Ring-Opening Methathesis Polymerization of (+)- and (±)-*endo*,*exo*-5,6-Dimethylbicyclo[2.2.1]hept-2-ene by Mo(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$

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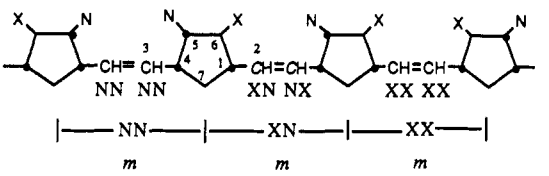
ABSTRACT: Ring-opened polymers of (+)- and (±)-*endo*,*exo*-5,6-dimethylbicyclo[2.2.1]hept-2-ene (1) having cis double bond contents between 5 and 85% were prepared using Mo(CH-*t*-Bu)(NAr)$(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2; OR = $OCMe_3$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$) complexes as initiators. The cis content of the polymers increased in proportion to the electron-withdrawing power of the alkoxide ligands. ^{13}C NMR spectra (125 MHz) of these polymers were interpreted in terms of the various possible diad structures. XX, XN (NX), and NN, where X and N refer to substituents derived from exo and endo methyl groups, *m* and *r* refer to the meso (isotactic) or racemic (syndiotactic) configuration of adjacent cyclopentane rings in the chain, and *tt*, *tc* (*ct*), and *cc* refer to the cis/trans double bond sequences. High-cis polymer made from 98% (+)-1 contained 78% *m* diads and had more than twice the optical rotatory power and a higher T_g (85 °C) than the high-trans polymer (48% *m* diads; T_g = 55 °C).

Introduction

Molybdenum alkylidene complexes of the type Mo(CHR′)(NAr)$(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2; OR = various alkoxides and phenoxides; R′ = CMe_3 or CMe_2Ph) (**2**) are useful initiators for the living ring-opening metathesis polymerization of cyclic olefins.[1-6] Recently, it has been shown that syn and anti rotamers can have dramatically different reactivities and that the rate at which they interconvert correlates with the cis/trans (*c*/*t*) content in polymers of 2,3-bis(trifluoromethyl)norbornadiene and 2,3-dicarbomethoxynorbornadiene.[7]

The microstructure of polynorbornenes and norbornadienes may be determined by ^{13}C NMR studies.[8] The polymers that have been studied include various methyl-substituted norborn-2-enes (*exo*-5-methyl,[9] *endo*-5-methyl,[10] *syn*- and *anti*-7-methyl,[5,11] 1-methyl,[12,13] 5,5-dimethyl,[14,15] *endo*,*endo*-5,6-dimethyl,[16] *exo*,*exo*-5,6-dimethyl,[16] and *endo*,*exo*-5,6-dimethyl[16]) as well as norbornene itself.[17,18] Polymers have been obtained that have a range of cis double bond contents (σ_c = 0–1) employing various classical metathesis catalysts as initiators. In all cases, one can observe *cc*, *ct* (*tc*), and *tt* pairs in the ^{13}C NMR spectra of polymers that contain appreciable proportions of both cis and trans double bonds. For polymers made from unsymmetrical monomers fine structure also arises from the presence of head–head (HH), head–tail (HT), and tail–tail (TT) structures. A third type of fine structure, which is observed only for some carbon nuclei in certain polymers, arises from the fact that neighboring cyclopentane rings in the polymer chain may have either an isotactic (*m*) or syndiotactic (*r*) relationship. Tacticity has been determined by ^{13}C NMR methods for polymers made from unsymmetrical monomers.[9,12-15] In these studies when partially resolved enantiomeric monomer mixtures are employed, the *m*/*r* ratio can be determined directly from the HT/HH ratio.

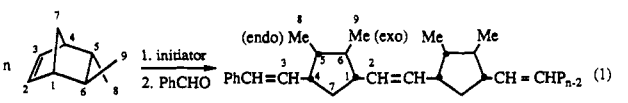
Poly(*endo*,*exo*-5,6-dimethylnorbornene) has been prepared previously, but only from (±)-**1**, using conventional initiators such as $RuCl_3$, $IrCl_3$, and WCl_6/Bu_4Sn; the resulting polymers had a rather limited range of σ_c (0–0.3).[16] Such polymers exhibit a form of HH, HT, and TT isomerism that is more conveniently defined in terms of the relative positions of the substituents derived from the *endo*-methyl (N) and *exo*-methyl (X) substituents in the monomer. Thus one may distinguish between NN, XN, and XX diads. The carbons on the X side of an XN diad

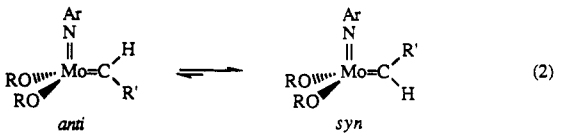


3 (derived from (±)-**1**; NX notation)

are designated as XN and have different chemical shifts from those on the N side, which are designated as NX. As drawn, all the tactic diads are *m* due to the opposite configuration of the allylic carbons on either side of the double bond. The double bonds may be *c* or *t*; note that adjacent cyclopentane rings will point in opposite directions in the trans isomer if the stereochemical relationship of the two allylic carbons is meso. The two central monomer units in **3** are derived from one enantiomer, and the outer two from the other enantiomer. The ^{13}C NMR spectra of the high-trans polymers showed evidence of *m*/*r* splittings, but the *m* and *r* assignments had to be made by analogy with related polymers.[16]

In the present work we report the preparation and polymerization of (+)-**1** (eq 1) as well as (±)-**1**, initiated by **2a**, **2b**, or **2c** (eq 2) to give polymers that have a much





2 a, OR = $OCMe_3$; **2b**, OR = $OCMe_2(CF_3)$; **2c**, OR = $OCMe(CF_3)_2$

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Table 1. Properties of Polymers Made from (+)-1 and (±)-1 Using Initiators 2a, 2b, or 2c[a]

monomer[b]	initiator	polymer	yield (%)	σ_c[c]	$10^{-4}M_n$[d]	$10^{-4}M_n$[e]	M_w/M_n	$[\alpha]_D$[h] (deg)	T_g (°C)
(+)-1	2a	(−)-3a	94	0.05	2.1	1.2[f]	1.03	−23.8	55
(±)-1	2a	3a	91	0.05	1.7	1.4	1.03		55
(+)-1	2b	(−)-3b	96	0.58	2.7	1.6	1.15	−31.7	75
(±)-1	2b	3b	93	0.44	1.5	1.5	1.13		71
(+)-1	2c	(−)-3c	97	0.85	3.8	2.4[g]	1.20	−53.6	85
(±)-1	2c	3c	95	0.85	0.9	1.2	1.19		79

[a] [1]/[2] = 100, except where indicated; [f,g] solvent = THF. Polymer was cleaved from the metal with benzaldehyde. [b] (+)-1: $[\alpha]_D$ = 72.8° (c = 2.8 g/dL in $CHCl_3$ at 20 °C; optical purity (ee) 96%). [c] Fraction of cis double bonds, as determined from the C_1 or C_8 fine structure in the ^{13}C NMR spectra. Infrared bands at 970 (trans) and 745 cm^{-1} (cis) provide qualitative confirmation for the cis and trans assignments. [d] Measured by absorbance detector (254 nm) relative to polystyrene standards. For 100% conversion of monomer, complete consumption of initiator, and allowance for $Me_3CCH=$ and =CHPh end groups, calculated M_n values would be 1.2×10^4. [e] Measured by on-line viscometry; calculated $M_n = 1.2 \times 10^4$. [f] [1]/[2] = 115; M_n(calcd) = 1.4×10^4. [g] [1]/[2] = 133; M_n(calcd) = 1.6×10^4. [h] Concentration = 2.8 g dL^{-1} in $CHCl_3$ at 20 °C.

