

# Highly Tactic Cyclic Polynorbornene: Stereoselective Ring Expansion Metathesis Polymerization of Norbornene Catalyzed by a New Tethered Tungsten-Alkylidene Catalyst

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**S** Supporting Information

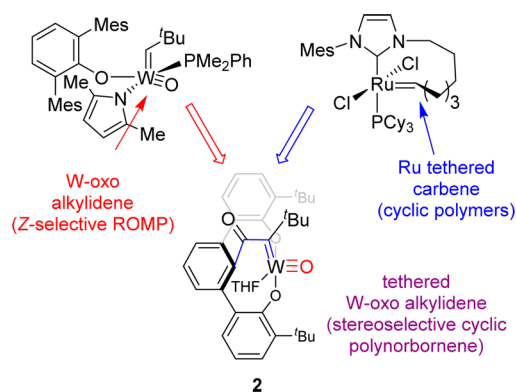
**ABSTRACT:** The tungsten alkylidene  $[^t\text{BuOCO}]\text{W}\equiv\text{C}(^t\text{Bu})$  (THF)<sub>2</sub> (**1**) reacts with CO<sub>2</sub>, leading to complete cleavage of one C=O bond, followed by migratory insertion to generate the tungsten-oxo alkylidene **2**. Complex **2** is the first catalyst to polymerize norbornene via ring expansion metathesis polymerization to yield highly *cis*-syndiotactic cyclic polynorbornene.

Ring-opening metathesis polymerization (ROMP) of norbornenes and norbornadienes can lead to a variety of microstructures depending on the resulting tacticity of the polymer (isotactic, syndiotactic, or atactic) and double-bond configuration (*cis* or *trans*).<sup>1</sup> Highly tactic polymers often present more well-defined properties, and therefore more value, than their atactic analogs.<sup>1c,2</sup> However, stereocontrolled ROMP of cyclic monomers still poses a challenge in polymer chemistry. Well-defined alkene metathesis catalysts of tungsten,<sup>3</sup> molybdenum,<sup>3</sup> and ruthenium<sup>1c,4</sup> were only recently discovered to initiate ROMP of norbornene monomers with high stereocontrol of tacticity and *cis/trans* ratio.

Perhaps even more challenging than stereocontrolled ROMP is the synthesis of cyclic polymers. Cyclic polymers exhibit remarkably different physical properties (e.g., lower intrinsic viscosity, higher glass transition temperature) compared to their linear counterparts of similar molecular weight.<sup>5</sup> Despite their interesting properties, laborious synthesis required for cyclic polymers has hindered development of this research field. Methods for the synthesis of cyclic polymers usually involve intramolecular coupling between the chain ends of linear precursors;<sup>6</sup> however, the inherent limitation of this method is the requirement of dilute conditions and long reaction times.<sup>7</sup> Recent discoveries in catalytic production of cyclic polymers offer exciting new avenues for their efficient production.<sup>8</sup> Grubbs' ring expansion metathesis polymerization (REMP) strategy overcomes some of the challenges in cyclic polymer synthesis.<sup>9</sup> REMP utilizes a cyclometalated alkylidene metal complex as the catalyst.<sup>9a,10</sup> In this case, the two ends of the growing polymer remain attached to the metal throughout the polymerization process, thus releasing a cyclic polymer upon intramolecular chain transfer.<sup>9</sup> Cyclic dendronized polymers<sup>11</sup> and cyclic brush polymers<sup>12</sup> employing norbornene-based macromonomers were synthesized via REMP using cyclic

ruthenium catalysts;<sup>13</sup> however, control over both tacticity and the *cis/trans* ratio is either not reported or absent.

Figure 1 outlines the design features of catalyst **2**. The catalyst combines the concept of tethering a M=C bond to a



**Figure 1.** Tethered tungsten-oxo alkylidene catalyst **2** design concept.

substitutionally inert ancillary ligand to promote REMP<sup>9,13</sup> with a tungsten-oxo alkylidene fragment known to promote *Z*-selective ROMP (Figure 1).<sup>14</sup> Herein, we report the first catalyst to promote stereocontrolled REMP to yield *cis*-syndiotactic cyclic polynorbornene.

