

solution. The ether solution was dried with anhydrous MgSO_4 and evaporated to dryness under rotary evaporator. The product was purified by silica gel column chromatography using ethyl acetate and pet. ether (1:3) as an eluent. Yield: 29%, mp 99-101 °C; $^1\text{H NMR}$ (CDCl_3) δ 8.86 (s, 1H, C₅-H), 7.47-7.96 (m, 5H, Ph), 3.32-3.47 (d, 6H, $\text{N}(\text{CH}_3)_2$); MS: m/e (relative intensity) 256 (M⁺, 28), 151 (25.6), 123 (42.2), 105 (100).

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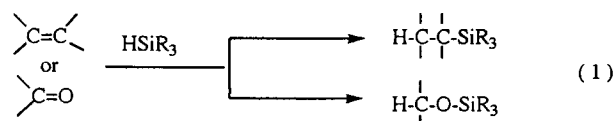
Hydrosilylation of Carbonyls and Alkenes with Alkylsilanes Catalyzed by Activated Metals

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The application of activated metals (M^*) to catalysis is an interesting and challenging subject in view of their unique reactivities, which have been extensively reported in the last decade.¹ Recently we reported the first successful utilization of activated nickel powder prepared from the reaction of NiI_2 with Li as a catalyst in hydrosilylation of alkenes with chlorosilane.²



However, hydrosilylation (1) on carbonyls-alkylsilane and alkene-alkylsilane with this activated nickel powders was not investigated. In continuation of our work, we have examined a broad range of activated metals that encompasses Zr^* , Mo^* , Ni^* for hydrosilylation reaction. We describe here the hydrosilylation of carbonyl compounds and alkenes with alkylsilanes catalyzed by activated metals prepared from this methods. Results are summarized at Table 1. The use of precious metals (Pt^3 , Pd^4 , Rh^5) can be circumvented by using a highly reactive metal powders as a catalyst for hydrosilylation. The highly activated metal powders such as Zr^* , Mo^* , Ni^* are readily prepared by the reaction of the corresponding anhydrous metal halides (Cl, Br, I) with equivalent of metals (Li, Na, Cd, Mg, Zn) in freshly distilled tetrahydrofuran (THF) or dimethoxyethane (DME). After refluxing these mixture under nitrogen atmosphere for 1 hr and cooling to room temperature, the finely divided metal appeared as black powders which settled down in a dark solution (in most cases). The activated metal in solution was used in this investigation without any further treatment. The silanes and substrates (catalyst : silanes : substrates = 1 : 2.5 : 2; molar ratio) were added to freshly prepared highly reactive metal solution and refluxed under nitrogen for 3-18 h. The resulting solution was then allowed to cool to room temperature and hexane was added to become a clear solution along with settled down the catalyst. Product isolation was straightforward. The solution was filtered to remove the catalyst through a pad of silica gel or filter paper using hexane-methylene chloride solvent as an eluent. Removal of the solvent under reduced pressure gave the corresponding hydrosilylating products. The reaction proceeded smoothly and without vigorous exothermic reaction in most cases. The final product mixture was free of polymer, containing only the unreacted reagents and the desired hydrosilylated product. Interestingly, commercially available metal powders such as nickel,

Table 1. Hydrosilylation of Carbonyls and Alkenes with Alkylsilanes Catalyzed by Activated Metals at Various Reaction Condition^a