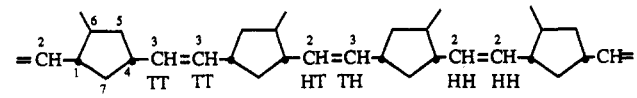
wider range of cis content (σ_c = 0.05–0.85) than heretofore obtained. Compounds **2a**, **2b**, and **2c** are known to be mixtures of anti and syn rotamers, with the syn rotamer being highly favored.[7] ^{13}C NMR spectra also were obtained at a higher frequency (125 MHz) than in previous studies (62.8 MHz),[16] and DEPT and HETCOR pulse sequences were also employed to assist in assignments. Therefore, a more accurate and detailed interpretation of the ^{13}C NMR spectra has become possible.

Results

Three polymers were prepared in >90% yields from (+)-1 and three from (±)-1. The cis content was determined from ^{13}C NMR spectra as described elsewhere;[16] the results are listed in Table 1. The polydispersities of the polymers are all low ($M_w/M_n < 1.2$), except for (−)-3, which suggests that these polymerization reactions are living and that the observed polymer structure is that produced in the primary polymerization reaction. M_n values determined by comparison with polystyrene standards were not consistent with the molecular weights calculated on the basis of the number of equivalents of monomer employed, but measurement of molecular weight by on-line viscometry gave molecular weight values close to those calculated, except for (−)-3c; the latter result suggests that a conformation other than a random coil is adopted by (−)-3c. T_g values increase with increasing cis content of the polymer, although not dramatically. Optical rotations of (−)-3a, (−)-3b, and (−)-3c are negative, while the optical rotation of the monomer is positive (Table 1), and increase in magnitude as σ_c increases. However, CD spectroscopy showed only a transition analogous to that found for the monomer. Apparently, if an ordered structure is adopted in solution, that structural form either is not inherently chiral, or if it is inherently chiral (e.g., a helix), one chirality is not favored over the other to a significant degree, even when the monomer itself is chiral.

The olefinic carbon regions in the spectra of the six polymers are shown in Figure 1a–f. The spectrum of high-trans 3a (Figure 1b) is similar to but better resolved than the reported spectrum of the polymer prepared employing $RuCl_3$;[16] three groups of resonances are observed for C_2 and three for C_3 in the approximate intensity ratio 1:2:1. Each group of C_2 resonances shows further incipient splitting. In the spectrum of high-trans (−)-3a (Figure 1a) the center C_2 resonance and the two outer C_3 resonances in Figure 1b are weak or missing, while the splitting of the two outer C_2 resonances is now well-resolved. Assignments made for high-trans polymer in previous work involved some assumptions.[16] Here we shall reconsider the problem *ab initio*.

A method that usually is reliable for making diad assignments is to compare the observed line positions with those predicted using known substitution parameters. We may start from the line positions in the polymer of *exo*-5-methylnorbornene (4),[9] renumbering to place the methyl



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groups in the 6-position, and add the *endo*-5-methyl substitution parameters derived from a comparison of the line positions for the polymers of norbornene[18] and *endo*-5-methylnorbornene.[10] The result of this exercise for both trans and cis polymers is shown in Table 2. To use this information, we must examine the types of diad structures possible in poly-(+)-1 and poly-(±)-1.

The only possibilities for poly-(+)-1 ((−)-3a, (−)-3b, and (−)-3c) are XX *r* and XN *m* for C_2 and NX *m* and NN *r* for C_3. For polymers made from (±)-1 (3a, 3b, and 3c) there are four additional possibilities: XX *m* and XN *r* for C_2 and XN *r* and NN *m* for C_3. Comparing Figure 1a with Figure 1b for the trans polymers ((−)-3a and 3a), one may therefore identify the central C_2 resonance in Figure 1b as a combination of XX *m* and XN *r*, while the outer resonances must be due to XX *r* and XN *m*. Likewise the central C_3 resonance, which is common to both Figure 1a and Figure 1b, must be assigned to a combination of NX *m* and NN *r*, while the outer resonances must be due to NX *r* and NN *m*. To decide which of the outer resonances is which in Figure 1b we may compare the predicted line positions (which take no account of *m*/*r* splitting) with the average positions of the four pairs of peaks. This results in the assignment of the trans peaks listed in Table 2. The predicted line positions are slightly displaced from the observed average *m*/*r* positions but the relative positions agree within 0.1 ppm. The *r*/*m* splittings for all four diads are in the same direction and of similar magnitude ($\delta_r - \delta_m = 0.18 \pm 0.05$ ppm). The intensities in Figure 1a indicate that the trans diads are atactic ($(\sigma_m)_t = 0.48$), while those in Figure 1b indicate that the structure is unbiased with respect to XN: (XN + NX)/(XX + NN) ~ 1.

The main peaks in Figure 1a arise from trans olefinic carbons in which the next nearest double bond is also trans (*tt*). However, the sample contains 5% cis double bonds and the small pairs of peaks upfield from the two main pairs between 134 and 133 ppm are ascribed to the corresponding structures for *tc* pairs. The inequality of the two components of these small signals in the spectrum of 3a suggests that, as in 3c (see below), the cis diads are predominantly isotactic (*m*). The shoulder and small peak slightly upfield from the main C_3 peak in Figure 1a are also probably accountable in terms of *tc* counterparts of the two overlapping *tt* peaks (NX *m* and NN *r*). All *tc*

