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Electronic Effects in Homogeneous Indenylzirconium Ziegler–Natta Catalysts

Nicoletta Piccolrovazzi,† Piero Pino,†,‡ Giambattista Consiglio,*,§ Angelo Sironi,⊥ and Massimo Moret⊥

Institut für Polymere and Technisch-Chemisches Laboratorium, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland, and Istituto di Chimica Strutturistica Inorganica, Università di Milano, Via Venezian, 21, I-20133 Milano, Italy

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A series of new bis(indenyl)zirconium(IV) complexes of the general formula $(\eta^5\text{-}4,7\text{-}X_2C_9H_5)_2ZrCl_2$ and $(\eta^5\text{-}4,7\text{-}X_2C_9H_5)_2Zr(CH_2C_6H_5)_2$ (where X = H, CH_3, OCH_3, and F) were synthesized in order to investigate the electronic effects of substituents on the nature of the catalytic species in homogeneous Ziegler–Natta catalysts. By use of poly(methylaluminoxane) as cocatalyst, the activity of these complexes as catalyst precursors in the polymerization of ethylene was examined. The substitution with electron-withdrawing groups resulted in a decrease of both molecular weights and productivity, whereas in the case of electron donors, like methyl groups, no significant change in productivity and average molecular weight was observed. These effects support the hypothesis of a polar or ionic character of the catalytic species. The molecular structure of $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$ was determined by X-ray diffraction. The complex crystallizes in space group $P2_1/c$ (No. 14) with cell parameters a = 10.786 (1) Å, b = 11.084 (2) Å, c = 21.602 (2) Å, β = 98.30 (1)°, Z = 4, R = 0.0220, and R_w = 0.0295.

Introduction

Since the discovery of Ziegler–Natta catalysis for olefin polymerization, a lot of attention has been paid to metallocenes of group IV elements as catalyst precursors for homogeneous systems.[1,2] Due to their low productivity, however, the applications of systems like $(\eta^5\text{-}C_5H_5)_2MX_2/AlR_nX_{3-n}$ were rather limited. With the recent development of poly(aluminoxanes) as cocatalyst,[3] this problem could be widely overcome and has led to the development of versatile homogeneous catalysts.[4] In fact, the use of chiral metallocenes as the catalyst precursors offers the possibility to prepare poly(α-olefins) having different stereochemical features.[5] Despite intensive studies over more than 30 years,[2–6] the nature of the catalytic centers in homogeneous Ziegler–Natta catalysts is still uncertain. For the $(\eta^5\text{-}C_5H_5)MX_2/AlR_nCl_{3-n}$ systems, kinetic studies[7] and the isolation[8] of an initial insertion product by use of trimethyl(phenylethynyl)silane as a model compound for an olefin, together with other evidence,[8–10] strongly support the hypothesis of a catalytic center having an ionic character. Also for the $(\eta^5\text{-}C_5H_5)_2MX_2$/aluminoxane system, ionic or strongly polarized catalytic species have been proposed, e.g., $[(\eta^5\text{-}C_5H_5)_2MCH_3]^+[Al_n(CH_3)_{n-1}O_nX_2]^-$ or $[(\eta^5\text{-}C_5H_5)_2MCH_3X]\cdot[Al_n(CH_3)_{n-1}O_nX]$.[10,11] Such species can be expected to be strongly influenced by the electronic surroundings and hence by the ligand field of the transition metal. Few efforts have been made until now to study the effect of substituents on the formation, stability, and behavior of the catalytic centers. The investigations were limited to alkyl-substituted indenyl complexes having the substituents on the C_5 ring and to cyclopentadienyl systems.[12,13] For these systems, however, electronic effects cannot be investigated separately from steric ones.[13] In order to study mainly the electronic effects of substituents on the behavior of the catalytic centers, we have designed a series of new substituted bis(indenyl)zirconium(IV) complexes. To avoid steric hindrance at the carbon atoms involved in the coordination to the transition metal, the carbon atoms of the C_6 ring were taken into account for substitution. Of the possible isomers, the 4,7-disubstituted

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† Institute für Polymere, ETH-Zentrum.

‡ Deceased July 9, 1989.

§ Technisch-Chemisches Laboratorium, ETH-Zentrum.

⊥ Università di Milano.

