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Titanium-Catalyzed Dehydrocoupling of Silanes: Direct Conversion of Primary Monosilanes to Titanium(0) Oligosilane Complexes with Agostic α-Si-H···Ti Interactions

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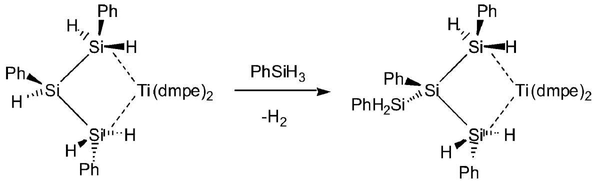
Polysilane high polymers have been attracting increasing interest owing to their potential applications as photoresists, photoinitiators, thermochromic materials, and precursors to silicon carbide.[1] In 1985, Harrod and co-workers discovered that group 4 metallocenes such as Cp_2TiMe_2 could catalyze the dehydrogenative coupling of primary organosilanes to linear poly(hydrosilanes), $H-(SiHR)_n-H$ with ∼140 SiHR units.[2] Since then, this reaction has been intensively studied, and many new catalysts have been discovered. The Si−Si bond-forming step in these dehydrocoupling reactions is thought to involve σ-bond metathesis reactions of metal silyl complexes with an entering hydrosilane.[2,3] Several group 4 silyl complexes have been isolated that serve as models of the intermediates responsible for the catalysis.[2,4] Silane dehydrocoupling reactions have found additional use in the derivatization of silicon surfaces.[5]

In the course of investigating the reaction chemistry of the 14-electron titanium(II) alkyl $TiMe_2(dmpe)_2$,[6] we found that it is a catalyst for the dehydrogenative oligomerization of primary arylsilanes. More importantly, we have been able to isolate several of the titanium-containing species that are formed in this reaction; these species document consecutive steps in the dehydrocoupling reaction and thereby provide intriguing insights into the inner workings of this process. Specifically, we find that treatment of solutions of $TiMe_2(dmpe)_2$ with 4 equiv of $PhSiH_3$ −20 °C for 4 h quantitatively yields a diamagnetic species of stoichiometry $Ti(Si_3H_5Ph_3)(dmpe)_2$ (**1**), which can be isolated as a purple solid.[7] The conversion of $TiMe_2(dmpe)_2$ to the trisilane complex **1** is accompanied by the formation of ∼1 equiv each of methane and $PhSiMeH_2$.[8] When solutions of **1** are incubated with $PhSiH_3$ in Et_2O at −20 °C for several weeks, a new compound of stoichiometry $Ti(Si_4H_6Ph_4)(dmpe)_2$ (**2**) is generated nearly quantitatively.[9] This tetrasilane species can also be isolated as a pure material.



1 **2**

The NMR spectra of **1** and **2** show that these two molecules are closely related. Both complexes give $^{31}P\{^1H\}$ NMR spectra that correspond to ABCD spin systems; the chemical shifts and coupling constants for **1** and **2** are very similar, though not identical. In both compounds, the presence of only one large J_{PP} coupling constant (∼50 Hz) suggests that the two dmpe ligands are arranged in a cis-octahedral fashion. In both compounds, there are eight PMe environments, a result which confirms that both compounds lack symmetry elements.

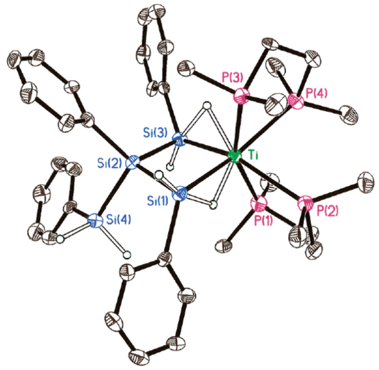


Figure 1. Molecular structure of $Ti(Si_4H_6Ph_4)(dmpe)_2$, **2**. Thermal ellipsoids are represented by the 30% probability surfaces. Selected bond distances (Å) and angles (deg): Ti−Si(1) 2.539(2), Ti−Si(3) 2.519(2), Ti−P(1) 2.529(2), Ti−P(2) 2.652(2), Ti−P(3) 2.511(2), Ti−P(4) 2.657(2), Ti−H(1A) 1.67(2), Ti−H(3A) 1.68(2), Si(1)−Si(2) 2.385(2), Si(2)−Si(3) 2.369(2), Si(2)−Si(4) 2.326(2), Si(1)−H(1A) 1.83(2), Si(1)−H(1B) 1.54(3), Si(3)−H(3A) 1.83(2), Si(3)−H(3B) 1.54(3), Si(4)−H(4A) 1.46(4), Si(4)−H(4B) 1.45(3), Si(3)−Ti−Si(1) 97.95(5), Si(2)−Si(1)−Ti 76.67(6), Si(3)−Si(2)−Si(1) 106.75(7), Si(2)−Si(3)−Ti 77.33(6).

The NMR spectra of **1** are consistent with a $PhSiH_2-SiPhH-SiPhH_2$ structure for the trisilane ligand, in which one hydrogen atom on each terminal silicon atom is involved in an agostic interaction with the titanium center.[10] The ^1H NMR spectrum of **2** is consistent with the presence of a tetrasilane ligand of stoichiometry $PhSi(SiH_2Ph)_3$, with a structure similar to that of **1** except that the hydrogen atom on the central silicon center is replaced with a SiH_2Ph group.

