Polymerization of Cyclopentene Using Metallocene Catalysts: Polymer Tacticity and Properties

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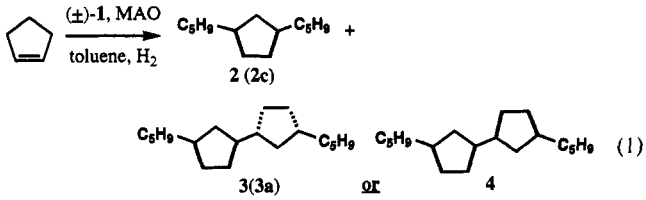
ABSTRACT: Hydro-oligomerization or polymerization of cyclopentene using racemic 1,2-ethylenebis(η^5-indenyl)zirconium dichloride (1) and methylaluminoxane leads to the production of poly(*cis*-1,3-cyclopentane) in which individual monomer units are incorporated in an isotactic manner. This was ultimately demonstrated through independent synthesis of the single, stereoisomeric tetramer produced under hydro-oligomerization conditions. In contrast to these result, hydro-oligomerization of cyclopentene with racemic 1,2-ethylenebis-(η^5-tetrahydroindenyl)zirconium dichloride (5) led to the production of oligomers in which cyclopentene is incorporated in a cis- and trans-1,3 manner. This was also confirmed through independent synthesis of some of these saturated oligomers. A mechanism is proposed to account for the isotactic insertion of cyclopentene and the formation of the various hydro-oligomers produced.

Introduction

Cyclopentene and other cyclic olefins can be polymerized using *rac*-ethylenebis(η^5-indenyl)zirconium dichloride (1) in the presence of methylaluminoxane (MAO) cocatalyst to give polymers without detectable ring opening.[1] Recently, we determined the microstructure of poly(cyclopentene) produced using this catalyst system; under hydro-oligomerization conditions a single trimer (2) and tetramer (3 or 4) are produced by cis-1,3 enchainment of the monomer (eq 1).[2]



(1)

While the mode of enchainment of cyclopentene has now been identified, the relative stereochemistry between two cyclopentane rings in the polymer (i.e., tacticity) has not been established.[1,2] Unlike prochiral monomers such as propylene, cyclopentene is not *a priori* expected to undergo isotactic insertion using a chiral catalyst.

In principle, the tacticity could be determined by identification of the tetramer formed under hydro-oligomerization conditions. Our previous attempts to do this in a direct manner were unsuccessful.[2] Compound 3 is achiral, whereas its isomer 4 is chiral; it had occurred to us that if one were to use an optically pure catalyst it should be possible to distinguish between these two structures based on the observation of optical activity of the tetramer fraction.

The resolution of catalyst 1, to our knowledge, has not been reported, whereas optically pure ethylenebis(η^5-tetrahydroindenyl)zirconium dichloride (5) is readily available.[3] We thus elected to study the polymerization and hydro-oligomerization of cyclopentene using both *rac*-5 and [*S*]-5. In this paper, we describe the results of these and related studies.

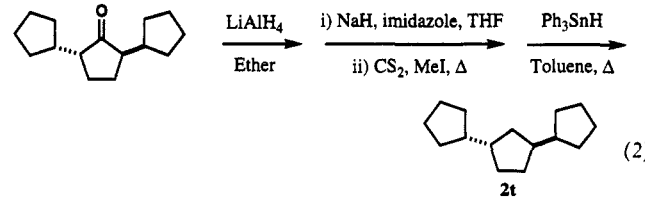
Results

Hydro-Oligomerization of Cyclopentene Using *rac*-5. Hydro-oligomerization of cyclopentene using *rac*-5 and methylaluminoxane was carried out in a toluene solution under conditions previously employed using *rac*-1.[2] The crude hydro-oligomer was fractionated by extraction with hot ethanol to isolate the lower molecular weight material.

In contrast to our previous results in which a single, stereoisomeric trimer and tetramer were produced (eq 1), the ethanol-soluble fraction contained two trimers (**2c**:**2t** in a 2.7:1 ratio by GC-MS; both with *m*/*e* 206) and five tetramers (**3a**:**3b**:**3c**:**3d**:**3e** in a 0.475:0.211:0.197:0.096:0.021 ratio by GC-MS; all with *m*/*e* 274) in addition to higher, hydro-oligomers. The major trimer and tetramer produced (**2c** and **3a**) using *rac*-5 had identical retention times and mass spectral fragmentation patterns as those produced using *rac*-1.[2] An identical product distribution was observed using optically pure, [*S*]-(+)-5. Although the tetramer fraction obtained from this polymerization was optically active, as it was composed of five different isomeric tetramers this is not surprising.

The trimeric and tetrameric fractions could be separated from the other oligomers present (see the Experimental Section), and the purified materials were additionally characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the trimer fraction is shown in Figure 1A; the major stereoisomer (**2c**) present is *cis*-1,3-dicyclopentylcyclopentane (2; cf. Figure 1B and Table 1), and the minor stereoisomer (**2t**) is obviously closely related in structure (Figure 1A).

Our previous synthesis of compound 2 although unambiguous was not stereoselective,[2] and therefore the corresponding trans isomer of 2 was also prepared (eq 2, see the Experimental Section for details). The spectrum



(2)

of this material is displayed in Figure 1C (Table 1); it is clear that the minor trimer (**2t**) produced using *rac*-5 is in fact *trans*-1,3-dicyclopentylcyclopentane. As far as we are aware, this is the first example of a trans "insertion" product being produced in olefin polymerization using homogeneous Ziegler–Natta catalysts.

The ^{13}C NMR spectrum of the tetramer fraction produced using *rac*-5 is displayed in Figure 2A. In the

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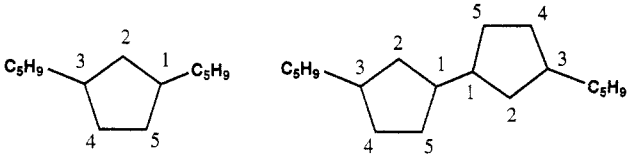
Table 1. Diagnostic ^{13}C NMR Chemical Shift Data for Compounds 2c, 2t, 3a–e, and 4[a]



	C1[b]	C3[b]	C1′[b]	C3′[b]	C2[b]	C2′[b]	C4′[b]	C5′[b]	C4	C5[b]
2c (cis)	*c*	46.75			38.84				30.73	*c*
3a (cis,cis)	46.59	46.75			38.73				30.73	30.61
4 (cis,cis)	46.63	46.76			38.84				30.71	30.59
3b (cis,trans)	46.60	46.73	45.57	45.10	38.56	36.41	32.38	32.26	30.73	30.66
3c (trans,cis)	46.60	46.76	45.56	45.09	38.84	36.43	32.35	32.29	30.71	30.45
3d (trans,trans)			45.46	45.13		36.51	32.49	32.20		
3e (trans,trans)			45.34	45.08		36.25	32.40	32.32		
2t (trans)			*c*	45.15		36.54	32.39	*c*		

[a] Spectra recorded in $CDCl_3$ at 50.3 MHz at 25 °C; chemical shifts are referenced with respect to $CDCl_3$. Only signals due to the carbon atoms of the central five-membered ring(s) are recorded (see the Experimental Section for a complete listing). [b] See diagram for numbering scheme, unprimed and primed carbons correspond to those atoms in a cis- and trans-1,3 cyclopentane ring, respectively. [c] Chemically equivalent to C3 (or C3′) and C4 (or C4′) in trimer.

