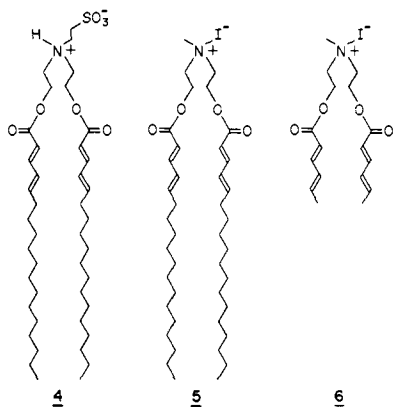


phore is not aggregated. The lipid phase transition is 11 °C for bilayers of **3a**,¹² therefore, the membranes were in the liquid analogous phase during the measurement at room temperature.

The longer chain disorbyl PC **3b** forms bilayer membranes with a phase transition at 33 °C.¹² The absorption maxima (room temperature) of **3b** in acetonitrile is the same as **3a**, 257 nm. However, in water the **3b** vesicles absorption shows a hypsochromic shift to 242 nm with a diminished extinction coefficient. This indicates the chain terminal sorbyl group is aggregated in the bilayer solidlike phase. When the vesicles are warmed above the phase transition temperature, 40 °C, the absorption shifts to 257 nm with a doubling of the extinction coefficient.

Previously we reported a 6000-fold difference in photosensitivity of lipid diacetylene bilayers as a function of the lipid structure.¹³ The reactivity of the phospholipid and dialkyl dimethylammonium halide analogues was interpretable based on the conformational preferences of these molecules. The glycerol backbone of phospholipids is approximately perpendicular to the plane of the bilayer with the two alkyl chains extending unequal distances into the bilayer membrane.¹⁴ The synthetic lipid dialkyl dimethylammonium salts¹⁵ have planes of symmetry, which suggest that both hydrocarbon chains penetrate equally into the bilayer membrane.

Indeed, the molecular assemblies of the symmetrical molecules **4** and **5** in water show a pronounced hypsochromic shift from the



monomer absorption maxima at 260 nm to approximately 235 nm ($\Delta\nu = 4000 \text{ cm}^{-1}$). This spectral effect is similar to that observed upon the formation of dimers and higher aggregates of dye molecules in monolayers and adsorbed on surfaces.¹⁶ The size of the shift indicates the aggregates in these vesicles are larger than dimers. We propose that the spectral shift is due to the bilayer induced close packing of the chromophores in these symmetric molecules. A test of this hypothesis is provided by the absorption of aqueous dispersions of **6**, which forms micelles in water. In contrast to the longer chain bilayer former, **5**, the absorption maximum of **6** in water is not shifted. Consequently, the chromophores have more freedom of motion in the micelle and are not constrained in a structure that favors aggregation. This is consistent with the view that amphiphile chain packing is looser and more disorganized in micelles than bilayers. In contrast to micelles, tightly organized assemblies of dienoyl-containing amphiphiles such as monolayers and multilayers should show short wavelength absorption due to aggregate formation. This prediction has recently been confirmed.¹⁷

(12) The phase transitions were measured for vortexed hydrated bilayers of the lipid (10 mg/mL) in a Hart scientific differential scanning calorimeter Model 701 at a scan rate of 20 °C/h for both heating and cooling.

(13) Lopez, E.; O'Brien, D. F.; Whitesides, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 305.

(14) Hitchcock, P. B.; Mason, R.; Thomas, K. M.; Shipley, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3036. Hitchcock, P. B.; Mason, R.; Shipley, G. G. *J. Mol. Biol.* **1975**, *94*, 297.

(15) Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3860.

(16) Mooney, W. F.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5712 and references therein.

(17) Laschewsky, A.; Ringsdorf, H., in press.

In summary, the unsymmetrical dienoyl PCs do not show evidence of bilayer-induced aggregation, whereas the symmetrical dimethyldialkylammonium halides favor chromophore aggregation with a pronounced hypsochromic absorption shift. These data demonstrate the utility of dienoyl lipids as probes of lipid chain packing in lipid assemblies.