These conclusions have been verified by a single-crystal X-ray diffraction study of the tetrasilane complex **2** (Figure 1).[11] The geometry about the titanium center is a distorted octahedron in which the two dmpe groups and a tetrasilane molecule act as chelating bidentate ligands. The tetrasilane is branched, $PhSi(SiPhH_2)_3$, and two of the $SiPhH_2$ groups are involved in agostic interactions with the titanium center. The Ti−Si(1) and Ti−Si(3) distances of 2.529(2) Å are shorter than those found in other titanium silyl (2.583(2)−2.765(8) Å)[4,12] or titanium silane (2.597(2)−2.891(2) Å)[4,13] complexes.[14] The Ti···Si(2) distance of 3.056(2) Å is probably too long for there to be a significant bonding interaction between these two atoms. Instead, the principal interaction is with the Si−H groups: the Ti−H(1A) and Ti−H(3A) distances, respectively 1.67(2) and 1.68(2) Å, are within the 1.45−1.96 Å range reported for terminal Ti−H distances[15] and the 1.59−1.82 Å range found for Ti···H−Si distances[4,13] in other complexes.

The geometries around Si(1) and Si(3) are distorted trigonal bipyramids in which the two hydrogen atoms occupy the axial sites. The H−Si(1)−H angle is 167.9(15)°, and the H−Si(3)−H angle is 163.8(16)°. For both Si(1) and Si(3), the Si−H distance to the

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bridging hydrogen, 1.83(2) Å, is considerably longer than the Si−H distance to the terminal hydrogen, 1.54(3) Å. The Si(4)−H distances, 1.46(4) and 1.45(3) Å, are typical of Si−H distances in hydrosilanes.[16] The 0.3 Å lengthening of the Si−H distances to the bridging hydrogen atoms reflects the agostic interactions with the Ti center.[16] The 0.1 Å lengthening of the Si−H distances to the terminal hydrogen atoms on Si(1) and Si(3) can be ascribed to the strong trans influence of their respective agostic hydrides, or to the higher effective coordination number of these silicon atoms.

The axial phosphorus atoms are bent away from the tetrasilane group to give a P(1)−Ti−P(3) angle of 157.53(6)°. The average Ti−P(axial) distance, 2.520(2) Å, and the average Ti−P(equatorial) distance, 2.654(2) Å, fall near the extremes of the 2.51−2.66 Å range observed for Ti−P distances in other six-coordinate complexes.[17] The longer Ti−P(equatorial) distances may be due to the trans influence of the tetrasilane group.

The NMR spectra of **2** afford additional information about the bonding between titanium and the tetrasilane molecule. The $^{1}J_{\mathrm{SiH}}$ coupling constants for the non-agostic $\mathrm{SiH_2Ph}$ group, 186 and 189 Hz, are consistent with those found in free silanes.[16] The $^{1}J_{\mathrm{SiH}}$ coupling constants for Si(1)−H(1B) and Si(3)−H(3B) are 127 and 133 Hz; these smaller $^{1}J_{\mathrm{SiH}}$ coupling constants are consistent with the 0.1 Å elongations of these bonds as described above. In contrast, the $^{1}J_{\mathrm{SiH}}$ coupling constants for Si(1)−H(1A) and Si(3)−H(3A) are less than 40 Hz; $^{1}J_{\mathrm{SiH}}$ coupling constants reported for M⋯H−Si complexes engaged in agostic interactions fall between 20 and 100 Hz.[16] The geminal $J_{\mathrm{H(A)H(B)}}$ coupling constants (13.7 Hz) are also in agreement with the structural data; these $^{2}J_{\mathrm{HH}}$ values are unusually large because the H(A)−Si−H(B) angles are nearly 180°.

The present results show that $\mathrm{TiMe_2(dmpe)_2}$ reacts with $\mathrm{PhSiH_3}$ to afford two titanium(0) products bearing coordinated oligosilane ligands; the latter are generated by dehydrogenative coupling promoted by the titanium center. An interesting mechanistic finding in this system is that the catalysis converts a linear trisilane to a *branched* tetrasilane. The titanium-containing products, $\mathrm{Ti(Si_3H_5Ph_3)(dmpe)_2}$ and $\mathrm{Ti(Si_4H_6Ph_4)(dmpe)_2}$, are the first molecules in which oligosilanes serve as chelating ligands and are rare examples of compounds in which a metal center is involved in two agostic M⋯H−Si interactions.[16−19]

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Supporting Information Available: Details of the characterization of **1** and **2**; X-ray crystallographic files for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Presumably $\mathrm{H_2}$ is also formed, but quantification was hindered because its chemical shift is the same as the Si−H resonance for $\mathrm{PhMeSiH_2}$.

(9) No $\mathrm{SiH_4}$ is formed in these reactions, but this product has been seen in some other systems.[4i] See also: Wu, F.; Jordan, R. F. *Organometallics* **2005**, *24*, 2688−2697.

(10) The ^{1}H NMR spectrum of **1** contains five equal-intensity Si−H resonances with complex line shapes. Two (at δ 4.50 and 4.75), due to hydrogen atoms that bridge between Si and Ti, are strongly coupled to all four phosphorus nuclei. The δ 4.50 resonance is coupled to a Si−H resonance at δ 6.25, and the δ 4.75 resonance is coupled to a Si−H resonance at δ 6.35. The H−H coupling constants of 14.5 Hz between these sites are consistent with gem H−Si−H couplings. The fifth Si−H resonance at δ 3.27 is a broad singlet and is assigned to the single Si−H group on the central silicon atom of the trisilane unit.

(11) Crystal data for $\mathrm{C_{36}H_{58}P_4Si_4Ti}$ (T = 198 K): monoclinic, space group $P2_1/n$, a = 11.8357(3) Å, b = 18.8226(5) Å, c = 18.9559(6) Å, β = 95.102(1)°, V = 4206.2(2) Å^3, Z = 4, wR_2 = 0.0779 for 433 variables and 5847 unique data.

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