

## HYDROSILYLATION OF CARBONYL COMPOUNDS CATALYSED BY RUTHENIUM COMPLEXES

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### SUMMARY

The ruthenium complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  catalyses the reaction of triethylsilane with ketones,  $\text{RR}'\text{CO}$ , and aldehydes,  $\text{RCHO}$ , to give the hydrosilylation products  $\text{RR}'\text{CHOSiEt}_3$  and  $\text{RCH}_2\text{OSiEt}_3$ , respectively, but it is not as effective a catalyst as  $[\text{RhCl}(\text{PPh}_3)_3]$ . The complex  $[\text{RuClH}(\text{PPh}_3)_3]$  was obtained by treatment of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  with triethylsilane, and  $[\text{RhCl}(\text{PPh}_3)_2(\text{CO})]$  was isolated from reaction between *p*-methoxybenzaldehyde and triethylsilane catalysed by  $[\text{RhCl}(\text{PPh}_3)_3]$ .

### INTRODUCTION

The appearance of preliminary accounts of the use of rhodium complex  $[\text{RhCl}(\text{PPh}_3)_3]^1$  and the ruthenium complex  $[\text{RuCl}_2(\text{PPh}_3)_3]^2$  as catalysts for the hydrosilylation of organic carbonyl compounds prompts us to report our observations on the use of the ruthenium complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  for this purpose. This study began as a side-development in our study of the reactions of acyl halides with silicon hydrides in the presence of transition metal catalysts<sup>3</sup>, but apart from making a brief comparison of the relative activities of the rhodium and ruthenium complexes we abandoned our work in this direction upon the appearance of the publication by Ojima and his colleagues<sup>1</sup>. The ruthenium complex appears to be less effective than the rhodium complex in all the cases examined, but nevertheless its use can lead to quite good yields of hydrosilylation products.

#### (1) Reactions with ketones

The results of reactions between various ketones and triethylsilane in equimolar proportions in the presence of a ca.  $7 \times 10^{-3}$  molar proportion of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  are shown in Table 1. The aliphatic ketones 2-heptanone and cyclohexanone reacted much more readily than the aromatic compounds acetophenone and *o*-methoxyacetophenone, while benzophenone did not react to any significant extent. Yields were not appreciably increased when a 2/1 molar ratio of silane to ketone was used. When water was not carefully removed from the ketones before use and excluded during the reaction, some hexaethyldisiloxane was also formed.

The silyl ethers produced readily undergo hydrolysis in aqueous alcohol to give the corresponding secondary alcohols.

TABLE 1

REACTIONS OF KETONES AND ALDEHYDES WITH TRIETHYLSILANE IN THE PRESENCE OF  $[\text{RuCl}_2(\text{PPh}_3)_3]$ 

Ketone or Aldehyde (mole)	$\text{Et}_3\text{SiH}$ (moles)	Catalyst (mmoles)	Temp ( $^\circ\text{C}$ )/ time (h)	Product	Yield (%)	
<i>n</i> - $\text{C}_5\text{H}_{11}\text{COMe}$	(0.0149)	0.015	0.10	90/3	<i>n</i> - $\text{C}_5\text{H}_{11}\text{CHMe}(\text{OSiEt}_3)$	71
cyclohexanone	(0.030)	0.031	0.10	80/3	$\text{C}_6\text{H}_{11}\text{OSiEt}_3$	74
$\text{PhCOMe}$	(0.050)	0.054	0.31	100/6	$\text{PhCHMe}(\text{OSiEt}_3)$	62
<i>o</i> - $\text{MeOC}_6\text{H}_4\text{COMe}$	(0.025)	0.026	0.15	90/3	<i>o</i> - $\text{MeOC}_6\text{H}_4\text{CHMe}(\text{OSiEt}_3)$	55
$\text{C}_6\text{H}_5\text{CHO}$	(0.025)	0.028	0.15	90/1.25	$\text{C}_6\text{H}_5\text{CH}_2\text{OSiEt}_3$	74
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	(0.025)	0.028	0.15	90/1.25	<i>p</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OSiEt}_3$	74
<i>o</i> - $\text{MeOC}_6\text{H}_4\text{CHO}$	(0.025)	0.028	0.15	90/1.25	<i>o</i> - $\text{MeOC}_6\text{H}_4\text{CH}_2\text{OSiEt}_3$	69
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	(0.025)	0.028	0.15	90/1.25	<i>m</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OSiEt}_3$	64
<i>o</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	(0.025)	0.028	0.15	90/1.25	<i>o</i> - $\text{ClC}_6\text{H}_4\text{CH}_2\text{OSiEt}_3$	61

