# Rare earth metal-based catalysts for the polymerization of nonpolar and polar monomers*

Jun Okuda[†], Stefan Arndt, Klaus Beckerle, Kai C. Hultzsch, Peter Voth, and Thomas P. Spaniol

*Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany*

*Abstract*: The synthesis of rare earth metal half-sandwich hydrido complexes $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ (Ln = Y, Lu) through $\sigma$-bond metathesis of the easily accessible alkyl complexes $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ was developed. The dimeric yttrium hydrido complexes are highly fluxional, and a monomer–dimer equilibrium is present. They were tested as single-site, single-component catalysts for the polymerization of ethylene and styrene, as well as alkyl acrylate and acrylonitrile. The hydrido complexes polymerize ethylene slowly and form isolable mono(insertion) products with styrene. The yttrium *n*-alkyl complexes $[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(R)(THF)]$ [R = $(CH_2)_nCH_3$, *n* = 3–9], prepared by the mono(insertion) of $\alpha$-olefins, initiate polymerization in a relatively controlled manner. Thus, styrene was polymerized by the *n*-alkyl complex to give atactic polystyrenes with somewhat enriched syndiotacticities.

## INTRODUCTION

Structurally well-characterized lanthanocene hydrides and alkyls of the type $[Ln(\eta^5-C_5R_5)_2X]_2$ (X = H, alkyl) have been attracting considerable interest as cocatalyst-free, homogeneous polymerization catalysts for both nonpolar and polar monomers [1]. Catalyst systems based on complexes with only one cyclopentadienyl ligand are expected to be even more active toward sterically demanding, functionalized monomers. Conventional synthesis of mono(cyclopentadienyl) rare earth complexes $Ln(\eta^5-C_5R_5)X_2(L)_n$, where at least one X ligand is a hydride or an alkyl, is often hampered by ate-complex formation due to the high Lewis acidity/electrophilicity [2]. Another complication lies in the uncontrolled formation of the thermodynamically more stable metallocene derivatives [3]. Thus, $\sigma$-bond metathesis with an appropriate cyclopentadiene and a lanthanide alkyl appeared to us to be a highly attractive synthetic pathway for these types of complexes [4].

## RESULTS AND DISCUSSION

In order to circumvent the problems associated with salt metathesis, we employed a lanthanoid tris(alkyl) complex $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu, Yb, Er, Tb), which allows the facile synthesis of the linked amido–cyclopentadienyl complex $Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)$ and the bis(alkyl) complexes $Y(\eta^5-C_5Me_4SiMe_2X')(CH_2SiMe_3)_2(THF)$ (X' = Me, Ph, $C_6F_5$) under very mild conditions in high yield (Scheme 1). These alkyl complexes are rather sensitive and cannot be stored for prolonged peri-

ods of time [5a]. The choice of $Ln(CH_2SiMe_3)_3(THF)_2$, which is significantly more reactive than $Ln\{CH(SiMe_3)_2\}_3$ was a trade-off against the problematic presence of tetrahydrofuran (THF) [4c]. Hydrogenolysis of the linked amido–cyclopentadienyl alkyl complexes with dihydrogen or phenylsilane cleanly leads to the dimeric hydrido complex $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ (Scheme 2).
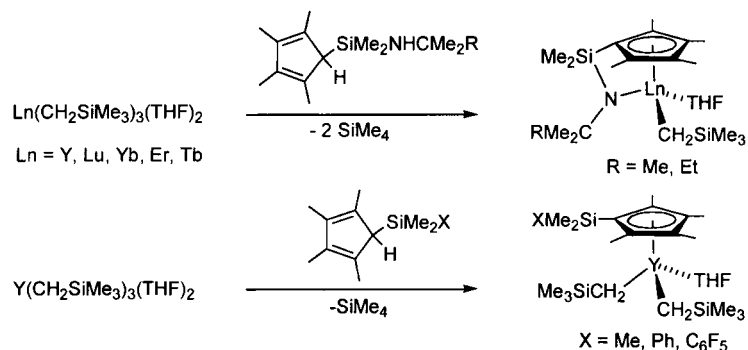


