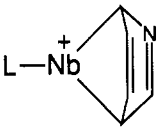
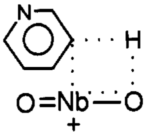
the presently observed values. Pyridine, but not benzene, cleavage by $Nb^+$ occurs simply because HCN elimination from pyridine requires 32 kcal/mol less energy than acetylene elimination from benzene, which also explains why nitrogen is not retained in the metal complex in any of the pyridine reactions.

Scheme I presents a mechanism for the reactions of $Ta^+$ with benzene, corresponding to the reverse of the cyclotrimerization of alkynes.[1,2] The reaction of $Ta^+$ with $C_6D_6$ generates the analogous deuterated products with a very small to negligible kinetic isotope effect ($k_H/k_D = 1.1 \pm 0.1$; see Figure 1), consistent with the formation of a tantalacyclopentadiene intermediate that does not require a C–H bond-cleavage step. The formation of the acetylene complex from "hot" $Ta^+$ involves subsequent decomposition of internally excited $TaC_4H_4^+$ by a retro-Reppe mechanism.[1] An analogous mechanism is proposed for the pyridine reactions.

The mechanism shown in Scheme I involves a "bent" ring system. Recent structural characterizations of a few tantalum–benzene complexes have shown the benzene distorted into a "boat" configuration with a 26° out-of-plane bend.[14] The two benzene carbon atoms bent toward the metal center have Ta–C distances close to that expected for σ-bonds. These complexes were synthesized by [2 + 2 + 2] cycloaddition reactions. Niobium cluster complexes have also been characterized which incorporate multiple boat benzene ligands, each with at least a 22.6° out-of-plane bend.[15] The $d^4$ $Nb^+$ and $Ta^+$ and the $d^2$ $NbN^+$ and $NbO^+$ systems all can form the Nb–C bonds (see structure III) necessary to initiate the ring-cleavage process. This is consistent with the condensed-phase observation that boatlike benzene structures are only observed for lower oxidation state early transition metals with two or more d electrons. The $d^0$ $NbO_2^+$ cannot form the necessary Nb–C bonds; thus, pyridine ring cleavage is not observed. However, many $d^0$ systems can activate C–H bonds through four-centered σ-metathesis transition states,[16] as in structure IV. In accord with this, $NbO_2^+$ slowly dehydrogenates pyridine.



III



IV

The primary benzyne and metallacyclopentadiene products will undergo subsequent reactions with either benzene or pyridine. Reactions out to 90 s and at pressures up to $1 \times 10^{-6}$ Torr have been investigated. $Ta^+$ reacts with benzene as many as four times while $Nb^+$ dehydrogenates up to three benzene molecules. Previous work on the reactions of halogenated benzene showed coupling of benzyne ligands to form metal ion–polyphenylene complexes.[3,4] To probe for coupling of the unsaturated ligands on $Ta^+$ we have performed collision-induced dissociation experiments on the $TaC_{10}H_8^+$ product of reaction 4.

$$TaC_4H_4^+ + C_6H_6 \rightarrow TaC_{10}H_8^+ + H_2 \qquad (4)$$

Observation of a small peak at the *m/e* value corresponding to naphthalene cation suggests the secondary formation of Ta(naphthalene)$^+$, most likely by a Diels–Alder mechanism. Subsequent reactions of $TaC_{10}H_8^+$ with benzene support the view of coupled hydrocarbon fragments that leave the metal center relatively unhindered. We are currently investigating the reactions of a variety of arenes with these metal cations to probe these interesting processes in more detail.

**Acknowledgment.** We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We gratefully acknowledge many helpful discussions with Professor David E. Wigley.

OM910732N

---

[14] (a) Wexler, P. A.; Wigley, D. E. *J. Chem. Soc., Chem. Commun.* **1989**, 664. (b) Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282. (c) Wexler, P. A.; Wigley, D. E.; Koerner, J. B.; Albright, T. A. *Organometallics* **1991**, *10*, 2319.