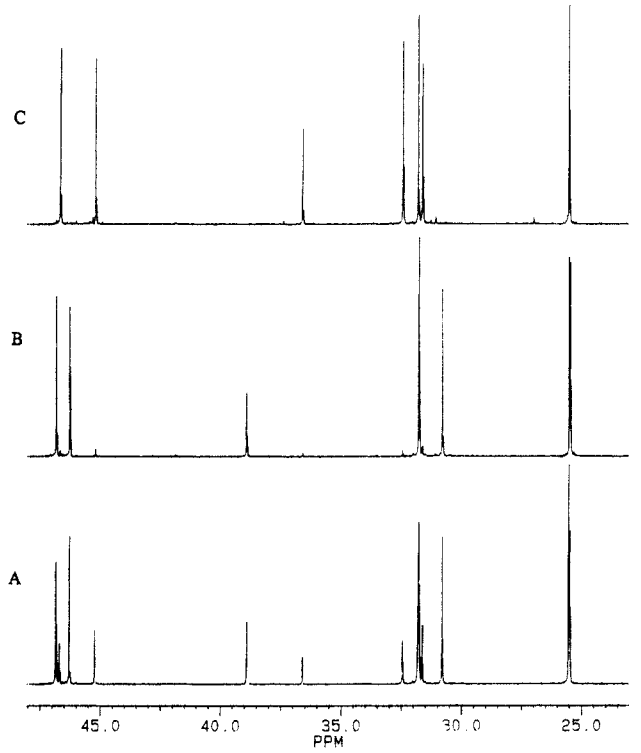


Figure 1. ^{13}C NMR spectra of the trimer products in a $CDCl_3$ solution at 50.0 MHz. (A) Spectrum of the trimer fraction obtained using catalyst **5**. (B) Spectrum of compound **2c**.[2] (C) Spectrum of compound **2t**.

region 35–40 ppm, in which resonances due to the central methylene carbons in **2c** and **2t** are found,[2] there are a total of seven resolved signals, the most intense of which corresponds to that of the single, symmetrical tetramer (**3a**) produced using *rac*-**1** as catalyst (Figure 2B and Table 1).[2] Of the remaining isomers present, two are clearly unsymmetrical (each giving rise to two signals in this region; Table 1) and are formed in equal amounts (**3b** and **3c**, parts C and D of Figure 2, respectively), whereas the remaining tetramers (**3d** and **3e**) are symmetrical with single central methylene resonances at 36.51 (Figure 2E) and 36.25 ppm, respectively (Table 1).

Authentic samples of all of these compounds were prepared as detailed in the Experimental Section. The major tetramer formed (**3a**) is the isotactic, cis–cis isomer (Chart 1), the two unsymmetrical tetramers (**3b** and **3c**) are the isotactic and syndiotactic cis–trans compounds,

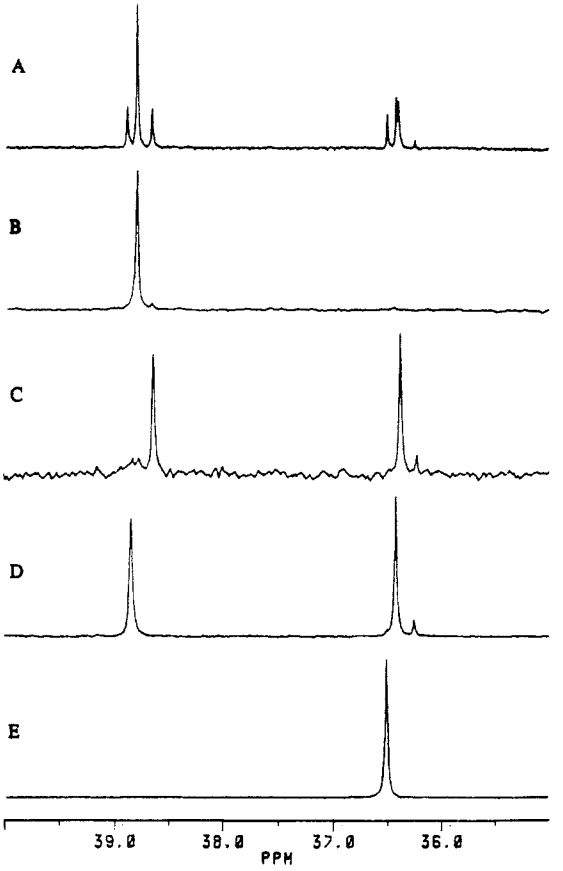


Figure 2. ^{13}C NMR spectra of tetramer products in a $CDCl_3$ solution at 50.0 MHz. (A) Spectrum of hydro-oligomerization product obtained using catalyst **5**. (B) Spectrum of compound **3a**. (C) Spectrum of compound **3b**. (D) Spectrum of compound **3c**. (E) Spectrum of compound **3d**.

respectively, compound **3d** is the syndiotactic trans–trans stereoisomer, and compound **3e** is the isotactic analogue of **3d**. From the relative amounts of **3a–e** formed (vide supra), the cis:trans ratio of the tetramer fraction can be calculated (2.1:1) and is somewhat reduced from that of the trimer fraction.

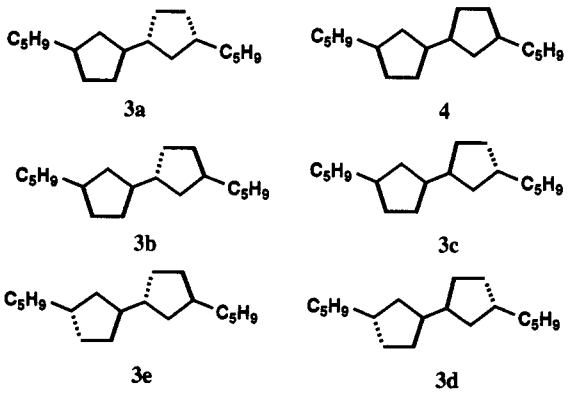
We had reported earlier that the putative syndiotactic cis,cis tetramer **4** was produced along with **3a** when the achiral catalyst Cp_2ZrCl_2 was employed under hydro-oligomerization conditions.[2] To verify this, this compound was also prepared as described in the Experimental

Table 2. Polymerization and Hydro-Oligomerization of Cyclopentene Using Catalyst 5 or 1 and Methylaluminoxane[a]

entry	Zr (mM)[b]	Al (mM)	C_5H_8 (M)	T (°C)	yield (g)[c]	% cis[d]	M_n[d]	2-C:3-C[e]	T_m (°C)[f]	% cryst[g]
1	5 (0.043)	94	1.46	25	0.80	60.5	1400			
2	5 (0.043)	31	1.46	25	0.74	59.6	1200			
3	5 (0.17)	94	1.46	25	2.03	60.6	920			
4	5 (0.17)	31	1.46	25	0.91	60.4	810			
5	5 (0.20)	100	1.13	0	1.74	68.0	900	91:9	160–285	25
6	5 (0.20)	100	1.13	25	2.73	62.0	600	79:21	125–250	19
7	5 (0.20)	100	1.13	50	1.88[h]	50.0	350	65:35	70–190	4
8	1 (0.36)	96	3.79	25	2.7	*i*	*i*	*i*	140–350	60
9[j]	5 (0.47)	74	3.73	25	6.1	63.0[k]	390[k]		40–80[k]	2[k]
10[j]	1 (0.33)	105	2.02	25	7.4	96.0[l]	390[l]		50–160[l]	34[l]

[a] All polymerizations were conducted in a toluene solution for 24 h unless otherwise noted. [b] Catalyst with concentration in parentheses. [c] Yield of unfractionated polymer. [d] Determined from the ^{13}C NMR spectrum (see text). [e] Ratio of 2-cyclopentenyl to 3-cyclopentenyl end groups. [f] Melting temperature range as determined by DSC or in an evacuated capillary tube. [g] % crystallinity as determined by WAXD. [h] The reduced yield of polymer at higher temperatures is due to the formation of large amounts of oligomers (i.e., dimer, trimer, tetramer, etc.) under these conditions. [i] Not determined due to insolubility of the polymer. [j] Conducted under 2.0 atm of H_2 for 12 h. [k] Data reported are for a fraction insoluble in acetone but soluble in hexane. [l] Data reported are for the fraction soluble in toluene.

Chart 1. Tetramers Formed by 1,3 Insertion of Cyclopentene



Section. Hence, all possible tetramers formed by 1,3 insertion have been prepared by unambiguous routes.

Polymerization of Cyclopentene Using *rac*-5. Some polymerizations of cyclopentene were conducted using catalyst 5, and the results are summarized in Table 2.

In contrast to the polymer produced using catalyst 1, the majority of these polymers were soluble in hot toluene or 1,2,4-trichlorobenzene (TCB). Analysis of these samples by ^{13}C NMR spectroscopy revealed the presence of diagnostic signals at 38.7 and 36.5 ppm due to cis- and trans-enchained monomer, respectively. The cis content of the polymer (as determined by integration of these signals) was found to be unaffected by catalyst or cocatalyst concentration within experimental error (Table 2, entries 1–4) but was higher at lower temperatures (entries 5–7). Note that the cis content in the polymers (61.5 ± 1.0%, entries 1–4) or hydro-oligomer (Table 2, entry 9) was somewhat lower than that found for the trimers (i.e., 2.7:1 or 73.0%) or even the tetramers (ca. 68%).

The number-average molecular weight (M_n) of these unfractionated polymers could be determined by ^{13}C NMR spectroscopy as both saturated and unsaturated end groups were detected. In all cases, low molecular weight material is produced (Table 2) and the usual dependency on polymerization temperature is observed (entries 5–7). Although we were unable to determine M_n for the polymer prepared using catalyst 1 (because of its insolubility), one can estimate from the published solid-state ^{13}C NMR spectrum of this material[1] that the molecular weight of this material is also low (M_n < 2000).

