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Hydrosilylation of olefins and dehydrogenative double silylation of conjugated dienes catalyzed by lanthanide–imine complexes

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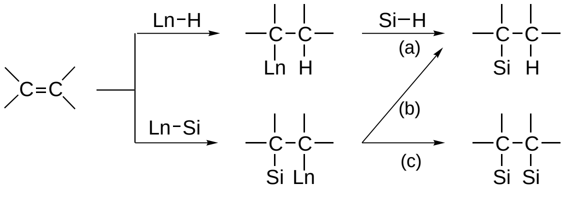
Abstract—Divalent lanthanide–imine complexes and a related species catalyzed the hydrosilylation of olefins with phenyl- and diphenylsilane. On the other hand, conjugated dienes were converted to 1,4-bissilyl-2-butenes and 3-silacyclopentenes, accompanied with hydrogen evolution, under similar conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Catalytic hydrosilylation and related reactions are important and efficient methods for the synthesis of organosilicon compounds.[1] In the last decade, trivalent lanthanocene catalysts have been used in this field, including cyclization/silylation of diene and triene systems, and exhibited unique regio-, chemo- and site-selectivities through the fine tuning of their steric and electronic environment.[2] These reactions have been proved to proceed via insertion of olefins to lanthanide hydride, followed by σ-bond metathesis as depicted in Scheme 1 (path a).[3] In contrast to late transition metal catalysts, there is no precedent for the process initiated by a lanthanide silyl species (path b). However, if the silyl species are added to olefins, this process may lead to double silylation, instead of hydrosilylation, owing to the polarity of hydrosilane in the σ-bond metathesis (path c).[4]



Scheme 1.

With such consideration in mind, we studied the reaction of olefinic compounds with hydrosilanes by using divalent lanthanide–imine complexes, [Ln(η^2-PhNCPh$_2$(hmpa)$_n$] (**1**), which can be simply prepared in situ from lanthanide metals (Yb and Sm) and aromatic imines,[5] and different catalytic activities from trivalent lanthanocenes in various reactions were exhibited; for example, dehydrogenative silylation of terminal alkynes,[6] hydrosilylation of imines[7] and intermolecular hydrophosphination of alkynes.[8] We report herein these results.

When styrene was treated with an equimolar amount of PhSiH$_3$ in the presence of **1a** (Ln = Yb, n = 4, 5 mol%)[9] in THF at −35°C for 20 h, 2-(phenylsilyl)ethylbenzene (**2a**) was formed in 85% yield together with polyphenylsilane after evolution of hydrogen, but the other regioisomer **3a**, a major product by lanthanocene catalysts,[2] was not detected (Eq. (1)). The reaction at room temperature gave **2a** in lower yield (33%) probably because of the predominant polymerization of the silane. No noticeable reaction was observed with SmI$_2$ (10 mol%) and without the catalyst **1a** even under refluxing conditions. Results on the hydrosilylation by using **1a** are summarized in Table 1 (method A). Phenylsilane could be substituted by diphenylsilane to afford 2-(diphenylsilyl)ethylbenzene (**2b**) in 76% yield (run 2), but triphenylsilane was inactive. In contrast to the reaction of styrene and 4-fluorostyrene (runs 1–3), this method was not applicable to electron-rich and substituted styrenes as well as α-olefins (runs 4–8).

Keywords: hydrosilylation; double silylation; lanthanide catalyst; olefins; conjugated dienes.

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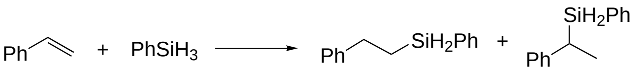
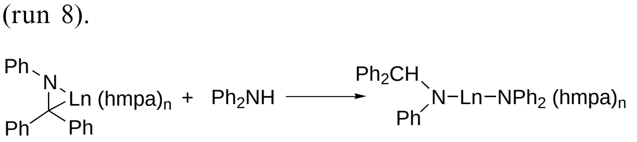


2a **3a**

(1)

The limitation was significantly improved by the addition of equimolar amounts of primary and secondary amines, particularly diphenylamine, whereby the imine complexes **1** would be changed to diamides **4** (Eq. (2)).[10] Thus, use of **4a** ($n=4$, 10 mol%) for the reaction of styrene with phenylsilane resulted in the reduction of the reaction time and an increase of the yield of **2a** to 95%.[11] As can be seen in Table 1 (method B), all styrene derivatives, including α- and β-methylstyrene, were converted to the expected products **2** in good yields, except for 4-methoxystyrene (run 5). In the reaction of 1-decene, the hydrosilylation did not occur with **4a**, but it could be conducted with the samarium catalyst **4b** ($n=0$) to afford the product **2h** in 79% yield (run 8).

