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Relative Rates of Hydrosilylation of Representative Alkenes and Alkynes by $Cp^*_2YMe\cdot THF$ and $[Cp^{TMS}_2YMe]_2$

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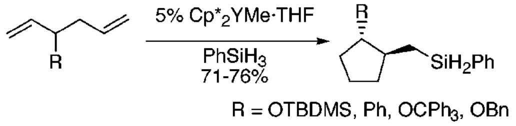
Reactivity in the hydrosilylation of alkenes and alkynes catalyzed by the organoyttrium catalysts $Cp^*_2YMe\cdot THF$ and $[Cp^{TMS}_2YMe]_2$ is generally determined by the steric environment of the substrate. Alkynes and conjugated alkenes show an increased reaction rate because of electronic effects; the magnitude of this increase is highly substrate dependent. The electron rich pyrrole system is particularly reactive, especially with the sterically open $[Cp^{TMS}_2YMe]_2$ precatalyst. For nonconjugated substrates, $Cp^*_2YMe\cdot THF$ is generally a more selective catalyst than $[Cp^{TMS}_2YMe]_2$.

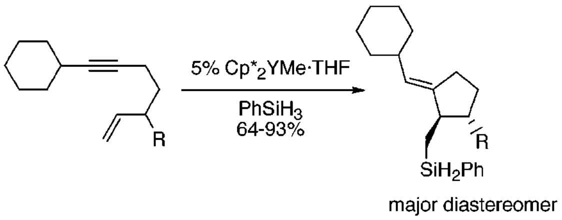
Introduction

Organolanthanide and group 3 organometallic compounds are emerging as potent catalysts in organic synthesis. Initially used for the polymerization and hydrogenation of simple alkenes,[1] these complexes have more recently catalyzed the cyclization/silylation of dienes, enynes, and trienes to produce more complex molecules.[1i] As the substrates become more complex, however, with multiple reaction sites available, the ability to predict the chemoselectivity of the reaction before preparing the starting material becomes a major concern.

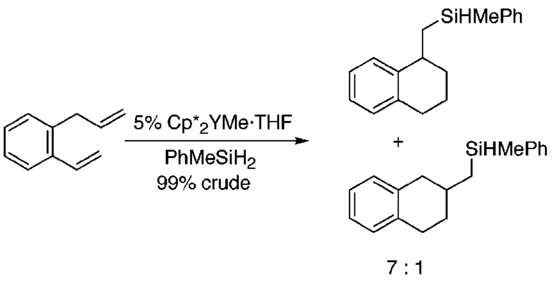
As seen in a sample catalytic cycle of the cyclization/silylation of a diene by $Cp^*_2YMe\cdot THF$ (Scheme 1), the substitution pattern of the product obtained will depend solely on the relative reactivity exhibited by the catalyst in the initial insertion event. Numerous experiments have qualitatively demonstrated that reactivity depends on the steric environment of the alkene or alkyne.[1d,2] For example, cyclization/silylation of substituted 1,5-dienes and many 1,6-enynes by $Cp^*_2YMe\cdot THF$ provide a single product from exclusive insertion at one select site of unsaturation (eqs 1 and 2),[2a,3] but alkynes and conjugated alkenes compete with less hindered alkenes to form mixtures of products (eqs 3 and 4).[4] Because this information was determined empirically, quantitative information for the relative rates of hydrosilylation of a variety of substrates was sought. The catalysts investigated in the studies described herein, $Cp^*_2YMe\cdot THF$ and $[Cp^{TMS}_2YMe]_2$, were chosen on the basis of their previously demonstrated effectiveness as selective hydrosilylation and cyclization/silylation catalysts. Relative rates of reaction were determined by the competition method.[5]



(1)



(2)



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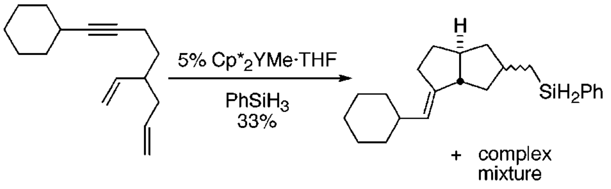

(4)

Results and Discussion

To determine the relative rates of hydrosilylation, 1 equiv each of two substrates was mixed with 1.2 equiv of silane, 0.5 equiv of dodecane as an internal standard, and 0.6−2.9 mol % catalyst in cyclopentane. Competition pairs were chosen such that the rate of the faster

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[1] (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (c) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (e) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (f) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765. (g) Qian, C.; Xie, Z.; Huang, Y. *J. Organomet. Chem.* **1987**, *323*, 285. (h) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (i) Molander, G. A. *Chemtracts* **1998**, *11*, 237 and references therein.

