



Synthesis, Structures and Ethylene Oligomerization Reactivity of Transition Metal Complexes Supported by Multidentate Amidine-Based Ligands

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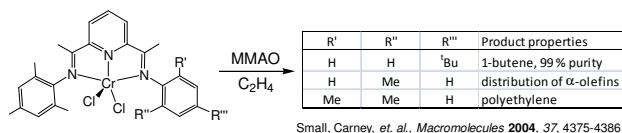
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Goals and Objectives

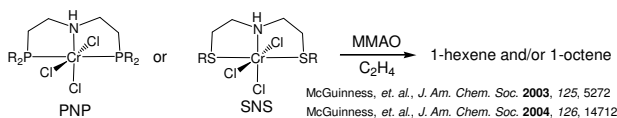
- > Synthesize new families of multidentate ligands and exploit their ability to coordinate transition metals
- > Develop new transition metal catalysts for olefin polymerization, including the oligomerization of ethylene to high purity α -olefins
- > Develop new tridentate ligands to serve as analogues of Sasol-type catalysts
- > Examine the impact of ligand structure (type, number and position of substituents) on catalyst performance
 - > Catalyst performance attributes include the following: catalyst productivity, purity of α -olefins and overall α -olefin selectivity

Background Information

- > Tridentate ligands figure prominently in recent chromium catalyzed olefin polymerization studies.
 - > Chromium pyridinebis(imine) complexes display high activities for ethylene oligomerization or polymerization, with polymer products being highly dependent on the ligand substituents.



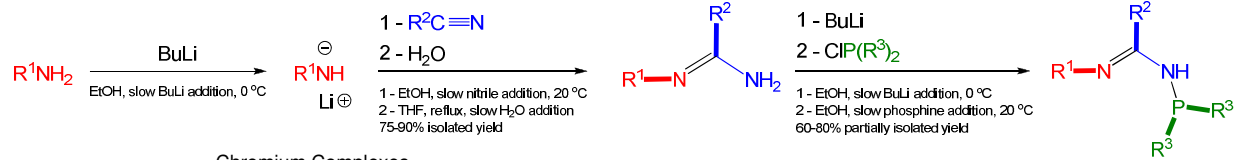
- > Sasol has demonstrated that chromium complexes supported by tridentate PNP and SNS ligands display high activities for ethylene oligomerization, including the uncanny ability to selectively produce 1-hexene and 1-octene (the highest value α -olefins).



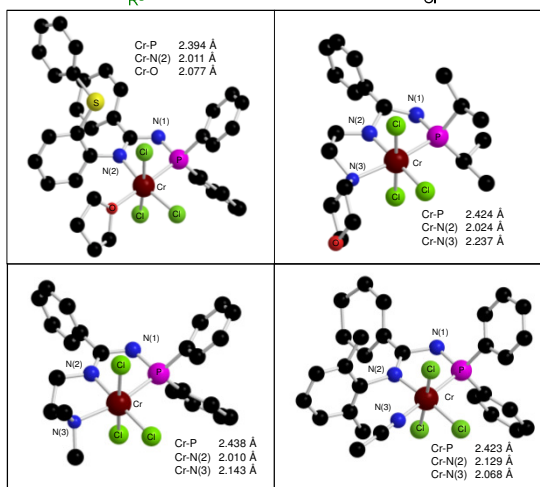
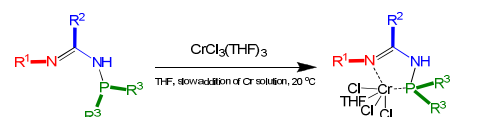
Experimental Details

- > Amidine ligand precursors were purified by crystallization or vacuum distillation and characterized by ¹H and ¹³C NMR spectroscopy.
- > N-phosphino amidine ligands were isolated as solids or viscous oils and characterized by ¹H and ¹³C NMR spectroscopy.
- > Transition metal complexes were isolated as greenish-blue to royal blue solids. Slow recrystallization provided samples suitable for x-ray analysis.
- > Polymerizations (MMAO co-catalyst) were performed in a 500 mL autoclave in using the reactor conditions indicated in the table.
- > Oligomeric products were analyzed by GC using the polymerization solvent as an internal standard.

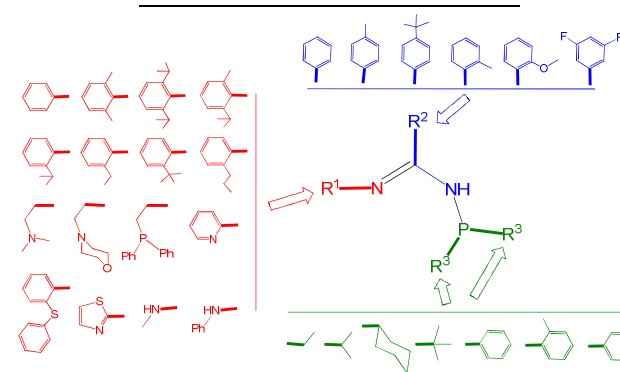
Multidentate Amidine-Based Ligands and Chromium Complexes: Synthesis and Structures



Chromium Complexes



Substituent Variation



Conclusions and Future Work

- > Ligand synthetic methods are modular and versatile, allowing for a large array of substituent combinations.
- > X-Ray crystallography and NMR spectroscopy of ligands and metal complexes confirm successful synthesis.
- > Surprisingly, chromium complexes supported by tridentate ligands (Sasol analogues) are not active polymerization catalysts.
- > However, chromium complexes supported by bidentate N-phosphino amidine ligands yield catalysts with high activity and product purity.
- > Continuing Work:
 - > Examine other ligand substituents and their effect on catalyst performance
 - > Prepare other transition metal (V, Fe, Ni, Pd, etc.) complexes using N-phosphino amidine ligands and examine their catalytic performance
 - > Conduct theoretical studies (DFT computations/molecular modeling) to help predict the impact of ligand modifications on metal complex geometry and catalytic behavior

Acknowledgements

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Selected Polymerization Data

R ¹	R ²	R ³	T (°C)	Activity (g/g cat-hr)	C ₆ fraction % α -olefin
CH ₂ CH ₂ NC ₆ H ₅ O	Ph	Ph	60	0	nd
CH ₂ CH ₂ PPH ₂	Ph	Ph	60	0	nd
CH ₂ CH ₂ NMe ₂	Ph	Ph	60	0	nd
CH ₂ CH ₂ NMe ₂	Ph	Ph	90	1000	92.9
C ₆ H ₄ -o-SPh	Ph	Ph	90	10400	98.0
Ph	p-MeC ₆ H ₄	Ph	60	4100	28.2
2,6-Me ₂ C ₆ H ₄	p-MeC ₆ H ₄	Ph	60	75100	96.2
2,6-Me ₂ C ₆ H ₄	p-MeC ₆ H ₄	ⁱ Pr	60	108000	99.3
2,6-Me ₂ C ₆ H ₄	p-MeC ₆ H ₄	ⁱ Pr	90	301200	99.4
2,6-Me ₂ C ₆ H ₄	p- ^t BuC ₆ H ₄	ⁱ Pr	60	481000	99.5

Polymerizations were performed for 30 minutes at 900 psi (850 psi ethylene, 50 psi hydrogen) in cyclohexane using MMAO as cocatalyst (Al:Cr = 1000)