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Catalytic Synthesis of Silicon Carbide Preceramic Polymers:
Polycarbosilanes

Final Technical Report

for Period March 1, 1991 - August 31, 1996

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TECHNICAL REPORT

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Project Title

"Catalytic Synthesis of Silicon Carbide Preceramic Polymers:
Polycarbosilanes"

Abstract

This effort has focused on the development of new systems for the catalytic formation of organosilicon monomers and polymers. Several new classes of ruthenium phosphine complexes containing one, two, or three silicon ligands have been prepared, and which exhibit unique catalytic reactivity for (1) the dehydrogenative coupling of tertiary alkyl silanes to polycarbosilanes, (2) dehydrogenative coupling of secondary and primary alkyl and aryl silanes to polysilanes, and (3) the dehydrogenative heterocoupling of silanes with substituted arenes to yield aryl silanes. In addition, germanium analogs of the ruthenium silyl complexes have been found to be effective catalysts for the unprecedented demethanative coupling of alkyl germanes to high molecular weight polygermanes. For each of these new reactions, key mechanistic features of the catalytic processes have been elucidated, and the complexes have been extensively studied in terms of relevant stoichiometric reactivity and structural features.

Catalytic Synthesis of Silicon Carbide Preceramic Polymers: Polycarbosilanes

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I. New Catalytic Reactions of Silicon and Germanium Compounds

A. Dehydrogenative Coupling of Trialkylsilanes to Carbosilanes

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 H-SiMe_3 at a very slow rate (<1 turnover per day at 150°C). However, this reaction is of fundamental interest, as it involves the catalytic activation and functionalization of an aliphatic C-H group. In addition, previous routes to polycarbosilanes involve harsh conditions and are rather unselective.

Significantly, a new class of trimethylphosphine ruthenium complexes was prepared that exhibit appreciably greater activity (>2 turnovers per hour). The seven-coordinate trihydride silyl complexes, $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiR}_3)$, are extremely stable, and have been fully characterized. The oligomeric carbosilanes produced using this catalyst are liquids at room temperature and contain up to ca. 5 silicon atoms.

linear and branched chains

B. Transfer Dehydrogenative Coupling of Trialkylsilanes in the Presence of Olefins

Preliminary studies of the mechanism of dehydrocoupling suggested that the principal turnover controlling process is *not* removal of two hydrogen atoms from the alkyl silane to the ruthenium center, but rather subsequent elimination of H_2 from the metal. In an important advance it was found that addition of a hydrogen acceptor such as *t*-butyl ethylene (3,3-dimethyl-1-butene) leads to an increase in the rate of dehydrocoupling of $\text{Me}_3\text{Si-H}$ at temperatures as low as 80°C . In addition

to the lower reaction temperatures and greater rate, this process leads to appreciably larger oligomers, with $M_n = 700\text{-}800$ dalton and average degree of polymerization of ca. 10. Remarkably, the dehydrocoupling catalyst, $(\text{Me}_3\text{P})_3\text{RuH}_3(\text{SiMe}_3)$, does not competitively catalyze the hydrosilylation of *t*-butyl ethylene (<1%).

Although ethylene coordinates too strongly to act as a hydrogen acceptor in this system, slightly larger olefins do show activity. However, reaction selectivity is reduced compared with *t*-butyl ethylene. Thus, *cis* and *trans* 2-pentene yield 90% carbosilanes and 10% olefin hydrosilylation products, and 1-hexene yields a carbosilanes/hydrosilylation ratio of 4:6. On the other hand, dehydrocoupling in the presence of cyclohexene yields carbosilanes with no hydrosilylation products, but disproportionation to benzene and cyclohexane is observed as a side reaction.

