ELSEVIER

Journal of Organometallic Chemistry 524 (1996) 275–279

Journal of Organometallic Chemistry

Preliminary communication

Organolanthanide catalyzed hydrogenation and hydrosilylation of substituted methylenecycloalkanes

Gary A. Molander *, Jörn Winterfeld

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

Received 3 January 1996; in revised form 22 February 1996

Abstract

This communication presents a study of the scope of the catalytic hydrogenation and hydrosilylation of chiral exomethylene-substituted cyclopentanes and cyclohexanes utilizing the organolanthanide precatalysts $Cp^*_2LnCH(SiMe_3)_2$ ($Cp^* = C_5Me_5$; Ln = Sm, Yb). Both reaction types are sterically driven and lead to the *cis*-diastereomer as the major product. Additionally, the hydrosilylation is regiospecific, the silane being placed exclusively at the terminal position of the double bond.

Keywords: Samarium; Ytterbium; Silicon; Lanthanides; Hydrogenation; Hydrosilylation

Organolanthanides and Group 3 organometallics [1] are effective homogeneous catalysts for olefin hydrogenation [2] and hydrosilylation [3]. The possibility of olefin insertion into Ln–H or Ln–C bonds, combined with σ-bond metathesis reactions transpiring through four center transition states, permits the development of a number of useful synthetic transformations. As an example, both catalytic hydrogenation and hydrosilylation reactions can be coupled to other organolanthanoid-catalyzed transformations (e.g., polyene cyclizations [2g,3d,3e]) for the construction of carbocycles and heterocycles. Unlike some transition metal-catalyzed processes [4], organolanthanide-catalyzed processes are typically not directed by polar groups, but appear purely steric in their selectivity patterns.

Building upon these characteristics and our interest to utilize the potential of organolanthanide and Group 3 organometallic catalysts for selective organic synthesis [2g,2h,3c,3d,3f], we initiated a program to examine the stereochemical features of the hydrogenation and hydrosilylation of substituted exomethylenecycloalkanes [5]. The catalytic cycle for both types of reactions mediated by the precatalysts $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Sm, Yb) [6] is outlined in Scheme 1. The generation of the active catalyst 'Cp^*_2LnH' as well as the individual steps in the process for the hydrogenation and the hydrosilylation respectively, are well documented [2a,2c,3a,7].

The hydrogenation reactions were typically carried out utilizing 3–5 mol.% of the precatalyst in cyclopentane under 3–4 atm of hydrogen pressure. The reactions were generally complete within 3 h [8]. The results are summarized in Table 1. In all of the reactions good to excellent yields were achieved in spite of the fact that many of the products were volatile and difficult to isolate.

In cases where bulky substituents flanked the exomethylene group of the cyclohexyl system, (e.g., **5c** and **5e**) as well as in the α-substituted methylenecyclopentanes (**1a** and **1b**), attack of the catalyst takes place exclusively from the less hindered Si-face, leading to the corresponding *cis*-product (Scheme 2).

For the sterically less hindered methylenecyclohexanes (**5a**, **5b**, and **5d**) the hydrogenation reaction loses some of its selectivity and does not lead exclusively to the *cis*-product. Improvement of the diastereoselectivities could be obtained by running the reactions at −20°C. Further lowering of the temperature led to a drastic increase in the reaction times.

Higher reaction temperatures were required for the hydrogenation of the substrates **5e** and **5f**. Intramolecular complexation of the electrophilic lanthanide center with either the arene π-system or the amine is perhaps

* Corresponding author.

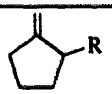
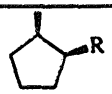
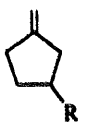
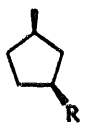
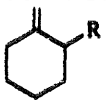
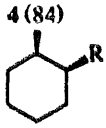
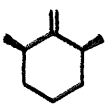
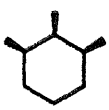
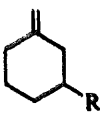
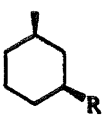
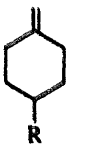
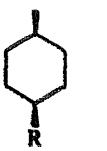
PII S0022-328X(96)06276-6

responsible for these results. The methoxy group in **5g** totally inhibits the catalytic reaction, presumably because a strong coordinative bond between the oxygen and the lanthanide center forms. There are considerable precedents for such interactions in lanthanide chemistry [10].