**Scheme 1**

The diamagnetic hydrido complexes of yttrium and lutetium were fully characterized by X-ray diffraction in the solid state and by variable-temperature NMR spectroscopy in solution. They are highly fluxional with respect to THF dissociation, monomer–dimer equilibrium, and rotation about the metal–metal axis. Two diastereomers, which differ in the relative configurations of the two metal centers within a square pyramidal coordination sphere, can be detected at lower temperatures.
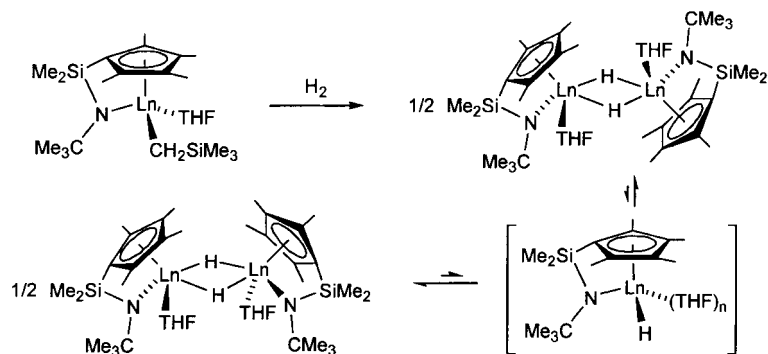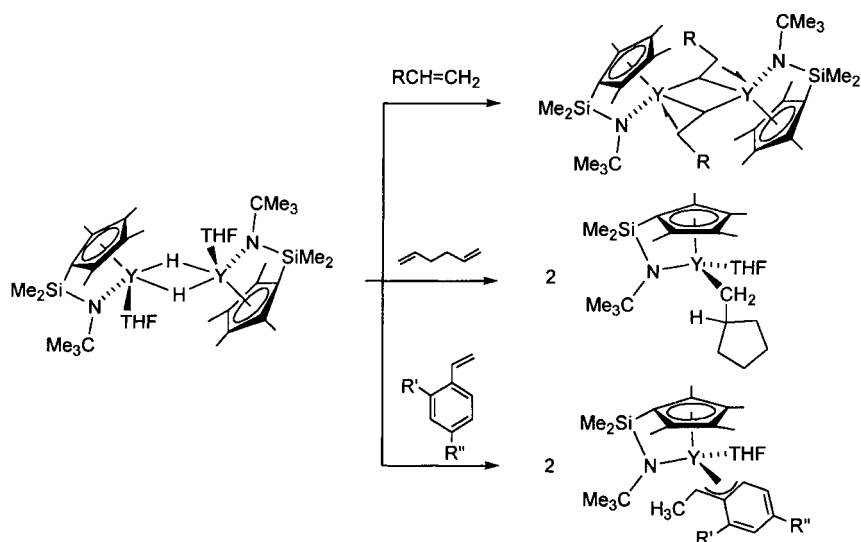


**Scheme 2**

The presence of monomeric units can be inferred from various scrambling reactions [5b]. Thus, mixing a benzene solution of $[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ with that of the lutetium analog at room temperature instantaneously gave a 1:2:1 statistical mixture containing the homo- and heterometallic complexes $[Ln(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ (Ln = Y, Lu) and $[YLu(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)_2(THF)_2(\mu-H)_2]$.

The hydrido complex $[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(THF)(\mu-H)]_2$ smoothly reacts with a variety of olefinic substrates (Scheme 3). Ethylene undergoes sufficiently slow sequential insertion at low temperatures (<–30 °C) to give a mixture of *n*-alkyl complexes $[Y(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)(\mu-R)]_2$, which can be independently synthesized by the reaction of α-olefin with the dimeric hydride. Initially, it was somewhat surprising that the crystals obtained from these reactions were THF-free. However, single-crystal structural analyses of a series of *n*-alkyl complexes revealed the presence of a β-agostic interaction which appears to alleviate the high Lewis acidity of the rare earth metal center. Few related structures of *n*-alkyl complexes have been reported in the literature [6]. The THF-free dimeric alkyl com-

plexes dissolve in THF to give the extremely sensitive and reactive monomeric *n*-alkyl complex [Y(η$^5$:η$^1$-C$_5$Me$_4$SiMe$_2$NCMe$_3$)(THF)(R)].



**Scheme 3**

Whereas ethylene is slowly polymerized by the hydrido complex at room temperature to give linear polyethylene with T$_m$ = 136 °C and activity of <1 kg polymer/mol Y•bar•h (Scheme 4), polymerization of α-olefins, dienes, or styrene does not occur, as stable mono(insertion) products form in these cases. In particular, styrenes with not more than one ortho-substituent give bright yellow 1-phenethyl complexes. An X-ray diffraction study of [Y(η$^5$:η$^1$-C$_5$Me$_4$SiMe$_2$NCMe$_2$Et)(THF)(CHMeC$_6$H$_4$$^t$Bu-4)] confirmed that the insertion occurred in a 2,1-fashion and that the phenyl ring is engaged in an η$^3$-coordination. Variable-temperature NMR spectroscopy further revealed fluxional behavior that includes THF dissociation, phenyl ring coordination, and rotation about the ipso- and α-carbon atom. These results are relevant to the mechanism of syndiospecific styrene polymerization by cationic mono(cyclopentadienyl)titanium(III) complexes. Here, an intermediate with 2,1-inserted monomer and an η$^4$-coordinated styrene is postulated [7].