[15] (a) Stollmaier, F.; Thewalt, U. J. *J. Organomet. Chem.* **1981**, *222*, 227. (b) The dication complex has a fold angle of 17.8°: Goldberg, S. Z.; Spivack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 110.

[16] Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

---

# Stereoselection Effects in the Catalytic Hydroamination/Cyclization of Aminoolefins at Chiral Organolanthanide Centers

Michel R. Gagné, Laurent Brard, Vincent P. Conticello, Michael A. Giardello,
Charlotte L. Stern, and Tobin J. Marks*
*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

*Received April 22, 1992*

*Summary:* The chiral organolanthanide complexes $Me_2Si(Me_4C_5)(C_5H_3R^*)LnE(SiMe_3)_2$ ($R^*$ = (–)-menthyl, (+)-neomenthyl; Ln = La, Sm; E = N, CH) serve as precatalysts for the enantioselective or diastereoselective hydroamination/cyclization of aminoolefins to chiral pyrrolidines and piperidines.

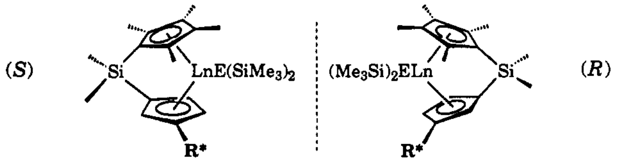
We recently reported[1a] on the synthesis, structural characterization, and efficacy (high enantiomeric excesses and turnover frequencies) as precatalysts for asymmetric olefin hydrogenation of the chiral organolanthanide complexes $Me_2Si(Me_4C_5)(C_5H_3R^*)SmCH(SiMe_3)_2$ (**1** and **3**; $R^*$

---

[1] (a) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Stern, C. L.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761–2762. (b) Symmetry labels refer to the planar chirality element associated with Ln coordination to the appropriate cyclopentadienyl enantioface.

0276-7333/92/2311-2003$03.00/0

**Chart I**[a]



[a] Legend: 1, Ln = Sm, R* = (−)-menthyl, E = CH; 2, Ln = Sm, R* = (−)-menthyl, E = N; 3, Ln = Sm, R* = (+)-neomenthyl, E = CH; 4, Ln = Sm, R* = (+)-neomenthyl, E = N; 5, Ln = La, R* = (+)-neomenthyl, E = N.

= (−)-menthyl, (+)-neomenthyl; Chart I).[1] Concerning potential stereocontrol in other organolanthanide-mediated transformations, we communicate here the first observations on asymmetric and diastereoselective aminoolefin hydroamination/cyclization processes[2] using these chiral alkyl as well as analogous, more easily prepared and purified, amido precatalysts.[3]

Hydrocarbyl precatalysts (*S*)-**1**-Sm and (*R*)-**3**-Sm were prepared as described previously;[1] amides (*S*)-**2**-Sm, (*R*)-**4**-Sm, and (*R*)-**5**-La were synthesized via reaction of the corresponding $Me_2Si(Me_4C_5)(C_5H_3R^*)LnCl_2Li$(solvent) complexes[1a] with $KN(SiMe_3)_2$[4] (for Ln = Sm, solvent = DME; for Ln = La, solvent = 2 $Et_2O$) and were characterized (including absolute configuration) by standard techniques, including CD (e.g., spectra of (*S*)-**2**-Sm and (*R*)-**4**-Sm are virtual mirror images).[4b] X-ray diffraction structural characterization of the representative complex (*S*)-**2**-Sm[5] confirms the absolute configuration and reveals a chiral, "bent-sandwich" structure having metrical parameters (Figure 1) similar to those of the E = CH analogues,[1,6-8] with planar $N(SiMe_3)_2$ ligation reminiscent of the analogous, achiral $Cp'_2Y$ complex (Cp′ = $\eta^5$-$Me_5C_5$).[7]