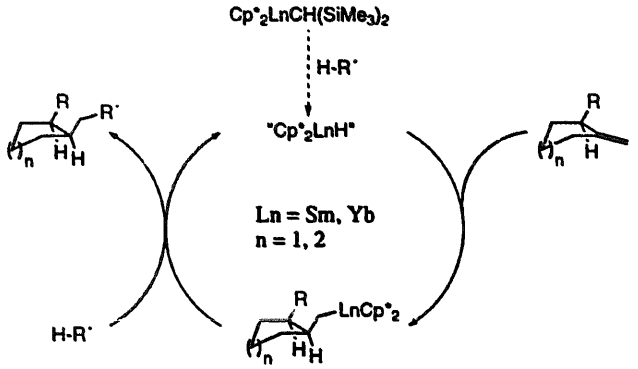
When both α-positions are alkylated, as in *cis*-1,3-dimethyl-2-methylenecyclohexane **7**, the olefin is virtually inert to organolanthanide-catalyzed hydrogenation, even at elevated temperatures (Table 1).

Increasing the distance between the exomethylene group and the substituent *R* decreases the stereoselectivity in the catalytic hydrogenation reactions. The best diastereoselectivities for the β- and γ-substituted methylenecycloalkanes **8a**, **8b**, and **10** could be obtained at −20°C and by utilizing the precatalyst $Cp_2^*YbCH(SiMe_3)_2$. The ratio of *cis*:*trans* isomeric products is 2%–3% better with this precatalyst than for the hydrogenations of these three substrates with the corresponding samarium catalyst under the same conditions. Unfortunately, the decreased ionic radius of Yb^{3+} compared with Sm^{3+} [11] demonstrated no remarkable positive effect on the hydrogenation of the α-substituted methylenecyclohexanes.

Table 1
Diastereoselective hydrogenation of substituted exomethylenecycloalkanes utilizing catalytic $Cp_2^*LnCH(SiMe_3)_2$(Ln = Sm, Yb)

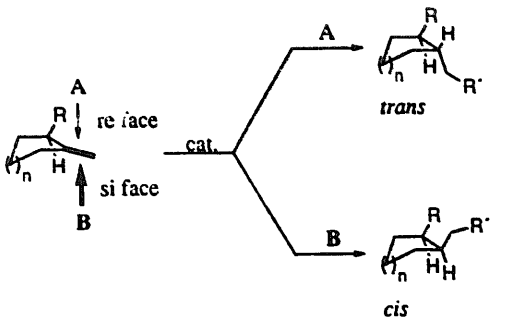
Entry	Substrate	Major product (% yield) [a]	Mol.% cat./ reaction temp. (°C)	Diastereoselectivity/ *cis*:*trans* [b]
				
1	**1a** R = *iso*-Bu	**2a** (84)	10/r.t. [c]	100:0
2	**1b** R = $CH_2C_6H_4Cl$-2	**2b** (32)	10/r.t. [c]	100:0
				
3	**3** R = n-Bu	**4** (84)	3/0 [c]	60:40
				
4	**5a** R = Me	**6a** (77)	3/−20 [c]	93:7
5	**5b** R = *iso*-Bu	**6b** (90)	3/−20 [c]	95:5
6	**5c** R = *tert*-Bu	**6c** (95)	5/r.t. [c]	100:0
7	**5d** R = Bn	**6d** (95)	3/−20 [c]	93:7
8	**5e** R = Ph	**6e** (96)	5/50 [c]	100:0
9	**5f** R = $(CH_2)_3NMe_2$	**6f** (76)	3/50 [c]	91:9
10	**5g** R = OMe	-	5/70 [c]	-
				
11	**7**	-	5/70 [c]	-
				
12	**8a** R = Me	**9a** (73)	3/−20 [d]	61:39
13	**8b** R = Et	**9b** (79)	3/−20 [d]	73:27
				
14	**10** R = *tert*-Bu	**11** (73)	3/−20 [d]	77:23

[a] Isolated yields of the diastereomeric mixture. [b] Ratios were determined on the crude reaction mixture by fused silica capillary gas chromatography. Satisfactory spectral data (^1H NMR, ^{13}C NMR, IR) and high-resolution mass spectrometry analysis were obtained on the compounds reported herein [9]. [c] $Cp_2^*SmCH(SiMe_3)_2$. [d] $CP_2^*YbCH(SiMe_3)_2$.



hydrogenation: R'= H
hydrosilylation: R'= SiH_2Ph

Scheme 1.

