Organometallics **2004,** *23,* 12−14

Alkene and Diene Hydrosilylations Catalyzed by Lanthanum Tris[bis(trimethylsilyl)amide][†]

Yoshikazu Horino and Tom Livinghouse*

Department of Chemistry, Montana State University, Bozeman, Montana 59717

Received September 30, 2003

Summary: Commercially available lanthanum tris[bis(trimethylsilyl)amide] has been shown to be a very effective catalyst for hydrosilylations of representative alkenes and dienes in the presence of $PhSiH_3$.

The catalyzed hydrosilylation of alkenes is one of the most versatile and efficient methods for the synthesis of alkylsilanes and their derivatives.[1] Recently, permethylmetallocene and related derivatives of the group 3 and lanthanide metals have been shown to be useful catalysts for this process and are complementary to classical platinum-based catalysts in this context.[2,3] The high sensitivity of group 3 metallocene complexes to air coupled with the comparative difficulty associated with their preparation have hindered the widespread use of these compounds in catalysis. We have previously disclosed that simple amido derivatives of the group 3 metals corresponding to the formula $Ln[N(TMS)_2]_3$ (**1**; Ln = lanthanide) are competent catalysts for intramolecular alkene hydroamination.[4] In this communication we show that commercially available **1b** (Ln = La) possesses high activity as a catalyst for the intermolecular hydrosilylation of alkenes as well as both conjugated and nonconjugated dienes.

Scheme 1

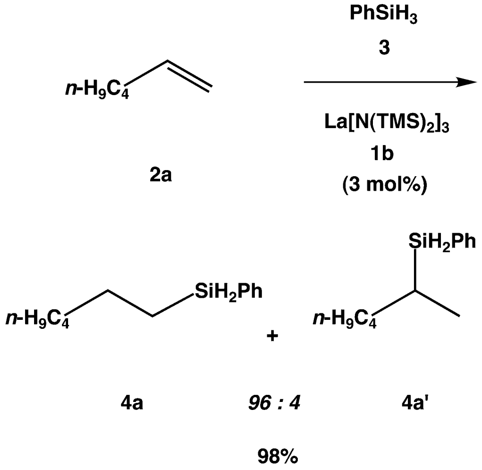
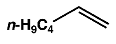
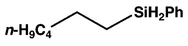
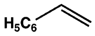
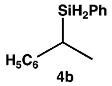
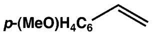
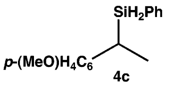
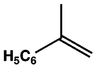
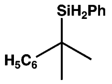
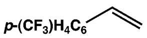


Table 1. Catalyzed Hydrosilylations of Alkenes

	Alkene	Reaction Conditions	Product	Isolated Yield (%)
1	 **2a**	25 °C, 40 h	 **4a**	98% (96 : 4)[a]
2	 **2b**	25 °C, 5 h	 **4b**	99% (>99 : 1)[a]
3	 **2c**	25 °C, 12 h	 **4c**	99% (>99 : 1)[a]
4	 **2d**	60 °C, 11 h	 **4d**	99% (>99 : 1)[a]
5	 **2e**	25 °C, 24 h	------------	< 5%

[a] Regioisomeric ratio.

We initiated this study by examining the group 3 amides $Y[N(TMS)_2]_3$ (**1a**) and **1b** as prospective catalysts for the hydrosilylation of 1-hexene (**2a**) with phenylsilane (**3**). Although exposure of **2a** to **3** in the presence of 3 mol % of **1a** (C_6D_6, 60 °C, 48 h) led to no reaction, *the use of **1b** (3 mol %, C_6D_6, 25 °C, 40 h) provided the anticipated alkylsilanes **4a** and **4a′** (**4a**:**4a′** = 96:4) in 98% isolated yield* (Scheme 1).[5,6] This result is consistent with the trend observed for permethyllanthanocene catalysts: i.e., a pronounced correlation between the increasing ionic radius of Ln^{3+} and increasing turnover frequency of hydrosilylation.[2b] It is interesting in this connection that other amidolanthanide complexes more closely related to **1b** (e.g., **1c** (Ln = Nd) and **1d** (Ln = Sm)) were found to possess comparatively low catalytic activity for the hydrosily-

---

* To whom correspondence should be addressed. E-mail: livinghouse@chemistry.montana.edu.

[†] This communication is dedicated to the memory of Heath Evans Freyer.

(1) Ojima, I. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: London, 1989, and references therein.

