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Diverse Pathways in Ring-Opening Ziegler Polymerization of an Annulated Methylenecyclopropane. A New Single-Site Chain Transfer Mechanism

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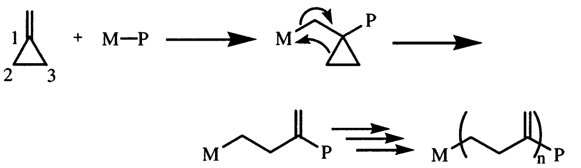
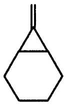
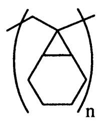
Electrophilic d^0/f^n metallocene centers are highly efficient catalysts for a variety of carbon−carbon bond-forming and bond-breaking transformations.[1] An unusual example is the d^0/f^n metallocene-mediated ring-opening Ziegler polymerization (ROZP) of strained methylenecycloalkanes in which sequential double bond insertions and β-alkyl shift ring-openings afford polyolefins with reactive *exo*-methylene functionalities (eq 1).[2] Recently, we reported a similar ring-opening polymerization pathway for 2-phenyl-1-methylenecyclopropane,[3] and subsequently there have been interesting reports on the polymerization of 2-phenyl-1-methylenecyclopropane mediated by late transition metal catalysts, which proceed via an entirely different ring-opening pathway.[4] To explore the scope and generality of ROZP, we have investigated a variety of substituted methylenecyclopropanes. In particular, we were interested in learning how substitution at the methylenecyclopropane 2- and 3-positions might influence the polymerization pathway. We report here preliminary observations on the single-site polymerization of 7-methylenebicyclo[4.1.0]heptane (**A**) and show that polymerization can be affected in a ring-unopening mode to produce homopolymer **B**, while copolymerizations of **A** with ethylene result in ring-opening of **A** to produce, via a new chain transfer mechanism, polymer **C** or **D** (depending on choice of catalyst used).

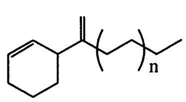


(1)

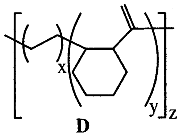

A



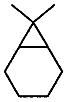
B



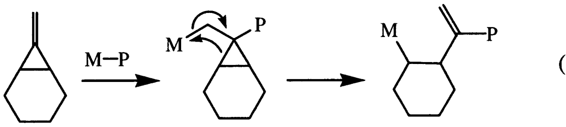
C



D

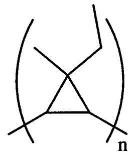

E

Polymerization of **A** mediated by the sterically encumbered metallocenium catalyst $(Me_5Cp)_2ZrMe^+MeB(C_6F_5)_3^-$ at 0 °C results in *ring-unopened* product **B** (Table 1, entry 1) as will be shown below. Interestingly, this material is insoluble in all solvents investigated, even at high temperatures. Because of the insolubility, structural characterization of **B** was carried out by solid-state CPMAS ^{13}C NMR, DSC, elemental analysis, FTIR, TGA, and XRD. Ring-opening of **A** via β-alkyl elimination should produce an *exo*-methylene functionality (eq 2);[2] however, the solid-state CPMAS ^{13}C NMR spectrum of **B** (Figure 1) shows no resonances assignable to unsaturated C centers (no signals downfield of δ 50 ppm). A dipolar dephasing pulse experiment[5] indicates that there is a quaternary ^{13}C resonance at δ 22 ppm, consistent with a ring-closed structure, whereas the quaternary ^{13}C after ring-opening would be olefinic (eq 2). Furthermore, the FTIR spectrum of **B** exhibits no absorptions corresponding to υ C=C modes (the 1500−2500 cm^{-1} region is featureless). Indeed, the FTIR and CPMAS NMR spectra exhibit parameters very similar to those reported for the saturated hydrocarbon 7,7-dimethylbicyclo[4.1.0]heptane (**E**);[6] the FTIR spectral similarity between **B** and **E** is shown in Figure S1 of the Supporting Information. Spectral broadening typically associated with solid-state NMR renders the 1,2-insertion vs 2,1-insertion regioselectivity assignment uncertain. For steric reasons, a 1,2-insertion pathway seems most probable since 2,1-insertion places a bulky tertiary C center directly on the metal.[7]



(2)

