

Catalytic Synthesis of Silicon Carbide Preceramic Polymers:  
Polycarbosilanes

Research Progress Report

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## TECHNICAL REPORT

Grant No. DE-FG02-91ER14173.A000

## Project Title

"Catalytic Synthesis of Silicon Carbide Preceramic Polymers:  
Polycarbosilanes"

## Abstract

Polycarbosilanes are the most successful and widely studied class of polymer precursors for silicon carbide, but traditional methods for their synthesis are inefficient and nonselective. This project is focused on developing transition metal catalysts for the synthesis of polycarbosilanes and other preceramic polymers. In recent work we have developed the first homogeneous transition metal catalysts for the dehydrogenative coupling of simple alkyl silanes to oligomeric and polymeric carbosilanes,  $H-(SiR_2CR'_2)_n-SiR_3$ . The coupling of alkylgermanes, however, yields the corresponding oligomeric poly(germanes) (Ge-Ge). Future work will help elucidate the mechanisms of these catalytic process, explore the use of hydrogen acceptors as reaction accelerators, and develop new and more active catalysts.

# Catalytic Synthesis of Silicon Carbide Preceramic Polymers: Polycarbosilanes

## Progress Report

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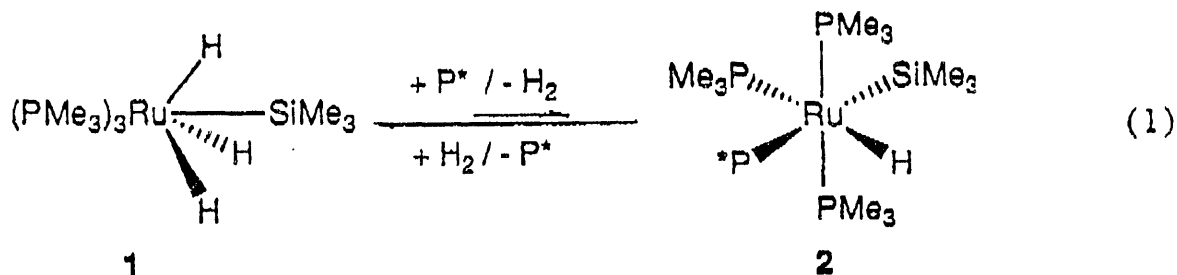
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Well-characterized ruthenium complexes of the type  $(PR_3)_3Ru(H)_3(SiR'_3)$  catalyze the dehydrogenation of trialkyl silanes at 150 °C to produce a distribution of linear and branched carbosilanes,  $H-(SiR_2CR'_2)_n-SiR_3$ . This research effort is focused on the detailed elucidation of the catalytic mechanism and the development of more active catalyst systems.

### I. Chemical Reactivity of Ruthenium Silyl Catalysts and Implications for the Catalytic Mechanism

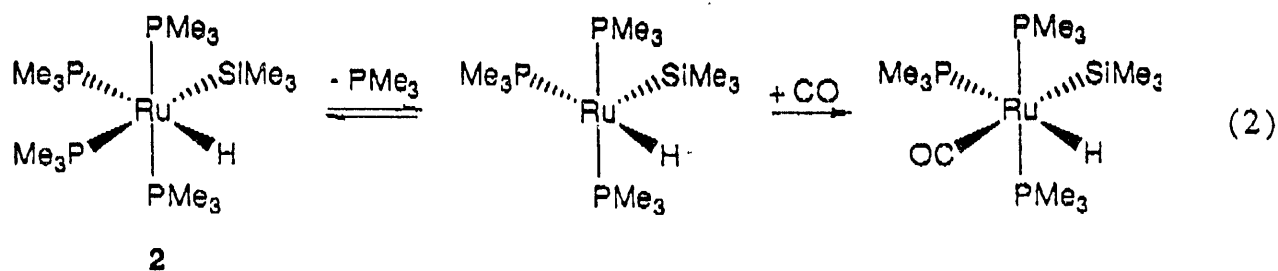
The seven-coordinate trihydride silyl complexes,  $(Me_3P)_3Ru(H)_3(SiR_3)$ , exhibit several properties which determine their relatively high catalytic activity. We have been systematically exploring the basic chemistry of this and related classes of ruthenium complexes to better understand the factors leading to the unique catalytic activity.