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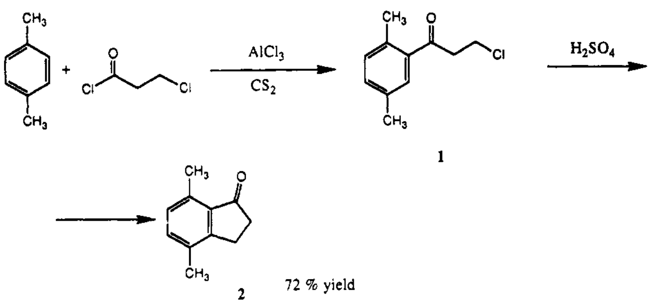
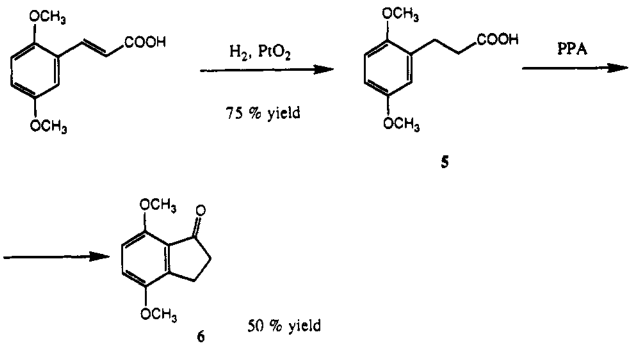
Scheme I



Scheme II

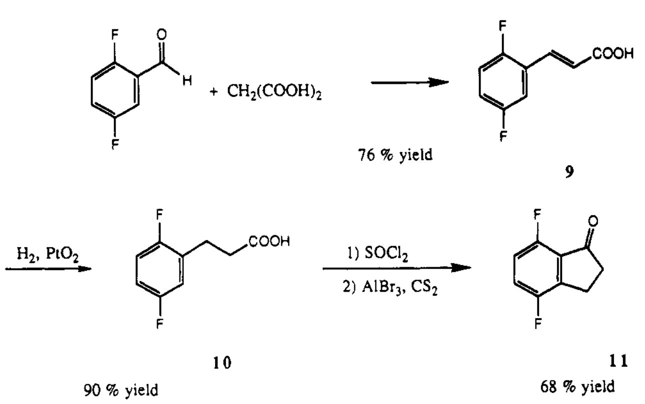


derivatives were chosen for this investigation. In this paper, we report on the synthesis and characterization of a series of zirconium compounds of the type $(\eta^5\text{-}4,7\text{-}X_2C_9H_5)_2ZrCl_2$ and $(\eta^5\text{-}4,7\text{-}X_2C_9H_5)_2Zr(CH_2C_6H_5)_2$. These systems have been also compared in the polymerization of ethylene in the presence of poly(methylaluminoxane) as cocatalyst.

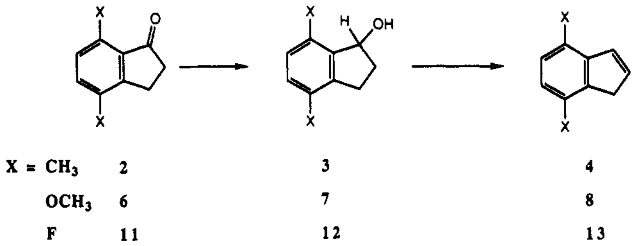
Results and Discussion

Synthesis of the Ligands. No direct derivatization of indene could be applied for the synthesis of the desired ligands in order to obtain pure 4,7-disubstituted isomers.[14] Starting with substituted benzene compounds, a series of 4,7-disubstituted indanones were prepared as a common ligand precursor. These indanones were then transformed through two reaction steps to the corresponding indenes (vide infra). 4,7-Dimethylindanone[15] (2) and 4,7-dimethoxyindanone[16] (6) (and the corresponding indenes 4 and 8) were already known in the literature; we have used some modification of the reported methods in order to improve the chemical yields. 2 was prepared according to Scheme I starting with *p*-xylene and 3-chloropropionyl chloride. An overall yield of 72% could be obtained by carrying out the reaction in two separate steps. The synthesis of 6, which has not been described in detail until now, was realized according to Scheme II. The steps are straightforward and, in spite of the rather low yield, do not present particular problems. The starting material for the synthesis of 4,7-difluoroindanone (11) was 2,5-difluorobenzaldehyde (Scheme III). In fact, attempts to synthesize the compounds following a reaction scheme similar to those applied for 4,7-dimethyl- and 4,7-dimethoxyindanone gave very low yields. A key step in this scheme is the Friedel–Crafts reaction, which gives only very low yields when PPA (poly(phosphoric acid)) or H_2SO_4 or $AlCl_3$[17] are used as the catalyst. Acceptable yields (~70%) were obtained only with $AlBr_3$ in CS_2. Reduction of the indanones and dehydratation in the presence of acids (Scheme IV) gave the desired indenes 4, 8, and 13.[18] For

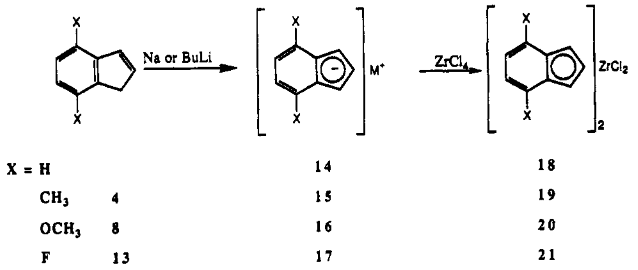
Scheme III



Scheme IV



Scheme V



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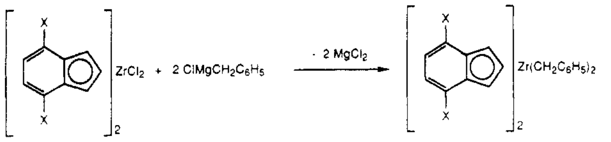
Scheme VI



X =		
H	18	22
CH_3	19	23
OCH_3	20	24
F	21	25

4,7-difluoroindene (**13**), secondary reactions such as oxidation and dimerization were avoided by removing the product from the reaction mixture immediately after formation through distillation.

