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Olefin hydrosilation catalyzed by zirconocene complexes *

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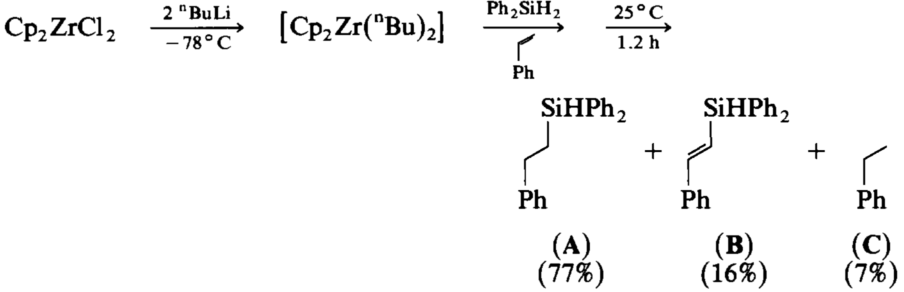
Abstract

The hydrosilation of olefins such as styrene, 1-hexene, and 2-pentene with diphenylsilane can be carried out with catalysts generated from zirconocene dichloride and two equivalents of butyllithium. Complete regioselectivity is observed as only terminal organosilicon products are produced (~ 90%). In the case of styrene, three major products are formed: diphenylphenethylsilane (77%), *trans*-1-diphenylsilyl-2-phenylethene (16%), and ethylbenzene (7%). The product distribution was found to be dependent on reagent concentrations: reactions run with excess diphenylsilane favored diphenylphenethylsilane; excess styrene favored *trans*-1-diphenylsilyl-2-phenylethene. Extensive H/D exchange is observed in the hydrosilation of styrene with Ph_2SiD_2.

Transition metal catalyzed olefin hydrosilation is a powerful method for the preparation of organosilicon compounds [1]. Many late transition metal complexes catalyze olefin hydrosilation, but few early transition metal hydrosilation catalysts have been reported [2]. Recently, during studies of the dehydrogenative coupling of hydrosilanes, Harrod observed the hydrosilation of styrene with phenylsilane in the presence of dimethylzirconocene [3]. Variable induction periods were observed with dimethylzirconocene as a catalyst precursor; products due to the dehydrogenative coupling of phenylsilane were also observed.

Herein we report our initial investigations on the activity and chemoselectivity of zirconocene complexes for olefin hydrosilation. We have found that catalysts generated from zirconocene dichloride and two equivalents of butyllithium (by the method of Negishi [4,5]), are active for the hydrosilation of styrene with diphenylsilane (eq. 1):



$Cp_2ZrCl_2 \xrightarrow[-78\,°C]{2\,{}^nBuLi} [Cp_2Zr({}^nBu)_2] \xrightarrow{Ph_2SiH_2} \xrightarrow[1.2\,h]{25\,°C}$

(1)

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[*] This manuscript is dedicated to the memory of Professor Piero Pino.

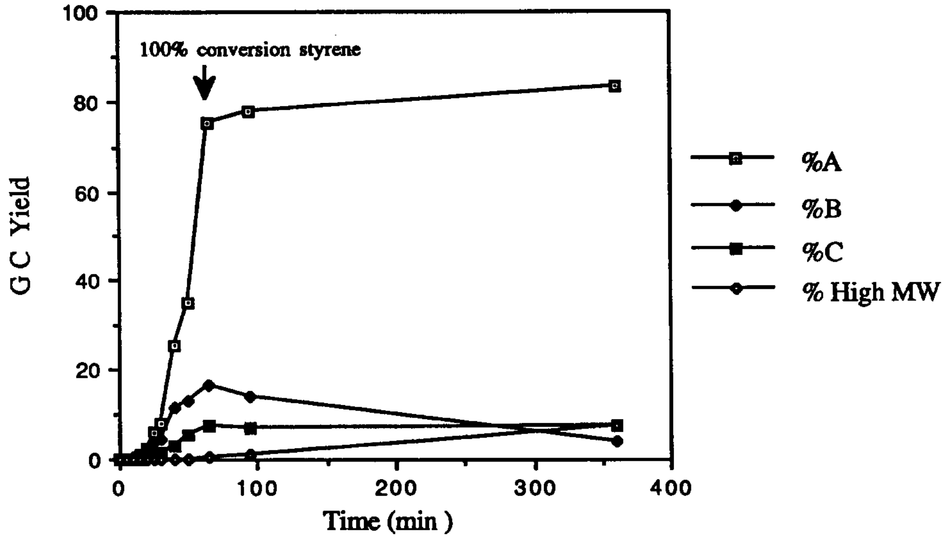

Fig. 1. Hydrosilation of styrene with diphenylsilane: reaction products versus time. A: diphenylphenethylsilane; B: *trans*-diphenylsilyl-2-phenylethene; C: ethylbenzene.