Run	Metal Activation	Substrates	Silane	Reaction Condition	Products(isolated)yields, (%)
1 ^b	NiI ₂ , Li, THF, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OSiEt ₃ (80)
2	Ni	PhCHO	Et ₃ SiH	reflux, 10h	no reaction
3	NiI ₂ , Li, THF, reflux, 1h	PhCH=CH ₂	Ph ₂ SiH ₂	reflux, 5h	PhCH ₂ CH ₂ SiHPh ₂ (80)
4	NiI ₂ , Na, THF, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OSiEt ₃ (4) ^f PhCH ₂ OH(96) ^f
5	NiI ₂ , Na, THF, reflux, 1h	PhCH ₂ OH	Et ₃ SiH	reflux, 4h	PhCH ₂ OSiEt ₃ (64)
6	NiI ₂ , Li, THF, reflux, 1h	PhCH=CH ₂	Ph ₂ SiH ₂	reflux, 5h	PhCH ₂ CH ₂ SiHPh ₂ (80)
7	NiI ₂ , Na, THF, reflux, 1h	PhCHO	Et ₃ SiH	sand bath heat 100 °C, 2h	PhCH ₂ OSiEt ₃ (25) ^f PhCH ₂ OH(75) ^f
8	NiI ₂ , Na, THF, Ultrasound ^c , 1h	PhCH ₂ OH	Et ₃ SiH	sand bath heat 100 °C, 2h	PhCH ₂ OSiEt ₃ (64)
9	NiI ₂ , Cd, THF, reflux, 1h	PhCHO	Et ₃ SiH	sand bath heat 100 °C, 3h	PhCH ₂ OSiEt ₃ (79)
10	NiI ₂ , Cd, THF, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 18h	PhCH ₂ OSiEt ₃ (50)
11	NiI ₂ , Li, THF, reflux, 1h	PhCH=CH ₂	Ph ₂ SiH ₂	reflux, 5h	PhCH ₂ CH ₂ SiHPh ₂ (80)
12	NiI ₂ , Li, THFPPPh ₃ ^f , reflux, 1h	PhCH=CH ₂	Ph ₂ SiH ₂	reflux, 5h	PhCH ₂ CH ₂ SiHPh ₂ (80)
13	NiI ₂ , Zn, THF, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OSiEt ₃ (3)
14	NiI ₂ , Na, THF, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OH(96) PhCH ₂ OSiEt ₃ (4) ^f
15	NiI ₂ , Mg, THF, reflux, 1h	PhCHO	Et ₃ SiH	sand bath heat 100 °C, 24h	PhCH ₂ OSiEt ₃ (13) ^{d,g}
16	ZrCl ₄ , Li, THF, stir, 1h	PhCH=CH ₂	Et ₃ SiH	reflux, 5h	PhCH ₂ CH ₂ SiEt ₃ (87)
17	ZrCl ₄ , Li, THF, stir, 1h	PhCHO	Et ₃ SiH	reflux, 5h	no hydrosilylation product ^h
18	ZrCl ₄ , Li, THF, stir, 1h	PhC≡CH	Et ₃ SiH	reflux, 5h	no hydrosilylation ⁱ
19	WCl ₆ , Li, THF, stir, 1h	PhCHO	Et ₃ SiH	reflux, 5h	no reaction
20	TiCl ₃ , WCl ₆ , THF, Li, stir, 1h	PhCH=CH ₂	Et ₃ SiH	ultrasound ^c , 2h	no reaction
21	TiCl ₃ , Zn, THF, reflux, 2h	PhCHO	Et ₃ SiH	reflux, 6h	no hydrosilylation product ⁱ
22	MoCl ₅ , Zn, DME, reflux, 1hr	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OSiEt ₃ (90)
23	MoCl ₅ , Zn, DME, reflux, 1hr	PhCH=CH ₂	Ph ₂ SiH ₂	reflux, 5h	PhCH ₂ CH ₂ SiHPh ₂ (80)
24	MoCl ₅ , Zn, DME, reflux, 1hr	Cyclohexanone	Et ₃ SiH	reflux, 5h	<i>c</i> -C ₆ H ₁₁ OSiEt ₃ (80)
25	MoBr ₃ , Li, DME, reflux, 1hr	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ COSiEt ₃ (17)
26	MoCl ₅ , Na, DME, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 5h	PhCH ₂ OSiEt ₃ (50) ^{d,k}
27	MoOCl ₄ , Zn, DME, reflux, 1h	PhCHO	Et ₃ SiH	reflux, 3h, 18h	PhCH ₂ OSiEt ₃ (16 ^{d,l} , 85)
28	MoOCl ₄ , Zn, DME, reflux, 1h	PhCHO	PhMe ₂ SiH	reflux, 6h	PhCH ₂ OSiMe ₂ Ph(79)
29	MoOCl ₄ , Zn, DME, reflux, 1h	PhCH ₂ OH	Et ₃ SiH	reflux, 3h	PhCH ₂ OSiEt ₃ (13) ^f