[2] (a) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415. (b) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (c) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347. (d) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123. (e) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266.

[3] Molander, G. A.; Retsch, W. H. *J. Am. Chem. Soc.* **1997**, *119*, 8817.

[4] (a) Nichols, P. J., Ph.D. Thesis, University of Colorado, 1997. (b) Retsch, W. H., Ph.D. Thesis, University of Colorado, 1997.

[5] (a) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 5080. (b) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.

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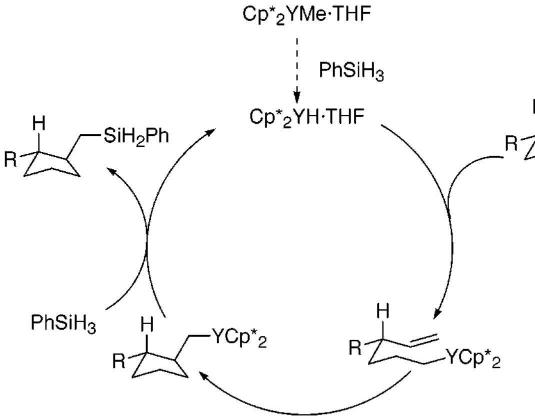
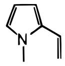
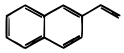
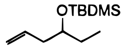
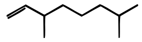
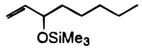
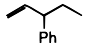
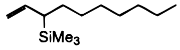
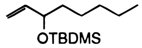
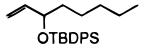
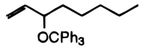
Scheme 1



[a] Defined as rate = 100. [b] Substrate is unreactive at the given temperature.

substrate was not more than 10 times greater than that of the slower; all rates were then normalized to a single substrate (typically 1-decene) which was arbitrarily defined as having a reaction rate = 100. The temperature for a group of substrates was chosen to provide reasonable reaction times (minutes or hours) so as to be consistent with what would realistically be used in a synthetic operation. It is important to note that because the reaction temperature used was different for each catalyst and/or type of substrate, one cannot necessarily compare values from two different columns in any of the following tables. While the reaction was in progress, samples were taken at various intervals to measure the amounts of substrates remaining against the internal standard. A wide variation in the overall reaction times and difficulty in sampling resulted in some deviation in the times at which the measurements were taken. However, as the Ingold–Shaw expression applies at any point during the reaction,[5] calculated relative rates will be comparable for measurements taken between 50 and 100% of reaction completion (i.e., until 1 equiv total of the substrates has reacted).

Table 1. Relative Rates of Hydrosilylation of Terminal Alkenes

entry	substrate	$Cp^*_2YMe \cdot THF$ (25 °C)	$[Cp^{TMS}_2YMe]_2$ (45 °C)
1		340	> 1000 [a]
2		34	700
3	1-decene	100 [b]	100 [b]
4		61	69
5		42	41
6		26	- [c]
7		25	39
8		16	12
9		7.5	21
10		7.1	14
11		0.79	7.5

[a] The rate was more than 10 times faster than 1-decene. This substrate could not be reacted in direct competition with vinylnaphthalene, as decomposition of vinylpyrrole occurs over the 1–3 days it takes for vinylnaphthalene competition reactions to reach 50% completion. [b] Rate defined as 100. [c] No reaction occurs at the given temperature.

Table 2. Comparison of Relative Rates of Hydrosilylation to *A* Values[a]

group	*A* value (kcal/mol)	$Cp^*_2YMe \cdot THF$ (relative rate at 25 °C)	$[Cp^{TMS}_2YMe]_2$ (relative rate at 45 °C)
$OSiMe_3$	0.74	26	*b*
Me	1.74	42	41
$SiMe_3$	2.5	16	12
Ph	2.8	25	39

[a] *A* values from reference 7. [b] Unreactive at the given temperature.