A diagnostic signal at 25.1 ppm (corresponding to two C atoms) due to saturated end groups[2] and three separate olefinic signals at 134.5, 130.4, and 130.0 ppm were observed. As the signals at 134.5 and 130.4 ppm were always in a 1:1 ratio, they were asigned to the olefinic carbons of a 2-cyclopentenyl end group by comparison to 3-cyclopentylcyclopentene (6, vide infra). The remaining signal was assigned, based on its chemical shift and by comparison to 4-cyclopentylcyclopentene (7, vide infra), to the two, accidentally equivalent, olefinic carbons of a 3-cyclopentenyl end group. Lower polymerization temperatures led to a decrease in the relative intensity of this signal (entries 5–7).

The ratio of saturated to unsaturated end groups (determined by integration of the spectrum obtained under inverse-gated decoupling conditions) was generally 1:1 within experimental error. This suggests that the principle mode of chain transfer in these polymerizations involves β-hydride elimination. The present results also suggest that formation of a 3-cyclopentenyl end group by this process is more energetically demanding than a 2-cyclopentenyl end group.

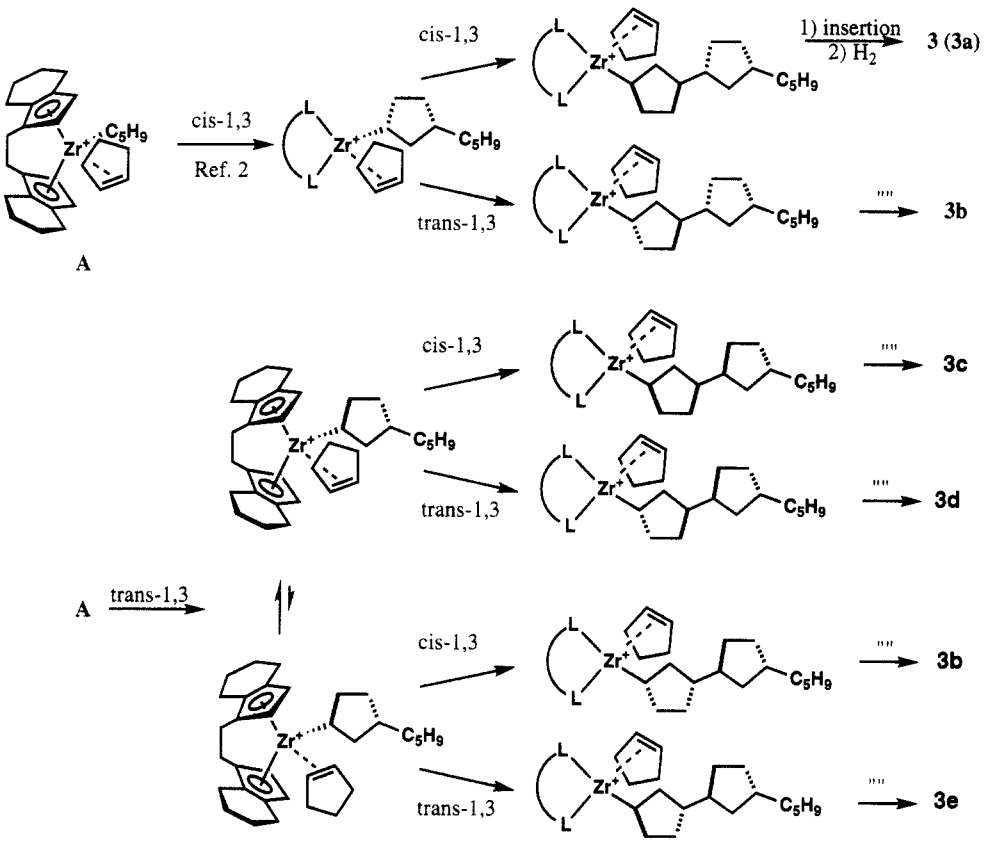
We note that the occurrence of competitive "trans insertion" in these polymerizations leads to the production of polymer with significantly lower crystallinity than observed for poly(cyclopentene) produced using catalyst 1 (Table 2, entries 6 and 8). As is evident from the table, the crystallinity (as determined by WAXD) and melting temperature decreases with decreasing cis content and molecular weight. Entries 9 and 10 demonstrate that, for similar degrees of polymerization, it is the cis content that most dramatically influences crystallinity as might be expected.

These results indicate that the high crystallinity and melting temperatures observed for isotactic, poly(*cis*-1,3-cyclopentane) produced using catalyst 1 are obviously the result of a very stable lattice; the extensive degradation observed during melting in air[1] is likely related to the fact that poly(cyclopentene) is oligomeric (i.e., maximum DP_n ~ 20–30) rather than polymeric.

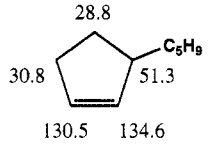
Isolation of Unsaturated Oligomers. To verify the above end-group assignments, a polymerization of cyclopentene was carried out at 25 °C using 5 at higher catalyst concentrations. Under these conditions, the average degree of polymerization is lower, and significant quantities of unsaturated dimers, trimers, etc., are formed as revealed by GC-MS of the toluene-soluble fraction.

The dimer fraction could be isolated by fractional distillation of the toluene-soluble portion and consisted of three components: 3-cyclopentylcyclopentene (6; 76%), 4-cyclopentylcyclopentene (7; 21%), and 1-cyclopentylcyclopentene (8; 3%). Although compound 7 has apparently not been reported in the literature, this symmetrical

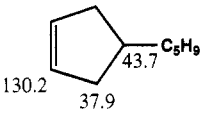
Scheme 1



compound was easily identified in the mixture by ^{13}C NMR spectroscopy. Diagnostic chemical shifts for **6** and **7** and their assignments are indicated in the diagram below and provide support for the end-group analyses reported above.[4]



6



7

The ratio of **6**:**7** was approximately the same as the ratio of 2-cyclopentenyl:3-cyclopentenyl end groups observed in a polymerization carried out at the same temperature using lower amounts of catalyst (i.e., 3.6:1 vs 3.8:1; see Table 2). Finally, for comparison purposes, polymerization of cyclopentene using catalyst **1** was performed under similar conditions. In this case, only **6** and **7** were produced in a ratio of 19:1.

Discussion

Isotactic Propagation. Isotactic insertion of cyclopentene using catalyst **5** could occur as is illustrated in Scheme 1. Insertion of cyclopentene probably arises from monomer coordination to the metal center and insertion in the manner indicated. This arrangement minimizes steric interactions between the five-membered ring of the monomer with the tetrahydroindenyl rings of catalyst **5** (or indenyl rings of catalyst **1**). Cis-1,3 insertion occurs via the mechanism postulated earlier, i.e., cis-1,2 insertion followed by β-hydride elimination to give an olefin–hydride complex which undergoes reinsertion with opposite regiochemistry.[2] Subsequent coordination and insertion of additional monomer in the same fashion leads to the production of **3a** under hydro-oligomerization conditions using catalyst **5** (or to isotactic polymer using **1**).

