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Detailed Terms
Z-Selective Olefin Metathesis Processes Catalyzed by a Molybdenum Hexaisopropylterphenoxyde Monopyrrolide Complex

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Abstract

The molybdenum-based monoaryloxide monopyrrolide (MAP) species, Mo(NAd)(CHCMe₂Ph)(C₄H₄N)(HIPTO) (2a), which contains “small” imido (Ad = 1-adamantyl) and “large” aryloxide (HIPTO = O-2,6(2,4,6-i-Pr₃C₆H₂)C₆H₃) ligands, catalyzes Z-selective metathesis reactions as a consequence of intermediate metallocyclobutane species not being able to have a (anti) substituent pointing toward the HIPTO group. ROMP of dicarbomethoxynorbornadiene (DCMNBD) with 2% 2a in toluene leads to >99% cis and >99% syndiotactic poly(DCMNBD), while ROMP of cyclooctene and 1,5-cyclooctadiene (300 equiv) with initiator 2a leads to poly(cyclooctene) and poly(cyclooctadiene) that have cis contents of >99%; all are previously unknown microstructures. Z-selectivity is also observed in the metathesis of cis-4-octene and cis-3-hexene by initiator 2a to give cis-3-heptene.

Monoaryloxide-pyrrolide (MAP) olefin metathesis catalysts, which can be prepared through addition of a phenol to a bispyrrolide species,¹ can be especially efficient for enantioselective olefin metathesis reactions. For example, mixtures of diastereomers of 1 (R = 1-adamantyl, R’ = Me, R” = Br) that are prepared in situ efficiently ring-close an intermediate.

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Supporting Information Available: Experimental details for the synthesis of all compounds and metathesis reactions, and details of the X-ray study. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.
in an enantioselective synthesis of the *Aspidosperma* alkaloid, quebrachamine,\(^{2a,2b}\) and catalyze \(Z\)-selective and enantioselective cross-metatheses.\(^{2c}\) \(Z\)-selectivity is proposed to be possible when olefin attacks at the metal \(trans\) to the pyrrolide in a \(syn\) complex to yield metallacyclobutane intermediates in which all substituents point toward the “small” axial imido ligand and away from the “large” axial OR’” group (equation 1, Pyr = pyrrolide). Studies involving tungsten\(^3\) or molybdenum\(^4\) MAP species support the proposals that (i) metallacyclobutanes that contain axial imido and alkoxide ligands are metathesis intermediates, and that (ii) the stereochemistry at the metal \(inverts\) as a consequence of each forward metathesis step (equation 1; \(R_1, R_2, R_3\) = alkyl groups).
If the mechanism proposed in equation 1 is correct, then ROMP of a substituted norbornadiene initiated by the appropriate MAP species should give rise to a cis,syndiotactic polymer, e.g., that shown in equation 2 (E = ester), a microstructure that is not known in pure form. Therefore we became interested in confirming the proposed transformation shown in equation 2, and if successful, in exploring other $Z$-selective reactions.

As the OR'' group we chose O-2,6-(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (hexaisopropylphenoxide = HIPTO$_6$) (see 2) in order to ensure that OR'' is sufficiently “large,” and adamantyl as the “small” imido substituent (R).$^{2c}$ Addition of HIPTOH to Mo(NAd)(CHCMe$_2$Ph)(C$_4$H$_4$N)$_2$ led to isolable syn-Mo(NAd)(CHCMe$_2$Ph)(C$_4$H$_4$N)(HIPTO) (2a: R’ = H) in good yield. Polymerization of dicarbomethoxynorbornadiene (DCMNBD) with 2% 2a in toluene, followed by quenching the
reaction with benzaldehyde, yielded a >99% cis, >99% tactic polymer with a C(7) resonance at 38.0 ppm in the $^{13}$C NMR spectrum in CDCl$_3$ (cf. 38.7 ppm for cis,isotactic polyDCMNBD$^5$) and an olefinic carbon resonance at 131.5 ppm (the same as in cis,isotactic polyDCMNBD$^5$). A similar highly tactic polymer was formed upon polymerization of 5,6-dicarboxymenthoxynorbornadiene (DCMenNBD). Since the inequivalent olefinic protons in poly(DCMenNBD) were not coupled, poly(DCMenNBD) prepared with 2a must be syndiotactic. Therefore we conclude that poly(DCMNBD) prepared with 2a as the initiator is also >99% cis and >99% syndiotactic (equation 3, Table 1). Poly(DCMNBD) prepared with an initiator that contains a dimethylpyrrolide (2b, R’ = Me, Table 1) was also >99% cis and >99% syndiotactic. Poly(DCMNBD) samples prepared with 2c, 3a, and 3b (Table 1) were found to have lower cis contents than poly(DCMNBD) prepared with 2a or 2b. Clearly the choice of “large” and “small” groups is critical for high Z content, as one might predict if the “all syn” metallacyclobutane intermediate must form (eq 1).