The relative rates of hydrosilylation of terminal alkenes by $Cp^*_2YMe \cdot THF$ and $[Cp^{TMS}_2YMe]_2$ are depicted in Table 1. In general, both catalysts show a decrease in the relative rate of hydrosilylation with an increase in the steric hindrance of the substrate. Even the rate of hydrosilylation of an allylsilane (entry 8, Table 1) is related to its steric bulk, despite the stabilizing effect silicon would have on any partial positive charge developing β to the silane.[6] When comparing relative rates of hydrosilylation to *A* values,[7] substrates with $OSiMe_3$ and $SiMe_3$ groups are disproportionately slower than one would expect (Table 2). This indicates that the yttrium catalysts are affected by steric bulk even somewhat removed from the double bond. This is particularly evident in the protected allyl alcohols where $Cp^*_2YMe \cdot THF$ is generally a less reactive catalyst than $[Cp^{TMS}_2YMe]_2$ (entries 6 and 9–11, Table 1). This reactivity difference can be attributed to the methyl groups on the cyclopentadiene rings of $Cp^*_2YMe \cdot THF$ which make its reactive site more crowded than that of $[Cp^{TMS}_2YMe]_2$. Consequently, it is more difficult for hindered substrates to approach the metal for insertion into the metal hydride bond. This difference may also be why a trimethylsilyl-protected allyl alcohol is unreactive with the more sterically open $[Cp^{TMS}_2YMe]_2$ at the given temperature (Table 1, entry 6); the oxygen is exposed enough to coordinate to yttrium and effectively inhibit the catalytic cycle.[8]

Electronic effects appear to affect the reaction rate only for vinylpyrrole and vinylnaphthalene (Table 1, entries 1 and 2). These conjugated substrates are hydrosilylated faster than the sterically less crowded 1-decene. This is in spite of the fact that hydrosilylations of styrene by various organoyttrium catalysts[9] and that of vinylpyrrole compounds by $[Cp^{TMS}_2YMe]_2$[10] do not proceed by the typical "1,2 addition" where the yttrium is added to the terminal carbon, but instead proceed via a sterically unfavorable "2,1 addition" resulting in yttrium addition to the more hindered carbon (Figure 1). As there is

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(6) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Lambert, J. B.; Wang, G. T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(7) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley & Sons: New York, 1994.

(8) For other examples of an $OSiMe_3$ group coordinating to a metal see (a) Chen, X.; Hortelano, E. R.; Eliel, E. L.; Frye, S. V. *J. Am. Chem. Soc.* **1990**, *112*, 6130. (b) Reetz, M. T.; Hüllmann, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1600.

(9) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, B. H.; Teuben, J. H. *Organometallics* **1998**, *17*, 284, and references therein.

(10) Molander, G. A.; Schmitt, M. H. Unpublished results.

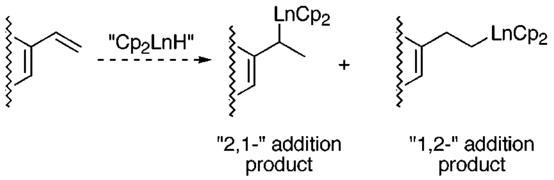
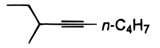
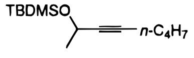


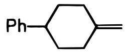
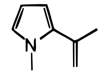
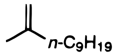
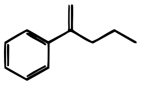
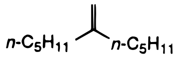
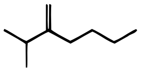
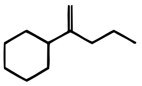
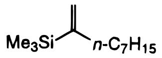
Figure 1. Regioisomers derived from olefin insertion of conjugated dienes into metallocene hydride complexes.