Synthesis of the Zirconium(IV) Dichloride Complexes. $(\eta^5\text{-}C_9H_7)_2ZrCl_2$ (**18**) was prepared according to the literature through metalation of indene to indenylsodium and reaction with $ZrCl_4$ (Scheme V)[19] and was purified by sublimation. In a similar way, also the substituted compounds were obtained. The metalation reaction was carried out in the case of **4** and **13** with metallic sodium, whereas in the case of **8** butyllithium was used. Due to the electron-withdrawing fluorine substituents, **13** shows a much higher reactivity as well as acidity than **4**. The freshly prepared solutions of the anions were reacted with the $ZrCl_4$/tetrahydrofuran adduct (or $ZrCl_4$/dimethoxyethane for **13**) in a 2:1 ratio to yield the corresponding zirconium(IV) dichloride complexes **19**, **20**, and **21** until now not reported in the literature. The crude reaction products **19** and **20** could be successfully purified by crystallization. Compound **21** showed very low solubility in the usual organic solvents, low thermal stability, and high sensitivity toward air in solution. Thus, purification by crystallization or sublimation was not successful.

Synthesis of the Zirconium(IV) Dibenzyl Complexes. The synthesis of these compounds was carried out through reaction of the corresponding chloride complexes with benzylmagnesium chloride (Scheme VI). The unsubstituted compound $(\eta^5\text{-}C_9H_7)_2Zr(CH_2C_6H_5)_2$ was already known in the literature.[20] For its preparation, only a slight excess of Grignard reagent was recommended; however, under these conditions, we could isolate a product that according to the spectroscopic data should be the monobenzyl derivative $(\eta^5\text{-}C_9H_7)_2ZrCl(CH_2Cl_6H_5)$. Therefore, we used a 1:5 molar ratio between the zirconium halide and the Grignard reagent for the transalkylation reaction. As expected, the dibenzyl derivatives showed a higher solubility than the dichlorides and were thus purified successfully by crystallization from toluene/*n*-hexane at −25 °C. The relatively high thermal and oxidation stability of the substituted and unsubstituted dibenzyl derivatives is in keeping with previous observations on similar $(\eta^5\text{-}C_9H_7)_2MR_2$ and $(\eta^5\text{-}C_5H_5)_2MR_2$ compounds.[21]

Crystal Structure of $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$. The crystal structure of $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$ (**25**) consists of discrete molecules with normal van der Waals interactions. Figure 1 reports an ORTEP view of the compound. The positional parameters are reported in Table I, while in Table II the relevant bond parameters are collected. The coordination geometry around the Zr(IV) ion, as defined by cp(A) and cp(B), the baricenters of the five-membered ring of the two F_2Ind ligands, and C(10A) and C(10B), the two η^1-benzyl carbon atoms, is pseudotetrahedral. Deviations from the ideal tetrahedral geometry occur because of an expansion of the cp(A)–Zr–cp(B) angle (129.95 (7)°) and of a contraction of the C(10A)–Zr–C(10B) one (95.44 (7)°). This behavior is similar to that found in the related $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$[22] compound but

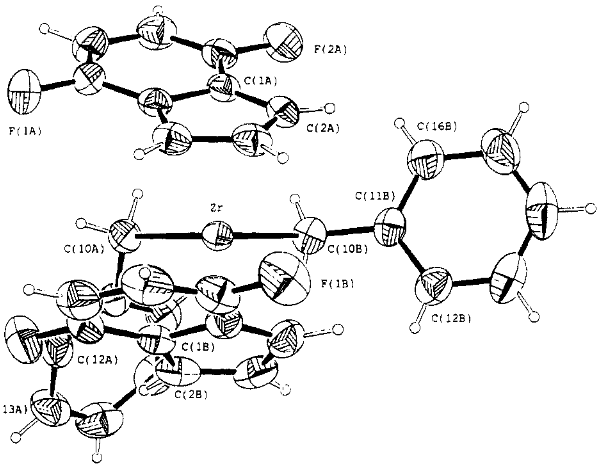


Figure 1. Molecular structure of compound $[F_2Ind]_2ZrBr_2$.

