



Transition Metal Complexes Incorporating Imine-Based Ligands for Selective Ethylene Oligomerization

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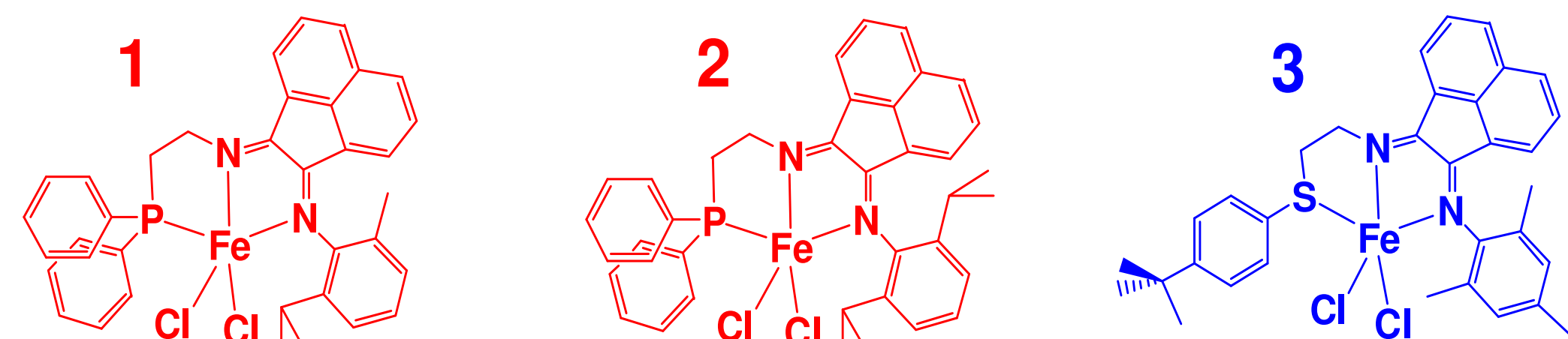
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Goals and Objectives

- Synthesize multidentate ligands and exploit their ability to coordinate early and late transition metals
- Develop transition metal catalysts for olefin polymerization, including the oligomerization of ethylene to high purity α -olefins
- Develop new ligands and metal complexes for the selective oligomerization of ethylene (1-hexene, 1-octene)
- Examine the impact of ligand structure (denticity, number and position of substituents, etc.) on catalyst performance
 - Catalyst performance attributes include the following: catalyst productivity, purity of α -olefins and overall α -olefin selectivity

Background Information

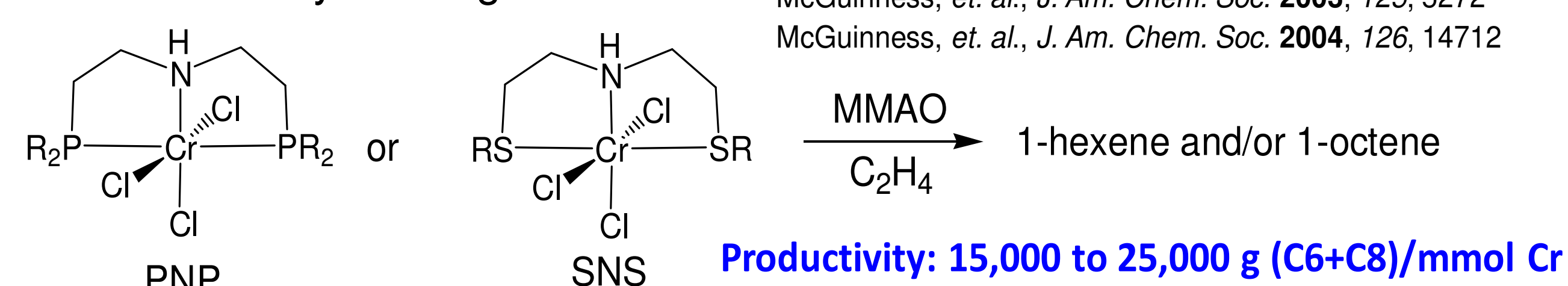
- α -olefins (C₄-C₂₀+) find wide commercial use (intermediates for polyolefins, detergents, flavors, fragrances, synthetic motor oils, etc.)
- Tridentate ligands figure prominently in metal catalyzed ethylene oligomerization studies
 - Iron(II) complexes supported by donor-modified α -diimine ligands