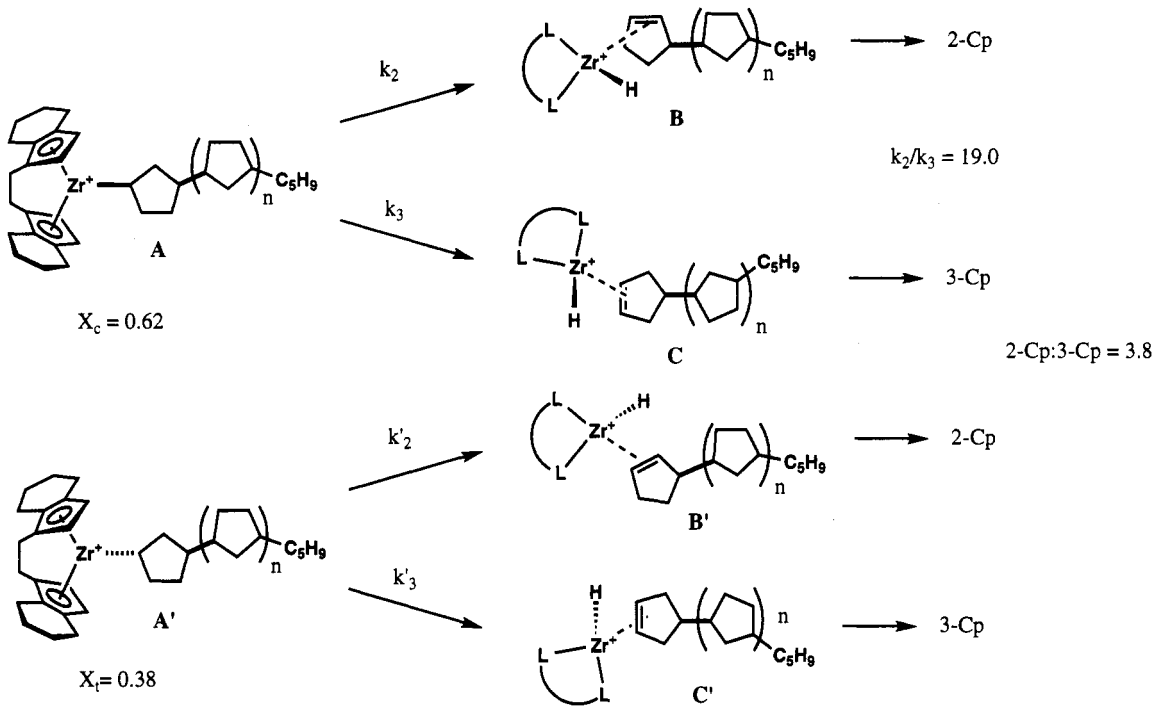
The other tetramers produced using catalyst **5**, with the exception of **3e**, could also form by isotactic placements of monomer in a similar manner as shown in Scheme 1. However, because trans insertion can occur either prior to or following a "normal" isotactic, cis-1,3 placement of monomer, two unsymmetrical tetramers will be produced in which the stereochemical relationship between the central five-membered rings is syndiotactic (**3c**) or isotactic (**3b**), respectively. Finally, two consecutive trans insertion processes lead to the production of syndiotactic, trans–trans tetramer **3d**.

The formation of **3e** (isotactic trans–trans) must arise by trans-1,3 insertion of coordinated monomer from the opposite orientation (Scheme 1; note that these two conformers are accessible without monomer dissociation from the metal as cyclopentene is not prochiral). As we do not detect the presence of **4** (syndiotactic cis–cis) in the mixture produced by catalyst **5** (or **1** for that matter) by NMR or GC-MS, insertion of cyclopentene into a growing chain in which the penultimate cyclopentane ring is trans to the metal must be less stereoselective than when it is cis.

Clearly, if **3e** is formed, then a portion of **3b** must also be produced by this process (i.e., cis-1,3 insertion from this same intermediate; Scheme 1). Based on the cis:trans ratio of the tetramers and the relative amount of **3e** formed, this portion can be estimated to be about 5% of the total tetramer distribution.

The selectivity for "isotactic" insertion of monomer when the penultimate ring is trans can then be calculated [i.e., (**3c** + **3d**)/(**3e** + 0.05)] and is equal to ~5:1. This is a surprisingly low number, particularly if it represents that intrinsic selectivity of the ligand framework (i.e., one would

Scheme 2



$$k'_2/k'_3 = \frac{X_t(2\text{-Cp:3-Cp}) + X_c(2\text{-Cp:3-Cp})/20 - X_c(19/20)}{X_t + X_c(19/20) - X_c(2\text{-Cp:3-Cp})/20} = \frac{0.38(3.8) + 0.62(3.8)/20 - 0.62(19/20)}{0.38 + 0.62(19/20) - 0.62(3.8)/20} = 1.14$$

expect chain-end effects to be minimal when the penultimate ring is trans to the metal center and to incoming monomer).

The implication is that chain-end effects are significant when the penultimate ring is cis to the metal as **4** is not present in detectable amounts.[5]

Chain-Transfer Reactions. As previously noted, two types of terminal unsaturation are present in polymers produced using catalyst **5**; the more predominant mode of chain transfer involves β-hydride elimination so as to give 2-cyclopentenyl end groups. As this process is an integral part of the mechanism proposed for cis-1,3 insertion (Scheme 2), this type of terminal unsaturation is observed (and expected) using both catalyst **5** and **1**.

Formation of a 3-cyclopentenyl end group requires that β-hydride elimination occurs with opposite regiochemistry from the common intermediate shown in Scheme 2. As this type of end group is observed using catalyst **1** but is clearly less predominant, it is clear that formation of this end group is facilitated when the metal is trans to the penultimate cyclopentane ring.

From the ratio of these two end groups (3.6:1) and the cis:trans ratio of the polymer (62:38) produced using catalyst **5**, it is possible to estimate the selectivity for formation of 2-cyclopentenyl vs 3-cyclopentenyl end groups when the metal is trans to the penultimate cyclopentane ring.[6] The results of this calculation (Scheme 2) indicate that the regioselectivity of β-hydride elimination is low when the penultimate ring is trans.[7]

Conclusions

Poly(cyclopentene) produced using catalyst **1** is isotactic, poly(*cis*-1,3-cyclopentane); thus the stereochemical issues associated with this "polymer" have now been resolved.

Trans-1,3 insertion of monomer is observed in polymerizations using the closely related catalyst **5**, and the various stereoisomeric tetramers formed under hydrooligomerization conditions have been identified through independent synthesis.

The mechanism of trans-1,3 insertion is of fundamental interest; our previous proposal for cis-1,3 insertion[2] is not compatible with the occurrence of this process.[8]

Also, it is not clear why catalyst **5** differs so dramatically from **1** in this respect. Future efforts will be directed toward these problems.

Finally, it is clear that poly(cyclopentene) is not a high MW polymer; this feature will probably limit the utility and durability of the homopolymer as a high-T thermoplastic.[9]

