Selective Catalytic Route to Bifunctional Silanes. Catalysis by Rhodium and Ruthenium Complexes of the Alcoholysis of Diarylsilanes and the Hydrosilylation of Carbonyl Compounds

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Summary Chlorotris(triphenylphosphine)rhodium(I) and dichlorotris(triphenylphosphine)ruthenium(II) are very effective catalysts for the alcoholysis of diarylsilanes and the hydrosilylation of carbonyl compounds, providing a selective route to diarylalkoxysilanes.

BIFUNCTIONAL organosilicon compounds are of interest.[1] Attempts to synthesize bifunctional alkoxysilanes led us to study the alcoholysis of diarylsilanes and the hydrosilylation of carbonyl compounds. These two reactions provide convenient syntheses of monofunctional alkoxysilanes.[2-4] However, heterogeneous catalysis was used in most cases but this was unsuitable for the preparation of $Ar_2Si(H)OR$.

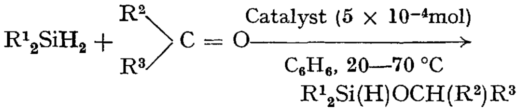
We report here the use of $(PPh_3)_3RhCl$ and $(PPh_3)_3RuCl_2$, which are known to activate alcohols,[5] as effective and selective homogeneous catalysts for the preparation of $R^1{}_2Si(H)OR^2$ [equation(1)]. The rhodium complex is the more efficient catalyst, and, in contrast with $Co_2(CO)_8$,[3] it also catalyses the reaction with phenols.

$$R^1{}_2SiH_2 + R^2OH \xrightarrow[C_6H_6,\ 20\ ^\circ C]{\text{Catalyst } (5 \times 10^{-4}\text{mol}} R^1{}_2Si\left\langle\begin{matrix} H \\ OR^2 \end{matrix}\right. + H_2 \quad (1)$$

Catalyst: $(PPh_3)_3RhCl$; $R^1 = Ph$, $R^2 = Me$, Pr^i, Bu^t; $R^1 = Ph$ and 1-naphthyl, $R^2 = Et$, Bu^t, $PhCH_2$, $PhCHMe$, $o\text{-}MeC_6H_4$.

Catalyst: $(PPh_3)_3RuCl_2$; $R^1 = Ph$, $R^2 = Me$.

The complexes are also selective catalysts for the hydrosilylation of carbonyl compounds [equation (2)].



$$R^1_2SiH_2 + R^2R^3C{=}O \xrightarrow[C_6H_6,\ 20\text{—}70\ ^\circ C]{\text{Catalyst } (5 \times 10^{-4} mol)} R^1_2Si(H)OCH(R^2)R^3 \quad (2)$$

Catalyst: $(PPh_3)_3RhCl$; R^1 = Ph, $R^2 = R^3$ = Me; R^1 = Ph and 1-naphthyl, R^2R^3 = Pr^n,H; Ph,H.
Catalyst: $(PPh_3)_3RuCl_2$; R^1 = Ph, $R^2 = R^3$ = Me.

While these studies were in progress the addition of triethylsilane to carbonyl compounds, using the rhodium complex as catalyst, was reported.[6] For this reaction also, the rhodium complex is the more efficient catalyst. Carbonyl compounds react more slowly than the corresponding alcohols and often with lower yields. However, diarylalkoxysilanes are formed exclusively, no dialkoxysilanes being detected. Hydrosilylation of acetophenone leads to a mixture of two products (I) and (II) [equation (3)]. Formation of (II) was not reported in the case of the hydrosilylation of acetophenone by triethylsilane.[6]

$$\text{Ph(1-naphthyl)}SiH_2 + \text{PhMeCO} \xrightarrow{(PPh_3)_3RhCl} \text{(1-naphthyl)SiH[OCH(Ph)Me] (I) (80\%)} + \text{Ph(1-naphthyl)SiH[OC(Ph)}{=}CH_2\text{] (II) (20\%)}$$

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