

1,2-Selective Hydrosilylation of Conjugated Dienes

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S Supporting Information

ABSTRACT: Selective 1,2-hydrosilylation of 1,3-dienes is a challenging problem in transition metal catalysis. Butadiene, specifically, would be a useful substrate because 3-butenylsilane products have promise as superior coupling reagents for hybrid organic/inorganic materials synthesis. We report the first selective 1,2-hydrosilylation of conjugated dienes including butadiene. Hydrosilylation proceeds through a Pt(II/IV) cycle, and selectivity is generated at a hexacoordinate Pt(IV) complex that favors η^2 -diene coordination and prevents π -allyl complex formation.

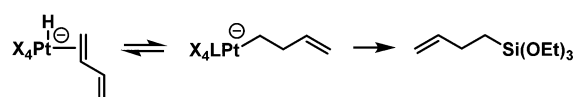
Despite the prevalence of transition metal-catalyzed olefin hydrosilylation methods,¹ no selective method for 1,2-hydrosilylation of 1,3-dienes has been reported.² Conjugated dienes represent a significant selectivity challenge because various coordination and insertion modes are accessible to a conjugated π -system at a transition metal catalyst. The prevalence of 1,4-selective additions may result from the likelihood of transition metals to form π -allyl intermediates upon migratory insertion of dienes into M–X bonds (Scheme 1).^{2,3} Products of 1,2-selective hydrosilylation, specifically 3-butenylsilanes derived from butadiene, would be valuable as superior coupling agents to link silicate-based materials to olefin polymers in hybrid materials synthesis.^{1d,4} Known catalysts cannot generate 3-butenylsilanes from an inexpensive and readily available feedstock, such as butadiene.⁵ Here, we report the first 1,2-selective hydrosilylation of conjugated dienes, including butadiene. Hydrosilylation by a platinum precatalyst bearing a cyclometalated phosphine ligand creates coordinative saturation at the catalyst following 1,2-migratory insertion and prevents π -allyl formation during the catalytic cycle, which leads to 1,2-selectivity.

Butenylsilanes, such as the product of 1,2-hydrosilylation of butadiene, can act as coupling agents to covalently link the surface of silicate-based sol-gel materials with hydrophobic olefin polymers.⁴ Coupling reagents contain a silicon group with hydrolyzable ligands and an α -olefin from which olefin polymerization can be initiated.^{4b} Although vinyltriethoxysilane and hexenyltriethoxysilane are currently used as coupling reagents, vinylsilanes are less active than α -olefins for initiating olefin polymerization,^{4c} and hexenylsilanes are produced from an expensive feedstock.⁶

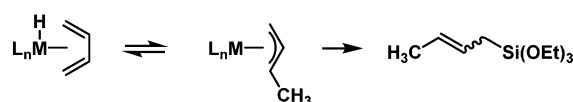
Selective 1,4-additions to dienes can be achieved with known catalysts by using the thermodynamic favorability of metal-allyl intermediates (products of 1,4- or 2,1-migratory insertion) over their σ -alkyl isomers (products of 1,2-migratory insertion).^{3a–g,1m} In contrast, 1,2-selective addition to conjugated dienes