### (2) Reactions with aldehydes

Reactions were carried out in similar fashion with aromatic aldehydes. Reactions occurred markedly more readily than with the ketones, and the results are shown in Table 1, from which it will be seen that yields of 61–74% of the silyl ethers are obtained. The ethers can be readily hydrolysed in aqueous ethanol to the corresponding primary alcohols.

### (3) Interaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ and triethylsilane

A solution of triethylsilane and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in benzene was refluxed for 14 h, and the purple solid which separated was shown to be the benzene adduct of the corresponding hydrido-chloride, *i.e.*  $[\text{RuClH}(\text{PPh}_3)_3\text{C}_6\text{H}_6]$ . The same complex without the benzene separated when a mixture of acetophenone, triethylsilane, and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  was kept at  $80^\circ$  for 2 h. It is likely that the  $[\text{RuClH}(\text{PPh}_3)_3]$ , which is known to be a very active catalyst for homogeneous hydrogenation<sup>4</sup>, is the effective catalyst in the carbonyl hydrosilylations.

### (4) Comparison of the rhodium and ruthenium catalysts

The reaction between cyclohexanone and triethylsilane in benzene was found to proceed rapidly and exothermically in the presence of  $[\text{RhCl}(\text{PPh}_3)_3]$ , whereas warming was needed to initiate the reaction when  $[\text{RuCl}_2(\text{PPh}_3)_3]$  was used. After both mixtures had been kept at  $70^\circ$  for 15 min, GLC analysis indicated that cyclohexyloxytriethylsilane had been formed in 90% yield with the rhodium catalyst but only in 14% yield with the ruthenium catalyst. After 3 h at  $70^\circ$ , a 76% yield was obtained with the ruthenium catalyst. Similarly, from *p*-methoxybenzaldehyde, after 10 min at  $70^\circ$  the silyl ether was formed in 94% yield with the rhodium catalyst but only 28% yield with the ruthenium catalyst. After 3 h at  $70^\circ$  the yield with the ruthenium catalyst reached 62%. After our work had been completed, Corriu and Moreau reported that the rhodium is more effective than the ruthenium complex<sup>2</sup>.

Diphenylsilane reacted very vigorously with cyclohexanone in the presence of  $[\text{RhCl}(\text{PPh}_3)_3]$  to give the silyl ether  $\text{C}_6\text{H}_{11}\text{OSiPh}_2\text{H}$ , along with only a small amount of a secondary product. With acetophenone, however, the reaction gave two

products, in ca 4/1 ratio; on the basis of the results obtained by Corriu and Moreau with (1-naphthyl)phenyl silane<sup>2</sup> these products are thought to be  $\text{PhMeCH}(\text{OSiPh}_2\text{H})$  and  $\text{CH}_2=\text{CPh}(\text{OSiPh}_2\text{H})$ , respectively.

Ojima *et al.* isolated  $[\text{RhHCl}(\text{SiEt}_3)(\text{PPh}_3)_2]$  from their reactions between carbonyl compounds and triethylsilane<sup>1</sup>. From the reaction between *p*-methoxybenzaldehyde, triethylsilane, and  $[\text{RhCl}(\text{PPh}_3)_3]$  we isolated instead yellow crystals of the carbonyl complex  $[\text{RhCl}(\text{PPh}_3)_2(\text{CO})]$ . This could possibly have been formed from  $[\text{RhClH}(\text{SiEt}_3)(\text{PPh}_3)_2(\text{CO})]$  (*cf.* ref. 5).

## EXPERIMENTAL

### General

All reactions involving the transition metal complexes were conducted under dry nitrogen. IR spectra were normally recorded with Nujol mulls on a Perkin-Elmer 457 Grating Spectrophotometer. NMR spectra were recorded at 60 MHz on a Varian A60 Spectrometer.