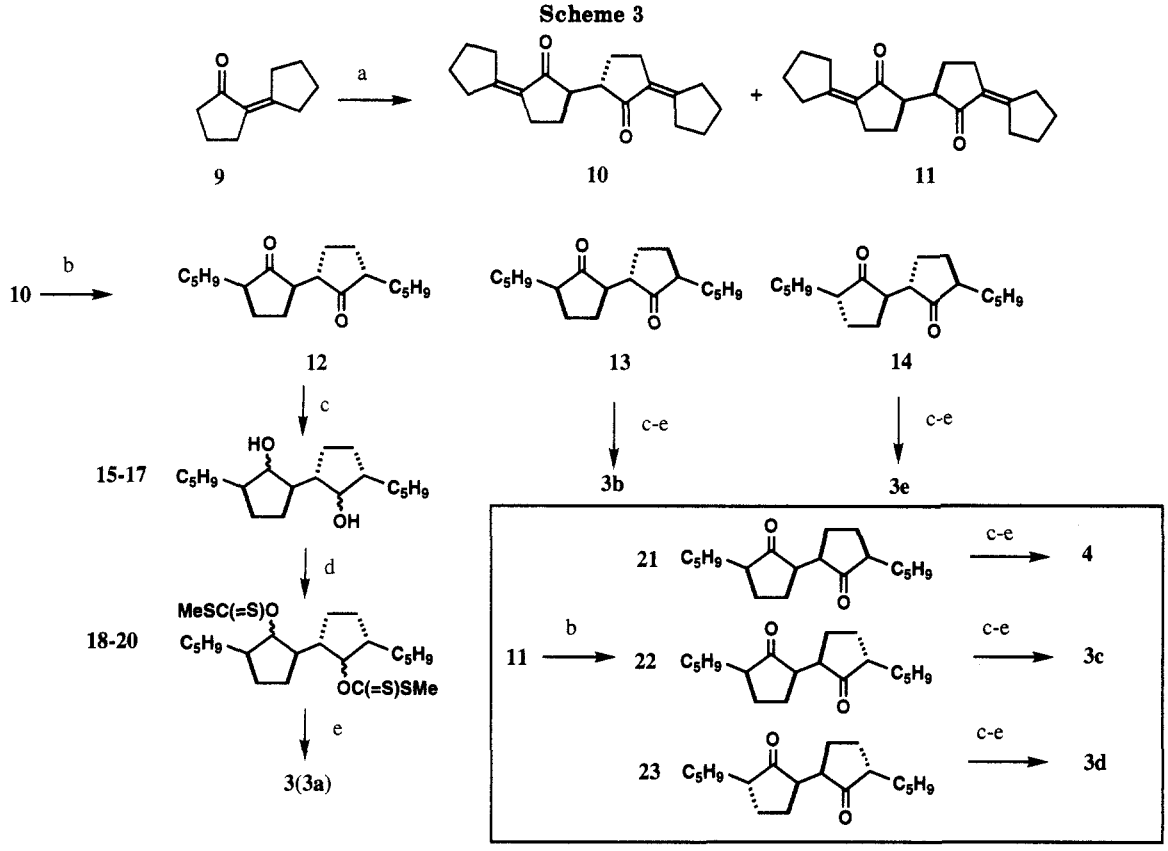
Experimental Section

All solvents and chemicals were reagent grade and purified as required. Tetrahydrofuran, diethyl ether, and toluene were dried by distillation from sodium benzophenone ketyl. DMF was dried by distillation from CaH_2. Cyclopentene (Aldrich, 97%) was dried by distillation from $LiAlH_4$ under nitrogen. Methylaluminoxane was obtained from Texas Alkyls as a solution in toluene and the solvent removed under high vacuum to obtain solid MAO used in the polymerizations. Metallocenes **1** and **5** and cyclopentanone **9** (Scheme 3) were prepared by the methods described in the literature.[10,11] All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 solution on either a Bruker AM-250 or AC-200 spectrometer; chemical shifts are referenced with respect to residual $CHCl_3$ or C_6D_5H. High-temperature (120 °C), quantitative ^{13}C NMR spectra were run with inverse-gated decoupling to minimize NOE in a 1,2,4-trichlorobenzene solution. Field/frequency lock was established using DMSO-d_6 or benzene-d_6, and chemical shifts were referenced with respect to these solvents. Spectra were recorded with a relaxation delay of 3 s and a digital resolution of 0.5 Hz/point corresponding to a data length of 32K. The pulse angle and acquisition time were 30° and 2 s, respectively. A sweep width of 0–160 ppm was used.

IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. Mass spectra were obtained using a Kratos MS-

Scheme 3



a. LDA, THF - 78° C; $FeCl_3$, DMF. b. H_2 (25 psi), 5% Pd/C, EtOH. c. $LiAlH_4$, Et_2O.
d. NaH, imidazole, THF; CS_2, MeI, Δ. e. Ph_3SnH, AIBN, toluene, 80 °C.

890 instrument at the University of Guelph. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with FID detectors and a 0.25 mm × 30 m, J&W Scientific DB-1701 capillary column. GC-MS analyses were obtained using a Hewlett-Packard 5890 Series II instrument equipped with a 5971A mass selective detector and a 0.32 mm × 25 m HP-5 column. Elemental analyses were determined by M.H.W. Laboratories of Phoenix, AZ.

Hydro-Oligomerization of Cyclopentene with *rac*-5. Hydro-oligomerization of cyclopentene (14.5 g) was conducted in a 300-mL, Parr autoclave at room temperature in 40 mL of a toluene solution containing 330 mg of MAO and 19 mg of (±)-5. The system was pressurized to 30 psi with hydrogen (Linde), and after 24 h, the vessel was vented and 200 mL of ethanol was added. The suspension was refluxed and allowed to cool to room temperature. The mixture was filtered to provide an insoluble white solid (4.6 g), whereas an oily solid (1.2 g) was obtained following concentration of the filtrate to dryness in vacuo. GC-MS analysis of the oily solid revealed the presence of a dimer, two trimers (27:73), and five tetramers (0.47:0.206:0.206:0.098:0.02) in a ratio of 1.9:1.4:1, respectively. Further purification was achieved by Kugelrohr distillation. This provided the trimers (0.4 g, bp 70 °C, 0.1 mmHg) and the tetramers (0.1 g, bp 110 °C, 0.04 mmHg, 99% pure by GC). Spectral data for the trimer fraction are as follows: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.7–0.9 (m, 1 H), 1.0–1.35 (m, 6 H), 1.4–2.0 (br m, 19 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) two sets of signals at δ 46.80, 46.23, 38.87, 31.75, 31.73, 30.77, 25.49, 25.45 and δ 46.66, 45.19, 36.57, 32.42, 31.78, 31.59, 25.49, and 25.45 in about a 3:1 ratio; IR (NaCl, neat) 2946 (s), 2906 (sh), 2864 (s), 1464 (sh), 1450 (m), 1362 (vw), 1331 (w), 1304 (sh), 1259 (vw), 932 (w), 894 (w) cm^{-1}. MS (EI): *m/e* 206 (M^+).

Polymerization of Cyclopentene with 5. A representative procedure follows (Table 2, entry 3): Cyclopentene (5.5 g, 80.73 mmol) and toluene (34 mL) were added to a 100-mL round-bottomed flask containing MAO (0.300 g, 5.17 mmol) under nitrogen. Compound 5 (4.0 mg, 9.38 μmol) dissolved in 14 mL of toluene was then added. The mixture was stirred at room temperature for 24 h, at which time methanol (ca. 0.1 mL) was added. The mixture was concentrated in vacuo to provide a tacky solid (2.03 g).

Isolation of Unsaturated Oligomers 6–8. To obtain samples of the dimer and trimer from the polymerization of cyclopentene with 1 and 5, the following experiments were carried out.

To a 50-mL flask was added MAO (0.3 g), toluene (25 mL), cyclopentene (12 mL), and 5 (58.6 mg). In the first hour, an exotherm of approximately 10 °C was observed. The polymerization was allowed to proceed for an additional 20 h at room temperature (25 °C). At this point, methanol (150 mL) was added to the polymerization mixture and the solid polymer was filtered. A portion of the toluene/methanol-soluble portion was analyzed using GC-MS and consisted of three volatile fractions with *m/e* 136, 204, and 272 (M^+) in a 1:1.2:3 ratio. The toluene/methanol-soluble fraction was then concentrated in vacuo (25–100 °C, 0.05 mmHg) ensuring that the toluene was being collected in a liquid nitrogen cold trap.

The distillate was then fractionally distilled at atmospheric pressure. Using a methanol/toluene azeotrope all of the toluene was removed, and the remaining methanol was extracted with pentane which was evaporated off at room temperature to afford the dimer fraction (10 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.8–2.6 (br m, 14 H) and three signals at 5.32 (br s, 1 H: 8), 5.66 (br s, 2 H: 7), 5.70 (br m, 2 H: 6) in a ratio of 1:7:25; ^{13}C NMR (50.3 MHz, $CDCl_3$) a set of signals at δ 134.61 (CH), 130.48 (CH), 51.29 (CH), 45.83 (CH), 32.14 (CH_2), 31.16 (CH_2), 30.81 (CH_2), 28.81 (CH_2), 25.51 (CH_2), and 25.31 (CH_2) due to 6 and another set at δ 130.24 (CH), 46.12 (CH), 43.68 (CH), 37.89 (CH_2), 31.42 (CH_2), and 25.44 (CH_2) due to 7; from the relative intensities of the two sets of signals these two compounds were present in a ratio of ~4:1.

A similar procedure was employed using 1 as the catalyst. A ^{13}C NMR spectrum of the purified dimer fraction revealed the presence of only 3-cyclopentylcyclopentene, whereas the ^{1}H NMR

spectrum revealed the presence of trace amounts of 4-cyclopentylcyclopentene (95:5 ratio).

***trans*-1,3-Dicyclopentylcyclopentane (2t).** [2*R*,5*R*]-2,5-Dicyclopentylcyclopentan-1-ol[2] was converted to the corresponding *S*-methylthiocarbonate, using the following procedure.[12]

The alcohol (0.42 g, 1.9 mmol) was added to NaH (0.091 g, 3.8 mmol) in 15.0 mL of dry THF, in a two-neck 50-mL round-bottomed flask equipped with a condensor. To this was added imidazole (4 mg, 0.06 mmol) in 1 mL of THF. The mixture was heated under nitrogen to reflux, and after 3 h carbon disulfide (0.6 mL, excess) was added and after a further 30 min at reflux CH_3I (0.6 mL, excess) was added. The solution was allowed to reflux for a further 30 min and then cooled to room temperature. Acetic acid (0.6 mL) was added to the reaction mixture prior to diluting with water. The product was extracted using dichloromethane, which was washed with dilute HCl, $NaHCO_3$, and water and finally dried over $MgSO_4$. After filtration, the filtrate was concentrated in vacuo and the mixture purified by flash chromatography on a silica gel column eluting with hexane, to provide the dithiocarbonate derivative (0.38 g, 64% yield) which was used *without further purification*: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86 (br, 1 H), 2.51 (s, 3 H), 2.1–0.7 (br m, 24 H); ^{13}C NMR (62.85 MHz, $CDCl_3$) δ 214.37, 92.00, 51.22, 49.76, 43.86, 40.06, 32.06 (2 C), 31.36, 30.76, 29.23, 28.09, 25.38, 25.30, 25.23, 24.99, 18.65; IR (NaCl, neat) 2948 (s), 2866 (s), 1450 (w), 1424 (sh), 1376 (vw), 1319 (vw), 1291 (vw), 1258 (sh), 1224 (s), 1189 (sh), 1050 (s), 963 (w), 908 (w), 894 (sh), 800 (w) cm^{-1}.

