HYDROSILYLATION OF OLEFINS CATALYSED BY ACTIVATED TITANOCENE PREPARED FROM THE REDUCTION OF TITANOCENE DICHLORIDE WITH EXCESS LITHIUM

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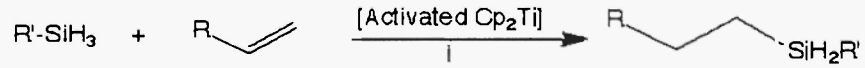
Abstract: Activated titanocene(Cp_2Ti^*) prepared by the reduction of titanocene dichloride with excess lithium in dimethoxyethane (DME) effectively catalyses the hydrosilylation of alkenes by alkyl- or phenylsilanes.

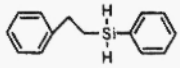
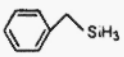
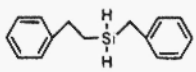
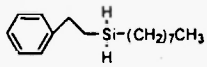
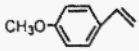
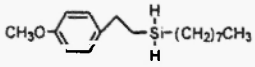
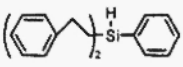
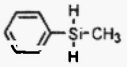
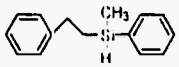
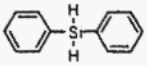
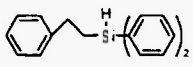
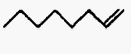
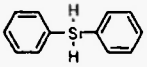
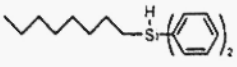
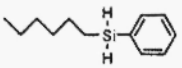
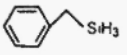
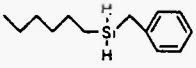
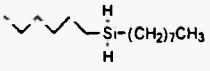
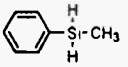
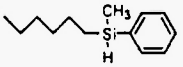
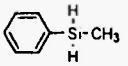
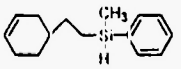
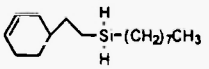
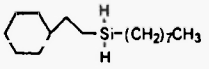
The transition metal catalyzed olefin hydrosilylation is one of the most important methods for the preparation of organosilicon compounds.[1] Many late transition metal complexes catalyze olefin hydrosilylation,[2] but few early transition metal hydrosilylation catalysts have been reported.[3] Recent results showed that early transition metallocenes, such as Cp_2MEt_2 (M = Ti,[3a] Zr[3a]), $Cp_2M(n\text{-}Bu)_2$ (M = Ti,[3e,f] Zr,[3a,d-f] Hf[3e,f]), Cp_2ZrMe_2[3a] and its complexes[3c], prepared by the treatment of Cp_2MX_2 (X = Cl, Br) with Grignard reagents are active catalyst precursors for olefin hydrosilylation. However, the methodology in the use of Cp_2MR_2 as a catalysts has some disadvantages including low yields, the required synthesis from a metallocene dichloride, the formation of polysilanes[4], the redistribution of alkylsilanes[4b], the hydrogenation of olefins[3d] and the fact that Cp_2ZrMe_2[3a] undergoes decomposition at room temperature. Apparently, a simpler method of preparation of the catalyst would be the generation in situ of an active and stable species directly from the metallocene dichloride. Our previous paper dealt with hydrosilylation of olefins[5] and carbonyls[5b]catalyzed by activated metal powders (Ni, Zr, Mo) prepared by the reduction of the corresponding metal halides (Cl, Br, I) with lithium or zinc. In this communication, we now report that the use of activated titanocene (Cp_2Ti^*) circumvent all the above disadvantages. The experimental results of organosilicon compounds prepared by the Cp_2Ti^* method are summarized in Table 1.



Scheme 1. *Reagents and conditions:* [Activated Cp_2Ti]; Cp_2TiCl_2-Li (1:3 molar ratio), DME, 25 °C, stirred for 1 h ; i, 1:1.2:0.1 molar ratio of alkene: alkylsilane: catalyst, 25 °C, stirred for 1 h. Experimental details; *see ref. 6*

