Palladium(II)-Catalyzed Olefin Addition Polymerizations of 3,3-Dialkyl-Substituted Cyclopropenes

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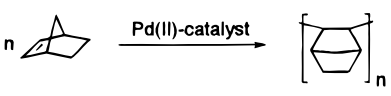
ABSTRACT: Ionic (η^3-allyl)palladium complexes containing bidentate 2,2′-bipyridyl, sparteine and C_2-symmetric bisoxazoline ligands and weakly coordinating anions catalyze the addition polymerization of 3,3-dialkylcyclopropenes. Poly(3,3-dimethylcyclopropene), poly(3-ethyl-3-methylcyclopropene) and poly(3-*n*-pentyl-3-methylcyclopropene) with molecular weights M_n(GPC) above 10 000 are formed which are nearly exclusively composed of triangular repeating units. In contrast, partial ring-opening occurs during polymerizations with ionic palladium tetrakis(nitrile) complexes $[Pd(RCN)_4][BF_4]_2$ which contain relatively labile nitrile ligands. The latter reactions lead to polymers which contain approximately 50% ring-opened unsaturated repeating units. The polymerizations carried out in the presence of the C_2-symmetric phenyl-substituted bisoxazoline ligand and with the (−)-sparteine-based catalyst lead to partially stereoregular polymers which contain a slight excess of meso units. Assignment of ^{13}C NMR spectra was aided with a quatercyclopropyl model compound composed of exclusively racemic units. The polycyclopropenes are partially crystalline and show a relatively good short term thermal stability with TGA investigations indicating onset of thermally induced weight loss above 280 °C.

Introduction

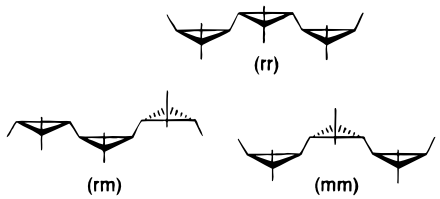
Homogeneous Ni(II)- and Pd(II)-based catalysts have recently emerged as a new versatile class of initiators for insertion polymerizations of linear and cyclic olefins. A large variety of macromolecular structures have become accessible through careful choice of the ligand sphere and the counterions in these late transition metal complexes. Polyolefins containing functional groups[1] and highly branched poly(α-olefins)[2] can be prepared with late metal catalysts bearing sterically bulky diimine ligands. A considerable number of Pd(II) compounds can be used for the synthesis of strictly alternating copolymers of α-olefins and carbon monoxide.[3−6] Furthermore, Pd(II) and Ni(II) catalysts can promote the olefin addition polymerization of strained bicyclic olefins (eq 1).[7,8] The bicyclic structure of the monomer remains intact,[9] and polymers with rigid structures are obtained. The driving force for these latter reactions is based on the release of ring strain[10] and the energy gained from converting a π-bond into a σ-bond.[11,12] Cyclic monomers previously used include norbornene, norbornadiene, 7-oxanorbornadiene, and their derivatives[7] and also polycylic olefins such as dicyclopentadiene,[7e,n] benzonorbornadiene,[7e] and *endo,exo*-1,4;5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.[7e]



(1)

Cyclopropenes appear to be interesting monocyclic monomers. They are highly strained (ring strain of cyclopropene = 55 kcal/mol)[10] and should produce polymers with fewer inequivalent ring carbon nuclei than those prepared from bicyclic monomers. Three different triad structures can be derived from cyclopropenes bearing two identical substituents at the 3-position (Scheme 1), provided the polymerization proceeds via 1,2-cis-insertion. 3,3-Disubstituted cyclopropenes should be very suitable for insertion polymerizations as they do not contain any β-hydrogens which could affect chain transfer reactions potentially leading to reduced polymer molecular weights.

Scheme 1



Unsubstituted cyclopropene is thermally unstable and undergoes spontaneous uncontrolled polymerization when kept above −78 °C.[13] A free-radical chain propagation mechanism and the formation of an addition polymer with the three-membered ring retained was suggested.[14] Reactions of cyclopropene derivatives with catalytic amounts of Pd(II) compounds including $PdCl_2$, (η^3-allyl)palladium chloride, and bis(benzonitrile)palladium chloride lead to the formation of cyclic dimers and oligomeric and polymeric byproducts.[15] Cyclooligomerizations via oxidative addition with Pd(0) complexes or Pd(0) intermediates and subsequent reductive elimination produce cyclic dimers, trimers, and tetramers based on 3,3-dialkylcyclopropenes.[16] Palladacycloalkanes containing two, three, and four cyclopropyl units were identified as stable intermediates in those reactions. Here, we describe high molecular weight polycyclopropenes, i.e., cycloaliphatic polyolefins composed of triangular repeating units, which are obtained with ionic Pd(II) catalysts.

Results and Discussion

Pd(II)-Catalyzed Polymerizations of 3,3-Dialkylcyclopropenes. Three 3,3-dialkyl-substituted cyclopropene monomers, **3a**−**c**, are prepared in 15−35% overall yields using a procedure which involves three reaction steps (Scheme 2).[17] The addition of in-situ generated dibromocarbene to the corresponding geminally disubstituted olefin leads to the formation of 1,1-dibromo-2,2-dialkylcyclopropanes **1a**−**c**. Reduction of compounds **1a**−**c** with Zn produces the monobromocy-

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Scheme 2. Synthesis of 3,3-Dialkyl-Substituted Cyclopropenes

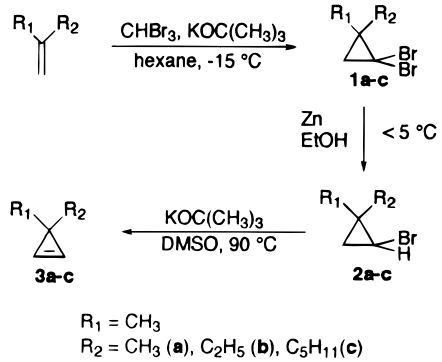


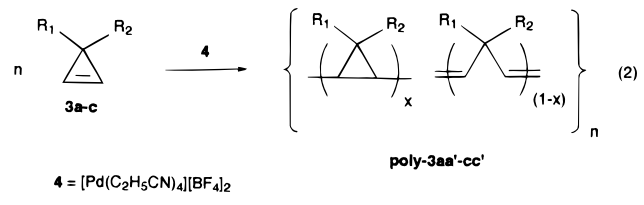
Table 1. Polymerization of 3,3-Dialkylcyclopropenes 3a−c Catalyzed by Pd Compound 4: Synthesis of Poly-3aa′−Poly-3cc′

entry	monomer	catalyst	[M]/[C][a]	*t*/h[b]	% yield[c]
1	**3a**	**4**	100/1	24	42
2	**3b**	**4**	10/1	24	65
3	**3b**	**4**	32/1	24	58
4	**3c**	**4**	10/1	24	40
5	**3c**	**4**	230/1	24	22

[a] Initial mole ratio of monomer to Pd^{2+} catalyst. [b] Reaction time at 20 °C, the temperature was previously raised from −90 to +20 °C. Reactions were carried out under nitrogen; solvent = CH_2Cl_2. [c] Polymer synthesis on a scale of 100−400 mg.

clopropanes **2a**−**c** which are subsequently transformed into the desired cyclopropene derivatives **3a**−**c** upon reaction with potassium *tert*-butoxide at 90 °C.

Initial polymerization studies of the highly strained cyclopropenes **3a**−**c** were carried out with $[Pd(C_2H_5CN)_4][BF_4]_2$. The reactions with this nitrile-based catalyst **4** proceed less selectively than the previous polymerizations of norbornene and its derivatives, and polymer structures comprising both cyclic and ring-opened repeating units are obtained (eq 2). The product based on 3,3-dimethylcyclopropene, **3a**, is only sparingly soluble, which indicates the presence of cross-linked structures. The polymers obtained from cyclic olefins **3b** and **3c** display a better solubility, and ^1H and ^{13}C NMR spectra show that both products are composed of approximately equal amounts of cyclic and ring-opened repeating units. The characteristic ^1H NMR signals at δ 5.45 and 0.65−0.45 (broad) correspond to the olefin protons of the ring-opened and the cyclopropane protons of the cyclic units of **poly-3bb′**, respectively.[18] Polymer yields in the range 22−65% are obtained when mole ratios of monomer/Pd catalysts between 10/1 and 220/1 are used for polymerization (Table 1).[19] The number average molecular weights of the chlorobenzene soluble fractions (T = 20 °C) range from 5900 to 16 600.[20]



4 = $[Pd(C_2H_5CN)_4][BF_4]_2$

$R_1 = CH_3$; $R_2 = CH_3$ (**3a**), C_2H_5 (**3b**), n-C_5H_{11}(**3c**)

In recent years, cyclopropenes have been shown to rearrange in the presence of Ti, Zr, W, Re, Ru, and Ir complexes to form transition metal vinylalkylidene complexes.[21] These rearrangements may suggest that a ring-opening olefin metathesis (ROMP) mechanism is responsible for the formation of the ring-opened units.

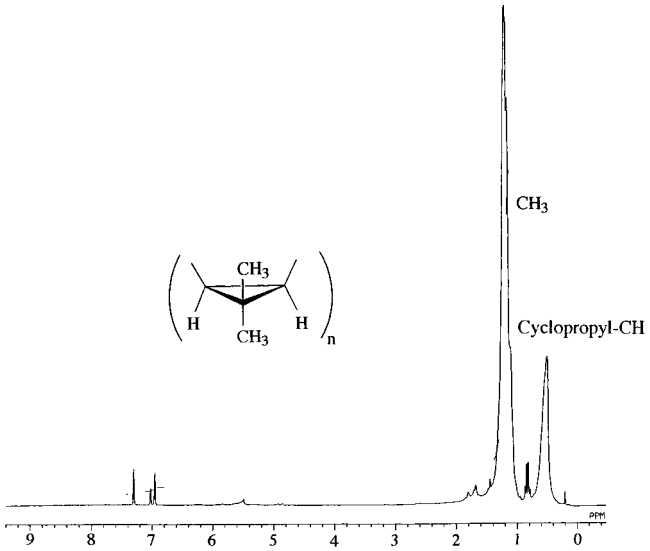
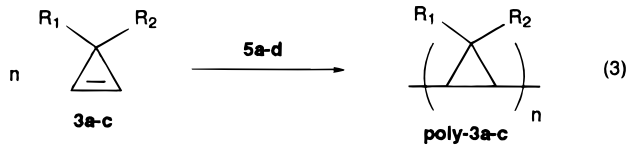


Figure 1. ^1H NMR spectrum (bromobenzene-d_5, 80 °C, 270 MHz) of poly(3,3-dimethylcyclopropene), **poly-3a**. The sample was prepared with the Pd catalyst **5b** (entry 8 of Table 2).