**Catalyst Synthesis and Characterization.** Previously reported, the tungsten alkylidene  $[^t\text{BuOCO}]\text{W}\equiv\text{C}(^t\text{Bu})$  (THF)<sub>2</sub> (**1**) supported by a trianionic pincer ligand<sup>15</sup> is the precursor for a highly active catalyst for polymerization of alkynes to give cyclic polymers.<sup>16</sup> Treating **1** with CO<sub>2</sub> at 55 °C for 12 h generates the tungsten-oxo alkylidene complex **2**, and the dinuclear species **3**, in a 9:2 ratio, respectively (Scheme 1).

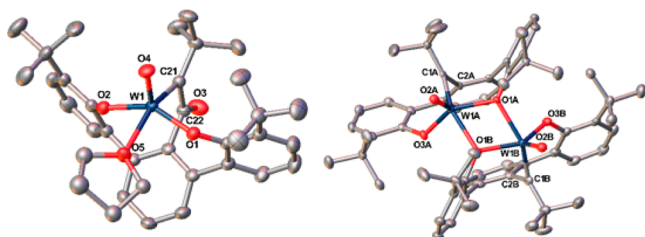
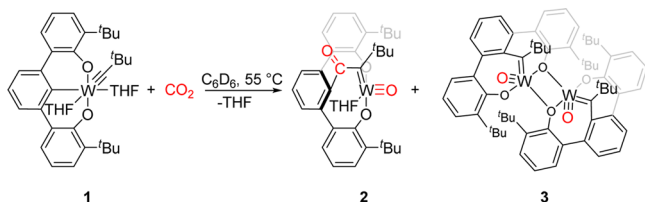
Complex **2** crystallizes preferentially in C<sub>6</sub>D<sub>6</sub>, resulting in single crystals amenable to X-ray diffraction. The tungsten ion in complex **2** (Figure 2) is square pyramidal ( $\tau = 0.12$ ).<sup>17</sup> The oxo group occupies the axial position (W1–O4 = 1.6948(15) Å) and the alkylidene (W1=C21 = 1.9503(19) Å), a THF ligand, and two aryloxides reside in the basal plane.

Scheme 2 depicts the proposed pathway for the formation of catalyst **2**. Carbonyl addition to tungsten alkylidynes bearing

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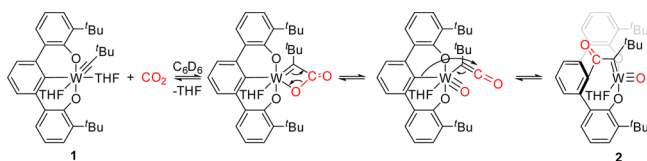
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## Scheme 1. Synthesis of Complexes 2 and 3



**Figure 2.** Left: Solid-state structure of **2** with H atoms, solvent molecules, and disorder on the coordinated THF omitted for clarity. Right: Solid-state structure of **3** with H atoms omitted for clarity. Thermal ellipsoids drawn at 50% probability.

## Scheme 2. Proposed Pathway for the Formation of Complex 2



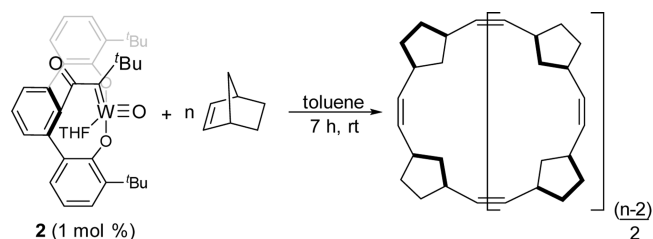
trianionic pincer ligands was recently reported by our group.<sup>18</sup> Thus, the first step involves cycloaddition and cleavage of CO<sub>2</sub> across the alkylidyne to give a tungsten-oxo-ketene intermediate. It is noteworthy to mention here that the cleavage of CO<sub>2</sub> across a metal–carbon triple bond is unprecedented, with only cycloaddition, but not cleavage, achieved by Fischer.<sup>19</sup> In contrast, CO<sub>2</sub> cycloaddition and cleavage across both early<sup>20</sup> and late<sup>21</sup> metal–carbon double bonds is more common. Strong support for the ketene intermediate comes in the form of an isolable analog employing an ONO<sup>3-</sup> trianionic pincer ligand.<sup>22</sup> However, in this OCO<sup>3-</sup> case, the ketene moiety is unstable and instead inserts into the metal–aryl bond of the pincer ligand to give **2**.

