and related α-silicon-substituted enols are now in progress.

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(20) E.g., $\mathrm{Mes_2CHCOCl + LiSiMe_3}$ in HMPA gave mostly **1c** and **6**. $\mathrm{Mes_2CHCHO + LiSiMe_3}$ gave mainly isomerization to $\mathrm{Mes_2C{=}CHOH}$ and not the alcohol which may be a precursor to **2c**. Other methods are under study.

Isolation, and Partial Characterization by XPS, of Two Distinct Catalysts in the Ziegler–Natta Polymerization of Ethylene

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Although Ziegler–Natta polymerization has been known for over 25 years and is widely used for the production of high-density polyethylene and isotactic polypropylene, the reactive catalytic intermediate(s) involved have not been characterized.[2–4] As part of our continuing studies of the use of X-ray photoelectron spectroscopy (XPS) in the characterization of the electronic properties of transition-metal complexes,[5] we have studied the homogeneous zirconocene-based[6] Ziegler–Natta polymerization of ethylene. We now report the first isolation and direct characterization of highly active Ziegler–Natta polymerization catalysts. This was accomplished through the use of our technique for the isolation and purification of reactive organometallic intermediates bearing macromolecular ligands.[8]

As shown in Table I, treatment of dichlorozirconocene (**1**), methylchlorozirconocene (**2**), or dimethylzirconocene (**3**) with methylaluminoxanes in toluene gave solutions of catalyst in which **1**, **2**, and **3** were all converted into new zirconium derivatives, which had the same zirconium(IV) binding energy.[9] This increase in binding energy relative to **1**, **2**, and **3** indicates that this catalyst is electron deficient (oxidized) in comparison to the three zirconocenes used as starting materials. This catalyst was very long-lived since, in the absence of oxygen and moisture, no change in the binding energy of this species could be detected after 10 days.[10] Exposure of this catalyst solution to an atmosphere of ethylene led to the immediate formation of polyethylene. After the initially formed catalyst had reacted with ethylene, no trace of material with a binding energy of 182.4 eV could be detected. Instead a new zirconium species with a binding energy of 182.1 eV was observed. This new material was also a catalyst for the polymerization of ethylene.

Table I. Binding Energies of Two Distinct Catalytic Species Obtained from **1**, **2**, and **3** Methylaluminoxanes and Ethylene in Toluene

	$\mathrm{Zr(3d_{5/2})}$ binding energies (±0.1 eV)		
compd	zirconocene (eV)	catalyst before ethylene addn (eV)	catalyst after ethylene addn (eV)
1	181.7	182.4	182.1
2	181.2	182.4	182.1
3	180.7	182.4	182.1

Table II. XPS Binding Energies of Substituted Zirconocenes

compd	compd no.	$\mathrm{Zr(3d_{5/2})}$ binding energy[a] (±0.1 eV)	Δ eV relative to **1**
$\mathrm{Cp_2ZrCl_2}$	**1**	181.7	0.0
$\mathrm{Cp_2Zr(Cl)(CH_3)}$	**2**	181.2	−0.5
$\mathrm{Cp_2Zr(Cl)[CH_2CH_2C(CH_3)_3]}$	**4**	181.3	−0.4
$\mathrm{Cp_2Zr(Cl)[CH{=}CHC(CH_3)_3]}$	**5**	181.3	−0.4
$\mathrm{Cp_2Zr(CH_3)_2}$	**3**	180.7	−1.0
$\mathrm{Cp_2Zr(Cl)[OCH(CH_3)_2]}$	**6**	181.6	−0.1
$\mathrm{Cp_2Zr[OCH(CH_3)_2]_2}$	**7**	181.5	−0.2
$\mathrm{[Cp_2ZrCl]O}$	**8**	181.5	−0.2
$\mathrm{Cp_2Zr(Cl)(H)}$	**9**	181.3	−0.4
$\mathrm{Cp_2ZrH_2}$	**10**	180.0	−1.7

[a] Measured in eV.

