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Preliminary communication

Reactions of hydropolysilanes with alcohols catalysed by tris(triphenylphosphine)chlororhodium

IWAO OJIMA, SHIN-ICHI INABA, TETSUO KOGURE

Sagami Chemical Research Center, 4-4-1 Nishi-Onuma, Sagamihara 229 (Japan)

MAKOTO MATSUMOTO, HIDEYUKI MATSUMOTO, HAMAO WATANABE and YOICHIRO NAGAI

Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)

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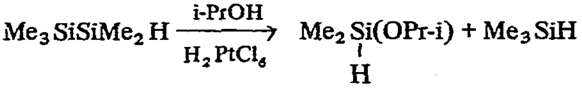
SUMMARY

$[RhCl(PPh_3)_3]$ is a very effective catalyst for the cleavage of Si–Si bonds by alcohols.

Cleavage of Si–Si bonds of polysilanes by bases in alcohols has been extensively investigated[1]. The noble metal derivatives chloroplatinic acid[2] and palladium(II) chloride[3] also appear to catalyse the reaction, and thus Urenovitch and West[2] reported that pentamethyldisilane underwent cleavage in isopropyl alcohol in the presence of chloroplatinic acid according to eqn. (1) as a side reaction accompanying hydrosilylation.



$$Me_3SiSiMe_2H \xrightarrow[H_2PtCl_6]{i\text{-}PrOH} Me_2\underset{\displaystyle H}{\underset{|}{Si}}(OPr\text{-}i) + Me_3SiH \qquad (1)$$

Reactions of this type are of potential value, since they may provide a convenient way of making monosilanes from polysilanes, we now report that the complex, tris(triphenylphosphine)chlororhodium is a very effective homogeneous catalyst for cleavage of hydropolysilanes such as pentamethyldisilane, 1,1,2,2-tetramethyldisilane, 1,1,2,2,3,3-hexamethyltrisilane and 1,2,3-trimethyl-1,2,3-triphenyltrisilane by a variety of alcohols. Results are summarised in Table 1, and it will be seen from the Table that the course of the reaction can readily be controlled by the relative amounts of reactants. For example, 1,1,2,2-tetramethyldisilane gave dimethylethoxysilane in 94% yield with one equivalent of ethanol at room temperature (eqn. 2), whereas it gave dimethyldiethoxysilane in 99% yield with an excess of ethanol at 50° (eqn. 3). In both cases, an equimolar quantity of dimethylsilane was captured by Dry-Ice trap. The diethoxy compound must have come from the

TABLE 1

REACTIONS OF POLYSILANES WITH ALCOHOLS IN THE PRESENCE OF TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM

Polysilane	*Alcohol*	*[Polysilane]/[Alcohol]*	*Conditions*	*Product*	*Yield (%)* [a]
$Me_3SiSiMe_2H$	i-PrOH	1	50°, 1h	$Me_2SiH(OPr\text{-}i)$	99 [b,c]
$H(Me_2Si)_2H$	MeOH	1	rt, 20 min	$Me_2SiH(OMe)$	94 [b,d]
$H(Me_2Si)_2H$	MeOH	4	rt, 3h	$Me_2Si(OMe)_2$	99 [e]
$H(Me_2Si)_2H$	EtOH	1	rt, 5 min	$Me_2SiH(OEt)$	94 [b]
$H(Me_2Si)_2H$	EtOH	4	50°, 4h	$Me_2Si(OEt)_2$	99 [e]
$H(Me_2Si)_2H$	i-PrOH	1	rt, 40 min	$Me_2SiH(OPr\text{-}i)$	96 [b]
$H(Me_2Si)_2H$	i-PrOH	4	50°, 9h	$Me_2Si(OPr\text{-}i)_2$	98 [e]
$H(Me_2Si)_2H$	t-BuOH	1	55°, 9h	$Me_2SiH(OBu\text{-}t)$	84 [b]
$H(Me_2Si)_2H$	$PhCH_2OH$	1	30°, 30 min	$Me_2SiH(OCH_2Ph)$	99 [b]
$H(Me_2Si)_2H$	PhOH	1	30°, 10 min	$Me_2SiH(OPh)$	98 [b]
$H(Me_2Si)_3H$	EtOH	2	50°, 30 min	$Me_2SiH(OEt)$	95 [b]
$H(Me_2Si)_3H$	i-PrOH	2	rt, 2h	$Me_2SiH(OPr\text{-}i)$	99 [b]
$H(Me_2Si)_3H$	i-PrOH	6	50°, 30 min	$Me_2Si(OPr\text{-}i)_2$	93 [e]
$H(PhMe)_3H$	MeOH	2	50°, 2h	PhMeSiH(OMe)	71 [b]
$H(PhMe)_3H$	MeOH	10	50°, 3h	$PhMeSi(OMe)_2$	87 [e]

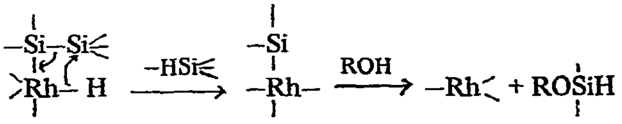
[a] Yields were determined by GLPC. [b] The yield was based on the amount of the respective alcohol. [c] Trimethylsilane was detected. [d] Dimethylsilane was detected. [e] The yield was based on the amount of the respective disilane.

$$HSiMe_2SiMe_2H + EtOH \xrightarrow{[Rh]} \underset{94\%}{Me_2HSiOEt} + Me_2SiH_2 \qquad (2)$$

$$HSiMe_2SiMe_2H \xrightarrow[{[Rh]}]{\text{excess EtOH}} \underset{99\%}{Me_2Si(OEt)_2} + Me_2SiH_2 \qquad (3)$$

ethanolysis[4] of dimethylethoxysilane first formed, a reaction which is known to be catalysed by this rhodium(I) complex[5].

A plausible mechanism for the cleavage reaction is depicted below; it involves initial formation of the disilyl derivative of the rhodium complex by the oxidative addition of the Si—H bond to the metal atom followed by the loss of a hydrosilane molecule in a β-elimination. The resulting silene complex[3,6] is likely to enter into the reaction with an alcohol to give the silene insertion product.



The course of the cleavage reaction is very similar in catalysis by both H_2PtCl_6 and $(Ph_3P)_3RhCl$, although the former catalyst gives only monoalkoxysilanes, and no dialkoxysilanes are produced even with an excess of the alcohols. On the other hand, the ethanolysis of pentamethyldisilane catalysed by $PdCl_2$ was reported[3] to give trimethylethoxysilane and dimethyldiethoxysilane. This observation may also be explained by the "silenoid" mechanism provided that the dehydrogenative condensation of trimethylsilane and dimethylethoxysilane with ethanol is very fast compared with the cleavage.

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