

Zirconium Complexes Supported by a Ferrocene-Based Ligand as Redox Switches for Hydroamination Reactions

 Yi Shen,^a Scott M. Shepard,^{a,b} Christopher J. Reed,^c and Paula L. Diaconescu^{a,*}

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The synthesis of (thiolfan*)Zr(NEt₂)₂ (thiolfan* = 1, 1'-bis(2,4-di-*tert*-butyl-6-thiophenoxy)ferrocene) and its catalytic activity for intramolecular hydroamination are reported. *In situ* oxidation and reduction of the metal complex results in reactivity towards different substrates. The reduced form of (thiolfan*)Zr(NEt₂)₂ catalyzes hydroamination reactions of primary aminoalkenes, whereas the oxidized form catalyzes hydroamination reactions of secondary aminoalkenes.

Redox-switchable catalysis is a field of growing importance, in which a redox-active functionality is incorporated within the framework of a metal complex.¹ Historically, the oxidation or reduction of a transition metal catalyst results in a change in the metal's oxidation state; this may result in compound degradation or loss of catalytic activity. As an alternative, the integration of a redox-active ligand into a metal complex provides a controllable way of tuning its electronic properties, potentially inducing selectivity or new catalytic activity with changing the redox state.^{1e-g} The activity of a metal complex supported by a redox-active ligand can be influenced *in situ* by the redox event occurring at the ligand via a chemical or electrochemical process. Redox switchable catalysis has been applied successfully to the ring-opening polymerization of cyclic esters and ethers,² and to olefin polymerization.^{1e, 3} Polymerization is so far the only area of redox switchable catalysis in which two orthogonal reactions could be coupled, resulting in the synthesis of block copolymers.^{2b-e, 2g-i, 2l, m, 4}

The first example using a metallocene redox switch in order to influence catalytic activity was reported by Wrighton and co-workers in 1995 (Figure 1).⁵ In that seminal work, the authors showed that a rhodium complex containing cobaltocene (reduced form) is a better catalyst for the hydrogenation of olefins than the corresponding compound incorporating cobaltocenium (oxidized form). The reverse trend was observed in the hydrosilylation of acetone. It is important to note that the two states of the catalytically active species did not achieve an on/off switch for either reaction.

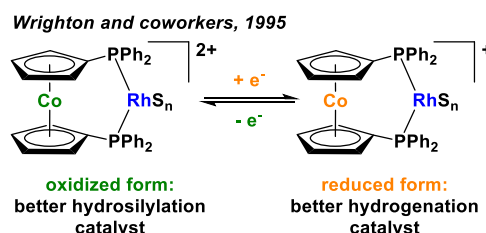


Fig. 1 The first reported example of a redox switchable catalyst.

Since then, several groups have become interested in applying redox switchable catalysis to organic synthesis using homogeneous catalysts.⁶ These efforts fall into two categories: (1) different reaction rates for the two catalytically distinct states that apply to a single reaction (including on/off switches); (2) different reaction rates for the two catalytically distinct states that apply to distinct reactions but without orthogonality, i.e., each catalytic state is active in both reactions but with different rates. The first category contains ring closing metathesis,^{6a, b, g, m} ring-opening metathesis polymerization,⁶ⁿ oxidation of dihydrogen,^{6c} oxazoline formation, furan formation, phenol formation,^{6i, o, p} cyclization of alkynes with furans,^{6r} hydroalkoxylation,^{6l} hydroamination,^{6q, r} hydrosilylation,^{6k} acetonitrile dissociation,^{6e} Kumada coupling,^{6h} Buchwald-Hartwig cross-coupling,^{6j} Mitsunobu reaction,^{6s} and allylic alcohol isomerization.^{6t} The only example in the second category is the comparative study of hydrogenation/hydrosilylation reported by Wrighton and coworkers and discussed above.⁵ Other examples similar to the second category but using a different type of external trigger are: ring closing metathesis and ring opening metathesis polymerization studied with a photoswitchable ruthenium complex,^{6f} and a hydrogenation and a dehydrogenative coupling performed by an acid-base triggered ruthenium complex.⁷ The last example is the only reported instance in which the two catalytic cycles were combined for assisted tandem catalysis.

