

# Catalytic Hydrosilylation of Terminal Alkynes Promoted by Organoactinides

Aswini K. Dash, Ji Quan Wang, and Moris S. Eisen\*

Department of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Haifa 32000, Israel

Received August 13, 1999

Organoactinide complexes of the type  $\text{Cp}^*_2\text{AnMe}_2$  (An = Th, U) have been found to be efficient catalysts for the hydrosilylation of terminal alkynes. The chemoselectivity and regioselectivity of the reactions depend strongly on the nature of the catalyst, the nature of the alkyne, the silane substituents, the ratio between the silane and alkyne, the solvent, and the reaction temperature. The hydrosilylation reaction of the terminal alkynes with  $\text{PhSiH}_3$  at room temperature produces the *trans*-vinylsilane as the major product along with the silylalkyne and the corresponding alkene. At higher temperatures (50–80 °C), besides the products obtained at room temperature, the *cis*-vinylsilane and the double-hydrosilylated alkene, in which the two silicon moieties are connected at the same carbon atom, are obtained. The catalytic hydrosilylation of  $(\text{TMS})\text{C}\equiv\text{CH}$  and  $\text{PhSiH}_3$  with  $\text{Cp}^*_2\text{ThMe}_2$  was found to proceed only at higher temperatures, although no *cis*-vinylsilane or double-hydrosilylated products were observed. When the catalytic hydrosilylation reaction is carried out using a 1:2 ratio of  $\text{PrC}\equiv\text{CH}$  to  $\text{PhSiH}_3$  with  $\text{Cp}^*_2\text{ThMe}_2$ , the yield of the double-hydrosilylated product is increased from 6 to 26%. When the same reaction is conducted using a 2:1 ratio between  $\text{PrC}\equiv\text{CH}$  and  $\text{PhSiH}_3$ , the alkene was found to be the major product with the concomitant formation of the tertiary silane  $\text{PrCH}\equiv\text{CHSi}(\text{HPh})(\text{C}\equiv\text{CPr})$ . For bulky silanes, nonselective alkyne oligomerization and trace amounts of the hydrosilylation products were produced. Mechanistic studies on the hydrosilylation of  $\text{PrC}\equiv\text{CH}$  and  $\text{PhSiH}_3$  in the presence of  $\text{Cp}^*_2\text{ThMe}_2$  show that the first step in the catalytic cycle is the insertion of an alkyne into a thorium–hydride bond. A delicate balance between alkyne protonolysis and  $\sigma$ -bond metathesis by the silane determines the ratio among the vinylsilanes, the double-hydrosilylated product, the silylalkyne, and the alkene. The kinetic rate law is first order in organoactinide, silane, and alkyne, with  $\Delta H^\ddagger = 6.3(3) \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -51.1(5) \text{ eu}$ . The turnover-limiting step is the release of the hydrosilylated product from the alkenyl–actinide complex. The key organoactinide intermediates for the *cis*-vinylsilane and the double-hydrosilylation products are the  $\text{Cp}^*_2\text{An}(\text{C}\equiv\text{CR})(\text{C}(\text{PhSiH}_2)=\text{CHR})$  (An = Th, U) complexes. These complexes have been trapped (for R = Pr) and characterized by spectroscopic methods and water poisoning experiments. A plausible mechanistic scenario is proposed for the hydrosilylation of terminal alkynes.

## Introduction

During the past decade, the chemistry of electrophilic  $d^0/f^0$  lanthanide and actinide organometallic compounds has been under intense investigation, reaching a high level of sophistication.<sup>1,2</sup> This broad interest originates from the novelty in their structure–reactivity relationships and the capacious opportunities in using these compounds, especially as homogeneous catalysts in demanding chemical transformations. For organolanthanides, many catalytic processes are known;<sup>3–10</sup> how-

ever, examples of organoactinide-catalyzed reactions are still limited to C–H activation<sup>11</sup> and hydrogenation,<sup>12</sup> and recently we have studied the hydroamination,<sup>13</sup> oligomerization, and selective dimerization of alkynes.<sup>14</sup> The metal-catalyzed hydrosilylation reaction, which is

(1) For general organolanthanide reviews, see: (a) Anwander, R.; Herrman, W. A. *Top. Curr. Chem.* **1996**, *179*, 1. (b) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247. (c) Schumann, H.; Meese-Marktschffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865 and references therein. (d) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283 and references therein.

(2) For general organoactinide reviews, see: (a) Edelmann, F. T.; Gun'ko, Y. K. *Coord. Chem. Rev.* **1997**, *165*, 163. (b) Ephritikhine, M. *New J. Chem.* **1992**, *16*, 451. (c) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds. Pergamon Press: Oxford, U.K., 1995; Chapter 2.

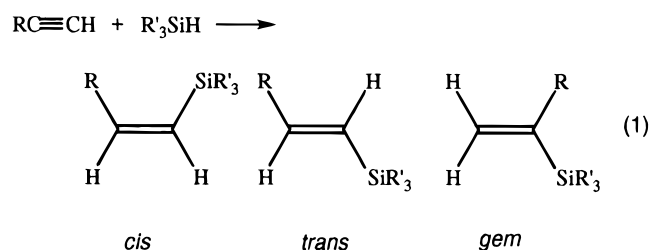
(3) For examples of the catalytic activity of organolanthanides in a variety of alkene and alkyne hydrogenations, see: (a) Roesky, P. W.; Denninger, U.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4486. (b) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 6, 4705. (c) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765. (d) Molander, G. A.; Winterfeld, J. J. *Organomet. Chem.* **1996**, *524*, 275. (e) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

(4) For examples of the catalytic activity of organolanthanides in dimerization, oligomerization, or polymerization, see: (a) Boff, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494. (b) Evans, W. J.; DeCoster, P. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929. (c) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (d) Ihara, E.; Nodono, M.; Yasuda, H.; Kanehisa, N.; Kai, Y. *Macromol. Chem. Phys.* **1996**, *197*, 1909. (e) Fu, P.-F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747. (f) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495 and references therein.

the addition of a Si–H bond across a carbon–carbon multiple bond, is one of the most important reactions in organosilicon chemistry and has been studied extensively for half a century. The hydrosilylation reaction has been used in the industrial production of organosilicon compounds (adhesives, binders, and coupling agents) and in research laboratories as an efficient route for the syntheses of a variety of organosilicon compounds, silicon-based polymers, and new types of dendrimeric materials.<sup>15</sup> Since the discovery of Speier's catalyst ( $\text{H}_2\text{PtCl}_6/\text{PrOH}$ ) in 1957,<sup>16</sup> catalytic asymmetric hydrosilylation, applied to organic syntheses, and new reactions related to hydrosilylation have been discovered and developed, mainly using late-transition-metal complexes.<sup>15,17–18</sup> More recently, metallocene complexes of either group 3 or 4, which exhibit distinctive features in comparison to late-transition-metal complexes, have been reported to catalyze the hydrosilylation reactions of unsaturated hydrocarbons very effectively.<sup>6,19</sup>

The versatile and rich chemistry of vinylsilanes has attracted considerable attention in recent years as these

compounds are considered to be important building blocks in organic synthesis.<sup>20</sup> For examples, electrophilic substitutions of the silyl moiety on vinylsilanes have been used for the stereoselective synthesis of substituted alkenes.<sup>20</sup> The heteroatom-substituted silyl moiety on vinylsilane provides a method for functional group transformation, as in the synthesis of phenylacetaldehyde from *cis*- $\text{PhCH}=\text{CHSi}(\text{OEt})_2$ .<sup>21</sup> The syntheses of vinylsilanes have been extensively studied, and one of the most convenient and straightforward methods is the hydrosilylation of alkynes.<sup>20,22</sup> In general, hydrosilylation of terminal alkynes produces three different isomers, *cis*, *trans*, and *geminal*, as a result of both 1,2- (*syn* and *anti*) and 2,1-additions, respectively, as shown in eq 1. The distribution of the products is found to vary



(5) For examples of the catalytic activity of organolanthanides in hydroamination, see: (a) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4871. (b) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295. (c) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770. (d) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707 and references therein.

(6) For examples of catalytic activity of organolanthanides in hydrosilylation see: (a) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (b) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Muhle, S.; Molander, G. A. *J. Organomet. Chem.* **1998**, *559*, 181. (c) Molander, G. A.; Dowdy, E. D.; Noll, B. C. *Organometallics* **1998**, *17*, 3754. (d) Onozawa, S.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177.

(7) Giardello, M. A.; King, W. A.; Nolan, S. P.; Porchia, M.; Sishta, C.; Marks, T. J. In *Energetics of Organometallic Species*; Martinho Simoes, J. A., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; pp 35–54.

(8) For examples of the catalytic activity of organolanthanides in hydroboration, see: (a) Anwender, R. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B.; Hermann, W., Eds.; VCH: Weinheim, Germany, 1997; Vol. 2, pp 866–892. (b) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121. (c) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

(9) Voskoboinikov, A. Z.; Beletskaya, I. P. *New J. Chem.* **1995**, *19*, 723.

(10) For examples of the catalytic activity of organolanthanides in ring-opening Ziegler polymerizations, see: (a) Jia, L.; Yang, X.; Seyam, A. M.; Albert, I. D. L.; Fu, P.-F.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 7900. (b) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, *27*, 4625.

(11) For examples of the catalytic activity of organoactinides in C–H activation processes, see: (a) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805. (b) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *7*, 1828.

(12) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515 and references therein.

(13) For examples of the catalytic activity of organoactinides in hydroamination, see: (a) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773. (b) Straub, T.; Frank, W.; Reiss, G. J.; Eisen, M. S. *J. Chem. Soc., Dalton Trans.* **1996**, 2541.

(14) For examples of the catalytic activity of organoactinides in oligomerizations, see: (a) Straub, T.; Haskel, A.; Eisen, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6364. (b) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3014. (c) Haskel, A.; Wang, J. Q.; Straub, T.; Gueta-Neyroud, T.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3025.

(15) (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, S.; Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 29, and references therein. (b) Reichl, J.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 197 and references therein. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (d) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 8, p 763.

(16) Speier, J. L.; Webster, J. A.; Bernes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(17) (a) Bruner, H.; Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric Synthesis*; Ojima, H., Ed.; VCH: New York, 1993; pp 303–322. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

considerably with the nature of the catalyst and substrates and also with the specific reaction conditions.<sup>20–23</sup>

A variety of mechanisms have been proposed for the hydrosilylation process, and one of the most widely accepted mechanisms was first proposed by Chalk and Harrod in 1965 for the Pt-catalyzed hydrosilylation of alkenes.<sup>23</sup> The key feature in the Chalk–Harrod mechanism (Scheme 1a) was the insertion of a coordinated alkene into a metal–hydrogen bond followed by reductive elimination of the alkyl and silyl ligands. If the intermediate alkyl complex undergoes reversible  $\beta$ -hydride elimination and reinsertion with opposite regio-

(18) (a) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (b) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421. (c) LaPonte, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906. (d) Adams, R. D.; Barnard, T. S. *Organometallics* **1998**, *17*, 2567. (e) Uozumi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137. (f) Widenhofer, R. A.; DeCarli, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3805. (g) Giraud, L.; Jenny, T. *Organometallics* **1998**, *17*, 4267. (h) Caporusso, A. M.; Barontini, S.; Pertici, P.; Vitulli, G.; Salvadori, P. *J. Organomet. Chem.* **1998**, *564*, 57.

(19) For group 4 complexes, see: (a) Eisen, M. S. In *The Chemistry of Organosilicon Compounds*; Apeloig, Y.; Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 3, Chapter 35, pp 2038–2122. (b) Eisen, M. S. *Rev. Inorg. Chem.* **1997**, *17*, 25. (c) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (d) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095. (e) Corey, J. Y.; Zhu, X. H. *Organometallics* **1992**, *11*, 672 (f). Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. For group 3 complexes, see: (g) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (h) Molander, G. A.; Nichols, P. J.; Noll, B. C. *J. Org. Chem.* **1998**, *63*, 2292. (i) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415.

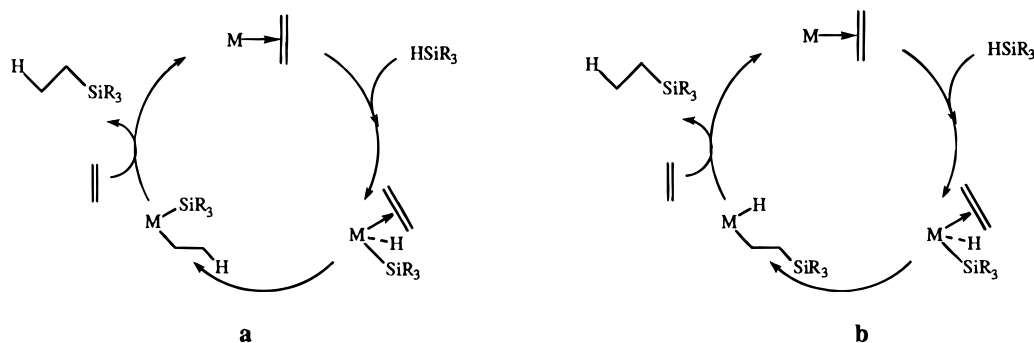
(20) (a) Fleming, I.; Dunogues, J.; Smithers, R. H. *Org. React.* **1989**, *37*, 57. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.

(21) (a) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443. (b) Tamao, K.; Yoshida, J.-I.; Takahashi, M.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kurita, A.; Kumada, M. *J. Am. Chem. Soc.* **1978**, *100*, 290.

(22) (a) Esteruelas, M. A.; Nurnberg, O.; Olivian, M.; Oro, L. A.; Werner, H. *Organometallics* **1993**, *12*, 3264. (b) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909. (c) Asao, N.; T. Sudo, Y. *J. Org. Chem.* **1996**, *61*, 7654.

(23) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 1133.

**Scheme 1. Chalk–Harrod (a) and Modified Chalk–Harrod (b) Mechanisms for the Hydrosilylation of Alkenes**



chemistry, then the Chalk–Harrod mechanism provides an explanation for the olefin isomerization and deuterium scrambling in the hydrosilylation reactions.<sup>15a</sup> However, this mechanism was unable to account for the formation of vinylsilanes from the hydrosilylation reaction of alkenes. In some cases vinylsilanes are produced more readily than the hydrosilylation product.<sup>24</sup> To explain this competing process, a number of different so-called modified Chalk–Harrod mechanisms have been proposed.<sup>25</sup> In the basic mechanism (Scheme 1b), a coordinated alkene inserts into a metal–silicon bond, forming a silaalkyl moiety. The subsequent reductive elimination of the  $\beta$ -silaalkyl group with the hydride ligand leads to the hydrosilylation products. A competing  $\beta$ -hydride elimination from the  $\beta$ -silaalkyl moiety allows the formation of vinylsilanes.

Although there is some evidence showing that the insertion of an alkene into a metal–hydrogen bond is faster than insertion into a metal–silicon bond, these findings are not enough to conclude that a Chalk–Harrod mechanism is more favorable than the modified Chalk–Harrod mechanism for late-transition-metal complexes.<sup>19a,b,26</sup> For organolanthanide and organoactinide complexes, the hydrosilylation of alkenes is proposed to proceed via the Chalk–Harrod type mechanism, except for the inclusion of a  $\sigma$ -bond metathesis instead of a classical oxidative-addition–reductive-elimination process.<sup>6a,19h</sup>

Recently we have reported that organoactinide complexes of the type  $\text{Cp}^*_2\text{AnMe}_2$  (An = Th, U) are active catalytic precursors for the linear oligomerization of terminal alkynes, and the extent of oligomerization was found to be strongly dependent on the electronic and steric hindrance of the alkyne substituents.<sup>14</sup> For example, bulky alkynes reacted with high regioselectivity toward dimers and/or trimers, whereas for nonbulky alkynes, the oligomerization afforded dimers to heptamers with total lack of regioselectivity. Addition of primary amines to the catalytic cycle allows us to control

the oligomerization reaction, producing selectively the formation of dimers and/or trimers.<sup>14c</sup> These findings prompted us to study the catalytic hydrosilylation reaction promoted by organoactinide complexes. Here we report a thorough study for the hydrosilylation reaction of terminal alkynes catalyzed by organoactinide complexes. We present a full discussion, including scope, stoichiometry and catalytic effects, substrate substituent, and metal effects. In addition, we have successfully trapped some of the key organometallic intermediates in the catalytic cycle. Kinetic and thermodynamic studies are presented as well, along with their mechanistic implications.

### Experimental Section

**Materials and Methods.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum ( $10^{-5}$  Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1–2 ppm  $\text{O}_2$ ). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. The hydrocarbon solvents THF-*d*<sub>6</sub>, benzene-*d*<sub>6</sub>, and toluene-*d*<sub>8</sub> were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs.  $\text{Cp}^*_2\text{AnMe}_2$  (An = Th, U) compounds were prepared according to the literature procedure.<sup>27</sup> Acetylenic compounds (Aldrich) were dried and stored over activated molecular sieve (4 Å), degassed and freshly vacuum-distilled.  $\text{PhSiH}_3$  (Aldrich) were dried and stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. NMR spectra for alkenes were confirmed by comparison with those in the published literature. For  $^{29}\text{Si}$  NMR,  $\text{Si}(\text{TMS})_4$  was used as internal standard ( $\text{SiMe}_3$  at  $-7.80$  ppm), and the experiments were measured using either the INEPT or DEPT program. GC/MS experiments were conducted in a GC-MS (Finnigan Magnum) spectrometer. The NMR experiments were conducted in Teflon-valve-sealed tubes (J. Young) after vacuum transfer of the liquids in a high-vacuum line. Microanalysis was carried out at the Hebrew University of Jerusalem.

**General Procedure for the Catalytic Hydrosilylation of Terminal Alkynes.** In a typical procedure, the specific alkyne and an equimolar amount of  $\text{PhSiH}_3$  were vacuum-transferred in a high-vacuum line into an J. Young NMR tube

(24) (a) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (b) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098. (c) Christ, M. L.; Sabo-Etienne, S.; Chaudert, B. *Organometallics* **1995**, *14*, 1082.

(25) Three main modified Chalk–Harrod mechanisms have been postulated: (a) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (b) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (c) Ruiz, J.; Bentz, P. O.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2709. (d) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151.

(26) (a) Bode, B. M.; Day, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 1552. (b) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510. (c) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *J. Am. Chem. Soc.* **1994**, *116*, 7258.

(27) (a) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (b) Aitken, C.; Barry, J. P.; Gauvin, F. G.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732.

containing 10 mg of Cp\*<sub>2</sub>AnMe<sub>2</sub> (An = Th, U) in 0.6 mL of THF-*d*<sub>8</sub> or C<sub>6</sub>D<sub>6</sub>. The sealed tube was then heated in an oil bath or kept at room temperature until 100% conversion of the alkyne was detected by the disappearance of the acetylenic hydrogen of the alkyne by <sup>1</sup>H NMR spectroscopy. The percentage of the converted products is given related only to the alkyne. The organic products were vacuum-transferred (10<sup>-6</sup> mmHg) to another J. Young NMR tube and sealed, and both the residue and volatiles were identified by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and 2D (COSY, C–H correlation, Si–H correlation, NOESY) NMR spectroscopy and GC-MS spectroscopy and by comparing with compounds known in the literature.

