

(CH₃)[HCr(CO)₃(C₅H₅)]₂; at 68 °C, $k = 2.2(3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Use of DCr(CO)₃(C₅H₅) 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 DCr(CO)₃(C₅H₅). 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 HCo(CO)₄ and HMn(CO)₅ to compare its behavior under catalytic and stoichiometric conditions.

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Crystal Structures and Stereospecific Propylene Polymerizations with Chiral Hafnium Metallocene Catalysts

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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-

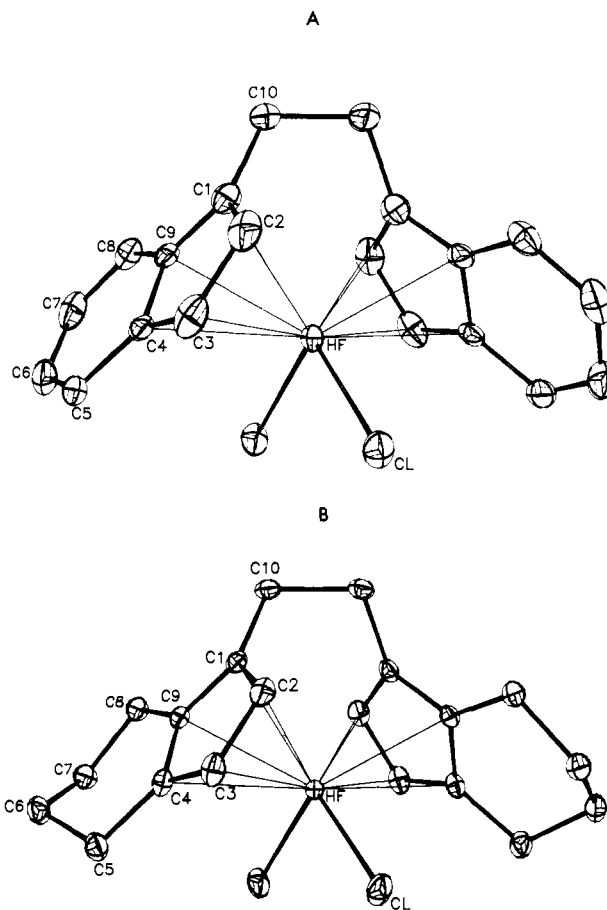


Figure 1. (a) Molecular structure of *rac*-Et[Ind]₂HfCl₂. (b) Molecular structure of *rac*-Et[IndH₄]₂HfCl₂. The atoms are represented by their 40% probability ellipsoids, and the figures depict the 1*R*-enantiomers.

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

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analogues. The molecular structures of *rac*-Et[Ind]₂HfCl₂ and *rac*-Et[IndH₄]₂HfCl₂ are displayed in Figure 1. The Hf–ring centroid distance in *rac*-Et[Ind]₂HfCl₂ is 0.02 Å longer, and its unit cell is 81.6 Å³ smaller than for *rac*-Et[IndH₄]₂HfCl₂. The presence of the *c*-glide plane in the monoclinic *C2/c* space group means that there are two sets of molecules with opposite chirality.¹⁵

The ligand–metal distances for *rac*-Et[IndH₄]₂MCl₂ increase in the order M = Zr > Hf >> Ti. The Hf–ring centroid distance and Hf–Cl length are 0.02 and 0.04 Å shorter, respectively, than the corresponding distances in *rac*-Et[IndH₄]₂ZrCl₂. The smaller Hf ionic radius is due to the 4f¹⁴ lanthanide contraction resulting from imperfect shielding of one electron by another in the same 4f subshell.¹⁶ The filled 4f orbital has been speculated to result in lower Lewis acidities for hafnocenes relative to zirconocene analogues.^{16a,17}

Polymerization Results. The yields and characterizations of the polypropylene samples are listed in Table I. The indenyl derivatives have higher activities, produce higher molecular weight polymers, and are less stereospecific than the tetrahydroindenyl complexes at equivalent polymerization conditions.^{1–3,11} This ligand effect is particularly pronounced for the smaller Ti complexes.^{1,2}

rac-Et[Ind]₂TiCl₂ is the only member of this series with a high activity at subambient conditions.¹ The higher fundamental activity for Ti is consistent with both the order of M–C σ -bond strengths (Ti < Zr < Hf)^{16a} and the increased stability of Ti(IV) at low temperatures.¹ On the other hand, the zirconium oligomerization and hafnium polymerization catalysts both have high activities at 30–80 °C because of their relatively more stable M(IV) oxidation states.

