

Redistribution of (Aryl, Benzyl, Octyl)silane and Dehydrogenative Coupling of Methylphenylsilane Using an Activated Metal Catalysts Prepared by the Reduction of Transition Metal Chlorides with Lithium Metal Powder

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Received November 9, 1999

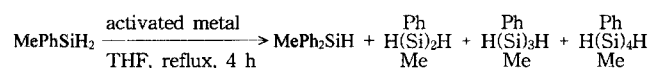
Activated metal powders (M^*), prepared by the reduction of the corresponding metal halide with alkali metal, have proven to be very useful in organic synthesis.¹ However, applications of these metal powders to organosilicon chemistry is only activated nickel (prepared from the reduction of nickel iodide with lithium) catalyzed for the dehydrogenative coupling of alkylsilanes² and for the hydrosilylation of alkenes with silanes.³ We reported earlier that the reaction of methylphenylsilane with styrene and with benzaldehyde using activated nickel (prepared by the reduction of NiI_2 with Li) produced the corresponding hydrosilylated products in high yields.⁴

In the course of studying the investigation of hydrosilylation using activated metal as a catalyst, we have found the redistribution reaction of organosilanes (aryl, benzyl, octyl) and the dehydrogenative coupling of methylphenylsilane using activated metal (M^* , prepared from the reduction of metal

chloride with lithium).

Results on the catalytic redistribution and dehydrogenative coupling of methylphenylsilane by the activated metal catalysts are summarized in Table 1.

We first expected that the reaction of methylphenylsilane with styrene by activated iron could give the hydrosilylation product, but they gave the redistributed silane, Ph_2MeSiH (21%) as well as dehydrogenative coupling dimer ($HSiPhMeSiPhMeH$, 43%), trimer ($HSiPhMeSiPhMeSiPhMeH$, 19%) and tetramer ($HSiPhMeSiPhMeSiPhMeSiPhMeH$, 3%) along with unreacted starting material (14%) by GLC analysis (run 1). Higher molecular weight polysilanes were not obtained. Using dimethoxyethane (DME) as a solvent did not improve the formation of polysilanes (run 2). When a mixture of methylphenylsilane and activated tungsten was refluxed for 4 h, redistributed product (Ph_2MeSiH , 71%) was formed mainly as well as dehydrogenative coupling products, ($HSiPhMeSiPhMeH$, 14%; $HSiPhMeSiPhMeSiPhMeH$, 15%) and starting material was all converted (run 3). We have also examined the catalytic activities of other activated metals for the formation of polysilylation from methylphenylsilane. However, noticeable polysilylation was not occurred using activated metals such as Ti, Cr, Mn and Zr (prepared by the reduction of $TiCl_3$, $CrCl_3$ and $MnCl_2$, respectively with Li powder). We have studied the reactivity of activated metal co-cata-



Scheme 1. Reagents and conditions: Activated metal was prepared by the reduction of metal halide with Li powder in THF (refluxed 2 h for metal activation); After metal activation, methylphenylsilane was added and refluxed again. For more details, see Experimental section.

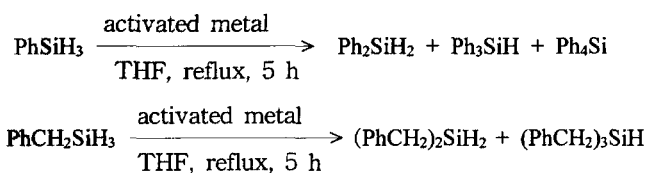
Table 1. Redistribution and Dehydrogenative Coupling of Methylphenylsilane Using an Activated Metal Catalyst Prepared by the Reduction of Metal Chloride with Lithium at Various Reaction Conditions^a

