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Exploiting Catalytic Dehydrogenative Coupling in the Synthesis and Study of Polysilanes

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Summary: A reinvestigation of the catalytic activity of Wilkinson's catalyst, $(Ph_3P)_3RhCl$ (**1**), for the dehydrogenative coupling reactions of secondary silanes has pointed the way toward the synthesis of key oligosilane reagents for structure property correlation studies of polysilanes. Implications are discussed for understanding the mechanisms of coupling and redistribution reactions of silanes mediated by such late metal centres. Also described are attempts to derivatize Si-H bonds in the resulting oligosilanes, which is highly relevant to the development of improved methods for the post-polymerization functionalization of polysilanes containing Si-H bonds.

Keywords: catalysis; functionalization of polymers; oligomers; polysilanes, transition metal chemistry

Introduction

Polysilanes are receiving considerable attention for properties that may render them useful in a variety of electronic and photonic device applications. These properties are a function of σ–delocalization along the polysilicon chain, and may be correlated with *all-transoid*, or *anti*, conformations along the polymer backbone (Figure 1).[1] While the ability to tune polysilane conformations with precision and predictability will be essential for the advancement of this promising class of materials, achieving rigorous conformational control in the intrinsically flexible polysilane chains presents significant synthetic challenges. In developing methods to control and optimize conjugation in polysilanes it is desirable to assess the effects of varying steric constraints on conformational preferences at the Si–Si bonds of discrete oligomers. However, a dearth of general, straightforward routes to small molecules containing Si-Si bonds has limited our ability to prepare homologous series of oligosilanes with the requisite, systematic structural modifications.[2]

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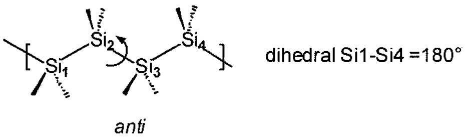


Figure 1. Polysilane conformation corresponding to σ-delocalization

Recently, we have focused on the synthesis of short oligosilanes with functional groups at the terminal silicons, which will allow us to incorporate these oligomers into a range of structural environments (Figure 2). Although 1,2-dichlorotetramethyldisilane, a byproduct of the direct synthesis route to dichlorodimethylsilane, is commercially available, few other such functionalized di- or oligosilanes, with reactive Si-X bonds are commercially available or easily accessible by synthetic means.[3] Wurtz reductive coupling of dichloromonosilanes (R_2SiCl_2) is not a viable route to α,ω-dichlorooligosilanes, since these reactive species are inevitably consumed to give longer chains or cyclic compounds.[2] Although there is precedent for the synthesis of 1,2-dihydrido-substituted disilanes through reductive coupling of $R_2Si(H)Cl$, these reactions are capricious and are frequently low yielding.[4]

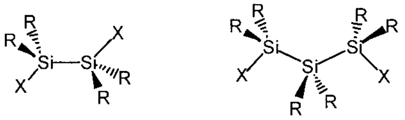
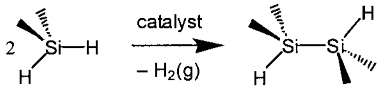


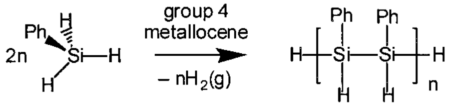
Figure 2. α,ω-Functionalized di- and trisilanes, where X = H, Cl, Br, OR', NR'$_2$.

Transition metal-catalyzed dehydrogenative coupling of hydrosilanes is a promising alternative to reductive coupling for the formation of Si-Si bonds (Eqn 1).[5] Since these catalysts are active principally for the coupling of primary (1°) or secondary (2°) silanes,[6] implicit in this method is the retention of reactive, terminal Si-H bonds in the catenated products.



(1)

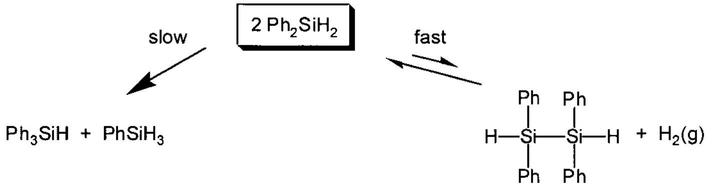
Most prominent among catalysts capable of dehydrogenative coupling of silanes are group 4 metallocene systems, which can produce relatively high MW polymers (degree of polymerization as high as 70-100 monomer units) from 1° aryl silanes (Eqn 2).[7] These early metal catalysts will give short oligomers from 2° silanes with aryl substituents, but decreased activities for these reactions, relative to those of the 1° silane substrates, necessitate prolonged reaction times and high temperatures.[3b] In addition, the established group 4 catalysts exhibit little or no activity for the coupling of dialkylsilanes.[8] Although many late transition metal complexes can effect the coupling of both aryl- and alkyl-substituted 1° and 2° silanes,[5] they have received less attention in this context, since they typically exhibit competing catalytic activities for both dehydrocoupling and substituent redistribution reactions of the silane substrates.[9] Notably, however, the coupling products resulting from late metal catalysis are almost invariably limited to short chains (2-5 silicons).[10] We therefore decided to examine this class of catalysts more closely for their potential utility in the production, on a synthetically useful scale, of Si-H functionalized oligosilane reagents.