**(1) Hydrosilylation of <sup>t</sup>BuC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>UMe<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>t</sup>BuC≡CH (0.638 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>8</sub> at room temperature for 48 h, producing *trans*-<sup>t</sup>BuCH=CHSiH<sub>2</sub>Ph (**1**; 47%), <sup>t</sup>BuC≡CSiH<sub>2</sub>Ph (**4**; 31%), and <sup>t</sup>BuCH=CH<sub>2</sub> (**7**; 22%).

**Characterization Data for **1**.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.05–7.17 (m, 3H, *o,p*-H Ph), 7.60–7.64 (m, 2H, *m*-H Ph), 6.39 (d, 1H, <sup>3</sup>J<sub>trans</sub> = 18.8 Hz, HCBu<sup>t</sup>), 5.62 (dt, 1H, <sup>3</sup>J<sub>trans</sub> = 18.8 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 3.2 Hz, HC(PhSiH<sub>2</sub>)), 4.79 (d, 2H, <sup>3</sup>J = 3.2 Hz, PhSiH<sub>2</sub>), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 164.1 (d, <sup>1</sup>J = 152 Hz, HCBu<sup>t</sup>), 135.6, 129.8, 128.3 (C–H Ph), 132.5 (s, CC<sub>5</sub>H<sub>5</sub>), 114.2 (d, <sup>1</sup>J = 141 Hz, HC(PhSiH<sub>2</sub>)), 32.2 (s, CMe<sub>3</sub>), 28.8 (q, <sup>1</sup>J = 128 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.62 (tt, <sup>1</sup>J<sub>Si–H</sub> = 198 Hz, <sup>3</sup>J<sub>Si–H</sub> = 7.3 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 190 (M<sup>+</sup>), 189 (M<sup>+</sup> – H), 175 (M<sup>+</sup> – CH<sub>3</sub>), 162 (M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>), 148 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>2</sub>), 133 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>3</sub>), 120 (M<sup>+</sup> – (CH<sub>3</sub>)<sub>3</sub>CCH), 105 (PhSi<sup>+</sup>, 100%).

**Characterization Data for **4**.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.35–7.40 (m, 3H, *o,p*-H Ph), 7.52–7.57 (m, 2H, *m*-H Ph), 4.85 (s, 2H, PhSiH<sub>2</sub>), 1.06 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.4, 130.2, 128.4 (C–H Ph), 132.5 (s, CC<sub>5</sub>H<sub>5</sub>), 73.6 (s, C≡CBu<sup>t</sup>), 67.3 (s, C≡CSiPh<sub>2</sub>), 35.6 (s, CMe<sub>3</sub>), 30.8 (q, <sup>1</sup>J = 128 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ –8.98 (tt, <sup>1</sup>J<sub>Si–H</sub> = 211 Hz, <sup>3</sup>J<sub>Si–H</sub> = 6.1 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 188 (M<sup>+</sup>), 187 (M<sup>+</sup> – H), 173 (M<sup>+</sup> – CH<sub>3</sub>), 159 (M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>), 145 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>), 131 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>3</sub>), 105 (PhSi<sup>+</sup>, 100%), 81 (M<sup>+</sup> – PhSiH<sub>2</sub>).

(b) According to the general procedure described above, 100% conversion was obtained after 24 h by the reaction of <sup>t</sup>BuC≡CH (0.638 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>8</sub> at 65 °C, producing **1** (15%), **4** (36%), **7** (7%), *cis*-<sup>t</sup>BuCH=CHSiH<sub>2</sub>Ph (**13**; 24%), and the double-hydrosilylation product <sup>t</sup>BuCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**16**; 19%).

**Characterization Data for **13**.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>8</sub>): δ 7.29–7.57 (m, 5H, Ph), 6.65 (d, 1H, <sup>3</sup>J<sub>cis</sub> = 14.95 Hz, HCBu<sup>t</sup>), 5.54 (dt, 1H, <sup>3</sup>J<sub>cis</sub> = 14.95 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 4.15 Hz, HCSiH<sub>2</sub>Ph), 4.76 (d, 2H, <sup>3</sup>J = 4.15 Hz, SiH<sub>2</sub>Ph), 1.16 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>8</sub>): δ 167.1 (d, <sup>1</sup>J = 150.2 Hz, HCBu<sup>t</sup>), 137.6, 133.1, 131.3 (C–H Ph), 132.6 (s, CC<sub>5</sub>H<sub>5</sub>), 118.4 (d, <sup>1</sup>J = 137.7 Hz, HCSiH<sub>2</sub>Ph), 42.7 (s, CMe<sub>3</sub>), 33.2 (q, <sup>1</sup>J = 125.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>8</sub>): δ 4.60 (t, <sup>1</sup>J = 210 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 190 (M<sup>+</sup>), 189 (M<sup>+</sup> – H), 175 (M<sup>+</sup> – CH<sub>3</sub>), 162 (M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>), 148 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>2</sub>), 133 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>3</sub>), 120 (M<sup>+</sup> – (CH<sub>3</sub>)<sub>3</sub>CCH), 105 (PhSi<sup>+</sup>, 100%).

**Characterization Data for **16**.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>8</sub>): δ 7.29–7.57 (m, 10H, Ph), 7.34 (s, 1H, HCBu<sup>t</sup>), 4.84 (s, 2H, SiH<sub>2</sub>Ph), 4.7 (s, 2H, SiH<sub>2</sub>Ph), 1.15 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>8</sub>): δ 180.2 (d, <sup>1</sup>J = 146.3 Hz, HCBu<sup>t</sup>), 137.2, 133.1, 131.6 (C–H Ph), 132.6 (s, CC<sub>5</sub>H<sub>5</sub>), 42.4 (s, CMe<sub>3</sub>), 33.0 (q, <sup>1</sup>J = 125.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>8</sub>): δ 30.22 (t, <sup>1</sup>J = 215.4 Hz, PhSiH<sub>2</sub>), 5.20 (t, <sup>1</sup>J = 210 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 296 (M<sup>+</sup>), 295 (M<sup>+</sup> – H), 281 (M<sup>+</sup> – CH<sub>3</sub>), 265 (M<sup>+</sup> – C<sub>2</sub>H<sub>6</sub> – H), 253 (M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>), 239 (M<sup>+</sup> – C(CH<sub>3</sub>)<sub>3</sub>), 219 (M<sup>+</sup> – C<sub>6</sub>H<sub>5</sub>), 187 (M<sup>+</sup> – PhSiH<sub>3</sub> – H), 183 (Ph<sub>2</sub>SiH), 131 (M<sup>+</sup> – PhSiH<sub>3</sub> – C(CH<sub>3</sub>)<sub>2</sub>), 105 (PhSi<sup>+</sup>, 100%).

**(2) Hydrosilylation of <sup>t</sup>BuC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>ThMe<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>t</sup>BuC≡CH (0.638 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at room temperature for 24 h, producing *trans*-<sup>t</sup>BuCH=CHSiH<sub>2</sub>Ph (**1**; 48%), <sup>t</sup>BuC≡CSiH<sub>2</sub>Ph (**4**; 28%), and <sup>t</sup>BuCH=CH<sub>2</sub> (**7**; 24%).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>t</sup>BuC≡CH (0.638 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at 78 °C for 12 h, producing **1** (21%), **4** (46%), and **7** (34%).

(c) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>t</sup>BuC≡CH (0.638 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in THF-*d*<sub>8</sub> at 65 °C for 12 h, producing **1** (21%), **4** (31%), and **7** (48%).

**(3) Hydrosilylation of <sup>i</sup>PrC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>UMe<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>i</sup>PrC≡CH (0.768 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>8</sub> at room temperature for 48 h, producing *trans*-<sup>i</sup>PrCH=CHSiH<sub>2</sub>Ph (**2**; 62%), <sup>i</sup>PrC≡CSiH<sub>2</sub>Ph (**5**; 27%), and <sup>i</sup>PrCH=CH<sub>2</sub> (**8**; 12%).

**Characterization Data for **2**.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.52–7.65 (m, 2H, *m*-H Ph), 7.05–7.22 (m, 3H, *o,p*-H Ph), 6.31 (dd, 1H, <sup>3</sup>J<sub>trans</sub> = 18.5 Hz, <sup>3</sup>J<sub>HH(Pr)</sub> = 5.9 Hz, HCPr<sup>i</sup>), 5.62 (dtd, 1H, <sup>3</sup>J<sub>trans</sub> = 18.7 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 3.32 Hz, <sup>4</sup>J<sub>H–H(Pr)</sub> = 1.66 Hz, HC(PhSiH<sub>2</sub>)), 4.78 (d, 2H, <sup>3</sup>J = 3.32 Hz, PhSiH<sub>2</sub>), 2.33 (m, 1H, CHMe<sub>2</sub>), 0.85 (d, 6H, <sup>3</sup>J = 6.69 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 160.4 (d, <sup>1</sup>J = 150.3 Hz, CHPr<sup>i</sup>), 135.7, 130.2, 128.3 (C–H Ph), 132.5 (s, CC<sub>5</sub>H<sub>5</sub>), 116.9 (d, <sup>1</sup>J = 140.1 Hz, CH(PhSiH<sub>2</sub>)), 34.78 (d, <sup>1</sup>J = 122.8 Hz, CHMe<sub>2</sub>), 21.55 (q, <sup>1</sup>J = 125.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 14.79 (t, <sup>1</sup>J = 199 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 176 (M<sup>+</sup>), 175 (M<sup>+</sup> – H), 159 (M<sup>+</sup> – CH<sub>3</sub>), 148 (M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>), 133 (M<sup>+</sup> – CH(CH<sub>3</sub>)<sub>2</sub>), 120 (M<sup>+</sup> – CHPr<sup>i</sup>), 105 (PhSi<sup>+</sup>, 100%), 98 (M<sup>+</sup> – C<sub>6</sub>H<sub>6</sub>), 69 (M<sup>+</sup> – SiH<sub>2</sub>Ph).

**Characterization Data for **5**.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.52–7.65 (m, 2H, *m*-H Ph), 7.05–7.22 (m, 3H, *o,p*-H Ph), 4.80 (d, 2H, <sup>5</sup>J = 1.07 Hz, PhSiH<sub>2</sub>), 2.16 (m, 1H, CHMe<sub>2</sub>), 0.97 (d, 6H, <sup>3</sup>J = 6.81 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.4, 129.8, 128.3 (C–H Ph), 132.5 (s, CC<sub>5</sub>H<sub>5</sub>), 78.6 (s, C≡CPr<sup>i</sup>), 67.8 (s, C≡CSiPh<sub>2</sub>), 34.7 (d, <sup>1</sup>J = 122.8 Hz, CHMe<sub>2</sub>), 22.5 (q, <sup>1</sup>J = 125.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ –9.0 (t, <sup>1</sup>J = 213 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 174 (M<sup>+</sup>), 173 (M<sup>+</sup> – H), 159 (M<sup>+</sup> – CH<sub>3</sub>), 145 (M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>), 131 (M<sup>+</sup> – CH(CH<sub>3</sub>)<sub>2</sub>), 119 (M<sup>+</sup> – CPr<sup>i</sup>), 105 (PhSi<sup>+</sup>, 100%), 96 (M<sup>+</sup> – C<sub>6</sub>H<sub>6</sub>), 67 (M<sup>+</sup> – SiH<sub>2</sub>Ph).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>i</sup>PrC≡CH (0.768 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>8</sub> at 65 °C for 24 h, producing **2** (4%), **5** (31%), **8** (35%), *cis*-<sup>i</sup>PrCH=CHSiH<sub>2</sub>Ph (**14**; 27%), and the double-hydrosilylation product <sup>i</sup>PrCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**17**; 2%).

**Characterization Data for **14**.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>8</sub>): δ 7.20–7.68 (m, 5H, Ph), 6.42 (dd, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz, <sup>3</sup>J<sub>HH(Pr)</sub> = 5.8 Hz, HCPr<sup>i</sup>), 5.57 (dt, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 4.15 Hz, HCSiH<sub>2</sub>Ph), 4.63 (d, 2H, <sup>3</sup>J = 4.15 Hz, PhSiH<sub>2</sub>), 2.37 (m, 1H, CHMe<sub>2</sub>), 1.03 (d, 1H, <sup>3</sup>J = 6.64 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>8</sub>): δ 162.7 (d, <sup>1</sup>J = 150.2 Hz, HCBu<sup>t</sup>), 138.4, 132.9, 131.1 (C–H Ph), 132.6 (s, CC<sub>5</sub>H<sub>5</sub>), 121.9 (d, <sup>1</sup>J = 140 Hz, HCSiH<sub>2</sub>Ph), 38.1 (d, <sup>1</sup>J = 126.8 Hz, CHMe<sub>2</sub>), 24.5 (q, <sup>1</sup>J = 125.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>8</sub>): δ 1.60 (t, <sup>1</sup>J = 195.5 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 176 (M<sup>+</sup>), 175 (M<sup>+</sup> – H), 159 (M<sup>+</sup> – CH<sub>3</sub>), 148 (M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>), 133 (M<sup>+</sup> – CH(CH<sub>3</sub>)<sub>2</sub>), 120 (M<sup>+</sup> – CHPr<sup>i</sup>), 105 (PhSi<sup>+</sup>, 100%), 98 (M<sup>+</sup> – C<sub>6</sub>H<sub>6</sub>), 69 (M<sup>+</sup> – SiH<sub>2</sub>Ph).

**Characterization Data for **17**.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>8</sub>): δ 7.72–7.60 (m, 4H, *m*-H Ph), 7.52–7.25 (m, 6H, *o,p*-H Ph), 6.82 (d, 1H, <sup>3</sup>J = 9.25 Hz, HCPr<sup>i</sup>), 4.66 (s, 2H, PhSiH<sub>2</sub>),

4.64 (s, 2H, PhSiH<sub>2</sub>), 2.64 (m, 1H, <sup>3</sup>J = 6.76 Hz, CHMe<sub>2</sub>), 1.18 (d, 6H, <sup>3</sup>J = 6.76 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>6</sub>): δ 174.0 (d, <sup>1</sup>J = 150.5 Hz, HCP<sup>r</sup>), 136.5, 130.6, 128.8 (C–H Ph), 132.8 (s, CC<sub>5</sub>H<sub>5</sub>), 116.9 (s, C(PhSiH<sub>2</sub>)<sub>2</sub>), 34.7 (d, <sup>1</sup>J = 122.8 Hz, CHMe<sub>2</sub>), 22.8 (q, <sup>1</sup>J = 125.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>6</sub>): δ 27.5 (t, <sup>1</sup>J = 198 Hz, PhSiH<sub>2</sub>), 7.3 (t, <sup>1</sup>J = 203 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 282 (M<sup>+</sup>), 281 (M<sup>+</sup> – H), 267 (M<sup>+</sup> – CH<sub>3</sub>), 251 (M<sup>+</sup> – 2CH<sub>3</sub>), 239 (M<sup>+</sup> – Pr<sup>r</sup>), 225 (M<sup>+</sup> – CHPr<sup>i</sup> – H), 205 (M<sup>+</sup> – C<sub>6</sub>H<sub>6</sub>), 173 (M<sup>+</sup> – PhSiH<sub>3</sub> – H), 148 ((CH<sub>3</sub>)<sub>2</sub>C=SiHPh<sup>+</sup>), 131 (M<sup>+</sup> – PhSiH<sub>3</sub> – Pr<sup>r</sup>), 105 (PhSi<sup>+</sup>, 100%).

**(4) Hydrosilylation of <sup>r</sup>PrC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>-ThMe<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>r</sup>PrC≡CH (0.768 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>-ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at room temperature for 24 h, producing *trans*-<sup>r</sup>PrCH=CHSiH<sub>2</sub>Ph (**2**; 42%), <sup>r</sup>PrC≡CSiH<sub>2</sub>Ph (**5**; 28%), <sup>r</sup>PrCH=CH<sub>2</sub> (**8**; 26%) and <sup>r</sup>PrCH<sub>2</sub>CH<sub>3</sub> (**10**; 5%).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>r</sup>PrC≡CH (0.768 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>-ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at 78 °C for 12 h, producing **2** (37%), **5** (38%), **8** (23%), and the double-hydrosilylation product <sup>r</sup>PrCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**17**; 2%).

(c) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>r</sup>PrC≡CH (0.768 mmol) and PhSiH<sub>3</sub> (0.637 mmol), catalyzed by Cp\*<sub>2</sub>-ThMe<sub>2</sub> (0.0187 mmol) in THF-*d*<sub>6</sub> at 65 °C for 12 h, producing **2** (33%), **5** (25%), **8** (36%), and **17** (6%).

**(5) Hydrosilylation of <sup>n</sup>BuC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>Ume<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>n</sup>BuC≡CH (0.684 mmol) and PhSiH<sub>3</sub> (0.716 mmol), catalyzed by Cp\*<sub>2</sub>-Ume<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>6</sub> at room temperature for 48 h, producing *trans*-<sup>n</sup>BuCH=CHSiH<sub>2</sub>Ph (**3**; 74%), <sup>n</sup>BuC≡CSiH<sub>2</sub>-Ph (**6**; 2%), and <sup>n</sup>BuCH=CH<sub>2</sub> (**9**; 24%).

**Characterization Data for 3.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.52–7.66 (m, 3H, *o,p*-H Ph), 7.11–7.17 (m, 2H, *m*-H Ph), 6.29 (dt, 1H, <sup>3</sup>J<sub>trans</sub> = 18.37 Hz, <sup>3</sup>J<sub>HH(Bu)</sub> = 6.25 Hz, HCBu<sup>n</sup>), 5.66 (dt, 1H, <sup>3</sup>J<sub>trans</sub> = 18.37 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 3.12 Hz, <sup>4</sup>J<sub>HH(Bu)</sub> = 1.55 Hz, HC(PhSiH<sub>2</sub>)), 4.77 (d, 2H, <sup>3</sup>J = 3.12 Hz, PhSiH<sub>2</sub>), 1.98 (dt, 2H, <sup>3</sup>J = 5.14 Hz, <sup>3</sup>J<sub>gem</sub> = 1.55 Hz, =CCH<sub>2</sub>), 1.20 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.8 (t, 3H, <sup>3</sup>J = 7.02 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 154.1 (d, <sup>1</sup>J = 150 Hz, HCBu<sup>n</sup>), 135.7, 129.8, 128.3 (C–H Ph), 132.4 (s, CC<sub>5</sub>H<sub>5</sub>), 120.4 (d, <sup>1</sup>J = 140 Hz, HC(PhSiH<sub>2</sub>)), 36.9 (t, <sup>1</sup>J = 125.4 Hz, =CCH<sub>2</sub>), 30.7 (t, <sup>1</sup>J = 126.3 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.5 (t, <sup>1</sup>J = 124.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 14.0 (q, <sup>1</sup>J = 125.6 Hz, CH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 14.04 (t, <sup>1</sup>J = 196.5 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 190 (M<sup>+</sup>), 189 (M<sup>+</sup> – H), 175 (M<sup>+</sup> – CH<sub>3</sub>), 161 (M<sup>+</sup> – CH<sub>3</sub>CH<sub>2</sub>), 147 (M<sup>+</sup> – CH<sub>2</sub>CH<sub>2</sub>-CH<sub>3</sub>), 133 (M<sup>+</sup> – Bu<sup>n</sup>), 120 (M<sup>+</sup> – CHBu<sup>n</sup>), 105 (PhSi<sup>+</sup>, 100%).