Table I. Positional Parameters and Their Estimated Standard Deviations for $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$[a]

atom	x/a	y/b	z/c	B, Å^2
Zr	0.17231 (1)	0.23152 (1)	0.389 24 (1)	2.41 9 (3)
F(1A)	0.1586 (1)	0.2908 (1)	0.585 68 (6)	4.99 (3)
F(2A)	0.5416 (1)	0.1197 (1)	0.470 12 (6)	4.29 (3)
F(1B)	−0.1327 (1)	−0.0252 (1)	0.342 90 (8)	5.84 (3)
F(2B)	−0.1237 (1)	0.4346 (1)	0.434 28 (7)	5.67 (3)
C(1A)	0.3252 (2)	0.1212 (2)	0.478 16 (8)	2.75 (3)
C(2A)	0.2732 (2)	0.0354 (2)	0.432 45 (9)	3.02 (4)
C(3A)	0.1455 (2)	0.0287 (2)	0.434 95 (9)	3.26 (4)
C(4A)	0.1123 (2)	0.1141 (2)	0.478 14 (9)	3.17 (4)
C(5A)	0.2249 (2)	0.1677 (2)	0.507 57 (8)	2.80 (3)
C(6A)	0.2549 (2)	0.2493 (2)	0.557 92 (9)	3.50 (4)
C(7A)	0.3736 (2)	0.2844 (2)	0.577 5 (1)	4.14 (5)
C(8A)	0.4723 (2)	0.2402 (2)	0.547 6 (1)	3.95 (4)
C(9A)	0.4472 (2)	0.1630 (2)	0.499 21 (9)	3.19 (4)
C(1B)	−0.0585 (2)	0.2960 (2)	0.363 02 (9)	3.16 (4)
C(2B)	0.0151 (2)	0.3672 (2)	0.327 02 (9)	3.73 (4)
C(3B)	0.0590 (2)	0.2898 (2)	0.283 72 (9)	4.11 (5)
C(4B)	0.0221 (2)	0.1713 (2)	0.293 15 (9)	3.84 (4)
C(5B)	−0.0571 (2)	0.1750 (2)	0.340 10 (9)	3.23 (4)
C(6B)	−0.1327 (2)	0.0890 (2)	0.365 5 (1)	4.00 (4)
C(7B)	−0.2030 (2)	0.1180 (2)	0.409 8 (1)	4.63 (5)
C(8B)	−0.2003 (2)	0.2360 (2)	0.434 4 (1)	4.74 (5)
C(9B)	−0.1284 (2)	0.3204 (2)	0.411 7 (1)	4.02 (4)
C(10A)	0.2330 (2)	0.4127 (2)	0.435 69 (9)	3.40 (4)
C(11A)	0.2356 (2)	0.5253 (2)	0.397 74 (9)	3.16 (4)
C(12A)	0.1463 (2)	0.6163 (2)	0.400 3 (1)	3.92 (4)
C(13A)	0.1441 (2)	0.7172 (2)	0.362 4 (1)	4.57 (5)
C(14A)	0.2303 (3)	0.7316 (2)	0.322 6 (1)	4.87 (5)
C(15A)	0.3197 (2)	0.6448 (2)	0.319 8 (1)	4.58 (5)
C(16A)	0.3225 (2)	0.5427 (2)	0.357 4 (1)	3.72 (4)
C(10B)	0.3365 (2)	0.2179 (2)	0.333 29 (9)	3.27 (4)
C(11B)	0.3682 (2)	0.1132 (2)	0.295 29 (8)	3.15 (4)
C(12B)	0.3036 (2)	0.0904 (2)	0.236 01 (9)	3.90 (4)
C(13B)	0.3292 (2)	−0.0087 (2)	0.201 8 (1)	4.84 (5)
C(14B)	0.4205 (2)	−0.0889 (2)	0.224 7 (1)	5.41 (5)
C(15B)	0.4888 (2)	−0.0682 (2)	0.282 2 (1)	5.32 (5)
C(16B)	0.4625 (2)	0.0312 (2)	0.3171 (1)	4.39 (5)

[a] *B* is reported for non-hydrogen atoms.

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Table II. Bond Distances (Å) and Selected Angles (deg) for $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$[a]