DSC and TGA data show that **B** undergoes decomposition prior to melting, with decomposition beginning at ∼310 °C (other hydrocarbon polymers with $T_m > T_{decomp}$ are known, including some polycycloolefins).[8] TGA data for **B** reveal ∼5% weight loss by 363 °C (10 °C/min ramp rate under N_2); DSC data show no features until the large decomposition exotherm at ∼310 °C (10 °C/min ramp rate). The low T_{decomp} of this hydrocarbon polymer (cf. polyethylene with 5% weight loss at 459 °C)[9] is further evidence that the majority of **B** cyclopropyl rings remain intact during polymerization; another polymer with enchained cyclopropyl rings, poly(3-ethyl-3-methylcyclopropene) (**F**), exhibits a similar ∼5% weight loss by 330 °C.[10] Unlike polymer **F**,[11] the FTIR spectra and TGA data for **B** remain unchanged over 20 months under ambient conditions. X-ray powder diffraction data (Ni-filtered Cu Kα radiation) for **B** exhibit a sharp reflection at $2\theta = 17.32°$, with a full width at half-maximum of 2.765°, indicating relatively high crystallinity, a lattice repeat spacing of ∼5.12 Å, and an average particle size/coherence length of ∼29 Å.[12] Elemental analysis is also in good agreement with formulation **B**.[13] It is not presently known whether the process that forms **B** is living; ring-opening of **A** during the polymerization could provide a pathway for termination through β-hydride elimination/chain transfer. The in-



F

10.1021/ma025717g CCC: $25.00

Table 1. Data for Copolymerizations of A and/or Ethylene[a]

entry	catalyst	temp (°C)	**A** (mmol)	ethylene press. (atm)	reaction time (min)	polymer yield (mg)	activity[b]	M_n (M_w/M_n)[c]	T_m (°C)	polymer formed	product **A**: ethylene
1	$(Me_5Cp)_2ZrMe_2$[d]	0	6.48	0	112	250	3.6		>310	**B**	
2	$(Me_5Cp)_2ZrMe_2$[e]	20	2.8	1.0	8	163	48.9	12500 (2.1)	128	**C**	1:219
3	$CGCZrMe_2$[e]	20	2.8	1.0	45	661	35.3	3900 (6.1)	105	**D**	1:113
4	$CGCTiMe_2$[e]	20	2.8	1.0	60	236	9.4	3300 (4.3)	90	**D**	1:32
5	$[(Me_5Cp)_2LuH]_2$[e,f]	20	2.8	1.0	45	72	3.8	24600 (2.1)	131	**D**	1:440

[a] Polymerizations carried out in 50 mL of toluene with 25 μmol of catalyst and 28 μmol of $[(C_6H_5)_3C^+B(C_6F_5)_4^-]$. [b] 10^{-3} g of polymer/(mol of catalyst atm h). [c] By GPC in 1,2,4-trichlorobenzene at 140 °C vs polystyrene standards. [d] Catalyst, 37 μmol, and $B(C_6F_5)_3$, 37.5 μmol used. [e] Copolymerization carried out with pseudo-first-order concentrations of monomer **A**. [f] No cocatalyst and 25 μmol of Lu used.

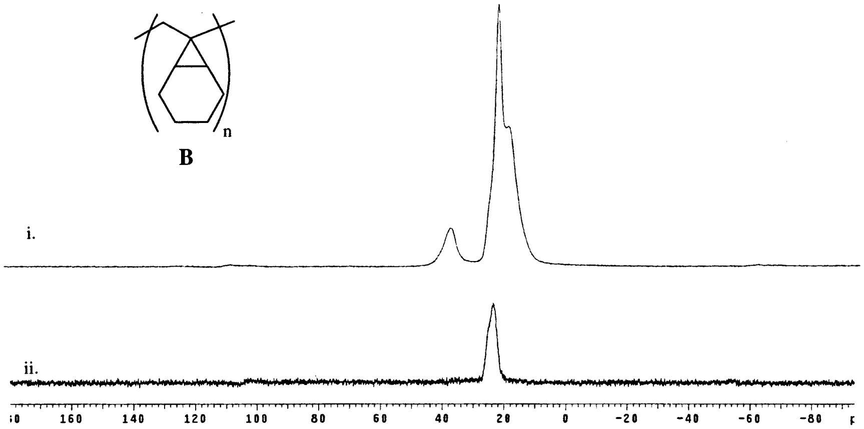
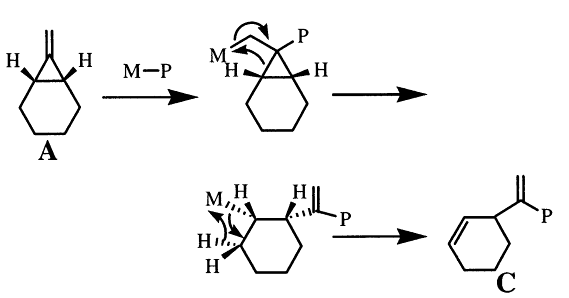


