

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 28-03-2013		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Apr-2012 - 31-Dec-2012	
4. TITLE AND SUBTITLE Final Report: STIR: Redox-Switchable Olefin Polymerization Catalysis: Electronically Tunable Ligands for Controlled Polymer Synthesis			5a. CONTRACT NUMBER W911NF-12-1-0127		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Brian K. Long			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Tennessee at Knoxville Office of Research 1534 White Avenue Knoxville, TN 37996 -1529			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 62021-CH-II.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Olefin polymerization catalysts containing redox-active moieties that may be tuned in situ via electrochemical or chemical oxidation and reduction were synthesized and examined. The redox capable functionalities were incorporated into specifically chosen ligand frameworks and metallated using organometallic reagents so as to produce precatalysts that could be activated using methylaluminumoxane, borane, or boronate-based activators. Those catalysts were shown to be active toward olefin polymerizations, their electrochemistry studied, and their in situ					
15. SUBJECT TERMS Catalysis, Redox-Switchable, Polymerization, Polyolefins					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Brian Long
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 865-974-6534

Report Title

Final Report: STIR: Redox-Switchable Olefin Polymerization Catalysis: Electronically Tunable Ligands for Controlled Polymer Synthesis

ABSTRACT

Olefin polymerization catalysts containing redox-active moieties that may be tuned in situ via electrochemical or chemical oxidation and reduction were synthesized and examined. The redox capable functionalities were incorporated into specifically chosen ligand frameworks and metallated using organometallic reagents so as to produce precatalysts that could be activated using methylaluminumoxane, borane, or boronate-based activators. Those catalysts were shown to be active toward olefin polymerizations, their electrochemistry studied, and their in situ switchability is currently underway yielding many promising results.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Zachary Sprigler	0.70	
FTE Equivalent:	0.70	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jennifer Rhinehart	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

**Final Report: STIR: Redox-Switchable Olefin Polymerization Catalysis:
Electronically Tunable Ligands for Controlled Polymer Synthesis**

Brian K. Long

Department of Chemistry University of Tennessee, Knoxville, TN 37996-1600

- 1. Forward** (optional – not included)
- 2. Table of Contents** (not included, report < 10 pages)
- 3. List of Appendices** (not applicable)

4. Statement of the Problem Studied

The development of olefin polymerization catalysts has had a profound influence on the world providing synthetic alternatives to traditional materials such as wood, steel, and glass. According to the American Chemistry Council, the U.S. production of polyethylene (PE) and polypropylene (PP) topped 53 billion pounds in 2011.¹ This extreme demand has ensured that olefin polymerization techniques and catalysts are continually evolving in the search for the next exceptional catalytic system.

Prior to the 1980's, olefin polymerization catalysts were heterogeneous mixtures of ill-defined structure having multiple active sites, each exhibiting different rates and selectivities.² The introduction of well-defined, homogeneous, single-site olefin polymerization catalysts has since opened new opportunities for understanding, controlling, and improving the synthesis of polyolefins. Group 4 metallocene-based catalysts dominated this area of research until the 1990's when non-metallocene catalysts were introduced based upon early and late transition metals.³ Unfortunately, the usefulness of these "post-metallocene" catalysts are often limited by various restrictions including functional group tolerance, uncontrolled/"non-living" behavior, and in the case of many group 10 catalysts, low activities and uncontrolled "chain-walking".^{4,5} In light of these limitations, we believe that the ability to modulate the electronic nature of a catalyst through the reduction or oxidation of an incorporated redox-active functionality may provide an attractive means of overcoming the problems associated with these post-metallocene catalysts.

The concept of redox-switchable catalysis (RSC) is a groundbreaking new area of research that promises to be a transformative tool in the field of olefin polymerization.⁶ The capability to modulate catalytic behavior via simple changes in oxidation state will bring unseen opportunities for catalyst control to the most widely used polymerization methodology in the world. To accomplish this, we sought to design and synthesize olefin polymerization catalysts containing redox-active moieties that may be tuned *in situ* via electrochemical or chemical oxidation and reduction (Figure 1). The redox capable functionalities were incorporated into specifically chosen ligand frameworks and metallated using organometallic reagents so as to produce precatalysts that could be activated using methylaluminoxane, borane, boronate-based activators, or in certain cases, no activator at all. These catalysts may provide a multitude of advantages, including the ability to modulate activity and reactivity *in situ*.