However, studies by Pfeffer et al.[22] on monoinsertions of cyclopropene derivatives into the Pd−C bond of a cyclopalladated dimethylbenzylamine Pd(II) complex have shown that insertions into Pd−C single bonds can be accompanied by ring-opening of the three-membered ring. The ring remains intact when substituted by two carbomethoxy groups; it opens when 3,3-dimethylcyclopropene is used for the insertion. Furthermore, a number of cyclopropane derivatives have been shown to undergo ring-opening induced by electrophilic attack of Pd(II) on the three-membered ring.[23] The latter results suggest that the unsaturated linear repeating units of **poly-3bb′** and **poly-3cc′** are more likely to be produced by secondary ring-opening due to electrophilic addition by Pd(II) rather than by a ROMP mechanism.[24]

A substantial improvement in the selectivity of the addition polymerization of cyclopropene monomers **3a**−**c** is achieved with the use of Pd(II) compounds **5a**−**d** (eq 3). These (η^3-allyl)Pd-complexes contain the nitrogen-based chelating ligands 2,2′-bipyridyl (in **5a**),[25] (−)-sparteine (in **5b**),[26] bis(phenyl)bisoxazoline (in **5c**),[27] and bis(*tert*-butyl)bisoxazoline (in **5d**)[27] which are more strongly bound to Pd(II) than the labile nitrile ligands in **4**. High molecular weight cycloaliphatic polyolefins **poly-3a**−**c** nearly exclusively composed of triangular repeating units are obtained when cyclopropenes **3a**−**c** are polymerized with these catalysts **5a**−**d**. Only very weak ^1H NMR signals in the range of 5.4 to 5.5 ppm (**poly-3a** in Figure 1) corresponding to the olefin protons of ring-opened repeating units are detected.



$R_1 = CH_3$; $R_2 = CH_3$ (**a**), C_2H_5 (**b**), n-C_5H_{11}(**c**)

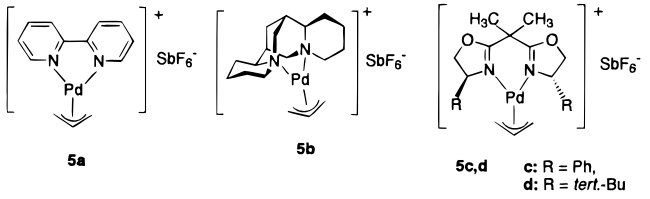


Table 2. Addition Polymerization of Cyclopropene Derivatives 3a−c Catalyzed by Pd Compounds 5a−d: Synthesis of Poly-3a−c

entry	monomer	catalyst	[M]/[C][a]	*t*/h[b]	% yield[c]
6	**3a**	**5a**	100/1	32	20
7	**3a**	**5b**	10/1	20	50
8	**3a**	**5b**	115/1	32	63
9	**3a**	**5c**	90/1	32	36
10	**3a**	**5d**	100/1	40	32
11	**3b**	**5b**	10/1	32	50
12	**3b**	**5b**	34/1	48	91
13	**3b**	**5b**	100/1	32	81
14	**3b**	**5c**	115/1	32	43
15	**3c**	**5b**	20/1	32	85
16	**3c**	**5c**	90/1	120	63
17	**3c**	**5d**	50/1	120	0

[a] Initial mole ratio of monomer to Pd^{2+} catalyst. [b] Reaction time at 20 °C, the temperature was previously raised from −80 to +20 °C. Reactions were carried out under nitrogen; solvent: CH_2Cl_2 in entries 6−8, 11−13, and 15−17; chlorobenzene in entries 9, 10, and 14. [c] Polymer synthesis on a scale of 130−400 mg.

Table 3. Molecular Weight Analysis of Poly-3a−c via Gel Permeation Chromatography

entry	polymer	M_n	M_w
3	**poly-3bb′**	5 900	7 700
5	**poly-3cc′**	16 500	28 600
6	**poly-3a**	16 500	32 000
8	**poly-3a**	19 000	31 000
10	**poly-3a**	16 600	35 000
13	**poly-3b**	39 600	68 000
15	**poly-3c**	42 000	99 000
16	**poly-3c**	54 000	104 000

[a] Analysis of the fraction soluble at 20 °C in chlorobenzene: 80 wt % of entry 3; 90 wt % of entry 5; 70 wt % of entries 6, 8 and 10; 60 wt % of entry 13; and 100% of entries 15, 16. [b] M_n and M_w are the relative number and weight average molecular weights, respectively, determined by gel permeation chromatography (GPC), calibrated with polystyrene standards.

Poly-3a−c are obtained in 20−91% yields from initial mole ratios of monomer to Pd between 10/1 and 115/1 (Table 2). The reaction temperature is 20 °C, and the reaction time is varied between 32 and 120 h. The steric bulk and the rigidity of the chelating ligand of the Pd catalyst as well as the size of the monomer substituents affect the polymerization behavior of the cyclopropene derivatives **3a−c**. Polymer yields (50−91%) are consistently higher with the sparteine-based catalyst **5b.**[28] Only 20% **poly-3a** is formed with the 2,2′-bipyridyl-based catalyst **5a**. These results indicate that catalyst stability and polymer yields decrease when catalysts with less bulky and less rigid chelating ligands are used. 3-*n*-Pentyl-3-methylcyclopropene undergoes polymerization with the phenyl-substituted bisoxazoline Pd(II) complex **5c**, but it remains unreacted (over a period of 120 h at 20 °C) when Pd(II) compound **5d** with the bulkier bis(*tert*-butyl)bisoxazoline ligand is used as the catalyst (compare entries 16 and 17 of Table 2). By contrast, 3,3-dimethylcyclopropene is sufficiently small to undergo insertion polymerization with complex **5d** (32% **poly-3a** in entry 10 of Table 2).

Poly(3-*n*-pentyl-3-methylcyclopropene), **poly-3c**, is completely soluble in chlorobenzene at 20 °C, and the relative number and weight average molecular weights of samples prepared from initial 20/1 and 90/1 mole ratios of monomer to catalyst ([M]/[C]) are M_n(GPC) = 42 000, M_w(GPC) = 99 000 (entry 15 of Table 3) and M_n(GPC) = 54 000, M_w(GPC) = 104 000 (entry 16 of Table 3), respectively.[29] These molecular weight values are higher than expected from the initial mole ratios of monomer to catalyst ([M]/[C]). The relatively high molecular weights and the broad molecular weight distributions suggest that initiation is considerably slower than chain propagation in the polymerizations according to eq 3. The cyclopropene polymerization is proposed to proceed by an insertion type mechanism presented in Scheme 3. Each of the first two cyclopropene insertion steps require a change in coordination mode of the corresponding hydrocarbon ligand from bidentate to monodentate. The terminal vinyl group (originating from the allyl ligand) and the free monomer can compete for coordination with Pd(II). Further chain propagation[30] is expected to proceed very rapidly, once the reaction has passed the slow stage of initiation.

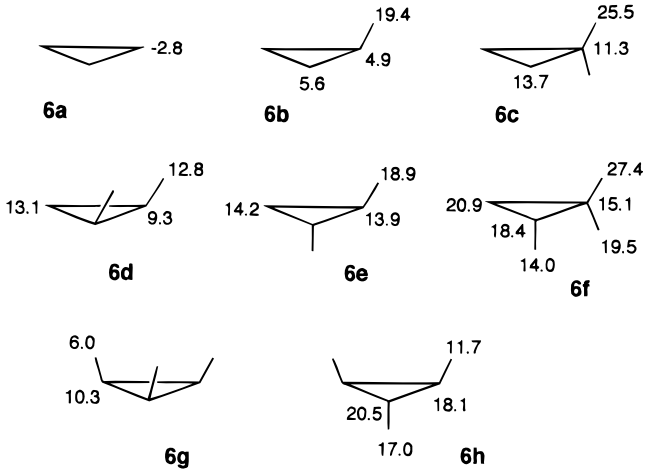
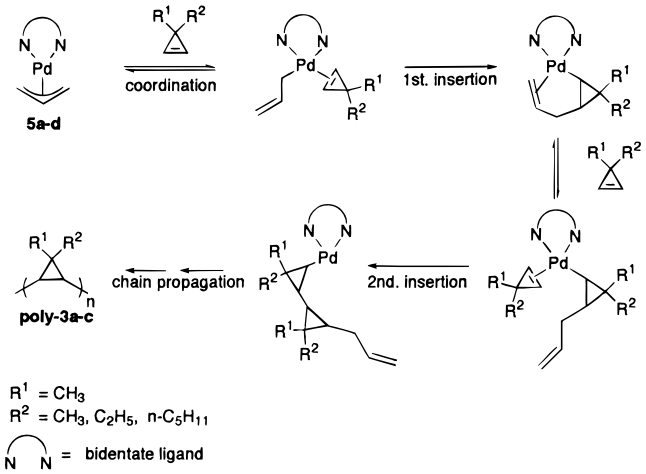


Figure 2. ^{13}C NMR shifts of cyclopropane derivatives **6a−h**,[33a,b] which serve as model compounds to aid the assignment of ^{13}C NMR spectra of **poly-3a**.

Scheme 3



Structural Analysis of Polycyclopropenes by NMR Spectroscopy. The ^1H NMR spectra of **poly-3a−c**[31] show characteristic broad signals at δ 0.65−0.45 ppm corresponding to the cyclopropyl protons, which indicate that the three-membered ring structure of the monomers is retained during the polymerization (^1H NMR spectrum of **poly-3a** displayed in Figure 1). ^{13}C NMR analysis reveals a polymer structure with 1,2-cis-linked triangular repeating units which agrees with an insertion mechanism for polymerization. This 1,2-cis structure contrasts with the trans-linked sequence of the cyclopropyl groups in the quater(cyclopropyl) unit of the naturally occuring antifungal agent FR-900848.[32]

Cyclopropane, **6a**,[33a] and methyl-, **6b**;[33a] 1,1-dimethyl-, **6c**;[33a] cis-1,2-dimethyl, **6d**;[33a] trans-1,2-dimethyl-, **6e**;[33a] 1,1,2-trimethyl-, **6f**;[33a] cis-1,2,3-trimethyl-, **6g**;[33b] and trans-1,2,3-trimethylcyclopropane, **6h**[33b] (Figure 2) serve as simple model compounds to aid assignment of

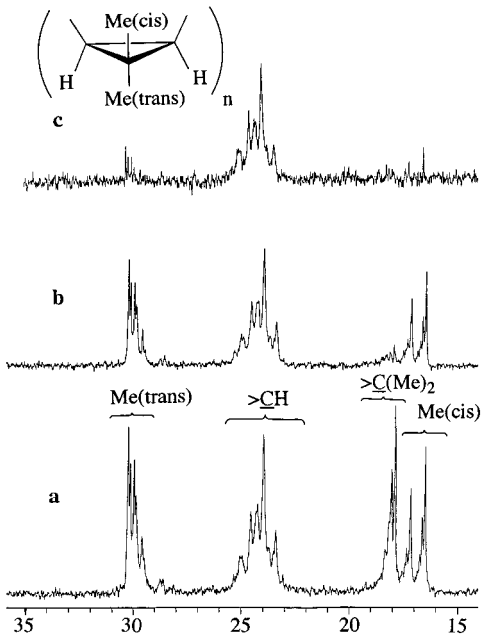


Figure 3. (a) ^{13}C NMR spectrum (bromobenzene-d_5, 80 °C, 67.8 MHz), (b) DEPT 135 NMR spectrum (showing the signals corresponding to CH_3 and CH), and (c) DEPT 90 NMR spectrum (signals corresponding to CH) of **poly-3a** prepared with Pd catalyst **5b** (entry 8 of Table 2).