Complex **3** is independently isolable from complex **2**. Further heating of the initial reaction mixture leads to complete conversion of **2** to **3**, as monitored by NMR spectroscopy. The initial formation of complex **2** and **3** in a 9:2 ratio and the eventual conversion of complex **2** into **3** upon heating suggest that the reaction is reversible and that complex **3** forms via attack at the  $\alpha$ -carbon of the ketenylide and subsequent loss of CO. Consistent with the mechanism, a sample of the headspace reveals CO as determined by GC-MS (see SI). The empirical formula of dimer **3** implies the loss of CO from **2**; however, the mechanism of this transformation is still under investigation. Addition of a few drops of THF to the reaction mixture of **2** and **3** prevents the conversion of **2** into **3** even upon heating, implying loss of THF is an integral step in the formation of **3**. Slow evaporation of a concentrated solution of **3** in a pentane/Et<sub>2</sub>O mixture yields single crystals suitable for X-ray diffraction. One of the aryloxides from the trianionic OCO<sup>3-</sup> pincer ligand bridges the two tungsten atoms (W<sub>1A</sub> and W<sub>1B</sub>, Figure 2). Bridges created by trianionic pincer ligands were noted in two previous structures

by our group<sup>23</sup> and Bercaw's.<sup>24</sup> Alkylidene W<sub>1A</sub>–C<sub>1A</sub> and W<sub>1B</sub>–C<sub>1B</sub> bond lengths of 1.884(4) and 1.885(4) Å are slightly shorter by 0.021(4) Å than the W=C double bond in the only related tetraanionic pincer OCO<sup>4-</sup> W-alkylidene.<sup>25</sup>

**REMP and Evidence for Stereoselectivity.** Treating **2** (1 mol %) with norbornene at room temperature yields *cis*-selective cyclic polynorbornene (>98% by <sup>1</sup>H NMR spectroscopy) after 7 h (Scheme 3). The reaction was quenched by dropwise addition

## Scheme 3. Polymerization of Norbornene by Catalyst 2 To Generate Cyclic Polynorbornene



of the reaction mixture into stirring methanol. The resulting polymer was isolated by filtration and dried under vacuum. Adding **3** (1 mol %) to norbornene at room temperature for 7 h yields polynorbornene in only 42% yield, with no *cis*-selectivity. Table 1 lists polymerization results as a function of the ratio of monomer to initiator **2**.

**Table 1.** Polymerization of Norbornene<sup>a</sup> by Catalyst **2** with Different Monomer/Catalyst Ratios

[mon/cat] <sub>0</sub>	[monomer] <sub>0</sub> <sup>b</sup>	yield (%)	% <i>cis</i> <sup>c</sup>	M <sub>n</sub> <sup>d</sup> (kDa)	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
25:1	0.1	97	97	126	1.24
50:1	0.1	97	97	197	1.25
100:1	0.1	92	98	248	1.21
200:1	0.1	60	97	578	1.29

<sup>a</sup>The appropriate amount of a 1 mg/mL solution of catalyst dissolved in toluene is added to 40 mg of norbornene dissolved in toluene and stirred for 7 h at room temperature. <sup>b</sup>mol L<sup>-1</sup>. <sup>c</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>d</sup>Determined by size exclusion chromatography equipped with multi-angle light scattering.

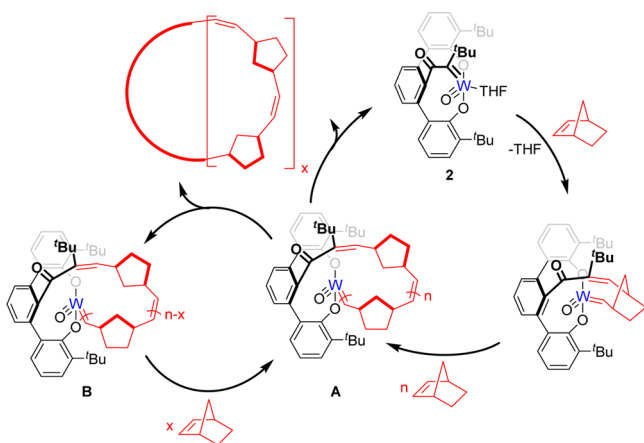
A mixture of **2** and **3** maintains the selectivity of **2** when treated with norbornene, suggesting initiation with catalyst **2** and propagation of the monomer are much faster than initiation by the more hindered complex **3**. Evidence for fast propagation relative to initiation comes from a sealed NMR tube polymerization experiment. Combining norbornene and **2** in C<sub>6</sub>D<sub>6</sub> results in polymer formation, but the <sup>1</sup>H NMR spectrum of the reaction mixture exhibits signals attributable to unreacted catalyst **2** (see Figure S17), thus indicating  $k_p > k_i$ .