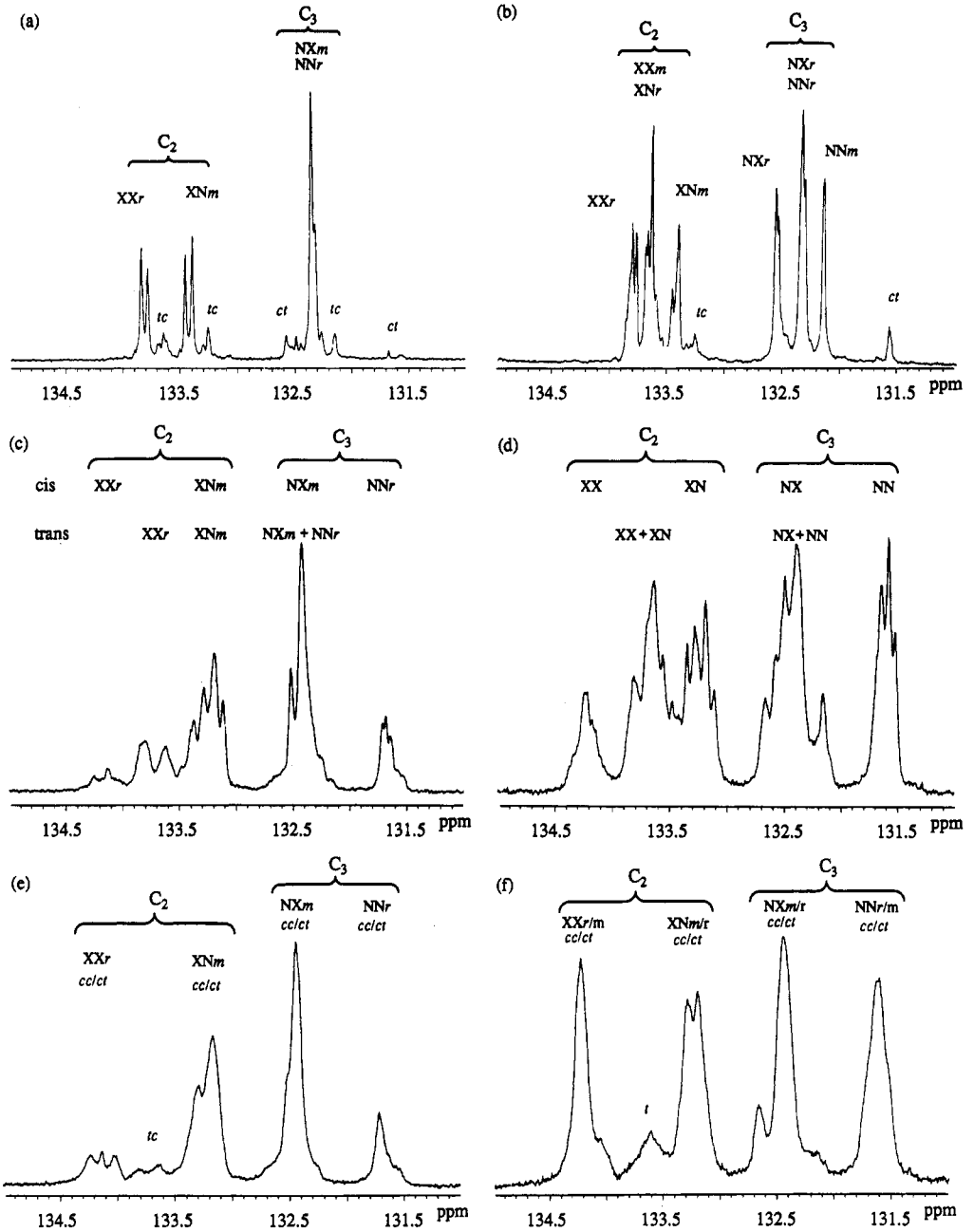

Figure 1. 125-MHz $^{13}C\{^1H\}$ NMR spectra of the olefinic carbons in polymers **3a–c**: (a) (−)-**3a**, $\sigma_c = 0.05$; (b) **3a**, $\sigma_c = 0.05$; (c) (−)-**3b**, $\sigma_c = 0.58$; (d) **3b**, $\sigma_c = 0.44$; (e) (−)-**3c**, $\sigma_c = 0.85$; (f) **3c**, $\sigma_c = 0.85$. In (d) only the main lines from (b) and (f) are marked. The other lines arise from *cc/ct* and *tt/tc* splittings.

peaks should have matching *ct* signals. Two of these are in the positions indicated; the others must be hidden.

The spectrum of **3c** (Figure 1f) consists of essentially four equal resonances for the cis diads. The predicted line positions of the outer lines (XX, NN) are in good agreement with those observed, while the inner lines are somewhat farther apart than predicted (Table 2). However, the overall agreement can be considered satisfactory, with the line order the same as for the trans resonances: XX, XN, NX, NN. There is no obvious *m/r* splitting, but it is readily apparent from the spectrum of (−)-**3c** (Figure 1e) that XN = NX > XX = NN; i.e., that $(\sigma_m)_c > (\sigma_r)_c$. It is estimated that $(\sigma_m)_c = 0.78$ for this polymer.

The spectra of the polymers of intermediate cis content, (−)-**3b** and **3b** (Figure 1c,d), are more complex because of *cc/ct* and *tt/tc* splittings. The correlation of line positions and assignments for the three polymers of (+)-**1** are given in Table 3. In Table 4 are listed the additional lines seen in the spectra of high trans (**3a**, Figure 1b) and high cis (**3c**, Figure 1f) polymers of (±)-**1**.

The line order for *r,m* deduced here is the same as that derived on a different basis in previous work,[16] but the line order XX, XN, NX, NN is different from thatpreviously deduced (XN, XX, NN, NX) on the assumption that the Ru-TFA-initiated trans polymer was fully XN biased. (Ru-TFA is a complex of approximate formula $Ru_2(CF_3CO_2)_4 \cdot 3H_2O$.)[11] The interpretation of the four-line spectrum of the olefinic carbons in the Ru-TFA-initiated polymer cannot yet be made because the relative line positions do not match exactly those reported here. (Note added in proof: It is now believed that the four-line spectrum of the olefinic carbons in the Ru-TFA-initiated polymer is to be interpreted in terms of an isotactic unbiased structure. Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J., unpublished work.) On the basis of how the lines match up, one of four outcomes is possible: (i) atactic, alternating XX–NN; (ii) syndiotactic, unbiased; (iii) isotactic, unbiased; (iv) atactic, fully XN biased. Further experimental work will be required to settle this issue.

Table 2. Predicted (from Shifts in 4) and Observed ^{13}C Chemical Shifts[a] (ppm) in the Spectra of 3a and 3c

carbon in 4		subst param	carbon in 3	pred	obs(av)	obs
			Trans Polymer (3a)			
C_2 HH	133.26	0.23	C_2 XX	133.49	133.75	133.81[c] *r*
				(0.21)[b]	(0.18)[b]	133.68 *m*
C_2 HT	131.45	1.83	C_2 XN	133.28	133.56	133.66 *r*
				(1.01)	(1.10)	133.45[c] *m*
C_3 TH	135.46	−2.89	C_3 NX	132.27	132.46	132.57 *r*
				(0.27)	(0.20)	132.34 *m*
C_3 TT	133.43	−1.43	C_3 NN	132.00	132.26	132.34 *r*
						132.16 *m*
			Cis Polymer (3c)			
C_2 HH	133.82	0.43	C_2 XX	134.25	134.22	
				(1.17)	(0.98)	
C_2 HT	131.92	1.16	C_2 XN	133.08	133.24	133.28[d]
				(0.39)	(0.81)	133.19[d]
C_3 TH	136.15	−3.46	C_3 NX	132.69	132.43	
				(1.01)	(0.82)	
C_3 TT	134.42	−2.74	C_3 NN	131.68	131.61	

[a] Listed in order of decreasing chemical shift. [b] Bracketed values are differences between successive shifts. [c] Split further into doublet (see Figure 1a), attributed to *rr*/*rm* triads for C_2 XX and *mm*/*mr* triads for C_2 XN. [d] The source of this splitting is not known.