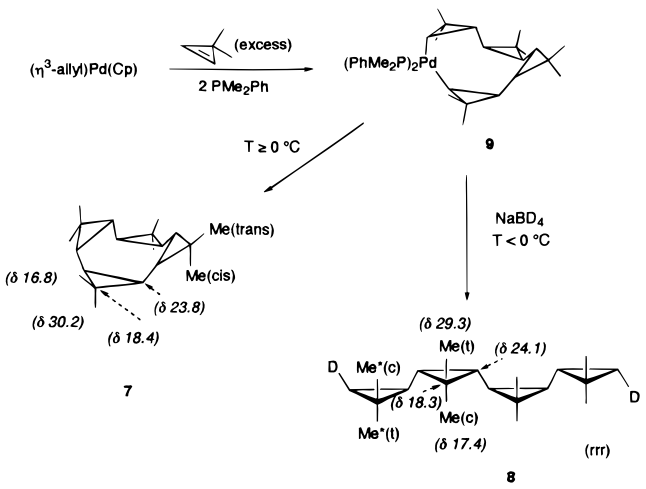
the ^{13}C NMR spectra of **poly-3a**. The γ-syn effect of a CH_3 group imposed on another CH_3 substituent leads to an upfield shift of $\Delta\delta = -6.0$ to -6.8 ppm and is approximately additive for a third methyl substituent (compare **6b** with **6d** and **6g**, and compare **6c** with **6f**). The γ-anti effect for the methyl substituents varies between $\Delta\delta = -1.9$ and $+1.9$ ppm (compare **6b** with **6e** and **6h**; also compare **6c** with **6f**). Accordingly, a substantial chemical shift difference of at least 8 ppm was predicted for the two methyl groups of 1,2-cis-linked repeating units of **poly-3a**.[34] By contrast, trans-1,2-linkages would render the methyl groups equivalent, as each would experience a γ-syn and a γ-anti interaction.

On the basis of the models of Figure 2 the ^{13}C NMR shifts of the all-1,2-cis-linked cyclotetramer 3,3,6,6,9,9,12,12-octamethyl-*anti*,*syn*,*anti*-pentacyclo-[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}]dodecane, **7**,[16c] are assigned as: δ 30.2 (Me(trans)), 23.8 (tertiary cyclopropyl-C), 18.4 (quaternary cyclopropyl-C), 16.8 (Me(cis)). The chemical shift difference for the two types of methyl substituents, Me(trans) and Me(cis), is $\Delta\delta = 13.4$ ppm in compound **7**.[34]

Similarly, the ^{13}C NMR spectrum of **poly-3a** (Figure 3a) displays signals which are assigned to the four different carbon atoms of the 3,3-dimethylcyclopropene repeating unit. The tertiary-CH carbons of the three-membered ring form the polymer main chain and give rise to a group of signals at δ 25.0−23.4 ppm. These carbons can be assigned from the DEPT 90 spectrum (Figure 3c). The quaternary cyclopropyl carbons correspond to the signals at δ 18.5−17.9 ppm, as these signals disappear in the DEPT 135 spectrum (Figure 3b). The group of resonances at δ 17.5−16.5 are assigned to the Me(cis) substituents which experience the γ-syn effects imposed by the two neighboring cyclopropyl units. The Me(trans) substituents are shifted downfield to δ 30.2−29.5 ppm due to the two γ-anti interactions with the neighboring repeating units.

Each of the four carbon nuclei of the repeating units of **poly-3a** (cyclopropyl-CH, quaternary cyclopropyl-C, Me(cis), and Me(trans)) gives rise to a group of three to eight partially resolved signals (67.8 MHz spectra). The observation of several signals for each of these carbon atoms reflects the presence of several stereochemical configurations in this cyclopropene-based polymer (see Scheme 1). Within each of the four groups of signals one signal shows a slightly more pronounced intensity (Figure 3a): δ 30.2 (Me(trans)), 24.0 (cyclopropyl-CH), 18.0 (quaternary cyclopropyl-C) and 16.6 (Me(cis)) which indicates that poly(3,3-dimethylcyclopropene) prepared with the sparteine-based catalyst **5b** is partially stereoregular. This stereoregularity is slightly more pronounced in **poly-3a** prepared with the phenyl-substituted bisoxazoline Pd catalyst **5c**.

Scheme 4. Synthesis of a Syndiotactic Tetramer Model Compound



The linear tetramer of 3,3-dimethylcyclopropene, 1,-12-dideuterioquater(3,3-dimethylcyclopropyl), **8**, with a syndiotactic sequence of three-membered ring units (rrr-tetrad)[35] serves as a model compound to assist in the assignment of the moderately predominant stereochemical configuration of **poly-3a**. The ^{13}C NMR signals at δ 17.4 and 29.3 corresponding to Me(c) and Me(t) of the internal cyclic units of **8** are very similar to those of the low-intensity signals of **poly-3a** but differ by nearly 1 ppm from the dominant Me(cis) and Me(trans) signals of the 3,3-dimethylcyclopropene based addition polymer in Figure 3a. This suggests that poly(3,3-dimethylcyclopropene) samples prepared with **5b** and **5c** contain a moderate excess of meso units (ca. 65% and 70% meso in **poly-3a** prepared with **5b** and **5c**, respectively).

Tetramer **8** (in addition to 20% cyclic compound **7**) is obtained by the reaction of (η^3-allyl)Pd(Cp) with an excess of 3,3-dimethylcyclopropene[16c] and subsequent reductive cleavage of the resulting palladacycle **9** with sodium borodeuteride at 0 °C (Scheme 4). An anti, syn, anti, syn arrangement of neighboring cyclopropane units in the cyclic precursor **9** corresponding to a syndiotactic sequence of repeating units has been previously established by X-ray analysis.[16d]

The relatively moderate degree of tacticity in **poly-3a** indicates that both catalytic site control and chain-end control contribute to the overall stereocontrol in the polymerization of **3a** catalyzed by **5b** and **5c**. At the current stage the origin of stereocontrol is still speculative.[36] It is suggested that in the case of the polymerization with the bisoxazoline-based catalyst **5c** the growing polymer chain points away from the moderately bulky phenyl substituents of the chelating ligand.[37] Both the polymer chain end and the phenyl substituents direct the relative orientation of the incoming cyclic monomer in order to keep steric interactions to a

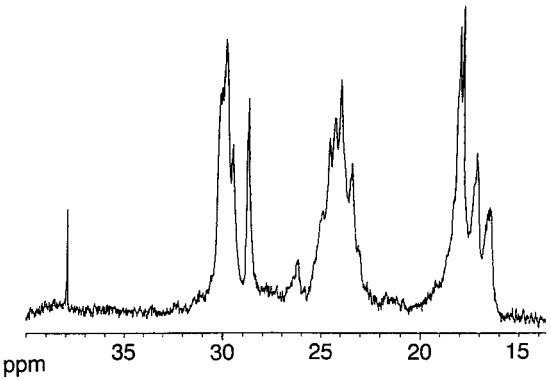
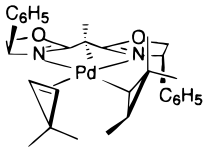


Figure 4. ^{13}C NMR spectrum (bromobenzene-d_5, 80 °C, 67.8 MHz) of **poly-3a** (entry 6 of Table 1) prepared with the achiral catalyst **5a** (signals at δ 37.9 and 28.7 correspond to small amounts of ring-opened units $=CHC(CH_3)_2CH=$).

minimum (structure **10**). By contrast, the use of Pd catalyst **5d** bearing two voluminous *tert*-butyl substituents leads to **poly-3a** with a predominantly atactic microstructure. The two bulky *tert*-butyl substituents exert a counteracting influence on the orientation of the cyclopropene monomer **3a**.



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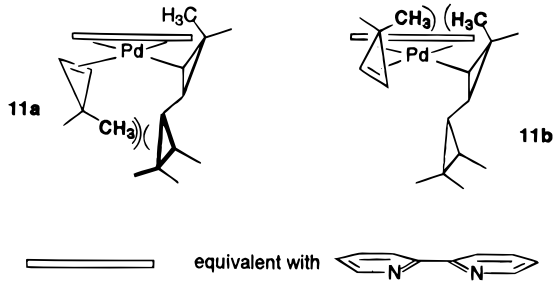
The ^{13}C NMR spectrum of **poly-3a** obtained with the achiral catalyst **5a** (Figure 4) shows signals of considerably reduced intensity at δ 30.2 and 30.1 (Me(trans)) and 16.7 ppm (Me(cis)) and more intense signals at δ 30.0, 29.9 and 17.3, 17.2 ppm. This indicates that approximately equal amounts of meso and racemic units are present (between 45% and 50% meso) corresponding to a predominantly atactic polymer microstructure.

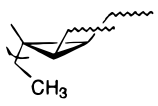
The atactic stereochemistry of **poly-3a** prepared with **5a** contrasts with the syndiotactic polymer configuration of alternating *p*-*tert*-butylstyrene/CO copolymers obtained with [(2,2′-bipy)Pd(CH_3)(CH_3CN)][BAr′$_4$].[4b] Again it is the higher rigidity of the growing polycyclopropene chain which is assumed to be responsible for the difference in the stereoselectivity of the polymerization. In contrast to the C_2-symmetric bisoxazoline ligand of **5c** the approximately planar 2,2′-bipyridyl ligand of **5a** (Scheme 5) does not impose any preferred orientation onto the polycyclopropene chain end attached to Pd(II). The Me(cis) group and the three-membered ring linked to the last inserted repeating unit point away from the Pd−C σ-bond in a fork-like fashion and are suggested to be positioned that they can sterically interact with the *syn*-CH_3 substituent of π-bonded **3a** to a similar extent. Then, both orientations **11a** (C-3 of **3a** down) and **11b** (C-3 of **3a** up) of the π-bonded cyclopropene monomer have a similar probability, and a polymer with low tacticity is obtained upon monomer insertion.

3-Ethyl-3-methylcyclopropene **3b** has two heterotopic faces and can approach the transition metal center of the catalyst with either the ethyl or the methyl substituted monomer face. Accordingly, the resulting poly-(3-ethyl-3-methylcyclopropene), **poly-3b**, contains additional stereochemical configurations to those presented in Scheme 1 as the ethyl substituent can be either cis (**3b,c**) or trans (**3b,t**) to the two neighboring cyclic units. Repeating units with trans-linked ethyl groups (**3b,t**) are slightly predominant due to moderately less hindered π-coordination of the methyl substituted monomer face during chain propagation.

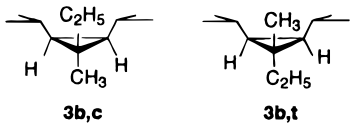
Scheme 5. Chain-End Control in Polymerization of 3a with 5a, Approximately Equal Probability for 11a and 11b



Scheme 6

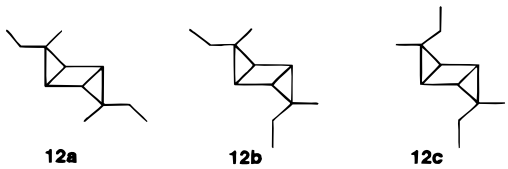


3b,t



3b,c **3b,t**

The mole fraction of **3b,t** repeating units is 0.65 for **poly-3b** prepared with the sparteine based catalyst (entries 11−13 of Table 2) and 0.60 (entry 14 of Table 2) for the polymer obtained with the phenyl-substituted bisoxazoline-Pd catalyst (as determined from the ^1H NMR spectrum). These values indicate that the ethyl-substituted face of **3b** is slightly less reactive. Similarly, the thermal dimerization of cyclopropene **3b** for 48 h at 110 °C leads to the formation of a 31/50/19 ratio of exo,exo-/exo,endo-/endo,endo-substituted 3,6-diethyl-3,6-dimethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexanes **12a**−**c**[38] which corresponds to a reactivity ratio of 56/44 in favor of the methyl-substituted face of **3b**.



