Catalytic Synthesis of Silicon Carbide Preceramic Polymers:
Polycarbosilanes

Research Progress Report

March 1, 1991 - October 31, 1991

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The Trustees of the University of Pennsylvania
Philadelphia, Pennsylvania 19104

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November, 1991

Prepared for

The U.S. DEPARTMENT OF ENERGY

AGREEMENT NO. DE-FG02-91ER14173.A000

MASTER

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TECHNICAL REPORT

Grant No. DE-FG02-91ER14173.A000

Project Title

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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, $H-(SiR_2CR'_2)_n-SiR_3$. Future work will help elucidate the mechanism of the 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:
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Progress Report

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DOE Grant No. DE-FG02-91ER14173.A000

The first homogeneous transition metal catalysts for the dehydrogenative coupling of simple alkyl silanes to oligomeric and polymeric carbosilanes, $\text{H}-(\text{SiR}_2\text{CR}'_2)_n-\text{SiR}_3$, have been developed and are under investigation. 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. Well-characterized ruthenium complexes of the type $(\text{PR}_3)_3\text{Ru}(\text{H})_3(\text{SiR}'_3)$ catalyze the dehydrogenation of trialkyl silanes at 150 °C to produce a distribution of linear and branched carbosilanes. Initial results suggested that transient metal silaolefin complexes of the type $\text{L}_n\text{Ru}(\eta^2-\text{R}_2\text{Si}=\text{CR}'_2)$ play a key role in the catalytic silane dehydrogenation and carbosilane formation. This research effort is focused on the detailed elucidation of the catalytic mechanism and the development of more active catalyst systems.

Progress

I. Synthesis, Structure and Activity of a New Class of Catalyst:
 $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiR}'_3)$

The first catalyst discovered for the synthesis of carbosilanes by dehydrogenative coupling of alkyl silanes was $(\text{Me}_3\text{P})_4\text{RuH}_2$. Although fairly stable to the catalytic conditions, this material coupled $\text{H}-\text{SiMe}_3$ at a very slow rate (<1 turnover per day). We have recently prepared a new class of trimethylphosphine ruthenium complexes, $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiR}_3)$ (eq 1), which are appreciably more active (>2 turnovers per hour). These seven-coordinate trihydride silyl complexes are extremely stable, and have been fully characterized, including single crystal X-ray diffraction studies of the SiMe_3 and $\text{SiMe}_2\text{CH}_2\text{SiMe}_3$ derivatives as shown below. Interestingly, the complexes can be unequivocally assigned as classical hydride complexes.

Oligomeric carbosilanes $\text{H}-(\text{SiMe}_2\text{CH}_2)_n-\text{H}$ with molecular weights up to 1000 ($n \leq 13$) have been prepared using this new catalyst.

II. Reactivity and Mechanistic Studies Relating to Catalytic Carbosilane Formation

Initial kinetics studies of the silane coupling indicate a rate law which is first order in $[\text{P}_3\text{RuH}_3(\text{SiMe}_3)]$ and independent of silane concentration. In addition, the reaction is inhibited by hydrogen pressure. This is consistent with a process involving a single ruthenium center, and in which the rate limiting step does not involve free $\text{Me}_3\text{Si-H}$. Additional studies of related stoichiometric reactions indicate that the requisite C-H activation step, apparently by β -hydrogen elimination from a Ru-silyl, is also *not* rate limiting; rather two other steps are more difficult: generation of a vacant coordination site adjacent to the Ru-silyl group and loss of H_2 from the metal following β -hydrogen elimination. This hypothesis was key in leading to the developments described in section IV.

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 (e.g. eq 2.) The observed trend for the rate of redistribution is: $\text{H} \gg \text{Cl} > \text{Ph} > \text{Me} \sim \text{CH}_2\text{SiMe}_3$. The rapid scrambling of hydrogen in particular has precluded detailed study of carbosilane formation in secondary silanes.

This process complicates analysis of the study of the carbosilane formation, but also raises several interesting mechanistic issues which we hope to address in the coming year (*vide infra*). In a very recent result, we have isolated the symmetrical bis(silyl) complex $(\text{Me}_3\text{P})_4\text{Ru}(\text{SiMeH}_2)_2$ and observed the redistribution to equilibrium mixtures containing the unsymmetrical complex $(\text{Me}_3\text{P})_4\text{Ru}(\text{SiMe}_2\text{H})(\text{SiH}_3)$ (eq 3.)

The most straightforward process to accomplish this scrambling would involve α -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 α - and β -elimination processes, thus suppression of the former and acceleration of the latter will favor catalytic silane coupling.

