

AreneCr(CO)₂(η²-HSiHPh₂) Complexes as Catalysts for the Si–H Bond Activation. Hydrolysis of the Si–H Bond and Dehydrogenative Coupling between Diphenylsilane and Nucleophiles

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The use of areneCr(CO)₂(η²-HSiHPh₂) complexes for the efficient catalysis of Si–H bond hydrolysis and, in general, the dehydrogenative coupling of diphenylsilane with nucleophiles is reported; this is the first example of a group VI transition-metal complex acting as a silylation catalyst, involving notably Si–H bond activation through η²-bonding of this group to the metal centre, without oxidative addition.

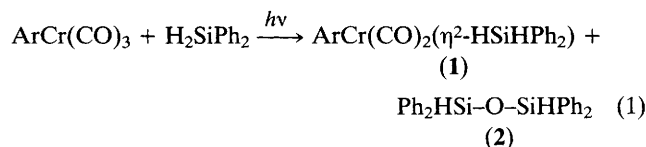
Transition metal catalysis of Si–Si bond formation from the Si–H bond^{1–10} is now well established, but there are fewer reports of Si–O–Si bond formation, which in certain cases accompanies the catalytic formation of a Si–Si bond;^{5,7,8} this was interpreted as resulting from Si–Si bond oxidation by atmospheric oxygen^{7,8} or by the simultaneous action of both atmospheric oxygen and water on the reaction mixture.⁵

We report here that hydrolysis of the Si–H bond, catalysed by areneCr(CO)₂(η²-HSiHPh₂) complexes, (1), is the basis of the Si–O–Si bond formation observed during the photochemical reaction of diphenylsilane and an arenechromium tricarbonyl.¹¹ The catalytic activity of the complexes (1) is not limited to the hydrolysis of diphenylsilane, but also extends to the dehydrogenative coupling of diphenylsilane with other nucleophiles. These are the first examples of a group VI transition metal acting as an efficient silylation catalyst. To our knowledge, only the group VIII transition metals and some of their derivatives and complexes are known to catalyse the dehydrocondensation of silanes with nucleophiles, in particular alcohols,^{12–15} amines,^{16–23} and thiols.^{24,25}

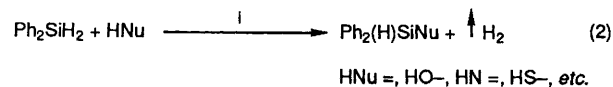
Furthermore the mechanism of Si–H bond activation by complexes (1) involves intermediate formation of an identified¹¹ 2e/3c bond to the metal, Cr–H–Si, *e.g.*, η²-bonding of the Si–H group to the metal centre, without oxidative addition. Such a mechanism was proposed by Crabtree *et al.*¹⁵ for the catalysis of silane alcoholysis by the complex [IrH₂S₂(PPh₃)₂]SbF₆, S = solvent. The 2e/3c character of the Cr–H–Si bond is greater than that of the Mn–H–Si bond, in isoelectronic manganese compounds,¹¹ leading to a greater decrease in electron density at the σSi–H bond for the chromium complex and, therefore, to a higher activation of this bond towards nucleophilic attack.

Arenechromium tricarbonyl can be photochemically hydro-silylated;¹¹ under the experimental conditions previously reported,¹¹ tetraphenyl-1,1,3,3-disiloxane, characterized by

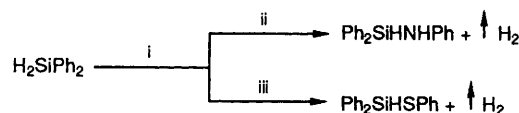
²⁹Si, ¹H NMR† and IR spectroscopies, always forms as a byproduct‡ [equation (1)]. In the absence of arenechromium tricarbonyl, under the same experimental conditions of UV irradiation, diphenylsilane remains unchanged.



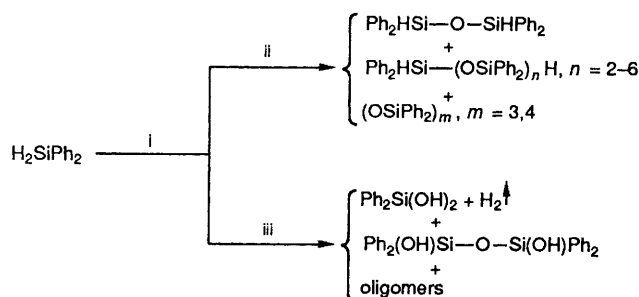
If the reaction mixture, essentially diphenylsilane and complex (1) is kept for an extended period in a Schlenk tube stoppered with a subseal at room temperature, diphenylsilane is completely consumed to give tetraphenyldisiloxane, (2), and its oligomers, Ph₂HSi–(OSiPh₂)_nH (*n* = 2–6) and (Ph₂SiO)_m (*m* = 3, 4), characterized by mass and IR spectroscopies. Tetraphenyl-1,1,2,2-disilane was not detected. Under the same experimental conditions, siloxanes were not detected by IR spectroscopy from a toluene solution of silane and arenechromium tricarbonyl. The previous results led us to conclude that the hydrosilyl complexes (1) are the intervening species in the formation of siloxanes and that their action is a catalytic one.



Reagent: i, catalytic amounts of BzCr(CO)₂(η²-HSiHPh₂).