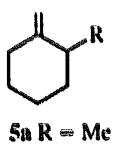
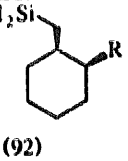
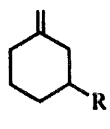
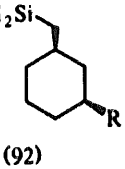
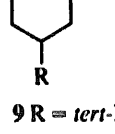
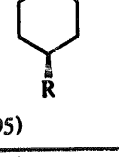


Scheme 2.

Because of the extreme Lewis acidity of the lanthanide catalyst, some isomerisation of the double bond (1%–2%) was observed in each of the hydrogenations and hydrosilylation reactions performed. The isomerised, endocyclic double bond isomers could not be hydrogenated nor hydrosilylated under the conditions.

Hydrosilylation reactions exhibited the same general characteristics as the hydrogenation reactions outlined above. In a typical hydrosilylation reaction, a substituted exomethylenecyclohexane and 1.1 equiv. of phenylsilane in the presence of $Cp_2^*SmCH(SiMe_3)_2$ provided an excellent yield of the corresponding *cis*-substituted (phenylsilyl)methylcyclohexane as the major diastereomer [12]. The results for these reactions using a variety of substrates are listed in Table 2. The reaction takes place with high regioselectivity, wherein the silyl group is delivered exclusively to the terminal position of the double bond. These results are in agreement with earlier findings that $Cp_2^*YCH(SiMe_3)_2$ mediated the

Table 2
Diastereoselective hydrosilylation of substituted methylenecycloalkanes utilizing catalytic $Cp_2^*SmCH(SiMe_3)_2$

Entry	Substrate	Major product (% yield) [a,b]	Diastereoselectivity / *cis*:*trans* [c]
			
14	5a R = Me	12a (92)	88:12
15	5b R = *iso*-Bu	12b (90)	93.5:6.5
16	5d R = Bn	12d (91)	93:7
17	5f R = $(CH_2)_3NMe_2$	12f (63)	93:7
			
18	7b R = Et	13b (92)	62:38
			
19	9 R = *tert*-Bu	14 (95)	60:40

[a] All reactions were performed with 5 mol % of the $Cp_2^*SmCH(SiMe_3)_2$ precatalyst at 70°C. [b] Isolated yields of the diastereomeric mixture. [c] Ratios were determined on the crude reaction mixture by fused silica capillary gas chromatography. Satisfactory spectral data (^1H NMR, ^{13}C NMR, IR) and high-resolution mass spectrometry analysis were obtained on the compounds reported herein [13].

hydrosilylation of a variety of aliphatic olefins with high selectivity for 1,2 addition [3c]. The hydrosilylations were performed at 70°C in order to achieve satisfactory reaction rates. At the same time, this leads to a minor loss of diastereoselectivity in these reactions compared with the corresponding hydrogenations. Variation of the lanthanide size, using $Cp_2^*YbCH(SiMe_3)_2$ instead of the corresponding samarium complex as a precatalyst, has only a minor influence on the stereoselectivity of the reaction.

The observation that the hydrosilylation of substituted exomethylenecyclohexanes (Scheme 1) takes precedence over the dehydrogenative polymerisation of the silane is significant because the latter is reported to be a facile process [7c,14]. Others have, however, noted the ability to perform the hydrosilylation selectively without polysilane formation [15]. Another particularly notable feature of the current work is that it represents one of the first successful hydrosilylation reactions of 1,1-disubstituted alkenes [1c,1e]. This olefin class is more sterically demanding than terminal olefins, and while several others have apparently not investigated this class [1a,1b], those who have generally report either very low yields under rigorous reaction conditions or altogether unsuccessful reactivity [15].

In conclusion, $Cp_2^*LnCH(SiMe_3)_2$ complexes (Ln = Sm, Yb) are efficient precatalysts for the diastereoselective hydrogenation and hydrosilylation of chiral exomethylene-substituted cycloalkanes. The reaction tolerates functional groups like tertiary amines or chlorides and proceeds with good yield. Additionally, the silylated products can be easily transformed into useful organic intermediates. For example, oxidation of the phenylsilane group proceeds readily to provide the corresponding alcohol [3d,15]. Further studies regarding organolanthanide-catalyzed hydrogenation and hydrosilylation reactions and their application to selective organic synthesis continue in these laboratories.