Hydrogen Atom Transfer Reactions of Transition-Metal Hydrides. Utilization of a Radical Rearrangement in the Determination of Hydrogen Atom Transfer Rates

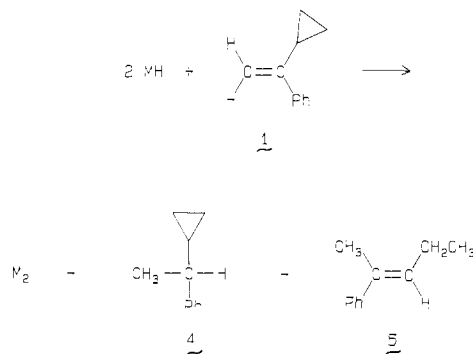
R. Morris Bullock* and Edward G. Samsel

Department of Chemistry
Brookhaven National Laboratory
Upton, New York 11973

Received March 18, 1987

The reaction of a transition-metal hydride with an unsaturated substrate is a critical step in several catalytic reactions. Commonly accepted mechanisms¹ for homogeneous hydrogenation and hydroformylation have traditionally involved even-electron intermediates conforming to the 16- and 18-electron rule.² Recently, kinetic and spectroscopic (CIDNP) evidence has been reported in support of odd-electron pathways for reactions of metal hydrides with substituted styrenes,³ anthracenes,⁴ allenes,⁵ and conjugated dienes,⁶ all of which form stabilized (benzylic or allylic) radicals. We report a new approach, in which metal hydrides are reacted with vinylcyclopropanes, which contain a radical clock.⁷

The reaction of α -cyclopropylstyrene (**1**, 0.052 M) with $\text{HCr}(\text{CO})_3(\text{C}_2\text{H}_5)$ (0.155 M) in benzene at room temperature resulted in hydrogenation of the carbon-carbon double bond as the predominant reaction and produced 1-cyclopropyl-1-



(1) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapters 10 and 12. (c) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; Chapter 1.

(2) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337-353.

(3) (a) Halpern, J. *Pure Appl. Chem.* **1986**, *58*, 575-584. (b) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335-8337. (c) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57-63. (d) Ungváry, F.; Markó, L. *Organometallics* **1982**, *1*, 1120-1125. (e) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299-311. (f) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222-223. (g) Bockman, T. M.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F. *J. Organomet. Chem.* **1985**, *279*, 165-169. (h) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1983**, *249*, 411-414. (i) Roth, J. A.; Wiseman, P. J. *J. Organomet. Chem.* **1981**, *217*, 231-234. (j) Nalesnik, T. E.; Freudenberger, J. H.; Orchin, M. *J. Mol. Catal.* **1982**, *16*, 43-49. (k) Roth, J. A.; Wiseman, P.; Ruzsala, L. *J. Organomet. Chem.* **1983**, *240*, 271-275.

(4) (a) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186-7188. (b) Sweany, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487-492.

(5) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* **1986**, *108*, 1689-1691.

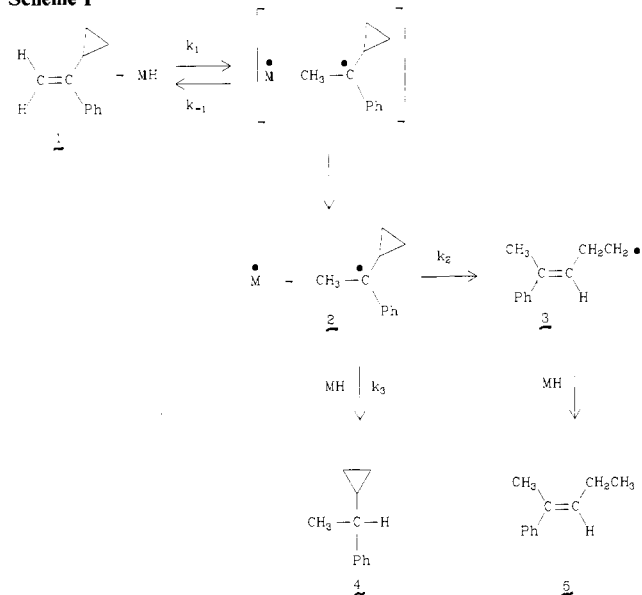
(6) (a) Connolly, J. W. *Organometallics* **1984**, *3*, 1333-1337. (b) Wasink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995-2002. (c) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1986**, 312-314.

(7) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317-323.