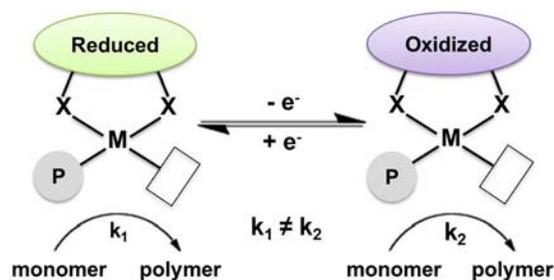


Figure 1. Overview of redox-switchable single-site olefin polymerization catalysts.

5. Summary of Most Important Results

Initial investigations focused on the modification and synthesis of known ligand frameworks where portions of the original ligand were replaced with redox functionality (Figure 2). The first choice for redox functionality was to incorporate one or more ferrocenyl moieties. Ferrocenyl derived ligands are well known and have applications ranging from materials⁷ to ligands for transition metal catalyzed carbon-carbon and carbon-heteroatom bond forming reactions.^{8,9} Their derivitization has been extensively studied, and perhaps most importantly, ferrocene's redox behavior is well understood as its $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ transition is easily obtainable electrochemically or through the use of many well-known chemical oxidants or reductants.¹⁰ Though ferrocene is an ideal target, our studies of Ni- and Pd-based catalysts hint that simpler ligands may also be appropriate to achieve redox-switching, which will be described in later sections of this report.

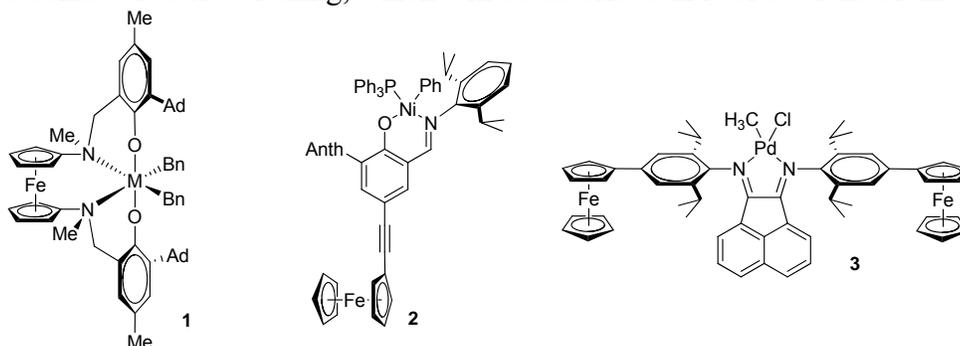


Figure 2. Targeted redox-switchable catalyst frameworks containing ferrocenyl moieties where M = Ti, Zr, or Hf, Ad = adamantyl, Bn = benzyl, and Anth = anthracenyl group.

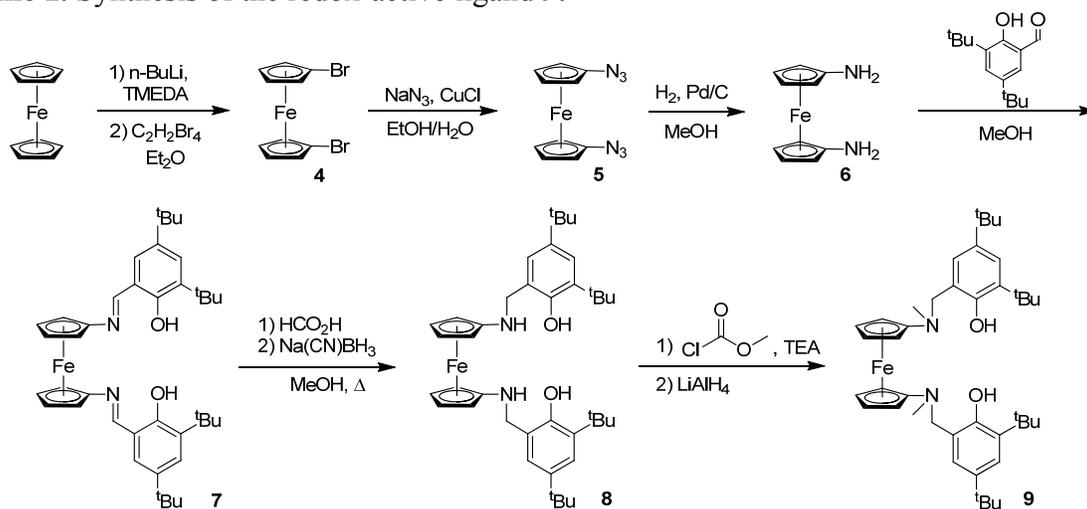
Catalyst framework **1** is a modified version of a tetradentate [ONNO] group 4 catalyst originally developed by Kol¹¹ and then later modified by Busico.¹² Though this system can produce polymers with narrow molecular weight distributions (PDI's),¹³ its propagation rates are often extremely slow when compared to metallocene-based polymerization catalysts, making it an attractive target for redox reactivity studies. Likewise, catalyst **2** is unique from **1** and **3** in that it falls into a class of so-called “neutral nickel” catalysts. These catalysts were originally developed by Grubbs¹⁴ around the turn of the century and drew significant attention, as they were found to propagate through a neutral Ni^{II} center rather than a traditional cationic metal center and without the need for an added activator.¹⁵ This unique ability to polymerize α -olefins without an activator will avoid any activator associated redox issues that could potentially arise. Their utility however, is drastically limited as they do not readily polymerize higher α -olefins and only polymerize ethylene at high-pressures, albeit somewhat slowly. This decreased

