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NEW RARE-EARTH COMPLEXES SUPPORTED BY TRIDENTATE AMIDINATE LIGAND WITH A PENDANT DIPHENYLPHOSPHINOXIDE GROUP. SYNTHESIS, STRUCTURES AND CATALYTIC ACTIVITY IN ISOPRENE POLYMERIZATION

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Introduction

In our previous studies we synthesized amidine with a pendant donor groups P=O (**1**) (**Fig. 1**). The bisalkyl complexes of yttrium and erbium were prepared. The ternary systems containing $[Ph_3C][B(C_6F_5)_4]$ and $[PhNHMe_2][B(C_6F_5)_3]$ demonstrated high catalytic activity at room temperature and ability to convert into polymer up to 10000 equivalents of monomer in 30-120 min achieving total conversions. More over these catalytic systems proved to be able to provide control of regio- and stereoselectivities of polymerization process enabling formation of polyisoprenes containing predominantly cis-1,4-units (96.6 %).

In this study, we report new versions of amidine (**2**) containing more bulky 2,6-diisopropyl phenyl fragment (**Fig.1**) to investigate the influence of coordination environment on the catalytic activity in polymerization of isoprene.

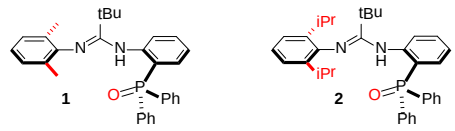


Figure 1. Amidines with pendant donor groups.

Results and discussion

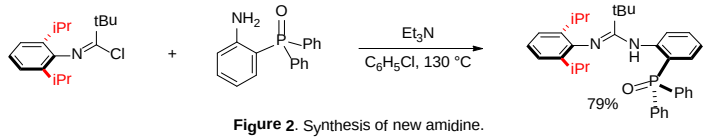


Figure 2. Synthesis of new amidine.

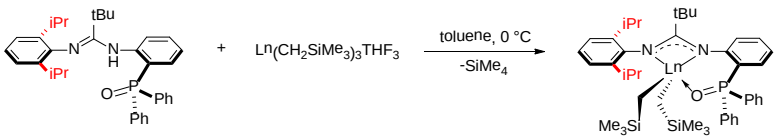
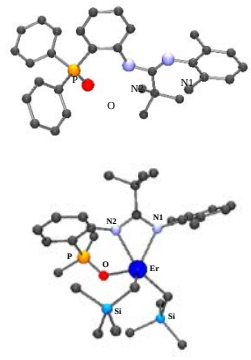


Figure 3. Synthesis of bisalkyl complexes of yttrium and erbium.

Ln=Y (45%) **3**
Er (62%) **4**

X-Ray diffraction

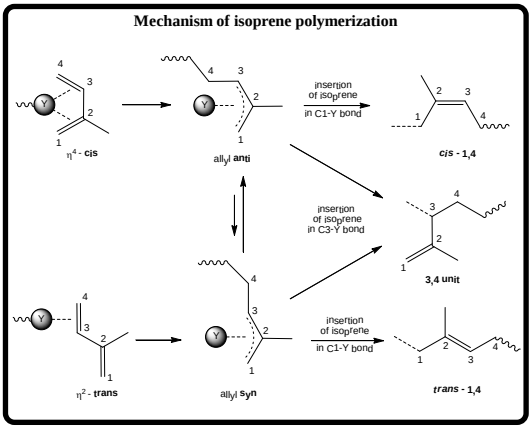


Catalytic tests in isoprene polymerization

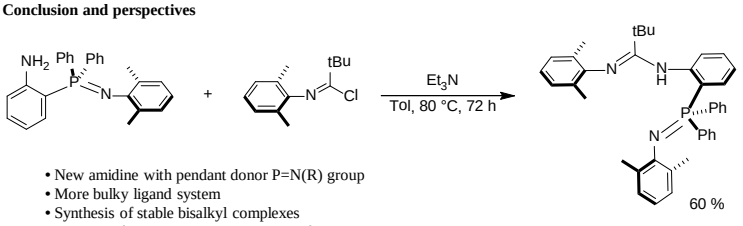
[Ln]	[Ln]/[Co-cat]/[Al^{i}Bu$_3$]/[IP]	Co-cat	t, min	Yield %	Cis-1, 4[a]	Trans-1, 4[a]	3, 4[a]	M_n[b] ($\times 10^{-3}$)	PDI[b]
Y	1:1:10:10000	$[PhNHMe_2][B(C_6F_5)_4]$	120	88	93,0	4,6	1,7	211,64	2,70
Y’	1:1:10:10000	$[PhNHMe_2][B(C_6F_5)_4]$	120	72	96,6	1,2	2,2	271.28	2,22
Er	1:1:10:10000	$[PhNHMe_2][B(C_6F_5)_4]$	120	92	98,5	0,5	1,0	206,74	3,48
Er’	1:1:10:10000	$[PhNHMe_2][B(C_6F_5)_4]$	120	73	93,5	3,9	2,7	484.13	2,49
Y	1:1:10:10000	$[Ph_3C][B(C_6F_5)_4]$	120	96	97,0	1,5	1,5	195,77	1,98
Y’	1:1:10:10000	$[Ph_3C][B(C_6F_5)_4]$	120	>95	92,2	4,3	3,4	1,04 % 70192,83 98,96 % 200,38	2,75 2,48
Er	1:1:10:10000	$[Ph_3C][B(C_6F_5)_4]$	120	96	90	4,5	5,5	88,95% 4526,27 11,05% 8,98	3,95 1,99
Er’	1:1:10:10000	$[Ph_3C][B(C_6F_5)_4]$	120	51	87,7	0,7	11,6	413,42	3,54

General conditions: Toluene, 25 °C, [Ln] = 0.01 mmol. a) Determined by ^{1}H and ^{13}C NMR spectroscopy. b) Determined by SEC in thf.

Mechanism of isoprene polymerization

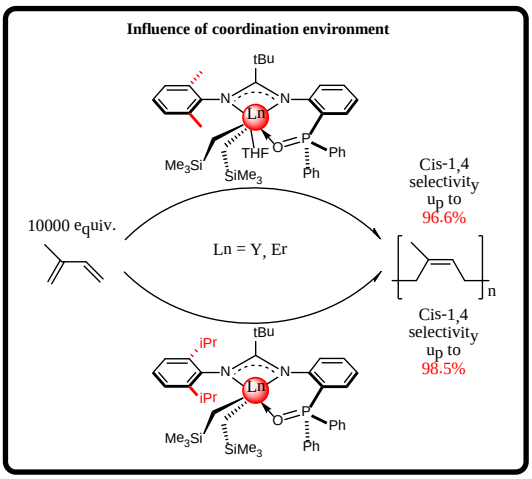


Conclusion and perspectives



- New amidine with pendant donor P=N(R) group
- More bulky ligand system
- Synthesis of stable bisalkyl complexes
- Increase of selectivity polymerization of isoprene

Influence of coordination environment



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