Table I. Reaction Conditions and Product Yields from the Reaction of Metal Hydrides with α -Cyclopropylstyrene (1)

MH	[MH], M	[1], M	conditions ^a	% yield ^b 4	% yield ^b 5
HCr(CO) ₃ (C ₅ H ₅)	0.155	0.052	4 d, 22 °C	85	7
HMo(CO) ₃ (C ₅ H ₅)	0.579	0.20	24 h, 65 °C	68	25
HMo(CO) ₃ (C ₅ H ₅)	0.545	0.20	2 h, 100 °C	43	48
HV(CO) ₃ (C ₅ H ₅)	0.571	0.20	50 h, 100 °C	23	65
HFe(CO) ₂ (C ₅ H ₅)	0.05	0.017	14 d, 22 °C	83	0.8
HFe(CO) ₂ (C ₅ Me ₅)	0.230	0.068	7 h, 65 °C	62	30
HFe(CO)(PMe ₃)(C ₅ H ₅)	0.264	0.093	20 h, 65 °C	17	64

^aIn benzene or toluene solvent (or deuterated analogues), except HFe(CO)₂(C₅H₅), which was carried out in hexane. ^bYields are based on consumed **1** and were determined by GC with an internal standard. Reactions were carried out to 97–100% conversion, except HFe(CO)(PMe₃)(C₅H₅), which was analyzed at 82% conversion.

Scheme I

phenylethane (**4**) in 85% yield. A small amount (7%) of the rearranged product (*E*)-2-phenyl-2-pentene (**5**) was also formed. HFe(CO)₂(C₅H₅) also reacted with **1** at room temperature to give a good yield of **4** and a trace of **5**. Several related metal hydrides react with **1** at 65–100 °C to produce substantial quantities of **5** in addition to **4**; results are summarized in Table I. We propose the mechanism shown in Scheme I, which involves hydrogen atom transfer from the metal hydride to **1**, followed by subsequent hydrogen atom transfer to the unrearranged (**2**) or rearranged (**3**) carbon-centered radicals.

Several lines of evidence argue against alternative mechanisms. The reactions proceed identically when carried out under vacuum or under 1 atm CO, indicating CO dissociation is unlikely. The similar reactivity of HCr(CO)₃(C₅H₅) ($pK_a = 13.3$)^{8a} and HFe(CO)₂(C₅H₅) ($pK_a = 19.4$)^{8b} rules out proton transfer reactivity of the hydrides^{8c} and subsequent carbocation rearrangement.⁹ Addition of [(C₅H₅)Cr(CO)₃]₂ to a solution of HCr(CO)₃(C₅H₅) and **1**, and photolysis into the 620-nm band of the dimer, resulted in no change in the rate of formation of **4** and **5**. A large rate acceleration would have been expected if the mechanism involved 17-electron (C₅H₅)Cr(CO)₃^{*} as a chain-carrying species.¹⁰

(8) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263. (b) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263. (c) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945–3953.

(9) (a) Sarel, S.; Ben-Shoshan, R. *Tetrahedron Lett.* **1965**, 1053–1058. (b) Sarel, S.; Breuer, E.; Ertag, S.; Salamon, R. *Israel J. Chem.* **1963**, *1*, 451–459. (c) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577–588.

The unsubstituted cyclopropylcarbinyl radical ring opening rearrangement¹¹ is a well-known radical clock⁷ ($k = 2.1 \times 10^8 \text{ s}^{-1}$ at 25 °C).¹² The substituted cyclopropylcarbinyl radical utilized in this study is a tertiary benzylic radical which rearranges more slowly. Our preliminary results from pulse radiolysis of (*c*-C₃H₅)(CH₃)(Ph)COCOCH₃ in hexane at 22 °C provide an estimate of $k_2 \approx 4 \times 10^5 \text{ s}^{-1}$ for this ring-opening rearrangement.¹³ The competition for radical **2** between rearrangement (first order, k_2) and trapping by MH (second order, k_3) predicts formation of more of the rearranged product **5** at lower [HCr(CO)₃(C₅H₅)]. Accordingly, a plot of [4]/[5] vs. [HCr(CO)₃(C₅H₅)] gives a straight line with a slope of $k_3/k_2 = 1.1 \times 10^2 \text{ M}^{-1}$. Use of the value of k_2 allows the calculation¹⁵ of the absolute rate constant for hydrogen atom transfer from HCr(CO)₃(C₅H₅) to **2** as $k_3 \approx 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. For HFe(CO)₂(C₅H₅) in hexane we estimate $k_3 \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A recent study of radical chain reactions by Darensbourg, Newcomb, and co-workers gave a measurement of $k = 1.81 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant of hydrogen atom transfer from HCr(CO)₃ to the 2,2-dimethyl-3-butenyl radical.¹⁷ This rate constant is very similar to an earlier estimate by Bergman et al. of $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of HV(CO)₃(C₅H₅)⁻ with the 2-allyloxyethyl radical.¹⁸ In contrast, rate constants for hydrogen atom donation from the main group hydride HSnBu₃ to simple alkyl radicals such as ethyl, isopropyl, or butyl span the narrow range of $(1.5\text{--}2.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹

