C-C Activation at Electrophilic d^0/f^n Centers. Facile, Regioselective β-Alkyl Shift-Based Ring-Opening Polymerization Reactions of Methylenecyclobutane

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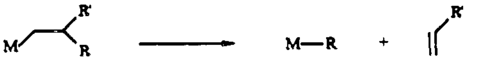
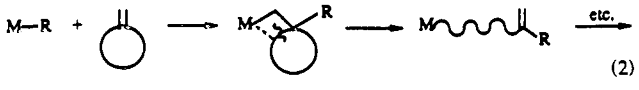
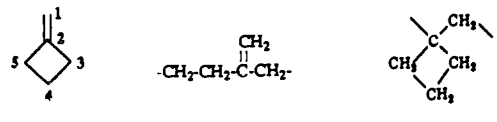
Facile β-alkyl eliminations are a distinctive feature of electrophilic d^0/f^n hydrocarbyl chemistry (e.g., eq 1)[1,2] and represent


(1)

deleterious termination channels in many α-olefin polymerization processes.[3] In principle, such transpositions might also provide an unusual *propagation pathway* to functionalized polyolefins by coupling strained monomer ring-opening to olefin insertion sequences (eq 2). In the presence of certain heterogeneous


(2)

Ziegler–Natta catalysts, methylenecyclobutane (**A**) was reported to undergo sluggish ($N_t \approx 0.03$ h^{-1}/25 °C) reaction to afford low-M_n polymers having mixed ring-opened/-unopened (**B** + **C**) or, in rare cases, predominately opened (**B**) microstructures.[4,5]


A **B** **C**

The ring-opened structures were tentatively ascribed to oxidative addition at the C3–C4/C4–C5 junctures of **A**.[5,6] We report here that electrophilic zirconocene cations[7,8] catalyze the rapid ($N >$ 400 h^{-1}/25 °C), regioselective ring-opening homopolymerization of methylenecyclobutane and its copolymerization with ethylene via C2–C3/C2–C5 scission, supportive of a new ring-opening β-alkyl shift polymerization mechanism.

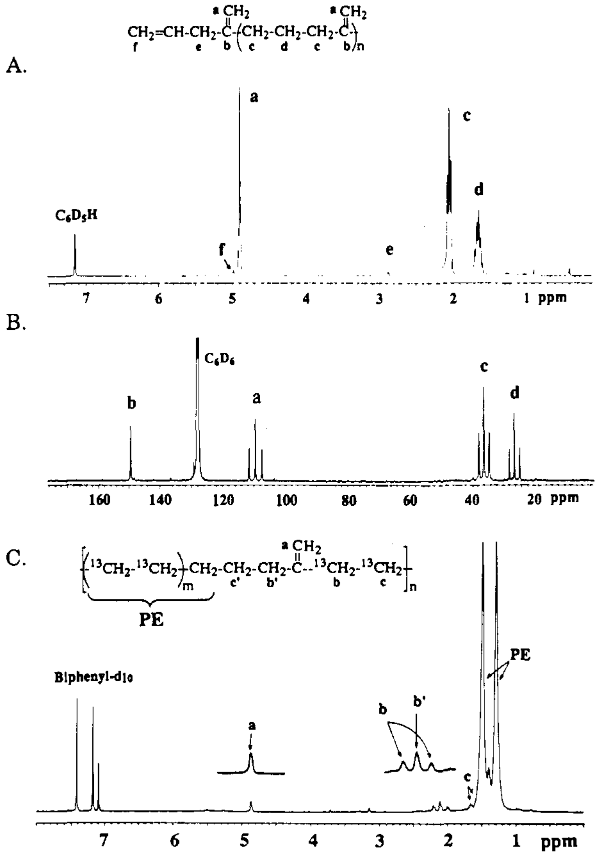


Figure 1. (a) ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of polymethylenecyclobutane produced by a $(1{,}2\text{-}Me_2C_5H_3)_2$-$ZrMe^+MeB(C_6F_5)_3^-$ catalyst (entry 2, Table I). (b) ^{13}C NMR spectrum (100 MHz, C_6D_6, 25 °C) of the polymethylenecyclobutane sample shown in a. (c) ^{1}H NMR (600 MHz, biphenyl-d_{10}, 140 °C) of the copolymer formed from methylenecyclobutane and $^{13}CH_2{=}^{13}CH_2$ (>99% ^{13}C; ~1.0:100 monomer ratio) with a $(1{,}2\text{-}Me_2C_5H_3)_2ZrMe^+MeB(C_6F_5)_3^-$ catalyst. The peak **a**:**b**:**b'** area ratios are 1.0:1.0:1.0 (±5%) (Scheme IB predicts 1.0:1.0:1.0).