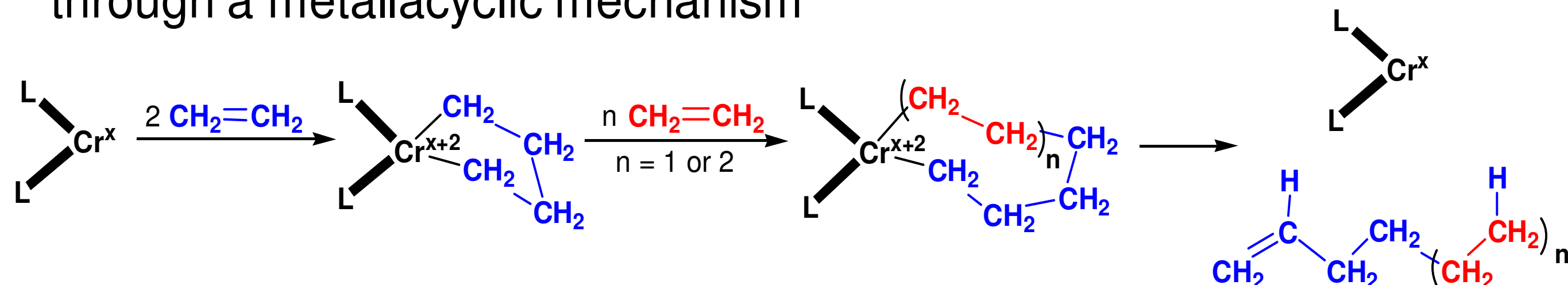
Compound	Productivity (g prod/mmol Fe)	K	C6 purity (%)	C8 purity (%)
1	35200	0.48	99.4	99.1
2	70600	0.60	99.4	99.1
3	91600	0.72	99.8	99.7

Small, Carney, et al., *Organometallics* 2010, 29, 6723; *Organometallics* 2007, 26, 1744; *Dalton Trans.* 2007, 2547

- Chromium complexes supported by tridentate PNP and SNS ligands for selective ethylene oligomerization



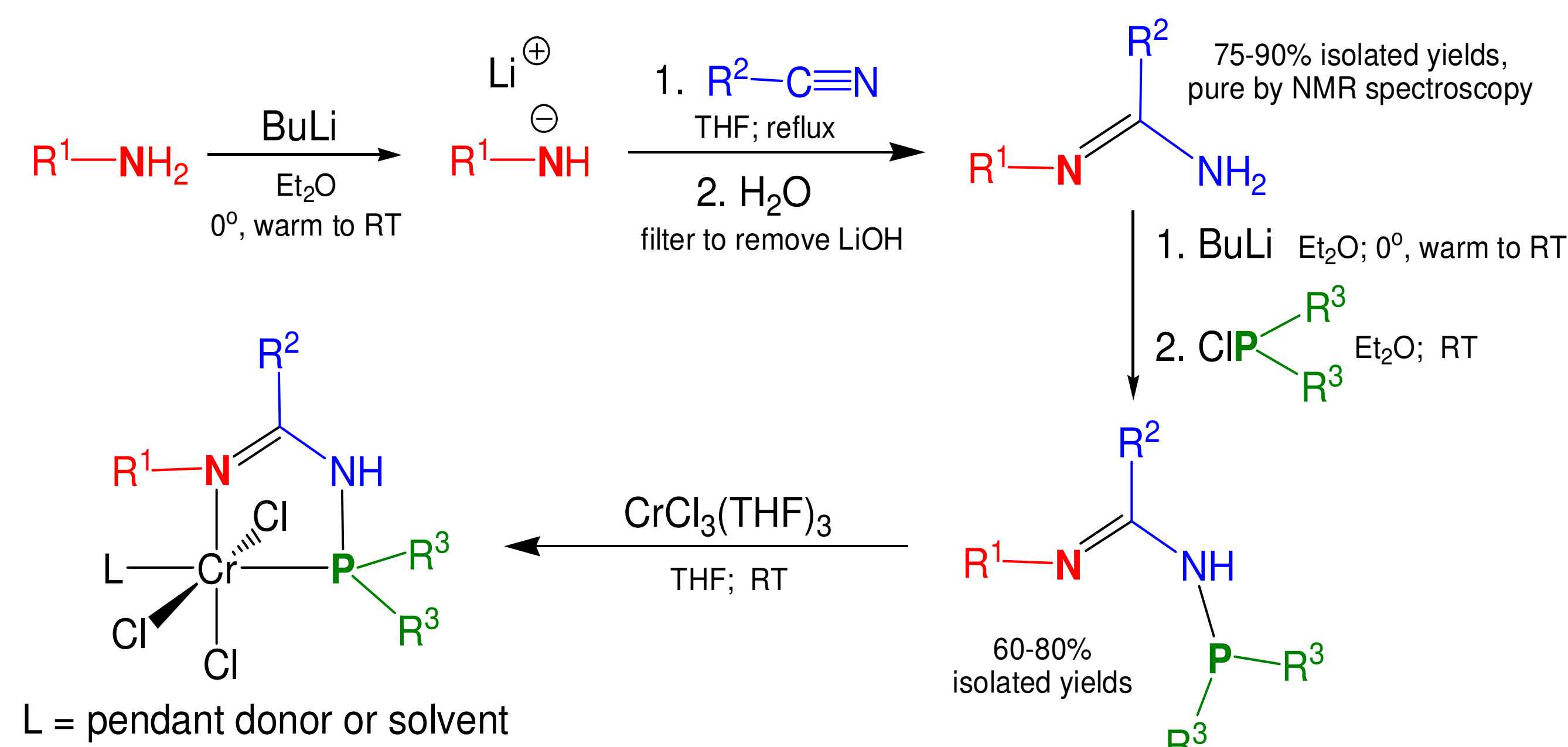
- Selective ethylene oligomerization (C₆ and C₈) presumably proceeds through a metallacyclic mechanism