Catalyst Stereospecificities. The polymer DSC melting points indicate that Hf produced polymers are slightly more stereoregular than those obtained with Zr (Table I). ¹³C NMR analyses of the polymers show that the racemic stereoisomers of Zr are 95–99% stereoselective (mole % of units with the same relative configuration = % N_A) at 80–20 °C.^{3,19} The soluble catalysts are therefore similar to heterogeneous δ -TiCl₃ systems in this respect.²⁰ However, *rac*-Et[IndH₄]₂ZrCl₂ and *rac*-Et[Ind]₂ZrCl₂ isomerization and/or decomposition products produce 6–15 wt % of perfectly atactic polymer at 20–80 °C, and their “as-polymerized” samples contain about 5% regioirregularities which are mostly stereoregular (meso).³

Polymer Molecular Weights. The chiral “zirconocenes” produce brittle polypropylene waxes at conditions where appreciable yields

can be obtained. The soluble chiral hafnium catalysts produce plastics with high molecular weights (Table I). The differences in the degrees of polymerization obtained with these two transition metals is remarkable because hafnium and zirconium typically produce similar chemistry.¹⁶ These are the first examples of filled 4f orbitals providing a useful advantage in a catalytic reaction.

Supplementary Material Available: Listings of crystal data, atomic coordinates, generated atomic coordinates for hydrogen atoms, bond distances and angles, geometry for the hafnium atoms, best planes, drawings of the unit cells, and temperature factors for the molecular structures as well as synthetic and polymerization procedures (11 pages); listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Synthesis of a Bilindionostilbenoparacyclophane as a Model for “Stretched” Bile Pigment Chromophores of Biliproteins¹

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The most primitive oxygen-producing phototrophic microorganisms, the cyanobacteria,² as well as the red algae (*Rhodophyceae*) and cryptomonads utilize highly specialized light-harvesting chromoproteins—the so-called phycobiliproteins—as photosensitizers of chlorophyll *a* in the primary process of photosynthesis.³ The chromophores of the phycobiliproteins (phycocyanins, phycoerythrins, and phycourobilins) belong to the class of bile pigments. However, two characteristic spectroscopic properties, namely intense fluorescence⁴ and a higher extinction of the visible absorption band with respect to the band in the near-UV range, differentiate native (i.e., not denatured) phycobiliproteins from free bile pigment chromophores. Both theoretical calculations^{5,6} and comparison with the UV–vis spectrum of isophorocobilin (an almost rigid bile pigment chromophore isolated from the butterfly *Papilio phorcas*)⁷ suggest that the enhanced absorption of phycobiliproteins in the visible range depends on the occurrence of “stretched” conformations of the chromophore molecules.⁸ Thus, in solution, the ratio of absorption of biliverdins and their 3,4-dihydro derivatives in the visible and UV range is higher in HMPTA than in CCl₄,⁹ probably because of the increase of “stretched” conformations in the former solvent at the expense of the energetically more favorable helical-shaped conformation of bile pigment molecules.¹⁰ However, the proof of a relationship between conformation of bile pigment molecules and their spectroscopic properties may be only furnished by a model which mimics the features of the phycobiliproteins without changing the structure of the chromophore. Such a prerequisite is fulfilled by

(12) The Hf complexes were prepared from 99.99% pure HfCl₄ on a metal–metal basis obtained from Research Organic/Inorganic Chemicals Co. with modifications (Supplementary Material) to the procedure described for preparation of the Zr analogues.¹⁴

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(15) The space group for *rac*-Et[IndH₄]₂HfCl₂ is the monoclinic *C2/c* with *a* = 16.328 (3) Å, *b* = 10.115 (2) Å, *c* = 14.296 (3) Å, β = 132.08 (2)°, and *D*_c = 1.95 g cm⁻³ for *Z* = 4. Least-squares refinement based on 1592 observed reflections led to a final *R* value of 0.027. We suggest that the zirconium complex (ref 14) also belongs to the space group *C2/c*. For *rac*-Et[Ind]₂HfCl₂, the space group is *C2/c* with *a* = 15.494 (2) Å, *b* = 10.612 (2) Å, *c* = 11.945 (2) Å, β = 121.71 (2)°, and *D*_c = 2.01 g cm⁻³ for *Z* = 4. Refinement based on 1527 observed reflections led to *R* = 0.030.

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