Acknowledgment

This research was supported by the National Institutes of Health. J.W. thanks the German Academic Exchange Service (DAAD) for a NATO postdoctoral fellowship.

References and notes

[1] (a) T.J. Marks, and R.D. Ernst, in G. Wilkinson, F.G.A. Stone, and E.W. Abel, (eds.), *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1982, Chapter 21; (b) W.J. Evans, *Adv. Organomet. Chem.*, *24* (1985) 131; (c) H. Schumann, in T.J. Marks, and I. Fragala, (eds.); *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, Reidel, Dordrecht, 1985, Chapter 1; (d) C.J. Schaverien, *Adv. Organomet. Chem.*, *36* (1994) 283; (e) H. Schumann, J.A. Meese-Marktscheffel, and L. Esser, *Chem. Rev.*, *95* (1995) 865.

[2] (a) W.J. Evans, J.H. Meadows, W.E. Hunter, and J.L. Atwood, *J. Am. Chem. Soc.*, *106* (1984) 1291; (b) H. Mauermann, P.N. Swepston, and T.J. Marks, *Organometallics*, *4* (1985) 200; (c) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, and T.J. Marks, *J. Am. Chem. Soc.*, *107* (1985) 8111; (d) C. Qian, Z. Xie, and Y. Huang, *J. Organomet. Chem.*, *323* (1987) 285; (e) C. Qian, Y. Ge, D. Deng, Y. Gu, and C. Zhang, *J. Organomet. Chem.*, *344* (1988) 175; (f) D. Stern, M. Sabat, and T.J. Marks, *J. Am. Chem. Soc.*, *112* (1990) 9558; (g) G.A. Molander, and J.O. Hoberg, *J. Am. Chem. Soc.*, *114* (1992) 3123; (h) G.A. Molander, and J.O. Hoberg, *J. Org. Chem.*, *57* (1992) 3266; (i) V.P. Conticello, L. Brard, M.A. Giardello, Y. Tsujii, M. Sabat, C.L. Stern, and T.J. Marks, *J. Am. Chem. Soc.*, *114* (1992) 2761; (j) M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagné, and T.J. Marks, *J. Am. Chem. Soc.*, *116* (1994) 10241.

[3] (a) I.P. Beletskaya, A.Z. Voskoboinikov, I.N. Parshina, and G.K.-I. Mogomedov, *Izv. Akad. Nauk. USSR*, (1990) 693; (b) T. Sakakura, H.-J. Lautenschlager, and M. Tanaka, *J. Chem. Soc. Chem. Commun.*, (1991) 40; (c) G.A. Molander, and M. Julius, *J. Org. Chem.*, *57* (1992) 6347; (d) G.A. Molander, and P.J. Nichols, *J. Am. Chem. Soc.*, *117* (1995) 4415; (e) P.-F. Fu, L. Brard, Y. Li, and T.J. Marks, *J. Am. Chem. Soc.*, *117* (1995) 7157; (f) G.A. Molander, and W.H. Retsch, *Organometallics*, *14* (1995) 4570.

[4] (a) J.M. Brown, *Angew. Chem. Int. Ed. Engl.*, *26* (1987) 190; (b) H. Takaya and R. Noyori, in B.M. Trost, (ed.) *Comprehensive Organic Synthesis*, Vol. 8, Pergamon, New York, 1991, Chapter 3.2; (c) A.H. Hoveyda, D.A. Evans, and G.C. Fu, *Chem. Rev.*, *93* (1993) 1307.

[5] The substituted methylenecycloalkane substrates were prepared from the corresponding ketones by Wittig chemistry according to the general procedure reported in the following: L. Fitjer, and U. Quabeck, *Synth. Commun.*, *15* (1985) 855.

[6] The precatalysts $Cp_2^*LnCH(SiMe_3)_2$ (Ln = Sm, Yb) were prepared from $Cp_2^*Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$ by treatment with $LiCH(SiMe_3)_2$ in toluene according to the literature. G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, and T.J. Marks, *J. Am. Chem. Soc.*, *107* (1985) 8091.