Improvements in the yields or the elimination of by-products (polysilane, dehydrogenative silylation and olefin hydrogenation) are significant in most cases. However, the most dramatic differences are those observed using Cp_2ZrR_2 (R=Et, Me, *n*-Bu) or Cp_2TiMe_2 as catalysts by Negishi and Takahashi.[3a] For example, when a mixture of 2-octene or 1-octene and diphenylsilane was stirred with Cp_2ZrEt_2 (prepared by the treatment of Cp_2ZrCl_2 with EtMgBr) in THF under nitrogen at 50 °C for 1 h, n-OctSiHPh$_2$ was produced in only 53% and 73% yields respectively (determined by GC). The hydrosilylation of 1-octene with phenylsilane under the same reaction conditions gave *n*-OctSiH$_2$Ph in only 41% yield. The use of $Cp_2Zr(n\text{-}Bu)_2$ in place of Cp_2ZrEt_2 led to a 75% yield of *n*-OctSiHPh$_2$ and a 10% yield of n-BuSiHPh$_2$ (determined by GC). The use of Cp_2ZrMe_2 led to only a 10% yield of *n*-OctSiHPh$_2$. However, when a mixture of 1-octene and diphenylsilane was refluxed in the presence of Cp_2Ti^* in DME under nitrogen for 2 h, n-OctSiHPh$_2$ was formed in 84% isolated yield (run 8). Using Cp_2Ti^*, hydrosilylation of 1-hexene with phenylsilane gave n-hexylSiH$_2$Ph in an 83% isolated yield (run 9). In each case, the reaction proceeded smoothly and was only moderately exothermic. In contrast to Cp_2ZrEt_2[3a], no hydrosilylation was observed when phenylsilane was reacted with 2-octene using Cp_2Ti^*. Alkene isomerization was also not observed using Cp_2Ti^*. We also found that DME was the best choice of solvent. Surprisingly, the hydrosilylation reaction did not occur at all when activated titanocene prepared in other solvents (such as THF, diethyl ether or benzene) was used as a catalyst. Using Cp_2Ti^*, the terminally silylated products were formed in over

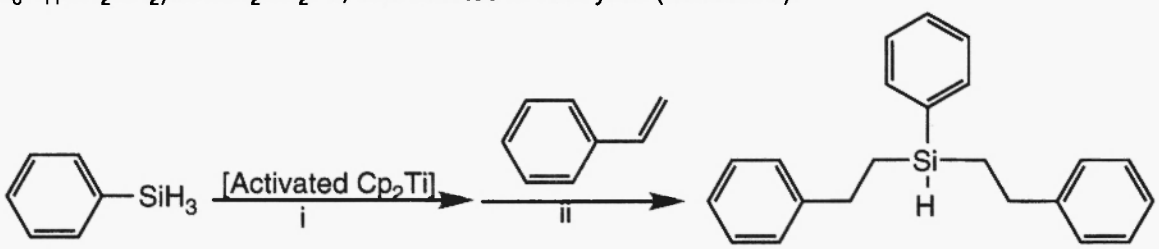
Table 1. Hydrosilylation of Olefins with Alkylsilanes Catalyzed by Activated Titanocene Prepared from Cp_2TiCl_2 - Li.[a]

Run	Olefins	Silanes	Product[b]	Yield(%)[c]
1				83
2				82
3		$CH_3(CH_2)_7SiH_3$		91
4		$CH_3(CH_2)_7SiH_3$		82
5[d]				87
6				78
7[e]				86
8[e,f]				84
9				83
10				82
11		$CH_3(CH_2)_7SiH_3$		86
12				80
13				82
14		$CH_3(CH_2)_7SiH_3$		86
15		$CH_3(CH_2)_7SiH_3$		81
16		$CH_3(CH_2)_7SiH_3$		93
17				86
18[g]		$CH_3(CH_2)_7SiH_3$		88

[a] 10 : 12.5 : 1 mmol of olefin : silane : catalyst (run 1-4, 8-10, 13-15, 17) and 12.5 : 10 : 1 mmol of olefins : silane : catalyst (run 6-7, 11-12, 16) in 5ml of DME. [b] Product are assigned by ^1H NMR, IR, Mass spectral data. [c] Isolated. [d] 22.5 : 10 : 1 mmol of olefin : silane : catalyst (run 5). [e] Refluxed for 2hr. [f] Yield was only 9% by GC when the reaction was run in THF for 1hr at 50°C rising Cp_2TiEt_2 as catalyst : see ref 3a. [g] 20% of dehydrogenative silylated product was also formed by GC along with hydrosilylated product : see ref 7.