Two other systems have been discovered that exhibit activity for catalytic transfer dehydrogenation. The new class of compounds $(\eta^6\text{-arene})\text{Ru}(\text{H})_2(\text{SiR}_3)_2$ and the previously known compounds $\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiR}_3)_2$ also catalyze the transfer dehydrocoupling of tertiary silanes using *t*-butylethylene as the hydrogen acceptor. In particular, the rather hindered silane $\text{Et}_3\text{Si-H}$ is coupled to the carbosilane dimer $\text{HSiEt}_2\text{CHMeSiEt}_3$ in reasonable yields. (eq 3)

C Polysilanes from Dialkylsilanes by Transfer Dehydrocoupling

In contrast to the reactions of tertiary silanes, secondary silanes, R_2SiH_2 , undergo transfer dehydrocoupling to produce polysilanes, $(\text{R}_2\text{Si})_x$. These silicon-silicon bonded polymers have been extensively studied for

their unusual electronic and optical properties. In the present case, coupling of Me_2SiH_2 in the presence of *t*-butyl ethylene and ruthenium phosphine catalysts gives a 75% yield of non-volatile polysilanes with $M_n = 892$ ($M_w/M_n = 1.6$), roughly corresponding to a formula " $(\text{Me}_2\text{Si})_{15}$ ". Interestingly, this appears to be the first system which couples secondary silanes beyond the dimer and tetramer stages.

The ^1H and ^{29}Si NMR suggest that significant redistribution of the Si-Si backbone has occurred, leading to a highly branched structure containing many $\text{Si}(\text{Si})_3(\text{Me})$ centers. This was confirmed by digesting the polymer with Br_2 , which yields large amounts of both Me_3SiBr and MeSiBr_3 .

D. Polygermanes from Trialkylgermanes by Demethanative Coupling

In very recent results we have observed that the bis(germyl complex) $\text{Ru}(\text{PMe}_3)_4(\text{GeMe}_3)_2$ is an effective catalyst for the preparation of high molecular weight polygermanes from trimethylgermane in high yields (80-90%). The coupling of the tertiary germane, HGeMe_3 , proceeds with loss of CH_4 and concurrent formation of Ge-Ge bonds, and appears to be the first instance of a catalytic *demethanative* coupling process. Absolute molecular weights (M_w) of the polygermanes have been determined by SEC/viscometry to range between ca. $10^4 - 10^5$. The polymers are highly branched, as indicated by intrinsic viscosity and hydrodynamic volume measurements, as well as by ^1H NMR and solubility properties. Alternatively, the ruthenium dimethyl complex, $(\text{PMe}_3)_4\text{RuMe}_2$ can be used directly as a precatalyst.

E. Transfer Dehydrocoupling of Alkylsilanes and Arenes to form Arylsilanes.

The concept of transfer dehydrocoupling, applied successfully to carbosilanes as described above, has also been used in the cross-coupling of silanes and arenes to aryl silanes. Thus, treatment of arenes, C_6H_5X ($X = CH_3, H, Cl, F, CF_3$) with Et_3SiH in the presence of *t*-butyl ethylene and either $(\eta^6\text{-arene})Ru(H)_2(SiR_3)_2$ or $Cp^*Rh(H)_2(SiR_3)_2$ catalysts leads to the formation of $C_6H_4XSIR_3$ with concurrent hydrogenation of *t*-butyl ethylene to *t*-butyl ethane. A 2:1 (statistical) mixture of meta- and para-isomers is observed in all cases. Activation of C-H bonds ortho- to substituents on the arene is apparently precluded by steric hindrance. Furthermore, the relative reactivity of the arene correlates well with substituent effects: arenes with electron-withdrawing groups are more reactive.

II. Synthesis and Structure of New Ruthenium Silyl Complexes as Catalysts and Model Systems.

A. Ruthenium Phosphine Complexes

The majority of the active catalysts developed for this project are ruthenium complexes containing a range of trimethylphosphine, hydride and silicon ligands. Some of these complexes were prepared initially as catalysts. However, studies of the catalytic cycles implied the intermediacy of less stable ruthenium silyl complexes, specifically ruthenium complexes containing two or more silicon ligands. 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: $P_4Ru(H)(SiR_3)$, $P_4Ru(SiR_3)_2$, $P_3Ru(H)_3(SiR_3)$, $P_3Ru(H)_2(SiR_3)_2$, $P_3Ru(H)(SiR_3)_3$ using sterically less demanding silyl groups. The basic relations between the different classes of complexes are shown in Scheme 1. At least one example of each of the complexes shown below have now been isolated and fully characterized, including single crystal X-ray diffraction studies of each representative structural type.