To assess the possibility of similar hydrogen atom transfer reactivity of a metal hydride to form a radical which does not benefit from benzylic stabilization, we reacted HCr(CO)₃(C₅H₅) with 2-cyclopropylpropene.²⁰ At 68 °C (under vacuum or 1 atm CO) the products were 2-methyl-2-pentene and isopropylcyclopropane (combined yields ~80%), with the unrearranged/rearranged product ratio increasing linearly with [HCr(CO)₃(C₅H₅)]. The kinetics of the reaction were found to conform to the rate law $-d[\text{CH}_2=\text{C}(c\text{-C}_3\text{H}_5)(\text{CH}_3)]/dt = k[\text{CH}_2=\text{C}(c\text{-C}_3\text{H}_5)-$

(10) For examples of radical chain mechanisms involving 17-electron organometallic radicals, see: (a) Brown, T. L., *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80–89. (b) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613–617. (c) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527–2532. (d) Edidin, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 948–953.

(11) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024–7026. (b) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877–1879. (c) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4. (d) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 8.

(12) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981–7984. For an earlier measurement by a different method, see ref 11a.

(13) Masnovi, J.; Samsel, E. G.; Bullock, R. M., unpublished data. Pulse radiolysis¹⁴ of a hexane or ethanol solution of (*c*-C₃H₅)(Ph)(CH₃)COCOCH₃ at 22 °C produces the radical anion, which then loses acetate anion to form the radical, (*c*-C₃H₅)(Ph)(CH₃)C^{*}. The decay of the absorbance of this radical ($\lambda_{\text{max}} = 310, 350, 410 \text{ nm}$) followed first-order kinetics and gave the rate of rearrangement as about $4 \times 10^5 \text{ s}^{-1}$. Details of this work and pulse radiolysis studies of several related esters will be published separately.

(14) For examples of formation of arylmethyl radicals by pulse radiolysis or γ -irradiation, see: (a) Hamill, W. H.; Guarino, J. P.; Ronayne, M. R.; Ward, J. A. *Discuss. Faraday Soc.* **1963**, *36*, 169–176. (b) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83–91. (c) Izumida, T.; Ichikawa, T.; Yoshida, H. *J. Phys. Chem.* **1980**, *84*, 60–63.

(15) Values of [HCr(CO)₃(C₅H₅)] used in this calculation are mean concentrations for individual runs. Use of an integrated form of the rate expression¹⁶ (to account for the change in [HCr(CO)₃(C₅H₅)] as the reaction proceeds) gave $k_3 = 5\text{--}6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

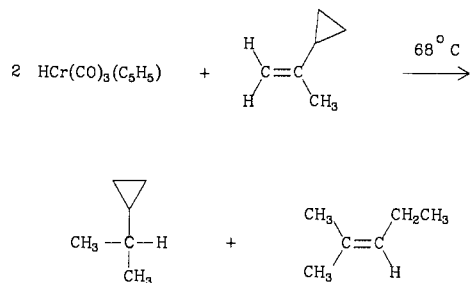
(16) (a) Rüchardt, C. *Chem. Ber.* **1961**, *94*, 2599–2608. (b) Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Suleman, N. K. *J. Org. Chem.* **1986**, *51*, 1446–1456. (c) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132–4134.

(17) Ash, C. E.; Hurd, P. W.; Darensbourg, M. Y.; Newcomb, M. *J. Am. Chem. Soc.* **1987**, *109*, 3313–3317.

(18) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902–7915.

