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Synthesis of Chiral Molybdenum ROMP Initiators and All-Cis Highly Tactic Poly(2,3-(R)$_2$norbornadiene) (R = CF_3 or CO_2Me)

David H. McConville, Jennifer R. Wolf, and
Richard R. Schrock*

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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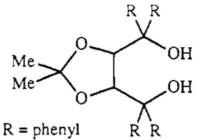
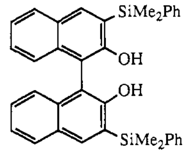
Controlling the stereochemistry of polymers prepared by ring-opening of norbornenes and norbornadienes has been a long standing problem,[1,2] one that ultimately could be solved by employing well-characterized catalysts with known structures and activities. Catalysts of the type Mo(CH-*t*-Bu)(NAr)(OR)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2)[3,4] have been shown to ring-open-polymerize 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) to give highly tactic all-trans poly(NBDF6) when OR = O-*t*-Bu (in toluene or THF)[5] and all-cis poly(NBDF6) with a tactic bias of ~74% when OR = $OCMe(CF_3)_2$ (in THF).[6] We show here that catalysts of this general type can be prepared that contain C_2-symmetric chiral diolate ligands and that poly(2,3-bis(trifluoromethyl)-norbornadiene) (poly(NBDF6)) and poly(2,3-dicarbomethoxynorbornadiene) (poly(DCNBD)) can be prepared using them that are >99% cis and >99% tactic.

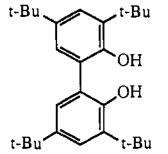
C_2-symmetric tartrate and BINO derivatives and related C_2-symmetric ligands have been widely and successfully used for enantioselective organic reactions in the past decade.[7–20] Addition of (+)-Ph_4tartH_2 to $Mo(CHCMe_2Ph)(NAr)(OTf)_2(DME)$[21,22] (DME = dimethoxyethane) in diethyl ether in the presence of triethylamine yielded $Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Ph_4tart](S)$ ((+)-**1**; S = a mixture of NEt_3 and dme; see supplementary material) in 70% yield. $Mo(CHCMe_2Ph)(NAr)[(-)\text{-}Ph_4tart](S)$ ((–)-**1**) and $Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Nap_4tart](S)$ ((+)-**2**; Nap = β-naphthyl) were prepared in an analogous manner. (±)-$BINO(SiMe_2Ph)_2H_2$ was prepared in a manner analogous to known SiR_3 derivatives[7] and treated with 2 equiv of KCH_2Ph[23] to give (±)-$BINO(SiMe_2Ph)_2K_2$, which when added to Mo(CH-*t*-Bu)(NAr)$(OTf)_2(DME)$[21,22] in THF gave crystalline Mo(CH-*t*-Bu)(NAr)[(±)-$BINO(SiMe_2Ph)_2$](THF) ((±)-**3**) in 70% yield.[24,25] Crystalline $Mo(CHCMe_2Ph)(NAr')[(\pm)\text{-}BINO(SiMe_2Ph)_2](THF)$ ((±)-**4**; Ar' = 2,6-$C_6H_3Me_2$) was prepared from (±)-$BINO(SiMe_2Ph)_2K_2$ and $Mo(CHCMe_2Ph)(NAr')(OTf)_2(DME)$[26] in a manner analogous to that used to prepare (±)-**3**. NMR spectra of (+)-**1**, (–)-**1**, and (+)-**2** show an H_α and C_α resonance for a single alkylidene rotamer, while NMR spectra of (±)-**3** and (±)-**4** suggest that they are mixtures of anti and syn rotamers.[27,28] (See supplementary material.)



