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Preliminary communication

Reactions of coordinated organosilanes: cobalt carbonyl complexes of ethynylhydrogenosilanes

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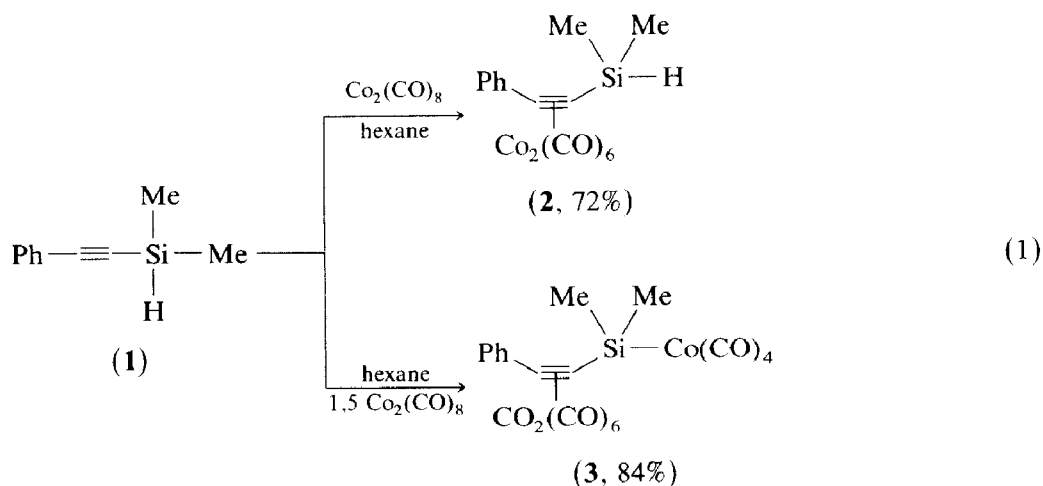
Abstract

Cobalt carbonyl complexes of mono-, di- and tri-ethynylsilanes containing silicon–hydrogen bonds are obtained by selective-coordination of the triple bond in ethynylhydrogenosilanes. The silicon–hydrogen bond of the coordinated ethynylsilanes reacts spontaneously with methanol, water, benzaldehyde, and phenylacetylene. The silicon–hydrogen bonds in the ethynylsilane-cobalt carbonyl complexes show enhanced reactivity in hydrosilylation.

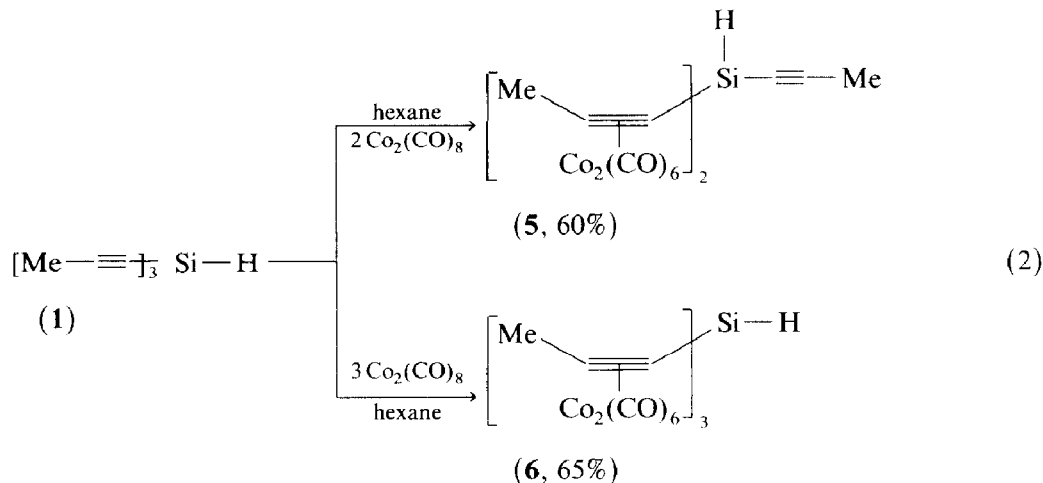
As part of our programme of study of organopolymetallic compounds and polymers, we decided to examine the reactivities of organosilanes coordinated to a transition metal center. It is well established that the reactivity at a carbon atom adjacent to a metal centre is noticeably affected [1] there have been few studies on the reactivity at a silicon atom in such a position. The *exo*-Si–H bond for silacyclopentadienyliron tricarbonyl complexes was found to be very reactive [2,3]. We now report preliminary results on the synthesis of cobalt complexes of hydro-mono-, di- or tri-ethynylsilanes and on the reactivity of the silicon–hydrogen bond in these compounds coordinated to cobalt.