**Characterization Data for 6.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.52–7.65 (m, 3H, *o,p*-H Ph), 7.11–7.17 (m, 2H, *m*-H Ph), 4.81 (s, 2H, PhSiH<sub>2</sub>), 1.97 (t, <sup>3</sup>J = 6.16 Hz, 2H, CH<sub>2</sub>), 1.20 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 0.71 (t, <sup>3</sup>J = 7.13 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.4, 130.2, 128.4 (C–H Ph), 132.4 (s, CC<sub>5</sub>H<sub>5</sub>), 75.6 (s, <sup>n</sup>BuC≡C), 67.2 (s, C≡CSiH<sub>2</sub>Ph), 30.5 (t, <sup>1</sup>J = 125.4 Hz, =CCH<sub>2</sub>), 22.1 (t, <sup>1</sup>J = 126.3 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 19.9 (t, <sup>1</sup>J = 124.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 13.6 (q, <sup>1</sup>J = 125.6 Hz, CH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ –9.17 (t, <sup>1</sup>J = 212.4 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 188 (M<sup>+</sup>), 187 (M<sup>+</sup> – H), 173 (M<sup>+</sup> – CH<sub>3</sub>), 159 (M<sup>+</sup> – CH<sub>3</sub>CH<sub>2</sub>), 146 (M<sup>+</sup> – C<sub>3</sub>H<sub>6</sub>), 131 (M<sup>+</sup> – Bu<sup>n</sup>), 105 (PhSi<sup>+</sup>, 100%).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>n</sup>BuC≡CH (0.684 mmol) and PhSiH<sub>3</sub> (0.716 mmol), catalyzed by Cp\*<sub>2</sub>-Ume<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>6</sub> at 65 °C for 24 h, producing **3** (5%), **6** (9%), **9** (16%), *cis*-<sup>n</sup>BuCH=CHSiH<sub>2</sub>Ph (**15**; 54%), and the double-hydrosilylation product <sup>n</sup>BuCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**18**; 3%).

**Characterization Data for 15.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>6</sub>): δ 7.30–7.65 (m, 5H, Ph), 6.61 (dt, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz,

<sup>3</sup>J<sub>HH(Bu)</sub> = 6.64 Hz, HCBu<sup>n</sup>), 5.75 (dt, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 4.15 Hz, HCSiH<sub>2</sub>Ph), 4.62 (d, <sup>3</sup>J = 4.15 Hz, 2H, PhSiH<sub>2</sub>), 2.20 (m, 2H, =CHCH<sub>2</sub>CH<sub>2</sub>), 1.50 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.9 (t, 3H, <sup>3</sup>J = 6.9 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>6</sub>): δ 156.8 (d, <sup>1</sup>J = 150.1 Hz, HCBu<sup>n</sup>), 138.8, 133.1, 131.1 (C–H Ph), 132.6 (s, CC<sub>5</sub>H<sub>5</sub>), 122.4 (d, <sup>1</sup>J = 146.3 Hz, HCSiH<sub>2</sub>Ph), 40.0 (t, <sup>1</sup>J = 125.6 Hz, =CHCH<sub>2</sub>), 34.1 (t, <sup>1</sup>J = 127.1 Hz, CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>), 25.7 (t, <sup>1</sup>J = 127 Hz, CH<sub>2</sub>CH<sub>3</sub>), 16.9 (q, <sup>1</sup>J = 123.8 Hz, CH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>6</sub>): δ 1.44 (t, <sup>1</sup>J = 195 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 190 (M<sup>+</sup>), 189 (M<sup>+</sup> – H), 175 (M<sup>+</sup> – CH<sub>3</sub>), 161 (M<sup>+</sup> – CH<sub>3</sub>CH<sub>2</sub>), 147 (M<sup>+</sup> – CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 133 (M<sup>+</sup> – Bu<sup>n</sup>), 120 (M<sup>+</sup> – CHBu<sup>n</sup>), 105 (PhSi<sup>+</sup>, 100%).

**Characterization Data for 18.** <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>6</sub>): δ 23.84 (t, <sup>1</sup>J = 208 Hz, PhSiH<sub>2</sub>), 4.14 (t, <sup>1</sup>J = 211 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 296 (M<sup>+</sup>), 295 (M<sup>+</sup> – H), 279 (M<sup>+</sup> – CH<sub>3</sub> – 2H), 265 (M<sup>+</sup> – CH<sub>3</sub>CH<sub>2</sub> – 2H), 239 (M<sup>+</sup> – Bu<sup>n</sup>), 145 (M<sup>+</sup> – PhSiH<sub>3</sub> – CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 131 (M<sup>+</sup> – PhSiH<sub>3</sub> – Bu<sup>n</sup>), 105 (PhSi<sup>+</sup>, 100%).

**(6) Hydrosilylation of <sup>n</sup>BuC≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>ThMe<sub>2</sub>.** (a) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>n</sup>BuC≡CH (0.684 mmol) and PhSiH<sub>3</sub> (0.716 mmol), catalyzed by Cp\*<sub>2</sub>-ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at room temperature for 24 h, producing *trans*-<sup>n</sup>BuCH=CHSiH<sub>2</sub>Ph (**3**; 56%), <sup>n</sup>BuC≡CSiH<sub>2</sub>-Ph (**6**; 22%), and <sup>n</sup>BuCH=CH<sub>2</sub> (**9**; 22%).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of <sup>n</sup>BuC≡CH (0.684 mmol) and PhSiH<sub>3</sub> (0.716 mmol), catalyzed by Cp\*<sub>2</sub>-ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at 78 °C for 12 h, producing **3** (43%), **6** (34%), and **9** (23%).

**(7) Hydrosilylation of (TMS)C≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>Ume<sub>2</sub>.** (a) According to the general procedure described above, the reaction of (TMS)C≡CH (0.556 mmol) and PhSiH<sub>3</sub> (0.557 mmol), catalyzed by Cp\*<sub>2</sub>Ume<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>6</sub> at room temperature for 48 h, produced *trans*-(TMS)CH=CHSiH<sub>2</sub>Ph (**11**; 8%) and (TMS)C≡CSiH<sub>2</sub>Ph (**12**; 16%).

**Characterization Data for 11.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.51–7.60 (m, 2H, *m*-H Ph), 7.05–7.12 (m, 3H, *o,p*-H Ph), 6.92 (d, 1H, <sup>3</sup>J = 22.4 Hz, HCTMS), 6.64 (dt, 1H, <sup>3</sup>J<sub>trans</sub> = 22.4 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 2.6 Hz, HC(PhSiH<sub>2</sub>)), 4.84 (d, 2H, <sup>3</sup>J<sub>HH(Si)</sub> = 2.6 Hz, PhSiH<sub>2</sub>), 0.09 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 158.9 (d, <sup>1</sup>J = 138.5 Hz, HCTMS), 140.8 (d, <sup>1</sup>J = 149.5 Hz, HC(PhSiH<sub>2</sub>)), 136.0, 135.8, 130.0 (C–H Ph), 138.2 (s, CC<sub>5</sub>H<sub>5</sub>), –0.45 (q, <sup>1</sup>J = 119 Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.46 (t, <sup>1</sup>J = 196 Hz, PhSiH<sub>2</sub>), GC/MS data: *m/z* 206 (M<sup>+</sup>), 205 (M<sup>+</sup> – H), 191 (M<sup>+</sup> – CH<sub>3</sub>), 178 (M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>), 161 (M<sup>+</sup> – 3CH<sub>3</sub>), 135 (PhSiH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 121 (PhSiH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 105 (PhSi<sup>+</sup>, 100%), 73 (Me<sub>3</sub>Si<sup>+</sup>).

**Characterization Data for 12.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.34–7.40 (m, 2H, *m*-H Ph), 7.05–7.12 (m, 3H, *o,p*-H Ph), 4.74 (s, 2H, PhSiH<sub>2</sub>), 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.5, 130.4, 128.4 (C–H Ph), 107.1 (s, C≡CSiH<sub>2</sub>Ph), 93.2 (s, C≡CTMS), –1.81 (q, <sup>1</sup>J = 120.5 Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ –9.8 (t, <sup>1</sup>J = 214.9 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 204 (M<sup>+</sup>), 203 (M<sup>+</sup> – H), 189 (M<sup>+</sup> – CH<sub>3</sub>), 163 (M<sup>+</sup> – C<sub>3</sub>H<sub>5</sub>), 145 (PhSiH<sub>2</sub>C≡CCH<sub>2</sub><sup>+</sup>), 135 (PhSiH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 121 (PhSiH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 105 (PhSi<sup>+</sup>, 100%), 73 (Me<sub>3</sub>Si<sup>+</sup>).

(b) According to the general procedure described above, 100% conversion was obtained by the reaction of (TMS)C≡CH (0.556 mmol) and PhSiH<sub>3</sub> (0.557 mmol), catalyzed by Cp\*<sub>2</sub>-Ume<sub>2</sub> (0.0186 mmol) in THF-*d*<sub>6</sub> at 65 °C for 24 h, producing **11** (6%), **12** (40%), *cis*-(TMS)CH=CHSiH<sub>2</sub>Ph (**19**; 26%), and (TMS)CH=CH<sub>2</sub> (**20**; 29%).

**Characterization Data for 19.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>6</sub>): δ 7.25–7.70 (m, 5H, Ph), 7.01 (d, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz, HCTMS), 6.64 (dt, 1H, <sup>3</sup>J<sub>cis</sub> = 13.3 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 4.4 Hz, HCSiH<sub>2</sub>Ph), 4.65 (d, 2H, <sup>3</sup>J<sub>HH(Si)</sub> = 4.4 Hz, H<sub>2</sub>SiPh), 0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>6</sub>): δ 160.7 (d, <sup>1</sup>J = 138.5 Hz, HCTMS), 144.5 (d, <sup>1</sup>J = 149.5 Hz, HCSiH<sub>2</sub>Ph), 138.5, 132.8, 130.9 (C–H Ph), 132.6 (s, CC<sub>5</sub>H<sub>5</sub>), 0.6 (q, <sup>1</sup>J = 116.6

Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>6</sub>): δ 6.56 (t, <sup>1</sup>J = 205 Hz, PhSiH<sub>2</sub>). GC/MS data: *m/z* 206 (M<sup>+</sup>), 205 (M<sup>+</sup> - H), 191 (M<sup>+</sup> - CH<sub>3</sub>), 178 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 161 (M<sup>+</sup> - 3CH<sub>3</sub>), 135 (PhSiH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 121 (PhSiH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 105 (PhSi<sup>+</sup>, 100%), 73 (Me<sub>3</sub>Si<sup>+</sup>).

**Characterization Data for 20.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.15 (dd, 1H, <sup>3</sup>J<sub>trans</sub> = 19.9 Hz, <sup>3</sup>J<sub>cis</sub> = 14.6 Hz, HCTMS), 5.88 (dd, 1H, <sup>3</sup>J<sub>cis</sub> = 14.6 Hz, <sup>2</sup>J<sub>gem</sub> = 4.4 Hz, HCH), 5.63 (dd, 1H, <sup>3</sup>J<sub>trans</sub> = 19.9 Hz, <sup>2</sup>J<sub>gem</sub> = 4.4 Hz, HCH), 0.03 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 140.1 (d, <sup>1</sup>J = 130.6 Hz, HCTMS), 131.0 (t, <sup>1</sup>J = 147.4 Hz, CH<sub>2</sub>), -2.2 (q, <sup>1</sup>J = 118 Hz, Si(CH<sub>3</sub>)<sub>3</sub>).

**(8) Hydrosilylation of (TMS)C≡CH with PhSiH<sub>3</sub> by Cp\*<sub>2</sub>ThMe<sub>2</sub>.** According to the general procedure described above, 100% conversion was obtained by the reaction of (TMS)C≡CH (0.556 mmol) and PhSiH<sub>3</sub> (0.557 mmol), catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in C<sub>6</sub>D<sub>6</sub> at 78 °C for 48 h, producing *trans*-(TMS)CH=CHSiH<sub>2</sub>Ph (**11**; 15%), (TMS)C≡CSiH<sub>2</sub>Ph (**12**; 46%), and (TMS)CH=CH<sub>2</sub> (**20**; 39%). No reaction was observed at room temperature.

**(9) Catalytic Hydrosilylation Reaction as a Function of Substrate Stoichiometry.** (a) In a typical procedure, 0.079 mL of <sup>3</sup>PrC≡CH (0.768 mmol) and 0.158 mL of PhSiH<sub>3</sub> (1.536 mmol) were vacuum-transferred in a high-vacuum line into a J. Young NMR tube containing 10 mg of Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in 0.6 mL of THF-*d*<sub>6</sub>. The sealed tube was then heated in an oil bath at 65 °C for 4 h, producing *trans*-<sup>3</sup>PrCH=CHSiH<sub>2</sub>-Ph (**2**; 52%), <sup>3</sup>PrC≡CSiH<sub>2</sub>Ph (**5**; 6%), <sup>3</sup>PrCH=CH<sub>2</sub> (**8**; 17%), and the double-hydrosilylation product <sup>3</sup>PrCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**17**; 26%).

(b) In a typical procedure, 0.079 mL of <sup>3</sup>PrC≡CH (0.768 mmol) and 0.04 mL of PhSiH<sub>3</sub> (0.384 mmol) were vacuum-transferred in a high-vacuum line into a J. Young NMR tube containing 10 mg of Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in 0.6 mL of THF-*d*<sub>6</sub>. The sealed tube was then heated in an oil bath at 65 °C for 4 h, producing *trans*-<sup>3</sup>PrC(H)=C(H)SiH<sub>2</sub>Ph (**2**; 20%), <sup>3</sup>PrC≡CSiH<sub>2</sub>Ph (**5**; 11%), <sup>3</sup>PrCH=CH<sub>2</sub> (**8**; 48%), <sup>3</sup>PrCH=C(SiH<sub>2</sub>-Ph)<sub>2</sub> (**17**; 9%), and *trans*-<sup>3</sup>PrCH=CHSi(HPh)C≡CPr<sup>+</sup> (**21**; 13%).

**Characterization Data for 21.** <sup>1</sup>H NMR (200 MHz, THF-*d*<sub>6</sub>): δ 7.41–7.70 (m, 2H, *m*-H Ph), 7.25–7.37 (m, 3H, *o,p*-H Ph), 6.41 (dd, 1H, <sup>3</sup>J<sub>trans</sub> = 18.5 Hz, <sup>3</sup>J<sub>HH(Pr)</sub> = 6.15 Hz, HCP<sup>+</sup>), 5.67 (dd, 1H, <sup>3</sup>J<sub>trans</sub> = 18.5 Hz, <sup>3</sup>J<sub>HH(Si)</sub> = 2.7 Hz, HCSiHPh), 4.76 (d, 1H, <sup>3</sup>J = 2.7 Hz, PhSiH), 2.67 (m, 1H, CCHMe<sub>2</sub>), 2.36 (septet, 1H, <sup>3</sup>J = 3.9 Hz, CHMe<sub>2</sub>), 1.19 (d, 6H, <sup>3</sup>J = 3.88 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, <sup>3</sup>J = 3.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (50 MHz, THF-*d*<sub>6</sub>): δ 160.1 (d, <sup>1</sup>J = 151 Hz, HCP<sup>+</sup>), 135.9, 130.7, 128.7 (C–H Ph), 132.5 (s, CC<sub>5</sub>H<sub>5</sub>), 119.3 (d, <sup>1</sup>J = 135 Hz, HCSiHPh), 77.4 (s, C≡CPr<sup>+</sup>), 76.51 (s, C≡CPr<sup>+</sup>), 35.4 (d, <sup>1</sup>J = 126.8 Hz, CHMe<sub>2</sub>), 35.2 (d, <sup>1</sup>J = 126.8 Hz, CHMe<sub>2</sub>), 22.9 (q, <sup>1</sup>J = 127 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 22.1 (q, <sup>1</sup>J = 127 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>6</sub>): δ 11.78 (d, <sup>1</sup>J = 212.4 Hz, PhSiH). GC/MS data: *m/z* 242 (M<sup>+</sup>), 241 (M<sup>+</sup> - H), 227 (M<sup>+</sup> - CH<sub>3</sub>), 214 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 199 (M<sup>+</sup> - Pr<sup>+</sup>), 186 (M<sup>+</sup> - <sup>3</sup>Pr - CH), 173 (M<sup>+</sup> - <sup>3</sup>PrCHCH, 100%), 157 (M<sup>+</sup> - 173 - CH<sub>3</sub> - H), 131 (PhSiH<sub>2</sub>C≡C<sup>+</sup>), 105 (PhSi<sup>+</sup>), 69 (M<sup>+</sup> - <sup>3</sup>PrC≡CSiHPh).

**(10) Effect of Silane Substituents on the Catalytic Hydrosilylation Reactions.** (a) In a typical procedure, 0.079 mL of <sup>3</sup>PrC≡CH (0.77 mmol) and 0.158 mL of Ph<sub>2</sub>SiH<sub>2</sub> (0.78 mmol) were vacuum-transferred in a high-vacuum line into a J. Young NMR tube containing 10 mg of Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The sealed tube was then heated in an oil bath at 78 °C for 24 h, producing <sup>3</sup>PrC≡CSiHPh<sub>2</sub> (**22**; 47%), *trans*-<sup>3</sup>PrCH=CHSiHPh<sub>2</sub> (**23**; 4%), <sup>3</sup>PrCH=CH<sub>2</sub> (**8**; 39%), and the alkyne oligomerization products (dimers–pentamers, 7%).

**Characterization Data for 22.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.10–7.78 (m, 10H, Ph), 5.51 (s, 1H, Ph<sub>2</sub>SiH), 2.37 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.0 (d, 6H, <sup>3</sup>J = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.5, 130.1, 128.3, 132.4, 77.1, 34.5, 22.6. <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 11.37 (d, <sup>1</sup>J = 212.4 Hz, Ph<sub>2</sub>SiH). GC/MS data: *m/z* 250 (M<sup>+</sup>), 249 (M<sup>+</sup> - H), 233 (M<sup>+</sup>

- CH<sub>3</sub> - 2H), 207 (100%, M<sup>+</sup> - Pr<sup>+</sup>), 182 (Ph<sub>2</sub>Si<sup>+</sup>), 172 (M<sup>+</sup> - C<sub>6</sub>H<sub>6</sub>), 105 (PhSi<sup>+</sup>).

**GC/MS Data for 23:** *m/z* 252 (M<sup>+</sup>), 251 (M<sup>+</sup> - H), 237 (M<sup>+</sup> - CH<sub>3</sub>), 224 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 209 (M<sup>+</sup> - Pr<sup>+</sup>), 196 (M<sup>+</sup> - CHPr<sup>+</sup>), 183 (M<sup>+</sup> - CHCHPr<sup>+</sup>), 174 (M<sup>+</sup> - C<sub>6</sub>H<sub>6</sub>), 105 (PhSi<sup>+</sup>).