(2) (a) Molander, G. A.; Retsch, W. H. *J. Am. Chem. Soc.* **1997**, *119*, 8817. (b) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (c) Hydrosilylations catalyzed by C_2-symmetric bis(silylamido) complexes of yttrium have been reported: Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661.

(3) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407 and references therein. (b) Hydrosilylations catalyzed by zirconocene complexes have also been described: Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095.

(4) (a) Kim, Y. K.; Livinghouse, T.; Bercaw, J. E. *Tetrahedron Lett.* **2001**, *42*, 2933. For the use of novel group 3 chelates to accelerate intramolecular aminoalkene hydroaminations, see: (b) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645. (c) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560.

(5) Marks has shown that the regioselectivity observed for the hydrosilylation of 1-alkenes with **3** catalyzed by lanthanocenes is highly dependent on the nature of the metal and its ligand environment.[2b]

(6) A general procedure for alkene and diene hydrosilylations is as follows: in an argon-filled glovebox, $La[N(TMS)_2]_3$ (**1b**; 18.6 mg, 0.03 mmol) and C_6D_6 (1.0 mL) were introduced into a J. Young NMR tube equipped with a Teflon screw cap and then phenylsilane (**3**; 119 mg, 1.1 mmol) and the appropriate alkene or diene (1.0 mmol) were added by microsyringe. The homogeneous reaction mixture was maintained at 25 and 60 °C, respectively, using an oil bath until the hydrosilylation reaction was judged complete by the disappearance of the appropriate olefinic resonances in the ^1H NMR spectrum. The product was purified by column chromatography on silica gel (5% CH_2Cl_2/95% hexane for elution) followed by removal of the solvents in vacuo.

10.1021/om0306168 CCC: $27.50
Publication on Web 12/09/2003

Scheme 2

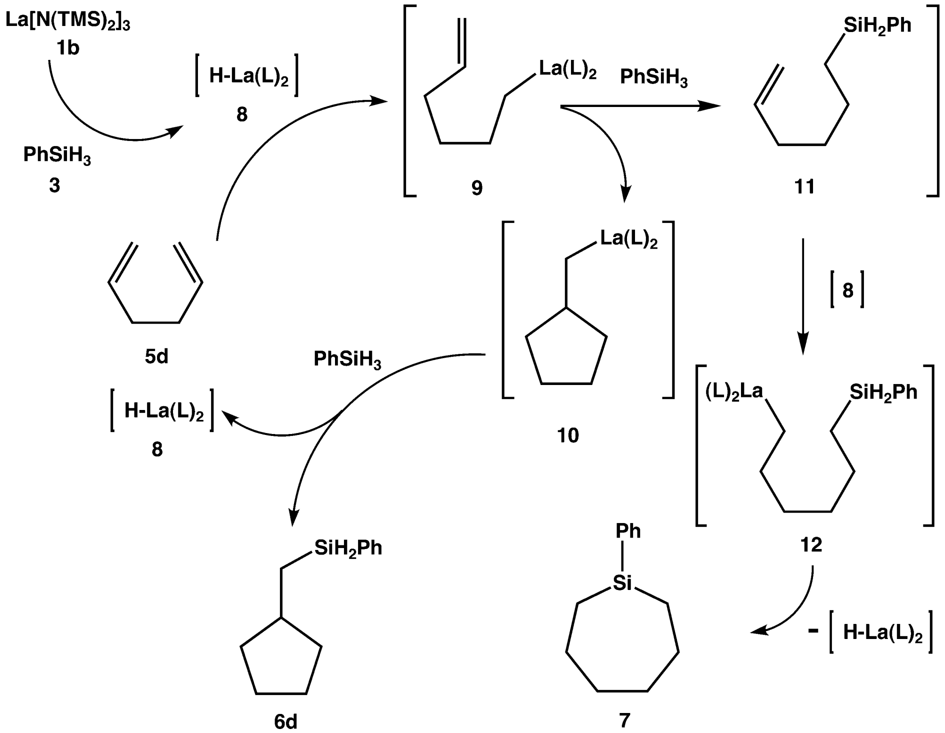
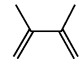
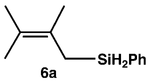
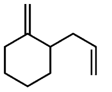
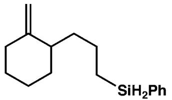
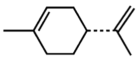
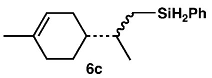
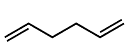
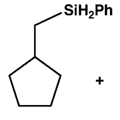
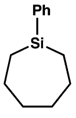