Slow addition of dicobalt octacarbonyl to a dilute solution of ethynylhydrogenosilanes resulted in selective coordination of the triple bond. Thus the reaction of (phenylethynyl)dimethylsilane (**1**) afforded complex **2**, which was isolated in good yield (eq. 1).

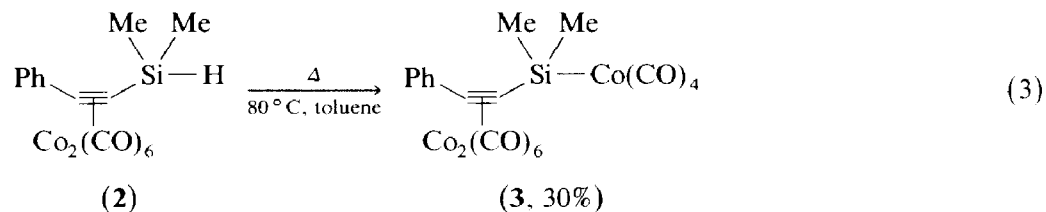
No oxidative addition of the Si–H bond to the cobalt was observed [4], but use of an excess of cobalt carbonyl gave complex **3** resulting from reaction at both the triple bond and the Si–H bond.



Selective coordination was also observed in the reaction of tripropynylsilane (4) with 2 or 3 mol of $\text{Co}_2(\text{CO})_8$, which gave the bis- and tri-alkynyl complexes 5 and 6 (eq. 2).