Table 3. Line Positions and Assignments for Olefinic Carbons (C_2, C_3) in Polymers (−)-3a (σ_c = 0.05), (−)-3b (σ_c = 0.58), and (−)-3c (σ_c = 0.85)

chem shift (ppm)			assignment[a]			
			trans		cis	
(−)-3a	(−)-3b	(−)-3c				
	134.25	134.24				
	134.14	134.13			C_2 *cc*/*ct*	XX *r*
	134.0[c]	134.03				
133.83[b]	133.82	133.81	C_2 *tt*	XX *rr*/*rm*		
133.78[b]						
133.68			C_2 *tc*	XX *rr*		
133.63	133.62	133.63	C_2 *tc*	XX *rm*		
133.45[b]			C_2 *tt*	XN *mr*/*mm*		
133.39[b]	133.37					
133.30			C_2 *tc*	XN *mr*		
133.26	133.29	133.28	C_2 *tc*	XN *mm*		
	133.19[b]	133.16[b]			C_2 *cc*/*ct*	XN *m*
	133.12	(sh)				
132.57			C_3 *tc*	(?)		
132.49	132.52	132.5[c]			C_3 *ct*	NX *m*
132.35[b]	132.42[b]	132.43[b]	C_3 *tt*	NX *m*	C_3 *cc*	NX *m*
				NN *r*		
132.17			C_3 *tc*	(?)		
131.71	131.67	131.71			C_3 *cc*/*ct*	NN *r*
131.60	131.64	131.6[c]				

[a] *cc*/*ct* implies that *cc* and *ct* resonances are resolved but individual assignments are uncertain; likewise for *rr*/*rm* and *mr*/*mm*. [b] Main peaks. [c] Shoulder.

^{13}C NMR spectra upfield of the olefinic carbon region for the six polymers are shown in Figure 2a–f. Consider first the spectra of the high-trans polymers (−)-**3a** and **3a** (Figure 2a,b). The spectrum of **3a** is a much better resolved version of that previously published (prepared employing $RuCl_3$).[16] Note in particular the considerable fine structure observed for the closely separated C_4 and C_5 resonances; only a single unresolved resonance was observed in the 62.9-MHz spectrum. Line positions and assignments are listed in Table 5. The overall assignments of resonances to C_1, C_6, C_4 and C_5, and C_7 were made by comparing observed and predicted shifts, as was done in the case of C_2 and C_3 (see above). Agreement is only within 1.5 ppm, which reflects the fact that the cumulative effect of *endo*-5-methyl and *exo*-6-methyl substitutions is not additive. The assignment for C_7 was confirmed by a DEPT experiment and the assignments for C_4 and C_5 were determined by means of a HETCOR 2D (^{13}C–^1H) experiment.

Table 4. Assignment and Line Positions for Olefinic Carbons in Polymers 3a (σ_c = 0.05) and 3c (σ_c = 0.85) for Those Resonances Not Listed in Table 3

chem shift (ppm)		assignment			
		trans		cis	
3a	3c				
	134.22			C_2 *cc*/*ct*	XX *m*[a]
133.68[b]		C_2 *tt*	XX *m*		
133.66[b]		C_2 *tt*	XN *r*		
	133.28			C_2 *cc*/*ct*	XN *r*[a]
	133.19				
132.57		C_3 *tt*	NX *r*		
132.14		C_3 *tt*	NN *m*		
	132.43			C_3 *cc*/*ct*	NX *r*[a]
	131.61			C_3 *cc*/*ct*	NN *m*[a]

[a] *m*/*r* unresolved. [b] Overlap with C_2 *tc* XX *r* peaks (Table 3) should be noted.

The fine structure in Figure 2a shows that the shifts for C_6, C_5, and C_8 are sensitive to *m*,*r* diads, while those for C_1, C_4, C_7, and C_9 are sensitive to *mm*, *mr*, *rm*, and *rr* triads, correlated with X,N structure in each case. It is clear from the relative intensities that the trans-centered diads are nearly atactic, as already concluded from the intensities for the olefinic carbons. Thus it is difficult to make absolute assignments; those shown in Table 5 are made from the relative intensities on the assumption that σ_m is slightly less than 0.5. Confirmation of these assignments would require the preparation of a more tactic high-trans polymer.

In **3a** (Figure 2b), there are four possible diad structures, as listed for C_6 in Table 5, and sixteen possible triad structures. Hence the spectrum is more complex and difficult to interpret because of the overlap of numerous lines. Thus the sixteen possible environments for C_7 give rise to three lines in the approximate ratio 2:6:8, while for C_1 and C_9 there is a somewhat different distribution. A curious feature of the spectrum in Figure 2a is the gap around 44.8 ppm. The intense resonance in this position in Figure 2b evidently stems mainly from C_5 NN *m* and NX *r* but may also contain a contribution from C_4 triads.

Let us now consider spectra of the high-cis polymers, (−)-**3c** and **3c** (Figure 2e,f). The line positions and assignments for the non-olefinic carbons are listed in Table 6. Small peaks due to the presence of 15% trans double bonds are marked on the spectrum in Figure 2e. A DEPT spectrum showed that the *c*-C_4 resonance overlapped with a small *t*-C_7 resonance. *c*-C_1 and *c*-C_5 are predicted to have very similar shifts, but in fact they are separated by ca. 1.1 ppm. *c*-C_1 was identified as the downfield resonance from its position relative to *t*-C_1: $\delta_t - \delta_c$ = 5.1 ppm, consistent with the range of values normally found for α-carbons in cis and trans isomers. Likewise $\delta_t - \delta_c$ = 5.7 ppm for C_4. These assignments were confirmed by a HETCOR 2D (^{13}C–^1H) experiment.