Zr–C(1A)	2.644 (1)	C(1A)–C(5A)	1.427 (2)	C(7B)–C(8B)	1.411 (3)
Zr–C(2A)	2.547 (2)	C(1A)–C(9A)	1.408 (2)	C(8B)–C(9B)	1.351 (3)
Zr–C(3A)	2.489 (2)	C(2A)–C(3A)	1.388 (2)	C(10A)–C(11A)	1.495 (2)
Zr–C(4A)	2.482 (2)	C(3A)–C(4A)	1.411 (3)	C(11A)–C(12A)	1.401 (3)
Zr–C(5A)	2.634 (2)	C(4A)–C(5A)	1.418 (2)	C(11A)–C(16A)	1.383 (3)
Zr–C(1B)	2.573 (2)	C(5A)–C(6A)	1.415 (2)	C(12A)–C(13A)	1.385 (3)
Zr–C(2B)	2.507 (2)	C(6A)–C(7A)	1.346 (3)	C(13A)–C(14A)	1.364 (4)
Zr–C(3B)	2.511 (2)	C(7A)–C(8A)	1.410 (3)	C(14A)–C(15A)	1.370 (3)
Zr–C(4B)	2.531 (2)	C(8A)–C(9A)	1.348 (3)	C(15A)–C(16A)	1.390 (3)
Zr–C(5B)	2.624 (2)	C(1B)–C(2B)	1.427 (2)	C(10B)–C(11B)	1.489 (2)
Zr–C(10A)	2.298 (2)	C(1B)–C(5B)	1.431 (2)	C(11B)–C(12B)	1.390 (3)
Zr–C(10B)	2.289 (2)	C(1B)–C(9B)	1.406 (3)	C(11B)–C(16B)	1.394 (3)
F(1A)–C(6A)	1.352 (2)	C(2B)–C(3B)	1.401 (3)	C(12B)–C(13B)	1.374 (3)
F(2A)–C(9A)	1.359 (2)	C(3B)–C(4B)	1.396 (3)	C(13B)–C(14B)	1.365 (4)
F(1B)–C(6B)	1.356 (2)	C(4B)–C(5B)	1.418 (3)	C(14B)–C(15B)	1.370 (4)
F(2B)–C(9B)	1.356 (2)	C(5B)–C(6B)	1.415 (3)	C(15B)–C(16B)	1.388 (3)
C(1A)–C(2A)	1.426 (2)	C(6B)–C(7B)	1.343 (3)		
cp(A)–Zr–cp(B)	129.95 (7)			cp(A)–Zr–C(10A)	104.7 (1)
C(10A)–Zr–C(10B)	95.44 (7)			cp(B)–Zr–C(10A)	108.9 (1)
Zr–C(10A)–C(11A)	121.1 (1)			cp(A)–Zr–C(10B)	104.4 (1)
Zr–C(10B)–C(11B)	126.8 (1)			cp(B)–Zr–C(10B)	108.1 (1)

[a] Numbers in parentheses are estimated standard deviations. cp(A) and cp(B) denote the centroids of the C_5 rings.

Table III. Ethylene Polymerization with $(\eta^5\text{-}C_9H_7)_2ZrX_2$/Poly(methylaluminoxane) Systems

X, [Zr], mol/L	Al/Zr	$p(C_2H_4)$, bar	T, °C	productivity, g PE/(g Zr·bar·h)	$10^{-5}M_n$	M_w/M_n	lit.
Bz, 3.1×10^{-5}	500	0.28	34	3.6×10^4	3.10	2.8	this paper
Cl, 1×10^{-7}	150000	5.00	60	6.8×10^5	6.04	2.2	29
CH_3, 3×10^{-7}	14000	3.04	50	7.1×10^5	3.95	2.2	10

Table IV. Ethylene Polymerization with $(\eta^5\text{-}4,7\text{-}X_2C_9H_5)_2Zr(CH_2C_6H_5)_2$/Poly(methylaluminoxane) Catalytic Systems[a]

X	productivity, g PE/(g Zr·bar·h)	M_n	M_w/M_n
H	4.3×10^4	320 000	2.73
CH_3	4.0×10^4	310 000	3.00
F	1.8×10^4	88 000	2.93
CH_3O	2.3×10^3	29 000	4.81

[a] Experimental conditions: see Experimental Section.