In order to evaluate the significance of the binding energy values of 182.4 and 182.1 eV obtained for the two catalytic materials, it is necessary to understand the effect of a wide variety of substituents on the $\mathrm{Zr(3d_{5/2})}$ binding energy of zirconocenes. Table II provides data which illustrate that replacement of the chloride of **1** by alkyl, alkoxyl, or hydride results in greater electron donation to the zirconium and, as a result, in a net reduction in binding energy relative to **1**. Since both active catalysts have binding energies which show that the zirconium is electron deficient relative to **1**, any simple exchange of one or more of these three ligands for the chlorides of **1** could not provide an intermediate which would be an active catalyst.

In order to ascertain whether one or more of the cyclopentadienide ligands might have been lost or replaced, the initial catalyst was also formed from either (η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)zirconium(IV) dichloride (**11**) or bis(η^5-pentamethylcyclopentadienyl)zirconium(IV) dichloride (**12**) and methylaluminoxanes. Both **11** and **12** gave catalysts which readily polymerized ethylene. In forming the active catalyst from **11** [$\mathrm{Zr(3d_{5/2})}$ binding energy = 181.4 eV], a change in binding energy to 181.9 eV before exposure to ethylene occurred (Δ eV = 0.5). In forming the active catalyst from **12** [$\mathrm{Zr(3d_{5/2})}$ binding energy = 181.0 eV], a change in binding energy to 181.7 eV before ethylene addition occurred (Δ eV = 0.7). These numbers can be compared to a change of 0.7 eV observed for the formation of active catalyst from **1**. These data provide convincing evidence that the cyclopentadienyl derived ligands are not lost in the formation of active catalyst.[11]

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[1] Division of Organic Chemistry of the American Chemical Society Fellow sponsored by the Rohm & Haas Company, 1986–1987. General Electric Co. Fellow, 1985–1986.

[2] For detailed reviews of Ziegler–Natta polymerization, see: (a) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (b) Quirk, R. P. *Transition Metal Catalyzed Polymerization, Alkenes and Dienes*; Harwood Academic Publishers: New York, 1983.

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[6] We chose to study a system recently developed by Kaminsky and co-workers[3c] which is based on variously substituted zirconocene halide and alkyl complexes as the catalyst and methylaluminoxanes as the cocatalyst. This catalytic system was chosen because it exhibits prolonged stability in solution, high activity for polymerization of ethylene and α-olefins, and extremely high overall yields of active catalytic centers.[7]

[7] Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

[8] Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380.

[9] The fact that **1**, **2**, and **3** were all converted into a material with the same binding energy, while providing very strong evidence for the formation of the same catalyst from all three precursors, does not *prove* the existence of a single species. The identity of the binding energies establishes that in all three examples the zirconium resides in the same electronic environment.

[10] After this same time period, no change was noted in the activity of the catalyst on the addition of ethylene. In addition, formation of this first catalyst followed by addition of ethylene for 1.0 h after the initially formed catalyst had stood for 0.0, 0.5, and 1.0 h gave similar yields of polyethylene (41, 40, and 43 kg per h per g of starting zirconium).

[11] This suggestion is consistent with the results obtained through the use of chiral catalysts: Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. See, also: ref 7.

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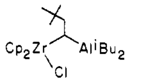
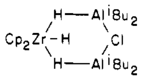
The significant question which remains to be answered centers on whether there is a suitable model system which is consistent with our Zr($3d_{5/2}$) binding energy for either the initially formed catalyst or the second catalytic species. Not surprisingly, compounds such as **13**[12] and **14**[13] were shown to be "electron-rich"



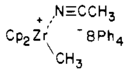
13

Zr($3d_{5/2}$) = 181.0 eV



14

Zr($3d_{5/2}$) = 181.3 eV



15

Zr($3d_{5/2}$) = 181.5 eV

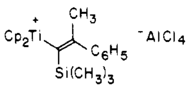
relative to both catalysts, as determined by the binding energies of 181.0 and 181.3 eV, respectively. Thus, structures closely related to **13** and **14** are not good models for either of the active species.