Scheme 1. Regioselectivity in Diene Hydrosilylation

This Work: 1,2-Addition



Conventional Hydrosilylation: 1,4-Addition



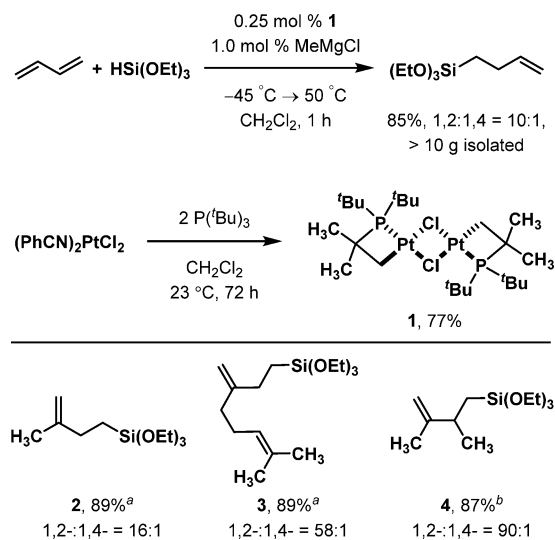
is rare. General methods for 1,2-addition are limited to two examples of diene hydro- and diboration reactions, and the factors leading to 1,2-selectivity in these cases are not understood.⁷ Few isolated examples of 1,2-hydrosilylation for specific substrates or as part of product mixtures have been reported, but 1,2-selectivity is substrate-dependent and does not extend to butadiene in any reported case.^{2,3g,8} We propose that a transition metal catalyst that excludes formation of π -allyl intermediates upon migratory insertion of 1,3-dienes would result in catalyst-controlled 1,2-selective addition (see σ -alkyl intermediate in Scheme 1). Because π -allyl ligands require two coordination sites while σ -alkyls require only one, π -allyl intermediates can be excluded by coordinative saturation at the transition metal catalyst.

Upon activation with methylmagnesium chloride, cyclometalated platinum complex **1**⁹ catalyzes the selective 1,2-hydrosilylation of butadiene with 10:1 selectivity for the 1,2-addition product (Scheme 2) and a turnover frequency (TOF) of 480/h at 50 °C. Precatalyst **1** is air- and moisture-stable and can be used for catalysis without special purification. Precatalyst **1** is activated with MeMgCl at –45 °C in dichloromethane, at which temperature transmetalation from the Grignard reagent proceeds more quickly than reaction with solvent. For hydrosilylation, diene and silane are added to the preactivated catalyst solution, and the vessel is sealed and heated to 50 °C until the reaction is complete. Butenylsilane products can be isolated by distillation of the reaction mixture without additional purification. A slight excess of diene, although unnecessary for full conversion, prevents isomerization of the 1,2-addition product to the 1,4-addition products after the reaction reaches full conversion. Selectivity for 1,2- versus 1,4-addition extends to substituted diene substrates and increases with diene substitution, reaching a maximum of 90:1 for 2,3-dimethylbutadiene (Scheme 2).

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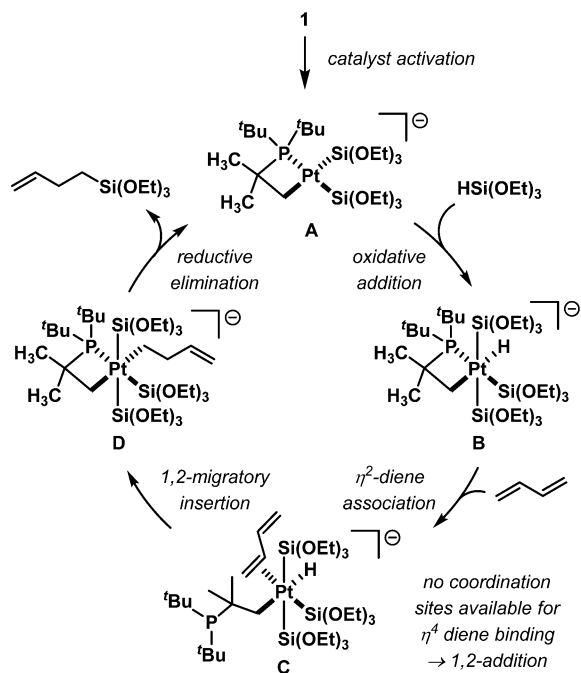
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Scheme 2. Hydrosilylation of Butadiene and Other 1,3-Dienes



