CHEMISTRY LETTERS, pp. 2375-2378, 1987.

Catalytic C-H Activation. Silylation of Arenes with Hydrosilane or Disilane by $RhCl(CO)(PMe_3)_2$ under Irradiation

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Direct silylation of arenes with triethylsilane or hexamethyldisilane were catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation.

Organosilicons have been revealed to be a versatile class of compunds in relation to photoresists, semiconductors, preceramics,1) reagents for organic synthesis,2) and bioactive compounds.3) Hence, synthesis of organosilicons is becoming increasingly important. The methods to form silicon-carbon bonds are, however, still limited to a few reactions such as organic halide-based Wurtz-type or Grignard reactions with halosilanes and hydrosilylation besides the Rochow process. On the other hand, similar chemical reactivities of hydrosilane to dihydrogen have been widely recognized.4) In addition, H/D exchange of hydrocarbons have been well documented.5) These considerations prompted us to examine the possibility of direct silylation of hydrocarbons with hydrosilane or disilane through H/Si exchange6) using $RhCl(CO)(PMe_3)_2$ which is capable of catalytic C-H bond activation under irradiation.7)

$$RH + R'_3SiH \longrightarrow RSiR'_3 + H_2 \qquad (1)$$

$$RH + R'_3SiSiR'_3 \longrightarrow RSiR'_3 + R'_3SiH \qquad (2)$$

Irradiation of a benzene solution (30 cm^3) containing triethylsilane (2.1 mmol) and $RhCl(CO)(PMe_3)_2$ (0.021 mmol) as the catalyst by means of a immersion type high pressure mercury lamp (UVL-100HA, Riko Corp.) for 16.5 h afforded triethylphenylsilane (177%/Rh) and biphenyl (304%/Rh),8) respectively. When the

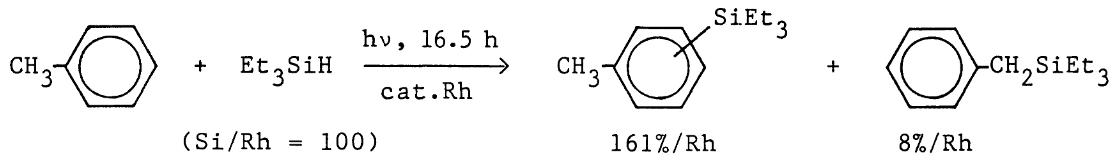
Si/Rh ratio was increased to 1000, triethylphenylsilane became the main product (Eq. 3).[9] A substantial amount of hydrogen (about 700%/Rh) was detected in the gas phase. The reaction mixture appeared homogeneous after the reaction. If the present reaction proceeded through the oxidative addition of hydrosilane to the rhodium species, a similar catalytic silylation is expected to occur in the use of disilane instead of hydrosilane. In fact, trimethylphenylsilane was formed by the reaction of benzene with hexamethyldisilane (disilane/Rh = 1000) (Eq. 4). Coexistance of the catalyst and the light was essential for the present silylations using monohydrosilane or disilane.

$$\mathrm{PhH} + \mathrm{Et_3SiH} \xrightarrow[\text{cat. Rh, 16.5 h}]{h\nu,\ \text{room temp}} \underset{376\%/\mathrm{Rh}}{\mathrm{PhSiEt_3}} + \underset{92\%/\mathrm{Rh}}{\mathrm{Ph\text{-}Ph}} \qquad (3)$$

$$\mathrm{PhH} + \mathrm{Me_3SiSiMe_3} \xrightarrow[\text{cat. Rh, 16.5 h}]{h\nu,\ \text{room temp}} \underset{323\%/\mathrm{Rh}}{\mathrm{PhSiMe_3}} + \underset{230\%/\mathrm{Rh}}{\mathrm{Ph\text{-}Ph}} \qquad (4)$$

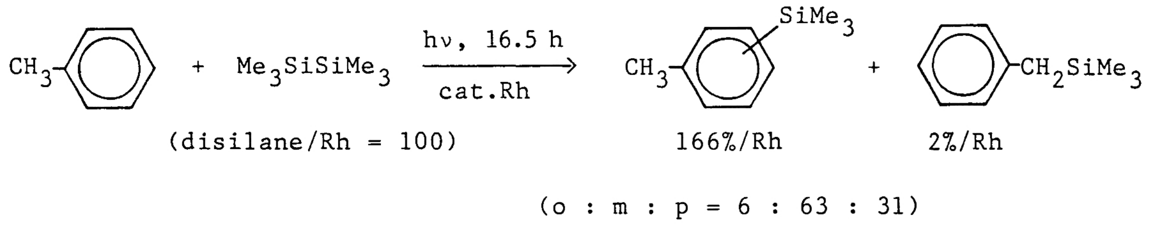
In the previous paper on the biaryl formation,[8] we postulated the existance of an aryl radical intermediate. However, the mechanism involving an aryl radical intermediate (Eq. 5) seemes to be unlikely for the present arylsilane formation, taking account of the precedent that the Si-Si bond cleavage did not occur in the reaction of hexamethyldisilane with phenyl radical.[10] In addition, a trimethylsilyl radical intermediate seems to be unlikely, either; toluene underwent the silylation of the aromatic ring in preference to the methyl group (Eqs. 6 and 7).[11] The regioisomeric ratios of tolylsilanes were