Table 2. Catalyzed Hydrosilylations of Dienes

	Diene	Reaction Conditions	Product(s)	Isolated Yield (%)
1	 **5a**	25 °C, 24 h	 **6a**	99%
2	 **5b**	60 °C, 9 h	 **6b**	95%
3	 **5c**	60 °C, 24 h	 **6c**	95%
4	 **5d**	25 °C, 48 h	 **6d** +  **7**	95% (4 : 1)[a]

[a] Isomeric ratio.

lation of **2a** with **3**. Alternative La^{3+} sources were subsequently examined and found to be inactive as catalysts for the hydrosilylation of **2a** with **3**. Accordingly, treatment of **2a** with **3** in the presence of 3 mol % of Cp_3La, LaI_3,[7] or $La(OTf)_3$ (C_6D_6, 60 °C, 48 h) failed to produce **4a** or **4a′**. A series of alkenes was then subjected to hydrosilylation with **3** in the presence of 3 mol % of **1b**. The results of this study are assembled in Table 1.

As is evident from these results, styrene substrates exhibit a pronounced bias for the formation of benzylic silanes (entries 2−4). In addition, the presence of a strongly σ-electron-withdrawing para substituent (CF_3) results in a significant depression of the reaction rate (entry 5). It is of interest that these results are entirely in accord with those obtained with sterically hindered lanthanocene catalysts.[2b,8] Hydrosilylation of one conjugated and three nonconjugated dienes was next examined. In consonance with the trend observed for styrenes, the reaction of 2,3-dimethyl-1,3-butadiene (**5a**) with **3** afforded allylsilane **6a**[9] in excellent isolated yield. The hydrosilylation of 2-allyl-1-methylenecyclohexane (**5b**)[11] and limonene (**5c**) proceeded with complete chemoselectivity to furnish the products derived from the addition of **3** to the least substituted alkene (in the case of **5c** as a mixture of diastereomers).[11] It is significant from a mechanistic standpoint that catalytic hydrosilylation of 1,5-hexadiene (**5d**) led to the formation of the (silylmethyl)cyclopentane **6d**[12] and the silacycloheptane **7** as a 4:1 mixture in 95% isolated yield (entry 4, Table 2).

Although the identity of the actual catalyst in these reactions has not been established, it is likely that reduction of the precatalyst **1b** by **3** initiates the catalytic cycle with concomitant generation of a lanthanum hydride of the type **8**. Anti-Markovnikov addition of **8** to **5d** should lead to the transient lanthanum alkyl **9**, which could partition between **10**, derived from intramolecular σ-bond metathesis, and **11**, resulting from intermolecular σ-bond metathesis between $PhSiH_3$ (**3**) and **9**. Final intermolecular σ-bond metathesis between **3** and **10** and intramolecular hydrosilylation catalyzed by anti-Markovnikov addition of **8** to the

---

[7] Evans has reported that SmI_3 is an efficient catalyst for the hydroboration of alkenes with catecholborane: Evans, D. A.; Muci, A. R.; Stürmer, R. *J. Org. Chem.* **1993**, *58*, 5307.

[8] (a) The ^1H and ^{13}C NMR spectral data for **4a**[8b] and the benzylic silanes **4b**−**d**[2b] are in complete accord with those reported in the literature. (b) Kobayashi, M.; Itoh, M. *Chem. Lett.* **1996**, 1013.

[9] Allylsilane **6a** was characterized by conversion to (2,3-dimethyl-2-buten-1-yl)dimethylphenylsilane[10] by treatment with CH_3Li (4 equiv).

[10] Fleming, I.; Rowley, M.; Cuadrado, P.; Gonzalez-Nogal, A. M.; Pulido, F. J. *Tetrahedron* **1989**, *45*, 413.

[11] Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347.

[12] Molander, G. A.; Dowdy, E. D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386.

alkene within **11** would ultimately lead to the observed products **6d** and **7** (Scheme 2).[13]

In conclusion, we have demonstrated that the commercially available[14] amide $La[N(TMS)_2]_3$ (**1b**) is a highly effective catalyst for representative hydrosilylations of alkenes and dienes with phenylsilane (**3**). The utilization of lanthanum amides possessing electronically and sterically varied ligand environments, as well as other lanthanum chelates, for stereoselective hydrosilylation and catalyzed hydroboration reactions will be described in the future.

Acknowledgment. Generous financial support for this research was provided by the National Institutes of Health and the National Science Foundation.

OM0306168

---

(13) An analogous catalytic cycle has been proposed in connection with the cyclization of 1,5- and 1,6-dienes in the presence of **3** and permethylyttrocene complexes: Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415.

(14) Available from Gelest Inc., 612 William Leigh Drive, Tullytown, PA 19007-6308.