Tunable Cooperative Effects in Multi-Center Catalysis for the Synthesis of New Materials. Binuclear Phenoxyiminato Polymerization Catalysts

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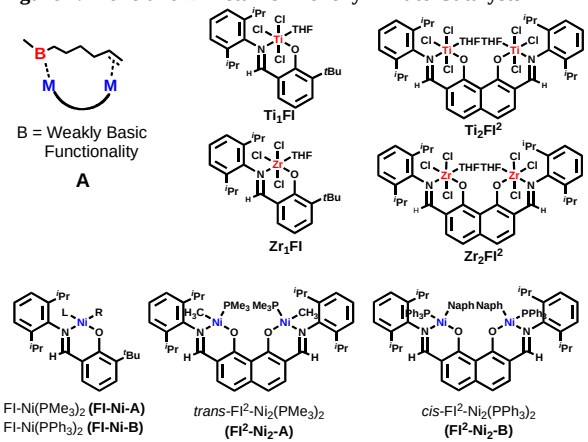
Introduction

Over the past few years, much research attention has focused on discovering more efficient and selective homogeneous catalytic processes enabled by cooperative effects between proximate active centers in multinuclear metal complexes. The origin of these effects for olefin polymerization processes is proposed to include non-negligible comonomer secondary binding to weakly basic groups on the olefin which modifies relative chain transfer rates and facilitates comonomer enchainment at the second, proximate metal center (e.g., **A)**. Here cooperative interactions significantly enhance styrene homopolymerization rates, modify enchainment regioselectivity, and greatly increase comonomer enchainment selectivity. These studies indicate that the degree of cooperativity between the two catalytic centers in these catalysts scales roughly inversely with intermetallic distance. [1]

To fully explore the nature of cooperativity effects on olefin polymerization , a new ligand structure was designed based mononuclear phenoxyiminato catalysts originally developed by Fujita[2] and Grubbs.[3] This new ligation enforces a close metal-metal contacts to maximize cooperativity effects. Utilizing electrophilic group 4 metals[4] and polar-monomer tolerant group 10 metals[5] in the present ligation environments, the scope of this cooperativity is explored via sterically crowded non-polar olefins and polar monomers, and in reaction media previously ineffective with the monometallic analogues.

Figure 1. Mono and Bimetallic Phenoxyiminato Catalysts



Materials and Methods

Polymerizations for the group 4 mono- and bimetallic systems were performed under an ethylene atmosphere with the desired amount of comonomer injected as required. Group 10 polymerizations were performed on a high-pressure line from 3.0-7.0 atm. Again, the desired amount of comonomer or polar solvent media was injected where applicable. All polymer microstructures were established by rigorous spectroscopic and analytical methodologies, including ^{1}H and ^{13}C NMR, DSC, GPC, and IR.

Results and Discussion

Ethylene homopolymerizations with group 4 binuclear catalysts are ~6x more active than their monometallic counterparts. In the case of copolymerizations, the bimetallic systems incorporate more than twice the amount of 1-hexene, and efficiently co-enchain methylenecyclohexane and methylenecyclopentane. Etheylene homopolymerizations with the group 10 systems also show increases in activity over the mononuclear catalysts. Additionally, they incorporate 4x the amount of functionalized norbornenes in ethylene copolymerizations and enchain up to 11 mol% of methacrylate as an ethylene comonomer.

Table 1. Representative Catalyst Activities and Polymer Properties

Entry	Catalyst	Comon.	Yield (g)	M_w[b]	M_w/M_n	Br/ 1000C	m.p °C	Activity[a]	Comon. Incorp.
1	**FI^2-Zr$_2$**	Hexene	0.150	98000	3.31	-	126	12	11
2	**FI-Zr**	Hexene	0.015	21000	9.61	-	125	1.0	7.4
3	**FI^2-Ti$_2$**	MCP	0.115	12100	4.01	-	126	15	0.7
4	**FI-Ti**	MCP	0.025	20200	20.2	-	128	3.4	0.4
5	**FI^2-Ni$_2$**	NB	0.558	66400	5.2	34	107	1.3	9
6	**FI-Ni**	NB	0.072	63200	2.3	9	124	0.3	3
7	**FI^2-Ni$_2$**	MA	0.722	6300	1.6	36	108	1.8	11
8	**FI-Ni**	MA	0	-	-	-	-	0	0

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