R_4tartH_2



$BINO(SiMe_2Ph)_2H_2$



Bipheno(t-Bu)$_4H_2$

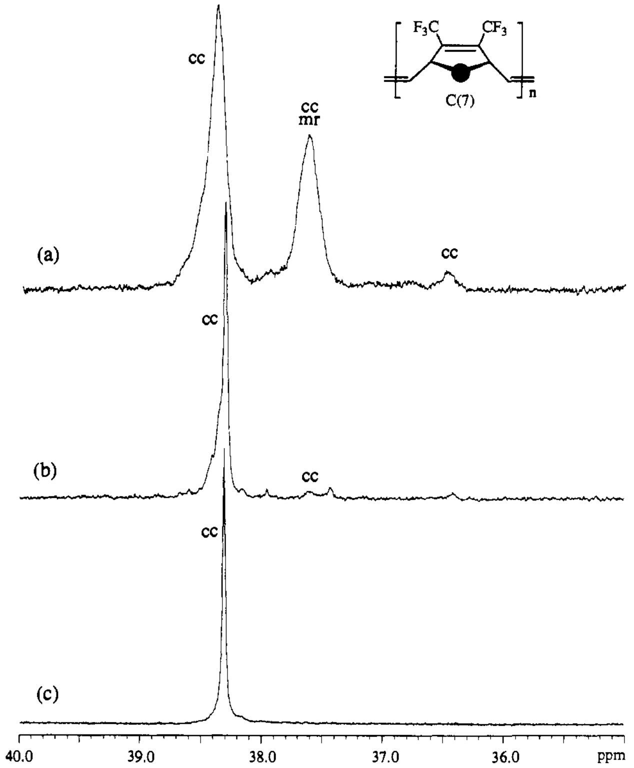


Figure 1. C(7) region of the 125.69-MHz ^{13}C NMR spectrum in acetone-d_6 of poly(NBDF6) prepared with initiator (a) $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$; (b) (+)-**2**; and (c) (±)-**4**.

The cis/trans ratio in poly(NBDF6) is determined readily and accurately by ^{13}C NMR,[5,6] while tacticity can be determined at the triad level by analyzing the resonances for C(7), as shown in Figure 1a.[6] The resonance at 38.38 ppm in Figure 1a can be assigned to C(7) in a tactic polymer (cc,mm or cc,rr triad), while that at 37.61 ppm can be assigned to C(7) in an atactic polymer (cc,mr triad).[6] The resonance at 36.44 is assignable to C(7) in

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Table I. Poly(2,3-bis(trifluoromethyl)norbornadiene)[a]

catalyst	cis (%)	cis tactic (%)	equiv	M_n[b]	M_w/M_n[b]	yield (%)
$Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$[c]	97	74	100	19 500	1.05	85
$Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Ph_4tart]$ (+)-**1**	98	88	100	14 000	1.05	95
$Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Nap_4tart]$ (+)-**2**[d]	97	97	100			85
$Mo(CH\text{-}t\text{-}Bu)(NAr)[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ (±)-**3**	71	86	100	11 200	1.06	87
$Mo(CHCMe_2Ph)(NAr')[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ (±)-**4**[e]	>99	>99	200			97

[a] All polymers were prepared in THF, unless otherwise noted. [b] Determined by GPC in THF versus polystyrene standards. [c] Prepared as described in ref 6. [d] Prepared in DME. [e] A 28 mer was found to be soluble in THF and had $M_n = 4900$ and $M_w/M_n = 1.09$.

Table II. Poly(2,3-dicarbomethoxynorbornadiene)[a]

catalyst	cis (%)	cis tactic (%)	equiv	M_n[b]	M_w/M_n[b]	yield (%)
$Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$[c]	98	73	100	16 400[d]	1.04[d]	86
$Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Ph_4tart]$ (+)-**1**[e]	93	93	100	23 000	1.60	85
$Mo(CHCMe_2Ph)(NAr)[(+)\text{-}Nap_4tart]$ (+)-**2**	93	97	100	51 500	2.38	80
$Mo(CHCMe_3)(NAr)[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ (±)-**3**	93	97	100	34 000	1.84	94
$Mo(CHCMe_2Ph)(NAr')[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ (±)-**4**	>99	>99	100	28 700[f]	1.28[f]	97
$Mo(CH\text{-}t\text{-}Bu)(NAr)[Bipheno(t\text{-}Bu)_4]$ **5**	>99	96	250	56 000	1.33	95

[a] All polymers were prepared in THF, unless otherwise noted. [b] Determined by GPC in CH_2Cl_2 versus polystyrene standards. [c] Prepared in DME as described in ref 4. [d] GPC analysis performed in THF. [e] Prepared in DME. [f] Prepared in CH_2Cl_2/THF (4:1).

a polymer whose tacticity is different than that which gives rise to the C(7) resonance at 38.38 ppm, while the minor broad resonances in Figure 1a can be ascribed to C(7) in ct triads.

