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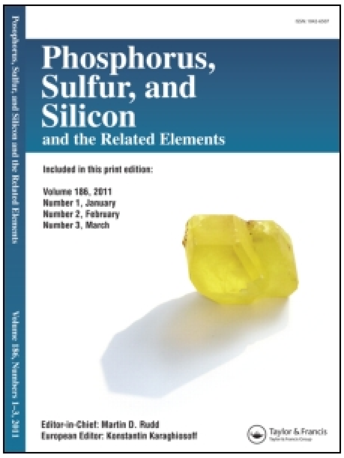

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Palladium(II) Catalysed Silicon-Oxygen Bond Formation Versus Rearrangement Reactions

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Phenylsilane and diphenylsilane undergoes rearrangement reactions by palladium catalysts such as Pd(TMEDA)Cl_2, Pd(TEEDA)Cl_2, $[Pd(PPh_3)]_2Cl_2$ (where TMEDA = tetramethylethylenediamine, TEEDA = tetraethylethylenediamine) at room temperature. However, the reductive Si-O bond forming reaction can be performed on hydrosilanes through competitive paths. The reactions of phenylsilane and quinonic compounds are catlaysed by Pd(TMEDA)Cl_2 (such as 1,4-benzoquinone, 1,4-napthoquinone) to give siloxanes, backbone of these siloxanes which contains rearranged phenylsilane units. The thin films of such oligomers has plot of resistance vs temperature profile resembling semiconductor.

Keywords: Phenylsilane; Pd-catalysts; rearrangement; dehydrogenative coupling

Introduction:

. The transition metal complexes containing silicon have interesting structural implications [1-2]. They also catalyse different type of organic reactions such as dehydrogenative coupling [3], hydrosilylation [4] and reduction reactions [5]. These reactions pass through different types of intermediates.

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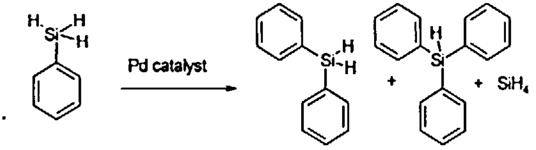
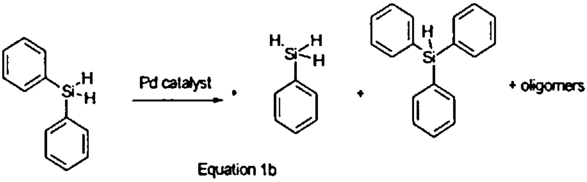
Polymerisation reactions of silicon compounds have been of special interest [6]. The dehydrogenative polymerisation of phenylsilane by early transition metal catalysts[7] and lanthanide catalysts [8] to polysilanes are extensively studied. The Si-Si bond formation[9] and rearrangement[10-11] of hydrosilane can independently proceed during the dehdrogenative coupling reactions. Based on our studies on Si-S bond forming reactions by Rh-catalyst [12-14] and Si-O bond forming reactions by palladium catalyst [15] we have extended the palladium catalysed reaction to Si-O bond forming reaction on phenylsilane .

Discussions:

The rearrangement reaction of phenylsilane (equation 1a) and diphenylsilane (equation 1b) can be represented by following equations:



Equation 1a



Equation 1b

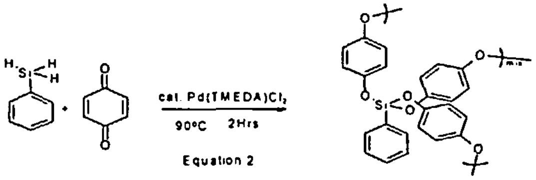
It is observed that these reactions are catalysed by various palladium(II) complexes. The results on the rearrangement of phenylsilane and diphenylsilane by different Pd-catalysts are shown in the table 1. The product ratios of the rearranged silanes are dependent on the ligand attached to palladium.