reactivity is presumably due to the further decreased electrophilic nature of the neutral salicylaldiminato ligated Ni^{II} center. Lastly, a final area of olefin polymerization research that could benefit from redox-tunable ligands is the use of cationic, late transition metal based catalysts similar to complex **3**. Brookhart pioneered this area with the introduction of Ni and Pd diimine catalysts in the late 1990's,¹⁶ opening up new possibilities for topological control during polymerizations.¹⁷ These systems are more tolerant towards functional groups and contaminants present in solvents and monomers; however, their activities are typically lower than metallocene-based catalysts, which can be attributed to the decreased electrophilicity of the metal centers.⁴

5a. Group IV Catalysts:

While catalyst **1** represents our ideal target, initial work for the development of this ligand scaffold was conducted using the commercially available *t*-butyl substituted salicylaldehyde to produce ligand **9** as outlined in Scheme 1. Our synthetic approach began with the derivitization of ferrocene via dibromination that was followed by copper catalyzed substitution using sodium azide. The azide moieties were reduced using standard hydrogenation conditions with hydrogen and palladium on carbon. Though the synthesis of 1,1'-diaminoferrocene has previously been reported in the literature,¹⁸ we found that in our laboratory, significant modifications were needed in order to produce useful amounts of diamine **6**. Condensation of this diamine onto two equivalents of 3,5-di-*t*-butylsalicylaldehyde furnished salen-like ligand **7**.¹⁹ The seemingly straight forward reduction of diimine **7** proved unusually difficult under typical conditions, although a stepwise procedure utilizing formic acid and sodium cyanoborohydride would yield air-sensitive compound **8** in good yields. Methylation was complicated by aminal formation between the amine and phenolic positions leading us to utilize a two-step procedure in which the amines were treated with methylchloroformate before being fully reduced with lithium aluminum hydride to yield target ligand **9**.

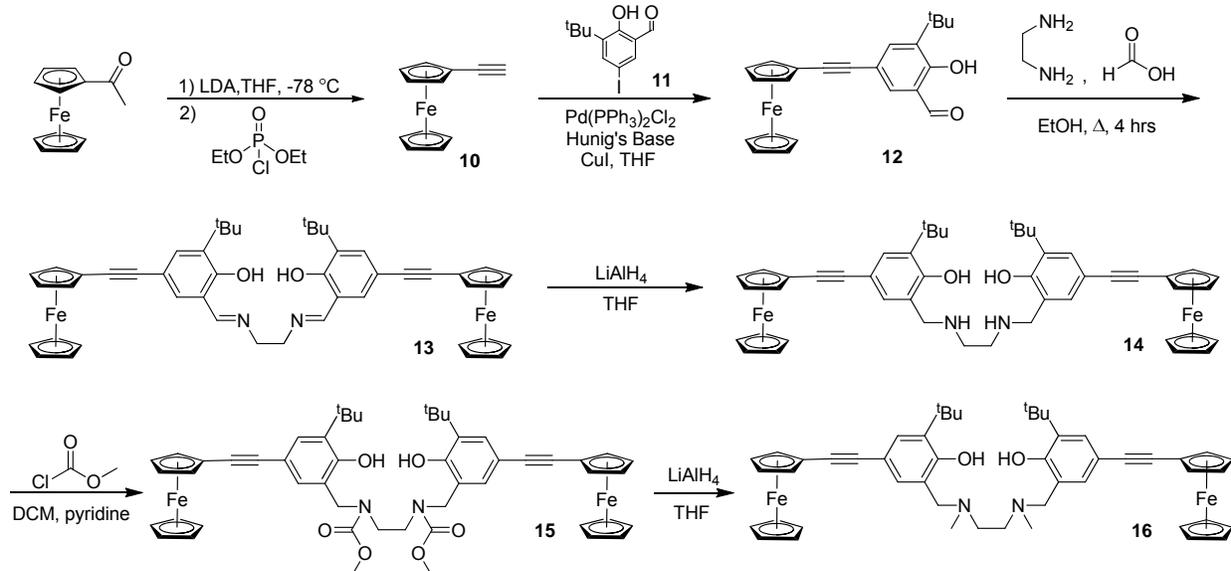
Scheme 1. Synthesis of the redox-active ligand **9**.