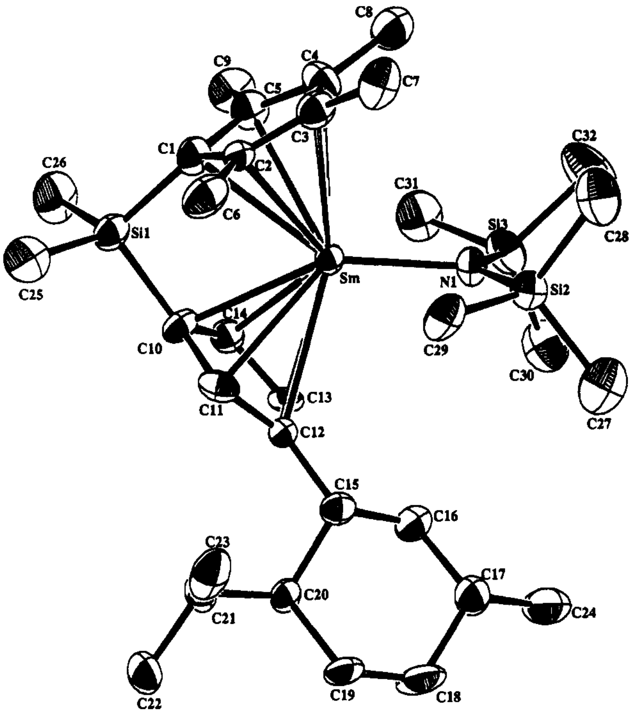


**Figure 1.** Perspective ORTEP drawing of the non-hydrogen atoms of (*S*)-$Me_2Si(Me_4C_5)[C_5H_3$((−)-menthyl)]$SmN(SiMe_3)_2$ ((*S*)-**2**-Sm). All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density.

**Table I. Rate, Product Enantiomeric Excess, and Product Absolute Configuration Data for the Catalytic Hydroamination/Cyclization of Aminopent-4-ene (6), 2,2-Dimethyl-1-aminopent-4-ene (7), and 2,2-Dimethyl-1-aminohex-5-ene (8)**[a]

| entry no. | precatalyst[b] | temp, °C | $N_t$, h$^{-1}$ | product % ee (sign) |
|---|---|---|---|---|
| | Compound 6 | | | |
| 1 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | 25 | 33 | 62 (+)[c] |
| 2 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | 0 | | 72 (+)[c] |
| 3 | (*R*)-**3**-Sm/(*R*)-**4**-Sm | 25 | 62 | 52 (−)[c] |
| 4 | (*R*)-**3**-Sm/(*R*)-**4**-Sm | 0 | | 58 (−)[c] |
| 5 | (*R*)-**5**-La | 25 | | 31 (−)[c] |
| | Compound 7 | | | |
| 6 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | 25 | 84 | 53 (+)[d] |
| 7 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | 0 | | 61 (+)[d] |
| 8 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | −30 | | 74 (+)[d] |
| 9 | (*R*)-**3**-Sm/(*R*)-**4**-Sm | 25 | | 51 (−)[d] |
| 10 | (*R*)-**3**-Sm/(*R*)-**2**-Sm | 0 | | 54 (−)[d] |
| 11 | (*R*)-**3**-Sm/(*R*)-**4**-Sm | −30 | | 64 (−)[d] |
| 12 | (*R*)-**5**-La | 25 | | 14 (−)[d] |
| | Compound 8 | | | |
| 13 | (*S*)-**1**-Sm/(*S*)-**2**-Sm | 25 | ~2 | 15 (−)[e] |
| 14 | (*R*)-**3**-Sm/(*R*)-**4**-Sm | 25 | | 17 (−)[e] |

[a] Conditions: [substrate]/[catalyst] = 100–150; solvent pentane; 100% conversion and >95% regiospecificity by GLC and $^1H$ NMR measurements. $N_t$ calculated for 3 half-lives. [b] Within experimental error, the E = CH and N precatalysts give identical results. [c] Based upon $[\alpha]_D^{20}$ = −20.0° for (*R*)-(−)-2-methylpyrrolidine.[10,11] [d] Based upon $[\alpha]_D^{20}$ = −24.3° for (*R*)-(−)-2,4,4-trimethylpyrrolidine.[11,12] [e] References 11 and 12.