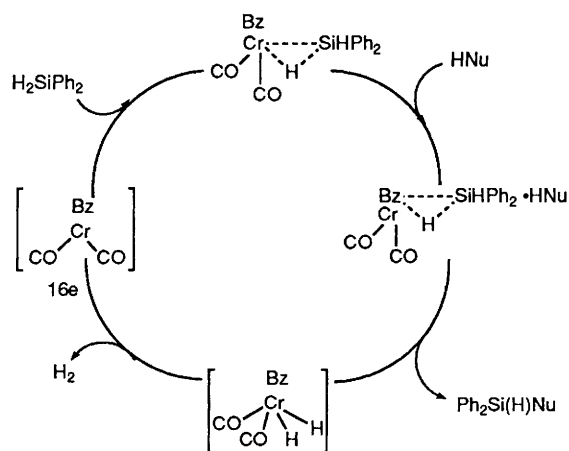
Scheme 2. Catalyst and reagents: i, BzCr(CO)₂(η²-HSiHPh₂) (5 mol%/H₂SiPh₂); ii, PhNH₂; iii, PhSH.



Scheme 1. Reagents and conditions: i, BzCr(CO)₂(η²-HSiHPh₂) (5 mol%/H₂SiPh₂); ii, atmospheric air; iii, HOH.

† ²⁹Si, ¹H NMR ([²H₈]toluene, 25 °C; δ in ppm/trimethylsilane, *J* in Hz; H₂SiPh₂ internal ref. δ_{Si} –33.25; δ_H 5.04, δ_{Si}, ¹J(Si–H), and δ_H for (Ph₂SiH)₂O: –18, 59, 218, and δ_H 5, 87 (Si–H). For Ph₂SiHNHPh: –23, 68, 202 and 5, 74(Si–H), 3, 49(N–H); IR ν(N–H) 3383 cm^{–1}. For Ph₂SiHSPH: –5, 97, 222, and 5, 81(Si–H). In the case of Ph₂SiHNHPh mass spectroscopy gave the mass of the corresponding oxygen compound, (Ph₂SiH)₂O. Possibly, the metal complexes present in the reaction mixture catalyse Si–N bond cleavage, the latter being replaced in the presence of atmospheric air, by a Si–O bond.

‡ Cf. ref. 5 and ref. 26.



Scheme 3. Bz = benzene.

What is the source of oxygen? The use of $\text{ArCr}(\text{C}^{18}\text{O})_3$ and of H_2^{18}O for mass and IR spectroscopic analysis of the reaction mixture led to the conclusion that traces of water (atmospheric moisture diffused in the reaction vessel, water present in the commercial deuteriated solvents, glass OH-, etc.) are the oxygen suppliers. In fact, under anhydrous conditions (sealed tube, solvents, and deuteriated solvents distilled and stored over potassium) (1) is obtained accompanied only by negligible traces of (2). Thus, a solution of the hydrosilyl complex (1) in toluene, in a sealed tube at -40°C , is stable for several weeks; at room temperature under the same conditions it decomposes in a few hours.

A slight excess of water acts very vigorously, at room temperature, on a toluene solution of diphenylsilane in the presence of catalytic amounts of $\text{BzCr}(\text{CO})_2(\eta^2\text{-HSiHPh}_2)$ (Bz = benzene). Evolution of hydrogen and total disappearance of diphenylsilane are accompanied by formation of diphenylsilane diol, tetraphenyl-1,1,3,3,-diol-3,3-disiloxane, and oligomers, characterized by mass and IR spectroscopies (Scheme 1). No siloxanes were detected by IR spectroscopy from an aqueous toluene solution of diphenylsilane, kept for a month in air at room temperature. Scheme 1 summarises the results obtained.

In light of all previous results, we can conclude that the hydrosilyl complexes (1) are both highly oxophilic and efficient catalysts for dehydrogenative coupling of diphenylsilane with water. Their catalytic activity is not limited to the dehydrogenative coupling with water but it also applies to other nucleophiles [equation (2)].

In the presence of catalytic amounts of $\text{BzCr}(\text{CO})_2(\eta^2\text{-HSiHPh}_2)$, diphenylsilane reacts smoothly at room temperature in toluene with a slight excess of either aniline or thiophenol; during reaction evolution of hydrogen and the disappearance of diphenylsilane were observed (Scheme 2). The amino and thio derivatives were characterized by ^{29}Si and ^1H NMR, IR, and mass spectroscopies.[†] We suggest the catalytic mechanism of Scheme 3, operating via a 16 e species which involves the activation of the silane through η^2 -bonding of the Si-H group to the metal centre, without oxidative

addition, and subsequent attack on the $\eta^2\text{-HSiHPh}_2$ bond by the nucleophile.[§]

We thank Professor Gerard Jaouen for helpful discussions, Dr. Nicole Sellier and her staff, in particular J. Maurois, for mass spectroscopy, H. Le Pesant and Y. Besace for their technical assistance in IR and NMR spectroscopies.

Received, 29th January 1990; Com. 0/00429D

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§ $\text{Bz}(\text{CO})_2\text{H}_2$ is not known, but $\text{Cr}(\text{CO})_4\text{H}_4$ has been reported as a very unstable compound;^{27,28} it is invoked as an intervening species in the water gas shift catalysis.²⁹