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Redox Control of a Ring-Opening Polymerization Catalyst

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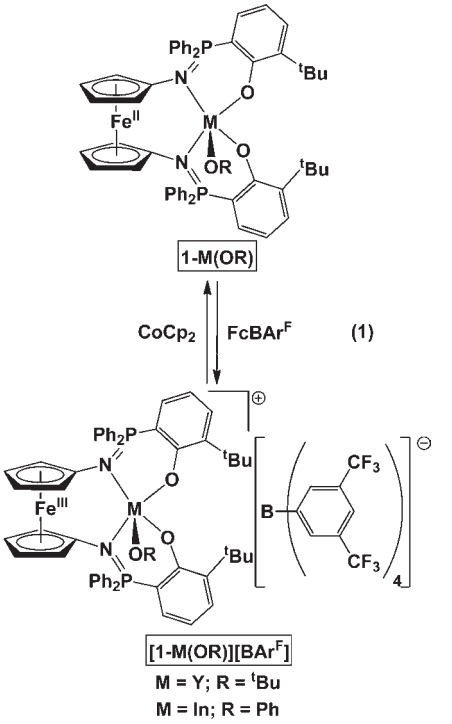
Supporting Information

ABSTRACT: The activity of an yttrium alkoxide complex supported by a ferrocene-based ligand was controlled using redox reagents during the ring-opening polymerization of L-lactide. The oxidized complex was characterized by X-ray crystallography and ^{1}H NMR, XANES, and Mössbauer spectroscopy. Switching in situ between the oxidized and reduced yttrium complexes resulted in a change in the rate of polymerization of L-lactide. Synthesized polymers were analyzed by gel permeation chromatography. Polymerization of trimethylene carbonate was also performed with the reduced and oxidized forms of an indium alkoxide complex. The indium system showed the opposite behavior to that of yttrium, revealing a metal-based dependency on the rate of polymerization.

In an effort to develop catalytic processes using external switches, organometallic complexes capable of reversible processes have been increasingly researched.[1−15] One method to modulate reactivity and selectivity is through the redox control of the supporting ligand in a metal complex. The goal of this research is to design a compound that exhibits orthogonal reactivity for different substrates by switching between the oxidized and reduced forms of a catalyst.

Although substrate selectivity has not been demonstrated in this context, a change in reactivity has been observed for systems containing ferrocene-derivatized ligands. Gibson et al.[7] reported that the rate of ring-opening polymerization of *rac*-lactide could be altered by changing the redox state of a ferrocenyl unit in a titanium salen bis(isopropoxide) catalyst. In addition, Plenio et al.[5] oxidized a ferrocenyl substituent in a Grubbs type catalyst, leading to its precipitation during a ring-closing metathesis reaction. In both cases, redox control was achieved by using a ferrocenyl functionalized ligand, with the ferrocenyl unit distant from the metal center, and a decrease in reactivity was observed after the oxidation of the ferrocenyl group.

Herein we report that an yttrium alkoxide phosfen complex (**1-Y(O^{t}Bu)**, eq 1, phosfen =1,1′-di(2-*tert*-butyl-6-diphenylphosphiniminophenoxy)ferrocene)[16] can be used to control the polymerization of L-lactide by using redox processes. The ferrocene unit is central to the backbone of the ligand and near the metal center; the proximity of the metal center to the ferrocene unit may be important in tuning the effect of ligand oxidation/reduction on the metal center of interest. In addition, the first example of increasing the reactivity of a polymerization catalyst through its oxidation is shown using an indium phosfen aryloxide (**1-In(OPh)**) and the oxidized analogue ([**1-In(OPh)**][**BAr^F**]).[10] The different rates of polymerization between the oxidized and reduced forms of the yttrium and indium complexes indicate that the control is metal dependent.



In order to achieve redox-switchable catalysis, the catalyst must be able to change reversibly between the oxidized and reduced forms. Electrochemical studies on **1-Y(O^{t}Bu)** ($E_{1/2}$= −0.28 V vs ferrocene) indicated that ferrocenium salts would be appropriate oxidants for the ferrocene backbone.[16] Consequently, the addition of 1 equiv of ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (FcBAr^F) to **1-Y(O^{t}Bu)** in tetrahydrofuran resulted in a dark green product, [**1-Y(O^{t}Bu)**][**BAr^F**] (eq 1), within minutes.