^a After refluxing a mixture of metal halide (1 mmol), metal (equivalent amount used) and 5 mL of solvent under nitrogen atmosphere for 1 hr and cooling to room temperature, olefin (2 mmol), silane (2.5 mmol) were injected and refluxed (see experimental for details). ^b For the hydrosilylation of alkenes with chlorosilane using activated nickel: see ref. 2. ^c Purchased nickel powder was used and purchased molybdenum, titanium, tungsten powders were also inert for hydrosilylation reaction. ^d GC yields. ^e Sonicated with laboratory cleaner for activation (run 8) and for reaction (run 20). ^f P(Ph)₃ (0.5 mmol) was used and PBu₃ and PEt₃ have not appeared to increase the yields. ^g 13% of *t*-stilbene was also isolated. ^h *t*-Stilbene was isolated in 90% and hydrosilylating product was not detected. ⁱ 1,3,5 and 1,2,4-triphenylbenzene were isolated in 90% combined yields (ratio of 42/58) by GC. ^j *t*-Stilbene was isolated in 80%. ^k *t*-Stilbene was formed in 11% by GC. ^l Refluxed for 3 h.

molybdenum and zirconium were inert under the same reaction condition even with an extended reaction time (run 2). Surprisingly, a single changes of reducing metal appears in drastic changes of reactivity of the resulting activated metal for hydrosilylation in case of nickel.⁶ For instance, the reaction of benzaldehyde with triethylsilane using activated nickel powders reduced by zinc gave benzyloxytriethylsilane in only 3% yield (run 13). Meanwhile, hydrosilylation of benzaldehyde with triethylsilane using activated nickel prepared from NiI₂ with Na in THF gave benzyl alcohol and benzyloxytriethylsilane in a ratio of 24 : 1 (run 4).

Hydrosilylation probably undergo via a benzyl alcohol in

this case. Therefore, coupling reaction of benzyl alcohol with triethylsilane was carried out using activated nickel prepared from the treatment of nickel iodide with sodium. As expected, benzyloxytriethylsilane was formed in 64% yield (run 5). Attempted hydrosilylation with activated nickel reduced by cadmium gave also hydrosilylating product (run 9, 10) along with stilbene (run 9) as by-product depending on reaction condition. However, the same reaction was carried out with activated nickel powder reduced by lithium gave hydrosilylating product in fair yield (run 1, 3, 11). Heating to 100 °C using pressure tube as a reactor after removal of solvent increased hydrosilylating product yields up to 29% in case

of the reaction of benzaldehyde with triethylsilane using activated nickel (run 6). Reducing metal such as magnesium yields reactive nickel but not as reactive as that prepared using lithium or cadmium (run 15). Amine such as triphenylphosphine is of limited value to improve the yield in our reaction condition compared with those of previous results (run 12).⁷ The choice of phosphine is quite significant in influencing the reactivity of activated metal. In general, the more electron donating the phosphine the more reactive towards hydrosilylation is the metal.⁸ However, the use of ligand such as PPh_3 , PBu_3 , PEt_3 has not appeared to increase the yields (run 12). No enhancement in the reactivity of the active nickel was observed on hydrosilylation under ultrasonic irradiation (run 8, 20) contrast to previous results.^{4,9} The reactivity of the activated nickel prepared in THF or DME appears to be identical. Although activated nickel showed the catalytic activity for the hydrosilylation on the reaction of alkene with trichlorosilane, activated zirconium, molybdenum, tungsten or titanium did not show the catalytic activity for the reaction of alkene with trichlorosilane. However, activated zirconium showed the catalytic activity on hydrosilylation of styrene with triethylsilane (run 16). Lithium was best choice of alkali metal to reduce the ZrCl_4 in this case. Mg or Zn did not reduce the ZrCl_4 . Attempted hydrosilylation of benzaldehyde with triethylsilane using activated zirconium or titanium resulted in the formation of stilbene (run 17, 21).¹⁰ Unexpected reaction took place in the attempted hydrosilylation reaction of phenylacetylene with triethylsilane using activated zirconium, 1, 2, 4 and 1,3,5-triphenylbenzene¹⁰ were formed from the cyclotrimerization of phenylacetylene instead of hydrosilylation product (run 18). Treatment of WCl_6 with equivalent amount of Li in THF produced activated tungsten. But activated tungsten was inactive for hydrosilylation (run 19).