Addition of diphenylsilane and styrene to a pre-formed toluene solution of di-n-butylzirconocene (generated *in situ* from zirconocene dichloride and ^{n}BuLi at $-78\,^\circ$C) followed by warming to room temperature, results in complete conversion of styrene and 93% conversion of diphenylsilane after 1.2 hours (65 turnovers, turnover frequency = 1.44 min^{-1}) [6*]. Three major products are formed: diphenylphenethylsilane (A, 77%), *trans*-1-diphenylsilyl-2-phenylethene (B, 16%), and ethylbenzene (C, 7%). Complete regioselectivity is observed; only terminal silyl products are produced. In addition to the hydrosilation, dehydrogenative silylation, and olefin hydrogenation products, traces of $(Ph_2SiH)_2$ and $Ph_2SiH(butyl)$ are also formed. The catalyst remained active for several days as repeated additions of silane and styrene were readily hydrosilated (10 days, 6 additions, > 450 turnovers).

Comparison experiments indicated that $Cp_2ZrCl_2/2$ ^{n}BuLi is a more active catalyst precursor than Cp_2ZrMe_2. Only traces of reaction products were detected after 15.5 hours at room temperature when dimethylzirconocene was employed for the hydrosilation of styrene with diphenylsilane; heating the reaction mixture to 70 °C resulted in complete conversion of styrene after 2 hours [7*]. In contrast, hydrosilation using the Cp_2ZrCl_2/BuLi procedure was complete after 50 min at 70 °C [8*].

The hydrosilation of styrene with diphenylsilane in the presence of Cp_2ZrCl_2/^{n}BuLi was monitored by GC (Fig. 1). Following complete conversion of styrene, a slow decrease in the concentration of vinylsilane **B** is observed while the concentration of alkylsilane **A** increases. Vinylsilane is completely consumed within two days, suggesting that it is slowly hydrogenated to alkylsilane **A**. The slow formation of higher molecular weight products is also detected during this time. These higher

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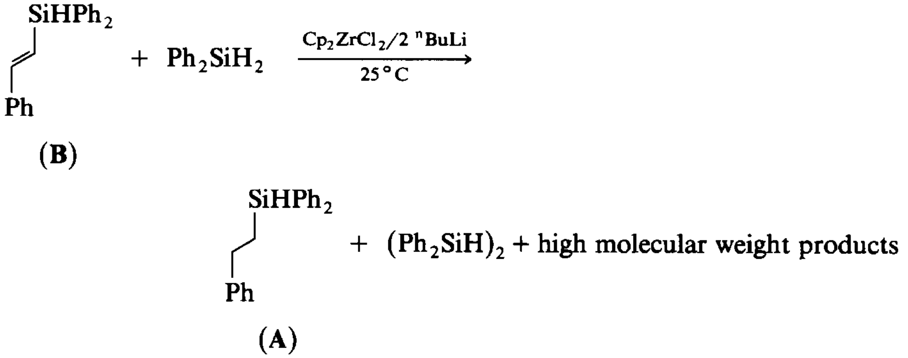
* Reference number with asterisk indicates a note in the list of references.

molecular weight products consist mainly of $(Ph_2SiH)_2$ along with traces of disilylalkyl compounds. The concentration of ethylbenzene, **C**, remained constant.

Control experiments were carried out to investigate the reactivity of alkylsilane **A** and vinylsilane **B** under the reaction conditions. 1 Equiv. vinylsilane **B** and 1.7 equiv. diphenylsilane were stirred in the presence of dibutylzirconocene at 25 ° C for 40 hours; > 95% conversion of vinylsilane was observed. Alkylsilane **A** was produced in ~ 62% GC yield along with $(Ph_2SiH)_2$ and higher molecular weight products which were not characterized (eq. 2).