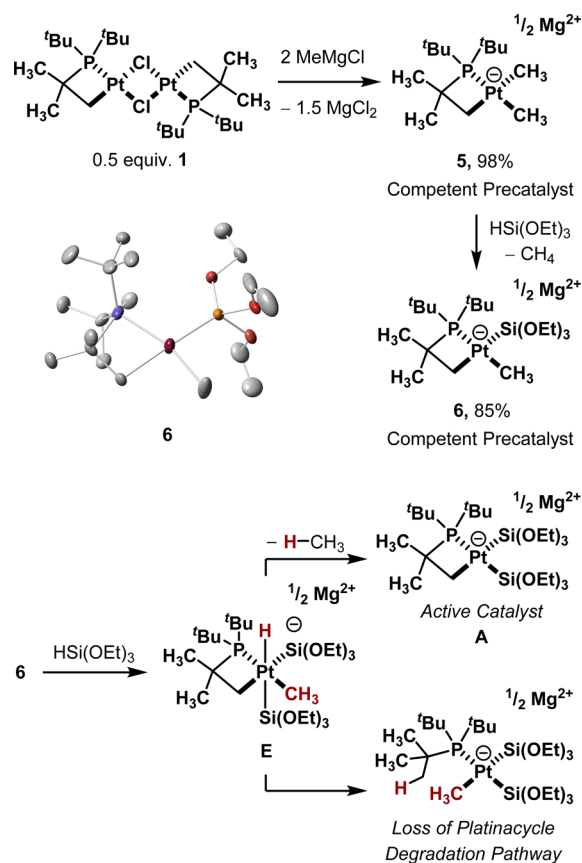
^aStandard conditions for substituted diene substrates: 1 mol% platinum precatalyst **6** (*vide infra*), 2.0 mol% MgCl₂(THF)₂, 1.0 equiv HSi(OEt)₃, DCM, -45 °C → 75 °C, 12 h. Optimization data for solvent, reductant, and silane are provided in the SI. ^bDCE, -45 °C → 125 °C. Precatalyst **6** was used for 1,3-dienes other than butadiene due to more reliable catalyst activation in those cases (see SI).

Scheme 3. Proposed Mechanism of 1,2-Hydrosilylation



We propose a Pt(II/IV) catalytic cycle to rationalize the selectivity for 1,2-addition (Scheme 3).¹⁰ Catalyst activation (*vide infra*) provides an electron-rich anionic Pt(II) complex (A) that can undergo oxidative addition of triethoxysilane to form coordinatively saturated Pt(IV) intermediate B. Because B is coordinatively saturated, a ligand must dissociate prior to diene coordination (C). Importantly, because the phosphine contained in the bidentate ligand is the only ligand which can readily dissociate from B, the incoming diene is restricted to η²-coordination. 1,2-Migratory insertion forms linear alkyl complex D, which may dissociate a ligand (such as the phosphine) to form

Scheme 4. Catalyst Activation

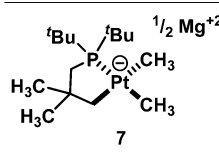
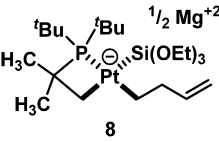
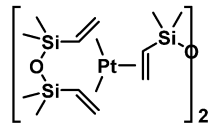


a pentacoordinate complex prior to reductive elimination of the desired 1,2-hydrosilylation product and regeneration of A.¹¹ Next we provide support for the proposed mechanism and evidence against a Pt(0/II) mechanism, typical for conventional Pt-catalyzed hydrosilylation.¹²