The use of activated metal powders prepared from the reduction of WCl_6 - ZrCl_4 with the equivalent of Li has also been studied in these system, but does not appear to have any noticeable effect even under ultrasonic irradiation (run 20). Activated molybdenum was prepared from the reaction of MoCl_5 with zinc or sodium in refluxing DME and was found to be very active as a catalyst for the reaction of benzaldehyde, cyclohexanone with triethylsilane to give the corresponding hydrosilylating product in high yield (run 22-26). We also found that MoCl_5 was a good metal halide compared with MoBr_3 . It should be noted that THF was not so good solvent as DME due to decomposition during the reduction of MoCl_5 with metal. In an extension of this work, we have studied the catalytic reactivity of activated molybdenum powder prepared from the reaction of MoOCl_4 with Zn (run 27-29). Using this activated molybdenum powders in DME under reflux for 6-14 h, benzyloxytriethylsilane and benzyloxymethylphenylsilane were isolated in 85% and 79% respectively (run 27, 28). Reaction of benzyl alcohol with triethylsilane also took place in the presence of activated molybdenum powders. But benzyloxytriethylsilane was found only 13% yield after reflux for 3 h and extension of reflux did not improve the yields (run 29). If the crude product were removed from the flask by decanting after catalyst settled down by addition of hexane, the activated metal catalysts such as Ni^* , Mo^* could be recycled many times (retained catalytic activities even after reuse 3 times). Moreover, there appears to be no limitation to scale-up. This unexpected reactivity

of activated metal in the hydrosilylation reaction may be due to the high surface area, some unique species, or a combination of two.¹¹ The process here is a facile means for the hydrosilylation reaction of alkene and aldehyde in high yield with activated metal.

In conclusion, we have demonstrated that activated metal can catalyze hydrosilylation of alkenes and carbonyl compounds with alkylsilane. These results show that yields are comparable or greater than those using precious metals. Furthermore, potential utility of activated metals would be expected in the use of direct formation of organometallic compounds in the metallic state as a reagent. The generality of this kind of reactions and to other activated metals-catalyzed transformation is under investigation and will be reported in the near future.

Experimental

Anhydrous metal halides and alkylsilanes were purchased from Aldrich, Junsei, Yakuri and Gelest. Tetrahydrofuran (THF) and dimethoxyethane (DME) were refluxed over sodium metal and benzophenone until the blue color of benzophenone ketyl was observed, then distilled just prior to use. High quality hydrocarbon solvents such as hexane or pentane were obtained by stirring the sulfuric acid for 3 days followed by distillation. Lithium powder (99%) was purchased from Aldrich Chemicals. ^1H NMR were obtained on a Bruker AC 80 spectrometer. Chemical shifts were reported in ppm downfield from TMS and coupling constant were obtained from first order analysis of the spectra. Infrared spectra were taken on a Jasco-A-1. Mass spectra (70 eV electron impact) were taken on a Finnigan 4510 instrument equipped with a Finnigan-incos data system. GLC was done with a Varian 3300 instrument equipped with a FID detector and stainless steel column packed with 10% OV-101, Chromosob W HP 80/100 (2 m \times 1/8 in). Flash column chromatography was carried out on Merck silica gel 60 (70-230 mesh). Thin layer chromatography was performed on silica gel plate (E. Merck, 60, No. 5539). Stirring of solutions was done with magnetic stirrers and all reactions were continuously stirred unless otherwise specified.

General procedure for the preparation of activated metal powders. In an example of a typical preparation for activated nickel powder is as follows. In a nitrogen 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 0.312 g (1 mmol) of Ni_2 and 0.014 g (2 mmol) of Li under a nitrogen atmosphere. 5 mL of freshly distilled THF was syringed into the flask. After refluxing for 1 hr, the finely divided metal appeared as black powders which settled down in a dark solution (in most cases). The activated metal in a dark solution was used in this investigation without any further treatment.