The efficacy of precatalysts **1**–**5** in asymmetric aminoolefin hydroamination/cyclization was assessed for two

---

(2) (a) Gagné, M. R.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294. (b) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109. (c) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716–1718.

(3) Communicated in part: Gagné, M. R.; Marks, T. J. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14; American Chemical Society: Washington, DC, 1989; INOR 32.

(4) (a) Synthesis of (*S*)-$Me_2Si(Me_4C_5)$[(−)-menthylCp]$SmN(SiMe_3)_2$ ((*S*)-**2**-Sm): A 50-mL flask with a Teflon inlet valve was charged with (*S*)-$Me_2Si(Me_4C_5)$[(−)-menthylCp]$Sm(\mu\text{-}Cl)_2Li$(DME) (0.781 g, 1.0 mmol) and $KN(SiMe_3)_2$ (0.200 g, 1.01 mmol). Toluene (30 mL) was added via syringe under an argon flush. The mixture was then stirred at 25 °C for 12 h, during which time a colorless solid precipitated from the clear, orange solution. The solvent was removed in vacuo and the resulting gummy solid dried for 12 h. Pentane (20 mL) was next condensed into the flask at −78 °C, the mixture was stirred at 25 °C for 20 min, and the solvent was removed in vacuo. This dissolution/evaporation procedure was repeated twice, after which the mixture was dissolved in 20 mL of pentane, the solution was filtered, and the colorless filtration residue was washed once with pentane (10 mL). The combined filtrate was then concentrated in vacuo to ca. 5 mL and the solution slowly cooled to −78 °C. Crystallization afforded 0.49 g (70% yield) of (*S*)-$Me_2Si(Me_4C_5)$-[(−)-menthylCp]$SmN(SiMe_3)_2$ as bright orange prisms. An additional 0.115 g (17%) of smaller orange prisms crystallized from the mother liquor by concentration and cooling to −78 °C (total yield 87%). The product was recrystallized from cold (−78 °C) pentane. $^1H$ NMR ($C_6D_6$): $\delta$ 14.15 (br s, 1 H), 11.03 (br s, 1 H), 6.60 (br s, 1 H), 4.37 (m, 1 H), 3.75 (m, 1 H), 2.73 (d, 3 H), 2.55 (s, 6 H), 2.51 (m, 1 H), 2.45–2.15 (m, 4 H), 2.25 (s, 3 H), 2.10 (s, 3 H), 1.53 (d, 3 H), 1.28 (q, 1 H), 0.95 (m, 1 H), 0.13 (d, 3 H), −4.45 (s, 3 H), −4.65 (s, 3 H), −6.82 (s, 9 H), −7.05 (s, 9 H). CD (heptane; $\lambda_{max}$ ([$\theta$]): 330 (+6385), 291 (+8010) nm. Anal. Calcd for $C_{32}H_{58}NSi_3Sm$: C, 55.58; H, 8.45; N, 2.03. Found: C, 55.46; H, 8.23; N, 1.70. (b) Supplementary Material.

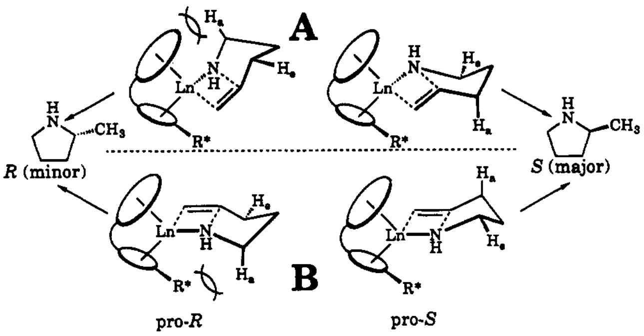
(5) Crystal data for (*S*)-**2**-Sm: $C_{32}H_{58}NSi_3Sm$, space group $P2_12_12_1$, $a$ = 10.217 (3) Å, $b$ = 19.103 (6) Å, $c$ = 19.456 (7) Å (−120 °C), $Z$ = 4. The structure was solved by direct methods and refined to $R(F) = 0.044$, $R_w(F) = 0.047$ ($R_w(F) = 0.056$ for the $R$ configuration) for 2621 reflections having $I > 3\sigma(I)$.