X = Ph (R = *n*-alkyl), CO$_2$$^t$Bu, CN
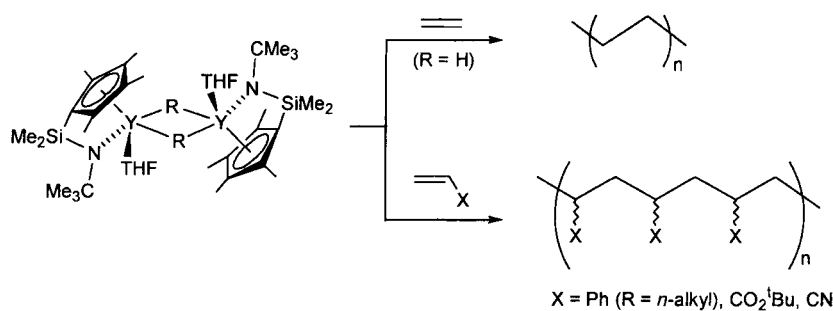
**Scheme 4**

The polymerization of styrene, however, cannot be initiated efficiently by the hydrido complex or the styrene insertion product, probably because the THF present in the system cannot be displaced by styrene. The *n*-alkyl complex of yttrium (but not that of lutetium and peculiarly, not the THF-free dimer) polymerized styrene in a controlled manner to give atactic polystyrene with low polydispersity. Thus, 50 equiv of styrene gives polystyrene with $M_n = 24\ 100$ and $M_w/M_n = 1.10$; $mm = 0$, $mr = 29.5$, $rr = 70.5\%$. This polymerization is not living, but sufficiently controlled (linear increase of molecular weights with conversion and monomer to yttrium ratio) to allow AB block copolymerization without considerable increase in molecular weight distribution. Thus, poly(styrene-*block-tert*-butyl acrylate) can be prepared by sequential addition of styrene and *tert*-butyl acrylate.

The yttrium hydrido complex polymerizes the polar monomers *tert*-butyl acrylate and acrylonitrile. *tert*-Butyl acrylate is polymerized at temperatures as low as –30 °C (i.e., well below the decomposition temperature) to give poly(*tert*-butyl acrylate) in high yields and with molecular weights $M_n > 20\ 000$. The molecular weight distributions of the resulting polymers are in the range of 1.5–2.0, and the polymer microstructure as determined by $^{13}C$ NMR spectroscopy is predominantly atactic. An intense red solution forms as soon as acrylonitrile is added to a toluene solution of the hydride, and the precipitation of yellow atactic polyacrylonitrile soon follows. This unusual color is ascribed to an intramolecular charge-transfer band of an $f^0d^0$-complex to an electron acceptor. According to GPC results, the polyacrylonitrile samples exhibit molecular weights in the range of $10^5$, but broad molecular distributions, >5. For the mechanism of the polar monomer polymerization, we propose a group-transfer-type polymerization involving enolate and keteniminato intermediates [8].

## ACKNOWLEDGMENTS

## REFERENCES

1. H. Yasuda and E. Ihara. *Adv. Polym. Sci.* **133**, 53 (1997).
2. H. Schumann, J. A. Meese-Marktscheffel, L. Esser. *Chem. Rev.* **95**, 865 (1995).
3. (a) K. C. Hultzsch, T. P. Spaniol, J. Okuda. *Organometallics* **16**, 4845 (1997); (b) K. C. Hultzsch, T. P. Spaniol, J. Okuda. *Organometallics* **17**, 485 (1998).
4. (a) M. Booij, N. H. Kiers, J. J. Heeres, J. H. Teuben. *J. Organomet. Chem.* **364**, 79 (1989); (b) Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko, V. G. Young. *Organometallics* **15**, 2720 (1996).
5. (a) K. C. Hultzsch, T. P. Spaniol, J. Okuda. *Angew. Chem. Int. Ed.* **38**, 227 (1999); (b) K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda. *Organometallics* **19**, 228 (2000); (c) S. Tian, V. M. Arrendondo, C. L. Stern, T. J. Marks. *Organometallics* **18**, 2568 (1999).
6. (a) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **116**, 4623 (1994); (b) C. J. Schaverien. *Organometallics* **13**, 69 (1994). (c) D. Stern, M. Sabat, T. J. Marks. *J. Am. Chem. Soc.* **112**, 9558 (1990).
7. A. Zambelli, L. Oliva, C. Pellecchia. *Makromol. Chem., Macromol. Symp.* **48/49**, 297 (1991).
8. H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura. *J. Am. Chem. Soc.* **114**, 4908 (1992).