The pattern of fine structure for the high-cis polymers is rather different from that of the trans polymers. On the one hand, there is a marked bias toward isotactic diads (see C_2 and C_3 spectra), making assignment of the fine structure in Figure 2e relatively easy. On the other hand, there is practically no *m*/*r* splitting of the individual XN, XX, NN, or NX signals in Figure 2f, except perhaps for C_4 NN (Table 6). C_6 and C_9 show no XX/XN splitting, nor does C_8 show an NN/NX splitting. However, C_1 is split (XX/XN), as are C_4 and C_5 (NN/NX), and C_7 shows triad sensitivity. The values of $(\sigma_m)_c$ derived from the C_1 and C_5 fine structure in Figure 2e were 0.77 and 0.78,

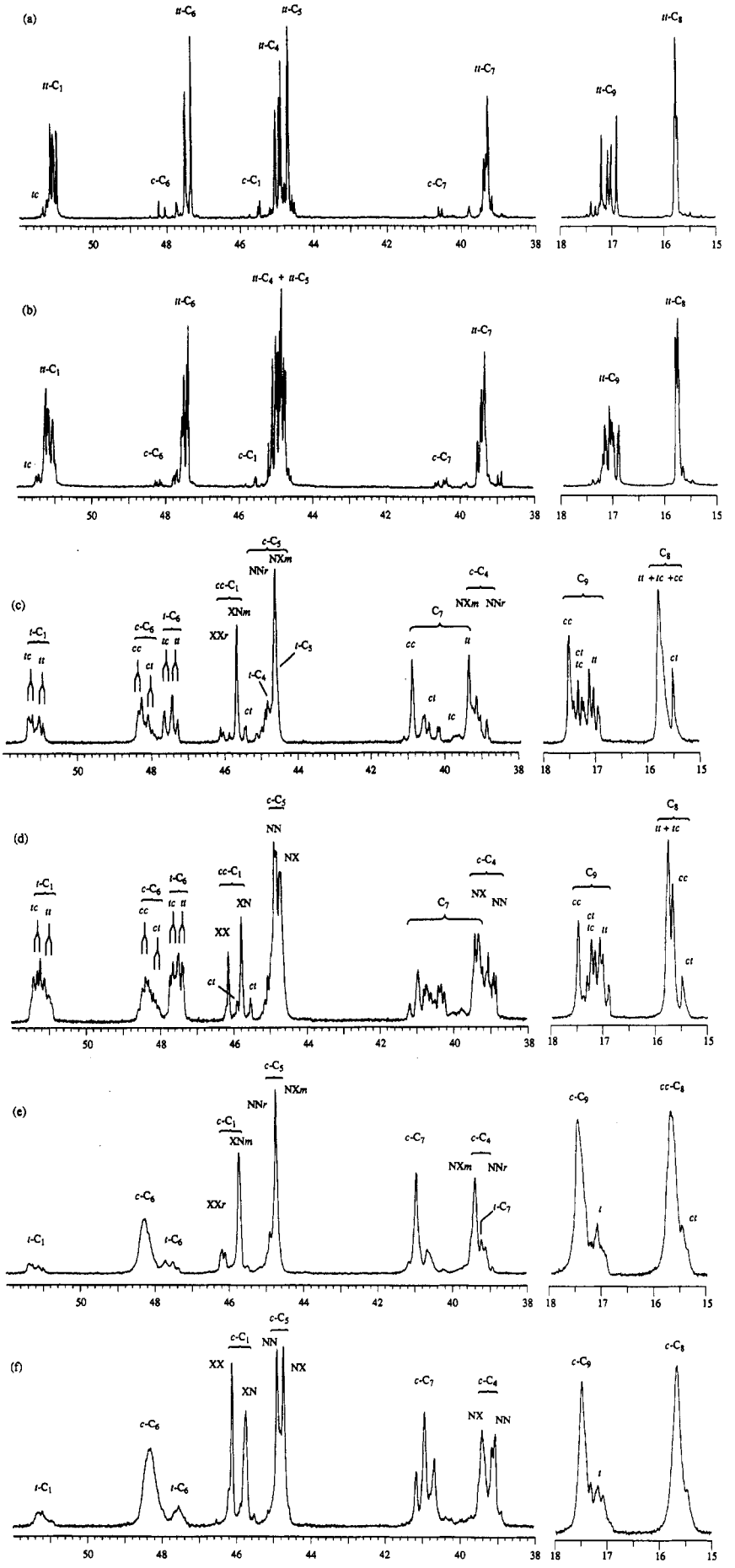

Figure 2. 125-MHz $^{13}C\{^1H\}$ NMR spectra of the ring and methyl carbons in polymers **3a–c**: (a) (−)-**3a**, $\sigma_c = 0.05$; (b) **3a**, $\sigma_c = 0.05$; (c) (−)-**3b**, $\sigma_c = 0.58$; (d) **3b**, $\sigma_c = 0.44$; (e) (−)-**3c**, $\sigma_c = 0.85$; (f) **3c**, $\sigma_c = 0.85$.

Table 5. Predicted and Observed Line Positions and Assignments for the Ring and Methyl Carbons in (−)-3a and 3a (Figure 2a,b) (Only *tt* Peaks Are Listed)

δ (ppm) for 4[a]	subst param[b] (ppm)	pred δ (ppm) for 3	carbon	obs δ (ppm) for (−)-3a	provisional assignment[c] for (−)-3a	obs δ (ppm) for 3a
				51.16	NN − XX *rr*	51.22
						51.17
						51.15
52.2	−1.1	51.1	C_1	51.09	XN − XX *mr*	51.13
				51.07	NN − XN *rm*	51.11
				50.99	XN − XN *mm*	51.02
				47.50	XN *m*	47.51
39.7	9.4	49.1	C_6		XN *r* / XX *m*	47.48 / 47.39
				47.33	XX *r*	47.36
						45.15
				45.06	NX − NX *mm*	45.08
				45.04	XX − NX *rm*	45.05
40.6	2.9	43.5	C_4	44.94	NX − NN *mr*	44.97
				44.89	XX − NN *rr*	44.92
						44.86[d]
						44.82[d]
41.0	4.9	45.9	C_5	44.71	NX *m*	44.75
				44.68	NN *r*	44.71
						39.49
				39.39	XN–XN *mm*	39.39
41.8	−2.2	39.6	C_7	39.33	XN–XX *mr*	39.31
				39.28[e]	NN–XN *rm*	
					NN–XX *rr*	
				17.20	XN − XN *mm*	17.17
			C_9(X)	17.09	NN − XN *rm*	17.08
				17.01	XN − XX *mr*	17.03
				16.91	NN − XX *rr*	16.92
			C_8(N)	15.77	NN *r*	15.79
				15.74	NX *m*	15.74

[a] Reference 9. Average values in the cases where there is fine structure. [b] On the basis of line positions for polymers of norbornene and *endo*-5-methylnorbornene. [c] Based on the assumption that $(\sigma_m)_t < 0.5$. The unassigned lines in the spectrum of **3a** arise from the presence of additional structures, not possible in (−)-**3a**; e.g., for C_1 the NN–XX sequences may be *mm*, *mr*, *rm*, or *rr*. Underlining in the table denotes the unit within which the relevant carbon is contained. [d] Assigned mainly to C_5 NN *m* and NX *r* but may contain a contribution from C_4. [e] Double-intensity peak arising from two of the possible four structures listed.