12a **12b** **12c**

The rotation of the ethyl substituents is less restricted in **3b,t** repeating units than in the **3b,c** units. Thus, **3b,t** units can adopt conformations with the ethyl-CH_3 positioned over the three-membered ring where the terminal protons experience the shielding effect of the cyclopropyl unit (Scheme 6). The ^1H NMR signal corresponding to ethyl-CH_3 of **3b,t** units is then shifted upfield to δ 1.05−0.98 ppm. The ethyl-CH_3 protons of **3b,c** are affected by a deshielding influence of the neighboring cyclopropene repeating units and give rise to a signal further downfield overlapping with the methyl-CH_3 protons at δ 1.25−1.15 (Figure 5a).

The ^1H and ^{13}C NMR spectra are assigned with the aid of a two-dimensional ^{13}C-^1H HETCOR NMR spectrum (Figure 5b). Characteristic is the correlation of the ^{13}C NMR shifts δ 11.6−11.3 ppm (ethyl-*C*H_3) with both ^1H NMR signals δ 1.05−0.98 (**3b,t** units) and 1.25−1.15 (**3b,c** units). In addition, the broad ^1H NMR signal

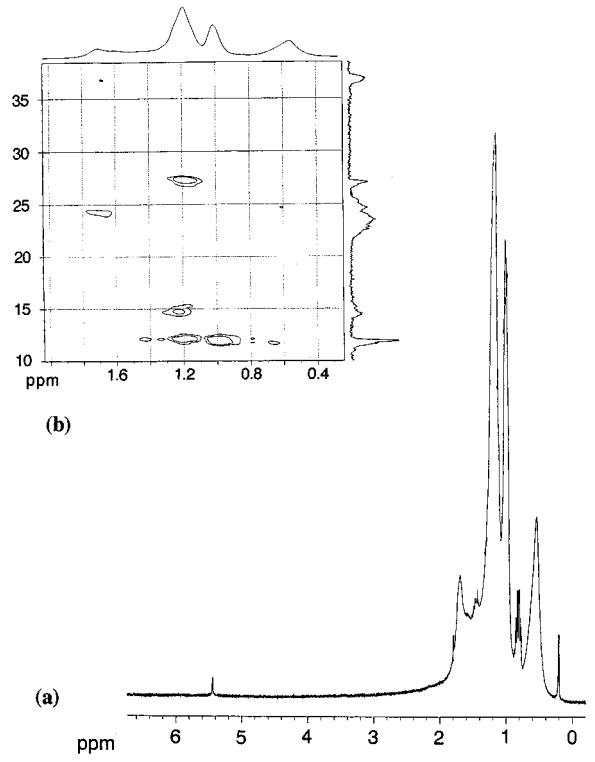


Figure 5. (a) ^{1}H NMR and (b) two-dimensional ^{13}C−^{1}H HETCOR NMR spectra (bromobenzene-d_5, 80 °C, 270 MHz) of poly(3-ethyl-3-methylcyclopropene), **poly-3b**, prepared with the Pd catalyst **5b** (entry 12 of Table 2).

δ 1.25−1.15 correlates also with the ^{13}C NMR resonances δ 26.8−26.5 (Me of **3b,c** units) and 15.0−14.0 (Me of **3b,t** units).[39]

Thermal Properties of Polycyclopropenes

Thermogravimetric analysis (TGA) of poly(3-ethyl-3-methylcyclopropene) and poly(3-*n*-pentyl-3-methylcyclopropene) show onset of weight loss at 280−300 °C (under nitrogen) and 5% weight loss at 330−350 °C. Both polymers decompose in one step, leaving approximately 0% residue at temperatures above 520 °C.

However, ring-opening of the three-membered ring already occurs upon prolonged storage at room temperature (despite the relatively high temperature for onset of weight loss in the TGA curves). Over a seven month period at 20 °C, 70% of the cyclic units of **poly-3b** open under predominant formation of [=CHC(CH_3)(C_2H_5)-CH=] repeating units with trans-linked carbon−carbon double bonds.[40] We assume that the slow ring-opening reaction at room temperature is initiated by the Pd-containing end groups. For comparison, thermal ring-opening of the more highly strained cyclic dimers of 3,6-diethyl-3,6-dimethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane **12a**−**c** proceeds at a substantially lower rate. Very slow rearrangement, i.e., 3% conversion to the trans- and cis-isomers of 3,6-diethyl-3,6-dimethyl-1,4-cyclohexadiene is detected (via ^{1}H NMR spectroscopy) after 48 h at an elevated temperature of 110 °C.[41]

Poly-3a−**c** samples prepared with Pd catalysts **5b** and **5c** are semicrystalline and show birefringence when viewed using the crossed polarizers of an optical microscope. The glass and melt transition temperatures T_g and T_m of poly(3-*n*-pentyl-3-methylcyclopropene), **poly-3c**, are 60 and 110 °C, respectively (recorded by DSC). In **poly-3a** and **poly-3b**, the glass and melt transitions occur at higher temperatures, and thermal ring-opening begins which obscures these thermal transitions.

Conclusion

The Pd(II)-catalyzed addition polymerization of three 3,3-dialkylcyclopropenes leads to macromolecular structures composed of triangular repeating units. Mixed polymer structures with three-membered ring units and ring-opened units are obtained with [Pd(C_2H_5CN)$_4$][BF_4]$_2$, a Pd-compound bearing comparatively small and labile nitrile ligands. With chelating nitrogen-based ligands on Pd(II), olefin addition predominates, and the resulting polymer contains nearly exclusively cyclic repeating units. Poly(cyclopropenes) containing a small excess of meso units are produced with Pd-complexes bearing chiral chelating ligands such as (−)-sparteine and 2,2-bis-(2-(4-(*S*)-phenyl-1,3-oxazolinyl))propane.

Experimental Section

General Procedures and Materials. All work involving air and/or moisture-sensitive compounds was carried out by using standard high-vacuum, Schlenk or drybox (M. Braun) techniques. NMR spectra were recorded on Jeol GX270 (270.05 MHz) and Bruker MSL300 (300.13 MHz) NMR spectrometers. Spectra were referenced to the solvent signals: δ 7.24 (^{1}H) and 77.00 (^{13}C) for $CDCl_3$, 5.32 (^{1}H) and 53.80 (^{13}C) for CD_2Cl_2, and 7.30 (^{1}H) and 131.50 ppm (^{13}C) for bromobenzene-d_5. ^{13}C NMR spectra in bromobenzene-d_5 were recorded at 80 °C. Gel permeation chromatographic (GPC) analysis utilized a Polymer Standards Service column, a Knauer HPLC Pump 64, and a Waters R401 differential refractometer. All GPC analysis were performed on solutions in chlorobenzene (0.4−0.7 g/dL). Calibration was based on five polystyrene standards ranging from M_n 5200 to 580 000 (M_w/M_n < 1.1). Thermogravimetric analysis was carried out under nitrogen on a Mettler TG 50 instrument at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) studies were performed at a heating rate of 10 °C/min. (under nitrogen) using Perkin Elmer DSC-7 and Mettler DSC-20 instruments. Dichloromethane and chlorobenzene were dried over CaH_2 and distilled; potassium *tert*-butoxide was sublimed at 150 °C and 0.01 Torr. Methanol (BDH), isobutylene (99%), 2-methyl-1-butene (98%), and 2-methyl-1-heptene (99%) (all from Aldrich), (−)-sparteine (Sigma), bromoform, 2,2-bis[2-[4-(*S*)-phenyl-1,3-oxazolinyl]]propane and 2,2-bis[2-[4-(*S*)-*tert*-butyl-1,3-oxazolinyl]]propane, sodium tetrachloropalladate(II) (99%), silver hexafluoroantimonate (98%), sodium borodeuteride (98% D), and 2,2′-bipyridyl (all from Aldrich) were used as obtained from the supplier. [Pd(C_2H_5CN)$_4$][BF_4]$_2$ was synthesized as previously described.[7a] (η^3-Allyl)[(−)-sparteine]palladium hexafluoroantimonate was prepared according to a procedure by Togni et al.[26] 3,3-Dimethylcyclopropene, **3a**, and the palladacycle bis(dimethylphenylphosphine)-3,3,6,6,9,9,13,13-octamethyl-11-pallada-*anti*,*syn*,*anti*,*syn*-pentacyclo-[10.1.0.0^{2,4}0.^{5,7}0.^{8,10}]tridecane, **9**, were obtained according to procedures by Nesmeyanova et al.[17b] and Binger et al.,[16c] respectively.

A reaction sequence similar to Binger et al. was used for the synthesis of **3b**.[17a]

Synthesis of 1,1-Dibromo-2-ethyl-2-methylcyclopropane, 1b. A three-necked 2 L flask equipped with an addition funnel was charged with potassium *tert*-butoxide (85.53 g, 0.76 mol) and hexane (700 mL). This mixture was cooled to −15 °C, and 2-methyl-1-butene (42.4 g, 0.61 mol) was added under stirring over a period of 20 min. Then, the addition funnel was rinsed with hexane (50 mL). A solution of bromoform (168.4 g, 0.67 mol) in hexane (60 mL) was added to the mixture at −15 °C over a period of 4 h. The mixture turned an orange-brown color and was gradually warmed to room temperature and stirred for 12 h. The solution was poured onto water (900 mL) and extracted with dichloromethane (5 × 200 mL). The combined organic fractions were dried over $MgSO_4$, the dichloromethane removed using a rotary evaporator, and the product was distilled under vacuum, bp 72 °C (14 Torr). Yield = 121.5 g (83%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ 1.65 (m, J = 7.5 Hz, 2 H, CH_2CH$_3$), 1.39 (s, 1 H, cyclopropyl-C*H*), 1.38 (s, 1 H, cyclopropyl-C*H*), 1.33 (s, 3 H, CH_3), 1.04 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3).

^{13}C NMR (67.8 MHz, $CDCl_3$, 25°C): δ 39.7 (CBr_2), 34.7 ($>CH_2$), 31.8 (CH_3CH_2), 30.5 (quaternary cyclopropyl-*C*), 21.9 (CH_3), 10.7 (CH_2CH_3).