Although the trimethylsilyl derivative,  $(Me_3P)_3Ru(H)_3(SiMe_3)$  (1) is not an active coupling catalyst at temperatures less than ca. 150 °C, it does undergo ligand substitution reactions at much lower temperatures. For example,  $H_2$  loss occurs rapidly at 25 °C, as evidenced by exchange with  $D_2$ , CO, and isotopically labeled phosphine ( $P^* \equiv P(CD_3)_3$ ). However, the equilibrium constant for exchange of  $H_2$  with  $P^*$  is extremely small, demonstrating the high stability of 1 relative to the more sterically hindered octahedral tetrakis phosphine complexes, 2, as shown in eq 1.

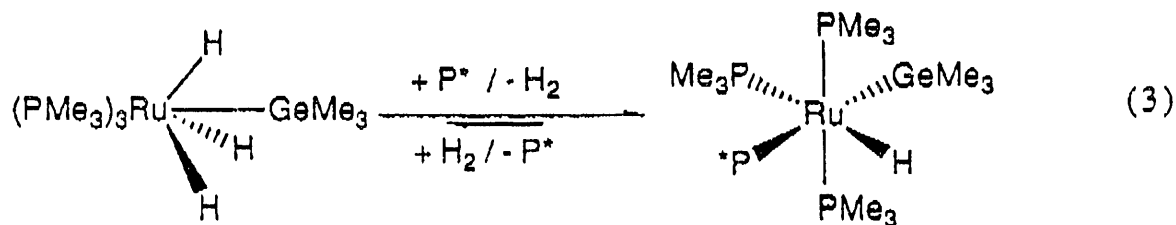


Remarkably, phosphine substitution is completely stereospecific and only leads to incorporation of isotopic label in the position trans to the silyl

group in 2. Similarly, treatment of isolated labeled 2 with CO leads to complete loss of P\* only, and formation of mer-P<sub>3</sub>Ru(CO)(H)(SiMe<sub>3</sub>) as the kinetic product (eq 2.) In other words, only the position trans to silyl undergoes exchange. It appears that SiMe<sub>3</sub> exhibits an extremely strong trans labilizing effect, greater even than hydride. This fact has great implications in the catalytic process, during which it is necessary to generate a vacant coordination site cis to the silyl for productive chemistry to occur.



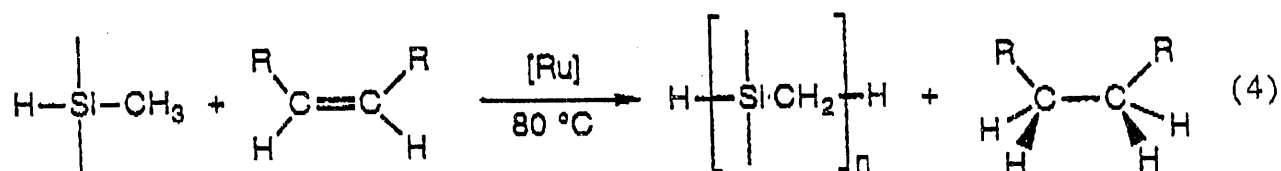
The stability of the seven-coordinate trihydrides relative to the octahedral P<sub>4</sub>Ru(H)(SiR<sub>3</sub>) complexes is determined largely by steric congestion. The octahedral complexes appear to be more stable, except with the larger tertiary silyl groups. Thus the equilibrium in eq 1 above lies quite far to the right for small silyl groups such as SiMe<sub>2</sub>H, SiMeH<sub>2</sub>, and SiH<sub>3</sub>. In these instances the trihydrides can only be generated by low temperature photolytic routes, which minimize the back-reaction to 2. Even the relatively small change from SiMe<sub>3</sub> to GeMe<sub>3</sub> greatly perturbs the balance; the Ru-Ge bond is slightly longer than the corresponding Ru-Si bond, hence the GeMe<sub>3</sub> group has a smaller cone angle. As a result, P<sub>3</sub>RuH<sub>3</sub>(GeMe<sub>3</sub>) and P<sub>4</sub>Ru(H)(GeMe<sub>3</sub>) are quite close in energy, and the former can only be isolated from the latter under a continuous hydrogen purge to remove PMe<sub>3</sub>.



## II. Acceleration of Silane Dehydrocoupling in the Presence of Hydrogen Acceptors.

Carbosilane formation is inhibited by the hydrogen produced, and mechanistic studies indicate that loss of H<sub>2</sub> from the metal following β-hydrogen elimination is to be a key step limiting the rate of dehydrocoupling. We have determined that addition of olefins as

hydrogen acceptors leads to rapid catalytic silane coupling at 80 °C, more than 70 °C below the temperature required in the absence of olefin (eq 4.) This results from the coupling of a second catalytic reaction, olefin hydrogenation, with the silane condensation process. Remarkably, olefin hydrosilylation does *not* successfully compete with olefin hydrogenation in the catalytic mixture.