### Preparations of Complexes

The complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  was made by Stephenson and Wilkinson's method<sup>6</sup>. The complex  $[\text{RhCl}(\text{PPh}_3)_3]$  was made by the method described by Osborn *et al.*<sup>7</sup>

TABLE 2

### PROPERTIES OF PRODUCTS

Compound	<i>B p</i> (°/mmHg)	$n_D^{20}$	$\nu(\text{Si}-\text{C})$ ( $\text{cm}^{-1}$ )	$\nu(\text{Si}-\text{O}-\text{C})$ ( $\text{cm}^{-1}$ )	Analysis Found ( <i>calcd</i> ) (%)	
					C	H
$n\text{-C}_5\text{H}_{11}\text{CHMe}(\text{OSiEt}_3)$	79/1.5	1.4309 <sup>a</sup>	1238	1077	67.6 (67.7)	13.4 (13.1)
$\text{C}_6\text{H}_{11}\text{OSiEt}_3$	78/2.0	1.4490 <sup>a</sup>	1238	1097	67.0 (67.2)	12.4 (12.2)
$\text{C}_6\text{H}_5\text{CHMe}(\text{OSiEt}_3)$	84/0.7	1.4801 <sup>a</sup>	1238	1094	71.1 (71.1)	10.2 (10.4)
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> CHMe(OSiEt <sub>3</sub> )	104/1.0	1.4864 <sup>a</sup>	1240	1097	67.5 (67.6)	9.7 (9.8)
$\text{C}_6\text{H}_5\text{CH}_2\text{OSiEt}_3$	72/0.35	1.4873 <sup>b</sup>	1239	1097	70.0 (70.2)	10.0 (10.0)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OSiEt <sub>3</sub>	90/0.15	1.4970 <sup>b</sup>	1243	1087	66.6 (66.6)	9.8 (9.6)
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OSiEt <sub>3</sub>	90/0.15	1.4872 <sup>b</sup>	1240	1084	66.3 (66.6)	9.6 (9.6)
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OSiEt <sub>3</sub>	77/0.10	1.5011 <sup>b</sup>	1239	1099	60.6 (60.8)	8.2 (8.2)
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OSiEt <sub>3</sub>	82/0.17	1.5010 <sup>b</sup>	1240	1105	60.6 (60.8)	8.2 (8.2)

<sup>a</sup> At 25°, <sup>b</sup> At 20°.

*Reactions with triethylsilane catalysed by [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>]*

(a) *Ketones*. The triethylsilane was added to a solution of the complex in the ketone under nitrogen. The solution gradually turned red on refluxing and a dark precipitate separated. After the time shown in Table 1 the solid was filtered off and the mixture fractionally distilled at reduced pressure, to give the silyl ether.

(b) *Aldehydes*. The reactions were carried out as described for ketones. The mixtures were initially red, but the colour changed to orange or bright yellow on refluxing and a bright yellow precipitate separated. The silyl ethers were isolated by fractional distillation at reduced pressure. The reaction conditions and the results are shown in Table 1. Some details of the products are listed in Table 2.

*Reactions of diphenylsilane*

(i) Diphenylsilane (0.022 mole) was added to cyclohexanone (0.020 mole) containing [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (100 mg., 0.11 mmole) A vigorous reaction occurred, and IR analysis showed that the ketone had wholly disappeared within a few minutes. Fractional distillation gave cyclohexyloxydiphenylsilane b.p. 160°/0.5 mmHg,  $n_D^{25}$  1.5488;  $\nu(\text{Si-H})$ , 2124 w(br);  $\nu(\text{Si-O-C})$ , 1081 s (br);  $\nu(\text{Si-Ph})$ , 1430 s (sp). (Found: C, 76.4; H, 7.9. C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>Si calcd.: C, 76.5; H, 7.9%).

(ii) Diphenylsilane (0.010 mole) was added to acetophenone (0.010 mole) containing [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (100 mg, 0.11 mmole) with cooling. A vigorous reaction occurred, and the ketone had entirely disappeared within a few minutes, as shown by IR analysis. GLC analysis showed the presence of two products of rather similar molecular weights in a ratio of 4/1; on the basis of results obtained by Corriu and Moreau<sup>2</sup> these were assumed to be PhMeCHOSiPh<sub>2</sub>H and CH<sub>2</sub>=CPhOSiPh<sub>2</sub>H.