The only chirality present in racemic initiators of type 2 and 3 is the stereogenic metal center. A stereogenic metal center should exert a powerful electronic control (olefin approach trans to pyrrolide, eqs 1 and 2) in a coordination polymerization reaction that is absent in the vast majority of other types of metal-catalyzed polymerizations. This “sterenogenic metal” (SM) control is distinct from enantiomorphic site control and chain-end control, which are both primarily steric in origin and arise from chirality in a ligand or in a polymer chain-end in the last-inserted monomer, respectively.
Poly(DCMNBD) samples prepared with 1a-1d (Table 1), in which OR‴ is the large, enantiomerically pure arylxide in 1, do not contain exclusively cis linkages. Evidently one or both of the two diastereomers (neglecting any chain end chirality) that must be formed sequentially in these circumstances is not (or are not) as Z-selective as 2a or 2b.

In order to explore the potential generality of Z-selective polymerization with 2a we turned to ROMP of cyclooctene and 1,5-cyclooctadiene (300 equiv). Poly(cyclooctene) was formed with a cis content of >99%. The T_m of cis-poly(cyclooctene) was found to be -10 °C, the temperature predicted by Feast in studies of cyclooctene polymers that contain various lower cis contents. We obtained poly(cyclooctene) with a cis content of 20% employing Mo(NAr)(CHCMe3Ph)(OCMe(CF3)2)2 as the initiator and 86% with 1b as the initiator. Poly(cyclooctadiene) was formed with a cis content of >99% (according to 13C NMR) when 2a was employed as an initiator. Poly(cyclooctadiene) prepared employing Mo(NAr)(CHCMe3Ph)(OCMe(CF3)2)2 as the initiator had a cis content of 15%. No T_m could be observed between 50 °C and -75 °C for cis-poly(cyclooctadiene), which is in accord with studies by Feast. We are not aware of any report of purecis-poly(cyclooctadiene) or cis-poly(cyclooctene) in the literature.

Z-selectivity is also observed in the metathesis of internal cis olefins with 2a as the initiator. Addition of 1% 2a to a 1:1 mixture of cis-4-octene and cis-3-hexene in diethyl ether leads to an equilibrium mixture that contains 50% cis-3-heptene after 8 hours at 22 °C (equation 4). The slow rate of the Z-selective reaction shown in equation 4 is consistent with the required formation of the highly sterically crowded “all-syn” metallacyclobutane intermediate (eq 1), but reactions that proceed via metallacyclobutane intermediates that lead to trans C=C bonds are even slower. Over a period of three days the cis olefins slowly isomerize to approximately a 1:1 cis/trans mixture.

\[
\begin{array}{c}
\text{cis-4-octene} + \text{cis-3-hexene} \\ \rightarrow \end{array} \quad \text{cis-3-heptene} \]