Synthesis of 1-Bromo-2-ethyl-2-methylcyclopropane, 2b. Zinc dust (200 g, 3.1 Mol) was dispersed in ethanol (450 mL), and the mixture was cooled to 0 °C. A solution of concentrated HCl (30 mL) in ethanol (70 mL) was added. Subsequently, a solution of 1,1-dibromo-2-ethyl-2-methylcyclopropane (75.0 g, 0.31 mol) in ethanol (100 mL) was added dropwise over a period of 3 h. Stirring was continued for an additional 2 h at 5 °C and for 20 h at room temperature. The mixture was filtered to remove the zinc and poured onto 3 L of water. A white precipitate formed which dissolved on addition of concentrated HCl (40 mL). The solution was extracted with pentane (5 × 200 mL), and the combined fractions were dried over $MgSO_4$. The pentane was removed by distillation. The ^{1}H NMR spectrum of the crude product showed that it contained approximately 9 mol % 1-ethyl-1-methylcyclopropane. The product was distilled under vacuum, bp 45 °C (28 Torr). Two pairs of enantiomers of 1-bromo-2-ethyl-2-methylcyclopropane are present. The predominant pair of enantiomers comprise the *R,R* and *S,S*-forms (60%, determined by ^{1}H NMR). Yield: 28.3 g (56%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C). *R,R*/*S,S*-enantiomers: δ 2.76 (dd, $J_{vic-cis}$ = 7.5 Hz, $J_{vic-trans}$ = 4.5 Hz, 1 H, C*H*Br), 1.23 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 1.16 (s, 3 H, CH_3), 0.90 (dd, $J_{vic-cis}$ = 7.5 Hz, J_{gem} = 6.5 Hz, 1 H, cyclopropyl-C*H*$^{(trans\ to\ Br)}$), 0.85 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.54 (dd, J_{gem} = 6.5 Hz, $J_{vic-trans}$ = 4.5 Hz, 1 H, cyclopropyl-C*H*$^{(cis\ to\ Br)}$. *R,S*/*S,R*-enantiomers: δ 2.77 (dd, $J_{vic-cis}$ = 7.5 Hz, $J_{vic-trans}$ = 4.5 Hz, 1 H, C*H*Br), 1.48 (m, 2 H, CH_2CH_3), 1.00 (s, 3 H, CH_3), 0.94 (t, J = 7.5 Hz, CH_2CH_3), 0.88 (dd, $J_{vic-cis}$ = 7.5 Hz, J_{gem} = 6.5 Hz, 1 H, cyclopropyl-C*H*$^{(trans\ to\ Br)}$), 0.56 (dd, J_{gem} = 6.5 Hz, $J_{vic-trans}$ = 4.5 Hz, 1 H, cyclopropyl-CH$^{(cis\ to\ Br)}$).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C). *R,R*/*S,S*-enantiomers: δ 31.6 (CH_3CH_2), 29.7 (*C*HBr), 22.3 (quaternary cyclopropyl-*C*), 22.2 (cyclopropyl-CH_2), 19.7 (CH_3), 10.5 (CH_2CH_3).

R,S/*S,R*-enantiomers: δ 30.6 (*C*HBr), 29.4 (CH_3CH_2), 22.7 ($>CH_2$), 21.8 (quaternary-cyclopropyl-*C*), 21.5 (CH_3), 10.7 (CH_2CH_3).

Side product 1-ethyl-1-methylcyclopropane. ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ 1.22 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 0.99 (s, 3 H, CH_3), 0.89 (t, J = 7.5 Hz, CH_2CH_3), 0.19 (d, J = 4.8 Hz, 4 H, cyclopropyl-CH_2).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 32.0 (CH_3CH_2), 22.3 (CH_3), 16.8 (quaternary *C*), 12.7 (cyclopropyl-CH_2), 11.0 (CH_2CH_3).

Synthesis of 3-Ethyl-3-methylcyclopropene, 3b. A 100 mL two-necked flask equipped with an addition funnel and a condenser was charged with potassium *tert*-butoxide (7.59 g, 67.6 mmol) and dimethyl sulfoxide (20 mL) under nitrogen. The mixture was heated to 90 °C, and 1-bromo-2-ethyl-2-methylcyclopropane (10.00 g, 61.3 mmol) was added one drop at a time from the addition funnel over a period of 3 h. After the addition of each drop, nitrogen was blown across the apparatus so that any 3-ethyl-3-methylcyclopropene which had formed was removed from the reaction flask (to keep secondary reactions to a minimum). The product was collected in a 30 mL Schlenk flask cooled in a −100 °C bath (liquid N_2/ethanol mixture), which was connected to the top of the condenser. The crude product collected in the Schlenk flask contained 10 mol % of *tert*-butanol (δ = 1.26, s). The monomer was purified by stirring over lithium aluminum hydride for 4 h and then vacuum transferred at 95 Torr.

Yield: 2.92 g (58%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ 7.34 (s, 2 H, =C*H*), 1.46 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 1.11 (s, 3 H, CH_3), 0.65 (t, J = 7.5 Hz, CH_2CH_3).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 121.9 (=*C*H), 32.5 (CH_3CH_2), 27.0 (CH_3), 21.4 (quaternary cyclopropyl-*C*), 11.3 (CH_2CH_3).

Synthesis of 1,1-Dibromo-2-*n*-pentyl-2-methylcyclopropane, 1c. The procedure used was very similar to the synthesis of **1b**: bromoform (58.2 g, 0.23 mol) in hexane (20 mL) was added to a mixture of 2-methyl-1-heptene (24.3 g, 0.2 mol), potassium *tert*-butoxide (28.1 g, 0.25 mol) and hexane (260 mL) at −15 °C over a period of 2 h. The mixture was then stirred at room temperature for 12 h. Then, addition to water (250 mL) and extraction with dichloromethane (5 × 150 mL) followed. The organic phase was dried over $MgSO_4$, the dichloromethane was removed by distillation, and the product was distilled: bp 76 °C (0.6 Torr); yield 45.3 g (80%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ 1.65−1.45 (bm, 4 H, 2 × CH_2 of *n*-pentyl), 1.39 (s, 1 H, cyclopropyl-CH), 1.38 (s, 1 H, cyclopropyl-CH), 1.33 (s, 3H, CH_3), 1.32−1.27 (bm, 4 H, 2 × CH_2 of *n*-pentyl), 0.88 (t, 3 H, CH_2CH_3).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 39.9 (CBr_2), 38.7 ($CH_3(CH_2)_3CH_2$), 34.8 (cyclopropyl-CH_2), 31.8 ($CH_3CH_2CH_2$), 29.7 (quaternary cyclopropyl-C), 26.1 ($CH_3(CH_2)_2CH_2$), 22.6 (CH_3CH_2), 22.5 (CH_3), 14.1 (CH_2CH_3).

Synthesis of 1-Bromo-2-*n*-pentyl-2-methylcyclopropane, 2c. A procedure similar to that for the preparation of **2b** was used. Zinc dust (35.5 g, 0.54 mol) was dispersed in ethanol (60 mL), followed by addition of a solution of concentrated HCl (5 mL) in ethanol (10 mL) and addition of dibromocyclopropane **1c** (17.5 g, 61.7 mmol) dissolved in ethanol (20 mL) at 0 °C over a period of 1 h. Stirring was continued for another 2 h at 5 °C and for 4 h at 20 °C. The mixture was filtered and poured onto 500 mL of water. Addition of concentrated HCl (3 mL), extraction with pentane (6 × 20 mL), drying over $MgSO_4$, and first atmospheric distillation to remove the pentane and then distillation of the crude product (containing 30 mol % of 1-*n*-pentyl-1-methylcyclopropane, bp 50 °C (29 Torr)) under vacuum yielded 1-bromo-2-*n*-pentyl-2-methylcyclopropane: bp 75 °C (6 Torr); yield 5.32 g (42%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C). *R,R*/*S,S* enantiomers (56%): δ 2.79 (dd, $J_{vic-cis}$ = 7.7 Hz, $J_{vic-trans}$ = 4.2 Hz, 1 H, CHBr), 1.48−1.16 (bm, 8 H, 4 × CH_2 of *n*-pentyl), 1.20 (s, 3 H, CH_3), 0.94 (dd, $J_{vic-cis}$ = 7.7 Hz, J_{gem} = 6.0 Hz, 1 H, cyclopropyl-CH$^{(trans\ to\ Br)}$), 0.86 (t, 3 H, $-CH_2CH_3$), 0.58 (dd, J_{gem} = 6.0 Hz, $J_{vic-trans}$ = 4.2 Hz, 1 H, cyclopropyl-CH$^{(cis\ to\ Br)}$).

R,S/*S,R* enantiomers (44%): δ 2.80 (dd, $J_{vic-cis}$ = 7.7 Hz, $J_{vic-trans}$ = 4.2 Hz, 1 H, CHBr), 1.48−1.16 (bm, 8 H, 4 × CH_2 of *n*-pentyl), 1.04 (s, 3 H, CH_3), 0.90 (dd, $J_{vic-cis}$ = 7.7 Hz, J_{gem} = 6.0 Hz, 1 H, cyclopropyl-CH$^{(trans\ to\ Br)}$), 0.88 (t, 3H, CH_2CH_3), 0.61 (dd, J_{gem} = 6.0 Hz, $J_{vic-trans}$ = 4.2 Hz, 1 H, cyclopropyl-CH$^{(cis\ to\ Br)}$).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C). *R,R*/*S,S* enantiomers: δ 39.0 ($CH_3(CH_2)_3CH_2-$), 32.0 ($CH_3CH_2CH_2-$), 30.2 (*C*HBr), 26.2 ($CH_3(CH_2)_2CH_2-$), 22.8 (CH_3CH_2-), 22.6 (cyclopropyl-CH_2), 21.2 (quaternary cyclopropyl-C), 20.3 (CH_3), 14.2 ($-CH_2CH_3$). *R,S*/*S,R* enantiomers: δ 36.5 ($CH_3(CH_2)_3CH_2-$), 32.1 ($CH_3CH_2CH_2-$), 30.7 (*C*HBr), 26.3 ($CH_3(CH_2)_2CH_2-$), 23.0 (cyclopropyl-CH_2), 22.8 (CH_3CH_2-), 22.2 (CH_3)), 21.4 (quaternary cyclopropyl-*C*), 14.2 ($-CH_2CH_3$).

Side product 1-*n*-pentyl-1-methylcyclopropane. ^{1}H NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 1.39−1.16 (bm, 8 H, 4 × CH_2), 0.98 (s, 3 H, (CH_3), 0.86 (t, J = 7.5 Hz, 3 H, $-CH_2CH_3$), 0.18 (m, 4 H, 2 × cyclopropyl-CH_2).

^{13}C NMR ($CDCl_3$, 67.8 MHz, 20 °C): δ 39.5 ($CH_3(CH_2)_3CH_2-$), 32.3 ($CH_3CH_2CH_2-$), 26.8 ($CH_3(CH_2)_2CH_2-$), 22.9 (CH_3CH_2-), 22.8 (CH_3)), 15.3 (quaternary cyclopropyl-*C*), 14.1 ($-CH_2CH_3$), 13.0 (2 C, cyclopropyl-CH_2).

Synthesis of 3-*n*-Pentyl-3-methylcyclopropene, 3c. Potassium *tert*-butoxide (3.0 g, 27 mmol) and dimethyl sulfoxide (6 mL) were placed (under N_2) in a 100 mL two-necked flask equipped with an addition funnel and a distillation bridge connected with a receiving flask (30 mL Schlenk flask) cooled to −78 °C. The pressure was then reduced to 100 Torr and kept constant. The solution was heated to 90 °C. 1-Bromo-2-*n*-pentyl-2-methylcyclopropane (5.0 g, 25 mmol) was added from the addition funnel within a period of 2 h. The crude product distilled as a colorless liquid from the reaction mixture during the addition and was collected in the receiving flask. It contained dimethyl sulfoxide (ca. 10%), *tert*-butanol (ca. 45%), and cycloolefin (ca. 45%). It was kept at −30 °C for 24 h during which time some of the *tert*-butanol crystallized. The supernatant liquid was filtered onto $LiAlH_4$ at −30 °C and then slowly warmed to room temperature. The pure cyclic olefin was isolated after vacuum transferring. Yield: 0.74 g (24%).