(2)

Coupling Reactions of 2° Silanes Catalyzed by Wilkinson's Catalyst

We have reexamined the reactions of 2° silanes in the presence of Wilkinson's catalyst, $(Ph_3P)_3RhCl$, **1**,[11] to identify optimal conditions (e.g. substrate, catalyst concentrations) to preferentially obtain the desired oligomers over redistribution products. We established a selective, high-yield route to 1,1,2,2-tetraphenyldisilane, **2**, via catalytic dehydrocoupling of diphenylsilane (Ph_2SiH_2), and, in doing so, identified general conditions for the coupling of a range of 2° silanes with little or no redistribution.[12] Our experiments demonstrated an extreme sensitivity of the chemoselectivity of this system to the rate at which the product dihydrogen is removed from reaction mixtures. Thus, production of di- and trisilanes is contingent on efficient removal of $H_2(g)$ from the reaction mixture, and thus continuously shifting a rapid, monomer-favoured equilibrium toward the desired products.[12] Because the equilibrium lies heavily toward monosilane, and because the rates of both coupling and hydrogenolysis are (apparently) extremely high, the presence of *any* residual hydrogen limits the amount of disilane produced, and, for aryl silanes (*vide infra*), allows the (slower) redistribution of substituents at silicon to occur (Scheme 1). The catalyst system is so sensitive to the local H_2 concentration that even the use of solvents in which the hydrogen has some limited solubility slows the production of coupled product relative to redistribution. Thus our dehydrocoupling reaction conditions include the use of neat substrate.



Scheme 1.

Along with mechanistic insights arising from this work (*vide infra*), we discovered that **1** has reasonably high activity for the dehydrogenative coupling of dialkylsilanes (R_2SiH_2, R = Et, *n*-Hex) to di- and trisilanes. Although the coupling turnover frequencies are slightly lower for these substrates than for Ph_2SiH_2, we observe *no* redistribution products in the reaction mixtures. This is in agreement with our experiments using $MePhSiH_2$ as substrate, in which we see facile transfer of the Si-Ph group (yielding redistribution products Ph_2MeSiH and $MeSiH_3$) relative to the Si-Me group (giving $PhMe_2SiH$ and $PhSiH_3$). It is also consistent with other reports of the relative ease of migration of groups at silicon, in the presence of transition metals.[10a,b,13] This Rh(I) catalyst system will allow the preparation of oligosilanes with a broad range of substituents, under mild conditions and at low catalyst concentrations.

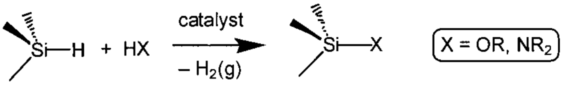
Mechanistic Implications

The mechanisms of the coupling and redistribution reactions of silanes at late metal centres remain a subject of some debate.[14] Our work clearly establishes distinct rate regimes for the two reaction types. That redistribution does *not* compete with coupling at a Rh(I) catalyst, under conditions allowing kinetic control (efficient $H_2(g)$ removal), was previously unrecognized, and should now provide insight in searching for likely catalytic intermediates (or for relevant, turnover-limiting steps) in these reactions. Our enhanced understanding of dehydrocoupling and redistribution processes has positioned us to further probe mechanisms for these reactions occurring at **1**. We are now examining, through catalyst modification, such issues as the role/fate of the chloride ligand in these reactions, the possibility of mononuclear versus dinuclear active species, and the precise nature of the Si-Rh interaction in the active species. This work will be reported in future publications.