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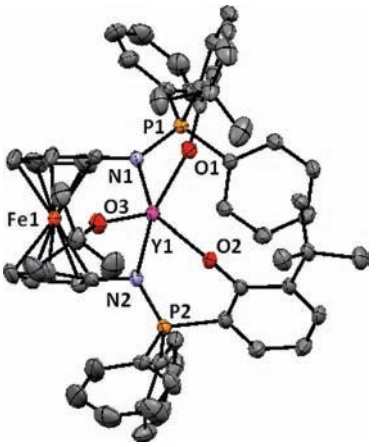

Figure 1. Thermal-ellipsoid (50% probability) representation of [**1-Y(O^{t}Bu)**][**BAr^F**]; hydrogen and anion atoms were removed for clarity.

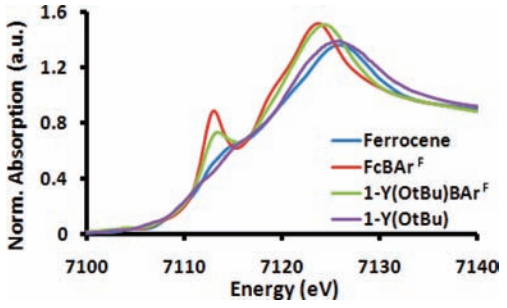

Figure 2. XANES spectra of the iron K-edge for ferrocene, FcBAr^F, [**1-Y(O^{t}Bu)**][**BAr^F**], and **1-Y(O^{t}Bu)**.

Table 1. GPC Data for the Polymerization of L-Lactide (0.2 M in Tetrahydrofuran) with 1-Y(O^{t}Bu) at Room Temperature

complex	equiv of LLA	time (h)	conversion	M_n[a,b] (kg/mol)	PDI
1-Y(O^{t}Bu)	100	3	74%	7.5	1.07
	200	8	76%	17.6	1.03
	300	10	70%	28.2	1.04
	500	47	64%	39.5	1.08
1-Y(O^{t}Bu)	100	2	51%	5.4	1.05
add **FcBAr^F**		0.5	51%	5.4	1.04
add **CoCp$_2$**		4	87%	7.6	1.06

[a] Samples were run in tetrahydrofuran with polystyrene standards. [b] A Mark–Houwink factor[23] of 0.58 was applied to the experimental molecular weights.

The ^{1}H NMR spectrum of the product was consistent with the presence of a paramagnetic species, as expected. [**1-Y(O^{t}Bu)**][**BAr^F**] could be reduced to **1-Y(O^{t}Bu)** within minutes in tetrahydrofuran through the addition of 1 equiv of $CoCp_2$ (see the Supporting Information (SI) for details).

X-ray quality crystals of [**1-Y(O^{t}Bu)**][**BAr^F**] were grown from a concentrated diethyl ether solution layered with *n*-pentane at −36 °C (Figure 1). X-ray absorption near edge structure (XANES) (Figure 2) and Mössbauer spectroscopic studies (see the SI for details) were carried out to determine the electronic structure of **1-Y(O^{t}Bu)** and [**1-Y(O^{t}Bu)**][**BAr^F**]. A pre-edge peak characteristic for ferrocenium salts was observed in the XANES spectra for [**1-Y(O^{t}Bu)**][**BAr^F**], but not for **1-Y(O^{t}Bu)**. The Mössbauer spectrum of [**1-Y(O^{t}Bu)**][**BAr^F**] exhibits two singlets at δ = 0.29(1) and 0.70(1) mm s^{-1}. The spectrum is consistent with the presence of iron(III) (the two singlets may be due to a difference in packing of the borate salt or solvent in the crystals). The Mössbauer spectrum of **1-Y(O^{t}Bu)** is similar to that of ferrocene and exhibits a doublet at δ = 0.52(1) mm s^{-1}. The data from XANES and Mössbauer spectroscopy indicate that [**1-Y(O^{t}Bu)**][**BAr^F**] contains an iron(III), while **1-Y(O^{t}Bu)** contains an iron(II) as part of the ligand backbone.

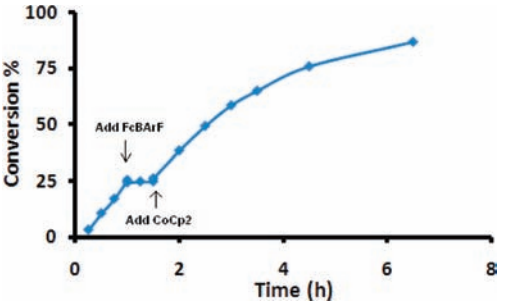

Figure 3. Plot of conversion (%) vs time for the polymerization of 100 equiv of L-lactide (0.2 M in tetrahydrofuran) with **1-Y(O^{t}Bu)** using in situ oxidation and reduction with FcBAr^F and $CoCp_2$, respectively.