Table 6. Predicted and Observed Line Positions and Assignments for the Ring and Methyl Carbons in (−)-3c and 3c (Figure 2e,f) (Only *cc* Peaks Are Listed)

δ (ppm) for 4[a]	subst param[b] (ppm)	pred δ (ppm) for 3	carbon	obs δ (ppm) for (−)-3c	assignment[c] for (−)-3c	obs δ (ppm) for 3c
40.7	9.2	49.9	C_6	48.24	XN *m* / XX *r*	49.28
				46.17	XX *r*	sh[d]
47.5	−1.2	46.3	C_1	46.09	XX *r*	46.08
				45.71	XN *m*	45.72
42.0	4.4	46.4	C_5	44.88	NN *r*	44.87
				44.71	NX *m*	44.71
				sh	NN–XX *rr*	41.14
43.0	−1.8	41.2	C_7	40.94	XN–XN *mm* / NN–XN *rm*[e]	40.91
				40.66	XN–XX *mr*[e]	40.66
				39.38	NX *m*	39.39
36.0	2.1	38.1	C_4	39.10	NN *r*	39.12
						39.04[f]
			C_9(X)	17.45	XN *m* / XX *r*	17.48
			C_8(N)	15.64	NN *r* / NX *m*	15.64

[a] See footnote *a* in Table 5. [b] See footnote *b* in Table 5. [c] Based on the fact that $(\sigma_m)_c = 0.78$ (from C_2 and C_3 intensities). [d] Shoulder. [e] *mr* and *rm* assignments may be reversed. [f] Assigned to NN *m*. No other resonances for **3c** show *m*/*r* splitting.

respectively, in good agreement with that derived from C_2 and C_3 (0.78). The fine structure for C_1, C_5, C_7, and C_4 in Figure 2f indicates at most only a slight NX bias in the high-cis polymer made from the (±)-monomer (NX/NN = XN/XX ~ 1.2). The approximately 1:2:1 intensity ratio for the C_7 peaks in Figure 2f indicates that the center peak in Figure 2e corresponds to two of the four triad structures listed in Table 6, but the detailed assignment is uncertain.

The spectra of the polymers of intermediate cis content, (−)-**3b** and **3b** (Figure 2c,d), indicate that the tacticities with respect to cis and trans double bonds are similar to those for the high-cis and high-trans polymers, respectively; i.e., $(\sigma_m)_c \sim 0.8$ and $(\sigma_m)_t \sim 0.5$. Therefore, to a first approximation the tacticities do not depend on the nature of the alkoxy ligands. Additional fine structure due to *cc*/*ct* and *tt*/*tc* splittings is indicated on the spectra. The intensities for the *tt* and *tc* structures are comparable, but that for *cc* is stronger than for *ct* (which is necessarily equal to *tc*). This means that (−)-**3b** and **3b** have a somewhat blocky cis/trans distribution, as commonly

found for metathesis polymerization of norbornene[17,18] and its derivatives.[9-16]

Discussion

One of the two important results that has been revealed in this study is that the cis content of polymers made from these norbornenes correlates with the electrophilicity of the initiator. Such a correlation also has been found when 2,3-bis(trifluoromethyl)norbornadiene and 2,3-dicarbomethoxynorbornadiene are the monomers employed; all-trans polymers are formed when OR = O-*t*-Bu[2] and all-cis polymers when OR = $OCMe(CF_3)_2$.[6] This work establishes that the formation of high-trans or high-cis polymers is not restricted to norbornadienes but appears to be a general feature of such catalysts of this type. One potentially important feature of catalysts is that the rate of isomerization of anti and syn alkylidene rotamers varies by many orders of magnitude, being relatively fast in **2a** ($\sim 1\ s^{-1}$) and slow in **2c**.[7] It is now believed that cis double bonds result from monomer addition to the syn alkylidene and that trans double bonds are formed upon addition of monomer to the anti alkylidene (or to some other more reactive intermediate during alkylidene rotamer isomerization), even though only syn rotamer can be observed readily in solution.[19] The trans content of the polymers prepared here employing **2a** is approximately the same as the trans content of poly[2,3-bis(trifluoromethyl)norbornadiene] prepared employing **2a**, but the cis content of the polymers prepared employing **2c** is only ~85% as opposed to essentially 100% in the case of poly[2,3-bis(trifluoromethyl)norbornadiene] prepared employing **2c**.[6] We could only speculate at this stage why **1** is not polymerized by **2c** to give 100% cis polymer.

It is interesting to note that in classical metathesis catalyst systems, all other things being equal, hard ligands such as trifluoroacetate tend to raise the cis content of the polymer.[20] However, the effect of the hard ligand can sometimes be overridden by steric or other factors. Thus with the present monomer, a ruthenium trifluoroacetate catalyst gives an all-trans polymer,[16] while with 1,7,7-trimethylnorbornene, **2c** also gives an all-trans polymer.[21] The latter result can be explained in terms of the relatively low reactivity of syn rotamers toward this bulky monomer; anti rotamers are by far the most reactive and a syn rotamer is the product of monomer insertion,[19] so that the rate of conversion of syn to anti rotamer becomes the rate-limiting step of the polymerization reaction.

A second important finding of the present work is that the trans diads are atactic while the cis diads in the same polymer have an isotactic bias. This is again consistent with the presence of two distinct propagating species, one adding monomer in two ways to give approximately equal proportions of *t*/*m* and *t*/*r* diads, the other adding monomer to give *c*/*m* diads in preference to *c*/*r* diads. As already discussed here, these two species are likely to be the anti and syn rotamers, respectively, of the propagating metal–alkylidene complex. Different tacticities with respect to cis and trans diads have been observed before with certain classical metathesis catalysts and interpreted in terms of two distinct propagating species,[11,20] though not of the same type as those proposed here. Poly[2,3-bis(trifluoromethyl)norbornadiene] prepared employing **2c**[6] shows a tactic bias of the same magnitude as that observed here for **3c**, but high-trans poly[2,3-bis(trifluoromethyl)norbornadiene] and poly[2,3-dicarbomethoxynorbornadiene] prepared employing **2a** are highly tactic.[2] Recently, we have proven that a variety of high-cis polynorbornadienes and norbornenes, including **1**, that can be prepared with a chiral (racemic) catalyst are isotactic, a result that is consistent with the conclusions reached here, and that all-trans poly[2,3-dicarboalkoxynorbornadienes] in which a chiral group (e.g., menthyl) is present in the ester are syndiotactic.[22] Isotacticity is believed to be the result of addition of monomer to the same Mo=C face in the syn rotamer of each intermediate in the polymerization reaction. In the absence of a chiral ligand on the metal, tacticity is determined by chain-end control. Apparently, the chain-end control that gives rise to all-trans syndiotactic polymers of 2,3-disubstituted norbornadienes is ineffectual in the case of polymerization of **1** by **2a**.