(19) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

(20) Several studies have demonstrated radical ring-opening rearrangement in reactions of 2-cyclopropylpropene: (a) Huyser, E. S.; Taliaferro, J. D. *J. Org. Chem.* **1963**, *28*, 3442–3445. (b) Lishanskii, I. S.; Vinogradova, N. D.; Guliev, A. M.; Zak, A. G.; Zvyagina, A. B.; Fomina, O. S.; Khachaturov, N. D. *Dokl. Akad. Nauk SSSR*, **1968**, *179*, 882–883. (c) Ratier, M.; Pereyre, M. *Tetrahedron Lett.* **1976**, 2273–2276. (d) Shellhamer, D. F.; McKee, D. B.; Leach, C. T. *J. Org. Chem.* **1976**, *41*, 1972–1976.



$(\text{CH}_3)[\text{HCr}(\text{CO})_3(\text{C}_5\text{H}_5)]$; at 68°C , $k = 2.2(3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Use of $\text{DCr}(\text{CO})_3(\text{C}_5\text{H}_5)$ led to the observation of an inverse isotope effect,^{3,4,6} $k_{\text{H}}/k_{\text{D}} \sim 0.5$. Additionally, the reversibility of the equilibrium^{3b} between the reactants and the caged radical pair was demonstrated by ^1H NMR observation of deuterium incorporation into the vinyl and methyl positions of 2-cyclopropylpropene when it was reacted with $\text{DCr}(\text{CO})_3(\text{C}_5\text{H}_5)$. To our knowledge this is the first direct experimental evidence for hydrogen atom transfer from a metal hydride to an alkene which cannot form a stabilized benzylic or allylic intermediate, and we are exploring the reactivity of this alkene with other metal hydrides. We are also studying the reactions of **1** with $\text{HCo}(\text{CO})_4$ and $\text{HMn}(\text{CO})_5$ to compare its behavior under catalytic and stoichiometric conditions.

Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Drs. Carol Creutz and Mark Andrews for helpful discussions and Prof. John Masnovi for the pulse radiolysis measurement.

Crystal Structures and Stereospecific Propylene Polymerizations with Chiral Hafnium Metallocene Catalysts

John A. Ewen* and Luc Haspeslagh

*Fina Oil and Chemical Company
Deer Park, Texas 77536*

Jerry L. Atwood* and Hongming Zhang

*Department of Chemistry, University of Alabama
Tuscaloosa, Alabama 35487*

Received May 11, 1987

Ligand effects on stereoregulation with homogeneous catalysts¹⁻³ have stimulated considerable interest in Ziegler-Natta propylene polymerizations with metallocene catalysts.⁴⁻¹¹ The major lim-

(1) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355-6364.

(2) Ewen, J. A. "Ligand Effects on Metallocene Catalyzed Polymerizations", In *Catalytic Polymerization of Olefins*; Keii, T.; Soga, K., Eds.; Elsevier, New York, 1986.

(3) Ewen, J. A.; Haspeslagh, L.; Elder, M. J.; Cheng, H. N. *Macromolecules*, in press.

(4) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto A. *Macromolecules* **1986**, *19*, 2703-2706.

(5) Corradini, P.; Guerra, G. "Steric Control in Ziegler-Natta Catalysts: Model Catalytic Sites for Isospecific and Syndiospecific Polymerization", In *International Symposium on Transition Metal Catalyzed Polymerizations*; Akron, OH, 1986.

(6) Pino, P. "Present Trends in Research on α -Olefins Polymerization", In *International Symposium on Transition Metal Catalyzed Polymerizations*; Quirk, R., Ed.; Akron, OH, 1986.

(7) Kaminsky, W. "Stereocontrol with New Catalysts", In *International Symposium on Transition Metal Catalyzed Polymerizations*; Akron, OH, 1986.

(8) Pino, P.; Rotzinger, E.; von Achenbach, E. "The Stereospecific Polymerization of α -Olefins: Recent Developments and Some Unsolved Problems", In *Catalytic Polymerization of Olefins*; Keii, T.; Soga, K., Eds.; Elsevier: New York, 1986.