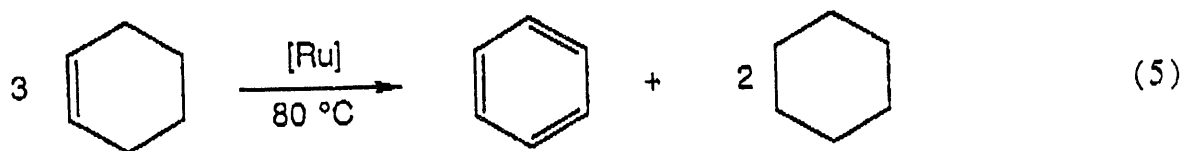


Several factors determine the suitability of the olefin for this process. The olefin must not bind sufficiently strongly to prevent catalysis, yet binding must be adequate to assure hydrogenation. For example, ethylene reacts with 1 to yield the bis(olefin) adduct  $(\text{PMe}_3)_3\text{Ru}(\text{H}_2\text{C}=\text{CH}_2)_2$ , which is completely inert under the reaction conditions. However, olefins such as neohexene (*t*-Butyl ethylene) and trimethylsilyl ethylene, which are substituted with a single, fairly large group are quite effective.

Deuterium labeling studies indicate the olefin interacts reversibly with 1 at relatively low temperatures, but that catalysis is achieved by an essentially irreversible alkane loss step at temperatures  $\geq 80\text{ }^\circ\text{C}$ . For example, reaction of neohexene with 1- $\text{d}_3$  at 25 °C gives rise to deuterium exchange into the olefinic positions (but no *neohexane*), indicating that olefin coordination and hydride migration occurs readily at temperatures ca. 60 °C below those at which catalysis is observed.

We have also discovered that cyclohexene is also a suitable hydrogen acceptor in this process. This is somewhat surprising, given the relatively small size of the olefin, and the presence of allylic hydrogens which might lead to competing side reactions. Although catalysis at 80 °C in the presence of cyclohexene is not as fast as with neohexene, the extremely low cost of the former makes it an attractive co-reactant.

Interestingly, under the reaction conditions cyclohexene also undergoes catalytic redistribution to benzene and cyclohexane. Although this reaction is of little consequence in the silane condensation, it is of interest with regard to the chemistry of C-H activation in general. Several



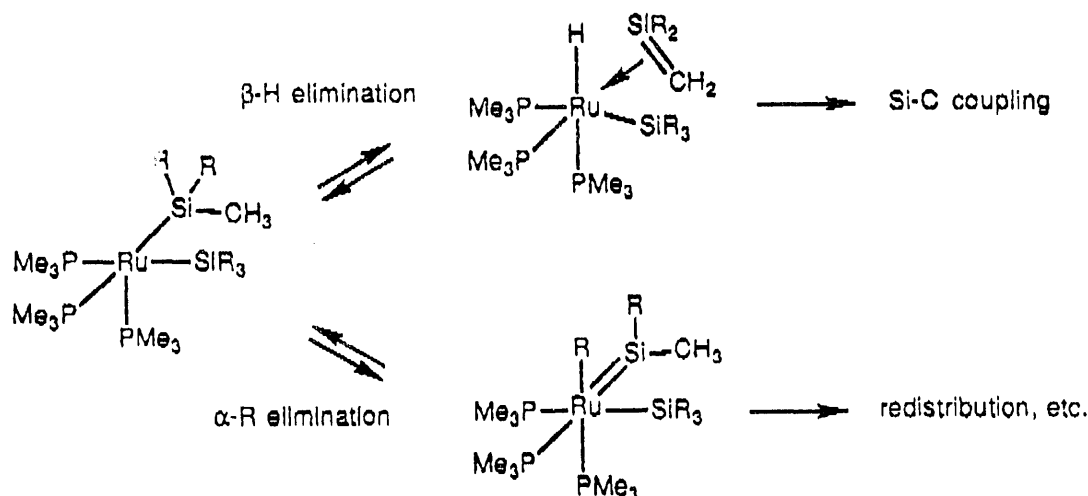
researchers are actively investigating so-called transfer dehydrogenation catalysts, but cyclohexene is not generally considered a feasible substrate,

due to the strong binding of intermediate cyclohexadiene to the catalyst. It would appear that the present ruthenium catalyst is sufficiently hindered to minimize binding of this intermediate.

