



# Strained metal bonding environments in methylindium dithiolates and their reactivity as initiators for the ring-opening polymerization of cyclic esters



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## ABSTRACT

We have synthesized indium complexes containing a variety of metal bonding environments through use of polyfunctional dithiolate ligands and examined their reactivity as initiators for the ring-opening polymerization of L-lactide, rac-lactide, ε-caprolactone and β-butyrolactone. The facile reaction of Me<sub>3</sub>In with the corresponding polyfunctional dithiols in toluene, thf or diethyl ether resulted in the formation of [MeIn(SOOS)]<sub>2</sub> (3), MeIn(SNNS) (4), [MeIn(ONS<sub>2</sub>)]<sub>3</sub> (5), MeIn(NNS<sub>2</sub>) (6), MeIn(NNS<sub>2</sub>Pr) (7) and MeIn(pyrS)<sub>2</sub> (8). The solid-state structures of 3 and 5 each show the corresponding ligand to be tridentate with an uncoordinated ligand O atom. Dimeric (3) and trimeric (5) structures result from short intermolecular In ... S interactions. All structures show five coordinate indium centres in distorted trigonal bipyramidal bonding environments, but with various arrangements of donor atoms (eq/ax): SSC/OS (3,5), SNC/NS (4), SSN/NC (6), SSC/NS (7) and SSC/NN (8). DFT studies of model MeIn(SMe)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> systems show the bonding environments in 4 and 6 to be highly strained, while the axial In–Me bond of 6 shows the longest bond distance and lowest vibrational frequency. Compound 5 provided the best control of the polymerization of L-lactide and rac-lactide in THF at 70 °C, and a small heterotactic enrichment was observed for the latter. Compounds 3 and 4 provided the best control of the polymerization of β-BL in toluene at 70 °C in toluene, and compound 3 provided the best control of the polymerization of ε-CL in toluene at 70 °C. In all cases, polymerization rates were low. This work demonstrates a systematic approach to exploring the modification and reactivity of main group metal bonding motifs, which has resulted in identification of two novel “strained” bonding environments for indium.

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## 1. Introduction

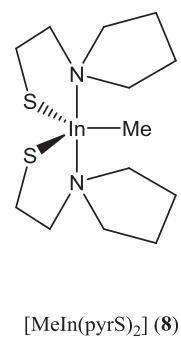
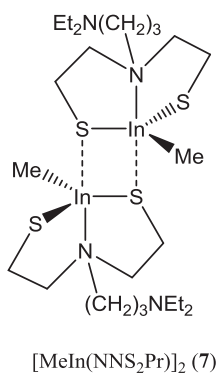
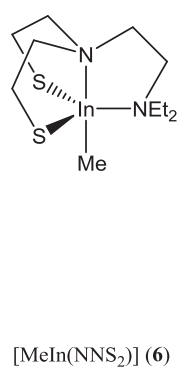
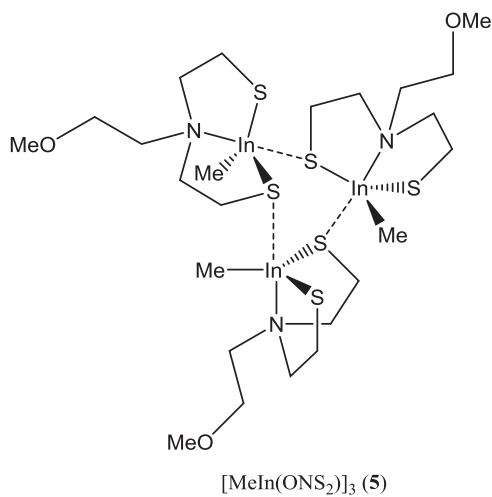
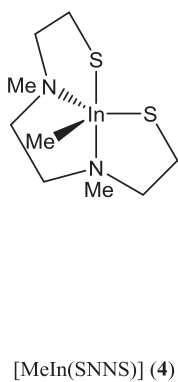
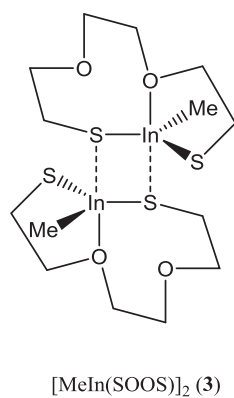
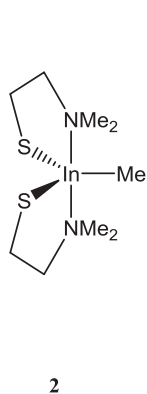
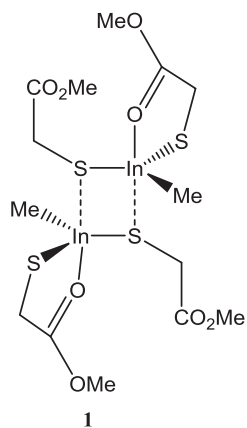
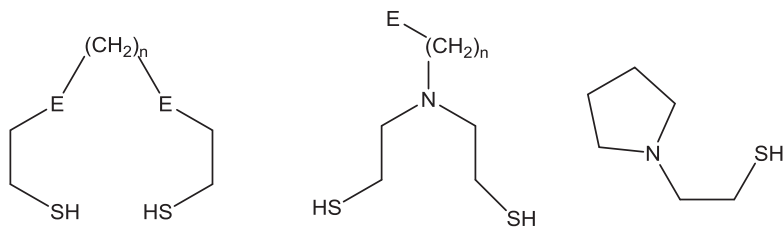
Over the past 20 years, interest in main-group element catalyzed ring opening polymerization (ROP) to obtain aliphatic polyesters has been steadily increasing due to applications in the pharmaceutical and commodity plastics industries [1–6], as has the prevalence of main group catalysis in small molecule chemistry [7]. Therefore, a primary focus of contemporary main group chemistry is the identification of reactive species for use as improved

alternatives to traditional transition metal-based catalysts in chemical processes [8]. Such studies often explore novel bonding situations for main group elements where reactivity is manipulated through electronic inductive effects of ligands or modification of the element's bonding environment. The latter is intimately related to electronic structure as the most stable structures for covalently bonded species must adhere to VSEPR rules and valence bond models [9].

While aluminum compounds displayed both early and continued success in catalyzing the ring opening polymerization of rac-lactide, ε-caprolactone and many other monomers [10,11], exceptional catalysts have more recently been prepared by the heavier indium analogues. In fact, ligand-supported indium

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