Run	Metal Activation	Silanes	Reaction Condition	Products (% GC yield)				Silane conversion (%) ^b
				Ph_2MeSiH	$\begin{matrix} Ph \\ H(Si)_2H \\ Me \end{matrix}$	$\begin{matrix} Ph \\ H(Si)_3H \\ Me \end{matrix}$	$\begin{matrix} Ph \\ H(Si)_4H \\ Me \end{matrix}$	
1 ^c	$FeCl_3$, Li, THF, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 3 h	21	43	19	3	86
2	$FeCl_3$, Li, DME, reflux, 2 h	$PhMeSiH_2$	DME, reflux, 3h	10	24	9	0	43
3	WCl_6 , Li, THF, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 4 h (1 h)	71(53)	14(14)	15(9)	0(0)	100(76)
4	$FeCl_3/WCl_6$, Li, THF/DME, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 5 h	10	69	8	1	88
5	$FeCl_3/WCl_6$, Li, THF, reflux, 2 h	$PhMeSiH_2$	DME, reflux, 4 h (1 h)	70(66)	12(18)	16(13)	2(0)	100(97)
6	Fe/W^d	$PhMeSiH_2$	THF, reflux, 5 h	No reaction				0
7	$FeCl_3/WCl_6$, Li, THF, ultrasound, 1 h	$PhMeSiH_2$	THF, reflux, 4 h	22	41	8	0	71
8	$FeCl_3/WCl_6$, Li, THF, ultrasound, 1 h	$PhMeSiH_2$	THF, ultrasound, 4 h	No	reaction			0
9	$FeCl_3/ZrCl_4$, Li, THF, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 3 h	2	12	6	2	22
10	$FeCl_3/TiCl_3$, Li, THF, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 4 h (12 h)	5(9)	19(26)	9(16)	1(2)	34(53)
11	$ZrCl_4/TiCl_3$, Li, THF, reflux, 2 h	$PhMeSiH_2$	THF, reflux, 4 h (8 h)	4(16)	27(32)	8(6)	1(1)	40(55)
12	$ZrCl_4/TiCl_3$, Li, DME, reflux, 2 h	$PhMeSiH_2$	DME, reflux, 4h	3	31	13	3	50

^a1 : 3 molar ratios of activated metal: silane were employed. ^bRest is remained starting material. ^cSimilar results were obtained in the presence of styrene. Hydrosilylated product was not detected. ^dA mixture of commercially purchased iron and tungsten were employed.

lysts system that gave the better result.^{1c,d} It appears that tungsten is the best choice of metal for the preparation of activated co-catalysts with iron for the formation of polysilane from methylphenylsilane. For example, when a mixture of methylphenylsilane and activated Fe-W (**warning**⁵) was refluxed for 5 h, the formation of polysilane was increased up to 78% (dimer, 69%; trimer, 8%; tetramer, 1%) and the formation of redistribution product was decreased to 10% (run 4) comparing with those results using Fe* and W* respectively (run 1 and 3). When the same reaction was carried out using dimethoxyethane (DME) as a solvent, the yields of polysilanes were decreased to 30% and redistribution product was increased up to 70% (run 5). Interestingly, commercially available iron-tungsten powder (iron or tungsten alone) gave no any redistribution products nor did polysilanes from alkylsilanes (MePhSiH₂, PhSiH₃, Ph₂SiH₂, PhCH₂SiH₃) under the same reaction condition even with an extended reaction time. Most of the alkylsilane was recovered (run 6). Ultrasonic waves are known to accelerate a variety of reactions, particularly those involving metals. We have extended our studies in this area to activated metal catalysis.⁶ We were able to prepare the F*-W* efficiently using common ultrasonic laboratory cleaner (run 7). However, the polysilanes was not formed when a mixture of methylphenylsilane and F*-W* in THF was sonicated using common ultrasonic laboratory cleaner (run 8). The yield of polysilanes from methylphenylsilane was not improved when the other activated co-catalysts prepared from a mixture of FeCl₃ and metal halides (such as TiCl₃, ZrCl₄) with Li powder were employed (run 9-10). Treatment of methylphenylsilane with Fe*-Cr* or Fe*-Mn* (prepared from the reduction of FeCl₃/CrCl₃ and FeCl₃/MnCl₂ with Lithium powder) resulted in the recovery of starting material.

We have also studied the redistribution and polysilylation of methylphenylsilane using other activated metal catalyst instead of Fe* system. We found that polysilanes from methylphenylsilane were formed only in less than 50% yield using Zr*-Ti* (run 11 and 12). So far, Fe* and Fe*-W* gave higher yields of polysilane from methylphenylsilane than any other activated metals. In an extension of this work, we have examined the reactivity of Fe*-W* to phenylsilane and benzylsilane. Interestingly, it appears that a single change the alkyl



Scheme 2. Reagents and conditions: Activated metal was prepared by the reduction of metal halide with Li powder in THF (refluxed 2 h for metal activation); After metal activation, silane was added and refluxed again. For more details, see Experimental section.

group on silicon gives different results.

For example, when a mixture of phenylsilane and Fe*-W* in THF was refluxed for 5 h, a broader redistributed phenylsilanes (Ph₂SiH₂, 41%; Ph₃SiH, 3%; Ph₄Si, 1%) are obtained along with unchanged phenylsilane (55%) by GLC (run 13). Phenylpolysilanes was not formed at all. Treatment of phenylsilane with Fe* alone in THF, diphenylsilane, triphenylsilane and tetraphenylsilane were formed in 19%, 51% and 6% respectively recovering with phenylsilane (run 14). Redistribution of phenylsilane with W* was also observed (run 15). Using Fe*-W*, diphenylsilane also redistributed to triphenylsilane and tetraphenylsilane in 50% and 26%, respectively, along with unchanged diphenylsilane (run 16). Instead of phenylated silane, we have examined the catalytic activities of Fe*-W* for the alkylated silanes such as benzylsilane and *n*-octylsilane.