[7] (a) P.L. Watson, *J. Chem. Soc. Chem. Commun.*, (1983) 276; (b) W.E. Piers, P.J. Shapiro, E.E. Bunel, and J.E. Bercaw, *Synlett* (1990) 74; (c) S.P. Nolan, M. Porchia, and T.J. Marks, *Organometallics*, *10* (1991) 1450; (d) N.S. Radu, and T.D. Tilley, *J. Am. Chem. Soc.*, *117* (1995) 5863.

[8] All reactions were carried out with strict exclusion of oxygen and water. In a typical procedure $Cp_2^*LnCH(SiMe_3)_2$ (Ln = Sm, Yb; 0.03 mmol), 2 ml of cyclopentane, and the olefin (1.0 mmol) were loaded into a 50 ml flask equipped with an Ace needle valve. The homogeneous mixture was cooled to −196°C, purged-filled three times with hydrogen and then allowed to warm to the desired reaction temperature (Table 1). After being stirred for 5 h the crude mixture was opened and filtered through a small plug of Florisil. The solvent was removed and the product was flash chromatographed with SiO_2 (10% $AgNO_3$) and hexanes or cyclopentane as the eluant.

[9] The ^{13}C NMR data of the diastereomers **6a**, **9a**, and **11** were compared with the literature values: W. Bremser, (ed.), *Carbon-13 [Carbon] NMR spectral data*, Verlag Chemie, Weinheim, 1981.

[10] For examples, see: (a) W.J. Evans, T.A. Ulibarri, and J.W. Ziller, *J. Am. Chem. Soc.*, *112* (1990) 219; (b) H. Schumann, J.A. Meese-Marktscheffel, A. Dietrich, and F. Görlitz, *J. Organomet. Chem.*, *430* (1992) 299; (c) B. Wang, D. Deng, and C. Qian, *New J. Chem.*, *19* (1995) 515.

[11] R.E. Shannon, *Acta Crystallogr.*, *A32* (1976) 751.

[12] All reactions were carried out with strict exclusion of oxygen

and water. In a typical procedure $Cp_2^*SmCH(SiMe_3)_2$ (0.05 mmol), 2 ml of cyclohexane, the olefin (1.0 mmol), and H_3SiPh (1.1 mmol) were loaded into a 50 ml flask equipped with an Ace needle valve. The homogeneous mixture was stirred for 12 h at 70°C. After filtration through Florisil the solvent was removed and the crude product was flash chromatographed with SiO_2 and hexanes as eluant.