General procedure of hydrosilylation with activated metal powders. 2.5 mmol of silanes and 2 mmol of substrates was injected to this slurry (above activated metal powders solution). The mixture was refluxed under nitrogen atmosphere for desired reaction times. The resulting solution was then allowed to cool to room temperature and hexane was added to become a visible solution along with settled the catalyst. Product isolation was straightforward. The solu-

tion was filtered to remove the catalyst through a pad of silica gel or filter paper using hexane-methylene chloride solvent as an eluent. Removal of the solvent under reduced pressure gave the corresponding hydrosilylating products. The yields are based on quantities obtained after this step. Some physical properties of the products are recorded below.

PhCH₂OSiEt₃: ¹H-NMR (CDCl₃) δ 7.28 (broad s, 5H), 4.72 (s, 2H), 0.97-0.68 (m, 15H). GC/Mass: no parent M⁺, 193 (M⁺-Et, 94), 163 (36), 135 (26), 91 (M⁺-OSiEt₃, 100), 65 (17). PhCH₂CH₂SiHPh₂: ¹H NMR (CDCl₃) δ 7.15 (broad s, 5H, benzylic ArH), 7.63-7.18 (m, 10H, Si ArH), 4.89 (t, *J*=3.7 Hz, 1H, SiH), 2.87-2.66 (m, 2H, Ph-CH₂), 1.63-1.37 (m, -CH₂Si). GC/Mass: no parent M⁺, 193 (M⁺-Et, 94), 163 (36), 135 (26), 91 (M⁺-OSiEt₃, 100), 65 (17). PhCH₂OSiMe₂Ph: ¹H NMR (CDCl₃) δ 7.68-7.20 (m, 10H), 4.69 (s, 2H), 0.39 (s, 6H). GC/Mass: no parent M⁺, 227 (M⁺-Me, 44), 197 (67), 164 (78), 149 (50), 135 (18), 91 (100), 65 (28). PhCH₂CH₂SiEt₃: ¹H NMR δ 7.1 (broad s, 5H), 2.48-2.70 (m, 2H), 0.3-1.3 (m, 17H). GC/MS, no parent M⁺, 191 (79) (M-Et)⁺, 163 (42), 133 (7), 105 (10), 87 (100). *c*-C₆H₁₁OSiEt₃: ¹H NMR (CDCl₃) δ 2.01-1.54 (m, 11H), 1.19-0.58 (m, 15H). GC/Mass: 214 (M⁺, 27), 185 (100), 156 (33), 103 (60), 75 (66).

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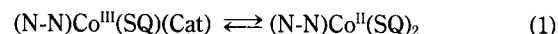
Distinct Oxidation-State Change Dependent on Remote Group of Coligand. (X₂-phen)Co(3,6-DBBQ)₂ (X₂-phen = 4,7-disubstituted-1,10-phenanthroline; 3,6-DBBQ = 3,6-di-*tert*-butyl-1,2-benzoquinone)

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Transition metal complexes containing quinone ligands have been elucidated to have metal- and quinone-localized electronic levels that are close in energy.¹ As a consequence, one of the most intriguing aspects of transition metal complexes of 1,2-semiquinonato (SQ) and catecholato (Cat) ligands is a unique facility for intramolecular electron transfer between the metal and chelated quinone ligands. This has been most prominently illustrated for the cobalt complexes, (N-N)Co^{III}(SQ)(Cat) where temperature- or photo-induced equilibria between the following redox isomers have been observed both in solution and in the solid state (1).² One isomer consists of Co(III) with one semiquinonato and one catecholato ligand and a diimine (N-N) ligand, and the other of Co(II) with two semiquinonato ligands and a diimine ligand. An intense band near 2500 nm (4000 cm⁻¹) assigned as Cat to Co(III) charge transfer has been characteristically observed for Co(III) forms.³⁻⁶ Moreover, for such complexes, the Co(III)/Co(II) transition temperature (T_c) has been found to be sensitive to the nature of the diimine coligands.⁶



In this paper, we describe an unexpectedly large change in oxidation state dependent upon the remote group X of