(6) (a) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110.

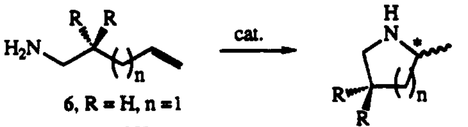
(7) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kajić-Prodić, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733.

(8) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558–9575.

Scheme I



aminopentenes and an aminohexene using the La and Sm precatalysts (eq 1).[9] Under identical conditions, turnover



(1)

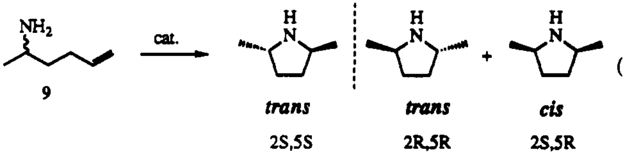
**6**, R = H, n = 1

**7**, R = $CH_3$, n = 1

**8**, R = $CH_3$, n = 2

frequencies are ~10× those of $Cp'_2Ln$ catalysts,[2] likely reflecting enhanced coordinative unsaturation at the metal center,[2a] and are indistinguishable for E = CH and N. This latter observation is compatible with in situ NMR studies which reveal rapid protonolytic displacement of the corresponding $HE(SiMe_3)_2$ fragment as turnover commences. Table I shows that **1**–**5** catalyze the asymmetric cyclization of substrates **6**,[10,11] **7**,[11,12] and **8**[11,12] with moderate to high enantioselectivities,[10-12] that % ee increases with decreasing temperature, that % ee increases with decreasing lanthanide ionic radius, and that (*S*)-**1**-Sm/(*S*)-**2**-Sm and (*R*)-**3**-Sm/(*R*)-**4**-Sm, (*R*)-**5**-La yield products of net *opposite* configuration except for entries 13 and 14 (vide infra). In situ NMR studies also indicate that (*S*)-**1**-Sm/(*S*)-**2**-Sm and (*R*)-**3**-Sm/(*R*)-**4**-Sm are configurationally stable (<5% epimerization) on the timescale of the catalytic experiments,[13] while kinetic measurements indicate $N_t$ is zero-order in olefin (intramolecular olefin insertion/cyclization is turnover-limiting[2]—also in accord with the observed **6** vs **7** *gem*-dimethyl effect on $N_t$) for ~3 half-lives. Rate law deviations occur at higher conversions, possibly reflecting competitive inhibition[2a] by the product. With regard to the possibility that cyclization is reversible, control experiments indicate that chiral products are not detectably epimerized by achiral catalysts under catalytic conditions. The gross aspects of enantioselection in the formation of the methylpyrrolidines can be explained on the basis of a pseudo-chair seven-membered transition state[2a,14,15] with the olefinic functionality approaching either along the central ring centroid–Ln–ring centroid bisector[1,16] (e.g., A; Scheme I) or approximately perpendicular to this direction (laterally), from the side away from R* (e.g., B). The importance of this type of seven-membered cyclic transition state in the stereodifferentiating step is further argued by the lower ee values and *identical* product absolute configurations observed in the cyclization of aminohexene **8** using (*S*)-**1**-Sm/(*S*)-**2**-Sm and (*R*)-**3**-Sm/(*R*)-**4**-Sm as precatalysts (Table I).

In principle, diastereoselective processes should also be mediated by chiral $Me_2Si(Me_4C_5)(C_5H_3R^*)Ln$ catalysts. We find that (*R*)-**3**-Sm/(*R*)-**4**-Sm effects the cyclization of 2-aminohex-5-ene (**9**; [substrate]/[catalyst] = 150; $N_t$ > 80 $h^{-1}$; 25 °C) to yield the $C_2$ auxiliary[17] *trans*-2,5-dimethylpyrrolidine[17] with >95% diastereoselectivity (eq 2).



