

Organometallics 2014 vol.33 N24, pages 7125-7134

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# Organolanthanide complexes supported by thiazole-containing amidopyridinate ligands: Synthesis, characterization, and catalytic activity in isoprene polymerization

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## Abstract

© 2014 American Chemical Society. Neutral bis(alkyl)-organolanthanide complexes supported by tridentate {N-,N,N} monoanionic 5-methylthiazole- or benzothiazole-amidopyridinate ligands have been prepared and completely characterized: (LThiaMe<sub>2</sub>)Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> [Ln = Lu<sup>3+</sup> (3), Er<sup>3+</sup> (7), Yb<sup>3+</sup> (8)] and (LBnThMe<sub>2</sub>)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (5). Similarly to related Y<sup>3+</sup> systems, the nature of the thiazole unit controls the ultimate catalyst stability in solution. In the diamagnetic Lu<sup>3+</sup> complex 5, a progressive and complete rearrangement of its metal coordination sphere takes place through a metal-to-ligand alkyl migration with subsequent benzothiazole ring-opening and generation of the Lu<sup>3+</sup> mono(alkyl)-arylthiolate species stabilized by a tetradentate {N-,N,N,S-} dianionic ligand. On the other hand, the 5-methylthiazole-containing complexes 3, 7, and 8 showed no evidence of any ligand rearrangement. Complexes 3-8 have been tested as homogeneous catalysts in isoprene (IP) polymerization, after activation with selected organoborates. Binary systems 3/TB and 7/TB [TB = tritylium tetrakis(pentafluorophenyl)borate] show the highest activity and living character toward IP polymerization, affording polymers with relatively high trans-1,4-selectivity (up to 76.4%), moderate molecular weights (M<sub>n</sub> up to 146'000 g/mol), and narrow polydispersities (M<sub>w</sub>/M<sub>n</sub>). Depending on the rare-earth ion of choice, a prevalent trans-1,4 (Lu<sup>3+</sup>, Er<sup>3+</sup>, Yb<sup>3+</sup>; up to 76.4%) or a dominant 3,4 (Y<sup>3+</sup>; 92.7%) polymer structure is observed. The influence of the ligand type, metal ion, and activator(s) on the ultimate catalyst activity and selectivity is discussed.

<http://dx.doi.org/10.1021/om500918y>

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