In addition to compound **9**, we felt that a derivative in which the ferrocenyl moiety was moved to the phenolic portion of the ligand might also be useful. Therefore, ligand **16** was targeted (Scheme 2) beginning with the formation of ethynylferrocene **10**.²⁰ This alkyne was then coupled onto iodo-compound **11** via standard Sonogashira cross-coupling conditions to yield salicylaldehyde **12** before being condensed onto ethylene diamine to yield salen-ligand **13**.²¹

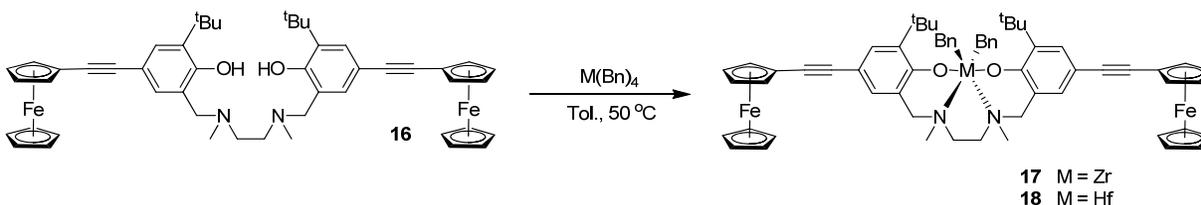
Reduction of the diimine was carried out using lithium aluminum hydride before undergoing a similar two-step methylation as described above to yield bisferrocenyl ligand **16**.

Scheme 2. Synthesis of the redox-active ligand **16**.



With ligands **9** and **16** in hand, metallation conditions were screened using standard reagents such as zirconium or hafnium tetrabenzyl. To our surprise, the incorporation of ferrocene into the backbone of ligand **9** seemed to have a deleterious effect on the metallation producing a complex mixture of species via ^1H NMR spectroscopy. Though we do not currently have confirmation, we speculate that the greatly increased N...N distance may be adversely affecting the C_2 bonding geometry of these ligand scaffolds. This postulation is supported by literature in which ligands similar to **9** and **16** report N–Zr–N bond angles of 103.3° and 70.2° respectively.^{19,11} This dramatic difference in bonding geometry may well account for our observations. To circumvent this issue, we proceeded to investigate ligand **16**, which left the coordination modes unchanged. Using conditions similar to Kol and co-workers for the metallation of Zr and Hf, two novel complexes were synthesized (Scheme 3).¹¹ Currently, precatalysts **17** and **18** are being evaluated for redox behavior and polymerization activity.

Scheme 3. Synthesis of the redox-active catalysts **17** and **18**.

