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Z-Selective Olefin Metathesis Processes Catalyzed by a Molybdenum Hexaisopropylterphenoxide Monopyrrolide Complex

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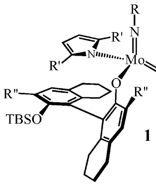
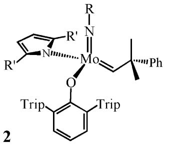
Monoaryloxide-pyrrolide (MAP) olefin metathesis catalysts, which can be prepared through addition of a phenol to a bispyrrolide species,[1] can be especially efficient for enantioselective olefin metathesis reactions. For example, *mixtures of diastereomers* of **1** (R = 2,6-*i*-$Pr_2C_6H_3$, R′ = Me, R″ = Br) that are prepared *in situ* efficiently ring-close an intermediate in an enantioselective synthesis of the *Aspidosperma* alkaloid, quebrachamine,[2a,b] and (when R = 1-adamantyl) 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 (eq 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 (eq 1; R_1, R_2, R_3 = alkyl groups).



1



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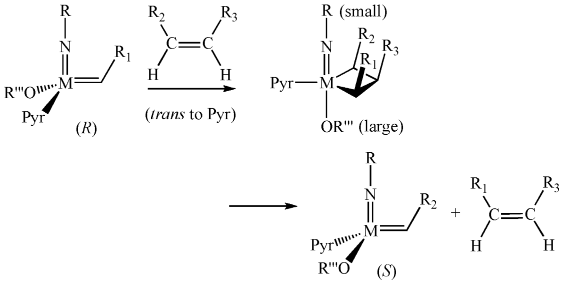
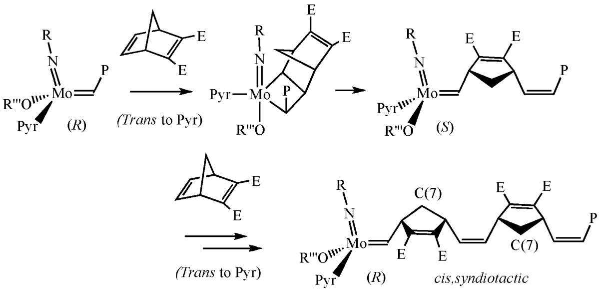
Trip = 2,4,6-i-$Pr_3C_6H_2$



(1)

If the mechanism proposed in eq 1 is correct, then ring-opening metathesis polymerization (ROMP) of a substituted norbornadiene initiated by the appropriate MAP species should give rise to a *cis,syndiotactic* polymer, e.g, that shown in eq 2 (*E* = ester), a microstructure that is not known in pure form.[5] Therefore we became interested in confirming the proposed transformation shown in eq 2 and, if successful, in exploring other *Z*-selective reactions.

As the OR‴ group we chose *O*-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (hexaisopropylterphenoxide = HIPTO[6]) (see **2**) to ensure that OR‴ is sufficiently "large" and adamantyl as the "small" imido substituent (R).[2c] Addition of HIPTOH to $Mo(NAd)(CHCMe_2Ph)(C_4H_4N)_2$[1a] led to isolable *syn*-$Mo(NAd)(CHCMe_2Ph)(C_4H_4N)$(HIPTO) (**2a**; R′ = H) in good yield. Polymerization of dicarbomethoxynorbornadiene (DCMNBD) with 2% **2a** in toluene, followed by quenching the reaction



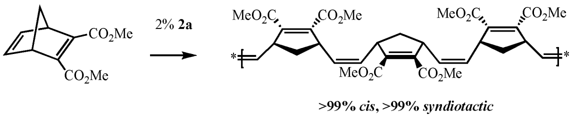
(2)

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-dicarbomenthoxynorbornadiene (DCMenNBD). Since the inequivalent olefinic protons in poly(DCMenNBD) were *not* coupled, poly(DCMenNBD) prepared with **2a** must be *syndiotactic*.[5] Therefore we conclude that poly(DCMNBD) prepared with **2a** as the initiator is also >99% *cis* and >99% *syndiotactic* (eq 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

Table 1. Synthesis of Poly(DCMNBD) with Various Initiators[a]

Initiator	R	R′	OR‴	*Cis* content
2a	Ad	H	HIPTO	>99%
2b	Ad	Me	HIPTO	>99%
2c	Ar	H	HIPTO	70%
3a	Ad	Me	TPP	83%
3b[b]	Ad	H	$OSiNaph_3$	44%
1a[b]	Ar	Me	Bitet; R″ = Br	65%
1b[b]	Ad	Me	Bitet; R″ = Br	70%
1c[b]	Ad	Me	Bitet; R″ = Me	90%
1d[b]	Ad	H	Bitet; R″ = $CHPh_2$	90%

[a] Ad = 1-adamantyl; Ar = 2,6-*i*-$Pr_2C_6H_3$; TPP = 2,3,5,6-Ph_4C_6H; Naph = 2-naphthyl; Bitet is the aryloxide shown in **1**. [b] Prepared *in situ*; see Supporting Information.