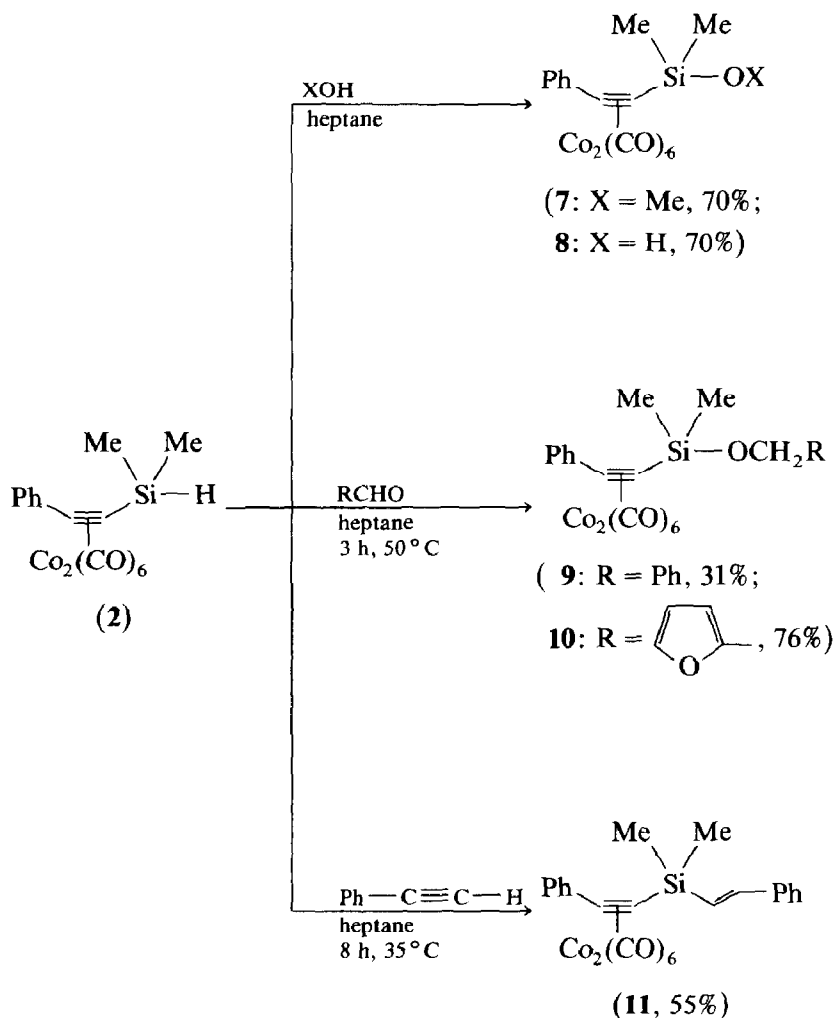


The complexes were isolated as stable crystalline compounds but showed low thermal stability in solution. Thermolysis of complex 2 gave complex 3 containing a silicon-cobalt bond (eq. 3), together with small amounts of $\text{Co}_4(\text{CO})_{12}$.



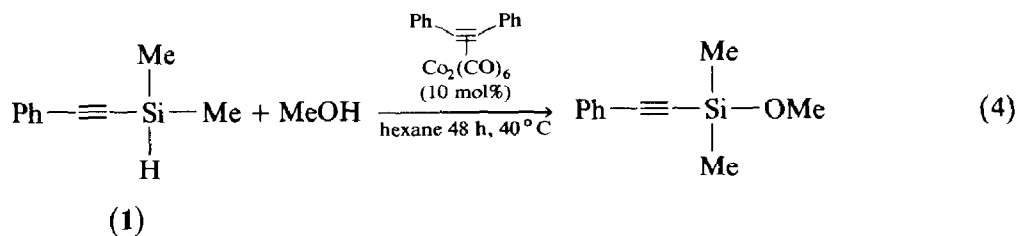
Hexane solutions of complex 2 were stable up to 60°C , but those of complex 6 slowly decomposed at 30°C .

We then turned to aspects of the reactivity of the coordinated organosilanes 2, 5 and 6, some reactions of the silicon-hydrogen bond in complex 2 are shown in Scheme 1. The Si-H bond of 2 was found to be cleaved rapidly by neutral methanol



Scheme 1. Reactions of complex 2.

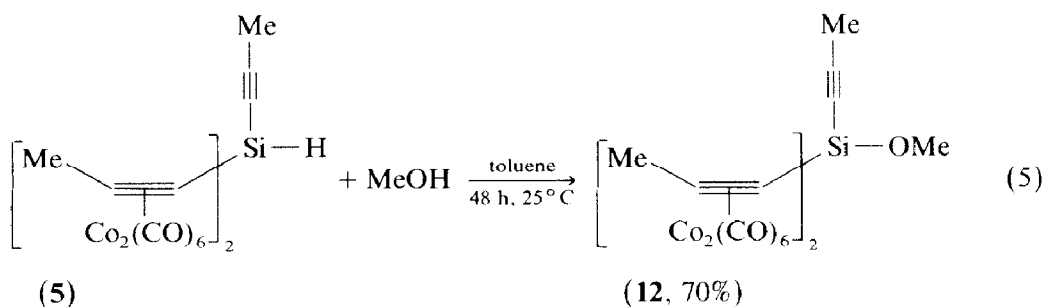
or water, to give high yields of methoxy- or hydroxy-silane, **7** or **8**. Such reactions of hydrogenosilanes with proton donors usually require a basic or transition metal catalyst [5]. Cobalt carbonyl is also a known catalyst for such reactions of the alcohols and amines [4,6,7] and so traces of cobalt carbonyl arising from the decomposition of complex **2** could act as a catalyst for the reaction of methanol and water even under mild conditions, and we found that the methanolysis of the ethynylhydrogenosilane (**1**) did take place in the presence of 10 mol% of diphenylacetylenecobalt carbonyl complex (eq. 4).