The dithiocarbonate (0.38 g, 1.22 mmol) in 2.0 mL of dry toluene was added dropwise to a refluxing solution of triphenyltin hydride (2.17 g, 6.1 mmol) in toluene (10.0 mL) over a 40-min period by a syringe pump. After the addition was complete, the mixture was refluxed for an additional 5 h and then cooled to room temperature. The solvent was removed in vacuo and the mixture chromatographed on silica gel eluting with hexane. The title compound is the first to elute under these conditions, and 170 mg (73%) of pure material was obtained: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.9–1.2 (br m, 6 H), 1.3–1.9 (br m, 20 H); ^{13}C NMR (62.85 MHz, $CDCl_3$) δ 46.61 (2 C), 45.15 (2 C), 36.54 (1 C), 32.39 (2 C), 31.75 (2 C), 31.57 (2 C), 25.48 (2 C), 25.46 (2 C); IR (NaCl, neat) 2940 (s), 2863 (s), 1449 (m), 1360 (vw), 1326 (w), 1258 (vw), 1227 (vw), 1200 (vw), 1120 (vw), 1022 (vw), 931 (w), 895 (w) cm^{-1}; MS (EI) *m/e* 206 (M$^+$). Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.51; H, 12.47.

Preparation of Compounds 3a–e and 4. The routes employed for the syntheses of these compounds are summarized in Scheme 3. The stereochemistry of key intermediates was determined by X-ray crystallography (i.e., compounds 11 and 18). Briefly, oxidative coupling of enone 9 provided two stereoisomeric dimers 10 and 11, which were separately transformed to the target compounds by a sequence involving hydrogenation, reduction of the carbonyl groups, and deoxygenation of the alcohols using a modification of Barton's procedure.[12]

[5*S*,5′*R*]- and [5*S*,5′*S*]-5,5′-Bis(2-cyclopentylidenecyclopentanone) 10 and 11. These compounds were prepared via oxidative coupling of compound 9 using a general literature procedure.[13]

To a 100-mL flask was added diisopropylamine (10.5 mL, 75.0 mmol) in dry THF (60 mL). This mixture was cooled to 0 °C prior to the addition of n-BuLi (27.4 mL, 2.6 M in hexane, 71.0 mmol). The solution was allowed to stir for 15 min before being cooled to −78 °C. 2-Cyclopentylidenecyclopentanone (10 g, 67.0 mmol) was then added dropwise over 20 min and allowed to react for 30 min prior to adding $CuCl_2$ (9.8 g, 73.0 mmol) in DMF (30 mL) over 20 min. The brown reaction mixture was then stirred for 30 min and allowed to warm to room temperature. The product was extracted using hexane which was washed with HCl, $NaHCO_3$, and water before drying over Na_2SO_4 and concentrating in vacuo. Two diastereomers were produced in equal quantities (analysis by ^{13}C NMR, total 1.7 g, 17% yield). The crude product was purified, and the isomers were separated by flash chromatography on a silica gel column eluting with hexane–ethyl acetate 25:1.

Racemic compound 11 was the first to elute and was recrystallized from hexane–ethyl acetate: mp 142–144 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.9 (t, J = 2.0 Hz, 2 H), 2.85–2.65 (br, 6 H), 2.55–2.35 (br, 4 H), 2.35–2.2 (br, 4 H), 2.1–1.9 (br m, 2 H), 1.9–1.5 (br m, 10 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 207.15, 158.91, 127.83, 49.63, 34.14, 32.56, 27.43, 26.89, 25.19, 22.24; IR (KBr disc) 2948 (s), 2871 (s), 1702 (s), 1639 (s), 1456 (m), 1417 (m), 1330 (w), 1299 (w), 1280 (w), 1253 (m), 1226 (m), 1167 (m), 1151 (sh), 1040 (m), 1019 (m), 991 (w), 947 (w), 882 (m), 862 (m), 730 (m), 701 (w), 631 (m), 563 (m), 427 (w) cm^{-1}; MS (EI) *m/e* 298 (M$^+$). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.54; H, 8.72. Found: C, 80.66; H, 8.87.

The meso isomer (10) was obtained as a pale yellow solid: mp 138–141 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.9–2.6 (br, 6 H), 2.6–2.4 (br, 4 H), 2.4–2.2 (br, 4 H), 2.2–1.9 (br m, 2 H), 1.4–1.5 (br m, 10 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 206.02, 158.87, 127.85, 50.42, 34.17, 32.52, 27.54, 26.89, 25.20, 23.98; IR (KBr disc) 2948 (s), 2868 (s), 1701 (s), 1637 (s), 1463 (w), 1438 (m), 1416 (m), 1309 (w), 1295 (w), 1256 (s), 1226 (m), 1173 (m), 1141 (m), 1114 (m), 1059 (w), 1018 (m), 988 (w), 958 (w), 880 (w), 848 (m), 805 (w), 725 (m), 693 (w), 620 (m), 556 (m) 470 (w) cm^{-1}; MS (EI) *m/e* 298 (M$^+$). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.54; H, 8.72. Found: C, 80.60; H, 8.73.

X-ray Structural Determination of Compound 11. Single crystals were obtained by slow cooling of a hot, saturated solution of this compound in 9:1 hexane–ethyl acetate. A crystal of dimensions 0.06 (100) × 0.06 ($\bar{1}$00) × 0.22 (010) × 0.22 (0$\bar{1}$0) × 0.30 (0$\bar{1}$2) × 0.28 (012) × 0.22 (01$\bar{4}$) mm was mounted on a Nicolet-Siemens R3m diffractometer. Intensity data were collected at 200 K with use of graphite-monochromated Mo Kα radiation. Accurate unit cell dimensions were determined with use of 25 general reflections ($20 < 2\theta < 30°$) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Absorption corrections to the data were made using a face-indexed numerical method (transmission factors 0.97–0.99).

The structure was solved by direct methods using Nicolet SHELXTLPLUS software and a DEC Microvax II computer. Following anisotropic refinement of all heavy atoms, the hydrogen atoms were included at calculated positions (using a riding model) with variable isotropic thermal parameters. The refinement converged with R = 0.0563 and R_w = 0.0657.[14]

Tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters, and structure factors are included as supplementary material.

[5*S*,2*R*,2′*S*,5′*R*]-, [5*S*,2*R*,2′*S*,5′*S*]-, and [5*R*,2*R*,2′*S*,5′*S*]-2,2′-Bis(5-cyclopentylcyclopentanone) (12–14). Compound 10 (0.61 g, 2.0 mmol) was suspended in absolute ethanol (23 mL) containing 73 mg of 5% Pd/C in a 300-mL, magnetically stirred, Parr autoclave. The reactor was purged with H_2 and then pressurized to 25 psi. After 2 h at 25 °C, the H_2 was vented and the reaction mixture was filtered through Celite and concentrated in vacuo. The crude material was separated by flash chromatography on a silica gel column eluting with hexane–ethyl acetate 20:1.

The first diketone to elute was a solid (0.10 g, 16% yield) and was identified as compound 14: mp 69–70 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.44 (t, J = 7.8 Hz, 2 H), 2.3–1.8 (br m, 10 H), 1.8–1.0 (br m, 18 H); ^{13}C NMR (62.85 MHz, $CDCl_3$) δ 219.50, 53.38, 50.27, 40.28, 30.67, 29.53, 25.48, 25.19, 24.87, 24.62; IR (NaCl, melt) 2949 (s), 2866 (s), 1726 (s), 1450 (m), 1357 (w), 1280 (w), 1244 (w), 1150 (w), 938 (w), 869 (w), 613 (w) cm^{-1}; MS (EI) *m/e* 302 (M$^+$). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.64; H, 9.83.

The second compound to elute was a liquid and was identified as isomer 13 (0.25 g, 40.3% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.75–2.55 (br m, 1 H), 2.5–2.3 (br m, 1 H), 2.3–1.0 (br m, 28 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 219.51, 219.42, 53.23, 51.56, 50.19, 49.02, 40.00, 39.96, 30.67 (2 C), 30.28, 29.19, 25.32, 25.11 (2 C), 24.84 (2 C), 24.71 (2 C), 24.62; IR (NaCl, thin film) 2949 (s), 2868 (s), 1734 (s), 1451 (m), 1338 (w), 1230 (w), 1151 (w) cm^{-1}; MS (EI) *m/e* 302 (M$^+$). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.54; H, 10.07.