Tacticity (*m* and *r*) and XX/XN/NN-type structures are related in the polymerization of (+)-**1** but are not necessarily related in the polymers derived from (±)-**1**. In the high-cis polymer **3c**, synthesized from (±)-**1**, no XN bias was found. This indicates that the two enantiomers are equally likely to add to the growing polymer chain. However, some selectivity for tacticity was found for these polymers (~4:1 *m*:*r* diads, evidenced by (−)-**3c**). This emphasizes that tacticity does not derive from XN-type selectivity; i.e., the chirality of the chain end is indifferent to the chirality of the incoming monomer. In other catalyst/monomer systems there is either little bias in favor of cis *m* (e.g., $WCl_6/SnBu_4$/*endo*,*endo*-5,6-dimethylnorbornene[16]) or a strong bias in favor of cis *r* (e.g., $ReCl_5$/*endo*,*endo*-5,6-dimethylnorbornene[16]).

Conclusions

The ^{13}C NMR spectra of polymers of *endo*,*exo*-5,6-dimethylnorbornene made with well-characterized molybdenum alkylidene complexes have been assigned in detail. The cis content correlates with the electron-withdrawing ability of the alkoxy ligands, maximizing for the most electron-withdrawing hexafluoro-*tert*-butoxide ligand. The cis-centered diads have an isotactic bias, $(\sigma_m)_c = 0.78$, but the trans-centered diads are atactic, $(\sigma_m)_t = 0.48$. There is no significant XN bias in either cis- or trans-centered diads.

Experimental Section

General Procedures. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. Pyridine was distilled from calcium hydride. The THF used for polymerization reactions was vacuum transferred from sodium benzophenone ketyl and passed through activated alumina prior to use. (−)-Dimenthyl fumarate was prepared by treating fumaric acid and *l*-(−)-menthol (2 equiv) with a catalytic amount of *p*-toluenesulfonic acid in toluene and heating the reaction mixture to reflux until no more water was evolved, as evidenced by separating the water in a Dean–Stark trap. After standard workup, the crude product (oil) was triturated with methanol to yield colorless crystalline material, which was used without further purification. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, Mo(CH-*t*-Bu)(NAr)[$OCMe_2(CF_3)$]$_2$, and Mo(CH-*t*-Bu)(NAr)[$OCMe(CF_3)_2$]$_2$ (Ar = 2,6-diisopropylphenyl) were synthesized as described in the literature.[23,24]

NMR chemical shifts are listed in ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out at room temperature using Shodex KF-802.5, -803, -804, -805, and -800P columns, a Knauer differential refractometer, and either a Spectroflow 757 absorbance detector (254 nm) or a Viscotek H-500 differential refractometer/viscometer on samples 0.1–0.3% w/v in THF that had been filtered through a Millex-SR 0.5-μm filter to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd., 1206 to 1.03 × 10^6 MW). GPC data were analyzed using a Unical 4.03 (Viscotek). A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine glass transition temperatures at a scanning rate of 20 °C/min. Optical rotation was measured at 20 °C with a Perkin-Elmer 24 polarimeter using a sodium lamp set at 589 nm (cell length = 1.0 dm).

Preparation of Monomer. (+)-(2*S*,3*S*)-Dicarbomenthoxynorborn-5-ene ((+)-**5**) was prepared by the asymmetric Diels–Alder reaction[25,26] of cyclopentadiene (0.608 mol) and *l*-(−)-dimenthyl fumarate (0.405 mol) in the presence of diethylaluminum chloride (0.446 mol) in toluene (500 mL) at −78 °C under argon. Standard workup procedures, followed by recrystallization from methanol gave (+)-**5** as colorless needles (yield 87%; $[\alpha]_D$ = +1.2°, *c* = 10.0 g/dL in $CHCl_3$): ^1H NMR ($CDCl_3$) δ 6.27 (dd, *J* = 5.6, 3.2, 1 H), 6.00 (dd, *J* = 5.5, 2.8, 1 H), 4.66 (ddd, *J* = *J'* = 10.9, 4.3, 1 H), 4.55 (ddd, *J* = *J'* = 10.9, 4.3, 1 H), 3.33 (dd, *J* = *J'* = 4.2, 1 H), 3.24 (broad, 1 H), 3.08 (broad, 1 H), 2.64 (dd, *J* = 4.5, 1.7, 1 H), 1.86–1.99 (m, 4 H), 1.57–1.68 (m, 6 H), 1.32–1.49 (m, 4 H), 0.76–1.06 (m, 6 H), 0.88 (d, *J* = 6.5, 6 H), 0.87 (d, *J* = 6.6, 3 H), 0.86 (d, *J* = 6.4, 3 H), 0.73 (d, *J* = 7.0, 3 H), 0.71 (d, *J* = 7.0, 3 H).

(+)-Norborn-5-ene-(2*S*,3*S*)-dicarboxylic acid ((+)-**6**) was prepared by hydrolysis of **5** (0.351 mol) in hot methanol (1 L) and potassium hydroxide (1.8 mol) at reflux for 14 h under argon. The crude reaction mixture was concentrated to a solid, treated with water (650 mL), and extracted with ether (3 × 280 mL) to remove methanol. The aqueous layer was acidified to pH = 1 and extracted with ether (3 × 280 mL). The ether layers were combined, dried, and concentrated, and the crude product was recrystallized from ethyl acetate/petroleum ether to give colorless crystals of (+)-**6** (86%; $[\alpha]_D$ = +134.8°, *c* = 5.0 g/dL in MeOH): ^1H NMR (THF-d_8) δ 10.68 (broad, 2 H), 6.22 (dd, *J* = 4.2, 3.2, 1 H), 6.06 (dd, *J* = 5.6, 2.7, 1 H), 3.30 (dd, *J* = *J'* = 4.1, 1 H), 3.17 (broad, 1 H), 3.06 (broad, 1 H), 2.58 (dd, *J* = 4.1, 1.6, 1 H), 1.60 (pseudodoublet, *J* = 8.3, 1 H), 1.36 (dd, *J* = 8.3, 1.8, 1 H).

Reduction of (+)-**6** (0.324 mol) with lithium aluminum hydride (1.05 mol) in ether (750 mL) at reflux under argon for 14 h yielded (−)-norborn-5-ene-(2*S*,3*S*)-dimethanol ((−)-**7**) as a colorless liquid after standard workup procedures. This was purified by vacuum distillation (103–104 °C/0.15 mmHg; 88%; $[\alpha]_D$ = −21.5°, *c* = 2.3 g/dL in $CHCl_3$): ^1H NMR ($CDCl_3$) δ 6.21 (dd, *J* = 5.67, *J'* = 3.15, 1 H), 5.96 (dd, *J* = 5.61, *J'* = 2.85, 1 H), 3.76 (dd, *J* = 9.77, *J'* = 5.51, 1 H), 3.65 (dd, *J* = 9.65, *J'* = 5.15, 1 H), 3.40 (dd, *J* = *J'* = 9.95, 1 H), 3.02 (dd, *J* = *J'* = 9.79, 1 H), 2.80 (broad, 1 H), 2.57 (broad, 1 H), 2.43 (s, 1 H), 1.93 (m, 1 H), 1.42 (broad, 2 H), 1.30 (m, 1 H).