Activation of precatalyst **1** with 2 equiv of methylmagnesium chloride at -45 °C generates electron-rich, anionic Pt(II) complex **5**, which reacts with triethoxysilane to give platinane **6** (Scheme 4). Platinanes **5** and **6** are isolable as air- and moisture-sensitive aggregates with MgCl₂(THF)₂ and have been characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy as well as by X-ray diffraction (XRD, **6**). Both **5** and **6** are competent precatalysts for 1,2-selective hydrosilylation, which indicates that these complexes are intermediates on the catalyst activation pathway (Table 1). Precatalyst **6** further reacts with triethoxysilane to form as yet unidentified products. We propose that precatalyst **6** further reacts with triethoxysilane by oxidative addition (E) to afford, after reductive elimination of methane (observed by GCMS), active catalyst A. Intermediate E has a second accessible C-H reductive elimination pathway available, which releases the cyclometalated arm of the phosphine ligand to form P(^tBu)₃ and leads to catalyst decomposition (Scheme 4). Consistent with this analysis, P(^tBu)₃ was observed during the early stages of hydrosilylation for precatalysts **1**, **5**, and **6** (see Supporting Information (SI)). Although degradation of homogeneous precatalysts can sometimes generate catalytically active metal nanoparticles,^{12c,13} adding elemental mercury had only a moderate effect on the observed selectivity and conversion of hydrosilylation using precatalyst **6** (Table 1). We conclude that catalysis by nanoparticulate platinum is unlikely to be the major pathway for hydrosilylation. However, because all

Table 1. Performance of Platinate and Pt(0) Precatalysts

$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{HSi}(\text{OEt})_3 \xrightarrow[0.5 \text{ mol } \% [\text{Pt}], \text{ Additive}]{\text{CH}_2\text{Cl}_2, 25 \text{ min.}, -45^\circ\text{C} \rightarrow 50^\circ\text{C}}$
 $\text{CH}_2=\text{CH}-\text{CH}(\text{Si}(\text{OEt})_3)-\text{CH}_2-\text{CH}=\text{CH}_2$

Precatalyst	Additive	Yield ^a	1,2:1,4 ^a
1 <i>standard conditions</i>	MeMgCl	86% ^{b,c}	10:1
5	MgCl ₂ (THF) ₂ ^d	64% ^b	9:1
	none	10% ^b	3:1
6	MgCl ₂ (THF) ₂ ^d	60% ^b	9:1
	1,4-Dioxane	2% ^b	3:1
	Hg ⁰ + MgCl ₂ (THF) ₂	52% ^b	8:1
	MgCl ₂ (THF) ₂ ^d	28% ^b	9:1
	MgCl ₂ (THF) ₂ ^d	65% ^b	10:1
	None	10%	1:10
	P(^t Bu) ₃	3%	1:8

Karstedt's Catalyst

^aYield and selectivity determined by integrating ¹H NMR resonances corresponding to the alkenyl H atoms vs TMS₂O (internal standard).

^bYield corresponds to conversion, as no other products are observed.

^cIsolated yield; reaction halted by 10 μL of *N,N'*-DMEDA after 25 min. ^dAdding MgCl₂(THF)₂ simulates conditions for catalysis with precatalyst **1**.

precatalysts showed decomposition during activation, we were unable to obtain reproducible kinetic data to determine a rate law, and we do not speculate as to the turnover-limiting step or the reversibility of proposed steps on the catalytic cycle.

Our data suggest that the magnesium counterion plays an active role in catalysis. *In situ* generation of precatalyst **6** results in a visibly homogeneous solution, whereas at the higher concentrations employed during isolation of **6**, MgCl₂(THF)₂ precipitated and was removed by filtration. X-ray data show that multiple aggregates of **6** with Mg²⁺ salts are formed under different conditions (see SI). Aggregation with fewer Mg²⁺ ions may explain why isolated precatalyst **6** shows significantly reduced activity and selectivity in the hydrosilylation of butadiene (Table 1). Notably, much of the loss in activity and selectivity can be recovered by adding MgCl₂(THF)₂ to reactions catalyzed by isolated **6**. We attribute the slight difference in yield with **6** + MgCl₂(THF)₂ compared to the *in situ* generated catalyst (from **1** + 2 MeMgCl) to the low solubility of MgCl₂(THF)₂ in the chlorinated solvents used in hydrosilylation. Adding ligand quantities of 1,4-dioxane, which binds strongly to Mg²⁺ and causes precipitation of magnesium halide salts,¹⁴ dramatically reduces conversion in the hydrosilylation of butadiene with **6** (Table 1).