The third diketone to elute (0.22 g, 35.5% yield) was identified as compound 12: mp 56–58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ

2.51 (t, J = 8.2 Hz, 2 H), 2.3–1.0 (br m, 28 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 219.54, 51.71, 48.98, 40.12, 30.70, 30.27, 25.28, 24.90, 24.82 (2 C). IR (KBr disc): 2947 (s), 2866 (s), 1728 (s), 1451 (m), 1315 (w), 1210 (w), 1169 (w), 1141 (w), 1004 (w), 934 (w), 860 (w), 607 (w), 529 (w) cm^{-1}; MS (EI) m/e 302 (M^+). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.32; H, 9.89.

2,2′-Bis(5-cyclopentylcyclopentanols) 15–17. Compound **12** (0.14 g, 0.46 mmol) was added to a 50-mL flask and dissolved in 20 mL of dry ether. To this was slowly added $LiAlH_4$ (58 mg, 1.5 mmol). The mixture was stirred for 40 min at room temperature and then cooled to 0 °C and quenched with water (0.05 mL), 1 M NaOH (0.05 mL), and water (0.15 mL). The crude product was filtered through silica gel and washed with ethanol to provide 0.13 g (93% yield) of the title compounds: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.0–3.8 (br m), 3.7–3.5 (br m) in a ratio of 1:1 (total 2 H), 2.0–0.7 (br m, 32 H); IR (KBr disc) 3609 (sh), 3462 (br s), 2945 (s), 2865 (s), 1449 (m), 1400 (w), 1329 (m), 1293 (w), 1271 (w), 1100 (w), 1057 (w), 1003 (w), 929 (w), 893 (w), 834 (m), 551 (m), 494 (m) cm^{-1}; MS (EI) m/e 306 (M^+). Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.44; H, 11.28.

Preparation of Bis(dithiocarbonates) 18–20. The general procedure developed by Barton et al. was used with modification.[12] Sodium hydride (0.04 g, 1.67 mmol) was added to a round-bottomed flask equipped with a condensor. To this was added a solution of imidazole (1.7 mg) and compounds **15–17** (0.13 g, 0.42 mmol) in THF (15 mL). This mixture was refluxed for 3 h prior to adding 250 μL of CS_2. After refluxing for a further 30 min, 250 μL of CH_3I was added. The mixture was heated at reflux for an additional 30 min, cooled to room temperature, and then diluted with water. The mixture was extracted using dichloromethane, and the organic phase was then washed with dilute HCl, $NaHCO_3$, and water and finally dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the mixture purified by flash chromatography on a silica gel column eluting with hexane–ethyl acetate (30:1) to provide a mixture of compounds (0.17 g, 80% yield) which were used without further purification for the preparation of compound **3a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.25–6.15 (br m), 5.78 (t, J = 5.4 Hz) in a ratio of 1:1 (total 2 H), 2.73 (s), 2.54 (s), 2.52 (s), in a ratio of 1:3:3 (total 6 H), 2.2–0.8 (br m, 30 H); IR (KBr disc) 2948 (s), 2868 (s), 1461 (sh), 1448 (w), 1421 (w), 1341 (w), 1320 (w), 1283 (w), 1215 (s), 1181 (sh), 1052 (s), 989 (w), 964 (w), 912 (w), 818 (w), 418 (w) cm^{-1}.

[5*R*,2*S*,1*S*,5′*S*,2′*R*,1′*R*]-2,2′-Bis[*O*-(*S*-methyldithiocarbonyl)-5-cyclopentylcyclopentan-1-ol] (18). The title compound was separated from the other isomers (**19** and **20**) by trituration of the mixture of these compounds with pentane. The crude solid obtained was recrystallized from ethyl acetate: mp 207 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 0.7–2.1 (br m, 30 H), 2.18 (s, 6 H), 6.2–6.4 (br m, 2 H); ^{13}C NMR (50.3 MHz, C_6D_6) δ 216.0, 89.80, 52.01, 46.82, 40.61, 33.61, 31.73, 29.27, 28.12, 25.66, 25.57, 18.78; IR (KBr disc) 2947 (s), 2867 (s), 1462 (vw), 1449 (w), 1422 (w), 1340 (w), 1320 (vw), 1312 (vw), 1340 (w), 1284 (w), 1247 (sh), 1216 (s), 1181 (sh) 1047 (s), 988 (w), 964 (w), 912 (w), 817 (w) cm^{-1}; MS (EI) m/e 486 (M^+). Anal. Calcd for $C_{24}H_{38}O_2S_4$: C, 59.21; H, 7.87. Found: C, 59.25; H, 7.87.

X-ray Structural Determination of Compound 18. Single crystals of this compound were obtained by slow evaporation of an ethyl acetate solution. A crystal of dimensions 0.50 (011, 0$\bar{1}\bar{1}$) × 0.24 (100, $\bar{1}$00) × 0.46 (0$\bar{1}$1, 01$\bar{1}$) mm was mounted on a Nicolet-Siemens R3m diffractometer. Intensity data were collected at 150 K with use of graphite-monochromated Mo Kα radiation. Accurate unit cell dimensions were determined with use of 25 general reflections ($20 < 2\theta < 30°$) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Absorption corrections to the data were made using a face-indexed numerical method (transmission factors 0.83–0.92).

The structure was solved by direct methods using Nicolet SHELXTLPLUS software and a DEC Microvax II computer. Anisotropic refinement of all heavy atoms allowed location of the hydrogen atoms from a difference map which were included in the refinement with fixed isotropic thermal parameters. The refinement converged with R = 0.0316 and R_w = 0.0355.

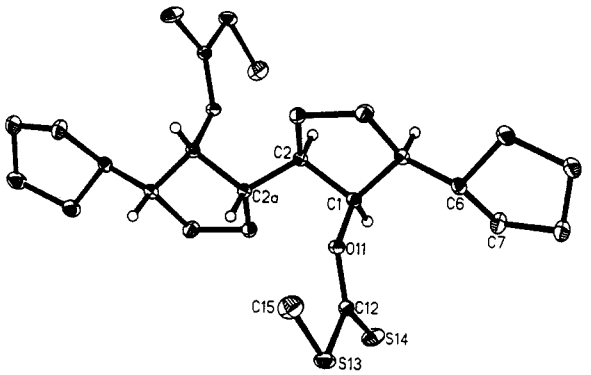


Figure 3. ORTEP diagram for bis(dithiocarbonate) **18** with 50% probability thermal ellipsoids depicted. H atoms on the terminal cyclopentane rings, the methylene carbons of the internal cyclopentane rings, and the dithiocarbonate methyl carbons have been removed for clarity.

The X-ray structure of this compound is depicted in Figure 3.[14] The structure of the hydrocarbon backbone corresponds to that of **3a**, and the dithiocarbonate groups have the relative stereochemistry expected for reduction of diketone **12** from the least hindered side of each carbonyl group. Tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters, and structure factors are included as supplementary material.

[1*R*,3*S*,1′*S*,3′*R*]-1,1′-Bis(3-cyclopentylcyclopentane) (3a). Compounds **18–20** (0.1 g, 0.21 mmol) in 5 mL of toluene were added to Ph_3SnH (1.4 g, 6 mmol) in 10 mL of toluene containing AIBN (20 mg) at 80 °C over 1.5 h using a syringe pump. After 2.5 h, the solution was concentrated in vacuo and the mixture was purified by flash chromatography on a silica gel column eluting with hexane to provide the title compound as the sole hydrocarbon product (17 mg, 30% yield): mp 91–92 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.6–0.85 (m, 2 H), 1.0–1.3 (m, 8 H), 1.4–2.0 (br m, 24 H); ^{13}C NMR (62.85 MHz, $CDCl_3$) δ 46.75, 46.59, 46.15, 38.73, 31.71, 30.73, 30.61, 25.43, 25.38; IR (KBr disc) 2944 (s), 2903 (sh), 2861 (s), 2838 (sh), 1464 (m), 1450 (m), 1445 (m), 1331 (w), 1316 (w), 1299 (vw), 1260 (w), 1097 (w), 1044 (w), 1023 (w), 935 (w), 892 (vw), and 882 (vw), 803 (w) cm^{-1}; MS (EI) m/e 274 (M^+). Anal. Calcd for $C_{20}H_{34}$: C, 87.52; H, 12.48. Found: C, 87.38; H, 12.69.

[1*R*,3*S*,1′*S*,3′*S*]-1,1′-Bis(3-cyclopentylcyclopentane) (3b). Compound **13** (0.24 g, 0.79 mmol) was reduced to a mixture of diols with $LiAlH_4$ using the procedure described above for the preparation of compounds **15–17**. The diol products were obtained in 85% yield and used without further purification.