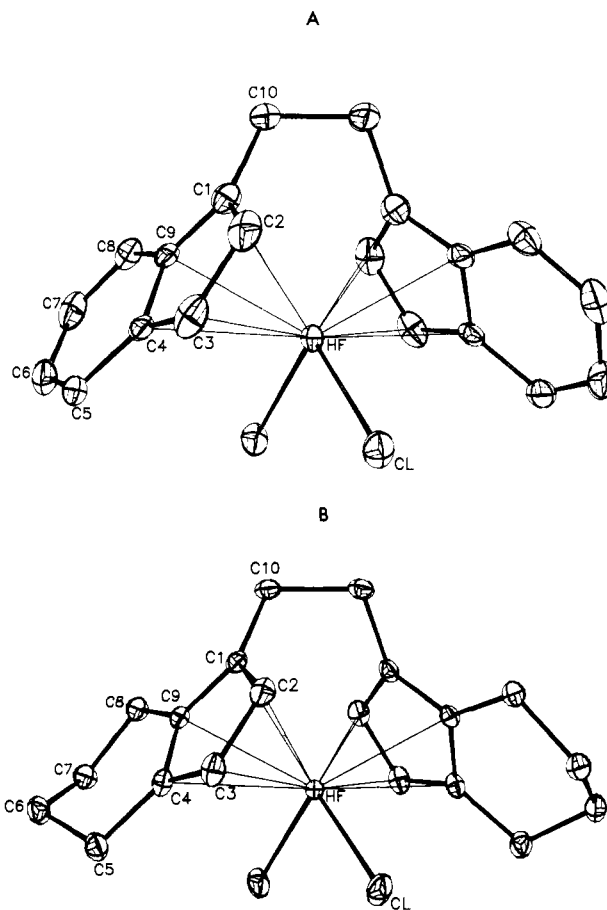


Figure 1. (a) Molecular structure of *rac*-Et[Ind]₂HfCl₂. (b) Molecular structure of *rac*-Et[IndH₄]₂HfCl₂. The atoms are represented by their 40% probability ellipsoids, and the figures depict the 1*R*-enantiomers.

Table I. Polymerization Results with Chiral Hf and Zr Metallocenes^a

metallocene (mg)	polym, T, °C	10 ⁻⁶ ·Rp, g/mol·M·h	10 ⁻³ ·M _w	M _w /M _n	mp, °C
Et[Ind] ₂ HfCl ₂ (0.17)	50	26.8	≥724	2.2	136
Et[Ind] ₂ HfCl ₂ (3.4)	50	43.6	304	2.3	136
Et[IndH ₄] ₂ HfCl ₂ (1.41)	50	9.1	150	2.2	142
Et[IndH ₄] ₂ HfCl ₂ (1.48)	80	34.8	42	2.4	127
Et[Ind] ₂ ZrCl ₂ (1.44)	50	21.2	28	2.1	134
Et[IndH ₄] ₂ ZrCl ₂ (1.45) ^b	80	25.5	9	2.1	117

^a Conditions: The polymerizations were studied in propylene/toluene mixtures unless otherwise stated. ^b Bulk propylene. See Supplementary Materials for additional details.

itations to development in this area have been that the titanium catalysts are unstable at conventional polymerization temperatures^{1,2} and that the zirconium analogues only produce low molecular weight oligomers in significant quantities.^{3,10,11}

In this contribution we describe the structures and the polymerization behavior of both *rac*-ethylenebis(indenyl)hafnium(IV) dichloride (*rac*-Et[Ind]₂HfCl₂) and *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium(IV) dichloride (*rac*-Et[IndH₄]₂HfCl₂). The results are compared to those with Ti and Zr analogues. The new Hf catalysts are the first metallocenes to provide high yields of high molecular weight isotactic polypropylene.

Crystal Structures. X-ray diffraction has confirmed that *rac*-Et[IndH₄]₂HfCl₂ is isostructural with the Ti¹³ and Zr¹⁴

(9) Kaminsky, W. "Preparation of Special Polyolefins from Soluble Zirconium Compounds with Aluminoxane as Cocatalyst", In *Catalytic Polymerization of Olefins*; Keii, T.; Soga, K., Eds.; Elsevier: New York, 1986.

(10) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. W. P. *Angew. Chem.* **1985**, *97*, 507.

(11) Kaminsky, W.; Kulper, K.; Niedoba, S. *Makromol. Chem.* **1986**, *187*, 377-387.