Reaction[9] of $(1{,}2\text{-}Me_2C_5H_3)_2ZrMe^+MeB(C_6F_5)_3^-$ (**1**)[8b] with **A** proceeds rapidly in toluene solution to yield, after workup, polymethylenecyclobutane (PMCB, Table I). ^{1}H and ^{13}C NMR spectra (Figure 1) reveal that the polymer microstructure is almost exclusively **B** (≥95%; minor traces of **C** may be present),[10] indicating high selectivity for a ring-opening pathway. The length of reaction time/extent of conversion has no detectable effect on selectivity (Table I). NMR analysis also indicates allylic end groups in all PMCB samples, consistent with chain transfer via conventional β-H elimination (Scheme IA).[3] Copolymerization of **A** with ethylene can be effected by rapidly stirring **A** neat or in toluene solution with **1** under 1.0 atm of ethylene (Table I).[9] Solubility data and ^{1}H and ^{13}C NMR spectroscopy are consistent with a copolymer having a ring-opened, random microstructure (Scheme IB) and indicate that x/y parallels monomer stoichiometries.

In regard to polymerization mechanism, it seems unlikely on the basis of known chemistry[7,8] that **1** can support two-election

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[1] (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–55. (b) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976–978.

[2] For a discussion of the thermodynamic constraints on such processes see: Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.

[3] (a) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025–1032. (b) Eshuis, J. J.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277–287.

[4] (a) Pinazzi, C. P.; Brossas, J. *Makromol. Chem.* **1969**, *122*, 105–122; **1971**, *147*, 15–33. (b) Pinazzi, C. P.; Brossas, J.; Clouet, G. *Makromol. Chem.* **1971**, *148*, 81–92.

[5] Rossi, R.; Diversi, P.; Porri, L. *Macromolecules* **1972**, *5*, 247–249.

[6] $Ti(CH_2Ph)_4$ and $RhCl_3$ effect homogeneous polymerization of **A** to yield polymers with mixed 1,4-isoprene, *cis*- and *trans*-1,4-pentadiene, and **B** microstructures.[5]

[7] For recent discussions of this field, see refs 3, 8, and: (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387, and references therein. (b) Bochmann, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992**, *424*, C5–C7, and references therein. (c) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413–1416, and references therein. (d) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910–3918, and references therein. (e) Eisch, J. J.; Caldwell, C. J.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417–3419, and references therein. (f) Taube, R.; Krukowa, L. *J. Organomet. Chem.* **1988**, *347*, C9–C11. (g) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875–7876.

[8] (a) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57–65, and references therein. (b) Yang, X.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625. (c) Dahmen, K. H.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* **1988**, *4*, 1212–1214.

[9] Under rigorously anaerobic/anhydrous conditions, a small quantity of catalyst was weighed into a 25-mL reaction flask. The flask was then attached to a vacuum line, and monomer and solvent were vacuum transferred in at −78 °C. The flask was back-filled with Ar and the mixture stirred at the desired temperature. Workup consisted of quenching with methanol, vacuum transfer of the volatiles, washing the product with toluene, and vacuum drying. Copolymerizations were carried out by replacing Ar with purified ethylene. NMR-scale experiments show that other zirconocene cations also effect methylenecyclobutane polymerization.

[10] Weak ^{1}H spectral features at δ = 1.0–1.5 and 1.8–1.9 are tentatively assigned to this microstructure.

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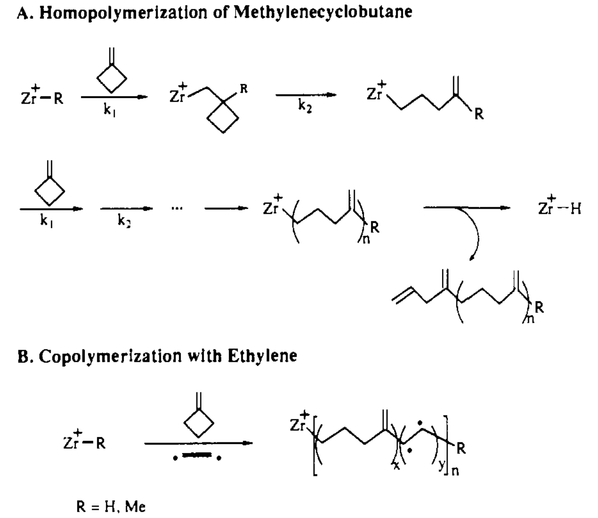
Table I. Polymerization of Methylenecyclobutane and Copolymerization with Ethylene Using $(1,2\text{-Me}_2C_5H_3)_2ZrMe^+MeB(C_6F_5)_3$ (**1**) as a Catalyst