X-ray data from single crystals of **6** show an interaction of Mg²⁺ with the O atoms of the triethoxysilyl ligand (see SI). We propose that the Mg²⁺ counterion assists reductive elimination from electron-rich Pt(IV) (**5** → **A**, **D** → **A**) by binding to triethoxysilyl ligands of the Pt(IV) anion. Mg²⁺ could also promote catalyst activation and/or hydrosilylation by binding to (EtO)₃SiH prior to oxidative addition, which would increase the electrophilicity of the Si–H bond and facilitate oxidative addition (**5** → **A**, **A** → **B**). Lewis acids have been shown to promote both oxidative addition¹⁵ and reductive elimination¹⁶ at transition metal complexes. Other silanes, such as Et₃SiH, are unreactive in hydrosilylation using precatalyst **1** (see SI), consistent with interaction of Mg²⁺ with the O atoms of triethoxysilane.

A key step in the proposed mechanism is dissociation of the phosphine ligand prior to diene ligation (**B** → **C**). As evidence for such a dissociation event, we synthesized an analogue of **5** with a 5-membered platinacycle (**7**). Hydrosilylation using platinate **7** as a precatalyst was significantly slower than using precatalyst **5** (Table 1, see SI). Because there is less angle strain in a 5-membered platinacycle (**7**) than a 4-membered platinacycle (**5**), the rate of phosphine dissociation from Pt should be slower for **7** than for **5**. If phosphine dissociation represents a step in the catalytic cycle prior to the turnover-limiting step, the rate of catalysis by the 5-membered platinacycle would be slower compared to that by the 4-membered platinacycle precatalyst, as observed in this system.

Pt-catalyzed olefin hydrosilylation often proceeds by Pt(0/II) cycles, such as the well-established Chalk–Harrod mechanism.¹² A Pt(0/II) cycle for the transformation described herein would include an intermediate such as **8** (Table 1). To probe this mechanistic possibility, we synthesized and tested anionic Pt(II) complex **8** as a precatalyst for the hydrosilylation of butadiene. Because significant decomposition is observed from precatalysts **1**, **5**, and **6**, if complex **8** were an intermediate on the catalytic cycle, then adding an amount of **8** equivalent to precatalysts **1**, **5**, and **6** would result in a much higher proportion of active catalyst and, therefore, a faster reaction rate. Complex **8** did not show improvement in rate or selectivity over the other tested precatalysts and decomposed to free tri-*tert*-butylphosphine during hydrosilylation (Table 1). Additionally, platinum complex **8** did not undergo reductive elimination at 50 °C in the presence of butadiene, which excludes this reductive elimination as a step in the catalytic cycle. These data demonstrate that the mechanism of butadiene hydrosilylation from **1** cannot proceed via a Chalk–Harrod-like Pt(0/II) cycle involving **8**.

To investigate whether precatalyst degradation produces a neutral monodentate phosphine complex of Pt(0) as the active catalyst, we tested an olefin-supported Pt(0) complex, Karstedt's catalyst,^{1b,17} as a precatalyst for hydrosilylation. Karstedt's catalyst was not selective for 1,2-addition (Table 1), alone or in the presence of P(^tBu)₃. If formation of Pt(0) or loss of cyclometalation were the critical event in catalyst activation, we would expect to see selectivity for 1,2-addition from a Pt(0) phosphine catalyst generated by another method.