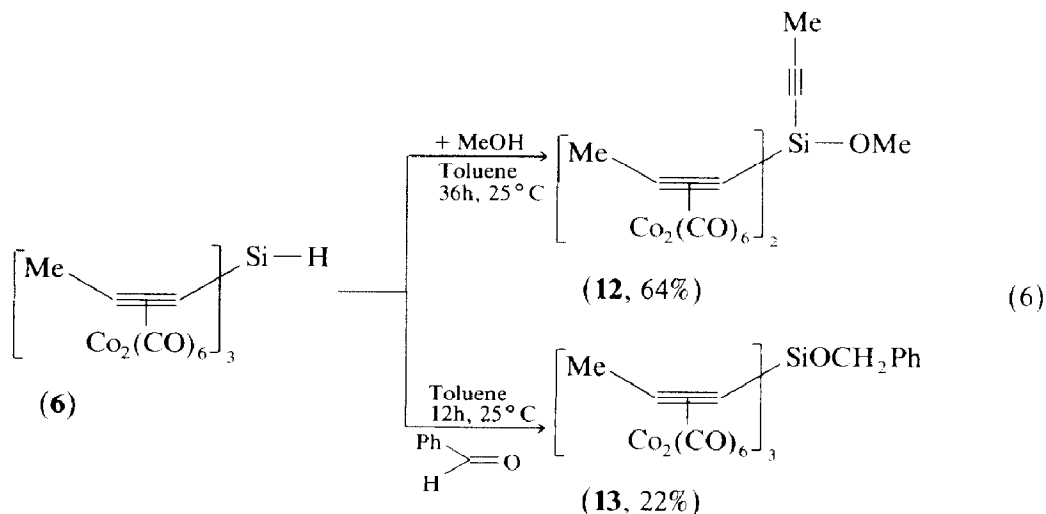
It is thus not clear whether the silicon–hydrogen bond of ethynylsilane does become more reactive upon complexation, as was observed for silole-iron carbonyl [2,3] and silylmethylcyclopentadienylcarbonyl complexes [8], or whether there is cobalt catalysis.

We also observed a hydrosilylation of benzaldehyde, furfural, and phenylacetylene. The reactions took place under mild condition to give compounds **9–11** respectively. In these cases no evidence for cobalt catalysis was obtained. In control experiments conducted in the presence of 10 and 15 mole% of diphenylacetylenecobalt carbonyl, no addition of hydroethynyl-silane **1** to benzaldehyde or to phenylacetylene at 40 or 50 °C was detected. Reactions in the presence of larger amounts of cobalt complexes or at higher temperatures resulted in the formation of several cobalt carbonyl species together with unchanged benzaldehyde or triphenylbenzene, the latter being derived from a cobalt catalysed cyclotrimerisation of phenylacetylene. The silicon–hydrogen bond in complex **2** thus appears to have an enhanced reactivity. However, no hydrosilylation took place with ketones or olefins.

It is noteworthy that the more hindered di- and tri-coordinated ethynylsilanes **5** and **6** were found to react under even milder reaction conditions; methanolysis of complex **5** yielded 70% of methoxysilane **12** at room temperature (eq. 5).



The methanolysis of complex **6** also gave 64% of the same complex **12** (eq. 6), with loss of one of the alkynyl cobalt carbonyl ligands. In contrast, the reaction with benzaldehyde gave the simple hydrosilylation product.



Neither complex **5** nor complex **6** carries out spontaneous hydrosilylation of phenylacetylene.

It is concluded that ethynylhydrogenosilane-cobalt carbonyl complexes, obtained by a coordination of the triple bond possess a reactive silicon-hydrogen bond so that reactions take place at the silicon center without added catalyst.

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