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Photoassisted C-H Bond Activation with $RhCl(CO)(PR_3)_2$ in the Presence of Isocyanides Leading to Catalytic Formation of Aldimines

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C-H bond activation of benzene and pentane in the presence of isocyanides was promoted by $RhCl(CO)(PR_3)_2$ to result in the isocyanides insertion into C-H bonds.

Activation and functionalization of C-H bonds of hydrocarbons have attracted considerable attention. In particular, creation of catalytic reactions through C-H bond activation is of fundamental importance in view of saving energy and resources consumed in chemical industries. However, examples of catalytic reactions are still limited. In addition, most of the reactions so far reported are of H/D exchange or of alkene formation through dehydrogenation of (cyclo)-alkanes in the presence of other types of alkenes as hydrogen acceptors (usually 3,3-dimethyl-1-butene).1) Neither of these reactions is, albeit the mechanistic importance, productive2) in their own right from synthetic viewpoints.

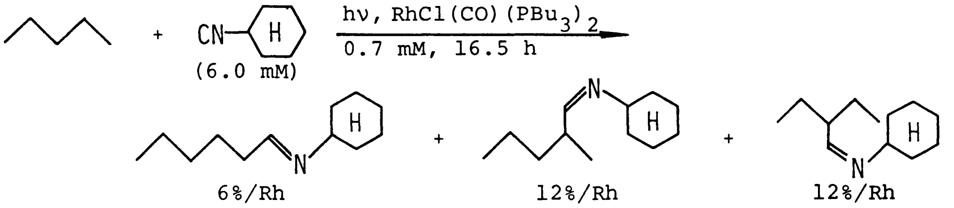
In the previous papers, we have reported productive functionalizations of hydrocarbons including the m- and terminal selective carbonylation of arenes and alkanes,3) terminal olefin synthesis,4) and dehydrogenative coupling of arenes yielding biaryls.5) All of these reactions are promoted by $RhCl(CO)(PMe_3)_2$ under irradiation. Further studies along this line have revealed that isocyanides are introduced into the C-H bond of benzene and pentane. Similar reactions of benzene have been disclosed in a very recent publication by Jones et al.6) The paper prompted us to report our results.

$$C_6H_6 + RNC \xrightarrow[\text{room temperature}]{h\nu,\ RhCl(CO)(PMe_3)_2} C_6H_5CH{=}NR + C_6H_5CH_2NHR\ (+\ C_6H_5C_6H_5) \quad (1)$$

When a benzene solution (30 ml) of cyclohexyl isocyanide (55 mM) and $RhCl(CO)(PMe_3)_2$ (0.7 mM) was irradiated in a Pyrex flask with a 100 W immersion type high pressure mercury lamp (UVL-100HA, Riko Corp.) for 16.5 h, N-benzylidenecyclohexylamine and biphenyl were formed in 9 and 27% yields respectively based on the rhodium complex. By reducing the isocyanide concentration down to 5 mM, the imine formation proceeded catalytically with respect to the rhodium complex to give 245%/Rh yield. A small amount of N-benzylcyclohexylamine (ca. 15%/Rh) was also formed.7) N-Benzylidenecyclohexylamine is known to reductively dimerize under irradiation in ethanol to yield 1,2-bis(cyclohexylamino)-1,2-diphenylethane.8) However, under the present reaction conditions, the reductive dimer was not formed at all. Prolonged reaction (36 h) with a supplemental addition of the isocyanide (0.12 mmol) at the 13.5 h reaction time increased the imine yield up to 467%/Rh.

Reactions of benzene (16.5 h) with methyl isocyanide (5 mM), t-butyl isocyanide (5.6 mM), and p-tolyl isocyanide (8.4 mM) afforded the corresponding imines in 38, 3, and 4%/Rh yields, respectively. The variant yields are presumably due to the differences in the structures, electronic natures, and/or the solubililities of the mixed phosphine/isocyanide complexes formed upon the addition of isocyanides to $RhCl(CO)(PMe_3)_2$; a precedent has disclosed that addition of isocyanide to $RhCl(CO)(PPh_3)_2$ affords either $[Rh(PPh_3)_2(CNR)_2]Cl$ or $[Rh(PPh_3)_2(CNR)_3]Cl$ depending on the structure of isocyanides.$^{9)}$

Extension of the $RhCl(CO)(PMe_3)_2$-cyclohexyl isocyanide system to the paraffin reactions was hampered by the insolubility of the phosphine/isocyanide complex formed upon mixing; irradiation of the heterogeneous mixture in pentane did not afford the imine(s) in detectable yield(s) by gas chromatography. The same problems were encounterd with the systems $RhCl(CO)(PMe_3)_2$-t-butyl isocyanide and $RhCl(CO)[P(CH_2O)CCH_3]_2$-cyclohexyl isocyanide. However, the complex formed from $RhCl(CO)(PBu_3)_2$ (0.7 mM) and cyclohexyl isocyanide appeared at least partly soluble in pentane. As shown in Eq. 2, irradiation really yielded the imines although not catalytic as yet.



(2)

To summarize, this communication offers the new clue to catalytic insertion of isocyanides into arene C-H bonds as well as the first example of the aldimine formation through paraffin C-H bond activation.

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