Derivatizing Si-H Bonds in Oligosilanes

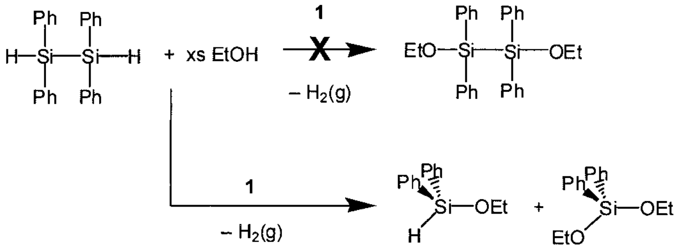
Another area of focus for us is the derivatization of the Si-H bonds in our coupled oligosilanes, to yield more substitutionally labile Si-X bonds (where X = Cl, Br, OR, NR_2) via halogenation, alcoholysis, or aminolysis reactions. This expands the range of methods available to us for the incorporation of these catenated units into conformationally constrained macrostructures. These studies are also helping us to refine techniques for the post-polymerization modification of higher MW polysilanes containing Si-H bonds.[15]

We are particularly interested in accessing Si-OR or Si-NR_2 oligosilane derivatives, since, while these functional groups are readily substituted by nucleophiles such as Grignards or alkyllithiums, they should exhibit milder reactivity and decreased hydrolytic sensitivity relative to analogous halide compounds. Catalytic dehydrogenative heterocoupling of monosilanes with alcohols or amines is known to be catalyzed by **1** and other late metals (Eqn 3),[5b] although we know of no examples of alcoholysis or aminolysis of Si-H bonds in compounds containing Si-Si bonds.



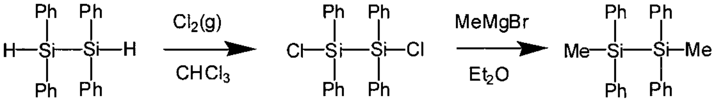
(3)

Nevertheless, based on this well established catalytic heterodehydrogenation chemistry, we envisaged a simple one-pot procedure for the preparation of 1,2-bis(ethoxy)tetraphenyldisilane, whereby, upon completion of the coupling reaction producing 1,1,2,2-tetraphenyldisilane, we could simply add ethanol to the catalytic reaction mixture. Conversion of Si-H to Si-OEt bonds should then proceed rapidly in the presence of residual Rh catalyst. We first tested this idea by adding ethanol to 1,1,2,2-tetraphenyldisilane, in the presence of **1**. However, instead of the desired bis(alkoxy)disilane, we obtained mixtures of two monosilanes: $Ph_2Si(OEt)H$ and $Ph_2Si(OEt)_2$ (Scheme 2), in varying ratios depending on the reaction time and the extent to which ethanol was added in excess.[16] Clearly, once $H_2(g)$ is formed from the heterodehydrocoupling reaction, a monosilane-disilane equilibrium is once again accessible, in the presence of Rh catalyst. Avoiding the competition of alcoholysis and catalytic Si-Si bond cleavage is a significant challenge, which we continue to address through the screening of other classes of alcoholysis catalysts,[17] including Lewis acids.[18]



Scheme 2.

In the meantime, we have begun to use established methods for Si-H bond halogenation on our di and trisilanes. For example, we have chlorinated 1,1,2,2-tetraphenyldisilane to give 1,2-dichlorotetraphenyldisilane using chlorine gas,[3a] as confirmed by characterization of its 1,2-dimethyl derivative, obtained from the *in situ* addition of methyl Grignard (Eqn 4).[19]



(4)

Conclusion

Our discoveries so far have pointed us toward understanding the challenges and conditions for preparing reactive oligosilane fragments via catalytic dehydrogenative coupling. They also indicate great potential for selectivity, in dehydrocoupling reactions catalyzed by **1**, through a careful balance of catalyst concentration and the method of removal of $H_2(g)$. These studies are laying the groundwork for us to develop general routes to new classes of polysilanes with enhanced conformational preferences.

[1] R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359.

[2] For leading references on the synthesis of small molecules containing Si-Si bonds, see M. A. Brook, "*Silicon in Organic, Organometallic, and Polymer Chemistry*" John Wiley & Sons, Inc., New York 2000, p.344.

[3] Examples of the preparation of *functionalized* oligosilanes include: (a) K. H. Pannell, J. M. Rozell, C. Hernandez, *J. Am. Chem. Soc.* **1989**, *111*, 4482; (b) J. Y. Corey, D. M. Kraichely, J. L. Huhmann, J. Braddock-Wilking, A. Lindeberg, *Organometallics* **1995**, *14*, 2704; (c) H. Sakurai, Y. Eriyama, Y. Kamiyama, Y. Nakadaira, *J. Organomet. Chem* **1984**, *264*, 229; (d) J. Zech, H. Schmidbaur, *Chem. Ber.* **1990**, *123*, 2087; (e) M. Söldner, A. Schier, H. Schmidbaur, *J. Organomet. Chem.* **1996**, *521*, 295

[4] See for example: H. J. S. Winkler, H. Gilman, *J. Org. Chem.* **1961**, *26*, 1265.

