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Olefin Hydrosilylation Catalysts Based on Allyl Bis(phenolato) Complexes of the Early Lanthanides

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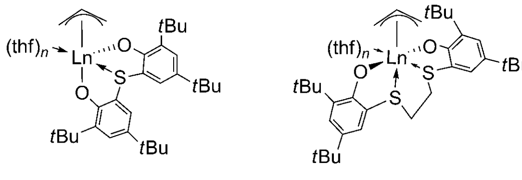
Dedicated to Professor Eiichi Nakamura on the occasion of his 60th birthday

Olefin hydrosilylation is commonly catalyzed by platinum compounds, such as the Speier[1a] or Karsted catalysts.[1b] Homogeneous late-transition-metal (Co, Rh, Pd, Pt) catalysts have been extensively optimized with respect to activity, regioselectivity, and stereoselectivity.[1c] Lanthanide complexes are also known to efficiently catalyze the hydrosilylation of olefins.[2] Their catalytic activity increases with the size of the central metal, as the crucial steps involve σ-bond metathesis. Therefore, inert ancillary ligands other than the ubiquitous metallocene frameworks are not numerous in the literature.[2,3]

Some time ago, sulfur-linked bis(phenolato) ligand scaffolds that contain two hard anionic oxygen donors along with a soft thioether moiety were introduced, and these scaffolds can be broadly modified in terms of their steric bulk.[4a–c] These scaffolds have allowed the development of efficient Group 4 metal catalysts for the stereoselective polymerization of styrene,[4d–f] and are also effective for supporting larger lanthanide central atoms, such as monomeric [Sm(tbmp)(OAr)(thf)][5] (tbmp = 6,6′-thiobis(2-*tert*-butyl-4-methylphenolate)) and silylamido complexes of scandium, yttrium, and lutetium $[Ln(L)\{N(SiMe_3)_2\}]$ (L = (OSSO)-type 1,ω-dithiaalkenediyl-bridged bis(phenolate) ligand).[6] The alkyl complexes of lutetium $[Lu(L)(CH_2SiMe_3)(thf)_n]$ (L = tbmp, mtbmp: 6,6′-methylenebis(sulfanediyl)bis(2-*tert*-butyl-4-methylphenolate), etbmp (6,6′-ethane-1,2-diylbis(sulfanediyl)bis(2,4-di-*tert*-butylphenolate)), $n = 1–2$) and the corresponding hydride complexes showed high activity and regioselectivity in the hydrosilylation of 1-hexene.[7] As non-metallocene hydride complexes of the lanthanides are extremely unstable and difficult to manipulate,[7c] we took advantage of the thermal stability of the tris(allyl) $[Ln(\eta^3\text{-}C_3H_5)_3(diox)]$ (Ln = Y, La, Ce, Pr, Nd, Sm; diox = 1,4-dioxane)[8–10] complexes for the synthesis of precatalysts. Herein, we report that non-metallocene allyl complexes of early rare-earth metals containing a 1,ω-dithiaalkenediyl-bridged bis(phenolate) ligand show high activity and regioselectivity as precatalysts for the hydrosilylation of styrene.

A series of allyl bis(phenolato) complexes $[Ln(L)(\eta^3\text{-}C_3H_5)(thf)_{1-2}]$ (L = tbbp, Y **1**, La **2**; L = etbbp, La **3**, Ce **4**, Nd **5**, Sm **6**) were synthesized in tetrahydrofuran by reacting the tris(allyl) complex $[Ln(\eta^3\text{-}C_3H_5)_3(diox)]$[10] with the bis(phenol) through propene elimination (Scheme 1). The ligands containing both one and two sulfur donor atoms in the backbone were found to be suitable as supporting ligands for the mono(allyl)-lanthanide fragment.



Ln = Y **1**, La **2**.
$n = 3–4$

Ln = La **3**, Ce **4**, Nd **5**, Sm **6**.
$n = 1–2$

Scheme 1. $[Ln(tbbp)(\eta^3\text{-}C_3H_5)(thf)_{3-4}]$ (Ln = Y **1**, La **2**) and $[Ln(etbbp)(\eta^3\text{-}C_3H_5)(thf)_{1-2}]$ (Ln = La **3**, Ce **4**, Nd **5**, Sm **6**).

The medium-sized yttrium as well as the largest lanthanide, lanthanum, were straightforwardly coordinated with the (OSO)-type bis(phenol) tbbp ligand. Recrystallization of yttrium complex **1** from a tetrahydrofuran/*n*-pentane mixture gave crystals suitable for X-Ray diffraction, which revealed that the geometry around the yttrium center could be best described as pentagonal bipyramidal with three tetrahydrofuran molecules in the plane (Figure 1).