(3)

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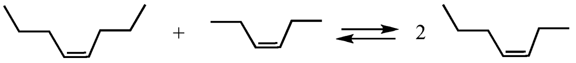
high *Z* content, as one might predict if the "all *syn*" metallacyclobutane intermediate must form (eq 1).

The only chirality present in racemic initiators of types **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 "stereogenic 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 aryloxide in **1**,[2] do *not* contain exclusively *cis* linkages. Evidently one or both of the two diastereomers[2−4] (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**.

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.[7] We obtained poly(cyclooctene) with a *cis* content of 20% employing $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ as the initiator and 86% with **1b** as the initiator. Poly(cyclooctadiene) was formed with a *cis* content of >99% (according to ^{13}C NMR) when **2a** was employed as an initiator. Poly(cyclooctadiene) prepared employing $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ as the initiator had a *cis* content of 15%. No T_m could be observed between 50 and −75 °C for *cis*-poly(cyclooctadiene), which is in accord with studies by Feast.[7] We are not aware of any report of *pure cis*-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 h at 22 °C (eq 4). The slow rate of the *Z*-selective reaction shown in eq 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 3 days the *cis* olefins slowly isomerize to approximately a 1:1 *cis/trans* mixture.



(4)

We prepared the unsubstituted tungstacyclobutane complex, $W(NAr)(C_3H_6)(C_4H_4N)(HIPTO)$ (Ar = 2,6-*i*-$Pr_2C_6H_3$), from $W(NAr)(CHCMe_2Ph)(C_4H_4N)_2(dme)$[8] in a manner analogous to that reported recently for related tungstacyclobutane species.[3] (The WNAr species was chosen because molybdacyclobutane species are relatively unstable toward the 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 the central ring of the HIPTO ligand is oriented "perpendicular" to the W−C_β vector (W−C2) of the WC_3 ring so that one set of 2,6 isopropyl groups in the HIPTO ligand are located "under" the WC_3H_6 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 significiant 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[9] 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.[10] Previous ROMP studies suggest that *anti* species may be orders of magnitude more reactive than *syn* species and that *trans* C═C bonds can form even though no *anti* alkylidene can be observed.[5c] 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."

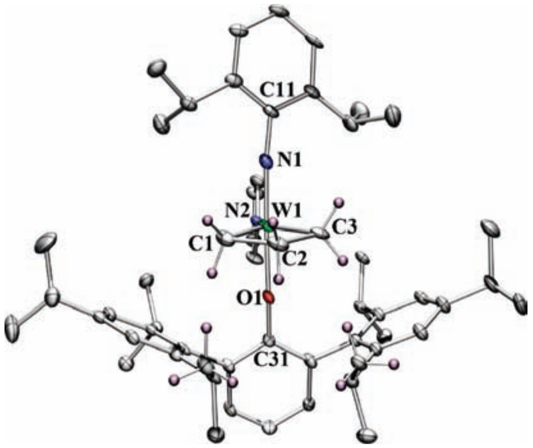


Figure 1. Thermal ellipsoid drawing of $W(NAr)(C_3H_6)(C_4H_4N)(HIPTO)$ (50% probability). Hydrogen atoms are removed for clarity except for those on C1, C2, C3, and 2 of the 12 HIPTO isopropyl methyl carbons.

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Note Added after ASAP Publication. The version of this paper published May 22, 2009, had an error in the first paragraph. The corrected version was published on May 26, 2009.

Supporting Information Available: Experimental details for the synthesis of all compounds and metathesis reactions, and details of the X-ray study. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hock, A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (b) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654.
(2) (a) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933. (b) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943. (c) Ibrahem, I; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844.
(3) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, web published 5/12/2009.
(4) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 58.
(5) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414. (c) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831. (d) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(6) Stanciu, C.; Olmstead, M. M.; Phillips, A. D.; Stender, M.; Power, P. P. *Eur. J. Inorg. Chem.* **2003**, 3495.
(7) Dounis, P.; Feast, W. J.; Kenwright, A. M. *Polymer* **1995**, *36*, 2787.
(8) Kreickmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.
(9) Recent studies of tungsten methylene MAP complexes[3] show that the methylidene ligand rotates readily about the W═C bond (10−100 s^{-1}), making it likely that *syn* and (unseen) *anti* isomers of monosubstituted methylidenes interconvert relatively rapidly.
(10) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R. *Chem. Rev.* **2009**, *109*, web published 3/13/2009.

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