Although reports of tandem catalysis⁸ are numerous, the number of examples of assisted tandem catalysis is relatively small,⁹ likely because of issues associated with reagent/substrate compatibility and the complexity in designing such a single 'multitasking' catalyst. As such, switchable catalysis may provide a general method for obtaining complex products. The first step in achieving assisted tandem switchable catalysis is to demonstrate that the two states of

^a Department of Chemistry & Biochemistry, University of California, Los Angeles

^b Current address: Department of Chemistry, Massachusetts Institute of Technology

^c Division of Chemistry & Chemical Engineering, California Institute of Technology

* Corresponding author, email: pld@chem.ucla.edu

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a catalyst show complementary on/off reactivity for each reaction. In the case of ring opening polymerization, the two substrates are rather similar and follow similar mechanisms. Therefore, we decided to take an analogous approach in order to develop applications to organic synthesis and focus on hydroelementation reactions.^{6f}

Zirconium catalysts were reported to exhibit hydroamination selectivity independent on the charge of the complex and the type of aminoalkene used. With few exceptions,¹⁰ neutral zirconium compounds exclusively catalyse reactions of primary aminoalkenes.¹¹ On the other hand, cationic zirconium complexes have displayed either no selectivity, where they catalyse both primary and secondary aminoalkenes,¹² or selective catalysis for secondary aminoalkenes.^{12a, 13}

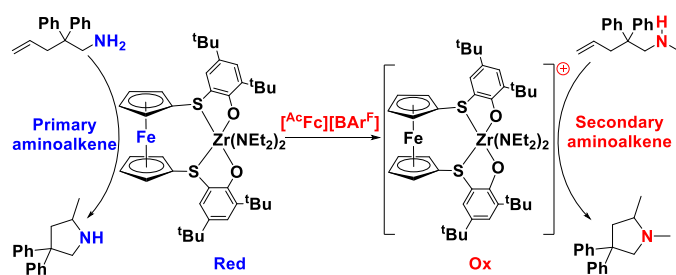


Fig. 2 A redox-active zirconium complex catalyses hydroamination reactions selectively.

Herein, we report the development of an [OSSO]-type zirconium complex, (thiolan*)Zr(NEt₂)₂ (thiolan* = 1, 1'-bis(2,4-di-*tert*-butyl-6-thiophenoxy) ferrocene), which can be switched *in situ* between a neutral and a cationic species when triggered by the oxidation/reduction of the ferrocene backbone. The two catalytic states generated by electron transfer react with different types of substrates (Figure 2).

The reaction of H₂(thiolan*) with Zr(NEt₂)₄ results in the clean formation of (thiolan*)Zr(NEt₂)₂,^{17,24} as confirmed by NMR spectroscopy (¹H NMR spectrum - Figure S1, ¹³C NMR spectrum - Figure S2, and heteronuclear single quantum coherence, HSQC, spectrum - Figure S3), and elemental analysis.

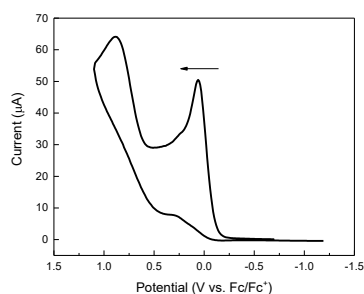


Fig. 3 Cyclic voltammetry diagram of (thiolan*)Zr(NEt₂)₂ recorded in *o*-F₂C₆H₄ at 100 mV s⁻¹ with 0.1 M [TPA][BARF] as the electrolyte and referenced to the Fc/Fc⁺ couple.

To investigate the redox properties of (thiolan*)Zr(NEt₂)₂, cyclic voltammetry experiments were performed in *o*-F₂C₆H₄ using [TPA][BARF] ([TPA][BARF] = tetrapropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) as an electrolyte, revealing two irreversible oxidation events (Figure 3). The electrochemical behaviour of (thiolan*)Zr(NEt₂)₂ contrasts that of the corresponding alkoxide complex, (thiolan*)Zr(O^{*i*}Bu)₂, which can be reversibly oxidized and reduced.^{2d} Although a cyclic voltammetry study of (thiolan*)Zr(O^{*i*}Bu)₂ was not reported, the titanium (thiolan*)Ti(O^{*i*}Pr)₂^{2d} and aluminium (thiolan*)Al(O^{*i*}Pr)₂^{2b} alkoxide complexes exhibit a reversible and quasi-reversible, respectively,

redox event near 0 V versus the Fc/Fc⁺ couple that was attributed to the oxidation of the ferrocene backbone. Therefore, a narrower region was chosen for the second scan from -0.5 to 0.5 V to isolate the corresponding oxidation peak, observed at 0.12 V versus the Fc/Fc⁺ couple, but it still did not result in a reversible event (Figure S42), indicating that the species that is generated is not reduced back to the starting compound.