Once the ferrocene and ferrocenium-based compounds were characterized, the polymerization of L-lactide with **1-Y(O^{t}Bu)** and [**1-Y(O^{t}Bu)**][**BAr^F**] was attempted since yttrium complexes are known catalysts for this reaction (Table 1).[17−22] At room temperature in tetrahydrofuran, **1-Y(O^{t}Bu)** polymerizes 100 equiv of L-lactide in 3 h with 74% conversion, while no conversion was observed in the presence of [**1-Y(O^{t}Bu)**][**BAr^F**] under the same conditions. In addition to polymerizing L-lactide, **1-Y(O^{t}Bu)** polymerized 100 equiv of *rac*-lactide in tetrahydrofuran at 70 °C. After 8 h, the polymerization reached 95% conversion, but no tacticity control was observed (see the SI for details).

Switching in situ between the oxidized and reduced forms of the yttrium complex was performed during the polymerization of 100 equiv of L-lactide (L-LA) in tetrahydrofuran at room temperature (Figure 3). After 1 h, the polymerization with **1-Y(O^{t}Bu)** reached 24% conversion. Upon the oxidation of **1-Y(O^{t}Bu)** with FcBAr^F, the polymerization halted. Once $CoCp_2$ was added to the reaction mixture, the polymerization resumed with the same rate as that before the switch was performed (see the SI for details). In situ switching was performed three consecutive times; it was found that there was minimal change in the rate of the reaction before or after changing the iron oxidation states (see the SI for details).

As detailed above, the catalyst containing the oxidized ligand decreases the rate of the polymerization reaction compared to the catalyst containing the reduced ligand. The same observation was made by the Gibson group when using a remote ferrocenyl unit.[7] The lack of activity of the oxidized catalyst was investigated by carrying out a stoichiometric reaction of [**1-Y(O^{t}Bu)**][**BAr^F**] with L-LA. The addition of 1 equiv of L-LA to a diethyl ether solution of [**1-Y(O^{t}Bu)**][**BAr^F**] led to the formation of a new species, which was unreactive toward further L-LA polymerization. This species was reduced with $CoCp_2$ to produce a diamagnetic product. We

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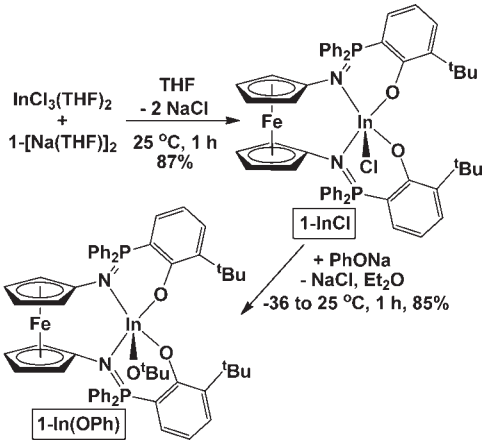
Scheme 1. Synthesis of 1-In(OPh)



hypothesize that the ^{1}H NMR spectrum of this product corresponds to the insertion of one lactide molecule (see the SI for details); further studies will be directed to the isolation and full characterization of this intermediate. This observation suggests that the insertion of the monomer is possible, but propagation with this new species is unfavorable. Single crystals suitable for X-ray crystallography could not be obtained.

The polymers obtained from the reactions with **1-Y(O^{t}Bu)** were characterized by gel permeation chromatography (GPC). The molecular weights correlate well with the corresponding theoretical molecular weights, and the PDIs are ca. 1.1; these data indicate a controlled polymerization process. ^{1}H NMR spectroscopy of a polymer formed from the reaction of **1-Y(O^{t}Bu)** and 50 equiv of L-lactide displayed *tert*-butoxide end groups, which suggests that the monomer inserts into the yttrium-alkoxide bond (see the SI for details). GPC analysis of the polymers produced by switching in situ between **1-Y(O^{t}Bu)** and [**1-Y(O^{t}Bu)**][**BAr^F**], once the reaction had reached 51% conversion, shows that the polymerization is also controlled when using redox agents, since the molecular weights correlate well with corresponding theoretical molecular weights, and the PDIs are ca. 1.1 (Table 1).

As mentioned above, our results indicate that the oxidation of ferrocene caused a decrease in the reaction rate compared to the reduced form of the metal complex; a similar result was reported by Gibson et al.[7] We became interested in determining whether the reverse effect (i.e., increased reactivity with a ferrocenium-containing metal complex) is possible. Reports of using electron-withdrawing groups to increase the rate of polymerization for aluminum complexes[24−28] indicated that a group 13 analogue of **1-Y(O^{t}Bu)** should be targeted.