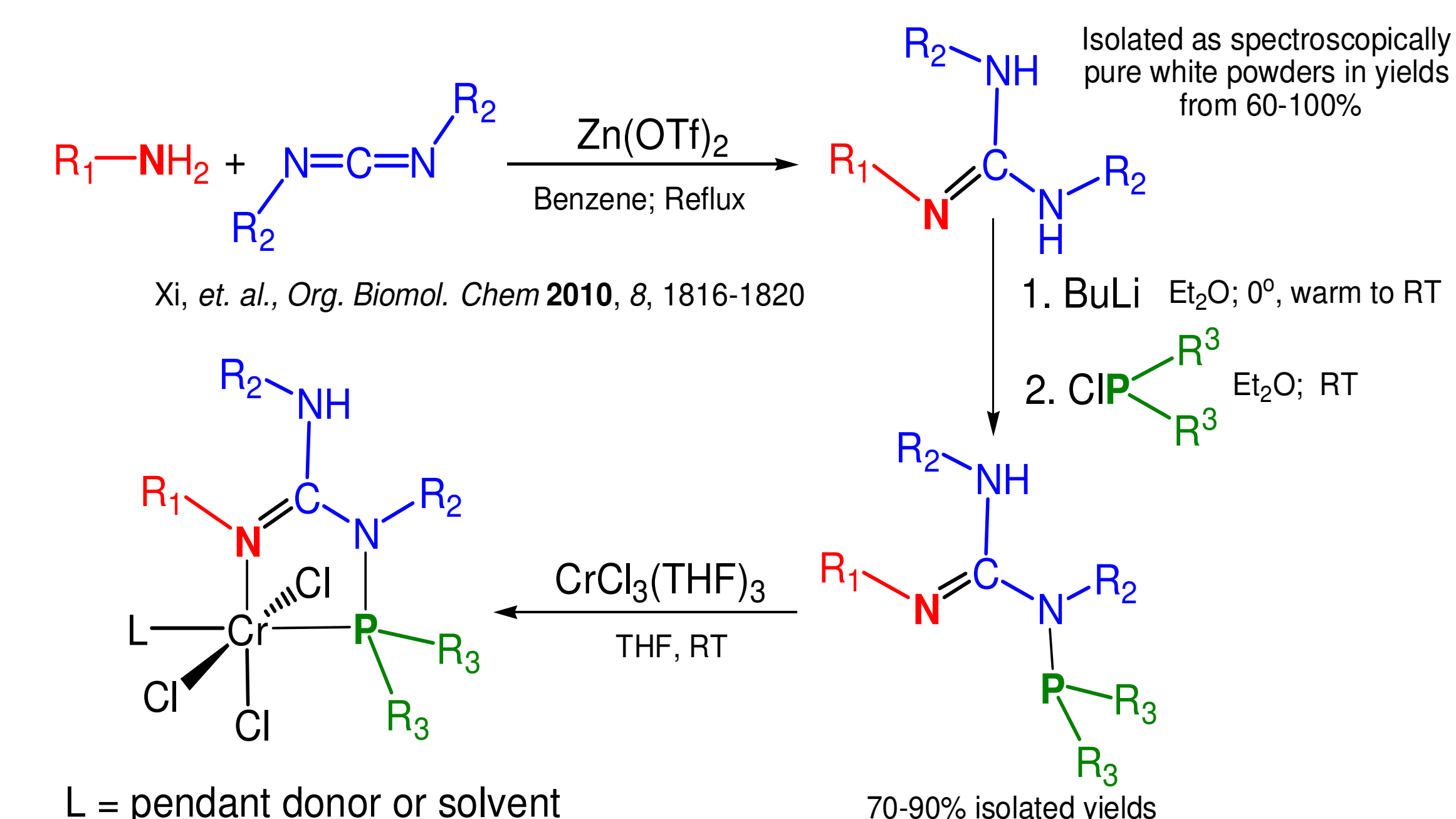
Experimental Details

- Ligand precursors were purified by recrystallization or vacuum distillation and characterized by ¹H and ¹³C NMR spectroscopy.
- N-phosphino amidine and guanidine ligands were isolated as solids or viscous oils and characterized by ¹H and ¹³C NMR spectroscopy.
- Chromium(III) complexes were isolated in nearly quantitative yield as greenish-blue to royal blue solids.