Other possible mechanisms exist, including variations on both Pt(0/II) and Pt(II/IV) cycles. However, none that we have considered explains the unprecedented selectivity for 1,2-hydrosilylation that we observe using precatalysts **1**, **5**, and **6**. Specifically, none is expected to prevent the formation of π -allyl intermediates. We propose that the platinacycle, which contributes both a non-dissociable ligand and a negative charge to the complex, is a key component that induces coordinative saturation and prevents π -allyl formation. In addition, the high

electron density of platينات **1**, **5**, and **6** allows access to the +IV oxidation state, which is not typical for platinum catalysts under the reducing conditions generated by large quantities of hydrosilane that are necessary for hydrosilylation.^{10,12}

In conclusion, we report the first general 1,2-selective hydrosilylation reaction of conjugated 1,3-dienes, including butadiene. We propose that the reaction proceeds through a Pt(II/IV) cycle and selectivity arises at a hexacoordinate Pt(IV) intermediate with a hemilabile phosphine ligand that favors η^2 -diene coordination and prevents formation of π -allyl intermediates. 1,2-Selective hydrosilylation of conjugated dienes may, after further development, enable the industrial synthesis of butenylsilanes that hold promise as coupling reagents to fuse silicates with olefin polymer materials.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Speier, J. L.; Webster, J. A.; Barnes, C. H. *J. Am. Chem. Soc.* **1957**, *79*, 974. (b) Karstedt, B. D. Ger. Offen. DE 2307085 A1, 1973. For reviews of recent progress in transition metal-catalyzed hydrosilylation, see: (c) Ojima, I.; Li, Z.; Zhu, J. Recent Synthetic Applications of Organosilicon Reagents. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp 1667–1792. (d) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-VCH Verlag: New York, 2000; Chapter 12. (e) Marciniak, B. *Silicon Chem.* **2002**, *1*, 155. (f) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1. (g) Marciniak, B.; Maciejewsky, H.; Pietraszuk, C.; Pawluć, P. In *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marciniak, B., Ed.; Springer: Berlin, 2010; Chapter 1. (h) Troegel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, *255*, 1440.
- (2) For reviews of 1,3-diene hydrosilylation, see: (a) Ojima, I.; Kogure, T. *Rev. Silicon, Germanium, Tin Lead Compd.* **1981**, *5*, 7. (b) Ojima, I. The Hydrosilylation Reaction. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Vol. 1, pp 1479–1526.
- (3) (a) Shiihara, I.; Hoskyns, V. F.; Post, H. W. *J. Org. Chem.* **1961**, *26*, 4000. (b) Mamedaliev, Y. G.; Mamedov, M.; Sadykh-Zade, S. I.; Akhmedov, I. M.; Salimov, M. A. *Azerb. Khim. Zh.* **1962**, *9*. (c) Takahashi, S.; Shibano, T.; Hagihara, N. *Chem. Commun.* **1969**, 161. (d) Hara, M.; Ohno, K.; Tsuji, J. *Chem. Commun.* **1971**, 247. (e) Takahashi, S.; Shibano, T.; Kojima, H.; Hagihara, N. *Organomet. Chem. Synth.* **1971**, *1*, 193. (f) Belyakova, Z. V.; Pomerantseva, M. G.; Popkov, K. K.; Efreanova, L. A.; Golubtsov, S. A. *Zh. Obshch. Khim.* **1972**, *42*, 889. (g) Swisher, J. V.; Zullig, C. *J. Org. Chem.* **1973**, *38*, 3353. (h) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143. (i) Wrighton, M. S.; Shroeder, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 6235. (j) Cornish, A. J.; Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1977**, *132*, 133. (k) Benkeser, R. A.; Merritt, F. M., II; Roche, R. T. *J.*

Organomet. Chem. **1978**, *156*, 235. (l) Hayashi, T.; Kabeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023. (m) Wu, J. Y.; Stanzl, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214.

(4) (a) Arkles, B. *CHEMTECH* **1977**, *7*, 766. (b) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1991. (c) Brook, M. A. *Silicon in Organic Organometallic and Polymer Chemistry*; Wiley-VCH Verlag: New York, 2000; Chapter 10. (d) Ab, R. I.; Padavettan, V. J. *Nanomater.* **2012**, 132424. (e) Cui, S.; Lin, B.; Liu, Y.; Liu, X.; Shen, X.; Han, G.; Zhou, X. *Curr. Nanosci.* **2012**, *8*, 797.