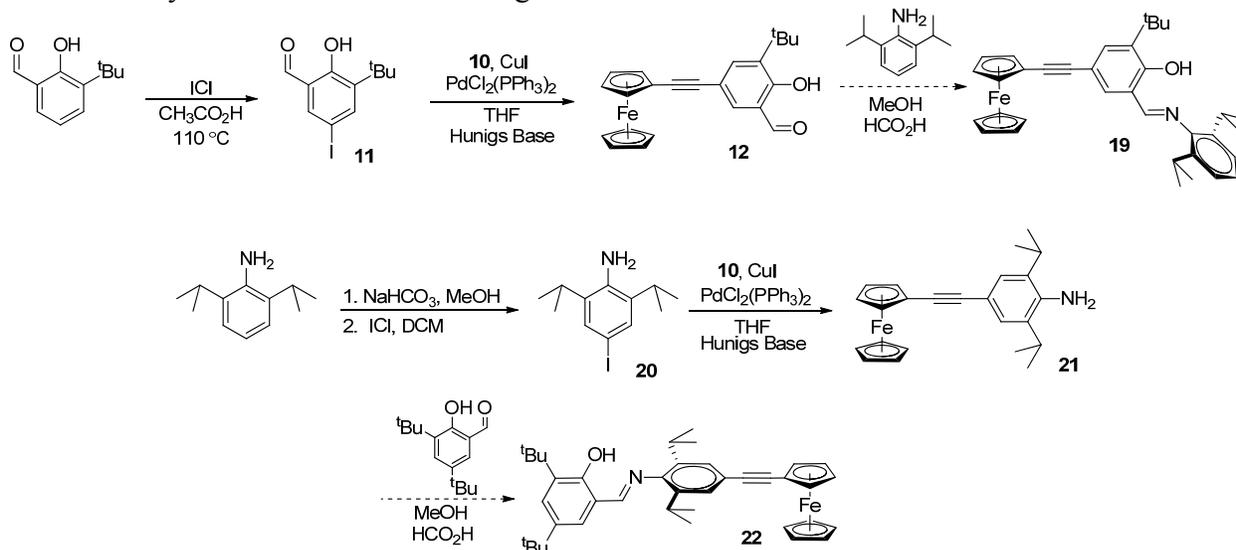


5b. Neutral Nickel Catalysts:

The synthesis of our targeted redox-active, neutral Ni ligands are outlined in Scheme 4. As with the group IV ligands shown above, there are two clear options for ferrocene incorporation. To incorporate the ferrocenyl moiety into the phenolic portion of ligand, salicylaldehyde **12** was synthesized under classic Sonogashira cross-coupling conditions. Likewise, aniline **21** was

synthesized via iodination of 2,6-diisopropylaniline followed by a similar Sonogashira cross-coupling reaction. To our surprise, we have found that the condensation reactions to produce ligands **19** or **22** lead to complex product mixtures and alternative routes to these salicylaldimines are currently being investigated.

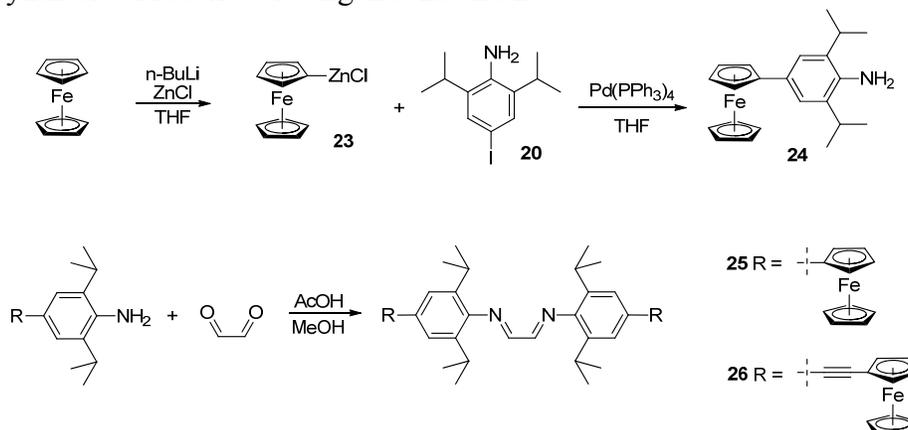
Scheme 4. Synthesis of neutral nickel ligands **19** and **22**.



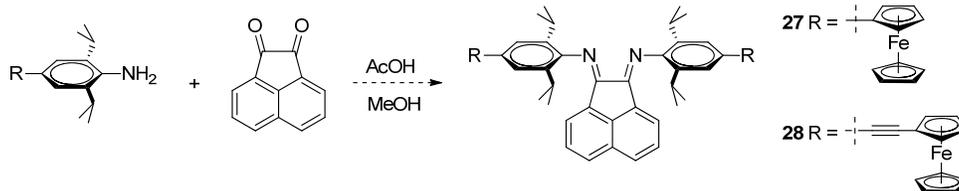
5c. Nickel and Palladium Cationic Catalysts:

To compliment aniline **21** (Scheme 4), aniline **24** was synthesized where the ethynyl moiety was removed. This was accomplished via a Negishi cross-coupling between iodoaniline **20** and zinc compound **23** that was generated *in situ*. With these in hand, the condensation of those anilines with glyoxal and 1,2-diones such as acenaphthenequinone was examined (Scheme 5). As expected, the condensation with glyoxal proceeded smoothly to yield ligands **25** and **26**, but unexpectedly, the condensation with acenaphthenequinone lead to complex product mixtures that were paramagnetic via ^1H NMR spectroscopy (Scheme 6). We believe that this is due to electron transfer from the ferrocenyl moieties to the easily reduced acenaphthenequinone, creating a quinone-based radical anion that ultimately prevents any condensation reactions.