The diols (120 mg, 0.39 mmol) were converted to the corresponding *S*-methyldithiocarbonate derivatives using the method described above for the preparation of compounds **18–20**. After purification by flash chromatography on silica gel, eluting with hexane–ethyl acetate 30:1, the mixture of products (180 mg, 94%) was directly employed in the next step.

The dithiocarbonate derivatives (100 mg, 0.205 mmol) were converted to the title compound using the procedure described above for the preparation of compound **3a**. After chromatography, 18 mg (32% yield) of the title compound was obtained as a solid: mp 65–67 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.0–1.3 (br m, 25 H), 1.3–1.0 (br m, 8 H), 0.95–0.6 (br m, 1 H); ^{13}C NMR (62.85 MHz, $CDCl_3$) δ 46.73, 46.60, 46.44, 46.20, 45.57, 45.10, 38.56, 36.41, 32.38, 32.26, 31.71, 31.69, 31.67, 31.54, 30.73, 30.66, 25.43 (3 C), 25.38; IR (KBr disc) 2943 (s), 2859 (s), 1449 (m) 1325 (w), 1260 (vw), 1201 (vw), 1103 (vw), 933 (w), 892 (w), 802 (vw), 695 (vw), 586 (vw) cm^{-1}. High-resolution MS. Calcd for $C_{20}H_{34}$: 274.26622. Found (EI): 274.26521.

[1*R*,3*S*,1′*R*,3′*R*]-1,1′-Bis(3-cyclopentylcyclopentane) (3c). Compound **11** (980 mg, 3.3 mmol) was hydrogenated over Pd/C as described above for the preparation of compounds **12–14**. The crude mixture of diketones was separated by chromatography on silica gel, eluting with hexane–ethyl acetate 30:1, to provide 390 mg (39% yield) of the unsymmetrical isomer **22** as revealed

by ^{13}C NMR. This diketone was reduced to a mixture of diols which were then converted to the title compound via the dithiocarbonate derivatives as described above (21% overall yield from diketone **22**): ^1H NMR (200 MHz, $CDCl_3$) δ 1.9–1.3 (br m, 25 H) 1.3–0.9 (br m, 8 H), 0.9–0.6 (br m, 1 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 46.76, 46.60, 46.46, 46.18, 45.56, 45.09, 38.84, 36.43, 32.35, 32.29, 31.73, 31.71, 31.69, 31.56, 30.71, 30.45, 25.42, 25.41 (2 C), 25.36; IR (neat, NaCl) 2942 (s), 2862 (s), 1449 (m), 1361 (w), 1324 (w), cm^{-1}. High-resolution MS. Calcd for $C_{20}H_{34}$: 274.26622. Found (EI): 274.26524.

[1*S*,3*S*,1′*S*,3′*S*]-1,1′-Bis(3-cyclopentylcyclopentane) (3d). The major symmetrical diketone (**23**; 210 mg, 0.70 mmol), prepared via hydrogenation of compound **11**, was converted to the title compound by an analogous series of reactions in 26% overall yield from this starting material: ^1H NMR (250 MHz, $CDCl_3$) δ 1.9–1.3 (br m, 26 H), 1.3–0.9 (br m, 8 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 46.64, 45.46, 45.13, 36.51, 32.49, 32.20, 31.73, 31.57, 25.39, 25.37; IR (NaCl, neat) 2939 (s), 2861 (s), 1448 (m), 1360 (vw), 1326 (w), 1305 (sh), 1227 (vw), 1119 (vw), 933 (w), 897 (w) cm^{-1}; MS (EI) *m/e* 274 (M^+). Anal. Calcd for $C_{20}H_{34}$: C, 87.52; H, 12.48. Found: C, 87.70; H, 12.54.

[1*R*,3*R*,1′*S*,3′*S*]-1,1′-Bis(3-cyclopentylcyclopentane) (3e). This material was prepared from diketone **14** using procedures described above: mp 49–50 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.9–1.25 (complex m, 30 H), 1.25–0.96 (m, 4 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 46.59, 45.34, 45.08, 36.25, 32.40, 32.32, 31.73, 31.55, 25.38, 25.36; IR (KBr disc) 2942 (s), 2859 (s), 1447 (m), 1325 (w), 1219 (w), 1037 (w), 934 (w), 893 (w), 729 (w), 696 (w), 586 (w), 450 (w) cm^{-1}; MS *m/e* 274 (M^+). Elem anal. Calcd for $C_{20}H_{34}$: C, 87.52; H, 12.48. Found: C, 87.51; H, 12.48.

[1*R*,3*S*,1′*R*,3′*S*]-1,1′-Bis(3-cyclopentylcyclopentane) (4). The minor symmetrical diketone (**21**; 50 mg, 0.17 mmol), prepared via hydrogenation of compound **11**, was converted to the title compound by an analogous series of reactions in 30% overall yield from this starting material: mp 38 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.9–1.35 (br m, 24 H), 1.35–0.9 (br m, 8 H), 0.9–0.6 (br m, 2 H); ^{13}C NMR (50.28 MHz, $CDCl_3$) δ 46.76, 46.63, 46.21, 38.84, 31.71 (2 C), 30.71, 30.59, 25.38, 25.33; IR (KBr disc) 2943 (s), 2903 (sh), 2860 (s), 1465 (m), 1447 (m), 1429 (sh), 1330 (m), 1250 (w), 1074 (w), 1022 (w), 997 (w), 934 (m), 894 (w), 727 (m), 697 (m) cm^{-1}; MS (EI) *m/e* 274 (M^+). Anal. Calcd for $C_{20}H_{34}$: C, 87.52; H, 12.48. Found: C, 87.36; H, 12.26.

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Supplementary Material Available: Tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters (18 pages); structure factors for both 11 and 18 (17 pages). Ordering information is given on any current masthead page.

References and Notes

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(4) Insufficient quantities of **8** were present in the mixture to obtain a decent ^{13}C NMR spectrum of this compound. Its presence was inferred from the ^1H NMR spectrum of the mixture (br m at δ 5.38).

(5) That chain-end effects are significant in polymerizations involving only cis-1,3 insertion is revealed by the finding that some **achiral** *ansa*-metallocene complexes (e.g., $en(Cp)_2ZrCl_2$, $Me_2Si(Cp)_2ZrCl_2$, and *meso*-$en(indenyl)_2ZrCl_2$) also produce highly isotactic polymer and hydro-oligomers. Kelly, W. M., unpublished results.

(6) One has to assume that the selectivity for formation of these two end groups when the metal is cis to this ring in **5** is the same as that observed using catalyst **1** (19:1). This is not unreasonable, given the similar steric demands of the tetrahydroindenyl and indenyl ligands.

(7) The determination of regioselectivity is probably not as straightforward as depicted in Scheme 2 in which a common intermediate is invoked for the formation of these two end groups. It is conceivable that olefin hydride complex **B′** is the **precursor** to the alkyl complex **A′** which then undergoes either further insertion of monomer or irreversible elimination to give olefin hydride complex **C′**. In addition, if chain transfer to, e.g., monomer, occurs competitively from **B′**, then the ratio of 2-cyclopentenyl:3-cyclopentenyl end groups will be dependent on monomer concentration. This is found to be the case (e.g., with $[C_5H_8]$ = 1.8 M, 2-Cp:3-Cp = 3.6:1, whereas with $[C_5H_8]$ = 4.5 M, 2-Cp:3-Cp = 7.9:1).

(8) The mechanism for trans-1,3 insertion could involve a reversible chain-transfer mechanism involving the unsaturated oligomers formed in these polymerizations or direct interconversion of cis to trans olefin hydride complexes prior to further propagation. These possibilities will be critically discussed elsewhere. Collins, S.; Kelly, W. M., manuscript in preparation.

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(14) Compound **11**: space group $C2/c$; $Z = 4$; $a = 17.267$ (3) Å, $b = 8.050$ (1) Å, $c = 12.488$ (1) Å, $\beta = 106.52$ (1)°; $V = 1664.1$ (4) Å^3 with $R = 0.0563$, $R_w = 0.0657$ for 1115 observed reflections with $F > 6.0\sigma(F)$. Compound **18**: space group $P2_1/c$; $Z = 2$; $a = 9.838$ (2) Å, $b = 13.844$ (2) Å, $c = 9.245$ (1) Å, $\beta = 92.64$ (1)°; $V = 1257.7$ (3) Å^3 with $R = 0.0316$, $R_w = 0.0355$ for 2347 observed reflections with $F > 6.0\sigma(F)$. For full details see the Experimental Section and the supplementary material.