Cyclic polynorbornene produced with catalyst **2** is syndiotactic (>98%), as determined by a comparison to <sup>13</sup>C NMR data of previously reported syndiotactic linear polynorbornene.<sup>26</sup> Tacticity is also supported by postfunctionalization of polynorbornene via bromination, as recently described by Schrock et al.<sup>26b</sup> The brominated polymer exhibits two doublets at 3.84 ppm ( $J = 11.2$  Hz) and 3.81 ppm ( $J = 10.3$  Hz) (Figure S24, top). Consistent with reported *cis*-syndiotactic polynorbornene, irradiating the methine protons at 2.61 ppm results in two singlets (Figure S24, bottom).<sup>26b</sup> Further evidence for high syndiotacticity comes from polymerization of the chiral monomer bis((menthyloxy)carbonyl)norbornadiene

(BMCNBD). COSY NMR is able to distinguish between isotactic and syndiotactic poly(BMCNBD). In the case of a *cis* isotactic sample, the olefinic protons are inequivalent and therefore couple in a COSY NMR spectrum. However, a *cis*-syndiotactic poly(BMCNBD) contains equivalent olefinic protons related by a  $C_2$  axis and thus do not couple.<sup>27</sup> Poly(BMCNBD) produced by **2** does not exhibit any coupling between the olefinic protons, indicating the polymer is syndiotactic (Figure S22).

Since the alkylidene in **2** is tethered to the ligand backbone, REMP is the expected mechanism of polymerization (Scheme 4). Through REMP, the growing polymer chain remains attached

#### Scheme 4. Proposed Mechanism of REMP of Norbornene To Give Highly *cis* and Syndiotactic Cyclic Polynorbornene



by both ends to the catalyst throughout the polymerization process (see intermediate **A**) and releases a cyclic polynorbornene after undergoing intramolecular chain transfer via backbiting. Though less probable, backbiting can occur to regenerate initiator **2**, or instead, backbiting can occur at any of the other  $C=C$  bonds to give intermediate **B**. The proposed mechanism is consistent with the observation of slow initiation/fast propagation since metathesis within complex **2** occurs at a disubstituted, sterically hindered (<sup>t</sup>Bu) alkylidene, whereas after the initial ring opening event, the new alkylidene is monosubstituted and relatively unhindered.

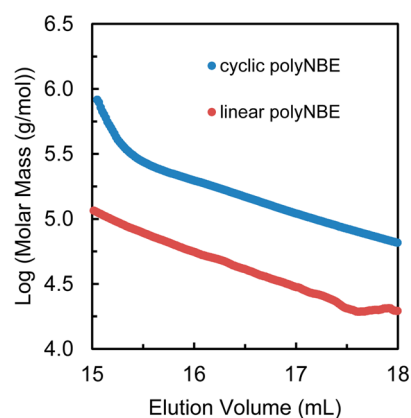
Size exclusion chromatography (SEC) equipped with multi-angle light scattering (MALS) and viscosity detectors provide compelling data for a cyclic topology. Cyclic polymers have lower intrinsic viscosities and smaller hydrodynamic volumes than their linear analogs. Catalysts that produce linear polynorbornene with high *cis* selectivity (>95%) and syndiotacticity (>95%) are known,<sup>28</sup> and a sample was synthesized utilizing Grubbs catalyst Ru(NHC(Ad)(Mes))(=CH(PhO<sup>i</sup>Pr))(η<sup>2</sup>-NO<sub>3</sub>) (**4**) (Table 2).<sup>29</sup>