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ 7.33 (ps, 2 H, =C*H*), 1.40 (t, 2 H, $CH_3(CH_2)_3CH_2$), 1.35−1.04 (bm, 6 H, 3 × CH_2),

1.11 (s, overlapping with the previous signal, 3 H, CH_3), 0.85 (t, 3 H, $-CH_2CH_3$).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 122.1 (olefin-*C*), 40.2 ($CH_3(CH_2)_3CH_2-$), 31.9 ($CH_3CH_2CH_2-$), 27.3 (CH_3)), 26.8 ($CH_3-(CH_2)_2CH_2-$), 22.8 (CH_3CH_2-), 19.8 (quaternary cyclopropyl-*C*), 14.1 ($-CH_2CH_3$).

Thermal Dimerization of 3-Ethyl-3-methylcyclopropene 3b to an Isomer Mixture of *exo,exo-*, *exo,endo-*, and *endo,endo*-3,6-Diethyl-3,6-dimethyl-*trans*-tricyclo[3.1.0.0^{2,4}]-hexane, 12a−c. 3-Ethyl-3-methylcyclopropene (600 mg, 7.3 mmol) was heated in a sealed flask for 16 h at 100 °C and subsequently for 48 h at 110 °C. Yield: 600 mg of product which contained 96% of a mixture of 3,6-diethyl-3,6-dimethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane isomers (composed of 31.2% exo,exo-, 49.6% exo,endo- and 19.2% endo,endo-isomers as determined by GC), 1% unreacted cyclopropene **3b**, and 3% 3,6-diethyl-3,6-dimethyl-1,4-cyclohexadiene.

^1H NMR (270 MHz, $CDCl_3$, 20 °C). exo,exo-isomer **12a**: δ 1.17 (s, 6 H, CH_3 (syn)), 1.08 (s, 4 H, cyclopropyl-CH), 1.06 (q, J = 7.3 Hz, 4 H, CH_3CH_2 (anti)), 0.87 (t, J = 7.3 Hz, 6 H, CH_2CH_3 (anti)). exo,endo-isomer **12b**: δ 1.60 (q, J = 7.3 Hz, 2 H, CH_3CH_2 (syn) of endo-unit), 1.18 (s, 3 H, CH_3 (syn) of exo-unit), 1.11 (d, J = 1.5 Hz, 2 H, cyclopropyl-CH of endo-unit), 1.09, (d, J = 1.5 Hz, 2 H, cyclopropyl-CH of exo-unit), 1.06 (q, J = 7.3 Hz, 2 H, CH_3CH_2 (anti) of exo-unit), 0.94 (t, J = 7.3 Hz, 3 H, CH_2CH_3 (syn) of endo-unit), 0.87 (t, J = 7.3 Hz, 3 H, CH_2CH_3 (anti) of exo-unit), 0.84 (s, 3 H, CH_3 (anti) of endo-unit). endo,endo-isomer **12c**: δ 1.61 (q, J = 7.3 Hz, 4 H, CH_3CH_2 (syn), 1.12 (s, 4 H, cyclopropyl-CH), 0.94 (t, J = 7.3 Hz, 6 H, CH_2CH_3 (syn)), 0.83 (s, 6 H, CH_3 (anti)).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C). exo,exo-isomer **12a**: δ 41.1 (2 C, quaternary cyclopropyl-C), 30.4 (2 C, CH_3CH_2 (anti)), 27.1 (4 C, cyclopropyl-CH), 12.7 (2 C, CH_3 (syn)), 11.2 (CH_2CH_3 (anti)). exo,endo-isomer **12b**: δ 41.0 (1 C, quaternary cyclopropyl-C of endo-unit), 40.6 (1 C, quaternary cyclopropyl-C of exo-unit), 30.4 (1 C, CH_3CH_2 (anti) of exo-unit), 28.5 (2 C, cyclopropyl-CH of endo-unit), 27.0 (2 C, cyclopropyl-CH of exo-unit), 22.2 (1 C, CH_3CH_2 (syn) of endo-unit), 20.2 (1 C, CH_3 (anti) of endo-unit), 12.6 (1 C, CH_3 (syn) of exo-unit), 11.2 (CH_2CH_3 (anti) of exo-unit), 11.0 (CH_2CH_3 (syn) of endo-unit). endo,endo-isomer **12c**: δ 41.4 (2 C, quaternary cyclopropyl-C), 28.4 (4 C, cyclopropyl-CH), 22.1 (2 C, CH_3CH_2 (syn)), 20.2 (CH_3 (anti)), 11.0 (CH_2CH_3 (syn)).

Assignment of spectra was aided by a two-dimensional ($^{13}C-^1H$) HETCOR NMR spectrum.

Synthesis of 3,6-Diethyl-3,6-dimethyl-1,4-cyclohexadiene (50.5/49.5 *trans*/*cis*-Diastereomer Mixture), Model Compounds for ^{13}C NMR Analysis. A sample of 3,6-diethyl-3,6-dimethyl-*trans*-tricyclo[3.1.0.0^{2,4}]hexane (isomer mixture of **12a−c**) was heated at 200 °C in a sealed flask for 48 h; quantitative conversion according to NMR was observed.

^1H NMR (270 MHz, $CDCl_3$, 20 °C). trans-isomer: δ 5.31 (s, 4 H, =CH), 1.27 (q, J = 7.5 Hz, 4 H, CH_3CH_2), 0.98 (s, 6 H, CH_3), 0.74 (t, J = 7.5 Hz, CH_2CH_3). cis-isomer: δ 5.36 (s, 4 H, =CH), 1.30 (q, J = 7.5 Hz, 4 H, CH_3CH_2), 0.99 (s, 6 H, CH_3), 0.72 (t, J = 7.5 Hz, 6 H, CH_2CH_3).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C). trans-isomer: δ 132.6 (=*C*H), 37.4 (quaternary-C), 35.1 (CH_3CH_2), 29.6 (CH_3), 10.0 (CH_2CH_3). cis-isomer: δ 133.0 (=*C*H), 37.2 (quaternary-C), 34.7 (CH_3CH_2), 29.8 (CH_3), 9.8 (CH_2CH_3).

Polymerization of 3-Ethyl-3-methylcyclopropene, 3b, with $[Pd(C_2H_5CN)_4][BF_4]_2$. Preparation of poly-3bb′ (Entry 3). A heavy-walled glass tube (30 mL volume) equipped with a female NS 14.5 joint and a Teflon valve was charged with 3-ethyl-3-methylcyclopropene **3b** (450 mg, 5.5 mmol). At −80 °C, a catalyst solution of $[Pd(C_2H_5CN)_4][BF_4]_2$ (86 mg, 0.17 mmol) in dichloromethane (5 mL) was added. The mixture was stirred and allowed to warm to 20 °C within 24 h. The solvent was removed until approximately 1 mL of solution remained. Then, the polymer was precipitated by addition to methanol (20 mL) and filtered. The resulting yellow solid was dried under vacuum. Yield: 260 mg, 58%. The fraction soluble in chlorobenzene at 20 °C (ca. 80 wt %) has a molecular weight M_n(GPC) = 5900, M_w/M_n = 1.31.

^1H NMR (270 MHz, C_6D_5Br, 80 °C): δ 5.45 (s, =CH), 1.75−1.55 (broad, CH_3CH_2 of cyclic unit) 1.48 (q, J = 7.3 Hz, CH_3CH_2 of opened unit), 1.25−1.15 (broad, CH_3 of cyclic unit), 1.15 (s, partially overlapped with previous signal, CH_3 of opened unit), 1.05−0.98 (broad, CH_2CH_3 of cyclic unit), 0.90 (t, J = 7.3 Hz, CH_2CH_3). In addition a small signal at δ 2.20−1.90 (broad) corresponding to additional rearranged units was observed.

Synthesis of Poly(3,3-dimethylcyclopropene), poly-3a, with Catalyst 5b (entry 8 of Table 2). A heavy-walled glass tube (30 mL volume) equipped with a female NS 14.5 joint and a Teflon valve was charged with 3,3-dimethylcyclopropene (540 mg, 7.9 mmol). The flask was placed in a −80 °C cooling bath, and a catalyst solution of [(η^3-allyl)((−)sparteine)palladium][SbF_6] (42 mg, 68 μmol) in dichloromethane (1 mL) was added. The mixture was allowed to warm to 20 °C over a period of 3 h. The colorless solution had turned slightly cloudy but not viscous yet. It was stirred for an additional 32 h at 20 °C during which time the viscosity increased. Chlorobenzene (2 mL) was added, and the cloudy solution was precipitated by addition to methanol (50 mL). The resulting white powdery solid was dried at 65 °C and 0.01 Torr. Yield: 340 mg (63%). GPC of the fraction soluble in chlorobenzene at 20 °C (ca. 70% of the sample): M_n(GPC) = 19 000; M_w(GPC) = 31 000. Softening range (hot stage optical microscopy): 180−200 °C.

^1H NMR (270 MHz, bromobenzene-d_5, 80 °C): δ 1.2 (bs, 6 H, 2 × CH_3), 0.5 (bm, 2 H, cyclopropyl-CH). (A weak signal at δ 5.5 corresponding to less than 5% $=CHC(CH_3)_2CH=$ was observed.)

^{13}C NMR (67.8 MHz, bromobenzene-d_5, 80 °C): δ 30.2, 30.1, 30.0, 29.9, 29.6, 29.5 (set of 6 signals corresponding to partially resolved stereochemical configurations (mmm, mmr, rmr, mrm, rrm and rrr) of Me(trans); δ 25.0, 24.9, 24.5, 24.3, 24.0, 23.7, 23.3, 23.0 (set of signals corresponding to partially resolved pentads of cyclopropyl-CH); δ 18.4, 18.3, 18.2, 18.1 (set of signals corresponding to partially resolved configurations of quaternary cyclopropyl-C), δ 17.5, 17.3, 17.2, 16.8, 16.7, 16.6 (set of signals corresponding to partially resolved configurations of Me(cis)). General peak assignment was aided by DEPT 135 (only showing signals corresponding to CH_3 and CH carbons) and DEPT 90 NMR spectra (exclusively showing resonances for CH-units). Reference: δ 131.5, C^{o-Ph} of bromobenzene-d_5.

Polymers of entries 6, 7, 9, and 10 of Table 2 were obtained in a similar fashion with Pd catalysts **5a,c,d**. The ^{13}C NMR spectrum of **poly-3a** prepared with **5a** (entry 6 of Table 2) contains additional signals at δ 136.4 (=*C*H), 37.9 (quaternary-C), 28.7 (CH_3) corresponding to ring-opened units with the structure $=CHC(CH_3)_2CH=$.

Synthesis of Poly(3-ethyl-3-methylcyclopropene), poly-3b, with Catalyst 5b (Entry 13 of Table 2). The same procedure was followed as described for the synthesis of **poly-3a** using the following starting materials: 3-ethyl-3-methylcyclopropene (160 mg, 1.95 mmol), [(η^3-allyl)((−)sparteine)-palladium][SbF_6] (12 mg, 19 μmol), and dichloromethane (1 mL), with monomer and catalyst mixed at −80 °C and then held for 32 h at 20 °C. Yield: 130 mg (81%). Softening range (hot stage microscopy) = 210−230 °C.

Thermogravimetric analysis shows onset of weight loss at 280 °C (under nitrogen) and 5% weight loss at 330 °C (TGA, 20 °C/min heating rate). DSC analysis shows an exothermic transition at 220 °C (heating rate of 10 °C/min) which corresponds to less selective ring-opening/rearrangement of the repeating units.

GPC of the **poly-3b** fraction soluble in chlorobenzene at 20 °C (ca. 60% of the sample): M_n = 39 600; M_w = 68 500.