entry	catalyst amount (μmol)	methylenecyclobutane amount (mmol)	ethylene pressure (1 atm)	solvent (*V*, mL)	*T* (°C)	reaction time (h)	yield of polymer (g)	methylenecyclo-butane:ethylene[b]	M_w (M_n)[c] × 10^3
1	7.33	27.0	0.0	toluene (10)	20	16	1.7 (100%)[a]		83.3 (38.5)
2	7.33	27.0	0.0	toluene (10)	20	5	1.1 (60%)[a]		
3	7.33	23.8	0.0	toluene (10)	−30	20	0.16 (9%)[a]		
4	7.33	23.8	1.0	none	20	0.17	0.84	0.81	89.9 (35.5)
5	7.33	8.3	1.0	toluene (15)	20	0.17	0.98	0.21	255.3 (152.0)
6	7.57	1.2	1.0	toluene (25)	20	0.12	0.60	ca. 0.002	

[a] Monomer conversion by ^{1}H NMR. [b] Ratio of methylenecyclobutane and ethylene incorporated into the copolymer as determined by ^{1}H NMR. [c] By GPC in 1,2,4-trichlorobenzene versus polystyrene.

Scheme I. Proposed Mechanisms for the Cationic Zirconocene-Catalyzed Ring-Opening Polymerization of Methylenecyclobutane and Copolymerization with Ethylene



(or one-electron)[11] oxidative addition–reductive elimination propagation sequences.[12] Furthermore, ^{1}H and ^{13}C NMR analysis of copolymerizations with excess $^{13}CH_2{=}^{13}CH_2$ indicates delivery of *one*-$^{13}CH_2$- unit adjacent to *every exo*-methylene group, compatible only with C2–C3/C2–C5 ring opening (Figure 1c, Scheme IB).[13] Combined with evidence for β-Me shifts in propylene polymerizations at similar cationic centers[3] and β-alkyl shift-based methylenecyclobutane → 1,4-pentadiene rearrangements at isoelectronic scandocene centers,[1b] the pathways of Scheme I seem most compatible with the present results. Additionally, kinetic measurements ([**1**] = 1.57–15.7 mM; [**A**] = 1.05–2.09 M) reveal that the homopolymerization of **A** obeys the rate law of eq 3, where $k = 4.1(1) \times 10^{-2}$ M^{-1} s^{-1} at −5.5 °C.

$$-\frac{d[\mathbf{A}]}{dt} = k[\mathbf{1}]^1[\mathbf{A}]^1 \qquad (3)$$

Interestingly, the turnover-limiting step under these conditions is monomer insertion rather than ring opening.

These results demonstrate that β-alkyl shift processes mediated by well-defined homogeneous catalysts represent an efficient propagation pathway for the synthesis of *exo*-methylene functionalized polyolefins. The generality of this new polymerization process is currently under investigation.

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(11) Methylenecyclobutane does not undergo homopolymerization with free radical initiators: (a) Hiraguri, Y.; Eudo, T. *J. Polm. Sci., Polym. Lett.* **1988**, *26*, 381–384. (b) Takemoto, K.; Izubayashi, M. *Makromol. Chem.* **1967**, *109*, 81–86.

(12) **A** is not polymerized by $B(C_6F_5)_3$. Conventional cationic initiators give predominantly ring-unopened or ring-contracted products.[4]

(13) ^{1}H (biphenyl-d_{10}, 142 °C): δ 4.90 (s, 2 H, -C($^{12}CH_2$)-), 2.10 (s, 2 H, -$^{12}CH_2C(CH_2)$-), 2.10 (d, $^1J_{C-H}$ = 123.6 Hz, -C(CH$_2$)$^{13}CH_2$-), 1.39 (d, $^1J_{C-H}$ = 117.1 Hz, polyethylene homopolymer block). ^{13}C (biphenyl-d_{10}, 142 °C): δ 36.0 (d, $^1J_{C-C}$ = 33 Hz), 30.0 (s, polyethylene homopolymer block). Assignments confirmed by 2D experiments.