A plot of log of molar mass vs elution volume (Figure 3) shows that the cyclic polynorbornene samples with the same molar

**Table 2.**  $M_n$ ,  $M_w/M_n$ , *cis*-Selectivity, and Tacticity of Cyclic/Linear Poly(NBE)

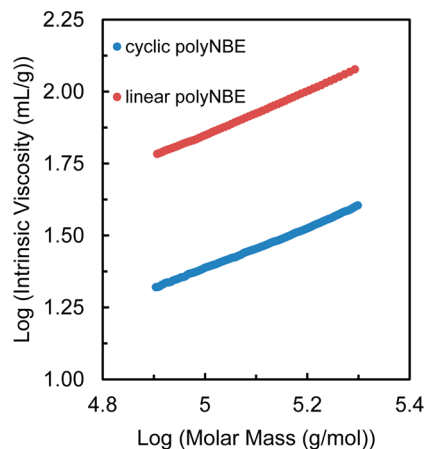
catalyst	$M_n^a$ (kDa)	$M_w/M_n$	% <i>cis</i> <sup>b</sup>	tacticity <sup>c</sup>
<b>2</b> (cyclic)	113	1.16	>98	syndiotactic
<b>4</b> (linear)	114	2.34	>95	syndiotactic

<sup>a</sup>Absolute molecular weights determined by SEC-MALS. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Determined by <sup>13</sup>C NMR spectroscopy.



**Figure 3.** Plot of log of molar mass vs elution volume.

mass elute later than their linear counterparts, consistent with their smaller hydrodynamic volume. A Mark–Houwink–Sakurada (MHS) plot ( $\log [\eta]$  vs  $\log M$ , where  $[\eta]$  is the intrinsic viscosity and  $M$  is the viscosity-average molar mass (Figure 4) confirms the lower intrinsic viscosity of the cyclic



**Figure 4.** MHS plot,  $\log [\eta]$  vs  $\log M$ .

polymers relative to the linear polymers. The experimental ratio  $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$  of 0.34 over a range of molecular weights is in good agreement with the theoretical value of 0.4.<sup>9a</sup> Additionally, MHS *a* parameters of 0.76 and 0.71 for the linear and cyclic samples, respectively, were determined from the slope of the MHS plots. This result indicates that both polymers behave as flexible random coils in solution, meaning the observed differences are caused by different behavior of the polymers in solution. In addition, a plot of mean square radius of gyration ( $\langle R_g^2 \rangle$ ) vs molar mass (see Figure S27) obtained for cyclic and linear samples of polynorbornene provides a  $\langle R_g^2 \rangle_{\text{cyclic}}/\langle R_g^2 \rangle_{\text{linear}}$  ratio of  $0.4 \pm 0.1$ , which is within the experimental error of the theoretical value of 0.5.<sup>30</sup>

In summary, tethering an alkylidene to a substitutionally inert ancillary ligand is an effective design for creating catalysts capable of REMP. Unique to this system, CO<sub>2</sub> cleavage across the metal–carbon triple bond of complex **1** leads to the tethered alkylidene catalyst **2**. Though other tethered group VI alkylidene complexes are known,<sup>10a</sup> complex **2** is the first to function as a REMP catalyst. Comparing the polymers produced by catalyst **2**, against *cis* and syndiotactic-rich linear analogs permits their conclusive assignment as cyclic polymers. To the best of our knowledge, this

is the first catalyst to produce cyclic polynorbornene with such high stereocontrol.<sup>13</sup> The *cis*-selectivity is presumably due to the steric congestion imposed by the <sup>t</sup>BuOCO<sup>4-</sup> ligand, and the observed syndiotacticity indicates addition of the monomer occurs with alternating stereoselectivity. The monomer adds to one face of the M=C bond first, and in the next addition, it adds to the opposite face of the alkylidene. This type of “stereogenic metal control” occurs when the configuration of the metal center changes after each monomer addition.<sup>14</sup> Complex **2** provides new avenues for exploration of not only cyclic polymers but also catalyst design. Considering the extensive history of early metal alkylidenes, surely other tethered versions can be designed to initiate REMP.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00014.

Crystallographic data (CIF)

Crystallographic data (CIF)

Experimental details and data (PDF)

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### Notes

The authors declare no competing financial interest.

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