- Typical polymerization conditions (MMAO co-catalyst): 0.40 L cyclohexane, 70° C, 50 psig H₂, 850 psig C₂H₄, Al:Cr = 500
- Oligomeric products were analyzed by GC using the polymerization solvent as an internal standard.

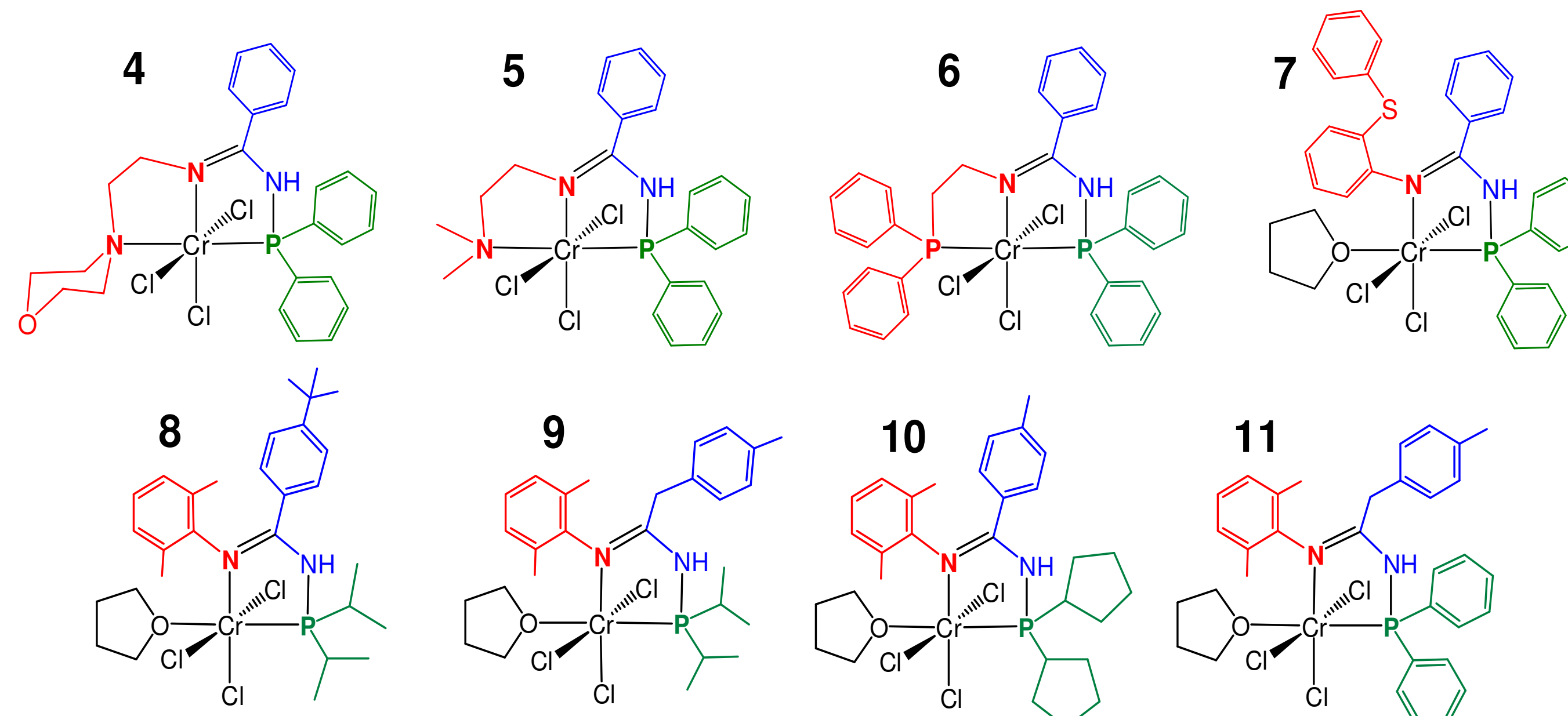
Synthesis of Phosphino-amidine Ligands and Chromium Complexes