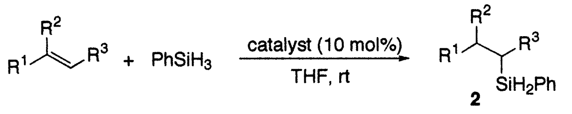


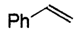
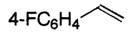
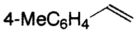
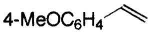
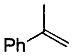
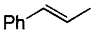
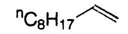
1a: Ln = Yb, **1b**: Ln = Sm **4a**, **b**

(2)

Various features of the reaction were elucidated through the improvement mentioned above. With respect to the catalyst activity of **4**, Yb was superior to Sm for the hydrosilylation of styrene, but the order was reversed for 1-decene. The HMPA ligand showed the promotive and inhibitory effect in the reaction of styrene and 1-decene, respectively. Moreover, regiochemistry in the reaction of styrene depended on the ligand, i.e. linear silane **2a** with HMPA and branched silane **3a** without the ligand were formed exclusively.

Table 1. Hydrosilylation of olefins



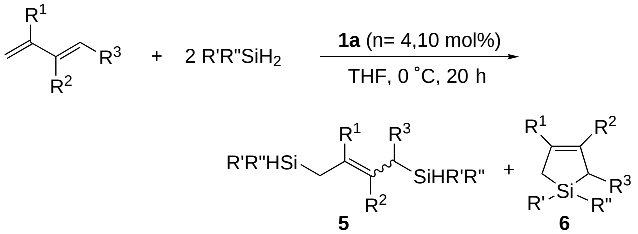
run	olefin	product and yield (%)[a]		
			method A[b]	method B[c]
1		**2a**	85[d]	95
2		**2b**[e]	76	90
3		**2c**	71	94
4		**2d**	10	88
5		**2e**	0	35
6		**2f**	26[f]	95
7		**2g**	0[f]	95
8		**2h**	0[f]	79[g]

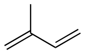
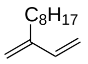
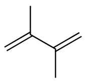
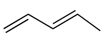
[a] GC yield. [b] Catalyst: **1a** (n = 6), silane / olefin = 1, 20 h. [c] Catalyst: **4a** (n = 4), silane / olefin = 2, 3 h. [d] Carried out with **1a** (n = 4, 5 mol%) at -35 °C. [e] Ph_2SiH_2 was used instead of $PhSiH_3$. [f] 50 °C. [g] Carried out with **4b** (n = 0) at 50 °C for 48 h.

Next, hydrosilylation of conjugated dienes was investigated (Table 2). The reaction of isoprene with phenylsilane (3 equiv.) in the presence of **1a** at 0°C for 20 h in THF gave 1,4-bis(phenylsilyl)-2-methyl-2-butene (**5a**) and 1-phenyl-3-methyl-3-silacyclopentene (**6a**) in 61 and 13% yields, respectively (run 1). The normally expected 1,4- and 1,2-hydrosilylation products were not detected at all, in contrast to trivalent lanthanocene catalysts that were reported to yield three 1,4-hydrosilylation products.[12] Use of equimolar or less amounts of the silane only caused a decrease of **5a** (ca. 20%) with similar yields of **6a**. The reaction with diphenylsilane also produced the products **5b** and **6b** in 57 and 16% yields, respectively (run 2). Similarly, the dehydrogenative double silylation took place in the reaction of 2-octyl- and 2,3-dimethylbutadiene (runs 3 and 4), wherein the silacyclopentene **6c** was formed as a major product in the former case.[13] Unfortunately, alkyl substituents on the terminal position seemed to significantly decrease the reaction efficiency as shown by 1,3-pentadiene (run 5). All products **5** were preferentially obtained as (*E*)-isomers. In addition, similar or somewhat better results were obtained with the diamide catalyst **4a**.[14]

These results clearly indicate that the reaction mode is completely different between olefins and conjugated dienes, which would be interpreted as follows. At first, since dehydrogenative oligomerization/polymerization

Table 2. Dehydrogenative double silylation of conjugated dienes[a]

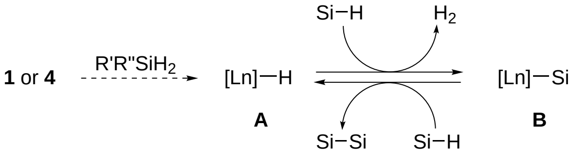


run	diene	hydrosilane	product, yield (%)[b] and E / Z ratio				
			5			**6**	
1		$PhSiH_3$	**5a**	61	(93 / 7)	**6a**	13
2[c]		Ph_2SiH_2	**5b**	57	(93 / 7)	**6b**	16
3		$PhSiH_3$	**5c**	18	(97 / 3)	**6c**	41
4		$PhSiH_3$	**5d**	60	(96 / 4)	**6d**	9
5		$PhSiH_3$	**5e**	19	(71 / 29)	**6e**	0