Table 3. Relative Rates of Hydrosilylation of Alkynes

entry	substrate	$Cp^*_2YMe{\cdot}THF$ (80 °C)	$[Cp^{TMS}_2YMe]_2$ (45 °C)
1	1-decene	100 [a]	100 [a]
2	2-decyne	1500	140
3	5-decyne	650	120
4		120	69
5		130	- [b]

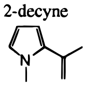
[a] Defined as rate = 100. [b] Unreactive at the temperature given.

Table 4. Relative Rates of Hydrosilylation of 1,1-Disubstituted Alkenes

entry	substrate	$[Cp^{TMS}_2YMe]_2$ (80 °C)
1		340
2		260
3		100 [a]
4		71
5		37
6		8.1
7		7.6
8		5.8

[a] Defined as rate = 100.

Table 5. Direct Comparison of Highly Reactive Substrates

entry	substrate	$Cp^*_2YMe{\cdot}THF$ (25 °C)	$[Cp^{TMS}_2YMe]_2$ (45 °C)
1	1-decene	100 [a]	100 [a]
2	2-decyne	670	140
3		- [b]	150

[a] Defined as rate = 100. [b] Substrate is unreactive at the given temperature.

evidence of organolanthanide compounds coordinating in a η^n- fashion to benzyl and styryl ligands,[11] it has been suggested that 2,1-addition may be a result of initial coordination of yttrium to the π bonds of the arene ring.[12] This initial coordination stabilizes the electron deficient metal center and lowers the energy of activation for olefin insertion, and in doing so directs the regiochemistry of the alkene insertion so that the yttrium remains near the arene at the more hindered olefin site. The unusual regiochemistry of reaction as well as the extraordinarily high rate of hydrosilylation for vinylpyrrole and vinylnaphthalene is consistent with such a substrate-directed reaction.[13] This initial coordination is also supported by the observation that electronic effects are particularly pronounced for $[Cp^{TMS}_2YMe]_2$, which should be better able to accommodate the arene as a ligand because it possesses more open space about the coordination sphere of the metal.

Alkynes generally insert more rapidly into the catalyst as seen by their faster relative rates of reaction (Table 3), but the overall reaction time is longer. The alkynes undergo faster insertion because they are typically less sterically hindered and more electronically rich. Once formed, however, the alkenylyttrium species is sterically crowded, resulting in slow σ-bond methathesis with the silane. Otherwise, alkynes follow the same general pattern of reactivity as terminal alkenes in that $Cp^*_2YMe{\cdot}THF$ is a less reactive catalyst than $[Cp^{TMS}_2YMe]_2$, and the more sterically hindered the substrate, the slower the relative rate of hydrosilylation. It is unclear why $[Cp^{TMS}_2YMe]_2$ is unreactive with a TBDMS protected propargyl alcohol (Table 3, entry 5). Perhaps ionization of this substrate by the Lewis acid catalyst is responsible.[4b]

The relative rates of hydrosilylation of 1,1-disubstituted alkenes were determined with $[Cp^{TMS}_2YMe]_2$ (Table 4). The precatalyst $Cp^*_2YMe{\cdot}THF$ reacts only slowly or not at all with these substrates.[2c] As with terminal alkenes and internal alkynes, steric effects dominate the relative rates with the exception of the pyrrole (Table 4, entry 2). The relative rate of hydrosilylation of the pyrrole is closer to that of the sterically less hindered methylenecyclohexane (Table 4, entry 1) than to the sterically similar conjugated α-propylstyrene (Table 4, entry 4). Surprisingly, the relative reaction rate of α-propylstyrene seems to be determined almost solely by its steric size, in contrast to vinylnaphthalene (entry 2, Table 1) which showed a higher electronically influenced reaction rate. This again points to the pronounced steric effects of substituents at the allylic position and beyond in various olefin substrates.

For a more direct comparison of the role played by electronic effects, 1-decene, 2-decyne, and *N*-methyl-2-(1-methylvinyl)pyrrole were compared at the same reaction temperature (Table 5). Electronic effects are clearly more important for the sterically open $[Cp^{TMS}_2YMe]_2$ than for $Cp^*_2YMe{\cdot}THF$ as evidenced by the similar reaction rate of the alkene, alkyne, and pyrrole. For $Cp^*_2YMe{\cdot}THF$, steric effects play a more important role as the unhindered alkyne inserts relatively quickly, whereas the electronically rich but sterically hindered pyrrole is unreactive at room temperature.