with different pertinent angles (cp(A)–Zr–cp(B) 120.8 (5)° and C_{Me}–Zr–C'_{Me} 96.9 (3)°) due to an increased steric crowding in **25**. The Zr–C bond distances (2.298 (2) and 2.289 (2) Å for benzyl A and B, respectively) compare well with those observed in other benzylzirconium complexes (see for instance ref 23). The Zr–C_α bonds are almost of the σ-type, as suggested by the values of the Zr–C_α–C_{ipso} angles (121.1 (1)° and 126.8 (1)°, ligands A and B, respectively) and by the absence of Zr···C_{ipso} significant interactions ($d_{Zr\cdots C_{ipso}} > 3.3$ Å). The other bond parameters within the benzyl groups are normal. The two 4,7-$F_2C_9H_5$ ligands are η^5-coordinated with mean Zr–C bond lengths of 2.559 and 2.549 Å, for A and B, respectively, in agreement with the value of 2.548 Å found in $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$ and with those usually found in other pseudotetrahedral $(\eta^5\text{-}C_9H_7)_2ZrR_2$ compounds. The Zr–C interactions involving the bridgehead carbon atoms are longer than the other carbon–metal bonds within the η^5-moiety, thus indicating an incipient $\eta^5 \rightarrow \eta^3$ distorsion. This feature is normally observed for η^5-indenyl complexes.[24] Its relevance in the substitution process kinetics on such complexes has been evidenced by Basolo.[25] The indenyl ligands of compound **25** show a folding of the allylic plane with respect to the least-squares plane of the six-membered ring (the pertinent dihedral angle being 7.3 and 7.6° for A and B, respectively). Furthermore, a slippage of the coordinated rings (Δ 0.19 and 0.12 Å for A and B, respectively) as defined by Faller et al.[24] is observed. The pattern of short and long C–C distances is consistent with a prevalence of the resonance structure depicted in Chart I, A. We have retrieved from the Cambridge Structural Database all the structurally characterized η^5-indenyl–metal complexes with $\sigma(d_{C-C}) \leq 0.005$ Å (compare Chart I, B, and for more details Table 6 in the supplementary material). From these data, it appears that the preference for the resonance structure of Chart I, A, is a general feature while the folding and the slippage have been observed in all cases but one. The data retrieved from the literature are representative of the geometry of the unsubstituted indenyl ligands. Therefore, they can be used to evidence the stereochemical effects of fluorine substitution (Chart I, C versus B). The C(8)–C(9) and C(1)–C(2) bond distances (and their equivalent C(6)–C(7) and C-(4)–C(5)) are shorter in the fluorine derivative by ca. 0.025 Å (ca. 8 σ). A larger statistical significance is found in the variations of the C–C–C angles at the ipso and ortho carbons of the six-membered rings which change by +3.6 and −1.6°, respectively. This is in good agreement with the prediction of +3.0 and −1.5°, obtained from Domenicano's rules. By taking into account the cooperative effect of the two fluorine atoms, these rules allow us to foresee the stereochemical effects of different substituents on benzene[26] (each of two fluorine atoms should affect the C–C–C angles at the ipso, ortho, meta, and para carbons by a shift of +3.4, −2.0, +0.5, and −0.4°, respectively).[27]

Ethylene Polymerization. The above-presented catalyst precursors together with poly(methylaluminoxane) as cocatalyst form highly active catalytic systems for the

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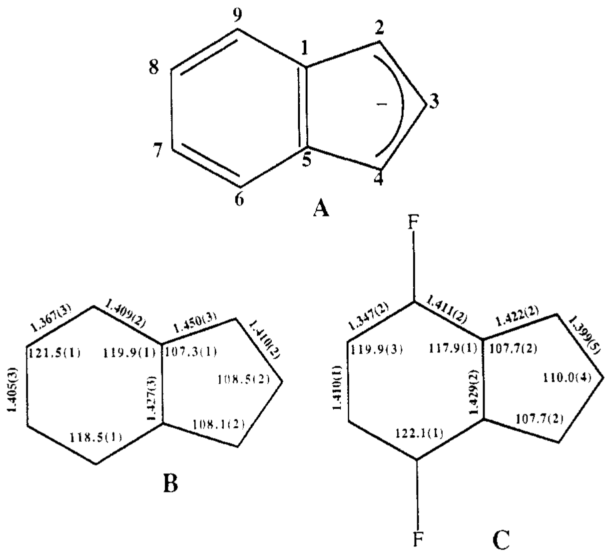
Chart I



polymerization of ethylene. Comparing the results obtained with $(\eta^5\text{-}C_9H_7)_2Zr(CH_2C_6H_5)_2$ with the data reported in the literature, lower productivities and lower average molecular weights may be observed (Table III). These differences are not only due to the different Zr(IV) derivatives used but mainly to the different reaction conditions and catalyst concentrations. In Table IV, a comparison of the substituted and the nonsubstituted catalysts in the polymerization of ethylene is presented. Each polymerization was repeated at least two times to check the reproducibility of the results. To guarantee an efficient temperature control especially during the first moments of the polymerization, low monomer pressures were used (0.28 ± 0.01 bar). Under these conditions, with a zirconium concentration of 3×10^{-5} mol/L, the temperature excursions can be limited to 1 °C. Poly(methylaluminoxane) from the same preparative batch was used for the polymerizations.

The results show a considerable influence of the electronic nature of the substituents on the behavior of the catalytic systems. Electron-withdrawing groups, like fluorine, lower both the productivity and the average molecular weight. No considerable variation of the productivity and the average molecular weight resulted from the substitution with methyl groups. In the case of $(\eta^5\text{-}4,7\text{-}(MeO)_2C_9H_5)_2Zr(CH_2C_6H_5)_2$, the situation is complicated by a coordination of the $[Al(CH_3)O]$ units of the cocatalyst to the methoxy groups of the catalyst precursor. This interaction was confirmed by ^1H NMR experiments. The coordination causes an enhancement of the inductive effect of the methoxy groups whereas the resonance effect is suppressed. Both the methoxy and fluorine substituents behave therefore as electron-withdrawing groups, leading to lower productivities and lower average molecular weights with these catalysts than with the nonsubstituted complexes.

