been formed through the hydrogenation of benzene.
11) In the reaction of a phenyl radical with toluene below 25 °C, the main product was methylbiphenyl without any detectable amount of 1,2-diphenylethane or diphenylmethane; C. S. Rondestvedt, Jr. and H. S. Blanchard, J. Am. Chem. Soc., 77, 1769 (1955).

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