(5) For alternate syntheses of triethoxysilyl-3-butene, see: (a) Yamamoto, K.; Nakajima, M.; Shiozawa, M.; Okumura, Y.; Koyama, T. *Jpn. Kokai Tokkyo Koho JP 01172391*, 1989. (b) Brondani, D. J.; Corriu, R. J. P.; Ayoubi, S. E.; Moreau, J. J. E.; Man, M. W. C. *Tetrahedron Lett.* **1993**, *34*, 2111. (c) Deschler, U.; Kleinschmit, P.; Wolff, S.; Tan, E. H. *Eur. Pat. Appl. EP 350600*, 1990.

(6) For syntheses of hexenylsilanes, see: (a) Takeaki, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, *183*, 1556. (b) Tanaka, H. *Jpn. Kokai Tokkyo Koho JP 2008174523*, 2008.

(7) For 1,2-selective hydroboration, see: (a) Zaidlewicz, M.; Meller, J. *Tetrahedron Lett.* **1997**, *38*, 7279. For 1,2-selective diboration, see: (b) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1997**, 689. (c) Kliman, L. T.; Mlynarski, S. N.; Ferris, G. E.; Morken, J. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 521.

(8) (a) Andrianov, K. A.; Bagratishvili, G. D.; Kantariya, M. L.; Sidorov, V. I.; Khananashvili, L. M.; Tsitsishvili, G. V. *J. Organomet. Chem.* **1965**, *4*, 440. (b) Nasiak, L. D.; Post, H. W. *J. Organomet. Chem.* **1970**, *23*, 91. (c) Fink, W. *Helv. Chim. Acta* **1971**, *54*, 1304. (d) Rericha, R.; Capka, M. *Collect. Czech. Chem. Commun.* **1974**, *39*, 144.

(9) Clark, H. C.; Goel, A. B.; Goel, R. G.; Goel, S. *Inorg. Chem.* **1980**, *19*, 3220.

(10) For a mechanism study of Pt(II/IV)-catalyzed hydrosilylation, see: Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510.

(11) For reductive elimination from 5-coordinate Pt(IV) complexes, see: (a) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456 and references therein. (b) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442. (c) Luedtke, A. T.; Goldberg, K. I. *Inorg. Chem.* **2007**, *46*, 8496.

(12) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510. (c) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693. (d) Faglioni, F.; Blanco, M.; Goddard, W. A.; Saunders, D. J. *Phys. Chem. B* **2002**, *106*, 1714.

(13) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(14) Schlenk, W.; Schlenk, W., Jr. *Ber. Dtsch. Chem. Ges. B* **1929**, *62B*, 920.

(15) (a) Ghosh, I.; Jacobi, P. A. *J. Org. Chem.* **2002**, *67*, 9304. (b) Shi, Y.; Peterson, S. M.; Haberaecker, W. W., III; Blum, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 2168. (c) Nakao, Y.; Idei, H.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, *131*, 15996. (d) Nakao, Y.; Idei, H.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, *131*, 5070. (e) Ohashi, M.; Shibata, M.; Saijo, H.; Kambara, T.; Ogoshi, S. *Organometallics* **2013**, *32*, 3631.

(16) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (b) Huang, J.; Haar, C. M.; Nolan, S. P.; Marcone, J. E.; Moloy, K. G. *Organometallics* **1999**, *18*, 297. (c) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (d) Nakamura, E.; Yamanaka, M.; Mori, S. *J. Am. Chem. Soc.* **2000**, *122*, 1826. (e) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576. (f) Yamamoto, T.; Aba, M.; Murakami, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1997. (g) Shen, Q. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7734. (h) Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2013**, *135*, 9612.

(17) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 438.