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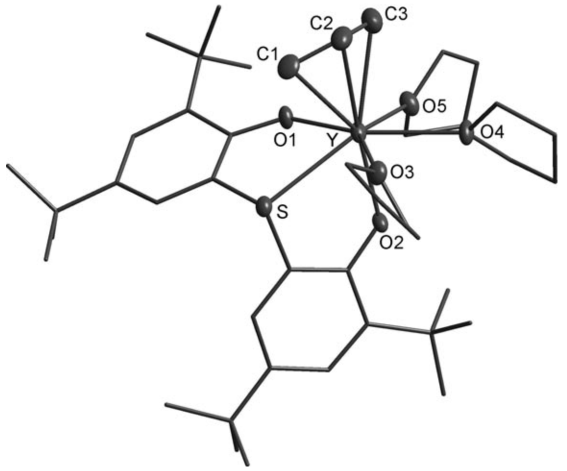


Figure 1. ORTEP diagram of [{Y(tbbp)(η^3-C_3H_5)(thf)$_3$}·thf] **1**. Thermal ellipsoids drawn at the 30 % probability level. Hydrogen atoms as well as the non-coordinated THF solvent molecules are omitted for clarity. thf = coordinated tetrahydrofuran.[15] IUPAC recommended differentiation between coordinated molecules (lower case) and non-coordinated solvent molecules (upper case).

The larger lanthanide metals lanthanum, cerium, neodymium, and samarium all accommodated the (OSSO)-type bis(phenolate) ligand. The tetrahydrofuran ligands were stable to substitution at room temperature. Variable-temperature ^{1}H NMR spectroscopy of **3** in [D_8]tetrahydrofuran showed the typical fluxional behavior for the allyl protons; distinct *syn* and *anti* protons could only be observed at −30 °C along with the multiplet for the methine proton (see the Supporting Information). Recrystallization of the lanthanum and cerium complexes **3** and **4** from a tetrahydrofuran/*n*-pentane solution led to monomeric bis(tetrahydrofuran) adducts [Ln(etbbp)(η^3-C_3H_5)(thf)$_2$] (Ln = La **3′**, Ce **4′**). Both compounds adopted a distorted-pentagonal-bipyramidal geometry in the solid state (Figure 2). One sulfur atom and the two oxygen atoms from the (OSSO)-type tetradentate ligand, and two tetrahydrofuran molecules were found in the equatorial plane, with the allyl group and the second sulfur atom of the (OSSO)-type ligand occupying the axial positions. Cerium complex **4**, which crystallized with an isotypic arrangement of the atoms as the lanthanum complex **3**, showed slightly shorter bonds (ca. 1 %) to the metal center.

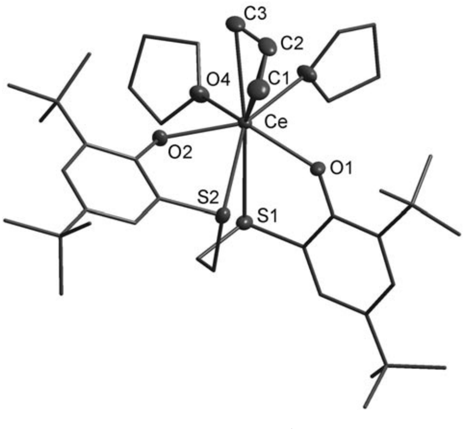


Figure 2. ORTEP diagram of [Ce(etbbp)(η^3-C_3H_5)(thf)$_2$] (**4**). Thermal ellipsoids drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.[15]

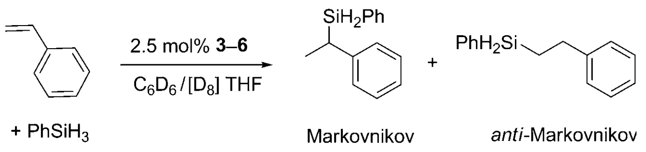
Table 1. Hydrosilylation of olefins catalyzed by early rare-earth metal bis(phenolato) complexes.[a]

Complex (metal)	$RSiH_3$	Olefin	*t* [h]	*T* [°C]	Conv. [%][b]	1,2:2,1[c]
3 (La)	Ph	1-hexene	18	25	> 99	94:6
4 (Ce)	Ph	1-hexene	14	50	> 99	93:7
5 (Nd)	Ph	1-hexene	9	50	> 99	93:7
6 (Sm)	Ph	1-hexene	16	50	> 99	95:5
3 (La)	Ph	1.5-hexadiene	48	25	> 99	95:5
4 (Ce)	Ph	1.5-hexadiene	14	50	> 99	91:9
4 (Ce)	*n*Bu	1.5-hexadiene	20	50	90	38:62
5 (Nd)	Ph	1.5-hexadiene	10	50	> 99	93:7
5 (Nd)	*n*Bu	1.5-hexadiene	17	50	92	67:33
3 (La)	Ph	styrene	< 30 min	25	> 99	3:97
4 (Ce)	Ph	styrene	< 20 min	25	> 99	3:97
5 (Nd)	Ph	styrene	3	25	> 99	5:95
6 (Sm)	Ph	styrene	7	50	> 99	6:94
4 (Ce)	Ph	*trans*-stilbene	14	50	51	–

[a] Reaction conditions: 40:1 substrate/precatalyst molar ratio, a silane/olefin ratio of 1.03:1 in C_6D_6 with a drop of [D_8]THF. [b] Calculated by ^{1}H NMR spectroscopy. [c] Ratio of the 1,2:2,1-regioisomers was determined by integration of the corresponding resonances in the ^{1}H NMR spectra.