(2)

Since the substrate of eq 2 is racemic, the product is racemic at 100% conversion as anticipated. Under identical conditions, achiral $Cp'_2Sm$ precatalysts afford only modest diastereoselection.[2a]

These initial catalytic C–N bond-forming results further illustrate the stereocontrol and unusual products that are accessible in chiral organolanthanide-catalyzed olefin transformations. The scope and mechanisms of such processes are under continuing investigation.

**Acknowledgment.** We thank the NSF for support of this work under Grant CHE9104112. V.P.C. and L.B. thank the NSF and Rhône-Poulenc, respectively, for predoctoral fellowships. We thank Professor Paul Loach for access to his CD spectrometer.

**Supplementary Material Available:** Text giving synthetic details and spectroscopic and analytical data, X-ray experimental details including tables of positional and anisotropic displacement parameters and tables of bond lengths and angles, and a figure showing the circular dichroism spectra of (*S*)-**2**-Sm and (*R*)-**3**-Sm (21 pages). Ordering information is given on any current masthead page.

OM920220O

---

(9) Typical preparative-scale catalytic reaction: In the glovebox, 78 mg (100 μmol) of (*S*)-**2**-Sm was loaded into a 15-mL round-bottom reaction flask equipped with a magnetic stirbar. At −78 °C, 2 mL of pentane was vacuum-transferred onto the catalyst, followed by 1.65 mL of **6** (1.27 g, 15 mmol). The clear, yellow solution was stirred under argon for 24 h at ambient temperature. The reaction mixture was then freeze–pump–thaw degassed and the volatiles vacuum-transferred into a separate flask. Pentane was removed on the rotary evaporator at 0 °C to afford 1.45 g (12.8 mmol, 86% yield, >95% pure by GC/MS) of 2-methylpyrrolidine. The optical rotation for this sample indicated 62% ee of (*S*)-(+)-2-methylpyrrolidine, $[\alpha]_D^{25}$ = +12.4° (*c* = 1.00 in 95% ethanol).

(10) Ringdahl, B.; Percira, W. E.; Craig, J. C. *Tetrahedron* **1981**, *37*, 1659–1662.

(11) (a) Optical purities verified by MTPA amide NMR assay.[11b] (b) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(12) (a) Absolute configuration assigned from the $[\alpha]_D$ value for the cyclization product of **6** and those of analogous pyrrolidines.[10,12b,c] (b) Craig, J. C.; Roy, S. K. *Tetrahedron* **1965**, *21*, 401–406. (c) Ripperger, H.; Schreiber, K. *Tetrahedron* **1965**, *21*, 407–412.

(13) (a) Epimerization products (*R*)-**1**-Sm/(*R*)-**2**-Sm and (*S*)-**3**-Sm/(*S*)-**4**-Sm have been synthesized independently and will be discussed elsewhere.[13c] (b) For the cyclization of **8** at ambient temperature by (*R*)-**3**-Sm/(*R*)-**4**-Sm, long reaction times (7–10 days) are required and a significant amount (~15–20%) of (*S*)-**3**-Sm/(*S*)-**4**-Sm[13c] is observed in the ¹H NMR spectrum. (c) Brard, L.; Conticello, V. P.; Gagné, M. R.; Giardello, M. A.; Stern, C. L.; Marks, T. J., unpublished results.

(14) (a) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406–9407. (b) Rigollier, P.; Young, J. R.; Fowley, L. A.; Stille, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 9441–9442. (c) Resconi, L.; Waymouth, R. W. *J. Am. Chem. Soc.* **1990**, *112*, 4953–4954. (d) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377–3378.

(15) The coordination of additional substrate molecules[2a] cannot be excluded.

(16) (a) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911–4914. (b) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515–5525. (c) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501–1505.

(17) (a) Harding, K. E.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920–3922. (b) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1977**, *42*, 1663–1664.