Scheme 5. Synthesis of redox-active ligands **25** and **26**.

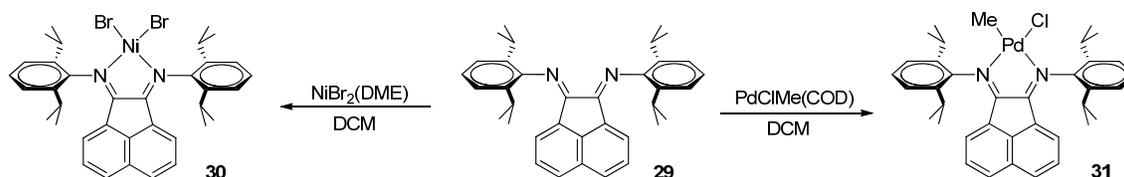


Scheme 6. Attempted synthesis of redox-active ligands **27** and **28**.



Inspired by our inability to produce ligands **27** and **28**, we decided to further investigate the redox behavior of simpler, acenaphthenequinone based catalysts, such as those originally reported by Brookhart and coworkers.¹⁶ Ligand **29** was synthesized via condensation of 2,6-diisopropylaniline with acenaphthenequinone and metallated using nickel(II) bromide dimethoxyethane adduct or chloromethyl(1,5-cyclooctadiene)palladium(II) to yield catalysts **30** and **31** respectively (Scheme 7).¹⁶ Nickel complex **30** is the subject of our completed redox studies and polymerization studies in the following sections.

Scheme 7. Synthesis of Brookhart catalysts **30** and **31**.



5d. Redox Behavior:

Though the redox behaviors of metal complexes with ligand **29** have been studied in the literature, most of those reports have been based on palladium dihalide species rather than Ni-based complex **30** or alkylated Pd species **31**.²² Cyclic voltammetry (CV) was utilized to examine the redox behavior of complex **30**. Those experiments demonstrated that a quasi-reversible reduction occurred at approximately -0.8 V relative to a ferrocene standard (see Figure 3). Subsequent CV experiments strongly support the hypothesis that the irregular electrochemical behavior seen between -1.4 V to -2 V and also the area between 1.4 V to -0.6 V is consistent with electrochemical-chemical-electrochemical (ECE) events that do not correspond to the desired oxidation/reduction at $E_{1/2} = -0.8$ V. With this information in hand, we were able to select appropriate oxidants and reductants from a broad spectrum of known reagents with initial focus being directed toward the use of cobaltacene as a reductant and $\text{Ag}(\text{B}(\text{C}_6\text{F}_5)_4)$ as an oxidant.¹⁰

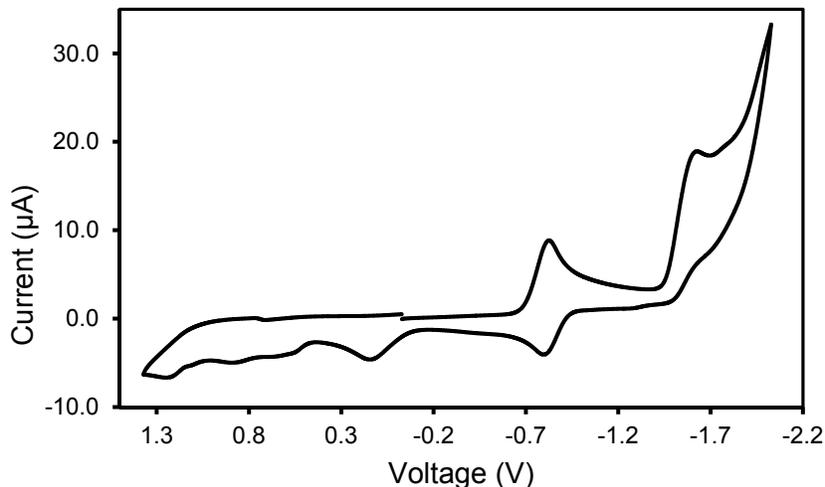
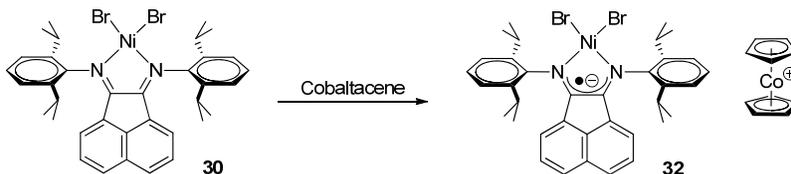