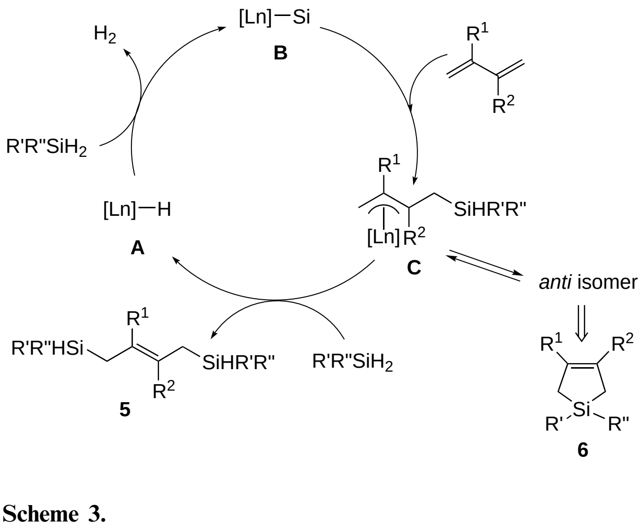
[a] Silane / diene = 3. [b] GC yield based on the diene. [c] Carried out at rt.

of $PhSiH_3$ and Ph_2SiH_2 was induced by the catalysts **1** and **4**, lanthanide hydride **A** and silyl species **B** would be generated in the reaction mixture (Scheme 2).[15] In the case of olefins, it is likely that the reaction was initiated by olefin insertion to the hydride species **A**, based on the regiocontrol by the HMPA ligand observed for the reaction of styrene. That is, π-coordination of the Ph ring to benzylic lanthanide metal after styrene insertion to Ln–H, which has been suggested to be a key factor to produce the branched product **3a**,[3] was disturbed by HMPA and, thus, linear product **2a** was formed instead. If styrene inserted to the silyl species **B**, a reverse ligand effect to produce **3a** and **2a** in the presence and absence of HMPA, respectively, could be observed.

On the other hand, the dehydrogenative double silylation would be initiated by the reaction of diene with the silyl species **B** to yield allylic lanthanide **C** (Scheme 3). Silylation of the *syn* isomer of **C** gave the product **5** and the hydride **A**, and the latter was converted finally to **B** by the reaction with another molecule of the silane with hydrogen evolution. Similarly, intramolecular silylation of the *anti* isomer of **C** would yield the silacyclopentene **6**. The reason for the change in the reaction mode by the two substrates still remains unclear. Alternatively, the two reactions may be explained by the addition of a silyl radical, followed by H abstraction from Si–H for olefin and Si abstraction for diene. However, this process seems less likely, because a radical reaction of dienes with hydrosilane was reported to yield hydrosilylation products,[16] and in fact, **5** and **6** were not formed by the reaction with AIBN.



Scheme 2.



Scheme 3.

In summary, it has been found that the imine complexes **1** and related diamide species **4** exhibit unique catalytic activity for the reaction of olefinic compounds with hydrosilanes, wherein the reaction mode is selected by the substrates. Particularly, double silylation of conjugated dienes with hydrosilanes, not with disilanes, has been achieved, though it involves restrictions on the substituents.

Acknowledgements

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4. Double silylation of alkenes and alkynes with disilanes is well known, but dehydrogenative double silylation with hydrosilanes has been rarely investigated, see: (a) Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603–5605; (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1–12.
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9. The isolated complex **1a** contains three HMPA ligands, see: Ref. 5. However, the real coordination number of **1** and **4** in solution is unknown, and thus, equivalents of this additive used for their preparation are tentatively shown as the coordination number (n).
10. Although the exact structure of **4** was not clear, formation of diamide species was confirmed by NMR. For example, on addition of PhMeNH to **1a** in THF-d_8, a signal at δ 160.2 (C=N) changed to δ 62.9 (CH–N) in ^{13}C NMR spectra and a new peak of the methine proton appeared at δ 5.5 in ^{1}H NMR, together with the change

of the Me group of the amine: δ 30.3 to δ 19.1 in ^{13}C NMR and δ 2.8 to δ 1.7 in ^{1}H NMR. In addition, a diamide species, prepared from LnI_2 (Ln = Yb and Sm) and lithium amides (2 equiv.), showed similar catalyst activities to a certain extent.

11. When 2 equiv. of Ph_2NH were added to **1a**, the yield of **2a** decreased to 47% yield.
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13. As shown in Scheme 3, preferential formation of the *anti* isomer of **C** over the *syn* isomer, owing to the octyl substituent, would be responsible for this selectivity.
14. For example, the reaction with **4a** ($n = 4$, 10 mol%, 0°C, 7 h) gave **5a** (69%) and **6a** (12%), **5d** (65%) and **6d** (8%), and **5e** (23%).
15. It has been reported that dehydrogenative polymerization of $PhSiH_3$ with trivalent lanthanocenes proceeds through these two intermediates, see: (a) Sakakura, T.; Lautenschlager, H.-J.; Nakajima, M.; Tanaka, M. *Chem. Lett*. **1991**, 913–916; (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543–2545; (c) Watson, P. L.; Tebbe, F. N. US Patent 4,965,386, *Chem. Abstr*. **1991**, 114, 123331p. Analogous reaction with Group 4 catalysts, see: Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc*. **1992**, *114*, 7047–7055.
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