Synthesis of Acyclic Phosphino-guanidine Ligands and Chromium Complexes



Polymerization Data – Amidine Complexes



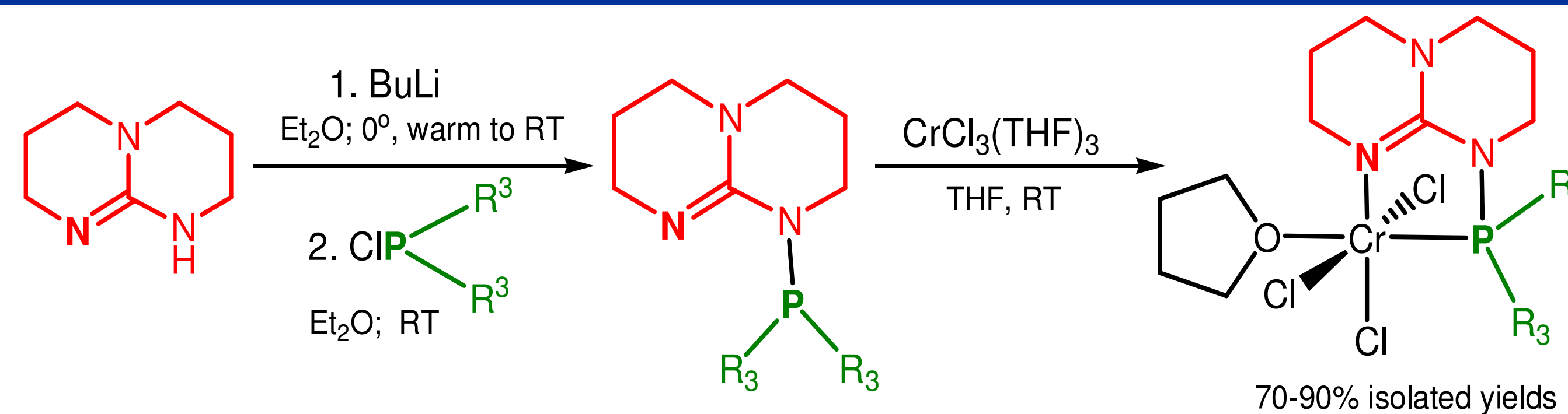
Compound	Productivity (g prod/mmol Cr)	% C6	% C8	C6 purity (%)	C8 purity (%)
4	0	nd	nd	nd	nd
5	5	nd	nd	nd	nd
6	7.5	nd	nd	nd	nd
7	540	86.9	2.5	98	83.4
8	25000	96.1	1.0	99.5	98.8
9	22600	93.9	3.2	99.7	99.3
10	34500	95.2	1.2	99.8	98.6
11	11700	61.6	36.0	96.5	99.1