Table1: Rearrangement of hydrosilanes by palladium(II) catalysts[\$]

Substrate = Phenylsilane			
Catalyst	Phenylsilane	Diphenylsilane	Triphenylsilane
$PdCl_2$	nil	36	63
$Pd(TMEDA)Cl_2$	nil	66	33
$Pd(TEEDA)Cl_2$	nil	59	41
Substrate = Diphenylsilane			
$PdCl_2$	1	82	17
$Pd(TMEDA)Cl_2$	98	nil	nil
$Pd(TEEDA)Cl_2$	100	nil	nil
$Pd(PPh_3)_2Cl_2$	5	94	nil

[\$] The reactions were carried out by mixing silane (0.1mmol) with palladium catalyst (0.001mmol) in dichloromethane (2cm^3). The reaction mixtures were stirred at 25°C for 30minutes. The products were analysed by GC using SE-30 column with oven temperature 180°C, detector and injector temperature 230°C.

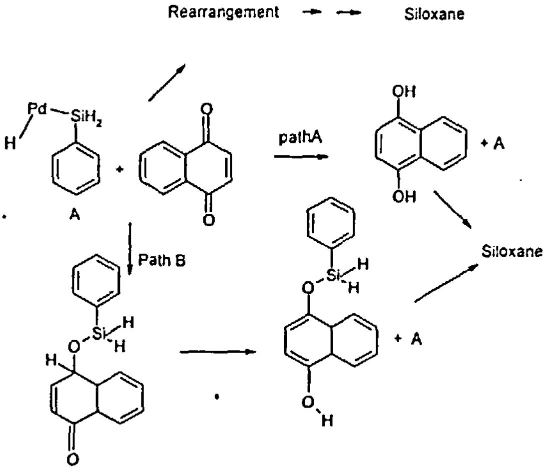
Recently we have shown that the palladium catalysed reactions of diphenylsilane with 1,4-benzoquinone gives Si-O bonded oligomers [15]. We have extended the reaction to coupling reactions of phenylsilanes with quinonic compounds. The catalytic reaction by $Pd(TMEDA)Cl_2$ led to Si-O bonded oligomers (equation 2). Mass spectral fragments showed it to be a low molecular weight oligomer (highest m/e at 857). The mass fragments corresponding to the unrearranged as well as rearranged



Equation 2

siloxanes having diphenylsilylene units in the siloxane backbone is observed. Similar reactions of diphenylsilane with 1,4-napthoquinone also gave siloxane oligomer (highest m/e 1007). The mass fragments of the diphenylsilylene unit are also observed in the backbone of the oligomer.

The oligomerisation of a quinonic compound can pass through two possible paths. The hydrogenation of a quinonic compound gives diol. The diol on subsequent dehydrogenative coupling reaction with silane can give siloxane (path A). It can



Scheme 2

also pass through reductive Si-O bond formation. Such a reduced species on aromatisation and dehydrogenative coupling can give siloxane (path B). The UV-visible spectra recorded at different time intervals helps in ascertaining such paths. In the reaction of 1,4-napthoquinone and phenylsilane (1:1 molar ratio) with Pd(TMEDA)Cl_2 (1mol%) as catalyst two isosebestic points at 390nm and at 330nm are observed. The isosebestic point at 330nm is assigned to the reduction of 1,4-napthoquinone to 1,4-napthalenediol. Thus, it is believed that these reactions proceeds through both the paths.

These oligomers have interesting electrical property and representative plot of the resistance vs temperature of film of one oligomer is shown in figure 1. Such profile might occur due to possible π-stacks of the aromatic rings of the siloxane backbone. Alternatively the delocalisation of electron through interaction of sp^2 carbon center of aromatic rings with Si-O bond may also be possible.

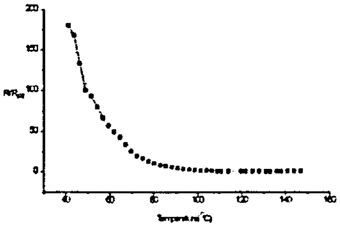


Figure 1: The plot of resistance(R) normalised to room temperature resistance (R_{RT}) of a film of oligomer prepared from phenylsilane with 1,4-napthoquinone by $Pd(TMEDA)Cl_2$ catalyst.

The oligomers are thermally stable below 150°C. They lose weight drastically above this temperature. For example the oligomer of 1,4-napthoquinone with phenylsilane loses 41% of its weight in the region of 180-300°C. The weight loss probably occurs from the loss of naphtholenic unit via degradation of the three dimensional network.

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