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Stereospecific Ring-Opening Metathesis Polymerization of Norbornene Catalyzed by Iron Complexes

Dmitry S. Belov,^[a] Logesh Mathivathanan,^[a] Melanie J. Beazley,^[b] William Blake Martin,^[c]

and Konstantin V. Bukhryakov*[a]

[a]	Dr. S. Belov, Dr. L. Mathivathanan, Dr. K. V. Bukhryakov				
	Department of Chemistry and Biochemistry				
	Florida International University				
	11200 SW 8th St., Miami, FL 33199, USA				
	E-mail: kbukhrya@fiu.edu				
[b]	Dr. M. J. Beazley				
	Department of Chemistry				
	University of Central Florida				
	4111 Libra Dr., Orlando, FL 32816, USA				
[c]	W. B. Martin				
	Department of Macromolecular Science and Engineering				
	Coop Western Reserve University				

2100 Adelbert Road, Cleveland, OH 44106, USA

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Abstract: Developing well-defined iron-based catalysts for olefin metathesis would be a breakthrough achievement in the field not only to replace existing catalysts by inexpensive metals but also to attain a new reactivity taking advantage of the unique electronic structure of the base metals. Here, we present two-coordinate homoleptic iron complex Fe(HMTO)₂ [HMTO = O-2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃] capable of performing ring-opening metathesis polymerization of norbornene to produce highly stereoregular polynorbornene (99% cis, syndiotactic). The use of heteroleptic Fe(HMTO)(RO) [RO = (CH₃)₂CF₃CO, CH₃(CF₃)₂CO, or Ph(CF₃)₂CO] prepared *in situ*, significantly increases the polymerization rate while preserving selectivity. The resulting polymers were characterized by ¹H and ¹³C NMR spectroscopy and gel permeation chromatography.

Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins is a widely applied method for the synthesis of useful polymers.^[1] Starting as a mysterious reaction where polymerization of norbornene (NBE) catalyzed by ill-defined Ti complexes that led to an unsaturated polymer seven decades ago,^[2] it is now a well-understood chemical transformation based on a robust mechanism involving transition metal alkylidene complexes.^[3] The first well-defined catalyst for polymerization of NBE contained Ti alkylidene was introduced by Grubbs in 1986.^[4] Shortly afterward, Schrock reported the first Ta alkylidene catalyst for ROMP, in 1987.^[5] Nowadays, commonly used homogeneous catalysts for ROMP of NBE are based on well-defined Ru,^[6] Mo, and W^[7-9] alkylidenes, which allow for the synthesis of highly stereoregular polyNBE.

Homogeneous complexes of other transition metals are also capable of performing ROMP of NBE, including third-row transition metals, such as Re^[10] and Os;^[11] second-row Zr^[12] and Nb;^[13] and first-row V.^[14]Attempts to use complexes based on other first-row transition metals, such as Fe, Co, and Ni, in the reaction with NBE lead to the formation of saturated polymers through addition polymerization.^[15] An alternative approach to obtain polyNBE is metal-free photoredox mediated ROMP, which uses an organic redox mediator and a vinyl ether initiator.^[16]

However, this method produces atactic polymers with low cis/trans selectivity.^[17]

Developing a new catalyst for ROMP based on Fe is highly desirable for four reasons: 1) Fe is the most common transition metal in the Earth's crust,^[18] and far less expensive than the precious metals that are currently used; 2) purification, isolation, and recycling of rare metals consume much energy and generate a tremendous amount of waste, leaving an enormous environmental footprint. Using Fe would significantly decrease the energy usage and waste generation making many industrial processes more environmentally-friendly;^[19] 3) Fe is incorporated in many biological systems and hence has relatively low toxicity, which is important in pharmaceutical, medicinal, and food industries;^[20] 4) the development of Fe catalysts will diversify our synthetic tools and may lead to new discoveries in the future.