[13] Characterization data for the hydrosilylation products: **12a:** IR (neat) 3068, 3010, 2922, 2852, 2132, 1428, 1116, 940, 890, 837; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 −7.57 (m, 2H), 7.41–7.34 (m, 3H), 4.35–4.30 (m, 2H), 1.82–1.71 (m, 2H), 1.59–1.41 (m, 6H), 1.37–1.27 (m, 2H), 0.92–0.89 (m, 2.34H), 0.86 (d, J = 6.9 Hz, 2.64H, *cis*-diastereomer); ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*-diastereomer, δ 135.12, 133.09, 129.42, 127.93, 36.94, 34.41, 31.85, 30.30, 24.39, 22.36, 14.61, 12.36; *trans*-diastereomer, δ 129.38, 41.50, 39.64, 35.69, 34.73, 26.82, 26.60, 20.39, 15.32; HRMS calcd for $C_{14}H_{22}Si$ 218.1491, found 218.1485. **12b:** IR (neat) 3068, 2952, 2923, 2853, 2132, 1465, 1428, 1116, 940, 862; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61–7.59 (m, 2H), 7.41–7.36 (m, 3H), 4.38–4.33 (m, 2H), 1.86–1.82 (m, 1H), 1.67–1.29 (m, 10H), 1.16–1.04 (m, 2H), 0.96–0.92 (m, 2H), 0.89 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*-diastereomer, δ 135.20, 133.12, 129.43, 127.94, 40.01, 37.91, 35.52, 31.75, 28.11, 24.89, 24.10, 23.43, 22.91, 22.68, 22.45, 9.72; *trans*-diastereomer, δ 43.35, 41.79, 34.74, 31.75, 26.37, 26.23, 25.06, 24.35, 22.68, 21.45, 15.22; HRMS calcd for $(M-H)^+ = C_{17}H_{27}Si$ 259.1882, found 259.1874. **12d:** IR (neat) 3065, 3024, 2924, 2853, 2131, 1449, 1153, 938; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62–7.60 (m, 2H), 7.43–7.39 (m, 3H), 7.31–7.28 (m, 2H), 7.22–7.16 (m, 3H), 4.46–4.36 (m, 2H), 3.12 and 2.18 (m, 0.14H, *trans*-diastereomer), 2.65 and 2.52 (ABX-system, J_{AB} = 13.4, J_{AX} = 5.2, J_{BX} = 9.5 Hz, 1.86 H, *cis*-diastereomer), 1.95–1.87 (m, 2H), 1.64–1.50 (m, 5H), 1.42–1.31 (m, 3H), 1.11–1.09 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*-diastereomer, δ 141.65, 135.21, 132.78, 129.49, 129.04, 128.13, 127.99, 125.53, 42.82, 36.42, 35.70, 30.95, 27.09, 23.66, 23.03, 10.34; *trans*-diastereomer, δ 141.42, 133.03, 129.25, 45.98, 40.26, 39.45, 34.61, 31.31, 26.31, 26.03, 15.55; HRMS calcd for $C_{20}H_{26}Si$ 294.1804, found 294.1803. **12f:** IR (neat) 3068, 2925, 2854, 2131, 1450, 1116, 941, 892, 858; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56–7.54 (m, 2H), 7.36–7.31 (m, 3H), 4.33–4.29 (m, 2H), 3.19 (t, J = 7.4 Hz, 2H), 2.18 (s, 6H), 1.87–1.81 (m, 1H), 1.52–1.20 (m, 13 H), 0.92–0.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*-diastereomer, δ 135.05, 132.86, 129.31, 127.81, 60.18, 45.42, 40.61, 35.40, 30.88, 27.90, 27.77, 25.53, 22.71, 21.89, 9.57; *trans*-diastereomer, δ 133.05, 60.30, 43.87, 38.87, 34.51, 31.47, 31.02, 26.30, 26.20, 24.42, 15.07; HRMS calcd for $C_{18}H_{31}NSi$ 289.2226, found 289.2211. **13b:** IR (neat) 3068, 2959, 2918, 2852, 2131, 1378, 1185, 1116, 940, 913, 845; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59–7.57 (m, 2H), 7.39–7.34 (m, 3H), 4.34–4.31 (m, 2H), 1.92–1.68 (m, 3H), 1.62–1.39 (m, 5H), 1.31–1.14 (m, 4H), 1.02–0.92 (m, 2H), 0.85 (q, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.18, 133.14, 133.05, 129.40, 127.92, 42.81, 39.58, 39.26, 36.14, 34.95, 34.38, 34.11, 32.44, 31.37, 30.10 29.78, 27.43, 26.42, 20.82, 18.95, 13.11, 11.86, 11.39; HRMS calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1638. **14:** IR (neat) 3068, 2938, 2866, 2132, 1428, 1365, 1117, 940, 875, 845; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57–7.55 (m, 2H), 7.40–7.34 (m, 3H), 4.32–4.29 (m, 2H), 2.00, 1.85, 1.73, 1.64, 1.50, 1.21, 1.04, and 0.94 (m, 12 H), 0.84 (s, 5.4H, *cis*-diastereomer), 0.82 (s, 3.6 H, *trans*-diastereomer); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.21, 135.17, 133.14, 132.95, 129.44, 129.39, 127.94, 48.48, 47.80, 36.63, 35.08, 32.77, 32.58, 32.37, 29.42, 27.58, 27.51, 21.09, 18.59, 9.61; HRMS calcd for $C_{17}H_{28}Si$ 260.1960, found 260.1972.

[14] (a) C.M. Forsyth, S.P. Nolan, and T.J. Marks, *Organometallics*, *10* (1991) 2543; (b) H.-G. Woo, J.F. Walzer, and T.D. Tilley, *J. Am. Chem. Soc.*, *114* (1992) 7047; (c) N.S. Radu, T.D. Tilley, and A.L. Rheingold, *J. Am. Chem. Soc.*, *114* (1992) 8293.

[15] (a) M.R. Kesti, M. Abdulrahman, and R.M. Waymouth, *J. Organomet. Chem.*, *417* (1991) C12; (b) M.R. Kesti, and R.M. Waymouth, *Organometallics*, *11* (1992) 1095.

[16] (a) K. Tamao, and N. Ishida, *J. Organomet. Chem.*, *269* (1984) C37; (b) S.H. Bergens, P. Nogeda, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, *114* (1992) 2121.