### III. Ruthenium-Catalyzed Redistribution of Silanes

The rapid Another important discovery regarding the reactivity of  $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiR}'_3)$  during the catalytic silane coupling process is that this compound also catalyzes the redistribution of groups on silicon. The observed trend for the rate of redistribution is:  $\text{H} \gg \text{Cl} > \text{Ph} > \text{Me} \sim \text{C}_6\text{H}_5\text{SiMe}_3$ . The rapid scrambling of hydrogen in particular has precluded detailed study of carbosilane formation in secondary and primary silanes.

The most straightforward process to accomplish this scrambling would involve  $\alpha$ -hydrogen elimination to generate a transient silylene complex  $(\text{H}-\text{Ru}=\text{SiR}_2)$ , followed by rapid 1,3-methyl migration between silicons.

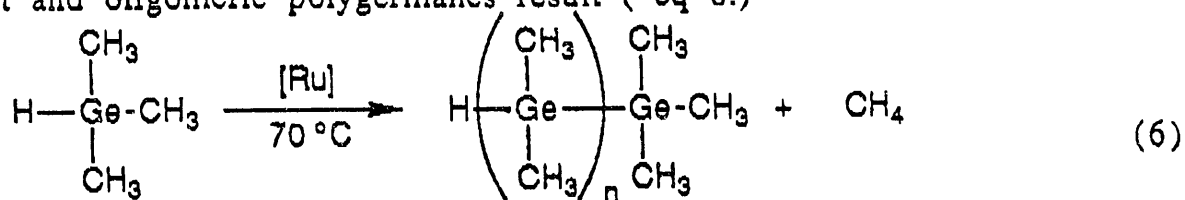


If this hypothesis is correct, the competition between silane coupling and redistribution can be analyzed as a competition between  $\alpha$ - and  $\beta$ -elimination processes, thus suppression of the former and acceleration of the latter will favor catalytic silane coupling. Unfortunately, the olefin-assisted catalysis exhibits the same relative rates for these two processes. Thus coupling of secondary silanes at  $80^\circ\text{C}$  in the presence of neohexene yields primarily redistribution (and not dehydrocoupling), identical to the reaction at  $150^\circ\text{C}$  in the absence of olefin.

### IV. Ruthenium-Catalyzed Coupling of Organogermanes

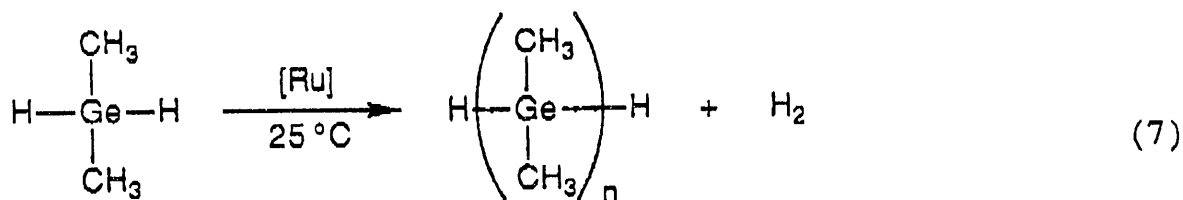
Although treatment of  $\text{Me}_3\text{Si}-\text{H}$  with 1 results in dehydrogenation and formation of carbosilanes, the corresponding germane,  $\text{Me}_3\text{Ge}-\text{H}$ , was

found to undergo a previously unknown transformation in which methane is lost and oligomeric polygermanes result (eq 6.)



This unprecedented "demethanative coupling" is readily understood in the context of the scheme presented above for silane redistribution: the relatively weak Ge-C bond undergoes cleavage through an  $\alpha$ -CH<sub>3</sub> migration in preference to the  $\beta$ -H elimination. Eventual germyl-to-germylene migration results in formation of new Ge-Ge bonds, and C-H reductive elimination yields the methane.

Consistent with this picture, Me<sub>2</sub>GeH<sub>2</sub> undergoes very rapid dehydrogenative coupling at 25 °C to form poly(dimethylgermylene). The greater catalytic rate appears to be consistent with the relative migratory aptitudes described above for the redistribution reactions.



### Publications

- (1) L. J. Procopio, B. Mayer, K. Plössl and D. H. Berry, "Polycarbosilanes from the Ruthenium-Catalyzed Dehydrogenative Coupling of Alkyl Silanes", *Polym. Prepr.* 1992, 33, 1241-1242.
- (2) L. J. Procopio, B. Mayer, K. Plössl and D. H. Berry, "Synthesis and Structures of Seven-Coordinate Ruthenium Silyl Complexes," manuscript in preparation.
- (3) K. Plössl and D. H. Berry, "Catalytic Synthesis Carbosilanes by Transfer Dehydrogenation of Alkyl Silanes," manuscript in preparation.

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