We prepared the unsubstituted tungstacyclobutane complex, W(NAr)(C3H6)(C4H4N)(HIPTO) (Ar = 2,6-i-Pr2C6H3), from W(NAr)(CHCMe3Ph)(C4H4N)2(dme) in a manner analogous to that reported recently for related tungstacyclobutane species. (The WNAr species was chosen because molybdacyclobutane species are relatively unstable toward loss of olefin and W=NAd complexes are unknown.) As shown in Figure 1, the imido and phenoxide ligands are located in axial positions, as expected. The plane of central ring of the HIPTO ligand is oriented “perpendicular” to the W-C2 vector (W-C7) of the WCl3 ring so that one set of 2,6 isopropyl groups in the HIPTO ligand are located “under” the WC3H6 ring. A space filling model shows that the three anti protons in the metallacycle are in close contact with isopropyl methyl group protons, making it unlikely that a metallacycle of this type could be formed readily if an anti substituent were present on an α or β carbon. The other set of 2,6-HIPTO isopropyl groups surround the pyrrolide ligand and force it to line up along the N1-W-O1 axis. The W-O-C bond angle is relatively large (W1-O1-C31 = 163.7(4)°), consistent with the significant steric demands of the HIPTO ligand.

“Mistakes” that yield trans C=C bonds can arise either when a cis olefin reacts with an (unseen) anti alkylidene to yield a syn(α)/syn(β)/anti(α) metallacyclobutane, or when a cis olefin attacks a syn alkylidene to yield an anti(α)/anti(β)/syn(α) metallacyclobutane. Anti alkylidenes in rare cases have been observed in the solid state or in solution. Preventing formation of any significant amount of product derived from a reaction that involves an anti...
alkylidene is likely to be a key aspect of $Z$-selectivity in MAP catalysts in which the imido $R$ group is “small” and the OR”' ligand is “large.”

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

**Acknowledgment**

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**References**


9. Recent studies of tungsten methylene MAP complexes show that the methyldiene ligand rotates readily about the W=C bond (10-100 s$^{-1}$), making it likely that syn and (unseen) anti isomers of monosubstituted methyldienes interconvert relatively rapidly.


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Figure 1.
Thermal ellipsoid drawing of W(NAr)(C₅H₆)(C₄H₄N)(HIPTO) (50% probability). Hydrogen atoms are removed for clarity except for those on C1, C2, C3, and two of the twelve HIPTO isopropyl methyl carbons.
### Table 1
Synthesis of poly(DCMNBD) with various initiators.\(^a\)

<table>
<thead>
<tr>
<th>Initiator</th>
<th>R</th>
<th>R'</th>
<th>or(\text{&quot;}^{a})</th>
<th>Cis content</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ad</td>
<td>H</td>
<td>HIPTO</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2b</td>
<td>Ad</td>
<td>Me</td>
<td>HIPTO</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>2c</td>
<td>Ar</td>
<td>H</td>
<td>HIPTO</td>
<td>70%</td>
</tr>
<tr>
<td>3a</td>
<td>Ad</td>
<td>Me</td>
<td>TPP</td>
<td>83%</td>
</tr>
<tr>
<td>3b(^b)</td>
<td>Ad</td>
<td>H</td>
<td>OSiNaph(_3)</td>
<td>44%</td>
</tr>
<tr>
<td>1a(^b)</td>
<td>Ar</td>
<td>Me</td>
<td>Bitet; R&quot; = Br</td>
<td>65%</td>
</tr>
<tr>
<td>1b(^b)</td>
<td>Ad</td>
<td>Me</td>
<td>Bitet; R&quot; = Br</td>
<td>70%</td>
</tr>
<tr>
<td>1c(^b)</td>
<td>Ad</td>
<td>Me</td>
<td>Bitet; R&quot; = Me</td>
<td>90%</td>
</tr>
<tr>
<td>1d(^b)</td>
<td>Ad</td>
<td>H</td>
<td>Bitet; R&quot; = CHPh(_2)</td>
<td>90%</td>
</tr>
</tbody>
</table>

\(^a\) Ad = 1-adamantyl; Ar = 2,6-i-Pr\(_2\)C\(_6\)H\(_3\); TPP = 2,3,5,6-Ph\(_4\)C\(_6\)H; Naph = 2-naphthyl; Bitet is the aryloxide shown in 1.

\(^b\) Prepared \textit{in situ}; see Supporting Information.