Under the same reaction condition, benzylsilane was redistributed to dibenzylsilane (74%) and tribenzylsilane (26%) respectively (run 17). But tetrabenzylsilane was not detected. However, the treatment of benzylsilane with Fe*, dibenzylsilane was formed exclusively (run 18). Similarly, *n*-octylsilane underwent redistribution to give di-*n*-octylsilane in 51% along with starting material and unidentified compound (run 19). This unexpected reactivity of activated metal compared to nonactivated ordinary metal in this system may be due to the high surface area, some unique species, or a combination of two.

In summary, we have shown that activated iron can catalyze the linear polysilylation of methylphenylsilane and redistribution of alkylsilane. The mechanism of redistribution and linear polysilane formation and the extension of these catalysts to the transformation of organic functional group are

Table 2. Redistribution of Arylsilanes, Benzylsilane and *n*-Octylsilane Using an Activated Metal Catalyst Prepared by the Reduction of Metal Chloride with Lithium at Various Reaction Conditions^a

Run	Metal Activation	Silanes	Reaction Condition	Products (% yield, GC)	silane conversion, (%) ^b
13	FeCl ₃ /WCl ₆ , Li, THF, reflux, 3 h	PhSiH ₃	THF, reflux, 5 h	Ph ₂ SiH ₂ , 41 Ph ₃ SiH, 3 Ph ₄ Si, 1	45
14	FeCl ₃ , Li, THF, reflux, 3 h	PhSiH ₃	THF, reflux, 18 h (5 h)	Ph ₂ SiH ₂ , 19(11) Ph ₃ SiH, 51(10) Ph ₄ Si, 6(0)	76(21)
15	WCl ₆ , Li, THF, reflux, 2 h	PhSiH ₃	THF, reflux, 15 h (8 h)	Ph ₂ SiH ₂ , 17(13) Ph ₃ SiH, 4(3) Ph ₄ Si, 1(1)	22(17)
16	FeCl ₃ /WCl ₆ , Li, THF, reflux, 2h	Ph ₂ SiH ₂	THF, reflux, 5 h	Ph ₃ SiH, 50 Ph ₄ Si, 26	76
17	FeCl ₃ /WCl ₆ , Li, THF, reflux, 3 h	PhCH ₂ SiH ₃	THF, reflux, 5 h	(PhCH ₂) ₂ SiH ₂ , 74(PhCH ₂) ₃ SiH, 26	100
18	FeCl ₃ , Li, DME, reflux, 3 h	PhCH ₂ SiH ₃	THF, reflux, 13 h	(PhCH ₂) ₂ SiH ₂ , 93(80) ^c (PhCH ₂) ₃ SiH. ⁷	100
19	FeCl ₃ /WCl ₆ , Li, THF, reflux, 3h	<i>n</i> -C ₈ H ₁₇ SiH ₃	THF, reflux, 12 h (5 h)	[<i>n</i> -C ₈ H ₁₇] ₂ SiH ₂ , 51(9)	51(9)

^a1 : 3 molar ratios of activated metal: silane were employed. ^bRest is remained starting material. ^cIsolated yield

the subjects of further study in these laboratories.

Experimental Section

Anhydrous metal halides and metal powders were purchased from Aldrich, Junsei and Yakuri Co. and used without further purification. Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled under nitrogen from sodium/benzophenone ketyl before use. Silanes were prepared by the reduction of the corresponding chlorosilane with lithium aluminum hydride in dry diethylether. Lithium powder (99%) was purchased from Aldrich Chemicals. ^1H NMR spectra were obtained on a Bruker AC 80 spectrometer. Chemical shifts were reported in ppm downfield from TMS and coupling constants were obtained from first order analysis of the spectra. Mass spectra (70 eV electron impact) were taken on a Finnigan 4510 instrument equipped with a Finnigan-incos data system and Jeol MS-SX102A system. GLC analyses were carried out on a Varian 3300 Model equipped with a FID detector and stainless steel column packed with 10% OV-101, Chromosob W HP 80/100 (2 m \times 8 in). Ultrasonic wave was introduced to reaction vessel using common ultrasound laboratory cleaner (Seung Dong, Model SD-100H).

General procedure for the preparation of activated iron and activated iron-tungsten. In an example of a typical preparation for activated iron powder is as follows. In an argon atmospheric glove box, a 100-mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with 0.162 g (1 mmol) of FeCl_3 and 22 mg (3.2 mmol) of Li under a nitrogen atmosphere. 5 mL of freshly distilled THF was syringed into the flask. After refluxing for 2 hr, the finely divided metal appeared as a black powders which settled down in a dark solution. The activated metal in a dark solution was used in this investigation without any further treatment. For the preparation of an activated iron-tungsten, 0.162 g (1 mmol) of FeCl_3 , 0.396 g (1 mmol) of WCl_6 and 66 mg (9.4 mmol) of Li were employed.

