$\psi[PO_2^-CH_2N^+]$ to other proteolytic enzymes are under investigation.

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Supplementary Material Available: Listing of synthetic procedures and experimental data relevant to the preparation of compound **7** (7 pages). Ordering information is given on any current masthead page.

Iso-Specific Ziegler–Natta Polymerization of α-Olefins with a Single-Component Organoyttrium Catalyst

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Three types of well-defined, homogeneous Ziegler–Natta α-olefin polymerization systems have been described recently: (1) two-component catalysts consisting of group 4 metallocene dihalides and a large excess of methylalumoxane cocatalyst;[1,2] (2) simpler two-component systems based on group 4 metallocene dialkyls with a stoichiometric (or near stoichiometric) amount of an activator such as $[C_6H_5(CH_3)_2NH^+][B(C_6F_5)_4^-]$,[3] $[(C_6H_5)_3C^+][B(C_6F_5)_4^-]$,[4] or $B(C_6F_5)_3$;[5] and (3) single-component catalysts such as Lewis base adducts of cationic group 4 metallocene alkyls[6] or the isoelectronic neutral group 3 or lanthanide metallocene hydrides or alkyls.[7] The group 4 metallocene/methylalumoxane and $[Cp_2MCH_3^+][B(R)(C_6F_5)_3^-]$ catalysts (M = Zr, Hf; R = C_6F_5, CH_3) exhibit higher activity in α-olefin polymerizations, and with the chiral, C_2-symmetric *ansa*-metallocene dihalide or dimethyl precursors (M = Ti, Zr, Hf) developed by Brintzinger, Ewen, Collins, and others, highly isotactic polypropylene is obtained.[1a-g,8] Unfortunately, the meso (C_s symmetric) isomer is normally formed along with the preferred chiral isomer in the synthesis of the metallocene dihalide.[8,9] Since the meso isomers generally produce atactic polypropylene and exhibit lower activity, a tedious separation of the meso isomer from the racemic isomer is normally required.

Herein we report the synthesis of the first iso-specific, single-component Ziegler–Natta polymerization catalyst, [*rac*-Me_2Si-(2-$SiMe_3$-4-$CMe_3C_5H_2)_2$YR]. Its simplicity makes it particularly

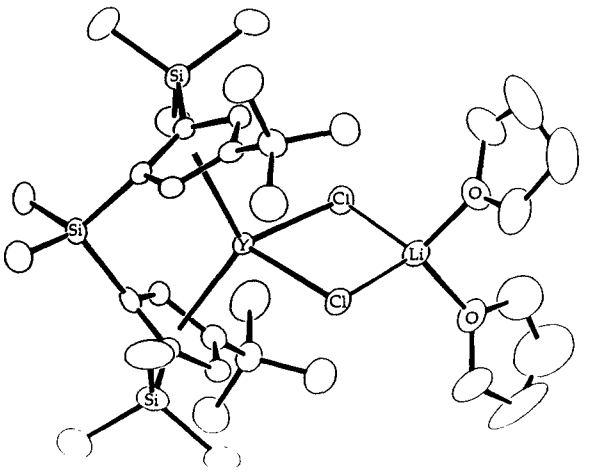

Figure 1. Molecular drawing of *rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$. All unlabeled atoms are carbon.

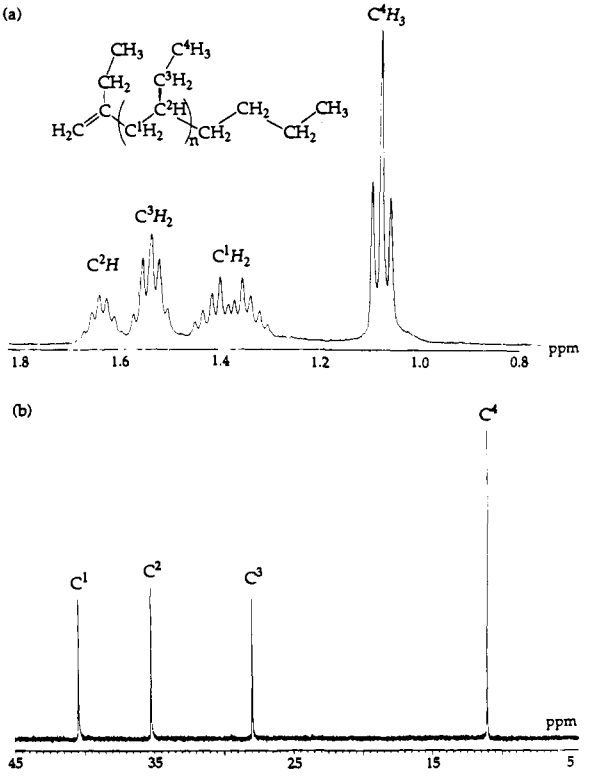

Figure 2. (a) ^1H NMR spectrum (400 MHz) (*o*-dichlorobenzene/benzene-d_6, 9:1 v:v, 100 °C) with tentative assignment of resonances. (b) ^{13}C NMR spectrum (100 MHz) (*o*-dichlorobenzene/benzene-d_6, 9:1 v:v, 100 °C) of poly(1-butene) obtained by polymerization of neat 1-butene at 25 °C with [*rac*-BpYH]$_2$.

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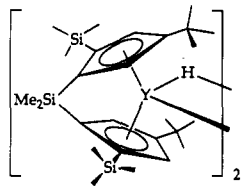
well suited to in situ mechanistic studies. Moreover, the $[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2]$ ligand has been designed to coordinate to yttrium to produce *only* the desired racemic isomer in the synthesis of the chloride precursor.