Recently, considerable attention has been devoted to the possible intermediacy of cationic zirconium[14] and titanium[15] species as active Ziegler-Natta polymerization catalysts.[16] In order to evaluate this concept, which was first proposed in 1965,[17] we studied the solvent complexed zirconium(IV) cationic species **15**,[14] which showed a Zr($3d_{5/2}$) binding energy of 181.5 eV. While this compound is more electron deficient than either **13** or **14**, it does not approach the values observed for both of the catalytic species formed from **1**, **2**, and **3**. Perhaps the best model for the formation of the first catalytic species is provided by examination of the first member of the titanium triad. Comparison of **16** with Eisch's

Cp_2TiCl_2

16

Ti($2p_{3/2}$) = 457.1 eV

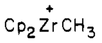


17

Ti($2p_{3/2}$) = 457.6 eV

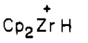
stable cationic titanocene **17** shows a 0.5 eV change *to a more electron-deficient titanium derivative*. This can be compared to a change of 0.7 eV in converting **1** into the initially formed zirconocene-derived catalyst.

On the basis of our data, we wish to suggest that the first formed catalytic species is **18** and the second formed catalytic species is



$Cp_2\overset{+}{Zr}CH_3$

18



$Cp_2\overset{+}{Zr}H$

19

⁻O-methylaluminoxane

20

19 (formed by β-hydride elimination from the attached polymer), with the methylaluminoxane anion **20** as the counterion in both cases.[16-18] In support of our proposal of **19** as the secondary catalytic species, we have shown that exposure of the initially formed catalyst **18** to hydrogen gas gave a material with a binding energy for Zr($3d_{5/2}$) equal to 182.2 eV.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this investigation.

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[18] Evolution of both hydrogen chloride gas and methane from the reaction of **1** with methylaluminoxanes, of methane from the reaction of **3** with methylaluminoxanes, of methane-d_3 from the reaction of **3**-d_6 with methylaluminoxanes, and of methane-d_1 from the reaction of **3** with methylaluminoxanes prepared from trimethylaluminum and deuterium oxide suggests, but does not prove, that the gegenion is an oxygen-based anion rather than an aluminum-based anion.

Asymmetric Hydrogenation of Trisubstituted Acrylic Acids Catalyzed by a Chiral (Aminoalkyl)ferrocenylphosphine-Rhodium Complex

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Although development of chiral phosphine-rhodium or ruthenium catalysts for asymmetric hydrogenation of olefins has resulted in so great a success as to make this reaction a practical approach to optically active compounds,[1-3] the olefinic substrates successfully used so far have been restricted, with a few exceptions,[4] to those containing a functional group such as carbonyl β to the olefinic double bond.[5-7] When designing chiral phosphine ligands, we have focused our particular attention on the selectivity being enhanced greatly by attractive interactions between functional groups on a substrate and on the chiral ligand.[8] Such reasoning prompted us to introduce an amino group on the chiral phosphine ligand that would provide an efficient catalyst for the rhodium-catalyzed asymmetric hydrogenation of unsaturated carboxylic acids. Here we report that chiral (aminoalkyl)ferrocenylphosphine ligands, (*R*)-*N*-methyl-*N*-[2-(dialkylamino)ethyl]-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamines (**1**),[9] give rise to high stereoselectivity as well as high catalytic activity in the hydrogenation of trisubstituted acrylic acids (tetrasubstituted olefins) where high stereoselectivity has

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[5] The high stereoselectivity is ascribed mainly to the chelate coordination by the functional group as well as the olefin in the diastereomeric transition state.[1,6,7]

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[9] The ferrocenylphosphines **1** were prepared by treatment of (*R*)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate with 5-15 equiv of 2-(dialkylamino)ethyl-*N*-methylamines in refluxing methanol.[8] The specific rotations ($[\alpha]^{25}_D$ (*c* 0.2-0.4, chloroform)) of **1a**, **1b**, **1c**, and **1d** are −333, −368, −297, and −325°, respectively.

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