*Comparison of ruthenium and rhodium catalysts*

(i) Cyclohexanone (0.015 mole) and triethylsilane (0.017 mole) reacted rapidly and exothermically when added to [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (50 mg, 0.054 mmole) in benzene (3 ml). When [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] was used, reaction began only on warming. The two mixtures were warmed together for 15 min in a bath at 70°, and the yields of cyclohexyloxy(triethyl)silane were shown to be 96 and 14%, respectively, as determined by GLC, using a column of SE30 on Chromasorb G at 180° with nitrogen as carrier gas and benzydrol as internal standard, in conjunction with a Pye Model 104 Chromatograph. When the mixture containing the ruthenium complex was kept at 70° for 3h, the yield was shown by GLC to have reached 76%.

(ii) Either [RhCl(PPh<sub>3</sub>)<sub>3</sub>] or [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (50 mg, ca. 0.05 mmole, in each case) was dissolved in *p*-methoxybenzaldehyde (0.010 mole) and triethylsilane (0.011 mole) was added. The mixtures were warmed for 10 min in a bath at 70°, and GLC analysis as in (i) showed that (*p*-methoxybenzyloxy)triethylsilane had been formed in 94% yield with the rhodium catalyst and in 28% yield with the ruthenium catalyst. The yield with the latter catalyst increased to 62% after 3 h at 70°.

*Examination of products from the catalytic complexes*

(i) A mixture of triethylsilane (2 ml) and [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (250 mg) in benzene (4 ml) was refluxed for 14 h. The purple precipitate was filtered off, washed with *n*-hexane, dried under vacuum, and found to be [RuH(Cl)(PPh<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>6</sub>]; m.p. 214°

(decomp) (lit.<sup>4</sup>, m.p. 218–220°);  $\nu(\text{Ru-H})$ , 2035 (lit.<sup>4</sup>, 2020);  $\delta(\text{Ru-H})$ , 855;  $\nu(\text{Ru-Cl})$ , 290 (lit.<sup>4</sup>, 282  $\text{cm}^{-1}$ ) (Found: C, 71.5; H, 5.2.  $\text{C}_{60}\text{H}_{52}\text{ClP}_3\text{Ru}$  calcd.: C, 71.8; H, 5.2%); the NMR spectrum confirmed that no  $\text{Et}_3\text{Si}$  groups were present. The product was soluble in chloroform; the colour of the solution changed from purple to green on exposure to the atmosphere

(ii) A mixture of acetophenone (0.025 mole), triethylsilane (2 ml, ca. 26 mmole), and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (250 mg, 0.2 mmole) was kept at 80° for 2 h. The purple crystals which separated were treated as under (i) and found to be  $[\text{RuH}(\text{Cl})(\text{PPh}_3)_3]$ , m.p. 210–212° (decomp);  $\nu(\text{Ru-H})$ , 2035  $\text{cm}^{-1}$ ;  $\delta(\text{Ru-H})$ , 855;  $\nu(\text{Ru-Cl})$  290  $\text{cm}^{-1}$  (Found: C, 70.2; H, 5.15.  $\text{C}_{54}\text{H}_{46}\text{ClP}_3\text{Ru}$  Calcd.: C, 70.2; H, 5.0%).

(iii) A mixture of triethylsilane (1.7 ml, 20 mmole), *p*-methoxybenzaldehyde (10 mmole), and  $[\text{RhCl}(\text{PPh}_3)_3]$  (103 mg, 0.10 mmole) was kept overnight at room temperature. The yellow crystals which separated were filtered off, washed with *n*-hexane, and dried under vacuum. The product was shown to be  $[\text{RhCl}(\text{PPh}_3)_2(\text{CO})]$  (35 mg), m.p. 195° (decomp.) [lit.<sup>8</sup>, m.p. 195° (decomp.)], by comparison with an authentic sample<sup>9</sup>;  $\nu(\text{C}\equiv\text{O})$  1969 s (br);  $\nu(\text{Rh-Cl})$ , 319  $\text{cm}^{-1}$  m (sp) (Found: C, 63.9; H, 4.4.  $\text{C}_3\text{H}_5\text{OClOP}_2\text{Rh}$  calcd.: C, 64.4; H, 4.4%).

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