Addition of $YCl_3(THF)_3$ to $Li_2[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2]$ (Li_2Bp), prepared by the addition of 2 equiv of Me_3SiCl to $Li_2[Me_2Si(3\text{-}CMe_3C_5H_3)_2]$[10] and subsequent deprotonation with 2 equiv of *n*-butyllithium, affords only the C_2-symmetric *ansa*-yttrocene compound, *rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ ($BpY(\mu\text{-}Cl)_2Li(THF)_2$), in ~48% isolated yield; <2% (^1H NMR) of the C_s meso isomer is detected. The results of a single-crystal X-ray structure determination for $BpY(\mu\text{-}Cl)_2Li(THF)_2$ are published elsewhere.[11] Inspection of the molecular drawing (Figure 1)[12] indicates that the unfavorable steric interactions between the $SiMe_3$ groups in the narrow portion of the Cp–M–Cp wedge are avoided only for the racemic isomer. Even for the favored racemic isomer, the two bulky $SiMe_3$ groups experience crowding from both the Me_2Si bridging unit and the opposite cyclopentadienyl ring.

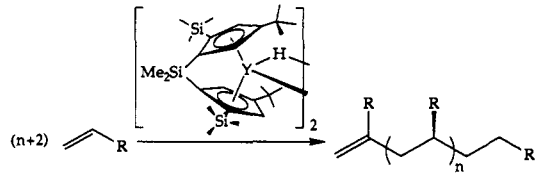
Lithium chloride and THF are conveniently removed by treatment of the lithium dichloroyttrate with the bulky lithium alkyl, $LiCH(Si(CH_3)_3)_2$, followed by hydrogenolysis to yield the colorless, crystalline hydride derivative [*rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}H)]_2$ ([*rac*-BpYH]$_2$) in ~35% isolated yield.



[*rac*-BpY-H]$_2$

[*rac*-BpYH]$_2$ is formulated as a dimer (almost certainly the homochiral *RR* and *SS* enantiomers, considering steric interactions) on the basis of a triplet in the ^1H NMR spectrum assigned to the two bridging hydride ligands (δ 4.87; $^1J_{^{89}Y\text{-}^1H}$ = 31 Hz; ^{89}Y, I = $^1/_2$, 100%). Solutions of [*rac*-BpYH]$_2$ prove to be remarkably unreactive toward PMe_3, and unlike other *ansa*-yttrocene hydride complexes,[13] no ligand redistribution resulting in a [Cp–$SiMe_2$–Cp]-bridged "spanover" dimer is observed after days in C_6D_6 solution (^1H NMR).

Propylene (25% v:v in methylcyclohexane) as well as neat 1-butene, 1-pentene, and 1-hexene are all polymerized, albeit rather slowly over a period of several days at 25 °C to afford modest molecular weight polymers.[14] Preliminary results indicate the following properties for the polymers produced: polypropylene (M_n 4200, PDI 2.32, T_m 157 °C, 97.0% mmmm); poly(1-butene) (M_n 8500, PDI 3.44, T_m 105 °C); poly(1-pentene) (M_n 20 000, PDI 1.99, T_m 73 °C); poly(1-hexene) (M_n 24 000, PDI 1.75, T_m <25 °C). Chain end analysis of the poly(α-olefins) by ^1H and



(R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$)

^{13}C NMR indicate geminally disubstituted olefinic end groups, consistent with chain propagation by 1,2 (primary) addition and termination by β-H elimination.[15] The moderately high melting point for the polypropylene sample as well as the ^{13}C NMR spectra of the polymers at the pentad analysis level shows a remarkably high degree of isotacticity for all polymers.[16] The ^{13}C and ^1H NMR spectra of a poly(1-butene) sample are shown in Figure 2.

rac-[BpYH]$_2$, the first *single-component*, iso-specific Ziegler–Natta catalyst so far as we are aware, is uniquely suited to a study of the subtle steric factors that govern the remarkably high stereospecificities exhibited in the polymerization of α-olefins by this and the related two-component, chiral group 4 catalyst systems. We plan to undertake the synthesis of related catalysts using the successful design feature responsible for the exclusive formation of the racemic isomers of $Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}CMe_3C_5H_2)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ and the catalysts derived therefrom.

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Supplementary Material Available: Experimental details describing the syntheses of Li_2Bp, $BpY(\mu\text{-}Cl)_2Li(THF)_2$, $BpYCH(SiMe_3)_2$, and [BpYH]$_2$, as well as information regarding α-olefin polymerizations and ^{13}C NMR analyses for the polymers (5 pages). Ordering information is given on any current masthead page.

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Observation of a 2-α-Enamine from a 2-(Methoxyphenylmethyl)-3,4-dimethylthiazolium Salt in Water: Implications for Catalysis by Thiamin Diphosphate-Dependent α-Keto Acid Decarboxylases

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During the past decade, several lines of evidence have suggested the intermediacy of a thiamin diphosphate (ThDP)-bound enamine on the pathway of pyruvate decarboxylase (PDC, EC 4.1.1.1),[1] starting with the observation of a new absorbance with λ_{max} near 440 nm, when the conjugated substrate analogue (*E*)-4-(4-chlorophenyl)-2-oxo-3-butenoic acid was employed.[2] Parallel with the accumulating evidence on PDC thiazolium compounds were synthesized, from which models for such enamines could be generated in nonaqueous media on addition of a strong, nonnucleophilic base. The structures of these enamines were established by UV–vis and NMR spectroscopy.[3a] Later, pK_a's of the con-

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