(b) In a typical procedure, 0.098 mL of <sup>3</sup>PrC≡CH (0.96 mmol) and 0.118 mL of PhMeSiH<sub>2</sub> (0.86 mmol) were vacuum-transferred in a high-vacuum line into a J. Young NMR tube containing 10 mg of Cp\*<sub>2</sub>ThMe<sub>2</sub> (0.0187 mmol) in 0.6 mL of C<sub>6</sub>D<sub>6</sub>. The sealed tube was then heated in an oil bath at 78 °C for 36 h, producing <sup>3</sup>PrC≡CSiHMePh (**24**; 31.1%) *trans*-<sup>3</sup>PrCH=CHSiHMePh (**25**; 2%), <sup>3</sup>PrCH=CH<sub>2</sub> (**8**; 20%), and the alkyne oligomerization products dimer (10%), trimer (traces), tetramers (1%), and pentamers (36%).

**Characterization Data for 24.** <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.10–7.70 (m, 5H, *o,p*-H Ph), 4.94 (q, 1H, <sup>3</sup>J = 4.14 Hz, PhMeSiH), 2.39 (m, 1H, CHMe<sub>2</sub>), 1.00 (d, 6H, <sup>3</sup>J = 7.48 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.39 (d, 3H, <sup>3</sup>J = 4.14 Hz, PhCH<sub>3</sub>SiH). <sup>13</sup>C-{<sup>1</sup>H} NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 134.7, 129.7, 128.2 (m, Ph), 132.4 (s, CC<sub>5</sub>H<sub>5</sub>), 79.9 (s, C≡CPr<sup>+</sup>), 78.6 (s, C≡CPr<sup>+</sup>), 34.8 (s, CHMe<sub>2</sub>), 22.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), -3.17 (s, PhCH<sub>3</sub>SiH). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 12.23 (d, <sup>1</sup>J = 223.4 Hz, PhMeSiH). GC/MS data: *m/z* 188 (M<sup>+</sup>), 187 (M<sup>+</sup> - H), 173 (M<sup>+</sup> - CH<sub>3</sub>), 161 (M<sup>+</sup> - C<sub>2</sub>H<sub>3</sub>), 145 (100%, M<sup>+</sup> - Pr<sup>+</sup>), 121 (M<sup>+</sup> - C≡CPr<sup>+</sup>), 105 (PhSi<sup>+</sup>).

**GC/MS Data for 25:** *m/z* 190 (M<sup>+</sup>), 189 (M<sup>+</sup> - H), 175 (M<sup>+</sup> - CH<sub>3</sub>), 162 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 147 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub> - CH<sub>3</sub>), 134 (M<sup>+</sup> - CHPr<sup>+</sup>), 121 (100%, M<sup>+</sup> - CHCHPr<sup>+</sup>), 105 (PhSi<sup>+</sup>), 69 (M<sup>+</sup> - PhSiHMe).

**(11) Synthesis of Cp\*<sub>2</sub>U(Me)(C≡CPr<sup>+</sup>)(**26**).** A 50 mL Schlenk tube was charged in the glovebox with 52 mg (0.097 mmol) of Cp\*<sub>2</sub>U<sub>2</sub>Me<sub>2</sub>. A 6 mL portion of C<sub>6</sub>H<sub>6</sub> was added to the Schlenk tube by vacuum transfer at -78 °C, and then 0.01 mL (0.097 mmol) of isopropylacetylene was vacuum-transferred. The solution was stirred at room temperature for 4 h. The reaction was monitored to completion by following the disappearance of the methyl signals of the starting complex. The mono(acetylide) complex Cp\*<sub>2</sub>U(Me)(C≡CPr<sup>+</sup>) (**1**) was formed together with the bis(acetylide) complex.

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.26 (s, 30H, Cp\*), -14.74 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.30 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), -37.39 (septet, 1H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CHMe<sub>2</sub>), -133.27 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.7 (s, C≡CCHMe<sub>2</sub>), 154.1 (s, C≡CCHMe<sub>2</sub>), 119.5 (s, C<sub>5</sub>Me<sub>5</sub>), 44.1 (d, <sup>1</sup>J = 122 Hz, CHMe<sub>2</sub>), -25.0 (q, <sup>1</sup>J = 125 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -29.5 (q, <sup>1</sup>J = 125 Hz, U-CH<sub>3</sub>), -45.2 (q, <sup>1</sup>J = 125 Hz, CH(CH<sub>3</sub>)<sub>2</sub>).

**(12) Synthesis of Cp\*<sub>2</sub>U(C≡CPr<sup>+</sup>)<sub>2</sub>(**27**).** A 50 mL Schlenk tube was charged in the glovebox with 52 mg (0.097 mmol) of Cp\*<sub>2</sub>U<sub>2</sub>Me<sub>2</sub>. A 6 mL portion of C<sub>6</sub>H<sub>6</sub> was added to the Schlenk tube by vacuum transfer at -78 °C, and then 0.02 mL (0.195 mmol) of isopropylacetylene was vacuum-transferred into the tube. The solution was stirred at room temperature for 4 h. The reaction was monitored to completion by following the disappearance of the methyl signal of the starting complex. The bis(acetylide) complex was also obtained quantitatively by addition of a second equivalent of isopropylacetylene (0.01 mL) to a solution of the mono(acetylide) complex Cp\*<sub>2</sub>U(Me)(C≡CPr<sup>+</sup>). Mp: 85 °C dec.

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 9.49 (s, 30H, Cp\*), -15.87 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), -38.03 (septet, 2H, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz, CHMe<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.0 (s, C≡CCHMe<sub>2</sub>), 154.0 (s, C≡CCHMe<sub>2</sub>), 119.1 (s, C<sub>5</sub>Me<sub>5</sub>), 39.7 (d, <sup>1</sup>J = 122 Hz, CHMe<sub>2</sub>), 19.4 (q, <sup>1</sup>J = 125 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -44.0 (q, <sup>1</sup>J = 125 Hz, CH(CH<sub>3</sub>)<sub>2</sub>).

**(13) Synthesis of Cp\*<sub>2</sub>Th(C≡CPr<sup>+</sup>)<sub>2</sub>(**28**).** A 50 mL Schlenk tube was charged in the glovebox with 50 mg (0.0939 mmol) of Cp\*<sub>2</sub>ThMe<sub>2</sub>. An 8 mL portion of C<sub>6</sub>H<sub>6</sub> was added to the Schlenk tube by vacuum transfer at -78 °C, and then 0.019 mL of isopropylacetylene (0.187 mmol) was vacuum-transferred into the tube. The solution was stirred at room temperature for 6 h. The reaction was monitored to completion by following the disappearance of the methyl signals of the

starting complex. The bis(acetylide) complex **3**, in the absence of an excess of alkyne, slowly decomposes at room temperature. Mp: 92 °C dec.

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 2.52 (septet, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CHMe<sub>2</sub>), 2.21 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.16 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 174.9 (s, C≡CCHMe<sub>2</sub>), 125.3 (s, C<sub>5</sub>Me<sub>5</sub>), 116.1 (s, C≡CCHMe<sub>2</sub>), 23.9 (q, <sup>1</sup>J = 125 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 21.6 (d, <sup>1</sup>J = 125 Hz, CHMe<sub>2</sub>), 11.7 (q, <sup>1</sup>J = 126 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

**(14) Synthesis of Cp\*<sub>2</sub>U(C≡CPr<sup>†</sup>)[C(PhSiH<sub>2</sub>)=C(H)Pr<sup>†</sup>]** (**29**). A 50 mL Schlenk tube was charged in the glovebox with 53 mg of Cp\*<sub>2</sub>U Me<sub>2</sub> (0.0985 mmol). A 10 mL portion of C<sub>6</sub>H<sub>6</sub> was added to the Schlenk tube by vacuum transfer at -78 °C followed by 0.02 mL of isopropylacetylene (0.195 mmol). The reaction mixture was stirred for 4 h, producing the bis(acetylide) complex Cp\*<sub>2</sub>U(C≡CPr<sup>†</sup>)<sub>2</sub>, as indicated by a change in color and also confirmed by spectroscopic methods. Then a 0.012 mL portion of PhSiH<sub>3</sub> (0.0985 mmol) was added by vacuum transfer, and the mixture was stirred for an additional 6 h, affording the quantitative formation of Cp\*U(C≡CPr<sup>†</sup>)-{C(PhSiH<sub>2</sub>)=CH(Pr<sup>†</sup>)}. Anal. Calcd for C<sub>36</sub>H<sub>52</sub>SiU: C, 57.60; H, 6.93. Found: C, 57.01; H, 7.00. Mp: 86 °C dec.

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 18.59 (s, 2H, <sup>1</sup>J<sub>H-Si</sub> = 192 Hz (satellites), PhSiH<sub>2</sub>), 9.67 (d, 2H, <sup>3</sup>J = 7.3 Hz, *o*-H Ph), 8.14 (t, 2H, <sup>3</sup>J = 7.3 Hz, *m*-H Ph), 7.83 (t, 2H, <sup>3</sup>J = 7.3 Hz, *p*-H Ph), 7.47 (d, 1H, <sup>3</sup>J = 5.7 Hz, =CH), 3.75 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -3.28 (d, 6H, <sup>3</sup>J = 6.8 Hz, =C-CH(CH<sub>3</sub>)<sub>2</sub>), -8.18 (m, 1H, =C-CHMe<sub>2</sub>), -15.87 (d, 6H, <sup>3</sup>J = 6.68 Hz, C-CH(CH<sub>3</sub>)<sub>2</sub>), -21.46 (septet, 1H, <sup>3</sup>J = 6.68 Hz, C-CHMe<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 247.8 (s, UC=CH), 231.0 (s, UC≡C), 162.1 (UC≡C), 138.4 (d, <sup>1</sup>J = 155 Hz, *o*-CH Ph), 135.6 (s, CC<sub>5</sub>H<sub>5</sub>), 135.5 (d, <sup>1</sup>J = 120 Hz, =CH), 130.9 (d, <sup>1</sup>J = 155 Hz, *m*-CH Ph), 129.8 (d, <sup>1</sup>J = 155 Hz, *p*-CH Ph), 128.3 (s, C<sub>5</sub>Me<sub>5</sub>), 107.3 (d, <sup>1</sup>J = 128.2 Hz, ≡C-CHMe<sub>2</sub>), 74.3 (d, <sup>1</sup>J = 128.2 Hz, =C-CHMe<sub>2</sub>), -24.9 (q, <sup>1</sup>J = 125.1 Hz, =C-CH(CH<sub>3</sub>)<sub>2</sub>), -32.7 (q, <sup>1</sup>J = 125.7 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -35.1 (q, <sup>1</sup>J = 125.1 Hz, ≡C-CH(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (79.5 Hz, C<sub>6</sub>D<sub>6</sub>): δ 34.33 (t, <sup>1</sup>J<sub>Si-H</sub> = 192 Hz, PhSiH<sub>2</sub>).

**(15) Synthesis of Cp\*<sub>2</sub>Th(C≡CPr<sup>†</sup>)[C(PhSiH<sub>2</sub>)=CH(Pr<sup>†</sup>)]** (**30**). A 50 mL Schlenk tube was charged into the glovebox with 52 mg of Cp\*<sub>2</sub>Th Me<sub>2</sub> (0.0977 mmol). A 10 mL portion of C<sub>6</sub>H<sub>6</sub> was added to the Schlenk flask by vacuum transfer at -78 °C followed by 0.02 mL of isopropylacetylene (0.195 mmol). The reaction mixture was stirred for 12 h at room temperature, producing the bis(acetylide) complex Cp\*<sub>2</sub>Th(C≡CPr<sup>†</sup>)<sub>2</sub>, as indicated by a change in color and confirmed by <sup>1</sup>H NMR spectroscopy. Then a 0.012 mL portion of PhSiH<sub>3</sub> (0.0985 mmol) was added by vacuum transfer and the reaction mixture was stirred for an additional 6 h, yielding quantitatively Cp\*Th(C≡CPr<sup>†</sup>){C(PhSiH<sub>2</sub>)=CH(Pr<sup>†</sup>)}. The color of the reaction mixture changed from pale yellow to dark red. Poisoning experiments with equimolar amounts of H<sub>2</sub>O allowed the production of the starting alkyne and the *cis*-hydrosilylated compound **14**. Anal. Calcd for C<sub>36</sub>H<sub>52</sub>SiUTh: C, 58.06; H, 6.99. Found: C, 56.70; H, 6.93. Mp: 90 °C dec.

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.80–7.82 (m, 2H, *m*-H Ph), 7.21–7.28 (m, 3H, *o,p*-H Ph), 6.79 (d, 1H, <sup>3</sup>J = 6.73 Hz, =CH), 5.27 (s, 2H, <sup>1</sup>J<sub>H-Si</sub> (satellites) = 203 Hz, PhSiH<sub>2</sub>), 3.17 (m, 1H, =CH-CHMe<sub>2</sub>), 2.68 (septet, 1H, <sup>3</sup>J = 6.94 Hz, ≡C-CHMe<sub>2</sub>), 2.07 (s, 30H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 1.26 (d, 6H, <sup>3</sup>J = 6.94 Hz, ≡C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.08 (d, 6H, <sup>3</sup>J = 6.44 Hz, =CH-CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>): δ 209.8 (s, ThC=CH), 156.8 (s, ThC≡C), 142.8 (d, <sup>1</sup>J = 119.2 Hz, ThC=CH), 135.8 (d, <sup>1</sup>J = 155 Hz, *o*-CH Ph), 129.3 (d, <sup>1</sup>J = 155 Hz, *m*-CH Ph), 135.3 (s, CC<sub>5</sub>H<sub>5</sub>), 128.2 (d, <sup>1</sup>J = 155 Hz, *p*-CH Ph), 123.8 (s, C<sub>5</sub>Me<sub>5</sub>), 120.6 (s, ThC≡C), 34.0 (d, <sup>1</sup>J = 129.2 Hz, =C-CHMe<sub>2</sub>), 24.18 (q, <sup>1</sup>J = 128.8 Hz, =C-CH(CH<sub>3</sub>)<sub>2</sub>), 22.7 (q, <sup>1</sup>J = 128.8 Hz, ≡C-CH(CH<sub>3</sub>)<sub>2</sub>), 21.8 (d, <sup>1</sup>J = 129.2 Hz, C-CHMe<sub>2</sub>), 11.6 (q, <sup>1</sup>J = 126.3 Hz, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). <sup>29</sup>Si NMR (79.5 Hz, C<sub>6</sub>D<sub>6</sub>): δ 5.9 (tdt, <sup>1</sup>J<sub>Si-H</sub> = 203.3 Hz, <sup>3</sup>J<sub>Si-H(C)</sub> = 23.2 Hz, <sup>3</sup>J<sub>Si-H(Ph)</sub> = 6.1 Hz, PhSiH<sub>2</sub>).

**(16) Kinetic Study of the Hydrosilylation of Terminal Alkynes with PhSiH<sub>3</sub>.** In a typical experiment, an NMR

sample was prepared as described in the typical NMR scale catalytic reactions section and maintained at -78 °C until kinetic measurements were initiated. The sealed tube was kept inside the probe of the NMR instrument, and at regular time intervals NMR data were acquired using eight scans with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration (*C*) was measured from the area (*A<sub>s</sub>*) of the <sup>1</sup>H-normalized signal of the solvent (*A<sub>b</sub>*). All the data collected could be convincingly least-squares-fit (*R* > 0.98) to eq 2, where *C*<sub>0</sub> (*C*<sub>0</sub> = *A<sub>s,0</sub>*/*A<sub>b,0</sub>*) is the initial concentration of substrate and *C*(*A<sub>s</sub>*/*A<sub>b</sub>*) is the substrate concentration at time *t*.

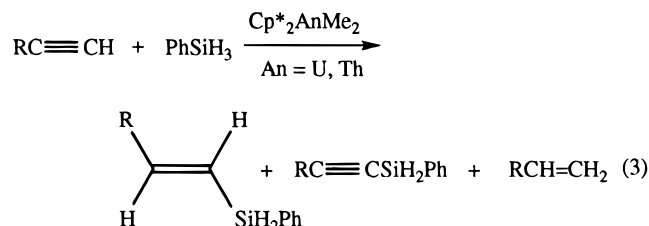
$$mt = \log(C/C_0) \quad (2)$$

The ratio of catalyst to substrate was accurately measured by calibration with internal FeCp<sub>2</sub>. Turnover frequencies (*N<sub>t</sub>*, h<sup>-1</sup>) were calculated from the least-squares-determined slopes (*m*) of the resulting plots. Typical initial alkyne and PhSiH<sub>3</sub> concentrations were in the range of 1.028–5.144 and 0.4264–4.264 M, respectively, and typical catalyst concentrations were in the range of 4.45–44.5 mM.

## Results

The goal of this investigation was to examine the scope, chemoselectivity, regioselectivity, actinide metal sensitivity, kinetics, and mechanism of the hydrosilylation reaction of terminal alkynes. This study represents an extension of the unique reactivities of organoactinides with alkynes in the presence of silanes and a complementary comparison to group 3, group 4, and organolanthanide chemistry.<sup>6,19</sup> In the following discussion, we focus on the reaction scope, metal effect, kinetics, rate law expression, and thermodynamics. We start the discussion with the reaction scope for the organoactinide-catalyzed hydrosilylation of terminal alkynes at room temperature.

**Organoactinide-Catalyzed Hydrosilylation of Terminal Alkynes. (i) Reaction Scope at Room Temperature.** The room-temperature reaction of Cp\*<sub>2</sub>-AnMe<sub>2</sub> (An = Th, U) with an excess of terminal alkynes RC≡CH (R = <sup>t</sup>Bu, <sup>i</sup>Pr, <sup>n</sup>Bu) and PhSiH<sub>3</sub> (alkyne:silane:catalyst = 40:40:1) in either benzene or tetrahydrofuran results in the catalytic formation of *trans*-vinylsilanes RCH=CHSiH<sub>2</sub>Ph (R = <sup>t</sup>Bu (**1**), <sup>i</sup>Pr (**2**), <sup>n</sup>Bu (**3**)), the dehydrogenated silylalkynes RC≡CSiH<sub>2</sub>Ph (R = <sup>t</sup>Bu (**4**), <sup>i</sup>Pr (**5**), <sup>n</sup>Bu (**6**)), and the corresponding alkenes RCH=CH<sub>2</sub> (R = <sup>t</sup>Bu (**7**), <sup>i</sup>Pr (**8**), <sup>n</sup>Bu (**9**)), as shown in eq 3



R = <sup>t</sup> Bu	<b>1</b>	<b>4</b>	<b>7</b>
<sup>i</sup> Pr	<b>2</b>	<b>5</b>	<b>8</b>
<sup>n</sup> Bu	<b>3</b>	<b>6</b>	<b>9</b>

**Table 1. Product Distributions of the Cp\*<sub>2</sub>AnMe<sub>2</sub> (An = Th, U) Catalyzed Hydrosilylation of Terminal Alkynes with PhSiH<sub>3</sub> at Room Temperature<sup>a</sup>**

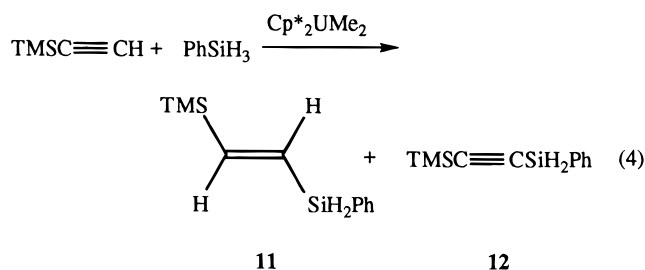
entry	cat.	R in RC≡CH	<i>trans</i> -RCH=CHSiH <sub>2</sub> Ph (%)	RC≡CSiH <sub>2</sub> Ph (%)	RCH=CH <sub>2</sub> (%)
1	Th	<sup>i</sup> Pr	42	28	26 (5) <sup>b</sup>
2	U	<sup>i</sup> Pr	62	27	12
3	Th	<sup>t</sup> Bu	48	28	24
4	U	<sup>t</sup> Bu	47	31	22
5	Th	<sup>n</sup> Bu	56	22	22
6	U	<sup>n</sup> Bu	74	24	2
7	Th	TMS	—	—	—
8	U	TMS	8	16	—

<sup>a</sup> When the reactions were carried out in either C<sub>6</sub>D<sub>6</sub> or THF-d<sub>8</sub> for both catalytic systems, no significant changes in the product selectivities were observed. <sup>b</sup> The number in parentheses corresponds to the alkane <sup>i</sup>PrCH<sub>2</sub>CH<sub>3</sub>.