Table 1 Intramolecular hydroaminations catalysed by (thiolan*)Zr(NEt₂)₂.^a

Entry		Reduced State		Oxidized State	
		Conversion	Time	Conversion	Time
1		95%	72 h		
2				0%	20 h
3		0%	16 h		
4				100%	20 h
5		0%	24 h		
6				0%	30 h
7		0%	18 h		
8				0%	20 h
9		0%	21 h		
10				0%	24 h
11		0%	20 h		
12				0%	21 h
13		99%	4 h		
14				99%	2 h
15		0%	20 h		
16				99%	1 h ^b
17		0%	21 h		
18				0%	24 h
19		0%	23 h		
20				99%	3 h ^b
21		66%	60 h ^c		
22				0%	21 h
23		0%	24 h		
24				77%	15 h ^b

^a Conditions: 10 mmol% (thiolan*)Zr(NEt₂)₂, 0.5 mL C₆D₆, 100 °C. Conversions were calculated from the corresponding NMR spectra using hexamethylbenzene (HMB) as an internal standard, except for entry 24, when the conversion was calculated by HRMS because of overlapping peaks in the corresponding NMR spectra. The oxidized state was generated *in situ* by the addition of 0.9 equiv. of [AcFc][BARF]. ^b Reactions were carried out in a 4:1 by volume C₆D₆:*o*-C₆H₄F₂ solution instead of C₆D₆. ^c Reaction was carried out in *o*-F₂C₆H₄.

Besides studying the electrochemical oxidation of (thiolfan*)Zr(NEt₂)₂, chemical oxidation studies were also carried out. [AcFc][BAR^F] (acetylferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), AgOTf, AgBF₄, AgBPh₄, and NOBF₄ were used as oxidants, and the addition of CoCp₂ was employed to reduce the chemically oxidized species. However, no reversible oxidation/reduction was observed according to ¹H NMR spectra (Figure S4). Furthermore, a determination of the solution state magnetic susceptibility using the Evans method¹⁴ of the oxidized species was unsuccessful due to the low solubility of this compound in benzene at ambient temperature. Adding a few drops of *o*-difluorobenzene resulted in loss of signal. However, elemental analysis agrees with the formula [(thiolfan*)Zr(NEt₂)₂][BAR^F] for the oxidized compound.

⁵⁷Fe Mössbauer spectroscopic studies at 80 K, with no applied magnetic field, indicate that both (thiolfan*)Zr(NEt₂)₂ and [(thiolfan*)Zr(NEt₂)₂][BAR^F] contain a low-spin iron(II) (Figure S43). An X-band electron paramagnetic resonance (EPR) spectrum acquired at 77 K indicates the presence of an organic radical (*g* = 2.006, Figure S44). Furthermore, UV-Vis spectra (Figure S45) of [(thiolfan*)Zr(NEt₂)₂][BAR^F] are different than those of (thiolfan*)Zr(NEt₂)₂ or [AcFc][BAR^F] supporting the Mössbauer results that [(thiolfan*)Zr(NEt₂)₂][BAR^F] does not contain an Fe(III) species, but the oxidation occurs on the organic portion of a ligand.

Nonetheless, these data are consistent with an oxidized species being generated with [AcFc][BAR^F], and it was reasoned that the coordination of a substrate may enhance the stability of the catalytically active species.