[5] (a) T. D. Tilley, *Comments Inorg. Chem.* **1990**, *10*, 37; (b) J. Y. Corey, in: "*Dehydrogenative Coupling Reactions of Hydrosilanes*", G. L. Larson, Ed., JAI Press Inc., 1991. Vol. 1, 327; (c) F. Gauvin, J. F. Harrod, H. G. Woo, *Adv. Organomet. Chem.* **1998**, *42*, 363; (d) J. A. Reichl, D. H. Berry, *Adv. Organomet. Chem.* **1999**, *43*, 197.

[6] An exception is the reported activity of a Pt catalyst in the coupling of 3° silanes to hexa-organo-substituted disilanes. M. Tanaka, T. Kobayashi, T. Hayashi, T. Sakakura, *Appl. Organomet. Chem.* **1988**, *2*, 91.

[7] (a) T. Imori, T. D. Tilley, *Polyhedron* **1994**, *13*, 2231; (b) V. K. Dioumaev, J. F. Harrod, *J. Organomet. Chem.* **1996**, *521*, 133.

[8] The activity of a titanocene-based catalyst for the coupling of $(n\text{-Pr})_2SiH_2$ has been reported, but requires the presence of cyclic olefins, which are hydrogenated in tandem with the coupling process. Complex product mixtures result, which include hydrosilation products. J. Y. Corey, X.-H. Zhu, *Organometallics* **1992**, *11*, 672.

[9] M. D. Curtis, P. S. Epstein, *Adv. Organomet. Chem.* **1981**, *19*, 213.

[10] See for example (a) M. D. Fryzuk, L. Rosenberg, S. J. Rettig, *Inorg. Chim. Acta* **1994**, *222*, 345. There are very few reports of late metal activities for the production of longer (DP>6) silicon chains. These include: (b) B. P. S. Chauhan, T. Shimizu, M. Tanaka, *Chem. Lett.* **1997**, 785; (c) F.-G. Fontaine, T. Kadkhodazadeh, D. Zargarian, *Chem. Commun.* **1998**, 1253.

[11] The reactivity of **1** and other Rh(I) phosphine complexes for dehydrocoupling of silanes, albeit invariably accompanied by redistribution reactions, was already established. (a) I. Ojima, S.-I. Inaba, T. Kogure, *J. Organomet. Chem.* **1973**, *55*, C7; (b) M. F. Lappert, R. K. Maskell, *J. Organomet. Chem.* **1984**, *264*, 217; (c) J. Y. Corey, L. S. Chang, E. R. Corey, *Organometallics* **1987**, *6*, 1595; (d) K. A. Brown-Wensley, *Organometallics* **1987**, *6*, 1590; (e) L. Rosenberg, M. D. Fryzuk, S. J. Rettig, *Organometallics* **1999**, *18*, 958.

[12] L. Rosenberg, C. W. Davis, J. Yao, *J. Am. Chem. Soc.* **2001**, *123*, 5120.

[13] P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 10462.

[14] The debate centres around whether a metal silylene ("M=Si") intermediate is involved in (or required for) Si-Si bond formation, or whether oxidative addition and reductive elimination steps involving only M-Si single bonds can be responsible for Si-Si coupling. See Reference 5.

[15] Our preliminary attempts, using methods described in references b-d below, to halogenate the Si-H bonds in poly(phenylsilane), $H\text{-}[SiPh(H)]_n\text{-}H$, have resulted either in low or incomplete substitution (Reference 15b) or in significant polymer degradation.(References 15c,d). (a) D. J. Harrison, L. Rosenberg, unpublished results; (b) J. P. Banovetz, Y.-L. Hsiao, R. M. Waymouth, *J. Am. Chem. Soc.* **1993**, *115*, 2540; (c) Reference 3a; (d) D. M. Friesen, R. McDonald, L. Rosenberg, *Can. J. Chem.* **1999**, *77*, 1931.

[16] J. Yao, L. Rosenberg, unpublished results.

[17] E. Lukevics, M. Dzintara, *J. Organomet. Chem.* **1985**, *295*, 265.

[18] J. M. Blackwell, K. L. Foster, V. H. Beck, W. E. Piers, *J. Org. Chem.* **1999**, *64*, 4887.

[19] (a) D. J. Harrison, L. Rosenberg, unpublished results. (b) An alternative technique for this halogenation involves the use of 4 equivalents of $CuCl_2$ in the presence of catalytic amounts of CuI; A. Kunai, T. Kawakami, A. Toyoda, M. Ishikawa, *Organometallics* **1992**, *11*, 2708.