(Table 1). Interestingly, for Cp\*<sub>2</sub>ThMe<sub>2</sub> and only for isopropylacetylene, the formation of the fully reduced alkane <sup>i</sup>PrCH<sub>2</sub>CH<sub>3</sub> (**10**) was observed.

Irrespective of the alkyl substituents and the metal center, the major product in the hydrosilylation reaction at room temperature is the *regio*- and stereoselective *trans*-vinylsilane, without any trace formation of the other two hydrosilylation isomers (*gem* or *cis*). For bulky alkynes (<sup>t</sup>BuC≡CH), the product distributions are nearly the same for both catalytic systems, whereas for other terminal alkynes, they vary from one catalytic system to another. It is worth pointing out that in the hydrosilylation reaction of the alkynes with Cp\*<sub>2</sub>ThMe<sub>2</sub> and PhSiH<sub>3</sub>, similar amounts of both the alkene and the corresponding silylalkyne are obtained. This result suggests a mechanistic pathway involving two organometallic complexes that are formed in a consecutive fashion, each one being responsible only for one of the products.

The reaction of Cp\*<sub>2</sub>UMe<sub>2</sub> with (TMS)C≡CH (TMS = Me<sub>3</sub>Si) and PhSiH<sub>3</sub> at room temperature is very slow, producing only, after 48 h, 8% and 16% of *trans*-(TMS)-CH=CHSiH<sub>2</sub>Ph (**11**) and the silylalkyne (TMS)C≡CSiH<sub>2</sub>Ph (**12**), respectively (eq 4). For the analogous

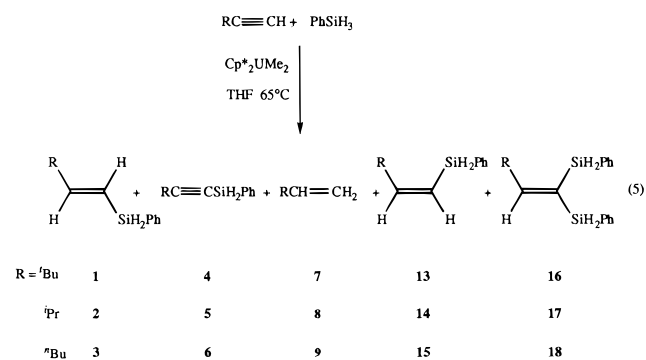


Cp\*<sub>2</sub>ThMe<sub>2</sub>, with (TMS)C≡CH and PhSiH<sub>3</sub> no hydrosilylation or dehydrogenative coupling products were observed under similar reaction conditions. In addition, neither the oligomerization dimer nor trimers of the (TMS)C≡CH were observed.<sup>14</sup>

**(ii) Reaction Scope at High Temperature.** At high temperature (65–78 °C), the chemoselectivity and the regioselectivity of the vinylsilanes formed in the organoactinide-catalyzed hydrosilylation of terminal alkynes with PhSiH<sub>3</sub> were found to be different, as compared to the hydrosilylation results obtained at room tempera-

ture. The reactions were found to be sensitive to the nature of the catalysts, the substituent on the alkyne and silanes, the stoichiometry of the substrates, and the polarity of the solvents.

The hydrosilylation of RC≡CH (R = <sup>t</sup>Bu, <sup>i</sup>Pr, <sup>n</sup>Bu) with PhSiH<sub>3</sub> catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub> (alkyne:silane:catalyst = 40:40:1) at high temperature (65–78 °C) produced, in addition to the hydrosilylation products at room temperature (eq 3), the corresponding *cis*-hydrosilylated compounds *cis*-RCH=CHSiH<sub>2</sub>Ph (R = <sup>t</sup>Bu (**13**), <sup>i</sup>Pr (**14**), <sup>n</sup>Bu (**15**)), and small to moderate yields of the *unexpected* double-hydrosilylation products RCH=C(SiH<sub>2</sub>-Ph)<sub>2</sub> (R = <sup>t</sup>Bu (**16**), <sup>i</sup>Pr (**17**), <sup>n</sup>Bu (**18**)), in which the two silyl moieties are attached to the same carbon atom (eq 5) (Table 2). For the bulky substituents (<sup>t</sup>Bu), a maxi-



imum yield of 19% for the double-hydrosilylation product <sup>t</sup>BuCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**16**), was obtained, whereas for <sup>n</sup>BuC≡CH or <sup>i</sup>PrC≡CH only ~3% of the corresponding double-hydrosilylated products **17** and **18** were obtained. The amounts of either the *cis* isomers **13**–**15** or the corresponding silylalkynes **4**–**6** are much higher than those of the *trans* isomers (**1**–**3**), which were the major hydrosilylated products at room temperature. These results strongly suggest a competing pathway toward the *cis* isomers at high temperature. A comparison of the concentrations of the silylalkyne and the corresponding alkene for each alkyne shows that each catalytic system gives a different ratio of the two products. This result suggests that, at high temperature, an additional competing route is responsible for the formation of both the alkene and the silylalkyne. Furthermore, it seems also possible that the silylalkyne may be transformed, during the catalytic cycle, to other products, inducing a lower concentration, as compared to the corresponding alkene (entries 2, 3, 5, 8, 11, and 12 in Table 2).

The corresponding hydrosilylation reactions using Cp\*<sub>2</sub>ThMe<sub>2</sub> with PhSiH<sub>3</sub> and the terminal alkynes RC≡CH (R = <sup>t</sup>Bu, <sup>i</sup>Pr, <sup>n</sup>Bu) (alkyne:silane:catalyst = 40:40:1), at high temperature, follow the regioselectivity and chemoselectivity as obtained for the hydrosilylation reaction at room temperature (eq 3). The only difference was found for isopropylacetylene, for which no fully hydrogenated alkane **10** was produced and the double-hydrosilylated product <sup>i</sup>PrCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> (**14**) was obtained in 2% yield (C<sub>6</sub>D<sub>6</sub>) or up to 6% (THF), as confirmed from the <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra. The use of a polar solvent increased the yield of the hydrogenated products RCH=CH<sub>2</sub> (**7** and **8**) as compared to that for the reaction carried out in C<sub>6</sub>D<sub>6</sub>, under similar reaction conditions (entries 1 and 2 or 4 and 5



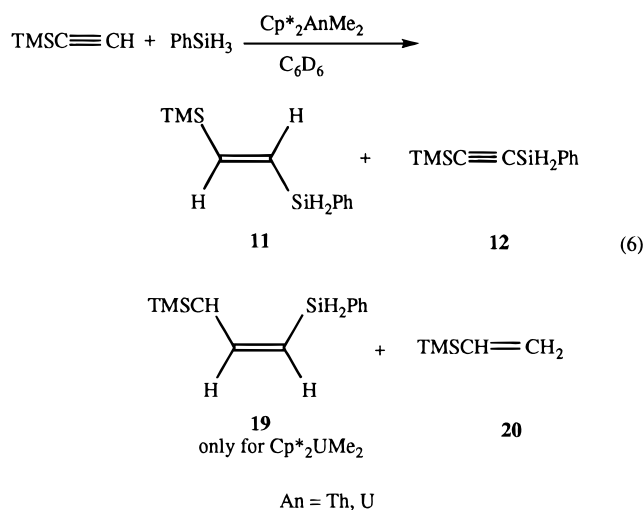
**Table 2. Product Distributions of the Cp\*<sub>2</sub>AnMe<sub>2</sub> (An = Th, U) Catalyzed Hydrosilylation of RC≡CH with PhSiH<sub>3</sub> at High Temperature<sup>a</sup>**

entry	cat.	R	solvent	RCH=C(SiH <sub>2</sub> Ph) <sub>2</sub> (%)	trans-RCH=CHSiH <sub>2</sub> Ph (%)	cis-RCH=CHSiH <sub>2</sub> Ph (%)	RC≡CSiH <sub>2</sub> Ph (%)	RCH=CH <sub>2</sub> (%)
1	Th	<sup>i</sup> Pr	C <sub>6</sub> D <sub>6</sub>	2	37	trace	38	23
2	Th	<sup>i</sup> Pr	THF	6	33	trace	25	36
3	U	<sup>i</sup> Pr	THF	2	4	27	31	35
4	Th	<sup>t</sup> Bu	C <sub>6</sub> D <sub>6</sub>	trace	21	trace	46	37
5	Th	<sup>t</sup> Bu	THF	trace	21	trace	31	48
6	U	<sup>t</sup> Bu	THF	19	15	24	36	7
7	Th	<sup>n</sup> Bu	C <sub>6</sub> D <sub>6</sub>	trace	43	trace	34	23
8	U	<sup>n</sup> Bu	THF	3	5	54	9	16
9	Th	TMS	C <sub>6</sub> D <sub>6</sub>	—	15	—	46	39
10	U	TMS	THF	—	6	26	40	29
11	Th <sup>b</sup>	<sup>i</sup> Pr	THF	26	52	trace	6	17
12	Th <sup>c</sup>	<sup>i</sup> Pr	THF	9	20 (13) <sup>d</sup>	trace	11	48

<sup>a</sup> The reactions were carried in either reflux of C<sub>6</sub>D<sub>6</sub> or THF-d<sub>8</sub>. <sup>b</sup> A stoichiometric ratio of 1:2 for <sup>i</sup>PrC≡CH:PhSiH<sub>3</sub> was used. <sup>c</sup> A stoichiometric ratio of 2:1 for <sup>i</sup>PrC≡CH:PhSiH<sub>3</sub> was used. <sup>d</sup> The number in parentheses corresponds to trans-<sup>i</sup>PrCH=CHSi(H)(Ph)C≡CPr<sup>i</sup>.

in Table 2). Whereas Cp\*<sub>2</sub>UMe<sub>2</sub> catalyzed the hydrosilylation of terminal alkynes at high temperature, yielding a mixture of both *cis*- and *trans*-vinylsilanes, *strikingly*, the analogue Cp\*<sub>2</sub>ThMe<sub>2</sub> afforded only the *trans*-vinylsilane.

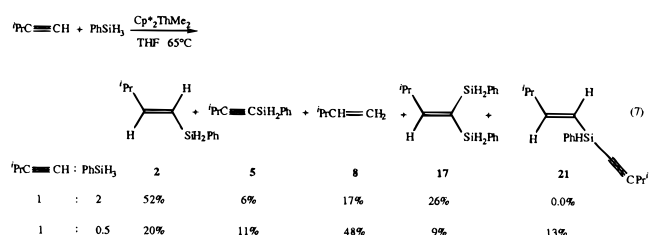
In the high-temperature hydrosilylation reaction of (trimethylsilyl)acetylene with PhSiH<sub>3</sub> catalyzed by Cp\*<sub>2</sub>UMe<sub>2</sub>, besides the *trans*-vinylsilane (**11**) and the silylalkyne (**12**) products, which were also obtained at room temperature, the *cis*-vinylsilane (**19**) and the olefin (TMS)CH=CH<sub>2</sub> (**20**) were obtained in good yields (eq 6 and Table 2). For Cp\*<sub>2</sub>ThMe<sub>2</sub>, in contrast to the room-



temperature reaction, in which no products were found, the same products as in the hydrosilylation reaction promoted by Cp\*<sub>2</sub>UMe<sub>2</sub> were formed except for the *cis*-vinylsilane (**19**) (eq 6). In neither case was the double hydrosilylation of (TMS)C≡CH observed.

**(iii) Effect of the Ratio of Alkyne to Silane.** A basic conceptual question regarding the effect of PhSiH<sub>3</sub> toward the formation of the different products was investigated by performing two parallel experiments. Two reactions were designed in which the concentration ratio between the catalyst and alkyne was maintained constant (1:40) but the concentration of PhSiH<sub>3</sub> as compared to that of the alkyne was either doubled or reduced to half. We have found that the chemoselectivity and regioselectivity of the products are highly dependent

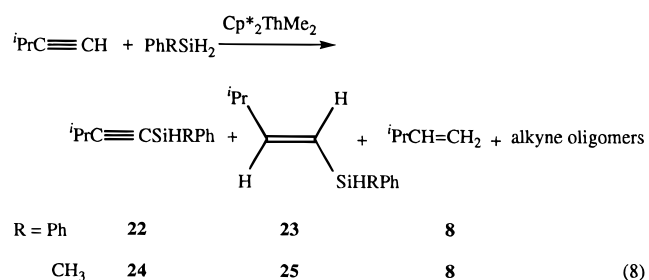
on the silane concentrations (eq 7).



Thus, when the hydrosilylation reaction is carried out using a 1:2 ratio of <sup>i</sup>PrC≡CH to PhSiH<sub>3</sub> with Cp\*<sub>2</sub>ThMe<sub>2</sub> in THF (65 °C), the *trans*-vinylsilane is the major product of the reaction (52%). The amount of the double-hydrosilylation product **17** is increased to 26%, as compared to the 6% obtained using a 1:1 ratio among the substrates (eq 7 and Table 2, entry 11). When the reaction is conducted under the same conditions, but with an opposite ratio between the substrates (<sup>i</sup>PrC≡CH:PhSiH<sub>3</sub> = 0.5), the olefin <sup>i</sup>PrCH=CH<sub>2</sub> (**8**) was found to be the major product. In addition to *trans*-<sup>i</sup>PrCH=CHSiH<sub>2</sub>Ph (**2**), <sup>i</sup>PrC≡CSiH<sub>2</sub>Ph (**5**), and the double-hydrosilylated olefin **17**, the tertiary silane *trans*-<sup>i</sup>PrCH=CHSi(HPh)(C≡CPr<sup>i</sup>) (**21**) was also observed. This last compound is obtained as the metathesis dehydrocoupling product from the reaction of the *trans*-alkenylsilane with the metal acetylide complex (vide infra).

#### (iv) Effect of the Silane Substituent in the Hydrosilylation Reaction at High Temperature.

The inductive and steric effects of the silane substituents for the Cp\*<sub>2</sub>ThMe<sub>2</sub>-catalyzed hydrosilylation reaction of <sup>i</sup>PrC≡CH were studied (eq 8, Table 3). Replacing



one hydrogen on PhSiH<sub>3</sub> by either an alkyl or a phenyl

**Table 3. Product Distributions of the Cp\*<sub>2</sub>ThMe<sub>2</sub> Catalyzed Hydrosilylation of <sup>i</sup>PrC≡CH with PhRSiH<sub>2</sub><sup>a</sup>**

entry	R	reacn time (h)	<sup>i</sup> PrC≡CSiHRPh (%)	<i>trans</i> - <sup>i</sup> PrCH=CHSiHRPh (%)	<sup>i</sup> PrCH=CH <sub>2</sub> (%)	alkyne oligomers (%)
1	H <sup>b</sup>	12	38	37	23	—
2	Ph	24	47	4	39	11
3	Me	36	31	2	20	47

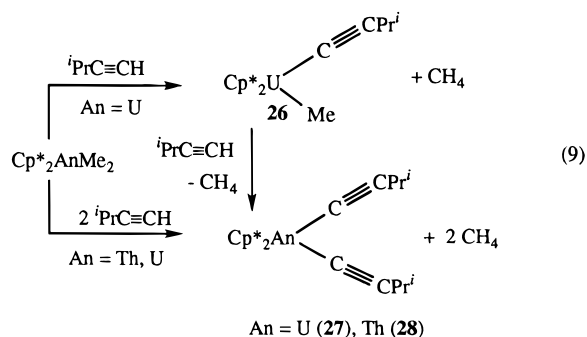
<sup>a</sup> The reaction was carried out in C<sub>6</sub>D<sub>6</sub> at 78 °C. <sup>b</sup> A yield of 2.2% of the double-hydrosilylation product <sup>i</sup>PrCH=C(SiH<sub>2</sub>Ph)<sub>2</sub> was observed.

ring generates a retardation in the rate of the hydrosilylation reaction as compared to the rate obtained utilizing phenylsilane. Moreover, the selectivities of the products were significantly different as compared to those obtained using PhSiH<sub>3</sub> as the hydrosilylating agent.

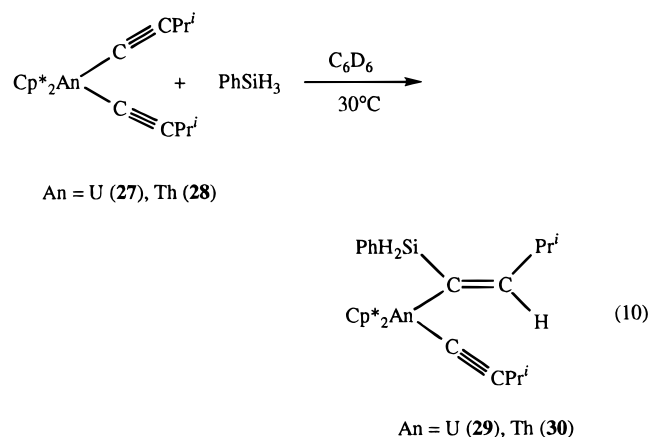
The reaction of an equimolar mixture of <sup>i</sup>PrC≡CH and Ph<sub>2</sub>SiH<sub>2</sub> in the presence of a catalytic amount of Cp\*<sub>2</sub>ThMe<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 78 °C produced the silylalkyne adduct <sup>i</sup>PrC≡CSiHPh<sub>2</sub> (**22**) and the alkene <sup>i</sup>PrCH=CH<sub>2</sub> (**8**) as the major products. Trace amounts of the hydrosilylation product <sup>i</sup>PrCH=CHSiHPh<sub>2</sub> (**23**) was identified by GC/MS spectroscopy, together with the alkyne oligomerization products (dimer–pentamers). The reaction of PhMeSiH<sub>2</sub> with <sup>i</sup>PrC≡CH under similar reaction conditions afforded large amounts of <sup>i</sup>PrC≡CSiHMePh (**24**), <sup>i</sup>PrCH=CH<sub>2</sub> (**8**), and alkyne oligomerization products (dimer–pentamers), in addition to a small quantity of *trans*-<sup>i</sup>PrCH=CHSiHMePh (**25**) (entries 2 and 3, Table 3). This result indicates that, for secondary silanes, the insertion of an alkyne into the active bis(acetylide)-actinide complex, inducing the oligomerization reaction,<sup>14</sup> is in competition with the dehydrogenative coupling reaction, producing the corresponding silylalkynes and the other observed products (vide infra).

