Synthesis and evaluation of sterically unencumbered CPAM group 4 metal complexes as pre-initiators for living coordination chain transfer polymerization

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We have previously reported that cyclopentadienyl, amidinate (CPAM) group 4 metal complexes of general formula, (η^5-C_5R_5)[κ^2-(*N,N*)-N(R^1)C(R^2)N(R^3)]MMe_2 (M = Zr and Hf) (**I**), can serve as pre-initiators for the living coordination polymerization (LCP) and living coordination chain transfer polymerization (LCCTP) of ethene, propene, linear and branched α-olefins and α,ω-nonconjugated dienes after 'activation' by a borate co-initiator, such as [$PhNHMe_2$][$B(C_6F_5)_4$] (**B1**). However, we are still motivated to: (1) increase the rate of propagation via a sterically less-encumbered CPAM supporting ligand environment, (2) extend LCP and LCCTP to first row derivatives (i.e. M = Ti), and (3) establish a highly efficient, inexpensive, and scalable synthesis of new amidinate ligands that are used to achieve (1) and (2). This talk will present the results of studies that have been successful in achieving these objectives, which include synthesis of several new derivatives of I that incorporate the easily synthesized N,N-dimethyl, phenyl amidinate (DMPA) ligand and its incorporation into the (η^5-C_5Me_5)(DMPA) Hf complex (**1**) and the (η^5-C_5H_5)(DMPA) Ti complex (**2**). After activation by **B1**, **1** is capable of the LCP of propene, 1-hexene, and vinylcyclohexane (VCH), with the last monomer providing isotactic poly(VCH) via stereoselective chain-end control. **1** is also capable of carrying out LCCTP with $ZnEt_2$ as the chain transfer agent. In contrast, the successful, albeit non-living, coordination polymerization of ethene, propene, and 1-hexene required activation of **2** with the borate, [Ph_3C][$B(C_6F_4)_4$] (**B2**).

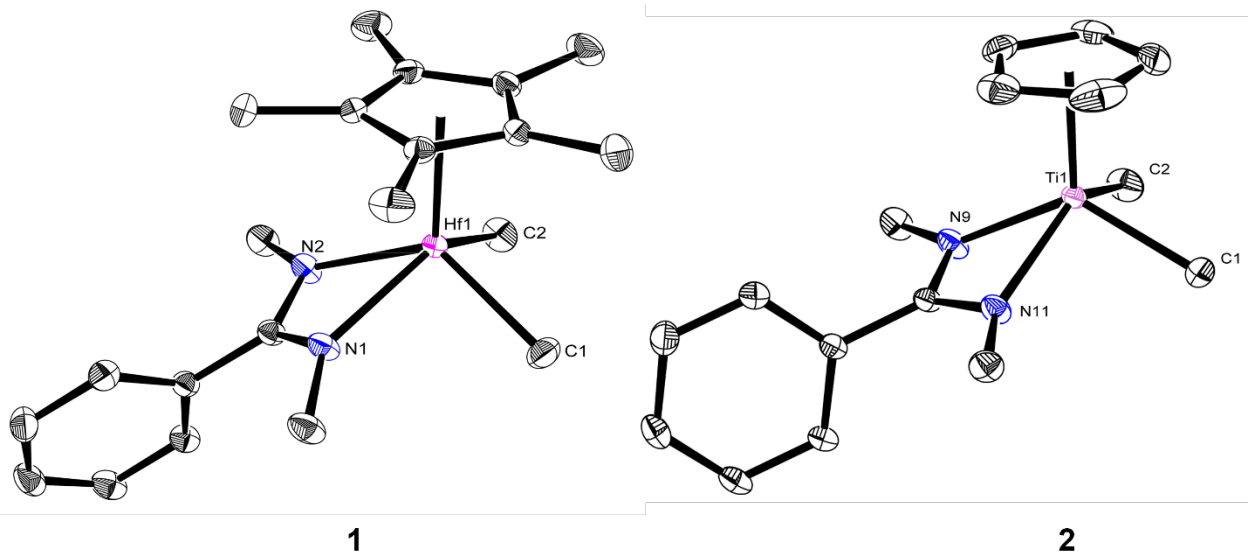

Figure 1. Crystal structures of **1** and **2** reported with 30% probability. Hydrogen atoms have been removed for the sake of clarity.