Redistribution and dehydrogenative coupling of methylphenylsilane with activated metal powders is illustrated. 3 mmol (0.41 mL) of methylphenylsilane was injected to this slurry (above activated metal powders solution). The mixture was refluxed under nitrogen atmosphere for desired reaction times. The solution was filtered to remove the catalyst through a pad of silica gel column (1 cm diameter \times 5 cm packed) using hexane-methylene chloride as an eluent. Some physical properties of redistributed silane (Ph_2MeSiH) and polysilanes (dimer, trimer and tetramer) from methylphenylsilane as well as products from other silanes are recorded below.

Ph_2MeSiH , m/z (EI), 198 (M^+ , 43), 163 (36), 120 (100), 105 (58), 79 (8), 53 (15); HSiMePhSiMePhH (dimer), ^1H NMR (CDCl_3) δ 7.53-7.26 (m, 10H, Ar-H), 5.00-4.96 (q, 1H, SiH), 0.41-0.40 (d, 3H, SiMe), m/z (EI), 242 (M^+ , 8), 197 (100), 163 (2), 149 (2), 121 (36), 105 (28), 79 (6), 43 (19); HSiMePh

SiMePhSiMePhH (trimer), m/z (EI), 362 (M^+ , 19), 317 (6), 240 (100), 197 (75), 164 (62), 105 (64), 43 (23); $\text{HSiMePhSiMePhSiMePhSiMePhH}$ (tetramer), m/z (EI), 482 (M^+ , 10), 361 (45), 284 (100), 240 (47), 197 (47), 105 (45), 43 (15).

Dibenzylsilane from benzylsilane with activated iron metal powders. $(\text{PhCH}_2)_2\text{SiH}_2$, ^1H NMR (CDCl_3) δ 7.19-6.99 (m, 10H, Ar-H), 3.92 (quintet, 2H, $J = 3.6$ Hz, SiH), 2.18 (t, 4H, $J = 3.6$ Hz, Si- CH_2 -Ar); m/z (EI), 212 (M^+ , 25), 121 (100), 91 (23), 43 (8).

Dibenzylsilane and tribenzylsilane from benzylsilane with activated iron-tungsten metal powders. $(\text{PhCH}_2)_2\text{SiH}_2$, selected ^1H NMR (CDCl_3) δ 7.19-6.99 (m, 10H, Ar-H), 3.92 (quintet, 2H, $J = 3.6$ Hz, SiH), 2.18 (t, 4H, $J = 3.6$ Hz, Si- CH_2 -Ar); m/z (EI), 212 (M^+ , 25), 121 (100), 91 (23), 43 (8). $(\text{PhCH}_2)_3\text{SiH}$; selected ^1H NMR (CDCl_3) δ 7.15-7.02 (m, 15H), 4.04 (septet, 1H), 2.13 (d, 6H); m/z (EI), 302 (M^+ , 34), 211 (100), 183 (6), 165 (2), 133 (81), 91 (26); mp 91.7 $^\circ\text{C}$ (lit.⁷, 91-93 $^\circ\text{C}$).

Diphenylsilane, triphenylsilane and tetraphenylsilane from phenylsilane. Ph_2SiH_2 and Ph_3SiH ; Selected ^1H NMR (CDCl_3) δ 7.59-7.32 (m, Ar-H), 5.0 (s, 1H, SiH), 4.92 (s, 2H, SiH); Ph_2SiH_2 , m/z (EI), 184 (M^+ , 74), 155 (6), 129 (2), 106 (100), 91 (2), 79 (11), 53 (17); Ph_3SiH , m/z (EI), 260 (M^+ , 21), 182 (100), 105 (23), 79 (6), 53 (6); Ph_4Si , m/z (EI), 336 (M^+ , 58), 259 (100), 182 (41), 105 (11), 79 (4), 53 (4).

Di-(*n*-octyl)silane from *n*-octylsilane. $[\text{n-CH}_3(\text{CH}_2)_6\text{CH}_2]_2\text{-SiH}_2$, m/z (EI), 256 (M^+ , 4), 211 (36), 143 (100), 99 (91), 59 (64), 43 (49).

Acknowledgment. Financial support for this work was provided by the Basic Sciences Research Institute Program, Ministry of Education of the Republic of Korea (BSRI-98-3433).

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- Warning:** The addition order should be obeyed. Lithium must be added to a mixture of $\text{FeCl}_3/\text{WCl}_6$ in THF. Otherwise, fire will be resulted when THF was added to a mixture of $\text{FeCl}_3/\text{WCl}_6$ /Li powder.
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