Summary

For the catalysts $Cp^*_2YMe{\cdot}THF$ and $[Cp^{TMS}_2YMe]_2$, the steric environment of the substrate determines the

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[11] (a) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

[12] Giardello, M. S.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

[13] Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.

relative rates of hydrosilylation with the exception of conjugated alkenes. Electronic effects cause an increased reaction rate for conjugated alkenes, although the magnitude of the increase is highly substrate dependent. The electron rich pyrrole system is particularly reactive, especially with an "open" $[Cp^{TMS}{}_2YMe]_2$ precatalyst. For nonconjugated substrates, $Cp^*{}_2YMe{\cdot}THF$ is generally a more selective catalyst than $[Cp^{TMS}{}_2YMe]_2$. The results reported herein not only demonstrate the reactivities that can be achieved in insertion reactions with these metallocene catalysts on a quantitative basis, but also illustrate in a dramatic fashion how reactivities and selectivities can be changed by relatively simple manipulations of the ligand system about the metal.

Experimental Section

The catalysts $Cp^*{}_2YMe{\cdot}THF$[14] and $[Cp^{TMS}{}_2YMe]_2$[15] were prepared by known methods. Substrates for Table 1, entries 2, 3, 5, and 7, and Table 3, entries 2 and 3, were commercially available. Substrates for Table 1, entry 1, and Table 4, entries 1−7, were prepared via a Wittig reaction from commercially available ketones.[16] Substrates for Table 1, entries 4, 6, and 9−11, were alcohols protected by conventional methods.[17] Preparations for all other substrates are described below. NMR chemical shifts are reported in ppm relative to TMS using the residual solvent resonance as an internal reference. All chemicals were dried, degassed, and stored in a Vacuum Atmospheres glovebox before use. Reactions were prepared in the glovebox and performed with rigorous exclusion of air and moisture. Reaction temperatures were maintained at ± 1 °C. Competition reactions were analyzed by GC, and relative rates were calculated from the amounts of starting materials remaining according to the Ingold−Shaw equation.[5]

Competition Reactions with $Cp^*{}_2YMe{\cdot}THF$. In a typical reaction, 2.00 mmol of each substrate, 2.5 mmol of $PhSiH_3$, 0.75 mL of cyclopentane, and 1.0 mmol of dodecane were mixed, and a sample of the solution was taken to determine time = 0 concentrations. Meanwhile, a mixture of 0.011−0.058 mmol (0.6−2.9%) of the catalyst and 0.75 mL of cyclopentane was prepared in a separate vial. After refrigerating both vials at −23 °C for 5.0 min the catalyst mixture was added dropwise to the substrate solution over 1−2 min. Samples were taken immediately after addition of the catalyst was complete and at various intervals throughout the course of the reaction. The samples were quenched by addition to a vial containing a small amount of Florisil. After dilution with MeOH and filtration through a glass wool plug, the amounts of substrates remaining were analyzed on a Hewlett-Packard 5890 GC with a 5% phenylmethylsilicone column using the dodecane as an internal standard. Relative rates were determined by applying the Ingold−Shaw equation: $k_A/k_B = (\ln[A]_0 - \ln[A]_t)/(\ln[B]_0 - \ln[B]_t)$[5a] where t was such that the reaction was 50−100% complete. Relative rates were normalized to 1-decene which was defined with rate = 100. Reaction pairs were chosen so that their relative rates were within 10 times of each other.

Competition Reactions with $[Cp^{TMS}{}_2YMe]_2$. In a typical reaction, 2.00 mmol of each substrate, 2.5 mmol of $PhSiH_3$, 1.0 mmol of dodecane, and 1.5 mL of cyclopentane were mixed, and a sample was taken to determine time = 0 concentrations. After addition of 0.012−0.045 mmol (0.6−2.3%) of the yttrium dimer the reaction was divided between two valved flasks, and both were quickly transferred to an oil bath at the appropriate temperature. The flasks were opened to the air (thus quenching the reaction) or taken to the glovebox to sample and then analyzed as above.