Sydora, et al., *ASC Catalysis* 2012, 2, 2452-2455

New Questions and Recent Work

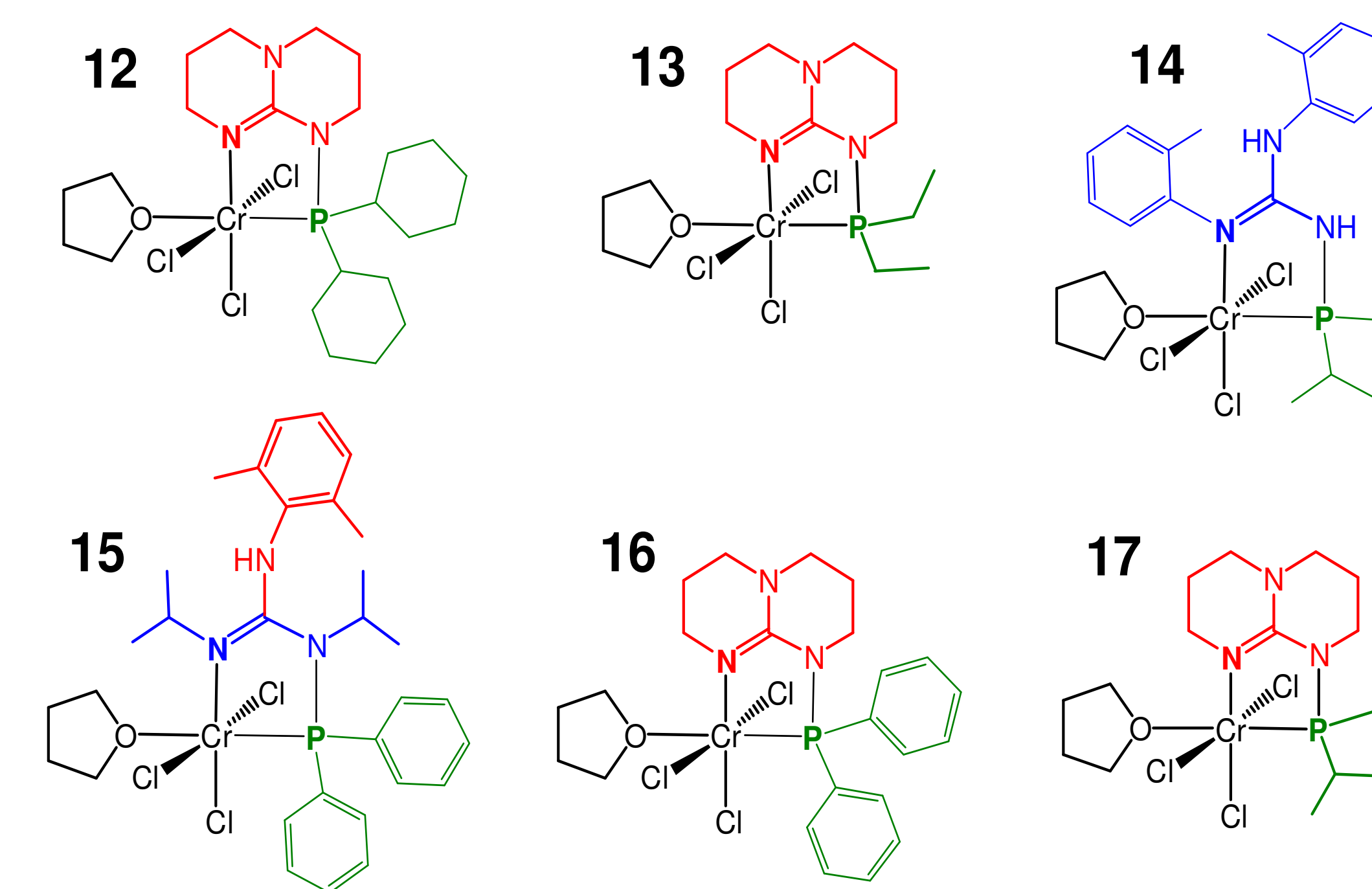
- Does heteroatom substitution in the ligand backbone (guanidine versus amidine) impact catalyst performance?
- A range of cyclic and acyclic phosphino-guanidines were synthesized.

Synthesis of Cyclic Phosphino-guanidine Ligands and Chromium Complexes



Dyer, et al., *Organometallics* 2008, 27, 5082-5087

Polymerization Data – Guanidine Complexes



Compound	Productivity (g prod/mmol Cr)	% C6	% C8	C6 purity (%)	C8 purity (%)
12	31	79.4	20.6	nd	nd
13	36	63.5	21.1	nd	nd
14	1440	60.7	26.9	94.1	96.7
15	38	71.7	12.3	nd	nd
16	520	37.0	41.7	44.7	85.0
17	9600	67.4	30.3	91.5	97.7

Conclusions

- Chromium complexes supported by phosphino-amidine ligands produce high activity catalysts for selective ethylene oligomerization.
- Chromium complexes supported by cyclic and acyclic phosphino-guanidine ligands can produce C₆ and C₈ selective catalysts (up to 97% C₆ + C₈), albeit with lower activity and product purity than those containing phosphino-amidine ligands.

Acknowledgements

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