^1H NMR (270 MHz, bromobenzene-d_5, 80 °C): δ = 1.7−1.4 (bm, $-CH_2CH_3$), 1.2−1.10 (bm, cyclopropyl-$C(C_2H_5)CH_3$ and $-CH_2CH_3$ of **3b,c**-repeating unit overlapping), 0.98 (bm, $-CH_2CH_3$ of **3b,t**-repeating unit), 0.55 (bm, cyclopropyl-CH). (δ = 5.45 (s, $=CHC(CH_3)(C_2H_5)CH=$, less than 5%).

^{13}C NMR (67.8 MHz, bromobenzene-d_5, 80 °C): δ 36.7−36.2 (CH_3CH_2- of **3b,t**-repeating unit), 26.8−26.5 ($>C(C_2H_5)CH_3$ of **3b,c**-repeating unit), 25−22 (unresolved group of signals, tertiary and quaternary cyclopropyl-C and CH_3CH_2- of **3b,c**-unit overlapping), 15.0−14.0 ($>C(C_2H_5)CH_3$ of **3b,t**), 11.6 ($-CH_2CH_3$) and 11.3 ($-CH_2CH_3$). Reference: δ 131.5, C^{o-Ph} of bromobenzene-d_5.

Polymers of entries 11, 12, and 14 of Table 1 were obtained in a similar fashion.

A polymer sample of **poly-3b** stored for seven months at 20 °C shows intense ^{13}C NMR signals (bromobenzene-d_5, 80 °C, 75.48 MHz) at δ 136.0 (=*C*H), 41.7 (quaternary-*C*), 35.0 (CH_3CH_2), 25.0 (CH_3) and 9.4 (CH_2CH_3) corresponding to (=CHC(CH_3)(CH_2CH_3)CH=) repeating units in addition to the signals assigned to the 3-ethyl-3-methylcyclopropene repeating units.

Synthesis of Poly(3-*n*-pentyl-3-methylcyclopropene), poly-3c, with Catalyst 5c (Entry 16 of Table 2). The same procedure was followed as described for the synthesis of **poly-3a** using the following starting materials: 3-*n*-pentyl-3-methylcyclopropene (270 mg, 2.17 mmol), Pd catalyst **3a** (17 mg, 0.024 mmol), and dichloromethane (2.5 mL), with monomer and catalyst mixed at −80 °C and then held for 120 h at 20 °C. Yield: 170 mg (63%), M_n(GPC) = 54 000; M_w(GPC) = 104 000; T_g = 55 °C; T_m = 110 °C (DSC).

^1H NMR (270 MHz, $CDCl_3$, 20 °C): δ 7.4−7.2 (very weak bm, Ar of Pd−bisoxazoline end group), 5.25 (very weak s, =C*H*C(CH_3)(C_5H_{11})C*H*=, less than 5%), 1.4−1.2 (bm, 8 H, 4 × CH_2), 1.05 (bs, 3 H, (cyclopropyl-C(*n*-C_5H_{11})C*H*$_3$), 0.86 (bm, 3 H, CH_2CH_3).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 44.0−43.6 (>C-(CH_3)CH_2− of **3c,t**-unit), 33.0−32.9 ($CH_3CH_2CH_2$− of **3c,c**-unit), 32.7−32.6 ($CH_3CH_2CH_2$− of **3c,t**-unit), 30.6−30.0 (>C-(CH_3)CH_2− of **3c,c**-unit), 26.8−26.6 (>C(C_5H_{11})CH_3 of **3c,c**-unit), 26.7−26.5 (>C(CH_3)CH_2CH_2− of **3c,c**-repeating unit, partially overlapped with previous signal), 26.3−26.0 (>C-(CH_3)CH_2CH_2− of **3c,t**), 24.0−21.0 (unresolved group of signals, tert tertiary and quaternary cyclopropyl-C of **3c,t** and **3c,c**), 22.8 (CH_3CH_2− of **3c,t** and **3c,c**, overlapping with the previous group of signals), 14.7−14.1 (>C(C_5H_{11})CH_3 of **3c,t**), 14.2 (−CH_2CH_3 of **3c,t** and **3c,c**).

The polymer of entry 15 (Table 2) was obtained in a similar fashion with catalyst **5b**.

Synthesis of [(η^3-allyl)(2,2′-bipyridyl)Pd^{II}][SbF_6], 5a.[25] A mixture of [(η^3-allyl)PdCl]$_2$ (303 mg, 0.828 mmol), $AgSbF_6$ (571 mg, 1.66 mmol), and dichloromethane (10 mL) was stirred for 1 h at 20 °C and subsequently filtered through a Whatman PTFE syringe filter with 0.45 μm pore size to remove the AgCl formed. This solution was added to a solution of 2,2′-bipyridyl (259 mg, 1.66 mmol) in dichloromethane (2 mL). An off-white colored precipitate formed almost immediately. After 30 min at 20 °C, the solvent was removed by cannula filtration, and the residue was dried under vacuum (0.01 Torr). Yield: 315 mg, 35%.

Anal. Calcd for $C_{13}H_{13}N_2PdSbF_6$ (539.40): C, 28.95; H, 2.43; N 5.19; F 21.13. Found: C, 28.73; H, 2.35; N, 5.25; F, 21.19.

^1H NMR (270 MHz, acetone-d_6, 20 °C): δ 9.02 (ddd, J_1 = 5.3 Hz, J_2 = 1.7 Hz, J_3 = 0.9 Hz, 2 H, H^3 and $H^{3'}$), 8.63 (ddd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, J_3 = 0.9 Hz, 2 H, H^6 and $H^{6'}$), 8.38 (ddd, J_1 = 8.3 Hz, J_2 = 7.7 Hz, J_3 = 1.7 Hz, 2 H, H^5 and $H^{5'}$), 7.81 (ddd, J_1 = 7.7 Hz, J_2 = 5.3 Hz, J_3 = 1.3 Hz, 2 H, H^4 and $H^{4'}$), 6.17 (tt, J_1 = 12.6 Hz, J_2 = 7.1 Hz, 1 H, internal allyl-CH), 4.46 (d, J = 7.1 Hz, 2 H, terminal allyl-CH^{syn}), 3.67 (d, J = 12.6 Hz, 2 H, terminal allyl-CH^{anti}).

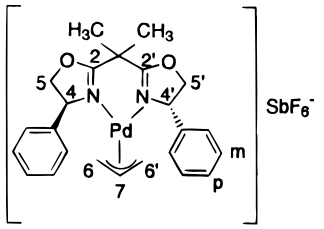
^{13}C NMR (67.8 MHz, acetone-d_6, 20 °C): δ 155.5 (C^1 and $C^{1'}$), 155.3 (C^6 and $C^{6'}$), 142.0 (C^4 and $C^{4'}$), 128.7 (C^5 and $C^{5'}$), 124.3 (C^3 and $C^{3'}$), 121.4 (allyl-CH), 63.2 (allyl-CH_2).

Synthesis of [(η^3-allyl)(2,2bis[2-[4(*S*)-phenyl-1,3-oxazolinyl]]propane)Pd^{II}][SbF_6], 5c (similar to a procedure by Pfaltz et al.[27]). A mixture of [(η^3-allyl)PdCl]$_2$ (63.7 mg, 0.17 mmol), bisoxazoline ligand (128 mg, 0.38 mmol), and dichloromethane (4 mL) was stirred for 10 min. A suspension of $AgSbF_6$ (119.7 mg, 0.35 mmol) in dichloromethane (1 mL) was added. The mixture was stirred for 1 h and subsequently filtered through a Whatman PTFE syringe filter with 0.45 μm pore size to remove the AgCl formed. The volume of the filtrate was reduced to approximately half of the original amount under reduced pressure, and diethyl ether (20 mL) was added to induce precipitation of the product. The palladium complex was isolated by filtration, washed with diethyl ether, and dried at 0.01 Torr. Yield: 105 mg (40%) of a white powder.

Anal. Calcd for $C_{24}H_{27}N_2O_2PdSbF_6$ (717.63 g/mol): C, 40.17; H, 3.79; N, 3.90; F, 13.38. Found: C, 40.32; H, 3.88; N, 3.93; F, 13.83.

^1H NMR (270 MHz, $CDCl_3$, 20 °C): δ 7.42−7.20 (m, 10 H, C_6H_5), 5.43 (bm, 2 H, allyl-CH^7, $CH^{4'\text{ or }4}$), 5.03−4.89 (dd, 1 H, $CH^{4\text{ or }4'}$ and overlapping unresolved pt, 2 H, $CH^{5\text{ and }5'}$), 4.29 (pt, J = 8.1 Hz, 2 H, $CH^{5\text{ and }5'}$), 3.40 (pd, J = 6.8 Hz, 1 H, $CH^{6\text{syn (or }6'\text{syn)}}$), 2.83 (dd, J_1 = 6.9 Hz, J_2 = 2.0 Hz, 1 H, $CH^{6'\text{syn (or }6\text{syn)}}$), 2.57 (d, J = 12.6 Hz, 1 H, $CH^{6'\text{anti (or }6\text{anti)}}$), 1.91 (d, J = 12.6 Hz, 1 H, $CH^{6\text{anti (or }6'\text{anti)}}$), 1.84 (s, 6 H, >C($CH_3$)$_2$).

^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 173.6 ($C^{2\text{ and }2'}$), 139.8 ($C^{\text{ipso−Ph}}$), 129.4 ($C^{o-\text{Ph}}$), 128.8 ($C^{m-\text{Ph}}$), 126.6 ($C^{p-\text{Ph}}$), 115.9 (C^7), 76.4 (C^4), 72.7 (C^5), 61.3 ($C^{6'\text{ or }6}$), 60.9 ($C^{6\text{ or }6'}$), 40.9 (>*C*(CH_3)$_2$), 26.5 (>C(*C*H_3)$_2$), 25.5 (>C(*C*H_3)$_2$).

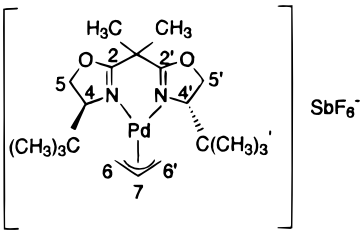


Synthesis of [(η^3-allyl)(2,2-bis[2-[4(*S*)-*tert*-butyl-1,3-oxazolinyl]]propane)Pd^{II}][SbF_6], 5d. Same synthetic procedure was used as for **5c**, with [(η^3-allyl)PdCl]$_2$ (51.7 mg, 0.14 mmol), bisoxazoline ligand (83.2 mg, 0.28 mmol), and 4 mL of dichloromethane and addition of a suspension of $AgSbF_6$ (97.2 mg, 0.28 mmol) in 1 mL of dichloromethane. Yield: 65 mg (34%) of a white powder.

Anal. Calcd for $C_{20}H_{35}N_2O_2PdSbF_6$ (677.65 g/mol): C, 35.45; H, 5.21; N, 4.45; F, 16.82. Found: C, 35.58; H, 5.19; N, 4.17; F, 15.63.