III. Synthesis and Reactivity of New Classes of Ruthenium Silyl Complexes.

Ruthenium complexes containing two or more silicon ligands are unquestionably key intermediates in the catalytic reactions described above. Therefore, as part of an effort to better understand the chemistry of this type of species we have prepared examples of new classes of ruthenium silyl complexes including: $\text{P}_4\text{Ru}(\text{H})(\text{SiR}_3)$, $\text{P}_4\text{Ru}(\text{SiR}_3)_2$, $\text{P}_3\text{Ru}(\text{H})_3(\text{SiR}_3)$, $\text{P}_3\text{Ru}(\text{H})_2(\text{SiR}_3)_2$, $\text{P}_3\text{Ru}(\text{H})(\text{SiR}_3)_3$. Complexes of with these stoichiometries are involved in the catalytic coupling of $\text{H}-\text{SiMe}_3$, therefore it is not surprising that the isolation of the complete series for SiMe_3 has not proven possible. Specifically, bis(silyl) complexes of the more hindered SiMe_3 groups could not be isolated, but the analogs have been prepared for relatively small silyl groups such as SiH_3 and SiMeH_2 . Finally, the unprecedented tris(silyl) complex $(\text{Me}_3\text{P})_3\text{Ru}(\text{SiH}_3)_3(\text{H})$ has been isolated in good yield from the photochemical reaction of $(\text{Me}_3\text{P})_4\text{Ru}(\text{H})_2$ with SiH_4 . This seven-coordinate complex is stereochemically non-rigid in solution at

room temperature, and variable temperature NMR studies suggest a non-symmetrical ground state structure, possibly containing a non-classical η^2 -silane ligand.

IV. Acceleration of Silane Dehydrocoupling in the Presence of Hydrogen Acceptors.

It was mentioned in Section II above that carbosilane formation is inhibited by the hydrogen produced, and that our mechanistic studies indicate that loss of H_2 from the metal following β -hydrogen elimination appears to be a key step limiting the rate of dehydrocoupling. In a very important breakthrough, we have recently determined that addition of neohexene (*t*-Butyl ethylene) as a hydrogen acceptor leads to rapid catalytic silane coupling at 80 °C, more than 70 °C below the temperature required in the absence of olefin (eq 4.) Neohexane (*t*-Butyl ethane), formed by hydrogenation of the olefin, is the only product formed in addition to the carbosilanes. Remarkably, hydrosilylation of the olefin does *not* successfully compete with olefin hydrogenation.

This discovery has several very significant implications. First of all, by coupling the silane *dehydrogenation* with olefin *hydrogenation*, H_2 is irreversibly removed from the reaction. This effectively drives the condensation equilibrium to completion, and should permit the formation of higher molecular weight carbosilanes without the necessity of removing hydrogen from the reaction. Secondly, the condensation can now be run at a much lower temperature, thus competing side reactions will be minimized and that the catalyst should survive for a much larger number of turnovers.

Future studies

Our first priority over the next year will be to explore and develop the silane coupling in the presence of hydrogen acceptors. The kinetics of trimethylsilane condensation using *t*-butyl ethylene as an acceptor will be examined, and the rate law determined. The stepwise or chain nature of the polymerization will be more accurately determined by following the average degree of polymerization as a function of percent conversion of monomer. The use of simpler olefins as hydrogen acceptors will also be explored. *t*-Butyl ethylene was originally chosen because it is too bulky to bind tightly to the metal center, and because there are no allylic hydrogens

which can be abstracted. Nonetheless, smaller olefins such as ethylene, propylene, etc. will be examined.

The milder catalytic conditions made possible using the hydrogen acceptor also mandates a re-examination of the coupling of silanes such as Me_2SiH_2 , PhMe_2SiH , and Me_2ClSiH , which undergo extensive redistribution at 150 °C.

The mechanism of the redistribution process itself will be probed using a variety of techniques, including a kinetics study of the exchange shown in eq 3, and the role of phosphine dissociate in the redistribution. In addition, the condensation of mixtures of $(^{13}\text{CH}_3)_3\text{Si-H}$ and $(^{12}\text{CH}_3)_3\text{Si-H}$ will be studied. In the latter, examination by ^{29}Si NMR of unconverted starting material for singly- and doubly-labeled silanes will indicate whether redistribution occurs competitively with coupling.

It may also prove feasible to use the redistribution reaction to adjust the Si/C ratio in the final carbosilanes. For example, coupling of $\text{Me}_3\text{Si-H}$ yields a carbosilane with a Si/C ratio of 3:1. Redistribution with SiH_4 (during or after the condensation step) could lower the Si/C ratio, and produce additional Si-H sites for subsequent cross-linking reactions.

Characterization of the structural and chemical properties of new ruthenium silyl complexes will also continue. In addition to standard single crystal X-ray diffraction studies, we have established a collaboration with Bob Bau at the University of Southern California and Tom Koetzle at Brookhaven National Laboratory, with the intent of determining the structures of the hydride complexes by neutron diffraction. Large crystals of $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiMe}_3)$ have already been grown for this purpose. The chemical reactivity of the new classes of complexes is also extremely relevant to the catalytic mechanism and will be studied in depth; In particular, the stereochemistry, rates, and activation parameters for ligand substitution bear directly on the catalytic process.

Other potential new catalysts which will be explored include carbonyl analogs such as *mer*- $(\text{Me}_3\text{P})_3(\text{CO})\text{Ru}(\text{H})(\text{SiMe}_3)$ and complexes of chelating and tripod ligands such as $(\text{tripod})\text{Ru}(\text{H})_3(\text{SiMe}_3)$ (e.g., tripod = *t*- $\text{BuSi}(\text{CH}_2\text{PMe}_2)_3$).

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