The very stable seven-coordinate trihydride silyl complex, $(\text{PMe}_3)_3\text{Ru}(\text{H})_3(\text{SiMe}_3)$, was also characterized by a single crystal neutron diffraction study by Dr. Tom Koetzel at Brookhaven National Laboratory, and found to exhibit a classical, Ru(IV) structure consisting of a tetrahedral arrangement of the phosphine and silyl groups, with the hydrides capping each of the three P_2Si faces.

B. New Arene Silyl Complexes

$(\eta^6\text{-Arene})\text{Ru}(\text{H})_2(\text{SiMe}_3)_2$ (arene = C_6Me_6 , *p*-cymene, C_6H_6) complexes were prepared by the reaction of Me_3SiH and the corresponding $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ complex. An X-ray structure analysis of the C_6Me_6 derivative shows the complex adopts a four-legged piano-stool geometry with a transoid disposition of hydride and silyl groups. The absence of any close intramolecular $\text{Si}\cdots\text{H}$ or $\text{H}\cdots\text{H}$ bonding interactions supports the formulation of **1a** as a classical Ru(IV) complex.

III. Mechanistic Considerations

The mechanisms of the various catalytic reactions described in Section I above have been probed by a variety of techniques, and these diverse processes share a several common aspects. All appear to be initiated by addition of an Si-H (or Ge-H) bond to the metal center, a step which renders subsequent (and more difficult) bond activation steps

intramolecular in nature (scheme 2.) Secondly, the apparent ease of subsequent bond activations in metal silyl intermediates follows the order: $\alpha\text{-Si-H} > \beta\text{-SiC-H} \gg \alpha\text{-Si-C}$. In contrast, the trend in the analogous reactions of germanes is inverted: $\alpha\text{-Ge-H} > \alpha\text{-Ge-C} \gg \beta\text{-GeC-H}$. In addition, the rate of dehydrogenative reactions appear to be limited by the unfavorable equilibrium constant for loss of hydrogen. The concurrent removal of hydrogen with a hydrogen acceptor, therefore, appears to increase the thermodynamics for the desired reaction, effectively rendering the reverse reaction irreversible.

A. Activation and Functionalization of C-H bonds in Alkyl Silanes: β -Hydrogen Elimination from Metal Silyls.

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 $\text{Me}_3\text{Si-H}$. The products distributions and isotopic labeling studies clearly indicate that the only C-H bonds activated are (1) in silanes that also contain an Si-H bond, and (2) are adjacent to the silicon center. This strongly suggests the mode of C-H activation is by β -hydrogen elimination to the metal in a silyl complex formed by prior Si-H addition.

B. Activation and Functionalization of Si-C and Si-H Bonds: α -Alkyl and α -Hydrogen Eliminations from Metal Silyls.

Although the coupling of tertiary silanes by $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_3(\text{SiR}'_3)$ is dominated by the activation of C-H bonds adjacent

to silicon, a secondary process involving intermolecular redistribution of alkyl groups between silicon centers leads to an equilibrium distribution of chains. For example, condensation of a dimeric carbosilane initially leads to a single tetramer (path a), but trimer and monomer are also produced by redistribution after longer reaction times (path b).

This process complicates analysis of the study of the carbosilane formation, but is strong evidence that the α -elimination of alkyl from silicon to the metal is occurring. The redistribution would then be the result of well-established 1,3-alkyl migrations between the transient silylene intermediate ($\text{Ru}=\text{SiR}_2$) and an adjacent silyl ligand.