95% yield (run 1-17, determined by GC) in most cases avoiding by-products (dehydrogenative silylation, polysilanes, olefin polymers and olefin hydrogenation) except the reaction of allyltrimethylsilane with *n*-octylsilane (run 18). Products (dehydrogenative silylated product : hydrosilylated product; 1 : 4, determined by GC) in this reaction were stirred for an additional hour under an atmosphere of hydrogen, the hydrogenative silylated product was hydrogenated to give the corresponding hydrosilylated product in 88% yield (run 18).[7]

In another controlled experiment using Cp_2Ti^*, we found that the reaction of phenylsilane with an excess of styrene (styrene : phenylsilane ratio 2.25 : 1) produced $PhSiH(CH_2CH_2Ph)_2$ in 77% yields (run 5) and no $PhSiH_2CH_2CH_2Ph$ was detected. However, when the styrene : silane ratio was changed to 1 : 1.25, the relative amounts were reversed. The yield of $PhSiH_2CH_2CH_2Ph$ was 83% (run 1) and no $PhSiH(CH_2CH_2Ph)_2$ was detected. An attempted preparation of the asymmetric organosilane by altering the olefin was very successful. For example, after the styrene : phenylsilane mixture (1 : 1.2 molar ratio) was stirred in the presence of Cp_2Ti^* for 1 hr, vinylcyclopentane was added and refluxed for another 1 hr. An asymmetric alkylsilane, $Ph(c\text{-}C_6H_{11}CH_2CH_2)SiHCH_2CH_2Ph$, was isolated in 70% yield (Scheme 2).



Scheme 2. *Reagents and conditions:* [Activated Cp_2Ti]; Cp_2TiCl_2-Li (1:3 mmol), DME, 25 °C, stirred for 1h ; i, 5: 6: 1 mmol of styrene: phenylsilane: catalyst, stirred for 1 h ; ii, vinylcyclohexane (6 mmol) was added, refluxed for 1 hr. 70% isolated yield

We also studied the reproducibility of the activated catalyst as follows; after removing the solvent under reduced pressure, hexane was added; the catalyst was recovered when the product mixture was removed from the reaction flask by decantation and the reaction flask was recharged with alkene, silane and DME after evaporation of the remaining hexane. The catalyst was reused without significant loss of activity. An excess of Li was essential for the preparation of highly activated titanocene to optimize the yields. For example, when the hydrosilylation of styrene with phenylsilane was carried out using the activated titanocene prepared by the treatment of Cp_2TiCl_2 with an equivalent of Li (1:2 molar ratio), β-phenethylphenylsilane was produced in 30% yield according to GC. The yields increased up to 83% using Cp_2Ti^* prepared by the treatment of Cp_2TiCl_2 with excess lithium (1:3 molar ratio) (run 1). The exact role of the excess lithium and the need for DME as a solvent are still unexplained at this stage. We have focused on the scope and synthetic potential of this reaction.

In summary, the hydrosilylation of alkenes with alkyl hydrosilanes was catalyzed by activated titanocene prepared by the reaction of titanocene dichloride with an excess of lithium in DME under very mild conditions. The hydrosilylation of alkynes and dienes using these reagents, as well as mechanistic studies, are in progress and will be reported in due course.

Acknowledgements

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References and Notes

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6. In a typical experiment, a well-dried solution of Cp_2TiCl_2 in DME (1 mmol in 5 ml) was treated with lithium powder (3 mmol). After stirring the mixture for 1 h at 25 °C under nitrogen, its color changed from deep red to a dark solution. 10 mmol of alkene and 12.5 mmol of alkylsilane were added, and the mixture was stirred for another 1 h at 25oC under nitrogen. Isolation of organosilicon compounds was straightforward: After removing the solvent under reduced pressure, hexane was added, and the solution was filtered through the pad of a silica gel column (1 cm dia x 5 cm packed) using hexane as an eluent to remove the catalyst. Evaporation of the solvent under reduced pressure gave the corresponding hydrosilylated products with >98% purity (Table 1). The yields are based on the quantity obtained after this step. All alkylsilanes were characterized by ^1H NMR, IR and Mass spectroscopy.
7. Product mixture was stirred for another one hour under an atmosphere of hydrogen, hydrogenative silylated product was hydrogenated to give the corresponding product. Hydrogenation of various alkenes under hydrogen were observed and similar result was already reported; see Scott, F.; Raubenheimer, H. G; Pretorius, G.; Hamese, A .M. *J .Organomet. Chem.* 1880, **384**, C17.

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