$$\begin{tikzcd} & \mathrm{R_3Si\cdot} \arrow[r, "\mathrm{ArH}"] & \mathrm{ArSiR_3} \\ \mathrm{Ar\cdot} \arrow[ur, "\mathrm{R_3SiSiR_3}"] \arrow[dr] & & \\ & \mathrm{ArSiR_3} & \end{tikzcd} \qquad (5)$$



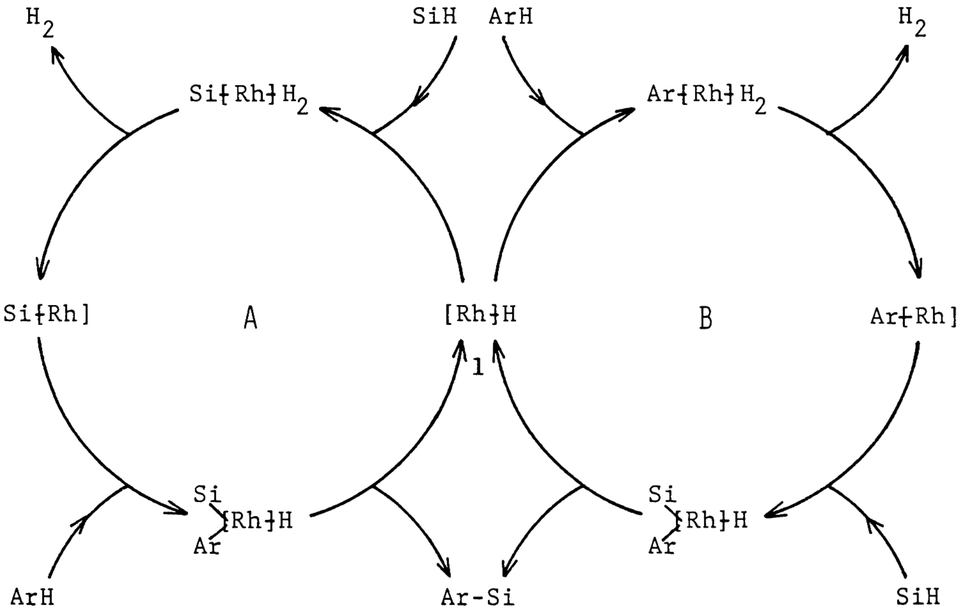
(6)

(o : m : p = 4 : 58 : 38)



(7)

similar to that obtained in the carbonylation (o : m : p = 2 : 64 : 34) catalyzed by the same complex.[8] If a free trimethylsilyl radical intervened in the catalysis, the tolylsilane formation should have resulted in a much higher ortho-selectivity (o : m : p = 39 : 42 : 19).[12] Scheme 1 represents tentative mechanisms for the reaction of monohydrosilane. The origin of the key rhodium hydride species **1** would be the oxidative addition of silanes or arenes to the photogenerated coordinatively unsaturated species $RhCl(PMe_3)_2$ followed by the reductive elimination of chlorosilanes or chlorcarenes. The reaction of disilane is presumably explained by a similar mechanism. In either mechanism A or B, the silicon-carbon bond forming process is the reductive elimination from an arylsilylrhodium complex. The reductive elimination of arylsilanes from arylsilylpalladium complexes was assumed in the reaction of aryl halides with hexamethyldisilane catalyzed by Pd(0).[13]



Scheme 1. ($[Rh] = Rh(PMe_3)_2$)

In conclusion, we have attained a direct and catalytic silylation of arenes with hydrosilane or disilane via rhodium-catalyzed C-H activation. The improvement of the catalytic activity is now under investigation.

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11) In both of the reactions (Eqs. 5 and 6), bitolyls were also formed (161 and 166%/Rh) with the regioselectivities similar to that observed in the dehydrogenative coupling without the silanes; see Ref. 8.
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(Received September 25, 1987)