Poly(NBDF6) prepared from (+)-**2** in DME (97% cis; Table I) precipitates as it is being formed. The fact that the polymer is relatively insoluble in DME, dichloromethane, toluene, and THF (although soluble in acetone) prevented determination of molecular weight and polydispersity by GPC. The C(7) region of the ^{13}C NMR spectrum of this polymer in acetone-d_6 (Figure 1b) shows primarily one carbon resonance (at 38.31 ppm), consistent with a tacticity of 97% for the all-cis triads (Table I) on the basis of the cc assignments shown in Figure 1b. Poly(NBDF6) prepared from (+)-**1** in DME or THF, which was identical to that prepared from (−)-**1** in DME or THF, was soluble in THF and had a lower all-cis tacticity (88%; Table I). (A higher enantioselectivity has been observed employing Nap_4tart as a chiral auxiliary instead of Ph_4tart in organic reactions.[14,17])

Poly(NBDF6) prepared using (±)-**3** as the initiator in THF is only ~71% cis, although the tacticity of the all-cis triads is relatively high (86%; Table I). However, poly(NBDF6) prepared from 200 equiv of NBDF6 and (±)-**4** as the initiator was >99% cis and was soluble only in acetone. Its ^{13}C NMR spectrum in the C(7) region is shown in Figure 1c. The narrow 38.31 ppm resonance is virtually the only C(7) resonance present. The ^1H NMR spectrum of this polymer is also relatively sharp and well-resolved. (See supplementary material.) Therefore we propose that this polymer is at least 99% tactic. The vastly improved cis/trans ratio and percent tacticity upon changing from isopropyl groups to methyl groups in the imido ligand of the initiator is striking. An oligomer of poly(NBDF6) (28 mer) prepared using (±)-**4** *is* soluble in THF and has a molecular weight (4900 versus polystyrene) and polydispersity (1.09) consistent with a living ROMP polymerization.

In order to test whether tacticity control is possible with other norbornadiene derivatives, we prepared samples of poly(2,3-dicarbomethoxynorbornadiene) using **1**, **2**, **3**, and **4** as initiators and compared them with poly(DCNBD) prepared employing $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ in DME[4] as shown in Table II. (^{13}C NMR spectra of poly(DCNBD) are closely analogous to those for poly(NBDF6).) The percent tacticity for poly(DCNBD) was at least as high as that for poly(NBDF6) in every case involving a chiral initiator.

Finally, we prepared $Mo(CH\text{-}t\text{-}Bu)(NAr)[Bipheno(t\text{-}Bu)_4]$ (**5**) by adding $Bipheno(t\text{-}Bu)_4K_2$ to $Mo(CH\text{-}t\text{-}Bu)(NAr)(OTf)_2(DME)$ in THF. The $Bipheno(t\text{-}Bu)_4$ ligand has been shown to "flip" rapidly on the NMR time scale in some lanthanide complexes,[29] although it is "locked" on the NMR time scale (300 MHz) in **5** at 25 °C. We were somewhat surprised to find that poly(DCNBD) (250 mer) prepared from **5** in THF was >99% cis and 96% tactic.

We have now proven by proton NMR that all cis polymers prepared from enantiomerically pure dicarboalkoxynorbornadienes are isotactic, while the all trans polymers are syndiotactic.[30] Therefore we believe that the all-cis, tactic polymers prepared here are also isotactic, and that a bias toward isotacticity by chain end control using $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ as the initiator is being enhanced by site control at a chiral metal center. Future studies will be aimed at determining under what conditions other monomers can be polymerized stereoselectively. One might also consider the possibility that catalysts such as (+)-**1** or (+)-**2** or enantiomerically pure versions of **3** or **4** could selectively polymerize or ring-close[31,32] one enantiomer in a racemic mixture.

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Supplementary Material Available: Experimental details and characterization data for compounds **1–5** and polymers NBDF6 and DCNBD (6 pages). Ordering information is given on any current masthead page.

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