Fe has attracted much attention since a well-defined Ru catalyst for olefin metathesis was developed. Grubbs attempted the synthesis of Fe complexes analogous to (PCy₃)₂Cl₂Ru=CHPh in 2001 using diazoalkanes, but instead of the formation of iron alkylidene, phosphazine complexes were formed.[21] To the best of our knowledge, no direct Fe analog of L₂Cl₂Ru=CRR' is known, where R = H, Alk, or Ar and L = phosphine or N-heterocyclic carbene (NHC). This can be explained by a weak iron-carbene bond; a theoretical calculation has indicated that the bond dissociation energy (BDE) of Fe=CH2 in (NHC)(PH3)Cl2Fe=CH2 is approximately one-half of the BDE of Ru=CH₂ in (NHC)(PH₃)Cl₂Ru=CH₂ (44.5 vs. 87.7 kcal/mol).^[22] Additionally, it has been shown that the formation of metallacyclobutane, the crucial intermediate in olefin metathesis, in the case of (NHC)(PH₃)Cl₂Fe=CH₂ is an endothermic process, unlike for (NHC)(PH₃)Cl₂Ru=CH₂.^[22] Furthermore, other calculations indicate that complexes L2Cl2Fe=CRR' should mainly favor alkene cyclopropanation over olefin metathesis, both thermodynamically and kinetically.^[23] Another theoretical work has shown that (NHC)Cl₂Fe=CHPh has an open-shell triplet ground state at the metal center and could be prone to radical chemistry rather than to olefin metathesis.^[24] However, other

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calculations suggest that complexes $L_2Cl_2Fe=CRR^\prime$ can promote olefin metathesis. $^{[25]}$

Despite the extensive theoretical^[22-27] and experimental studies^[15, 21, 28, 29] to the best of our knowledge, there are no successful examples of iron-catalyzed olefin metathesis. Here, we describe a Fe-based catalytic system capable of ROMP of NBE to produce highly stereoregular polyNBE (99% *cis, syndiotactic*).

As a starting point, we tested the possibility of *in situ* formation of (HMTO)₂Fe=CRR' from Fe(HMTO)₂ and carbene precursors in the presence of NBE. ROMP of NBE would indicate the formation of catalytically active alkylidene. Fe(HMTO)₂ was chosen for three reasons: 1) bulky 2,6-terphenoxide ligands allow the synthesis of low-coordinate Fe(II) complexes^[30, 31] without neutral *σ*-donor ligands, to avoid complications in the alkylidene formation;^[21, 28] 2) monodentate ligands facilitate the required geometry for intermediates. It has been shown for Mo and W that rigid bidentate^[32] and tridentate^[33] ligands prevent access to trigonal bipyramidal metallacyclobutane complex, a crucial intermediate for the cycloreversion step. 3) Mo and W-based alkylidene complexes containing 2,6-terphenoxide ligands have been extensively used in olefin metathesis for the past few years^[34] and exhibit unprecedented reactivity and selectivity.^[35]

 $Fe(HMTO)_2(1)$ was synthesized from $Fe[N(SiMe_3)_2]_2$ and two equivalents of HMTO-H in good yield (Scheme 1).



Compound **1** is a monomeric two-coordinate Fe complex, as determined by single-crystal X-ray diffraction (Figure 1). The bent structure of **1** (O1-Fe1-O2, 142.8(4)°) is in sharp contrast to the linear structure of Fe(TIPTO)₂ [TIPTO = O-2,6-(2,4-*i*-Pr₂C₆H₃)₂C₆H₃] where O1-Fe1-O2 is 180°.^[30] The bond distances Fe1-O1 (1.849(9) Å), Fe1-O2 (1.855(9) Å) and angles Fe1-O1-C1 (130.7(8)°), Fe1-O2-C25 (124.8(7)°) in **1** are similar to those in Fe(TIPTO)₂ [1.847(1) Å, 129.33(8)°]. The Fe1-C17, 2.569(9) Å, and Fe1-C31, 2.507(7) Å, distances indicate weak secondary interactions between Fe and carbon atoms in mesityl rings. Magnetic measurements showed that **1** has a μ_{eff} of 5.32 μ_{B} , corresponding to the high-spin *d*⁶ configuration.



Figure 1. Molecular structure of 1 with the displacement ellipsoids drawn at 30% probability level. Hydrogen atoms are not shown for clarity.

Nine carbene precursors (2-10, Table 1) have been tested in the presence of 1 and NBE in benzene at room temperature: diazocompounds 2 and 3, zwitterion 4 (:CF₂ carbene precursor),^[36] 5 (:CBr₂ carbene precursor), terminal acetylene 6 (vinylidene precursor),^[37] cyclopropene 7 (alkylidene precursor for Ru),^[38] phosphorus ylide 8 (alkylidene precursor for W),^[39] cycloheptatriene 9 (carbene precursor for Au),^[40] and norbornene oxide 10 (alkylidene precursor for Ru).^[41]

Table 1. Test of carbene precursors for ROMP of NBE.