**Stoichiometric Reactions and Trapping of the Key Organometallic Intermediate Complex.** To detect some of the key organometallic intermediates in the hydrosilylation process, a consecutive series of stoichiometric reactions were carried out, using the organoactinide precursor Cp\*<sub>2</sub>AnMe<sub>2</sub> (An = Th, U), <sup>i</sup>PrC≡CH, and PhSiH<sub>3</sub>. The stoichiometric reaction of PhSiH<sub>3</sub> with Cp\*<sub>2</sub>ThMe<sub>2</sub> induced the dehydrogenative coupling of the silane to the dimer and trimer, as already reported in the literature.<sup>27</sup> Since we have not been able to detect any traces of these dimers or oligomers for either organometallic complex, we decided to start the stoichiometric reaction studies from the addition of 1 and/or 2 equiv of <sup>i</sup>PrC≡CH to a benzene solution of Cp\*<sub>2</sub>AnMe<sub>2</sub> at room temperature.

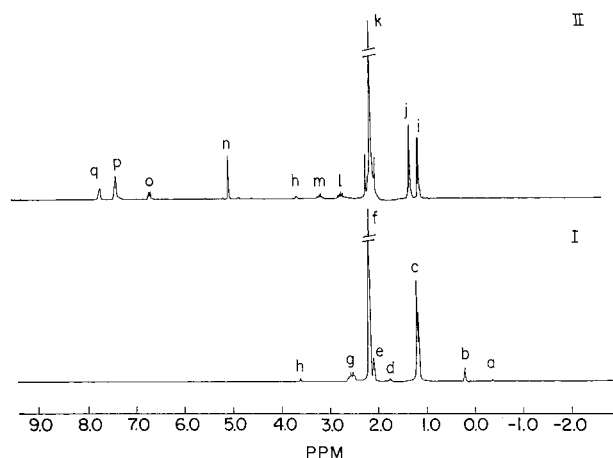
The reactions of the organoactinide metallocene complexes Cp\*<sub>2</sub>AnMe<sub>2</sub> (An = Th, U; Cp\* = C<sub>5</sub>Me<sub>5</sub>) with alkynes in stoichiometric amounts allow the preparation and characterization of mono- and bis(acetylide) complexes of organoactinides, as described in eq 9.



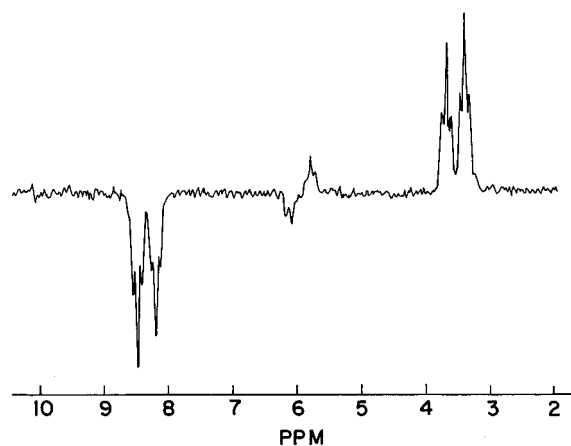
When an equivalent amount of <sup>i</sup>PrC≡CH was added to a benzene solution of Cp\*<sub>2</sub>U<sub>2</sub>Me<sub>2</sub> at room temperature, methane gas evolved, leading to the formation of the orange mono(acetylide) methyl complex Cp\*<sub>2</sub>U(C≡CPr<sup>i</sup>)(Me) (**26**). This transient species was found to be very reactive, and the consecutive addition of a second equivalent of <sup>i</sup>PrC≡CH converted complex **26** rapidly into the deep red-brown bis(acetylide) complex Cp\*<sub>2</sub>U(C≡CPr<sup>i</sup>)<sub>2</sub> (**27**). Due to the paramagnetic behavior of the uranium(IV) complexes and the rapid electron spin–lattice relaxation times, chemically and magnetically nonequivalent ligand protons in **26** and **27** exhibit generally sharp, well-separated signals and can be readily resolved in the <sup>1</sup>H NMR spectra. Attempts to spectroscopically trap any other mono(acetylide) methyl organoactinide complexes were unsuccessful. For thorium, the reaction with stoichiometric amounts of <sup>i</sup>PrC≡CH produced half the amount of the bis(acetylide) complex Cp\*<sub>2</sub>Th(C≡CPr<sup>i</sup>)<sub>2</sub> (**28**). Addition of 1 equiv of PhSiH<sub>3</sub> at room temperature to a benzene solution of any of the bis(acetylide) organoactinide complexes afforded the quantitative formation of the silylalkenyl acetylide actinide complexes Cp\*<sub>2</sub>An(PhSiH<sub>2</sub>C=CH<sup>i</sup>Pr)(C≡C<sup>i</sup>Pr) (An = U (**29**), Th (**30**)), which were found to be intermediates in the catalytic cycle for the hydrosilylation reactions (eq 10).



The formation of such an intermediate was indicated by the change in color of the reaction from orange to dark orange-brown for complex **29** and from pale yellow to dark red for **30**. Both of the complexes were found to be stable in their solutions for long periods of time under an inert atmosphere. The structures of **29** and **30** were unambiguously confirmed by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy as well as by NOE experiments. The <sup>1</sup>H NMR spectra of **29** and **30** each displayed, in addition to the signals for the phenyl and Cp\* protons, two signals for the CH<sub>3</sub> protons (two different isopropyl groups), two signals for the CH–(CH<sub>3</sub>)<sub>2</sub> protons, and one signal for each of the olefinic CH and silane (SiH<sub>2</sub>) protons. Figure 1 shows the comparison of the <sup>1</sup>H NMR



**Figure 1.** (I)  $^1\text{H}$  NMR spectrum of  $\text{Cp}^*_2\text{Th}(\text{C}\equiv\text{CPr}^i)_2$  in  $\text{THF}-d_8$  (signals marked as d and h). The signals marked a and e correspond to the methyl and  $\text{Cp}^*$  signals of remaining  $\text{Cp}^*_2\text{ThMe}_2$ . Signal b corresponds to  $\text{CH}_4$ , and the signals c, f, and g, correspond to the  $\text{CH}_3$ ,  $\text{Cp}^*$ , and CH hydrogens of  $\text{Cp}^*_2\text{Th}(\text{C}\equiv\text{CPr}^i)_2$ , respectively. (II)  $^1\text{H}$  NMR spectra of  $\mathbf{30}$  in  $\text{THF}-d_8$ . Signals i, j, and l, m correspond to the  $\text{CH}_3$  and CH hydrogens of the two different isopropyl groups, respectively. Signals k, n, and o correspond to the  $\text{Cp}^*$ ,  $\text{SiH}_2$ , and vinylic CH protons, respectively. Signals p and q correspond to the aromatic hydrogens.

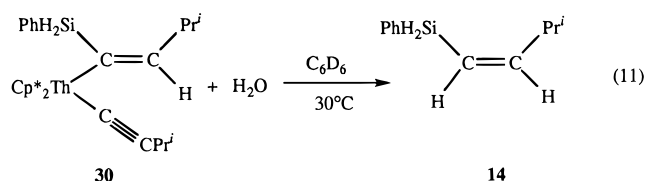


**Figure 2.**  $^{29}\text{Si}$  INEPT spectrum of complex  $\mathbf{30}$  at 300 K.

spectra for complexes  $\mathbf{28}$  and  $\mathbf{30}$ . In Figure 1(II), the downfield doublet signal at 6.79 ppm ( $^3J = 6.73$  Hz) is assigned to the olefinic proton, split by the CH proton of the isopropyl group, indicating that both isopropyl and olefinic proton moieties are in *gem* positions in the organometallic complex.

The signal at 5.27 ppm corresponds to the  $\text{SiH}_2$  protons ( $^1J_{\text{SiH}}(\text{satellite}) = 203$  Hz). Interestingly, the proton-coupled  $^{29}\text{Si}$  NMR of  $\mathbf{30}$  (Figure 2) displays a triplet signal at 5.9 ppm ( $^1J_{\text{Si-H}} = 203.3$  Hz), which is split into a doublet due to the *trans* vinylic hydrogen ( $^3J_{\text{Si-H}} = 23.19$  Hz), which is also split into a triplet by the *ortho* hydrogens of the phenyl ring ( $^3J_{\text{Si-H}} = 6.19$  Hz). For the corresponding complex  $\mathbf{29}$ , the signal is observed at 34.33 ppm ( $^1J_{\text{Si-H}} = 192$  Hz). Low-temperature INEPT measurements ( $-50$  °C) induced neither a broadening of the signals nor a reduction in the  $J$  couplings. This result argues that even at low temperature no  $\eta^2\text{-Th-H-Si}$  interactions are detected, indicating the rapidity of such a process if operative.<sup>19a</sup> The geometric arrangement of the silyl group with regard

to the isopropyl group in the organometallic complex was found to be *cis*. The full stereochemical assignment of the signals, in each of the complexes, was confirmed by NOE experiments. For example, irradiation at the CH proton of the isopropyl group in the silylalkenyl moiety in  $\mathbf{30}$  enhanced the corresponding  $\text{PhSiH}_2$  and methyl signals in the  $^1\text{H}$  NMR by 3.12% and 1.56%, respectively. A corroboration for the stereochemistry of the organometallic intermediate  $\mathbf{30}$  was found by a quenching experiment of  $\mathbf{30}$  with  $\text{H}_2\text{O}$ . The addition of an equimolar amount of water to complex  $\mathbf{30}$  generated the corresponding *cis*-vinylsilane product  $\mathbf{14}$  (eq 11).



Further addition of a second equivalent or even an excess of  $\text{PhSiH}_3$  or alkyne to complex  $\mathbf{29}$  or  $\mathbf{30}$  did not change the complex into a new organometallic compound. After long periods of time, some decomposition of the complexes was observed and the *gem* dimer was found in the reaction mixture. This result strongly suggests that, at room temperature, neither the silane nor the alkyne is able to induce the  $\sigma$ -bond metathesis or protonolysis of the hydrosilylated alkene or the alkyne. The addition of an excess of alkyne at room temperature to complex  $\mathbf{30}$ , *only* in the presence of  $\text{PhSiH}_3$ , yields the *trans*-hydrosilylated alkyne, alkene, silylalkyne, and bis(acetylide) complex. This result indicates that the silane is responsible for the  $\sigma$ -bond metathesis of a different organometallic complex leading to the *trans*-hydrosilylated product, which must be in equilibrium with the organoactinide complex  $\mathbf{30}$ . This equilibrium is proposed due to the *trans* stereochemistry of the observed products as compared to the expected *cis* stereochemistry, if the intermediate organoactinide  $\mathbf{30}$  were to undergo protonolysis. This result also corroborates a consecutive pathway for the formation of the silylalkyne and alkene as presented in the room-temperature scope of the reaction (vide supra).

When complex  $\mathbf{30}$  is warmed with  $\text{PhSiH}_3$ , the double-hydrosilylation compound  $\text{RCH}=\text{C}(\text{SiH}_2\text{Ph})_2$  is produced. This result indicates that  $\text{PhSiH}_3$  is not the protonolytic source, suggesting that the possible Th-Si bond is not formed. When complex  $\mathbf{29}$  is warmed with 1 equiv of alkyne, the *cis*-vinylsilane product is obtained. Similar reaction of  $\mathbf{29}$  with 1 equiv of  $\text{PhSiH}_3$  produces the double-hydrosilylation product. These high-temperature results account for the alkyne as the major protonolytic agent, whereas the Si-H bond will induce the  $\sigma$ -bond metathesis, producing the double-hydrosilylation product and the corresponding organometallic hydrides.

**Kinetic Studies on the Hydrosilylation of  $^i\text{PrC}\equiv\text{CH}$  with  $\text{PhSiH}_3$  Catalyzed by  $\text{Cp}^*_2\text{ThMe}_2$ .** A kinetic study of the  $\text{Cp}^*_2\text{ThMe}_2$ -catalyzed hydrosilylation of  $^i\text{PrC}\equiv\text{CH}$  with  $\text{PhSiH}_3$  in  $\text{C}_6\text{D}_6$  was carried out by in situ  $^1\text{H}$  NMR spectroscopy. The reaction of an  $\sim 40$ -fold excess of  $^i\text{PrC}\equiv\text{CH}$  was monitored with constant phenylsilane and catalyst concentration at 303 K, until

complete disappearance of the normalized  $\text{C}\equiv\text{CH}$  ( $\delta$  1.83 ppm) signal in the  $^1\text{H}$  NMR. The turnover frequency of the reaction was calculated from the slope of the kinetic plots of substrate to catalyst ratio vs time. When the initial concentrations of  $\text{PhSiH}_3$  and catalyst were held constant and the concentration of the alkyne was varied over a 10-fold concentration range, a plot of the reaction rate vs alkyne concentration displayed a linear dependence, indicating that the reaction has a first-order dependence on alkyne.<sup>28</sup> When the concentrations of the alkyne and catalyst were maintained constant and the concentration of  $\text{PhSiH}_3$  was varied over a 10-fold concentration range, a plot of the reaction rate vs silane concentration also displays a linear dependence indicating that the reaction has a first-order dependence on silane.<sup>28</sup> When the concentrations of alkynes and  $\text{PhSiH}_3$  were kept constant and the concentration of the catalyst was varied over a 10-fold concentration range, a plot of the reaction rate vs precatalyst concentration indicated the reaction to be first order in catalyst.<sup>28</sup> When all these facts are taken together, the empirical rate law expression for the  $\text{Cp}^*_2\text{ThMe}_2$ -catalyzed hydrosilylation of  $^i\text{PrC}\equiv\text{CH}$  with  $\text{PhSiH}_3$  can be given by eq 12. The derived rate constant for the production of **2** at 30 °C is  $k = [1.13(5)] \times 10^{-3} \text{ s}^{-1}$ .

$$\nu = k[^i\text{PrC}\equiv\text{CH}][\text{PhSiH}_3][\text{Cp}^*_2\text{ThMe}_2] \quad (12)$$

A similar kinetic dependence on alkyne,  $\text{PhSiH}_3$ , and catalyst concentrations is observed over a 30–80 °C temperature range. The derived activation parameters  $E_a$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  from an Eyring analysis are 6.9(3) kcal  $\text{mol}^{-1}$ , 6.3(3) kcal  $\text{mol}^{-1}$ , and 51.1(5) eu, respectively.<sup>28</sup>

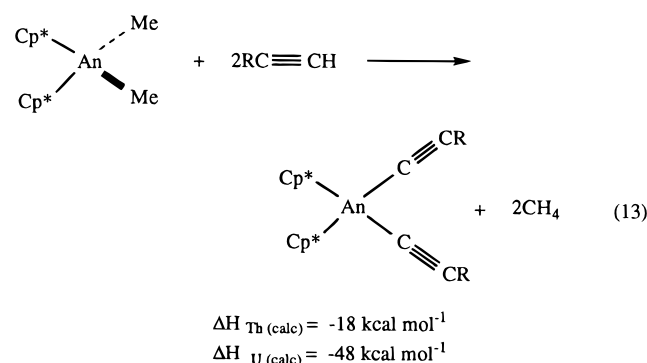
## Discussion

The discussion of the results will be presented by starting with some controlling experiments detailed in the literature that show the versatility of these organoactinides toward the hydrosilylation reaction. Then we will present a thorough discussion regarding the formation of the organoactinide bis(acetylide) complexes, the key organoactinide mono(acetylide) silaalkenyl complexes, the reaction scope, and the mechanistic implications.

**Controlling Experiments.** The catalytic reaction of the actinides  $\text{Cp}^*_2\text{AnMe}_2$  (An = Th, U) with an excess of terminal alkynes, at high temperature ( $T > 80$  °C) and in the absence of silanes, induces the alkyne oligomerization reaction (dimers–heptamers).<sup>14a,b</sup> In this process the bis(acetylide) complexes, which are rapidly formed at room temperature, were found to be the active species. The reaction of  $\text{Cp}^*_2\text{UMe}_2$  with an excess of  $\text{PhSiH}_3$  in the absence of alkyne, induces the dehydrogenative coupling of the silane toward oligomers, whereas the reaction with  $\text{Cp}^*_2\text{ThMe}_2$  produces the dehydrogenated dimer and the corresponding  $[\text{Cp}^*_2\text{ThH}(\mu\text{-H})_2]$ .<sup>27</sup> Interestingly, for these types of organoactinides no actinide–silyl complexes have been isolated. The uranium–silicon bond dissociation enthalpies have been measured to be as low as ca.  $37 \pm 3$  kcal

$\text{mol}^{-1}$ , arguing presumably for the high reactivity of these actinide–silyl bonds.<sup>29</sup> Since no dehydrogenative coupling products of  $\text{PhSiH}_3$  or alkyne oligomers are observed for the catalytic reaction between alkyne and  $\text{PhSiH}_3$ , we focus our studies on the stoichiometric reactions, at room temperature, starting from the bis(acetylide) complexes.

**Synthesis of Bis(acetylide) and Mono(acetylide)–Silaalkenyl Actinide Complexes: Stoichiometric Reactions.** The  $\sigma$ -bond metathesis reaction of the acidic proton of a terminal alkyne with an organoactinide complex of the type  $\text{Cp}^*_2\text{AnMe}_2$  (An = Th, U) is a fast reaction which is thermodynamically driven by the elimination of methane. A number of bis(acetylide) complexes can be easily prepared and characterized.<sup>13b,14</sup> The enthalpy of reaction for such a process is highly exothermic and can be calculated from tabulated bond disruption energies that have been measured for these organoactinide complexes (eq 13).<sup>29a,30</sup>



The mono(acetylide) complex was only observed, as a transient organometallic moiety, for the uranium complex with isopropylacetylene (**26**). Stoichiometric reactions for other alkynes did not form the mono(acetylide) complex but rather the bis(acetylide) complexes, indicating that the second  $\sigma$ -bond metathesis has an energy of activation much lower than that of the corresponding first  $\sigma$ -bond metathesis. The symmetric NMR spectra which are obtained for these bis(acetylide) complexes, similarly to other early-transition-metal bis(acetylide) complexes,<sup>31</sup> indicate that they do not form bridging acetylide species as in the group 3/organolanthanide complexes. Interestingly, only when  $\text{Cp}^*_2\text{HfCl}_2$  is reacted with an excess of  $\text{NaC}\equiv\text{CH}$  is the mono(acetylide) bridging complex  $\text{Cp}^*_2(\text{C}\equiv\text{CH})\text{HfC}\equiv\text{CHf}(\text{C}\equiv\text{CH})\text{Cp}^*_2$  obtained.<sup>32</sup>

The reaction of either **27** or **28** with  $\text{PhSiH}_3$  induced the quantitative isolation of complex **29** or **30**, for uranium and thorium, respectively. These complexes are formed by the  $\sigma$ -bond metathesis of complexes **27** and **28** by the silane, forming the corresponding actinide

(29) (a) King, W. A.; Marks, T. J. *Inorg. Chim. Acta* **1995**, *229*, 343. (b) Radu, N. S.; Engeler, M. P.; Gerlach, C. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 3261.