The values for the productivity and the number-average molecular weight allow us to make a rough estimation of the polymerization rate and the ratio of the polymerization rate over the chain termination rate. The comparison of the results for the substituted catalysts with the unsubstituted system **22** shows that by substitution with fluorine groups the polymerization rate is lowered; under the assumption that both catalyst precursors give the same number of active centers, the chain termination rate seems not influenced considerably. In the case of the methoxy-substituted complex **24**, steric effects due to the coordination of the cocatalyst and/or a combined influence of electronic and steric effect may cause the decrease in the polymerization rate. In the dimethyl system **23**, the electronic and steric effects of the methyl groups either may be compensating each other or may be too small to be observed. However, speculations about the possible mechanistic implications of the reported results appear at the moment unwarranted due to the lack of knowledge on the possible effects of the substitution on the different reaction steps leading to the formation of the polymers.

Narrow molecular weight distributions (2.7–3.0) were found by GPC measurements, with the exception of the dimethoxy system **24**. The cocatalyst consists of a mixture of poly(methylaluminoxane) chains with different lengths and a certain amount of trimethylaluminum. Because of the complex nature of the cocatalyst in the $\{\eta^5\text{-}4,7\text{-}(MeO)_2C_9H_5\}_2Zr(CH_2C_6H_5)_2/MAO$ system (vide infra), various complexation equilibria can be expected, leading to different types of catalytic centers and thus to a broader molecular weight distribution.

Conclusions

In this paper, the nature of new substituted bis(indenyl)zirconium(IV)–X_2 catalyst precursors has been investigated. A considerable influence especially of electron-withdrawing groups on the behavior of the catalytic species was observed. These results are in keeping with the proposed polar nature of the active catalytic species, which in our opinion can be described as tight ion couple or as containing a strongly polarized [Zr]–X–[Al] species. The effect of substituents on the propylene polymerization and on the rate profile in ethylene polymerization will be discussed elsewhere.

Experimental Section

General Aspects. An inert atmosphere was used for the synthesis and purification of substituted indenes only when specified in the experimental part.

All manipulations for the synthesis and purification of the zirconium complexes as well as the preparation of the poly(methylaluminoxanes) and the ethylene polymerizations were carried out under N_2 or Ar atmosphere in dried solvents and vessels by using standard Schlenk techniques. The solvents were freshly distilled under N_2 from drying agents as follows: Na/K alloy for tetrahydrofuran, toluene, 1,2-dimethoxyethane (DMOE), and *n*-hexane; $LiAlH_4$ for diethyl ether and *n*-pentane; P_2O_5 for dichloromethane. The deuterated solvents were dried over activated molecular sieves prior to use. Starting materials were Fluka products.

The NMR spectra were recorded on a Bruker AM 300 WP or on a Bruker WH 90; the chemical shifts were referred to the usual standards. The microanalysis was performed at the microanalytical laboratories of the ETH-Zürich and/or at Dornis und Kolbe (Muelheim a.d.R.).

Synthesis of Substituted Indenes. 1-(2,5-Dimethylphenyl)-3-chloropropanone (1).[15b] The reaction was carried out under N_2. To a suspension of $AlCl_3$ (60 g, 0.45 mol) in CS_2 (125 mL) was added a solution of 1,4-dimethylbenzene (25 mL, 0.20 mol) and 3-chloropropionyl chloride (20 mL, 0.21 mol) in CS_2 (25 mL) dropwise under magnetical stirring over 45 min. The color changed from green to yellow to red, and the evolution of hydrogen chloride was observed. The suspension was stirred for 3 h at room temperature and then poured on ice (500 g). The mixture was extracted with Et_2O (3×), and the combined organic phases were washed with an aqueous solution of $NaHCO_3$ and with water, dried, filtered, and evaporated. Forty grams of yellow oil was obtained, which was used without further purification for the following reaction.

4,7-Dimethylindanone (2).[15a] To concentrated sulfuric acid (220 mL, 2.64 mol) was added the above reaction product **1** dropwise over 15 min under N_2 and with magnetic stirring at room temperature. The color changed from yellow to red to green, and evolution of hydrogen chloride was observed. The solution was heated and stirred at 80 °C for 1 h. The mixture was cooled to room temperature, poured on ice (500 g), and extracted with Et_2O (3×). The combined organic phases were washed with an aqueous solution of $NaHCO_3$ and with water and dried. The solvent was removed by vacuum distillation. The crystallization of the crude product from methanol yielded 72% (23 g, 0.14 mol) of **2**; mp 77 °C. MS: *m/e* 160 (M^+).

4,7-Dimethylindanol (3).[15d] The reaction was carried out under N_2 in dried vessels and solvents. To a suspension of $LiAlH_4$ (2.00 g, 53 mmol) in Et_2O (350 mL) was added a solution of **2** (22 g, 0.138 mol) in Et_2O (100 mL) dropwise under magnetical stirring while the temperature was maintained at 25 °C. After the addition, the mixture was heated at reflux temperature for 1 h. The suspension was hydrolyzed at 0 °C by addition of (1) H_2O (2 mL), (2) a 15% aqueous solution of NaOH (2 mL), and (3) H_2O (3.6 mL). After filtration, the solution was dried and evaporated. The crystallization of the product from petroleum ether yielded 85% (19 g, 0.117 mol) of white **3**; mp 67–68 °C. MS: *m/e* 144 ($M^+ - H_2O$).