4	entry	additive	polyNBE, NMR conversion, %
	1	none	16
	2	2	5
	3	3	10
	4	4	15
	5	5	5
	6	6	10
	7	7	11
	8	8	<1
	9	9	15
	10	10	5

We were somewhat surprised to find that **1** can catalyze ROMP of NBE. Additives do not improve polymerization, which suggests the formation of active species in the presence of NBE only. Furthermore, the resulting polymer (entry 1, Table 1) is 99% *cis, syndiotactic*.^[8]

Complex 1 has been analyzed by ICP-MS to eliminate the possibility that trace quantities of adventitious metals catalyze ROMP. The content of Ru (< 1 ppt), Mo (0.008 ppm), W (0.01 ppm), and V (0.88 ppm) is insignificant to affect polymerization (see SI for details and additional control experiments).

The reaction of **1** with NBE was tested in the presence of alcohols to examine how the formation of mixed Fe alkoxides *in situ* can affect ROMP. The results are summarized in Table 2. Mixed Fe alkoxides that contain HMTO and fluorinated alkoxides $(CH_3)_2CF_3CO$, $CH_3(CF_3)_2CO$, or $Ph(CF_3)_2CO$ improve the reaction rate with constant selectivity (entry 3, 4, and 9, Table 2). Interestingly, the use of fluorinated alcohol with hydrogen at α -carbon atom (CF₃)₂CHOH leads to a decrease of selectivity (entry 8, Table 2). The most efficient catalyst is the mixed alkoxide Fe(HMTO)(Ph(CF₃)₂CO) (entry 9, Table 2), which was confirmed by ¹H NMR, thus, when **1** reacted with 1 equiv. of Ph(CF₃)₂COH

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in C_6D_6 at 22 °C, the proton signals of a new complex along with free HMTO-H signals immediately appeared (see SI for details).

The resulting polymers have high molecular weights (MW) and polydispersity indexes (PDI) based on gel permeation chromatography (GPC), which suggests that the rate of the propagation is higher than that of initiation. The formation of the active species in the presence of NBE is a relatively slow process, as a result, most of the Fe complex stays intact during the ROMP, which was confirmed by ¹H NMR. The reaction of Fe(HMTO)(Ph(CF₃)₂CO) with NBE in benzene at 70 °C produces a smaller polymer with lower yield (entry 10, Table 2) as compared to the reaction at 22 °C suggesting decomposition of the active species on the growing polymer chain depends on the solvent. Thus, the reaction in toluene at 22 °C produces a smaller

 Table 2. Test of additives, solvents, and temperature for ROMP of NBE.

polymer with a conversion comparable to the reaction in benzene (entry 12, Table 2). Surprisingly, Fe(HMTO)(Ph(CF₃)₂CO) can catalyze ROMP of NBE at -35 °C in toluene. The reaction is slower but gives a higher MW compare to the reaction at 22 °C. This observation confirms that the stability of the active species decreases at higher temperatures (entry 11-13, Table 2). Notably, the nature of the active species remains the same since the highly stereoregular polymers are obtained in all cases. The reaction of Fe(HMTO)(Ph(CF₃)₂CO) with NBE in benzene at 22 °C at a shorter reaction time (4 and 14 hours, entry 14 and 15, Table 2) produces a larger polymer with lower PDI. We assume that the formed active species have a short lifetime and, presumably, decompose after termination. Newly formed active species produce smaller polymer due to decreasing of the concentration of NBE, leading to growing PDI over time.

		<u> </u>	10 mol % 1	→ ,			
			10 mol % additive C ₆ D ₆ , 22 °C, 24 h	+ eie eurod			
		NDE		cis,synai			
entry	additive	temp., °C	conv., % ^[a]	cis/trans	tacticity	Mn (g/mol) ^[b]	M _w /M _n
1	none	22	17	99:1	syndiotactic	262800	2.33
2	(CH ₃) ₃ COH	22	0	-	-	-	-
3	(CH ₃) ₂ CF ₃ COH	22	42	>99:1	syndiotactic	663400	2.05
4	CH ₃ (CF ₃) ₂ COH	22	48	>99:1	syndiotactic	470600	2.29
5	(CF ₃) ₃ COH	22	20	>99:1	syndiotactic	625000	2.11
6	allyl(CF ₃) ₂ COH	22	3	-	-	-	-
7	(CH ₃) ₂ CHOH	22	0		-	-	-
8	(CF ₃) ₂ CHOH	22	42	91:9	syndiotactic	590000	2.22
9	Ph(CF₃)₂COH	22	84 (81) ^[c]	>99:1	syndiotactic	930700	1.97
10	Ph(CF ₃) ₂ COH	70	28	>99:1	syndiotactic	362100	2.33
11	Ph(CF ₃) ₂ COH ^[d]	-35	43	>99:1	syndiotactic	565700	2.36
12	Ph(CF ₃) ₂ COH ^[d]	22	75	>99:1	syndiotactic	416000	2.66
13	Ph(CF ₃) ₂ COH ^[d]	100	10	>99:1	syndiotactic	82300	3.31
14	Ph(CF ₃) ₂ COH ^[e]	22	62	>99:1	syndiotactic	1141800	1.57
15	Ph(CF ₃) ₂ COH ^[f]	22	74	>99:1	syndiotactic	1038700	1.65
16	3,4-dihydro-2H-pyran	22	15	-	-	-	-
17	benzaldehyde	22	0	-	-	-	-
18	acetophenone	22	7	-	-	-	-
19	benzophenone	22	12	-	-	-	-