Compound (−)-**7** (16.2 mmol) was treated with *p*-toluenesulfonyl chloride (65.0 mmol) in 50 mL of dry pyridine at room temperature for 14 h. The reaction was worked up by standard procedures, and the product was recrystallized from ethyl acetate/hexane to give (+)-norborn-5-ene-(2*S*,3*S*)-dimethanol bis(4-methylbenzenesulfonate) ((+)-**8**) as colorless crystals (91%; $[\alpha]_D$ = +52.6°, *c* = 5.0 g/dL in $CHCl_3$): ^1H NMR ($CDCl_3$) δ 7.72–7.77 (m, 4 H), 7.32–7.35 (m, 4 H), 6.11 (dd, *J* = 5.7, 3.2, 1 H), 5.78 (dd, *J* = 5.7, 2.7, 1 H), 4.00 (dd, *J* = 10.0, 6.6, 1 H), 3.89 (dd, *J* = *J'* = 9.2, 1 H), 3.73 (dd, *J* = 9.5, 6.6, 1 H), 3.57 (dd, *J* = *J'* = 9.6, 1 H), 2.83 (broad, 1 H), 2.63 (broad, 1 H), 2.44 (s, 6 H), 1.86 (m, 1 H), 1.41 (dd, *J* = 9.2, 2.1, 1 H), 1.27 (dd, *J* = 9.2, 1.4, 1 H), 1.15 (m, 1 H).

(+)-(5*R*,6*R*)-Dimethylnorborn-2-ene ((+)-**1**) was prepared by the reduction of (+)-**8** (19.8 mmol) with lithium aluminum hydride (198 mmol) in ether (300 mL) at reflux for 1 day under argon. The reaction mixture was cooled in an ice bath and then treated with 50 mL of saturated ammonium chloride solution. The inorganic solids were separated by filtration and washed with ether. The combined ethereal solutions were washed twice with sodium thiosulfate (10% w/w) solution followed by saturated sodium chloride solution. The ether solution was dried over $CaCl_2$, and ether was removed by distillation at atmospheric pressure. The product was distilled from sodium under argon at atmospheric pressure (128 °C; 57%; $[\alpha]_D$ = +72.8°, *c* = 2.8 g/dL in $CHCl_3$). The optical purity of (+)-**1** was found to be 96% (ee) according to GC analysis using a Chrompack CP-Cyclodextrin-β-2,3,6-M-19 column: ^1H NMR ($CDCl_3$) δ 6.20 (dd, *J* = 5.7, 3.1, 1 H), 5.96 (dd, *J* = 5.8, 2.7, 1 H), 2.59 (broad, 1 H), 2.31 (broad, 1 H), 1.46–1.51 (m, 2 H), 1.35–1.39 (m, 1 H), 1.06 (d, *J* = 6.8, 3 H), 0.85–0.88 (m, 1 H), 0.80 (d, *J* = 6.9, 1 H).

Polymerization of 1. Polymerizations of 100 equiv of (+)-**1** or (±)-**1** using **2a**, **2b**, or **2c** were conducted in THF at room temperature. The following is a typical example. A solution of (+)-*endo*,*exo*-5,6-dimethylnorborn-2-ene (**1**) (300 mg, 2.45 mmol) in 6.00 mL of THF was added in one portion to a rapidly stirred solution of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (**2a**) (12 mg, 0.0245 mmol) in 6.00 mL of THF at room temperature and the mixture was stirred for 20 min. The living polymer was quenched by adding benzaldehyde (15 μL). After 30 min, the reaction mixture was added dropwise to 150 mL of methanol. The colorless precipitate was isolated by centrifugation or filtration, washed with methanol, and dried under vacuum overnight. In all cases, yields were greater than 90%. GPC analyses, optical rotation, and glass transition temperatures are presented in Table 1. Samples for ^{13}C NMR spectra were further purified by a second precipitation from THF into methanol. All optical rotations were measured at a concentration of 2.8 g/dL in $CHCl_3$ at 20 °C.

^{13}C NMR Spectra. $^{13}C\{^1H\}$ spectra on polymer samples (8–9 w/v% in $CDCl_3$) were obtained at 125.7 MHz on a Varian VXR-500 instrument at 25 °C with spectral widths of 25 000 Hz and an acquisition time of 1.30 s. All chemical shifts were determined relative to TMS. The DEPT $^{13}C\{^1H\}$ NMR spectra were obtained at 62.9 MHz on a Bruker AC-250 instrument with spectral widths of 20 000 Hz, polarization transfer angle (Θ_y) of 135°, and acquisition time 0.41 s. The HETCOR 2D ^{13}C–^1H spectra were obtained at 75.4 MHz (^{13}C) using a Varian Unity 300 instrument with spectral widths of 11 270 Hz, 2D spectral widths of 2018 Hz, and an acquisition time of 0.09 s.

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References and Notes

(1) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.
(2) Bazan, G. C.; 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.
(3) Bazan, G. C.; Oskam, J. H.; Cho, H.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.
(4) Bazan, G. C.; Schrock, R. R.; Cho, H.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.
(5) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Khosravi, E.; Kenwright, A. M.; Marshall, E. L.; Mitchell, J. P. *Makromol. Chem.* **1992**, *193*, 2103.
(6) Feast, W. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.
(7) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.
(8) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.
(9) Ivin, K. J.; Lapienis, G.; Rooney, J. J. *Polymer* **1980**, *21*, 436.
(10) Ivin, K. J.; Lam, L. M.; Rooney, J. J. *Makromol. Chem.* **1981**, *182*, 1847.
(11) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1985**, *28*, 255.
(12) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Br. Polym. J.* **1984**, *16*, 21.
(13) Hamilton, J. G.; Ivin, K. J.; McCann, G. M.; Rooney, J. J. *Makromol. Chem.* **1985**, *186*, 1477.
(14) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245.
(15) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *Makromol. Chem.* **1982**, *183*, 1629.
(16) Greene, R. M. E.; Ivin, K. J.; McCann, G. M.; Rooney, J. J. *Makromol. Chem.* **1987**, *188*, 1933.
(17) Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545.
(18) Greene, R. M. E.; Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Makromol. Chem.* **1986**, *187*, 619.
(19) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.
(20) Hamilton, J. G.; Ivin, K. J.; McCann, G. M.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1379.
(21) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Mol. Catal.*, in press.
(22) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.
(23) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(24) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.
(25) Furuta, K.; Iwanaga, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4507.
(26) Hamanaka, N.; Seko, T.; Miyazaki, T.; Naka, M. *Tetrahedron Lett.* **1989**, *30*, 2399.