To investigate the reactivity of (thiolfan*)Zr(NEt₂)₂ in intramolecular hydroamination reactions, a catalytic amount (10 mol%) of (thiolfan*)Zr(NEt₂)₂ was added to a J-Young NMR tube with the aminoalkene/alkyne of interest and an internal standard, hexamethylbenzene(HMB), and the reaction mixture was heated to 100 °C in C₆D₆. Control experiments were performed with [AcFc][BAR^F] in order to determine if the oxidant can act as a catalyst for the reactions of interest by itself. No conversion of **1a** (Table 1) to **1b** was observed when heated to 100 °C for 20 h in presence of catalytic amount of [AcFc][BAR^F] (Figure S34). However, full conversion of **2a** (Table 1) to **2b** was observed under the same reaction condition (Figure S35). To understand further the reasons behind this observation, several experiments using catalytic amounts of AcFc, FcPF₆, NaBAR^F, or [Fc][BAR^F] were performed with **2a**. After 19 hours, no conversion was observed in the presence of AcFc (Figure S36). After 2 hours, a partial conversion (34%) was observed with NaBAR^F (Figure S37), a full conversion was observed with [Fc][BAR^F] (Figure S38), and no conversion was observed with FcPF₆ (Figure S39). The peaks corresponding to acetylferrocene were observed in the ¹H NMR spectra of control reactions catalysed by [AcFc][BAR^F], and a peak corresponding to ferrocene was observed in the ¹H NMR spectra of control reactions catalysed by FcPF₆ and [Fc][BAR^F]. A possible explanation is that the aminoalkene reduced [AcFc][BAR^F] to acetylferrocene and the reaction was catalysed by a Brønsted acid.¹⁵ Michon and co-workers reported that HBF₄, generated *in situ* from AgBF₄ catalysed the hydroamination of secondary aminoalkynes.¹⁶ Similarly, when [AcFc][BAR^F] served as a precatalyst in the hydroamination reactions, HBAR^F was generated *in situ* and combined with the amine substrate to generate an ammonium [BAR^F] salt as the active catalyst. The difference in reaction rates likely resulted from the difference in solubility of the [BAR^F] precatalysts. Therefore, we decided to use a ratio of zirconium compound to the oxidant of 10:9 molar equivalents. By premixing the oxidant (9 mol%)

with (thiolfan*)Zr(NEt₂)₂ (10 mol%) before the addition of a substrate, we ensured that all [AcFc][BAR^F] was consumed to form the corresponding oxidized species. The results reported in Table 1 account for these modifications.

The reactivity studies show that (thiolfan*)Zr(NEt₂)₂ can catalyse the cyclization of the primary aminoalkene **1a** in 72 h (Table 1, entry 1), while the oxidized species showed no conversion after 20 h (Table 1, entry 2). In contrast, (thiolfan*)Zr(NEt₂)₂ showed no reactivity toward the secondary aminoalkene **2a** (Table 1, entry 3), but the oxidized species can catalyse the cyclization of **2a** in 20 h (Table 1, entry 4). Similarly, a 66% conversion of **11a** was achieved in the presence of (thiolfan*)Zr(NEt₂)₂ after 60 h in *o*-DFB (Table 1, entry 21), while the oxidized species showed no conversion after 21 h (Table 1, entry 22). (thiolfan*)Zr(NEt₂)₂ showed no reactivity toward **12a** (Table 1, entry 23), but 77% conversion was achieved in 15 h in the presence of the oxidized species (Table 1, entry 24). Furthermore, the hydroamination of the secondary aminoalkyne **8a** (Table 1, entry 16) and secondary aminoalkene **10a** (Table 1, entry 20) could only be catalysed by the oxidized catalyst. Unfortunately, (thiolfan*)Zr(NEt₂)₂ was not active towards other secondary aminoalkene substrates: no conversion was observed for substrates **3a-6a** with either state of the catalyst (Table 1, entries 5-12). However, the results obtained with **1a** and **2a** indicate that there is selectivity between primary and secondary aminoalkenes triggered by the oxidation state of the zirconium catalyst. Unfortunately, the selectivity was lost with primary aminoalkynes: **7a** cyclized in the presence of both the reduced and oxidized species (Table 1, entries 13-14).

In our search for redox-switchable catalysts for organic transformations, (thiolfan*)Zr(NEt₂)₂ was successfully synthesized and characterized. We found that (thiolfan*)Zr(NEt₂)₂ catalyses the hydroamination of primary aminoalkenes, whereas an oxidized species generated *in situ* catalyses the hydroamination of secondary aminoalkenes. The selectivity of the two oxidation states observed in these reactions will form the basis of developing redox switchable catalysts for assisted tandem reactions.

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Conflicts of interest

There are no conflicts to declare.

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