[a] by ¹H NMR. [b] GPC data in THF vs. polystyrene standards. [c] Isolated yield. [d] Reaction in toluene-d₈. [e] 4h. [f] 14h.

We have attempted to elucidate the mechanism of Fe catalyzed ROMP of NBE. Three possible mechanisms were considered: involving Fe alkylidene, photoredox mediated ROMP, and carbonyl-olefin metathesis.

The first considered mechanism involves the formation of Fe alkylidene in the presence of NBE *in situ*. According to computational studies,^[23, 26] Fe alkylidene and metallacyclobutane of the active catalyst are low spin complexes. However, the formation of low spin, diamagnetic species, was not detected by

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NMR during the catalysis in our case. The addition of cyclooctene or octa-1,7-diene (see SI for the full list of tested substrates) during the reaction does not lead to the formation of polycyclooctene or cyclohexene, which one can expect to observe if the reaction of **1** and NBE produced an active Fe alkylidene. The origin of the tacticity of polyNBE is an essential question in the Fe catalyzed ROMP involving alkylidenes. In the case of Mo and W catalysts, the formation of *cis*, *syndiotactic* polymers is achieved through stereogenic metal control, where the inversion of the configuration at the chiral four-coordinated metal center proceeds with each insertion.^[7] The same principle does not apply to the mononuclear Fe alkylidene formed from NBE and **1** containing two identical HMTO groups. The formation of polynuclear iron clusters that contain chiral metal center seems plausible explanation.

The second mechanism is the redox-initiated ROMP mentioned previously.^[16] This mechanism involves oxidation of a vinyl ether to form radical cation to initiate ROMP in the presence of a photoredox mediator. The addition of 3,4-dihydro-2H-pyran does not improve the reaction rate (entry 16, Table 2). Furthermore, redox-initiated ROMP produces atactic polymers due to the radical intermediates, which is not the case in our system. It is noteworthy, we have never observed any evidence of radical reactions, e.g., alkene cyclopropanation or radical olefin polymerization. Additionally, the presence of light does not affect the ROMP of NBE with **1**.

The third mechanism is based on the recently developed carbonyl-olefin metathesis (COM),^[42] where Fe complex acts as a Lewis acid. Although Fe-mediated COM has not been applied for ROMP of NBE yet,^[43] we tested the possibility of this mechanism by adding carbonyl compounds to the reaction (entry 17-19, Table 2). However, no improvement of ROMP was observed, suggesting that this mechanism is implausible.

Our studies demonstrate that Fe-based alkoxide complexes can catalyze ROMP of NBE to produce highly stereoregular polyNBE (>99% *cis, syndiotactic*). The use of heteroleptic Fe(HMTO)(RO), where RO is (CH₃)₂CF₃CO, CH₃(CF₃)₂CO, or Ph(CF₃)₂CO prepared *in situ*, significantly increases the rate of the reaction compared to homoleptic Fe(HMTO)₂ while preserving stereoselectivity. The formation of polyNBE with high MW and PDI indicates that the rate of propagation is higher than the rate of initiation. The stability of active species strongly depends on the solvent and temperature. However, the nature of the active catalyst remains unclear. The reaction may involve polynuclear iron clusters and/or a yet unknown mechanism, and requires further investigations.

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COMMUNICATION

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Homoleptic iron complex catalyzes ring-opening metathesis polymerization of norbornene to yield highly stereoregular polynorbornene (99% *cis, syndiotactic*). The influence of solvent, temperature, and additives was examined.