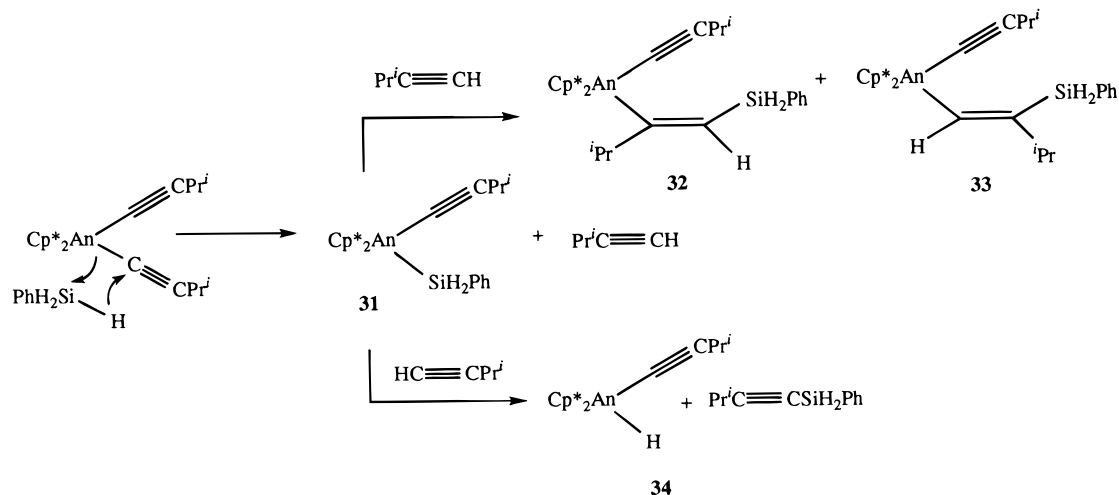
(30) (a) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. *ACS Symp. Ser.* **1990**, *428*, 159. (b) Marthino Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.

(31) For related group IV bis(acetylide) compounds, see: (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Augermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. (b) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.

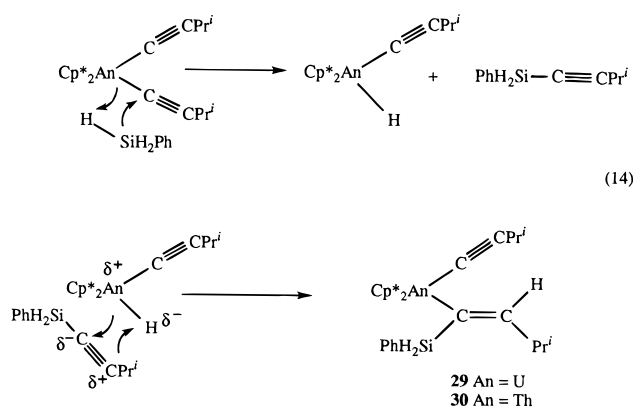
(32) Southard, G. E.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1996**, *15*, 5, 4667.

(28) See the Supporting Information for kinetic and thermodynamic plots.

**Scheme 2. Plausible Organoactinide Intermediates Expected in the Stoichiometric Hydrosilylation of Terminal Alkynes through a Transient Organoactinide–Silicon Bond**



hydrides and the silylalkyne, which rapidly reinsert to produce **29** or **30** (eq 14). For the thorium complex a



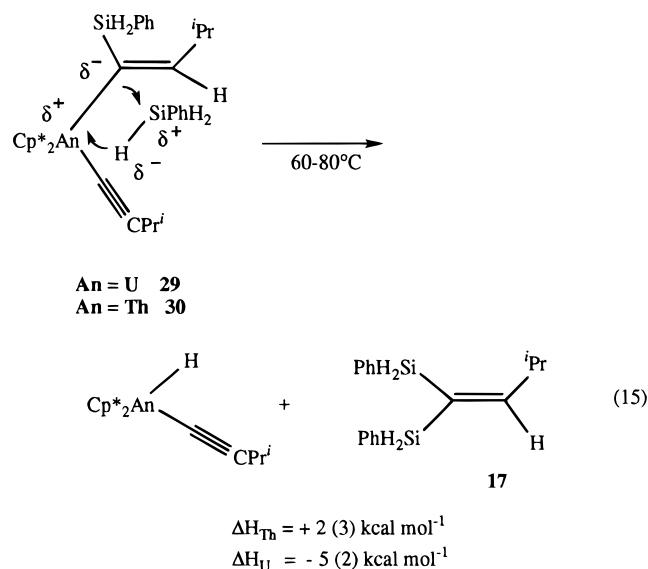
hydride signal at 13.64 ppm is observed, which has a chemical shift similar to that for the thorium hydride  $[\text{Cp}^*_{2}\text{Th}(\mu\text{-H})_2]$  (19.20 ppm),<sup>27</sup> although our attempts to trap this organometallic complex were unsuccessful.

The obtained regioselective mode of insertion for  $\text{PhSiH}_2\text{C}\equiv\text{CPr}^i$  approaching the actinide hydride complex is fully electronically favored, as expected for the polarization of the organoactinides and the  $\pi^*$  orbital of the alkyne.<sup>33</sup> In addition, since the insertion followed a four-center transition state mechanism, a *cis* stereochemistry between the two alkyne substituents is expected, as corroborated by the  $\text{H}_2\text{O}$  poisoning experiment and the high-temperature reactions with alkyne or silane. A similar regioselective insertion of  $(\text{TMS})\text{C}\equiv\text{CH}$  into an organothorium alkenyl complex has been observed in the organoactinide-catalyzed oligomerization of alkynes.<sup>14</sup>

Theoretically, the formulation of the organoactinide–silane intermediate **31** is also possible, as described in Scheme 2. Complex **31** could be obtained from the corresponding bis(acetylide) complex. The low bond enthalpy calculated for an actinide–silicon bond (high

reactivity) would be expected to induce the rapid formation of either the acetylide alkenyl complex with a *trans* or *gem* stereochemistry, **32** or **33**, respectively, or the hydride complex **34**. If this mechanism is operative, we can conclude that this is not a major route to products because (i) the quenching experiments with water gave exclusively the *cis*-vinylsilane, (ii) under the stoichiometric conditions, the addition of silane did not induce the protonolysis of the acetylide–alkenylsilane complex (**29** or **30**), arguing how difficult the production of complex **31** will be, (iii) no *gem* hydrosilylated product was obtained (if complex **33** is an intermediate, it would be observed), (iv) no *cis* hydrosilylated products can be obtained from complex **31**, and (v) no *cis* double-hydrosilylated products are observed (the result of  $\sigma$ -bond metathesis from complex **32** or **33**).

The reactions of complexes **29** and **30** at high temperature with silane yield the double-hydrosilylated product (eq 15). This  $\sigma$ -bond metathesis reaction is

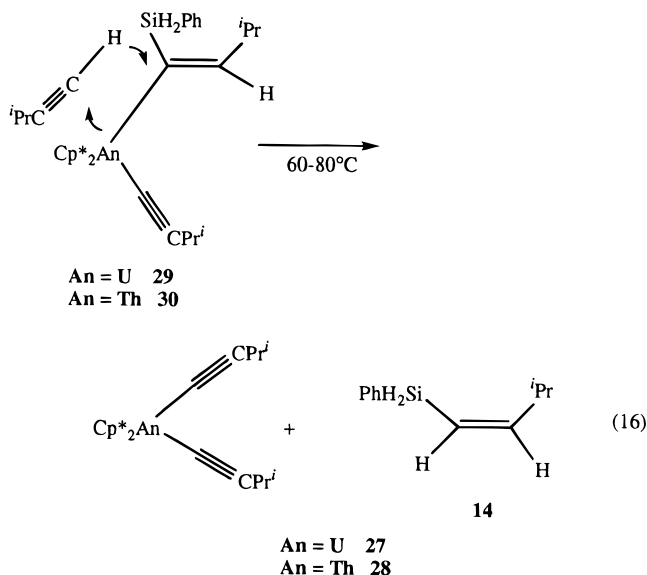


(33) For reviews, see: (a) Fleming, I. *CHEMTRACTS: Org. Chem.* **1993**, 6, 113. (b) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; pp 57–225. (c) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, 118, 3838 and references therein.

stereoselectively favored due to the putative polarization of the  $\text{PhSiH}_3$  toward the metal center, as well as the preferred thermodynamics, as compared to the protonolysis by the silane producing complex **31** and the *cis*

hydrosilylated product ( $\Delta H_{\text{Th}} = +15(4)$  kcal mol<sup>-1</sup>;  $\Delta H_{\text{U}} = -3(2)$  kcal mol<sup>-1</sup>).<sup>30</sup>

The most remarkable and puzzling observation regards the products of reaction of complexes **29** and **30** with alkyne at either low or high temperature. The reaction at high temperature (65–80 °C) yields the expected *cis*-hydrosilylated product. This reaction is the protonolysis of **29** or **30** by the alkyne, producing the bis(acetylide) organoactinide complex (eq 16). The reac-



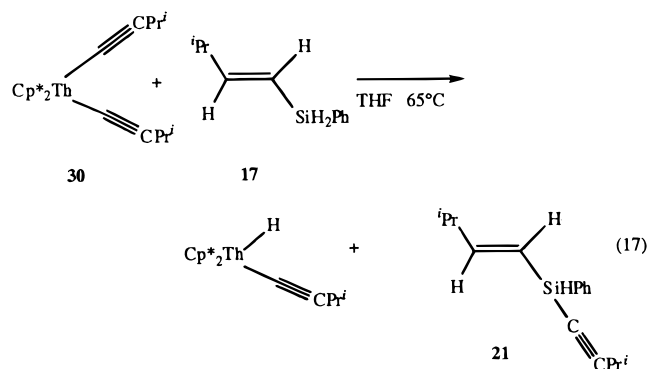
tion at room temperature in the presence of alkyne and silane yields exclusively the *unexpected trans* isomer. Thus, an operative competitive mechanism should be in equilibrium, giving the different hydrosilylation products at different temperatures.

**Catalytic Reaction Scope and Mechanism.** The present catalytic results for the hydrosilylation of terminal alkynes with PhSiH<sub>3</sub> producing, at room temperature, the *trans*-hydrosilylated product and, at high temperature, the *cis* and the double-hydrosilylation products besides the hydrogenated alkyne and the intermediate silylalkyne, demonstrate the ability to tailor the hydrosilylation reaction catalyzed by organoactinides.<sup>34</sup> Moreover, this is the first time in which organoactinides or any other metal complexes have been able to catalyze the double hydrosilylation of alkynes in which the two silyl groups are in *gem* positions.<sup>35</sup>

With regard to the alkynes, (TMS)C≡CH exhibits at room temperature a total lack of reactivity with PhSiH<sub>3</sub> in the presence of Cp\*<sub>2</sub>ThMe<sub>2</sub>; however, at high temperature it produced the *trans*-vinylsilane, the silylalkyne, and the alkene. Interestingly, no *cis* or double-

hydrosilylation products are observed as compared to other alkynes under the same catalytic conditions (entries 7 and 9 in Tables 1 and 2, respectively). This type of reactivity is found in general as the result of a kinetic effect. Therefore, this result strongly suggests, and again corroborates, an equilibrium between an organometallic complex, similar to **30**, in which the <sup>i</sup>Pr group is replaced by a TMS moiety (**35**), with the organometallic complex **36** (Scheme 3). Complex **36** is obtained by the insertion of the silylalkyne into a hydride complex. Complex **36** is able to react with another alkyne, yielding the alkene and the bis(acetylide) complex (protonolysis route) or to react with a silane, producing the organometallic hydride and the *trans* product ( $\sigma$ -bond metathesis route). The low activity obtained for (TMS)C≡CH argues for a high energy of activation to perform either the metathesis or protonolysis of complex **36**, as compared with the energy required for other alkynes.

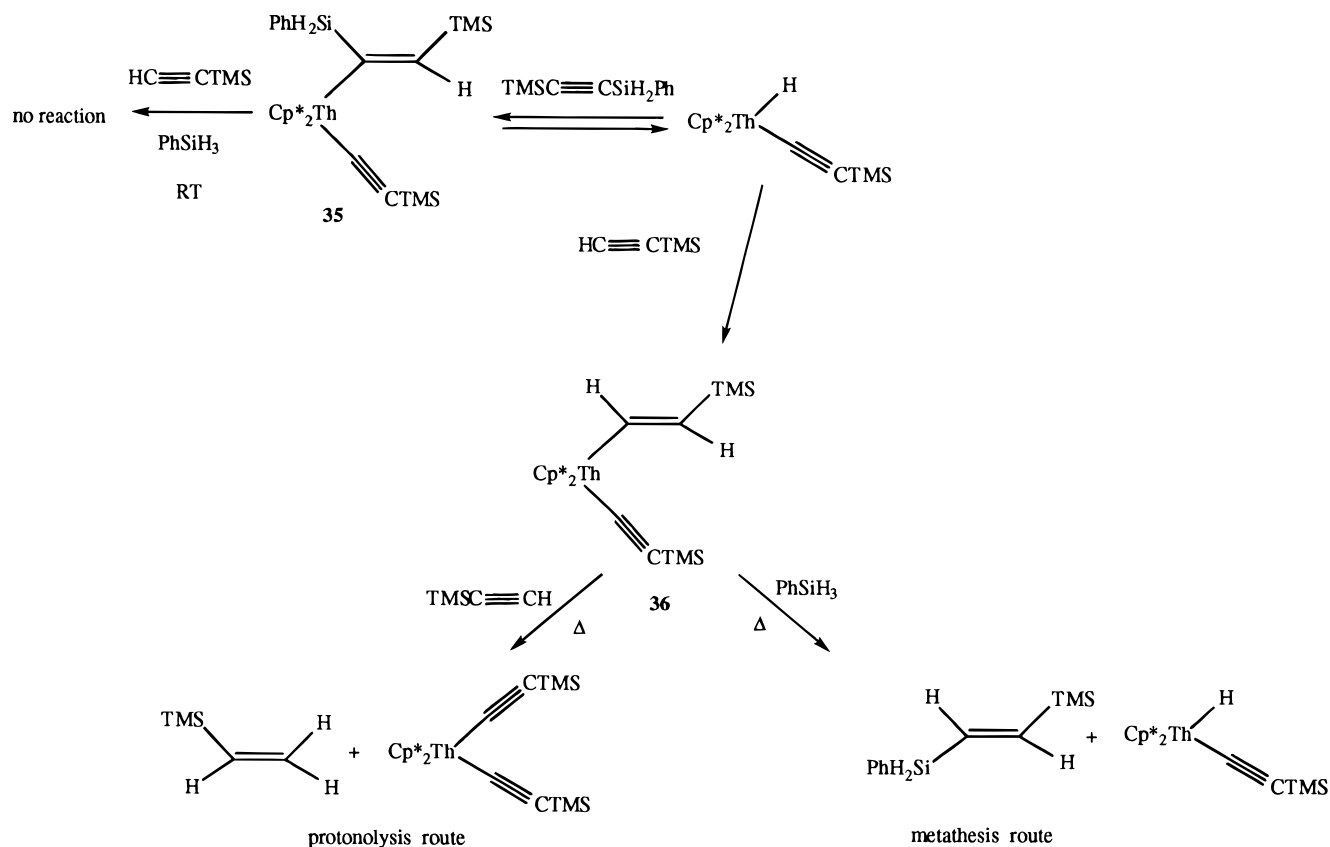
The ratio between the silane and the alkyne seems to govern the kinetics toward the different products. Thus, when the PhSiH<sub>3</sub>:<sup>i</sup>PrC≡CH ratio is 2, the *trans* and double-hydrosilylation products are the major products (metathesis route) (entry 11 in Table 2). When the same ratio is halved, large amounts of the alkene are obtained. This result is consistent with an organometallic structure similar to that of **36** (Scheme 3). An increase in the alkyne concentration will route the reaction toward the alkene and the bis(acetylide) complex (protonolysis route). The large concentration of the bis(acetylide) complex will be able to react with the *trans*-vinylsilane product, allowing the formation of **21** and the corresponding hydride complex (eq 17).



The absence of the expected oligomerization products under these PhSiH<sub>3</sub> starving conditions indicates that the metathesis reaction of the bis(acetylide) complex with the hydrosilylated product (eq 17) is much faster than that of the insertion of an alkyne into the bis(acetylide) complex. This is a plausible route, as indicated by the higher temperature needed to run the oligomerization reactions as compared to the hydrosilylation.<sup>14</sup> Interestingly, by using more bulky silanes such as Ph<sub>2</sub>SiH<sub>2</sub> and PhMeSiH<sub>2</sub> a large retardation in the kinetics toward the hydrosilylated products is noticed. It seems that the secondary silanes are unable to induce the metathesis of the organometallic alkenyl complex, yielding the hydrosilylated *trans* product (metathesis pathway as described in Scheme 3). The silylalkyne and the alkene are the major products (pro-

(34) The hydrosilylation of terminal alkynes by organoactinides is not operative due to the rapid competing oligomerization of the alkyne.<sup>4</sup> For internal alkynes, only Cp\*<sub>2</sub>YR has been reported as an active catalyst, producing both (*E*)- and (*Z*)-vinylsilanes.<sup>6,19</sup>

(35) The bis-silylation of a C–C triple bond is a reaction in which two Si–C bonds are created in the same molecule. Palladium complexes are the most often used catalysts. The mechanism consists of the oxidative addition of the Si–Si bond to palladium(0) and the transfer of the two organosilyl groups to the C–C triple bond in a *cis* stereochemistry, regenerating the palladium(0). See ref 19a and: (a) Murakami, M.; Yoshida, T.; Ito, Y. *Organometallics* **1994**, *13*, 2900. (b) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408. (c) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (d) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224.