Figure 3. Cyclic voltammogram of Ni-based complex **30**. CV's were ran in DCM with tetrabutylammonium hexafluorophosphate electrolyte and referenced to a ferrocene standard.

In addition to understanding the electrochemical behavior of these complexes, understanding the structure of the reduced catalyst will be of utmost importance to interpreting any observed behavior. At this point, we believe that a ligand based radical anion is obtained as is depicted in Scheme 8. Though we do not have sufficient evidence of this hypothesis at this time, it is supported by literature reports,²² and we are actively investigating the species generated upon reduction of complex **30** with cobaltacene via electron paramagnetic resonance (EPR), single crystal X-ray spectroscopy, and various other techniques.

Scheme 8. Proposed reduction of Ni complex **30** to ligand-based radical anion **32**.



5e. Polymerization and Differentiation of Reduced and Oxidized Catalysts:

Both catalysts **30** and **32** were screened for polymerization activity using 1-hexene as the monomer. 1-Hexene is an ideal starting monomer as it is a liquid at room temperature facilitating rapid screening and data collection without the need for cumbersome, high pressure polymerization reactors. Due to the dihalide nature of catalyst **30**, these polymerizations were activated using methylaluminoxane though plans to eliminate the need for this problematic activator are in place for future cationic Ni- and Pd-based catalyst architectures.

To our delight, oxidized catalyst **30** and reduced catalyst **32** were easily distinguishable via simple kinetic studies such as the one shown in Figure 4. Though this data was recently obtained and several control experiments remain to be run, analysis of this data clearly shows that the oxidized catalyst **30** consumes 1-hexene at a much greater rate, $t_{1/2} = 26 \pm 6$ min., than that of the reduced catalyst **32**, which has a $t_{1/2} = 247 \pm 52$ min. Encouraged by these results, we remain careful to assign this differentiation to catalyst redox state without careful examination of the polymeric materials produced and concrete knowledge of the structure of reduced species **32**.

Such investigations are currently being performed and will provide considerable insight into our operating hypothesis.

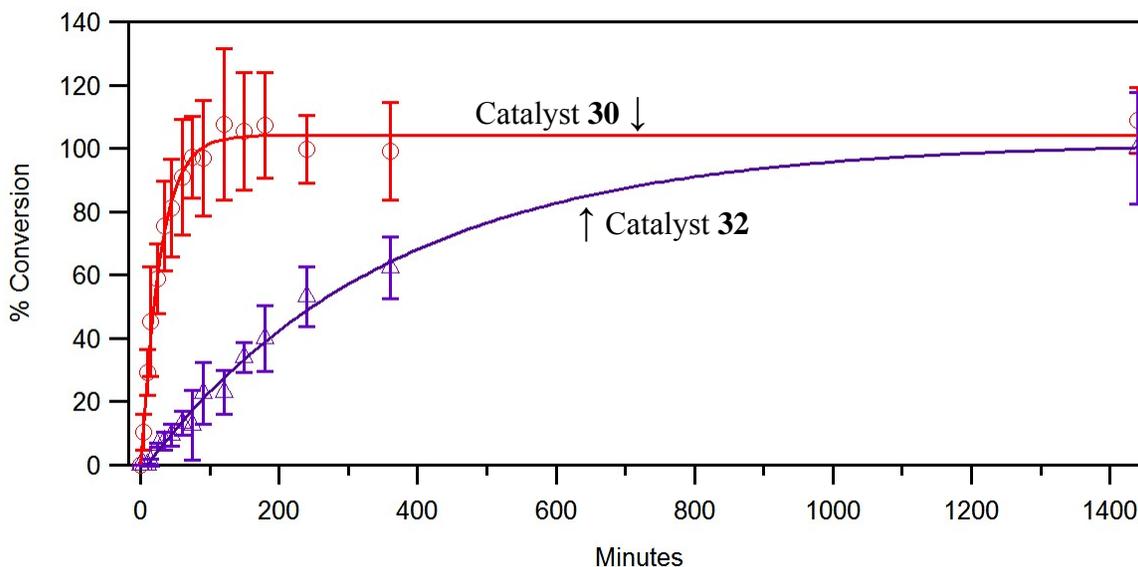


Figure 4. A plot of conversion versus time for the polymerization of 1-hexene with oxidized catalyst **30** (○) and reduced catalyst **32** (Δ).