The mono(allyl) complexes [Ln(etbbp)(η^3-C_3H_5)(thf)$_{1-2}$] (Ln = La **3**, Ce **4**, Nd **5**, Sm **6**) were tested in the hydrosilylation reactions of different olefins (Table 1). Hydrosilylation of 1-hexene with phenylsilane using complexes **3–6** led to the formation of 93–95 % of the *anti*-Markovnikov or primary product. The regioselectivity did not differ significantly from metal to metal, but the conversion time was different, with the neodymium complex **5** being the fastest. 1,5-Hexadiene was hydrosilylated with phenylsilane and *n*-butylsilane. With phenylsilane, the regioselectivity for the formation of the linear disilylated product was found to be between 91 (**4**) and 95 % (**3**). Full conversion was achieved at 50 °C within 10–14 hours. With *n*-butylsilane, only 67 % linear product was formed for the neodymium complex **5** and 38 % for the cerium complex **4**. The reaction time was also slower than that with phenylsilane.

The hydrosilylation of styrene with phenylsilane were remarkably efficient (Scheme 2). The regioselectivity was highest with the lanthanum **3** and cerium **4** compounds and full conversion was achieved in less than 30 minutes at room temperature, giving 97 % Markovnikov or secondary product. Neodymium complex **5** gave full conversion within 3 hours and samarium **6** compound required 7 hours and higher temperatures for the reaction to proceed to comple-



Scheme 2. Hydrosilylation of styrene with phenylsilane.

tion. The selectivity of the samarium compound **6** was only slightly lower. The hydrosilylation of the less-reactive substrate *trans*-stilbene with phenylsilane catalyzed by the cerium compound **4** gave 51 % conversion after heating at 50 °C for 14 hours.

In conclusion, we have shown that the larger early-lanthanide allyl complexes can serve as versatile catalyst precursors for the hydrosilylation of olefins. When optimized, both activity and regioselectivity could approach values for late-metal catalysts. To the best of our knowledge,[7c,11–13] lanthanum and cerium compounds **3** and **4** are among the most-active, regioselective homogeneous rare-earth metal catalysts for the hydrosilylation of styrene. At least in the case of readily available cerium this catalyst system would offer some advantage over precious metal catalysts.[14] Investigations into the asymmetric hydrosilylation of styrene using catalysts with the chiral, enantiopure variant of the (OSSO)-type ligand are currently underway.[4f]

Experimental Section

3: A solution of etbbpH_2 (151 mg, 0.3 mmol) in THF (5 mL) was added dropwise to a solution of [La(η^3-C_3H_5)$_3$(1,4-dioxane)] (105 mg, 0.3 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h, then concentrated to 3 mL under vacuum, and stored at −30 °C for crystallization for a few days. Pale-yellow crystals of **3** (186 mg, 82 %) were obtained after decantation of the supernatant and drying under vacuum. ^1H NMR ([D_8]THF): $\delta = 1.23$ (s, 18 H, *p*-*t*Bu), 1.41 (s, 18 H, *o*-*t*Bu), 1.78 (m, 6 H, β-thf), 2.49 (br. s, 2 H, anti-CH_2CHCH_2), 2.77 (s, 4 H, SCH_2CH_2S), 3.18 (br. s, 2 H, syn-CH_2CHCH_2), 3.62 (m, 6 H, α-thf), 6.10 (quint, $^3J_{HH} = 12.1$ Hz, 1 H, CH_2CHCH_2), 7.13 (d, $^4J_{HH} = 2.5$ Hz, 2 H, C3-H), 7.15 ppm (d, $^4J_{HH} = 2.5$ Hz, 2 H, C5-H). ^{13}C NMR ([D_8]THF): $\delta = 26.37$ (β-thf), 30.02 (o-*t*Bu, $C(CH_3)_3$), 32.12 (p-*t*Bu, $C(CH_3)_3$), 34.58 (p-*t*Bu, $C(CH_3)_3$), 35.96 (o-*t*Bu, $C(CH_3)_3$), 38.23 (SCH_2CH_2S), 68.22 (α-thf), 73.84 (CH_2CHCH_2), 119.99 (C2), 125.53 (C5), 129.21 (C3), 137.27 (C4 and C6), 147.18 (CH_2CHCH_2), 169.20 ppm (C1). Anal. Calcd. for $C_{37}H_{57}LaO_3S_2$ (*M*: 752.90 g mol^{-1}): C 59.03, H 7.63; Found: C 58.58, H 7.63. Diffraction quality crystals of the bis(THF)-adduct **3′** were obtained from an n-pentane/THF mixture at −40 °C.[15]

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Keywords: allyl ligands · hydrosilylation · lanthanides · olefins · styrene

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[15] CCDC 736509 (**1**), 736510 (**3**), and 736511 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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