4-[(1,1-Dimethylethyl)dimethylsiloxy]-1-hexene. 4-[(1,1-Dimethylethyl)dimethylsiloxy]-1-hexene was prepared from 1-hexen-4-ol and *tert*-butyldimethylsilyl chloride using standard reaction conditions.[16] Purification by flash chromatography (silica gel, hexanes) and kugelrohr distillation (11 mmHg, 74−84 °C) resulted in the isolation of 4.76 g (88%) of 4-[(1,1-dimethylethyl)dimethylsiloxy]-1-hexene (98% pure by GC analysis): R_f 0.29; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84−5.75 (m, 1H), 5.04−4.98 (m, 2H), 3.60 (quint, J = 5.74, 1H), 2.18 (t, J = 7.20, 2H), 1.47−1.37 (m, 2H), 0.87 (s, 9H), 0.85 (t, J = 7.57, 3H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.54, 116.47, 73.18, 41.45, 29.46, 25.89 (3C), 18.16, 9.64, −4.44, −4.55; IR (neat) 3077.9, 1640.7, 1434.0, 1360.6, 1254.2, 1058.0, 910.4 cm^{-1}; HRMS calcd for $C_{12}H_{26}OSi$ $(M - CH_3)^+$ 199.1518, found 199.1516; LRMS (EI) m/z 173 (17), 157 (44), 129 (33), 115 (16), 99 (51), 73 (100), 59 (28), 41 (38), 29 (23).

3-(Trimethylsilyl)-1-decene. 3-(Trimethylsilyl)-1-decyne was prepared from 1-decyne.[18] Clean reduction of the alkyne to 3-(trimethylsilyl)-1-decene was achieved by hydroboration by dicyclohexylborane[19] followed by removal of the borane with methanol.[20] This compound has been previously reported in the literature.[21]

3-Methyl-4-nonyne. 3-Methyl-4-nonyne was prepared by alkylation of 3-methyl-1-pentyne with butyl iodide.[2b] This compound has been previously reported in the literature.[22]

2-[(1,1-Dimethylethyl)dimethylsiloxy]-3-decyne. 3-Decyn-2-ol was prepared from 1-octyne and acetaldehyde.[4b] The alcohol was protected as the *tert*-butyldimethylsilyl ether by standard methods.[16] Purification by flash chromatography (silica gel, 20:1 hexanes:ethyl acetate) followed by kugelrohr distillation (0.3 mmHg, 79−89 °C) resulted in the isolation of 5.08 g (93%) of 2-[(1,1-dimethylethyl)dimethylsiloxy]-3-decyne (98% pure by GC analysis): R_f 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (q, J = 6.43, 1H), 2.15 (td, J = 6.96, 1.87, 2H), 1.48−1.23 (m, 11H), 0.95−0.81 (m, 12 H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.70, 82.81, 59.24, 31.36, 28.64, 28.52, 25.85 (3C), 25.78, 22.57, 18.68, 18.27, 14.03, −4.56, −4.91; IR (neat) 2232.7, 1159.3, 1101.6 cm^{-1}; HRMS calcd for $C_{16}H_{31}OSi$ $(M - H)^+$ 267.2144, found 267.2134; LRMS (EI) m/z 268 (0.1), 253 (4), 211 (80), 167 (100).

2-(Trimethylsilyl)-1-nonene. *tert*-Butyllithium (13.0 mL, 1.7 M, 22.1 mmol) was slowly added to THF (20 mL) at −78 °C. (1-Bromovinyl)trimethylsilane (2.07 g, 11.6 mmol) was slowly added, and the solution was stirred for 1.5 h. After iodoheptane (2.26 g, 10.0 mmol) was slowly added, the reaction was allowed to warm to room-temperature overnight. The mixture was quenched with aqueous $NaHCO_3$, extracted with pentane, washed with water and brine, and dried over $MgSO_4$. Purification by flash chromatography (silica gel, hexanes) followed by distillation (19 mmHg, 54 °C) resulted in the isolation of 0.80 g (40%) of 2-(trimethylsilyl)-1-nonene (100% pure by GC analysis). Spectral data matched that reported in the literature.[23]

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