^1H NMR (270 MHz, $CDCl_3$, 20 °C): δ 5.72 (pseudo-tt, J_1 = 12.2 Hz, J_2 = 6.6 Hz, 1 H, allyl-CH^7), 4.54−4.42 (m, 4 H, $CH_2^{5\text{ and }5'}$), 4.15 (dd, J_1 = 6.8 Hz, J_2 = 2.2 Hz, 1 H, allyl-$CH^{6'\text{syn (or 6syn)}}$), 4.06 (dd, J_1 = 6.8 Hz, J_2 = 2.2 Hz, 1 H, allyl-$CH^{6\text{syn (or }6'\text{syn)}}$), 4.03 (dd, J_1 = 7.5 Hz, J_2 = 5.5 Hz, 1 H, $CH^{4'\text{ (or }4)}$)), 3.90 (dd, J_1 = 8.6 Hz, J_2 = 4.4 Hz, 1 H, $CH^{4\text{ (or }4')}$), 3.36 (d, J = 12.6 Hz, 1 H, allyl-$CH^{6'\text{anti (or 6anti)}}$), 3.02 (d, J = 12.0 Hz, 1 H, allyl-$CH^{6\text{anti or (6'anti)}}$), 1.72 (s, 3 H, >C($CH_3$)$_2$), 1.64 (s, 3 H, >C($CH_3$)$_2$), 0.94 (s, 9H, C($CH_3$)$_3$, 0.88 (s, 9 H, C($CH_3'$)$_3$.

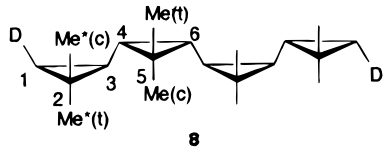
^{13}C NMR (67.8 MHz, $CDCl_3$, 20 °C): δ 175.2 ($C^{2'\text{ or }2}$), 174.7 ($C^{2'\text{ or }2}$), 116.3 (C^7), 76.7 (C^4), 71.1 (C^5), 65.7 ($C^{6'\text{ (or }6)}$), 62.4 ($C^{6\text{ (or }6')}$), 40.3 (>*C*(CH_3)$_2$), 34.23 (*C*(CH_3)$_3$), 34.18 (*C*(CH_3)$_3$), 25.47 (>C(*C*H_3)$_2$), 25.23 (C(*C*H_3)$_3$), 24.85 (>C(*C*H_3)$_2$).



Synthesis of (rrr)-1,12-dideuterioquater(3,3-dimethylcyclopropyl), 8 for ^{13}C NMR Analysis. The palladacycle bis(dimethylphenylphosphine)-3,3,6,6,9,9,13,13-octamethyl-11-pallada-*anti,syn,anti,-syn*-pentacyclo[10.1.0.0.^{2,4}0.^{5,7}0^{8,10}]tridecane **9** (30 mg, 46 μmol) [16c] was dissolved in dichloromethane (8 mL) at 0 °C to give a pale yellow solution. Sodium borodeuteride (5 mg, 0.12 mmol) and methanol-d_1 (80 μL) were added at 0 °C. The mixture was stirred and warmed up to 20 °C within 1 h during which time it turned dark brown. After an additional 1 h at 20 °C, the mixture was filtered through silica, and the solvent was removed at 0.01 Torr to give an off-white colored solid composed of 1,12-dideuterioquater(3,3-dimethylcyclopropyl) (80% by ^1H NMR) and the cyclic tetramer 3,3,6,6,9,9,12,12-octamethyl-*anti,syn,anti*-pentacyclo-[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}]dodecane, **7**, (20%). Yield: 8 mg (63%).

^1H NMR (270 MHz, bromobenzene-d_5, 80 °C) of the linear tetramer **8**: δ 1.09 (s, 6 H, Me), 1.07 (s, 6 H, Me), 1.05 (s, 6 H, Me), 1.04 (s, 6 H, Me), 0.52 (d, J = 8.6 Hz, 2 × cyclopropyl-CH), 0.48 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 2 × cyclopropyl-CH), 0.42 (pt, J = 8.2 Hz, 2 × cyclopropyl-CH), 0.27 (m, 2 × cyclopropyl-CH).

^{13}C NMR (67.8 MHz, bromobenzene-d_5, 80 °C) of the linear tetramer **8**: δ 29.3 (Me(t)), 29.2 (C^4), 27.8 (Me*(t)), 24.1 (C^6), 22.1 (t, C^1, $J_{C-D} = 24.3$ Hz), 21.7 (Me*(c)), 21.1 (C^3), 18.3 (C^5), 17.4 (Me(c), 15.7 (C^2) (The presence of the two deuteriums simplifies assignment of the two terminal cyclopropyl units. Assignment was further aided by a DEPT-90 spectrum).



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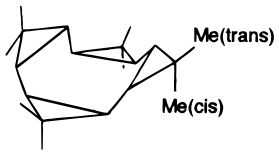
(^{1}H NMR (270 MHz, bromobenzene-d_5, 80 °C) of the cyclic tetramer **7**: $\delta = 1.11$ (s, 12 H, CH_3(cis)), 1.10 (s, 12 H, CH_3-(trans)), 0.35 (s, 8 H, cyclopropyl-CH).)

(^{13}C NMR (67.8 MHz, bromobenzene-d$_5$, 80 °C) of the cyclic tetramer **7**: $\delta = 30.2$ (Me(trans)), 23.8 (tert. cyclopropyl-C), 18.4 (quaternary cyclopropyl-C), 16.8 (Me (cis).)



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(19) Polymer yields decrease when the initial mol ratio of monomer to catalyst is increased (Table 1) due to the unselective nature of the polymerization when catalyst **4** is used.

(20) Relative number average molecular weights of the parts of **poly-3bb′** and **poly-3cc′** soluble in chlorobenzene at 20 °C (between 60 and 90 wt %); calibration with polystyrene samples.

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(24) Treatment of **poly-3a** (83.5 mg, 1.19 mmol) with catalyst **4** (52.7 mg, 0.11 mmol) in chlorobenzene at 20 °C for 24 h resulted in ring-opening of the cyclopropene repeating units. The ^{1}H NMR spectrum of the resulting ring-opened polymer shows the olefinic signal at δ 5.45. The signal due to the cyclopropane ring protons of **poly-3a** at δ 0.65−0.45 disappears after reaction with **4**.

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(28) Many of the cyclopropene polymerizations of Table 2 were precipitation polymerizations. As a result, direct relationships between polymer molecular weights and initial mole ratios of monomer to catalyst or polymer yield and reaction time are difficult to establish.

(29) **Poly-3a,b** samples (entries 7−14) are only partially soluble at 20 °C in chlorobenzene.

(30) Chain propagation is being driven by both the release of ring strain and the energy gained from converting a π-bond into a σ-bond.

(31) Polycyclopropenes **poly-3a,b** are completely soluble in bromobenzene-d_5 at 80 °C, and NMR spectra are recorded at this elevated temperature. **Poly-3c** is soluble in $CDCl_3$ at 20 °C.

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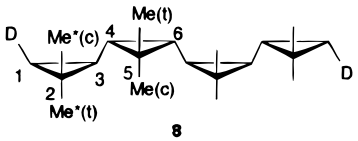
(34) The large ^{13}C NMR shift difference for Me(cis) and Me(trans) is a result of the rigidity of the polymer structure. There is no rotation about the C−C bonds which are part of the three-membered rings.

(35) The presence of the two deuteriums simplifies the ^{13}C NMR assignment of **8**. The DEPT 90 spectrum shows only those carbons bearing one hydrogen (deuterium) atom, C^1, C^3, C^4, C^6 of **8** (and the CH at δ 23.8 of cyclic tetramer **7**). C^1 at δ 22.1 ppm is easily assigned since the signal is a 1:1:1 triplet due to the coupling with the deuterium nucleus ($J_{C-D} = 24.3$ Hz). (C^1 has two extra δ-carbons than the unsubstituted cyclopropyl carbon (δ 20.9 ppm) of 1,1,2-trimethylcyclopropane, **6f** in Figure 2). C^6 is in an almost identical environment (minus one δ-effect) as the CH carbons of the cyclic tetramer and consequently shows a signal δ 24.1 closest to that of the tertiary cyclopropyl-C of **7** (δ 23.8). Nucleus C^4 of **8** experiences one γ-syn effect less than C^6 (of **8**) which shifts C^4 downfield to δ 29.2. C^3 of **8** has one β- and two γ-carbons less than C^6 (of **8**) and accordingly is shifted upfield to δ 21.1. The quaternary carbon C^5 shows a signal at δ 18.3 which is very close to the quaternary carbon of the cyclic tetramer **7** (at δ 18.4). The other quaternary carbon C^2 of **8** is shifted upfield to δ 15.7, as it has one β and two γ-carbons less than C^5 (of **8**). Both Me*(c) (δ 21.7) and Me*(t) (δ 27.8) can be compared with the geminal methyl groups of 1,1,2-trimethylcyclopropane **6f** (δ 19.5 and 27.4 in Figure 2) as they experience only two additional δ-effects. Me(t) at δ 29.3 and Me(c) at 17.4 of **8** are in almost the same environment as Me(trans) and Me (cis) of **7**. (They differ slightly due to a difference in the shielding/deshielding effects induced by the neighboring terminal cyclopropane units.)



8

(36) (a) Some achiral metallocene catalysts produce atactic polycyclopentene while others have been described to form isotactic cyclopentene polymers.[36b] However these polycyclopentenes are 1,3-linked polymers in contrast to the present 1,2-linked polycyclopropenes and are not really suited as a model for discussing chain-end control as the exclusive mechanism of stereocontrol. (b) Kelly, W. M.; Collins, S. *Macromolecules* **1994**, *27*, 4477.

(37) It is suggested that the dimethyl-substituted C-3 carbon of **3a** preferably points downward in structure **10** leading to an excess of isotactic (meso) structural units upon insertion. In contrast to alternating copolymerizations of *p-tert*-butylstyrene with CO, the chain-end control mechanism in the polymerizations of **3a** is not completely overridden because of a bigger steric contribution by the structurally rigid cycloaliphatic polymer chain end of **poly-3a**. In the α-olefin/CO copolymerizations, a linear polymer structure is obtained which is more flexible than **poly-3a**, and catalytic site control exerted by appropriate C_2-symmetric ligands (when present in a single enantiomeric form) clearly dominates over the chain end control mechanism.[4b] In case of an equimolar mixture of *R,R* and *S,S*-ligands, enantiomeric site control operates in concert with chain-end control producing a syndiotactic copolymer. [4a]

(38) Cyclodimers **12a**−**c** are also formed in the reaction of 3-ethyl-3-methylcyclopropene, **3b**, with palladium(0) bis(dibenzylideneacetone) at 40 °C.[16a] They are the predominant reaction products in addition to small amounts of cyclotrimers and cyclotetramers.

(39) Similar to **poly-3a**, there is a chemical shift difference of more than 10 ppm for the two different types of methyl substituents in **poly-3b**. Likewise, the CH_2-carbons of the ethyl substituents show peaks (overlapped by resonances corresponding to the three-membered ring carbons) at δ 23.9−22.9 when they are cis to the polymer main chain (**3b,c** units) and signals at δ 36.7−36.2 when they are in a trans position (**3b,t** units).

(40) The ^{13}C NMR signal at δ 41.8 ppm corresponds to quaternary carbon atoms linked to trans carbon−carbon double bonds. This chemical shift value compares with δ 37.4 and 37.2 for the quaternary carbons α to the cis double bonds of *trans*- and *cis*-3,6-diethyl-3,6-dimethyl-1,4-cyclohexadiene, respectively. In the latter compounds, the ^{13}C NMR signals are shifted upfield due to the γ-syn effect.

(41) This corresponds to an approximate rate constant k_1 of 10^{-7} s^{-1} (at 373 K).

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