Figure 1. (i) CPMAS ^{13}C NMR spectrum (6.5 kHz, 20 000 transients) of polymer **B** (there are spinning sidebands $\delta \sim 190$ ppm and $\delta \sim -64$ ppm). (ii) Dipolar dephasing[5] CPMAS ^{13}C NMR spectrum (6.5 kHz, 8500 transients) of polymer **B** (there are spinning sidebands $\delta \sim 102$ ppm and $\delta \sim -55$ ppm).

solubility of **B** precludes GPC analysis of the molecular weight and polydispersity, and spectral signatures for end group features in the CPMAS NMR or FTIR spectra of **B** are below the detection limits.

Attempts to produce a completely ring-opened homopolymer of **A** have been unsuccessful. A variety of catalysts were examined at 20 and 0 °C, and GC/MS of the reaction mixtures revealed only products with molecular weights corresponding to dimers.[14] If **A** undergoes insertion and then ring-opening (via β-alkyl elimination), the product is expected to contain a cyclohexyl ring bound directly to the metal (i.e., eq 2). We speculate that olefin insertion into such an encumbered metal−secondary carbon bond would be slow, and hence β-hydride elimination would predominate over chain propagation, thus yielding only dimers or oligomers.

Copolymerizations of **A** with ethylene mediated by a variety of d^0/f^n catalysts afford polymer **C** or **D**. Polymerization data are summarized in Table 1 (entries 2−5), and representative ^1H and ^{13}C NMR spectra of polymer **C** are shown in Figure 2 (see Figure S2 for NMR spectra of **D**). All copolymerizations were run with a pseudo-first-order excess of monomer concentration. A proposed polymerization mechanism for **C** and **D** formation (Scheme 1) invokes ethylene enchainment until monomer **A** is eventually incorporated (step i), at which point either ring-opening (step ii) or additional ethylene insertion (step iv) occurs. Intramolecular step ii appears to predominate over step iv for all catalysts at room temperature. After step ii, β-hydride elimination/chain transfer (step iii) produces **C** (there are in principle two possible pathways for β-hydride elimination/chain transfer, but because the bridge-head C−H units of **A** are *syn*-disposed, only product **C** is observed (eq 3)), or ethylene insertion can occur (step v), producing **D**. Only step iii is observed with catalyst $(Me_5Cp)_2ZrMe^+MeB(C_6F_5)_3^-$, whereas with sterically more open $Me_2Si(Me_4Cp)(^tBuN)TiMe^+B(C_6F_5)_4^-$ and $Me_2Si(Me_4Cp)(^tBuN)ZrMe^+B(C_6F_5)_4^-$ (known for the ability to enchain bulky α-olefins)[15] steps iii and v are competitive. This latter contention is supported by GPC data showing the product produced by $(Me_5Cp)_2ZrMe^+MeB(C_6F_5)_3^-$ to be monomodal (PDI ~ 2), whereas the products produced by $Me_2Si(Me_4Cp)(^tBuN)TiMe^+B(C_6F_5)_4^-$ and $Me_2Si(Me_4Cp)(^tBuN)ZrMe^+B(C_6F_5)_4^-$ are multimodal (PDI > 4). If structure **H** proceeds via step v to form **J**, **J** is expected to mediate subsequent ethylene polymerization until step i occurs (thus producing a polymer with roughly twice the molecular weight than if step v had not occurred). For the neutral organolanthanocene $[Cp^*_2LuH]_2$, step v predominates over step iii; this fact combined with the fact that $[Cp^*_2LuH]_2$ has the least propensity to undergo insertion of **A** (relative to ethylene) yields the highest molecular weight product polymer of the catalysts examined.