**Scheme 3. Protonolysis and  $\sigma$ -Bond Metathesis Routes for the High-Temperature Hydrosilylation of (TMS)C=CH with PhSiH<sub>3</sub> Catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub>**


nolysis pathways), whereas only trace amounts of the *trans*-hydrosilylated product are observed. This result is also in agreement for a situation similar to that depicted in Scheme 3. The low reactivity of the secondary silanes and their intrinsic inability toward the  $\sigma$ -bond metathesis route to produce the corresponding vinylsilane seem to be responsible for allowing the production of alkene and the bis(acetylide) complex, which may either react slowly with the silane, producing the silylalkyne and the corresponding hydride, or react with an alkyne, yielding the observed oligomers.<sup>14</sup>

Regarding the rate, the present hydrosilylation process exhibits larger turnover frequencies as compared to Cp\*<sub>2</sub>YCH<sub>3</sub>.<sup>19i</sup> The yttrium complex is able to induce the hydrosilylation reaction of internal alkynes preferentially toward the *E* isomer, although in some case the *Z* isomer is found in similar quantities. Mechanistically, the active species for the yttrium hydrosilylation of internal alkynes is proposed to be the corresponding hydride. For alkenes, the hydrosilylation reaction promoted by organolanthanides of the type Cp\*<sub>2</sub>LnR (Ln = Sm, La, Lu) proceeds with similar turnover frequencies, as compared to the organoactinides with terminal alkynes. Mechanistically, the lanthanide hydrides have been proposed as the primordial pathway toward the hydrosilylated products.<sup>6a</sup>

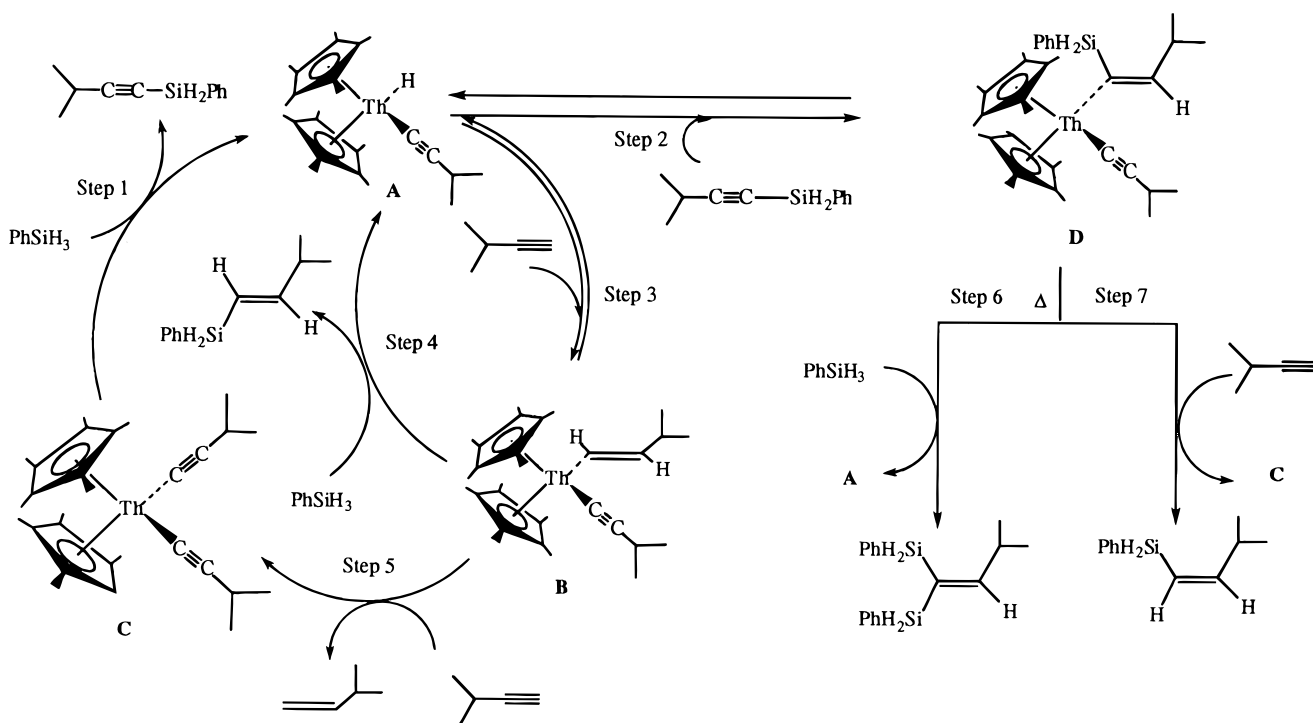
A plausible mechanism for the hydrosilylation of terminal alkynes catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub> is described in Scheme 4.

The mechanism presented in Scheme 4 consists of a sequence of well-established elementary reactions, such as insertion of acetylene into a metal–hydride  $\sigma$ -bond,

$\sigma$ -bond metathesis by a silane, and protonolysis by an acidic alkyne hydrogen. The precatalyst Cp\*<sub>2</sub>ThMe<sub>2</sub> in the presence of alkyne is converted to the bis(acetylide) complex **C** (eq 9). Complex **C** reacts with PhSiH<sub>3</sub>, yielding the silylalkyne and the organoactinide hydride **A** (step 1), which is in equilibrium with the intermediate **D** after reinsertion of the silylalkyne with the preferential stereochemistry (step 2).<sup>36</sup> Complex **D** was found to be the predominant complex under alkyne and silane starvation. Although  $\beta$ -H elimination is not a favored process in organoalkylactinide chemistry, interestingly, the reaction of complex **30** with <sup>t</sup>BuC≡CH and PhSiH<sub>3</sub> produces only *trans*-<sup>t</sup>BuCH=CHSiH<sub>2</sub>Ph (**1**) and the corresponding silylalkyne (**4**), supporting the equilibrium between complexes **A** and **D**. Complex **A** rapidly inserts an alkyne, producing the alkenyl acetylide organothorium complex **B** (step 3), which is presumably in rapid equilibrium with complex **A** (as indicated by the first-order dependence on alkyne). For example, in the hydrogenation of alkenes by the metallocene thorium bis(hydride) complex, this insertion step has been found to be in rapid equilibrium.<sup>12</sup> Complex **B** will react with PhSiH<sub>3</sub>, as the rate-determining step producing the hydride and the *trans*-hydrosilylated product (step 4). Under the catalytic conditions, complex **B** may also react with a second alkyne, producing the alkene and the bis(acetylide) complex **C** (step 5). A similar insertion of the alkene into complex **A** with the concomitant

(36) Under the catalytic conditions, trace amounts of PhSiH<sub>2</sub>Me are produced and characterized by <sup>1</sup>H NMR and GC/MS techniques, indicating that the Cp\*<sub>2</sub>ThMe<sub>2</sub> or the mono(acetylide) Cp\*<sub>2</sub>ThMe(C≡CR) is able to react with PhSiH<sub>3</sub>, yielding the corresponding hydride.

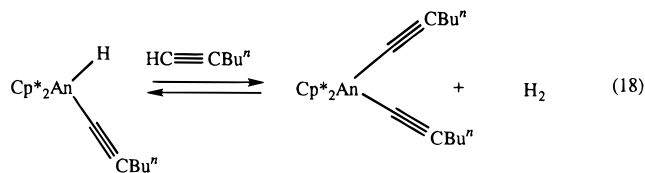
**Scheme 4. Plausible Mechanism for the Room- and High-Temperature Hydrosilylation of Isopropylacetylene with PhSiH<sub>3</sub> Promoted by Cp\*<sub>2</sub>ThMe<sub>2</sub><sup>a</sup>**



<sup>a</sup> The transformation of the Cp\*<sub>2</sub>ThMe<sub>2</sub> complex into the bis(acetylide) complex is described in eq 9 and omitted for clarity.

reaction with an additional alkyne, will produce the double-hydrogenated product (**10**), as found for isopropylacetylene. At high temperature, complex **D** may react with a silane (step 6), yielding complex **A** and the double-hydrosilylation product, or with an alkyne (step 7), yielding complex **C** and the *cis* isomer. Thus, the reaction rate law presented in eq 12 is compatible with rapid, operationally irreversible phenylsilane metathesis with complex **C**, rapid preequilibrium involving the hydride and alkenyl complexes **A** and **B**, and a slow metathesis by the PhSiH<sub>3</sub> inducing the *trans* product. It is important to point out that, for the thorium complex, step 6 is much faster than step 7, since the *cis* product is obtained in trace amounts. The rate law presented in eq 12 is operative for the production of the hydrosilylated compound **2**, between 30 and 80 °C. It is important to point out that, since other pathways are observed at higher temperatures, the kinetics for each possible product may change as a function of temperature.

The mechanistic pathway proposed takes into account the similar yields for the alkene and silylalkyne catalyzed by the thorium complex even when the alkyne concentration is in excess (in this case the sum of the silylated products is equal to the amount of the alkene). For the thorium or uranium complexes, the amount of the hydrosilylated product is either similar to or larger than that of the alkene. For example (entry 6, Table 1), at room temperature the amount of 1-hexene (2%) is much lower than that of the corresponding silylalkyne (24%), indicating that an optional competing equilibrium route should be operative, responsible for the transformation of the hydride complex back to the biacetylide complex, allowing the production of the silylalkyne without producing the alkene (eq 18).



The activation energy parameters for the hydrosilylation of <sup>t</sup>PrC≡CH with PhSiH<sub>3</sub> promoted by Cp\*<sub>2</sub>ThMe<sub>2</sub> are characterized by a rather small enthalpy of activation ( $\Delta H^\ddagger = 6.3(3)$  kcal mol<sup>-1</sup>,  $E_a = 6.9(3)$  kcal mol<sup>-1</sup>) and a large negative (even for an intermolecular reaction) entropy of activation ( $\Delta S^\ddagger = -51.1(5)$  eu,  $\Delta G^\ddagger = 21.5(6)$  kcal mol<sup>-1</sup> at 298 K). These parameters suggest a highly ordered transition state with considerable bond making to compensate for bond breaking. Thus, the process proceeds with a high degree of entropic reorganization on approaching the transition state. The low enthalpy of activation indicates that the  $\sigma$ -bond metathesis of the alkenyl complex by PhSiH<sub>3</sub>, which is the rate-determining step, is faster as compared to the insertion of an alkyne into the bis(acetylide) complex ( $\Delta H^\ddagger = 11.1(3)$  kcal mol<sup>-1</sup>), which will produce alkyne oligomers. On the basis of the obtained results, we can argue that the formation of the silylalkyne and the corresponding organoactinide hydride and the concomitant alkyne insertion forming the alkenyl complex are faster steps than the metathesis reaction of the alkenyl complex yielding the *trans*-vinylsilane.

**Solvent Effect.** Recently the use of polar solvents to allow the stereoselective controlling of vinylsilanes obtained by the hydrosilylation of terminal alkynes by [Rh(COD)Cl<sub>2</sub>]<sub>2</sub> has been reported.<sup>22c</sup> When the hydrosilylation reaction is conducted in polar and/or protic solvents (EtOH, DMF), the (*Z*)-vinylsilane is obtained as the predominant species due to the stabilization of a



**Table 4.**  $^{29}\text{Si}$  NMR Chemical Shifts (ppm) for the Si–H-Containing Products Obtained in the Hydrosilylation of  $\text{RC}\equiv\text{CH}$  with  $\text{PhSiH}_3$  Promoted by  $\text{Cp}^*_2\text{AnMe}_2$  (An = U, Th)

entry	R	$\text{RCH}=\text{C}(\text{SiH}_2\text{Ph})_2$	$\text{trans-RCH}=\text{CHSiH}_2\text{Ph}$	$\text{trans-RCH}=\text{CHSi}(\text{H})\text{-}(\text{Ph})\text{C}\equiv\text{CR}$	$\text{cis-RCH}=\text{CHSiH}_2\text{Ph}$	$\text{RC}\equiv\text{CSiH}_2\text{Ph}$
1	$^t\text{Bu}$	30.2 (t, $^1J = 215$ Hz) 5.2 (t, $^1J = 210$ Hz)	15.6 (tt, $^1J = 198$ Hz, $^3J = 7.3$ Hz <sup>a</sup> )		4.6 (t, $^1J = 210$ Hz)	-8.98 (tt, $^1J = 211$ Hz; $^3J = 6.1$ Hz <sup>a</sup> )
2	$^i\text{Pr}$	27.5 (t, $^1J = 198$ Hz) 7.3 (t, $^1J = 203$ Hz)	14.7 (t, $^1J = 199$ Hz)	11.7 (d, $J = 212$ Hz)	1.6 (t, $^1J = 196$ Hz)	-9.0 (t, $^1J = 213$ Hz)
3	$^n\text{Bu}$	23.8 (t, $^1J = 208$ Hz) 4.1 (t, $^1J = 211$ Hz)	14.0 (t, $^1J = 196$ Hz)		1.4 (t, $^1J = 195$ Hz)	-9.1 (t, $^1J = 212$ Hz)

<sup>a</sup> Only in these compounds were the  $^3J$  couplings of the *ortho* hydrogens with the silicon atom observed.

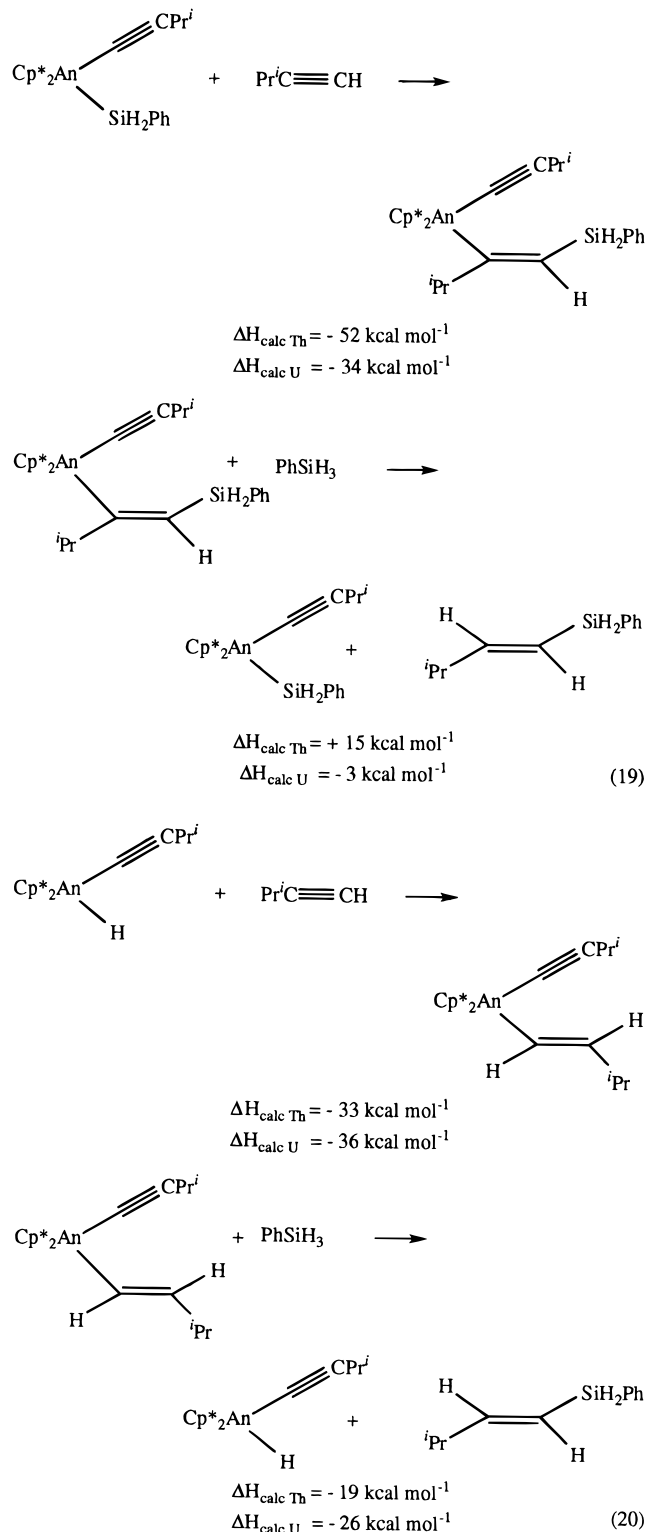
zwitterionic intermediate. However, using less polar solvents, such as  $\text{CH}_3\text{CN}$ , the *E* isomer is the predominant species obtained. For organoactinides, the use of polar solvents (THF) did not induce any changes in stereoselectivities but produced a significant shift in the yields of the alkenes as compared to the reaction carried out in  $\text{C}_6\text{H}_6$ . Thus, in polar solvents, the protonolysis of the metal–alkenyl complex by the alkyne (step 5 in Scheme 4) is much faster than the  $\sigma$ -bond metathesis of the phenylsilane (step 4 in Scheme 4), possibly due to the solvent–silane interactions.<sup>37</sup>

Thermodynamically, it is very interesting to compare the enthalpy of the reactions for the possible silane and hydride intermediates toward the formation of the *trans* hydrosilylation product as presented in eqs 19 and 20, respectively.

The calculated enthalpies of reaction for the insertion of an alkyne into an actinide–silane bond (eq 19) ( $\Delta H_{\text{Th}} = -52$  kcal mol<sup>-1</sup>;  $\Delta H_{\text{U}} = -34$  kcal mol<sup>-1</sup>) or into an actinide–hydride bond (eq 20) ( $\Delta H_{\text{Th}} = -33$  kcal mol<sup>-1</sup>;  $\Delta H_{\text{U}} = -36$  kcal mol<sup>-1</sup>) are expected to be rapid and exothermic. However, the protonolysis by the silane, yielding back the An–Si bond and the *trans* product (eq 19), is for thorium an endothermic process ( $\Delta H_{\text{Th}} = +15$  kcal mol<sup>-1</sup>), as compared to the exothermic  $\sigma$ -bond metathesis (eq 20) of the thorium alkenyl complex by the silane ( $\Delta H_{\text{Th}} = -19$  kcal mol<sup>-1</sup>), yielding the corresponding Th–H bond and the *trans* product. For the corresponding uranium complexes, the latter processes are exothermic, although the  $\sigma$ -bond metathesis route (eq 20) is by far more exothermic ( $\Delta H_{\text{U}} = -26$  kcal mol<sup>-1</sup>) than the protonolysis route (eq 19) ( $\Delta H_{\text{U}} = -3$  kcal mol<sup>-1</sup>).

**$^{29}\text{Si}$  Chemical Shift Behavior.** We have shown that many types of silicon-containing organic compounds are obtained in the hydrosilylation of terminal alkynes promoted by organoactinide complexes. Table 4 compiles the different  $^{29}\text{Si}$  chemical shifts for the corresponding Si–H-containing products.

In the double-hydrosilylation products, the downfield  $^{29}\text{Si}$  signal was found to correspond to the silicon atom that is in the position *trans* to the alkyl group. These signals (23–30 ppm) appear at a lower field as compared to those of similar silicon atoms in the *trans*-vinylsilane compounds (14–16 ppm). No major changes are observed in the chemical shifts of the silicon atom *cis* to the alkyl group in the double-hydrosilylation product as compared to the *cis*-vinylsilane (2–8 ppm). As expected, silicon atoms at the vinylic positions (*cis* or *trans*) are deshielded as compared to silicon atoms



(37) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, Chapter 7, pp 355–430.

bonded to alkyne sp carbons as in the silylalkyne products ( $\sim -9$  ppm).<sup>19</sup>

### Conclusions

In conclusion, we have shown that organoactinides are active species for the hydrosilylation of terminal alkynes by a mechanism that consists of several insertions and  $\sigma$ -bond metathesis. A delicate balance between alkyne protonolysis and  $\sigma$ -bond metathesis by the silane determines the ratio among the silaalkyne, alkene, and *trans*-hydrosilylated product. The present work represents the first study on the synthetic, spectroscopic, kinetic, and reactivity properties of bis(acetylide) organoactinide complexes in the presence of silanes. It provides insights into the mechanistic process and stability of the key intermediate compounds, providing a basis for the rational modification of the metallocene complexes for future organoactinide arrays. It also lays the groundwork necessary to understand the approach to control the hydrosilylation reaction to obtain selec-

tively and catalytically only desired products. The striking difference in reactivity of the thorium complex as compared to the corresponding uranium complex may be a result of the involvement of the f orbitals for the latter complex.

**Acknowledgment.** The research was supported by the Israel Science Foundation, administered by the Israel Academy of Sciences and Humanities under contract **67/97-1**, by the Fund for the Promotion of Research at the Technion, and by the Technion VPR Fund. A.K.D. thanks the Technion for a postdoctoral fellowship.

**Supporting Information Available:** Figures giving kinetic and thermodynamic plots for the hydrosilylation of isopropylacetylene with phenylsilane catalyzed by Cp\*<sub>2</sub>ThMe<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990655C