(2)

In another control experiment, the alkylsilane **A** was stirred in the presence of dibutylzirconocene for 39 hours. No reaction was observed. These results suggest that Si–C bond formation is not reversible and that vinylsilanes are hydrogenated to alkylsilanes under these conditions.

A series of experiments were carried out to study the effects of different reagent concentrations on the product distribution. When $[Ph_2SiH_2]/[\text{styrene}] > 1$, selectivity for alkylsilane increased and when $[Ph_2SiH_2]/[\text{styrene}] < 1$, selectivity for vinylsilane increased. Thus, the chemoselectivity between alkyl- and vinylsilane can be controlled by altering the reaction conditions.

The hydrosilation of 1-hexene, 2-pentene, and cyclohexene was investigated. The aliphatic olefins 1-hexene and 2-pentene are readily hydrosilated [6*] after 8 hours to produce terminal silyl products in ~ 90% yield (GC); approximately 10% of the olefin is hydrogenated in each case. In contrast to styrene, no vinylsilane is detected during the reaction of the aliphatic olefins. Monitoring results revealed that *cis*-2-pentene is preferentially hydrosilated over *trans*-2-pentene. Cyclohexene yielded only traces of silylated products; the major products were $(Ph_2SiH)_2$ and cyclohexane (< 15% yields, 24 hours).

Extensive deuterium scrambling was observed when styrene was hydrosilated with Ph_2SiD_2. In this particular reaction, Ph_2SiD_2 and styrene were added to a pre-formed dibutylzirconocene solution. After 24% conversion of styrene, the reaction was quenched and the products and reactants isolated and analyzed by NMR [9*]. The isolated diphenylsilane consisted of 46% Ph_2SiH_2, 42% Ph_2SiHD and 12% Ph_2SiD_2. Each of the three olefinic H(D) sites of the unreacted styrene contained 39–43% deuterium incorporation and there was extensive deuterium incorporation into the products [10*]. Extensive H/D exchange after only 24% conversion of styrene implies that H/D exchange is much faster than hydrosilation.

In conclusion, $Cp_2ZrCl_2/2\ ^nBuLi$ readily hydrosilates olefins with diphenylsilane to yield terminal organosilanes. Chemoselectivity for hydrosilation was achieved by employing a secondary silane to suppress the silane coupling reactions which are observed with primary silanes [3]. The development of the $Cp_2ZrCl_2/2\ {}^nBuLi$ procedure avoids the induction periods which are observed when dimethylzirconocene is employed as the catalyst precursor. The formation of vinylsilane during the hydrosilation of styrene, the rapid H/D exchange, and olefin isomerization of 2-pentene attest to the complexity of this catalytic system. Further studies are underway to investigate the scope of group IV metallocenes as hydrosilation catalysts and to probe the mechanism of this reaction.

Acknowledgements. We gratefully acknowledge partial support from the NSF-MRL Program through the Center for Materials Research at Stanford University and the Department of Education for a GAANN Fellowship for M. Kesti.

References and notes

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5 While these studies were underway, other workers reported a similar procedure: L.S. Chang and J.Y. Corey, Organometallics, 8 (1989) 1885; J.Y. Corey, X.H. Zhu, T.C. Bedard and L.D. Lange, Organometallics, 10 (1991) 924.

6 Experimental conditions: $[Cp_2ZrCl_2/2\ {}^nBuLi]_i = 0.011\ M$, $[Ph_2SiH_2]_i = 0.71\ M$, $[\text{olefin}]_i = 0.71\ M$. All reactions were run under N_2 using either standard Schlenk techniques or inside a dry box. All products were fully characterized by GC/mass spectroscopy, ^1H, ^{13}C NMR, and microanalysis ($\leqslant 0.4\%$).

7 Product distribution (GC): **A**, 81%; **B**, 10%; **C**, 9%.

8 Product distribution (GC): **A**, 80%; **B**, tr; **C**, 8%; higher molecular weight products, ~12%.

9 Separate signals for the silicon hydrides Ph_2SiH_2 and Ph_2SiHD were obtained. Percentages were calculated by comparison of the integral regions of the appropriate proton signals with the *ortho* phenyl protons (internal standard).

10 The reaction products, ethylbenzene and diphenyl(butyl)silane, were not isolated. A H/D mass balance analysis using the percentages calculated by NMR is within experimental error.