It is clear that α -elimination processes dominate over β -hydrogen elimination in the dehydrocoupling of secondary and primary silanes. In these instances carbosilane (Si-C bond) formation is not observed, but rather chain growth resulting from creation of Si-Si bonds occurs. This result, combined with the high degree of concurrent redistribution, strongly implicates a rapid α -elimination of Si-H bonds to the metal, and Si-Si bond formation by silyl to silylene migration.

Finally, perhaps the most convincing evidence for the efficacy of the α -alkyl elimination step is the remarkable facile demethanative coupling of tertiary germanes described in section I-D. No other process for cleaving Ge-C bonds would appear plausible. The reversal of the relative rates of α - and β - elimination processes between germanium and silicon is most likely the result of the weaker Ge-C bonds and the greater stability of the low valent $\text{M}=\text{ER}_2$ species in the case of germanium. In addition, the rapid rates and high molecular weights achieved for the demethanative coupling provides further evidence for the irreversibility of alkane loss, as opposed to hydrogen loss in the slower dehydrocoupling processes.

C. The Role of Olefins as Hydrogen Acceptors

We have seen that the addition of *t*-butylethylene and other olefins leads to a significant increase in the rate of dehydrocoupling processes. Remarkably, the dehydrocoupling catalyst, $(\text{Me}_3\text{P})_3\text{RuH}_3(\text{SiMe}_3)$, does not competitively catalyze the hydrosilylation of *t*-butylethylene. In the absence of olefin, $(\text{Me}_3\text{P})_3\text{RuH}_3(\text{SiMe}_3)$ is indefinitely stable and unreactive in neat $\text{Me}_3\text{Si-H}$ at 80 °C. The olefin, therefore, acts as more than merely a sponge for hydrogen produced by dehydrocoupling, and must actively remove H_2 from the ruthenium center to facilitate carbosilane formation.

Furthermore, the catalyst does not apparently react with excess *t*-butylethylene at lower temperatures. However, labeled catalyst undergoes a rapid regioselective H/D exchange with *t*-butylethylene at 25 °C (scheme 3.) indicating that the olefin does react with the metal as far as alkyl formation, but that addition of a second silane and irreversible alkane elimination requires substantially higher temperatures.

Scheme 3. Selective H/D exchange with prior to irreversible alkane loss.

IV. Publications based on DOE support

1. L. J. Procopio and D. H. Berry, "The Dehydrogenative Coupling of Trialkylsilanes Mediated by Ruthenium Phosphine Complexes: Catalytic Synthesis of Carbosilanes," *J. Am. Chem. Soc.* **1991**, *113*, 4039-4040.
2. 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.
3. L. J. Procopio, Ph.D. Thesis, 1991, University of Pennsylvania.
4. P. I. Djurovich, P. J. Carroll, and D. H. Berry, "Synthesis, Structure, and C-H Bond Activation Chemistry of $(\eta^6\text{-arene})\text{Ru}(\text{H})_2(\text{SiMe}_3)_2$ Complexes," *Organometallics* **1994**, *13*, 2551-2553.
5. P. I. Djurovich, A. Dolich, and D. H. Berry, "Transfer Dehydrogenative Coupling of Alkylsilanes Catalyzed by Ruthenium and Rhodium Complexes: A New Si-C Bond Forming Process," *J. Chem. Soc., Chem. Commun.* **1994**, 1897-1898.
6. D. H. Berry and P. I. Djurovich, "Method for Synthesizing Arylsilanes," U.S. U.S. Patent No. 5,508,460, April 16, 1996.
7. P. Hong, Ph.D. Thesis, **1995**, University of Pennsylvania.
8. J. A. Reichl, C. M. Popoff, L. A. Gallagher, E. E. Remsen and D. H. Berry "Ruthenium-Catalyzed Demethanative Coupling of HGeMe_3 : A High Yield Route to Polygermanes," *J. Am. Chem. Soc.* **1996**, *118*, 9430.