(3)

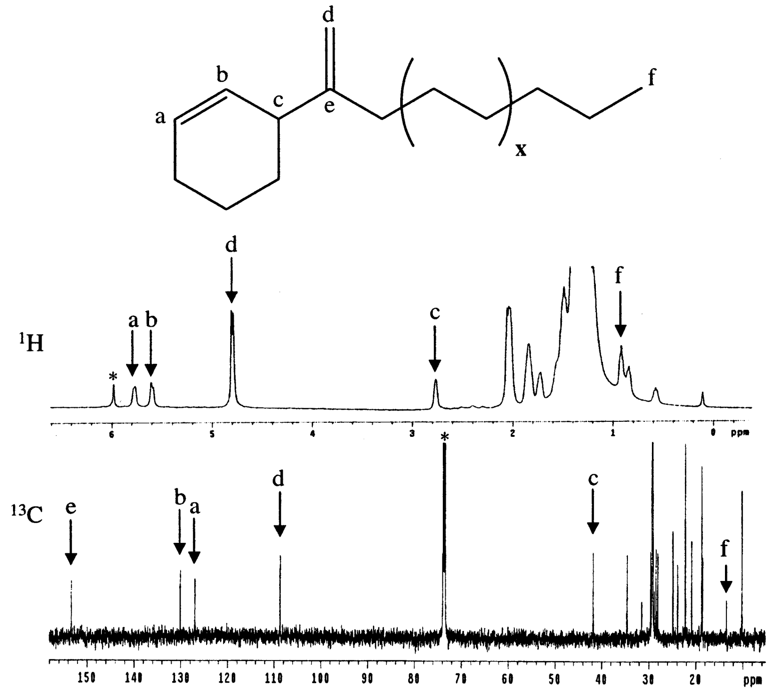
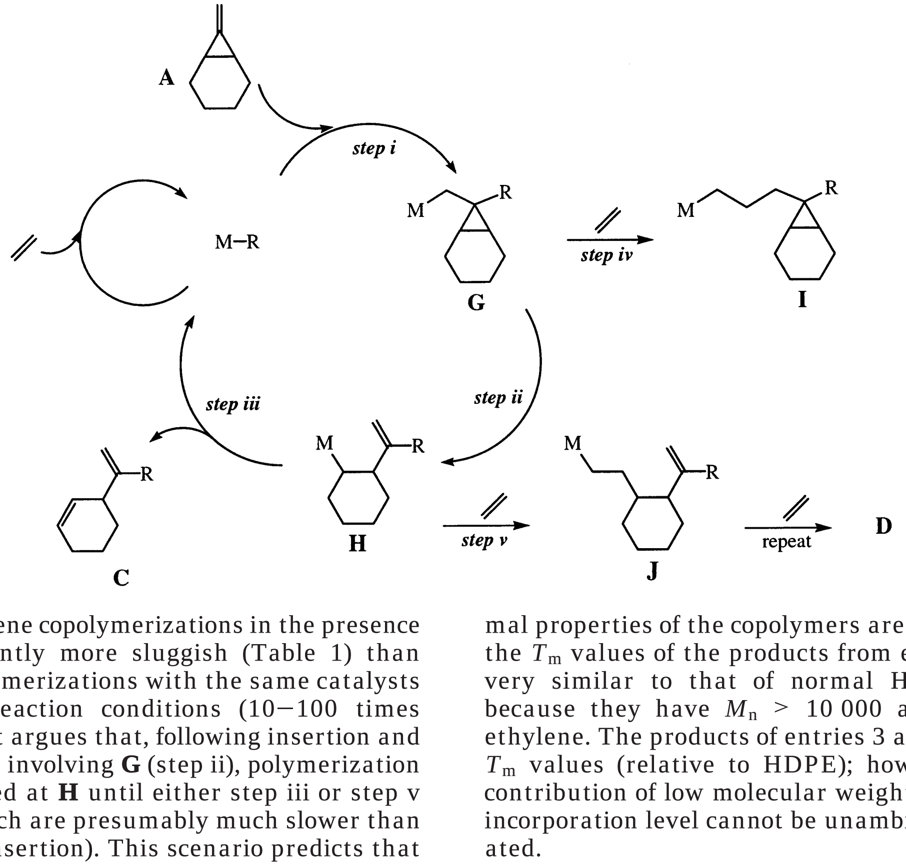


Figure 2. ^{1}H and ^{13}C NMR spectra of polymer **C** in $D_2Cl_4C_2$ at 125 °C.