In order to ensure the formation of a mononuclear species, a larger metal center than aluminum, indium (ionic radius 0.80 Å),[29] was chosen; such complexes would be analogous to the yttrium (ionic radius 0.90 Å) complexes **1-Y(O^{t}Bu)** and [**1-Y(O^{t}Bu)**][**BAr^F**]. Also, indium complexes are known catalysts for the ring-opening polymerization of lactide.[30−36] **1-In(OPh)** was synthesized similarly to **1-Y(O^{t}Bu)**: the salt metathesis reaction between $InCl_3(THF)_2$ and $[Na(THF)]_2$[phosfen] (**1-Na$_2$(THF)$_2$**) led to the formation of InCl(phosfen) (**1-InCl**), which underwent a second salt metathesis reaction with sodium phenoxide (NaOPh) to give **1-In(OPh)** (Scheme 1). The oxidized complex [**1-In(OPh)**][**BAr^F**] was obtained upon the addition of 1 equiv of FcBAr^F to **1-In(OPh)** at room temperature in toluene, after minutes of stirring. [**1-In(OPh)**][**BAr^F**] had a ^{1}H NMR spectrum consistent with that of a paramagnetic species and could be reduced with 1 equiv of $CoCp_2$ to produce **1-In(OPh)** (see the SI for details). The Mössbauer spectra for the indium complexes display a doublet for **1-In(OPh)**, which is similar to the spectrum for ferrocene, and a singlet for [**1-In(OPh)**][**BAr^F**], a characteristic of an oxidized iron center. The Mössbauer spectra support the assignment that [**1-In(OPh)**][**BAr^F**] contains iron(III), while **1-In(OPh)** contains iron(II) as part of the ligand backbone.

With **1-In(OPh)** and [**1-In(OPh)**][**BAr^F**] in hand, ring-opening polymerizations of cyclic esters were performed. The polymerizations of ε-caprolactone and L-lactide were slow with both **1-In(OPh)** and [**1-In(OPh)**][**BAr^F**]. As a result, the polymerization of 100 equiv of trimethylene carbonate was carried out at room temperature, in benzene-d_6. After 1 day, **1-In(OPh)** reached 2% conversion, while [**1-In(OPh)**][**BAr^F**] reached 49% conversion under the same conditions. These results suggest that withdrawing electrons from indium through the oxidation of the ligand backbone increased the rate of polymerization of trimethylene carbonate.

For comparison, at room temperature, **1-Y(O^{t}Bu)** and [**1-Y(O^{t}Bu)**][**BAr^F**] polymerized 100 equiv of trimethylene carbonate within minutes in benzene-d_6. When the polymerizations were performed at −78 °C in THF, **1-Y(O^{t}Bu)** transformed 29% of the starting material, while [**1-Y(O^{t}Bu)**][**BAr^F**] reached only 3.5% conversion. Therefore, for the yttrium complexes, the rate of polymerization decreased when the complex containing ferrocenium was employed; these results are the opposite of those observed for indium. The difference in reactivity between the yttrium and indium complexes suggests that the change in reactivity observed as a result of oxidizing the ferrocene backbone is metal dependent. We hypothesize that, in the case of yttrium, although substrate coordination may be more favorable with the more electrophilic metal center ([**1-Y(O^{t}Bu)**][**BAr^F**]), the activation barriers for alkoxide migration and ring opening are higher than for the less electrophilic metal center (**1-Y(O^{t}Bu)**). In the case of indium, it is possible that the effect is reversed; however, one study with aluminum also indicates that electron-withdrawing substituents can decrease polymerization activity.[37] These data suggest that the explanation for the change in the rate of polymerization due to the electron-donating or -withdrawing abilities of a ligand may not be general. In-depth DFT calculations could shed light on this proposal and will be reported in due course.

In conclusion, we described the first example of redox control with a catalyst containing ferrocene in the proximity of a metal center. This arrangement may allow tuning the reactivity of the oxidized and reduced forms of a metal complex. The rate of ring-opening polymerization of L-lactide with an yttrium alkoxide phosfen catalyst was altered by switching in situ the redox state of the ferrocene moiety. In addition, the first experimental evidence of increasing the activity of a metal complex during the ring-opening polymerization of a cyclic ester by oxidizing the ferrocene substituent is presented. The results discussed in this paper are an important step toward the ultimate goal of achieving substrate selectivity through redox-switchable catalysis.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, NMR spectroscopy, Mössbauer spectroscopy, and X-ray crystallography data. This material is available free of charge via the Internet at http://pubs.acs.org.

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