5f. Conclusions:

A set of group 4 and group 10 single-site olefin polymerization catalysts containing redox-active moieties were synthesized. Their use as redox-switchable olefin polymerization catalysts is actively being pursued in an effort to determine how oxidation state and catalyst structure affect polymerization performance. Currently, much of our work has centered on the use of catalysts **30** and **31** based on acenaphthenequinone-derived ligands to facilitate this study. Those catalysts were evaluated via CV, demonstrating a quasireversible redox transition at an easily achievable -0.8 V relative to ferrocene standards. Furthermore, we have begun polymerization studies with those catalysts to ascertain differentiation between oxidized catalyst **30** and its reduced analogue **32**. Initial results have been extremely promising showing marked differences in 1-hexene polymerization when monitoring percent conversion versus time. The results show that the oxidized catalyst consumes 1-hexene significantly faster than catalyst **32**. With this said, we are cautious to assign the observed activity behavior solely to changes in ligand oxidation state until further control experiments are performed.

In sum, the ability to tune a redox-active catalyst may open new avenues to increased catalyst activity as well as block copolymer synthesis with improved physical properties relative to currently available polymers. The materials produced may ultimately lead to new high performance adhesives, elastomers, binders, thermoplastic elastomers, rheology modifiers, permeation selective membranes, and high strength, light-weight structural materials for numerous applications.²³

6. Bibliography

¹ Annual report of the American Chemical Council, **2011**.

² Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252.

³ Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

-
- ⁴ Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203.
- ⁵ Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.
- ⁶ Allgeier, A. M.; Mirkin, C. A. *Angew. Chem. Int. Ed.* **1998**, *37*, 894–908.
- ⁷ Masson, G.; Lough, A. J.; Manners, I. *Macromolecules*, **2008**, *41* (3), pp 539–547.
- ⁸ Limmert, M. E.; Roy, A. H.; Hartwig, J. F. *J. Org. Chem.*, **2005**, *70*, 9364–9370.
- ⁹ Hartwig, J. F. *Acc. Chem. Res.*, **2008**, *41*, 1534–1544.
- ¹⁰ Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.
- ¹¹ Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707.
- ¹² Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Togrou, M. *Macromolecules* **2003**, *36*, 3806–3808.
- ¹³ Cipullo, R.; Busico, V.; Fraldi, V.; Pellicchia, R.; Talarico, G. *Macromolecules*, **2009**, *42*, 3869–3872.
- ¹⁴ Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149–3151.
- ¹⁵ Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Banslebenof, D. A. *Science* **2000**, *287*, 460.
- ¹⁶ Johnson, L. K.; Killian, C.K.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.
- ¹⁷ Guan, Z. *Chem. Asian J.* **2010**, *5*, 1058–1070.
- ¹⁸ Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics*, **2000**, *19*, 3978–3982.
- ¹⁹ Shafir, A.; Fiedler, D.; Arnold, J. *J. Chem. Soc., Dalton Trans.*, **2002**, 555–560.
- ²⁰ Doisneau, G.; Balavoine, G.; Fillebeenkhan, T., *J Organomet Chem* **1992**, *425*, 113–117.
- ²¹ Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410–7411.
- ²² a) Baker, R. J.; Farley, R. D.; Jones, C.; Mills, D. P.; Kloth, M.; Murphy, D. M. *Chem. Eur. J.* **2005**, *11*, 2972–2982, b) van Asselt, R.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organometallics* **1997**, *16*, 317–328, c) Kern, T.; Monkowius, U.; Zabel, M.; Knör, G. *Eur. J. Inorg. Chem.* **2010**, 4148–4156, d) Gao, B.; Gao, W.; Wu, Q.; Luo, X.; Zhang, J.; Su, Q.; Mu, Y. *Organometallics* **2011**, *30*, 5480–5486, e) Klein, R. A.; Elsevier, C. J.; Hartl, F. *Organometallics* **1997**, *16*, 1284–1291.
- ²³ Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15327–15332.

7. Appendices (none)