Scheme 1. Proposed Catalytic Cycle for the Copolymerization of A and Ethylene



In general, ethylene copolymerizations in the presence of **A** are significantly more sluggish (Table 1) than ethylene homopolymerizations with the same catalysts under identical reaction conditions (10−100 times slower). This result argues that, following insertion and β-alkyl elimination involving **G** (step ii), polymerization is essentially halted at **H** until either step iii or step v occurs (both of which are presumably much slower than normal ethylene insertion). This scenario predicts that polymer molecular weights will be depressed by increasing **A** concentrations, since **A** acts as a chain transfer agent in competition with step v. Polymerizations with all catalysts examined evidence decreased product molecular weight with increasing concentrations of **A**; however, the standard linear relationship[16] expected between M_n and $[\mathbf{A}]^{-1}$ should not strictly apply unless the participation of step v is negligible (product molecular weight would otherwise be multimodal). The thermal properties of the copolymers are as expected. Thus, the T_m values of the products from entries 2 and 5 are very similar to that of normal HDPE (~135 °C)[17] because they have $M_n > 10\,000$ and contain >99% ethylene. The products of entries 3 and 4 have very low T_m values (relative to HDPE); however, the relative contribution of low molecular weight ($M_n < 5000$) vs **A** incorporation level cannot be unambiguously differentiated.

In summary, the scope of ROZP has now been expanded to include 2,3-disubstituted methylenecyclopropanes. Methylenecyclopropanes have >40 kcal/mol of ring strain,[18] which is a major factor driving the ring-opening process in ROZP homo- and copolymerizations;[2] thus, it is not surprising that the majority of enchained monomers underwent ring-opening in all our previous studies with methylenecycloalkanes.[2,3,19] In the present case, it is surprising that monomer **A** affords a homopolymer with negligible ring-opening. Note that the tentative pathway proposed in Scheme 1 is based on our previous mechanistic results with methylenecyclopropane and methylenecyclobutane using group 4 or organolanthanide catalysts.[2] Monomer **A** is an interesting example of a chain transfer agent that is actually incorporated into the polymer prior to terminating chain growth, while simultaneously creating a new reactive end group. **A** demonstrates that new pathways previously unobserved in ROZP are accessible and include ring-unopened polymerizations as well as polyolefin capping.

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Supporting Information Available: Details of experimental procedures, FTIR spectra of **B** and **E**, and NMR spectra of **D**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(7) (a) Rigorous differentiation between coordinative/insertive and carbocationic polymerization mechanisms is sometimes nontrivial.[7b] All current evidence points to the present homo- and copolymerizations being coordinative/insertive: (i) in the carbocationic polymerization of isobutene, Cp_2ZrMe_2 is far more active as the precatalyst than $Cp^*_2ZrMe_2$,[7b] whereas in our system $Cp^*_2ZrMe_2$ is active and Cp_2ZrMe_2 is ineffective; (ii) while $(C_6H_5)_3C^+B(C_6F_5)_4^-$ is an active initiator for the carbocationic polymerization of isobutene at 0 °C, it exhibits negligible reaction with **A**; (iii) the observed ethylene copolymerizations are inconsistent with a cationic pathway.[7b] (b) Baird, M. C. *Chem. Rev.* **2000**, *100*, 1471−1478 and references therein.

(8) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, *9*, 1413.

(9) Polyethylene made under identical conditions as **A** (same catalyst, solvent, temperature, but 1 atm of ethylene instead of **A**).

(10) Rush, S.; Reinmuth, A.; Risse, W.; O'Brien, J.; Ferro, D. R.; Tritto, I. *J. Am. Chem. Soc.* **1996**, *118*, 12230−12231.

(11) Over 7 months ∼70% of the cyclopropyl rings in **F** are reported to open under ambient conditions (see ref 10).

(12) Average particle size/coherence length as expressed by the Scherrer equation in: Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969; pp 335−337.

(13) Calcd: C, 88.82; H, 11.18. Found: C, 88.93; H, 11.18.

(14) Previous work showed that reaction of methylenecyclopropane with $[(Me_5Cp)_2MH]_2$ (M = Sm, La) results in a dimeric product (see refs 2a and 2c).

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(19) The ring-unopened polymerization of methylenecyclobutane mediated by a heterogeneous catalyst has been proposed (Pinazzi, C. P.; Brossas, J. *Makromol. Chem.* **1969**, *122*, 105), and very recently, Ni-catalyzed ring-unopened polymerization of 2-phenyl-1-methylenecyclopropane has been reported (see ref 4a).

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