
Unprecedented 1,4-Methyl Group Migration in a Rhodium-catalysed Hydrosilylation of Ketones by 1,2-Bis(dimethylsilyl)benzene

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A rhodium-catalyzed hydrosilylation of ketones afforded a mixture of alkoxy-silanes, 1-(ROSiMe₂)-2-(HMe₂Si)C₆H₄ and 1-(ROSiHMe)-2-(Me₃Si)C₆H₄; the latter resulted by 1,4-methyl group migration during the hydrosilylation.

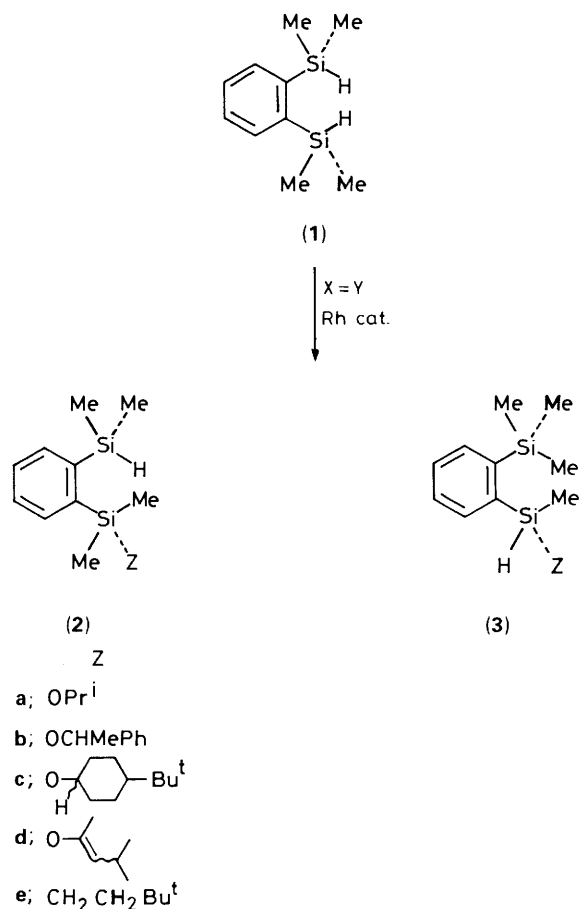
Rearrangements of alkyl groups in organosilicon compounds which have received extensive study,¹ generally result in random scrambling of the alkyl moieties by intermolecular redistribution reactions. Here we report an unprecedented

migration of a methyl group in the rhodium-catalyzed hydrosilylation of ketones with 1,2-bis(dimethylsilyl)benzene (**1**). This is the first example of a formal 1,4-methyl group migration in organosilicon chemistry.²

Table.

Run	Substrate (X = Y)	Time (h)	Product (Ratio)	Yield ^b (%)
1	Acetone	2.5	(2a) + (3a) (5:4)	74 (>99)
2	Acetophenone	3	(2b) + (3b) (1:1)	50 (>99)
3	4-t-Butylcyclohexanone	18	(2c) + (3c) (2:1)	54 ^c (>99)
4	Mesityl oxide	22	(2d) + (3d) (2:1)	(>99)
5	t-Butylethylene	48	(2e)	75 (>99)

^a All reactions were carried out in benzene or [²H₆]benzene at room temperature. ^b Owing to the sensitivity to moisture of the product especially in the presence of the rhodium catalyst, the isolated yields were significantly decreased. The figures in parenthesis are the yields determined by n.m.r. for reactions carried out in [²H₆]benzene. ^c The yield was determined after hydrolysis.



Scheme.

A benzene solution of (1) and an equimolar amount of acetone in the presence of RhCl(PPh₃)₃ (1 mol%) as catalyst at room temperature for 3 h afforded not only the expected hydrosilylation product (2a) but also a product resulting from transfer of a methyl group from one silicon atom to the other (3a). The latter was isolated pure by preparative g.l.c. $\delta_{\text{H}}(\text{C}_6\text{D}_6, 270 \text{ MHz})$ 0.30 (s, 9 H, SiMe₃), 0.40 (d, 3 H, SiHMe, *J* 2.4 Hz), 1.09 (d, 3 H, OCHMe, *J* 6.8 Hz), 1.11 (d, 3 H, OCHMe, *J* 6.8 Hz), 3.93 (sept, 1 H, OCH, *J* 6.8 Hz), 5.55 (q, 1 H, SiH, *J* 2.4 Hz), and 7.22, 7.61, and 7.84 (m, 4 H, phenyl); $\delta_{\text{C}}(\text{C}_6\text{D}_6, 67.8 \text{ MHz})$ -0.6 (MeSiO), 1.4 (SiMe₃), 25.4, 25.5 (OCHMe), 66.9 (OCH), and 129.1, 134.7, 135.1, 143.4, and 146.4 (phenyl); δ_{Si} (53.5 MHz,

C₆D₆) -9.54 (SiOPrⁱ), and -3.44 (SiMe₃); *m/z* 179 (*M* - SiMe₃), 252 (*M*), 253 (*M* + 1), and 254 (*M* + 2).

Various ketones reacted with (1) to give a mixture of alkoxy-silanes (see Table). The ratios of the rearranged products (3) to the usual hydrosilylation products (2) were in the range 1:1 to 1:2. The reaction of 4-t-butylcyclohexanone afforded a mixture of *cis*- and *trans*-silyl ethers. Hydrolysis of this mixture gave *cis*- and *trans*-4-t-butylcyclohexanol in a ratio of 1:1. The hydrosilylation of mesityl oxide proceeded by 1,4-addition. Both the stereo- and regio-chemical results are consistent with those observed in the rhodium-catalyzed hydrosilylations with trialkylsilanes such as PhMe₂SiH.^{3,4} It is noteworthy that reactions with (1) were much faster than that with PhMe₂SiH: *t*_{1/2} at 30 °C in the reaction with acetone; (1) 1 h, PhMe₂SiH, >2 days. Thus, the hydrosilylation of ketones with (1) compared with that with PhMe₂SiH shows not only a substantial rate enhancement but also an unusual migration of the methyl group.

Controlled experiments revealed no thermal interconversion between either (1) and 1-(Me₃Si)-2-(MeH₂Si)C₆H₄ or between (2) and (3), either in the absence or in the presence of the rhodium catalyst; this indicates that the methyl group migration is kinetically produced during the rhodium-catalyzed hydrosilylation. Interestingly, hydrosilylation of olefins with (1) afforded the corresponding monosilylation product (2e) without formation of any rearranged products. Since hydrosilylation of nitriles with (1) reported by Corriu *et al.*⁵ did not result in the methyl group migration, the ketone function seems to be essential. We are currently investigating the mechanistic aspects of this fascinating rearrangement.

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