4,7-Dimethylindene (4).[15d] To a solution of **3** (19.00 g, 0.12 mol) in benzene (150 mL) was added a few crystals of *p*-toluenesulfonic acid. The solution was heated to reflux temperature and stirred until 2 mL of water had been separated. The solution was washed with aqueous $NaHCO_3$, dried, filtered, and evaporated. The remaining liquid was purified by distillation (8 mmHg, 93–97 °C), yielding 71% of **4** (12 g, 84 mmol). MS: *m/e* 144 (M^+). ^1H NMR (90 MHz, ppm in $CDCl_3$): δ 7.2–6.8 (m, 3 H), 6.5 (dt, 1 H), 3.2 (t, 2 h), 2.4 (s, 3 H), 2.3 (s, 3 H).

3-(2,5-Dimethoxyphenyl)propionic Acid (5).[16a] To a solution of *trans*-3-(2,5-dimethoxyphenyl)propenic acid (25 g, 0.12 mol) in EtOH (700 mL) was added PtO_2 (420 mg). The reaction vessel was set under hydrogen atmosphere and connected with a gas buret. The mixture was stirred at room temperature until no more hydrogen takeup was observed (4 h). The catalyst was removed by filtration and the solution evaporated. The crystallization of the reaction product from benzene yielded **5** (75%) as white crystals; mp 66 °C. MS: *m/e* 210 (M^+). ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 12.00–11.30 (br s, 1 H), 6.80–6.68 (m, 3 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 2.91 (m, J = 7 Hz, 2 H), 2.65 (m, J = 7 Hz, 2 H).

4,7-Dimethoxyindanone (6).[16a] To poly(phosphoric acid) (38 g) was added **5** (1.22 g, 5.8 mmol). The viscous mixture was heated to 60 °C and stirred mechanically for 30 min. The color changed from yellow to dark brown. The reaction mixture was cooled and poured on ice (400 g). The obtained yellow suspension was extracted with Et_2O (3 × 10 mL) and neutralized with a saturated solution of $NaHCO_3$. The organic solution was dried, filtered, and evaporated. The recrystallization of the reaction product gave **6** as small white needles. From the basic aqueous solution, a small amount of **5** could be precipitated on acidification with HCl. A yield of 50% was calculated for the reaction. MS: *m/e* 192 (M^+). ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 6.99 (d, 1 H), 6.73 (d, 1 H), 3.90 (s, 3 H), 3.85 (s, 3 H), 2.97 (m, 2 H), 2.67 (m, 2 H).

4,7-Dimethoxyindanol (7).[16a] The reaction was carried out under N_2 in dried vessels and solvents. Under temperature control to a stirred suspension of $LiAlH_4$ (2.1 g, 55 mmol) in Et_2O (100 mL) was added a solution of **6** (9.00 g, 64 mmol) in Et_2O (500 mL)/THF (400 mL). The solution was stirred for 2 h at room temperature and then hydrolyzed by addition of (1) H_2O (2.1 g), (2) 15% aqueous solution of NaOH (2.1 g), and (3) H_2O (6.3 g). The suspension was filtered, and the solution was dried, filtered again, and evaporated. The reaction product was recrystallized from Et_2O/*n*-hexane, yielding 85% (10.56 g, 54 mmol) **7** as white needles. MS: *m/e* 194 (M^+). ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 6.66 (dd, 2 H), 5.46 (dd, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.02 (m, 1 H), 2.74 (m, 1 H), 2.44 (m, 1 H), 2.01 (m, 1 H).

4,7-Dimethoxyindene (8).[16c] A solution of **7** (7.87 g, 40 mmol) and a few crystals of *p*-toluenesulfonic acid in benzene (250 mL) was prepared under N_2. The solution was heated and stirred at reflux temperature for 30 min. The eliminated water was distilled from the reaction mixture as soon as it formed. The solution was washed with aqueous $NaHCO_3$, with water, dried, and evaporated. The obtained yellow solid was purified by chromatography on silica gel with a mixture of *n*-hexane/Et_2O (from 7:1 to 4:6) as eluent, yielding 57% (4.03 g, 22.9 mmol) **8** as fine white needles; mp 58–59 °C. MS: *m/e* 176 (M^+). ^1H NMR (300 MHz, ppm in C_6D_6): δ 7.27 (dt, 1 H), 6.58 (d, 1 H), 6.49 (d, 1 H), 6.21 (dt, 1 H), 3.48 (s, 3 H), 3.47 (s, 3 H), 3.36 (m, 2 H). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): 150 (1 C), 148.68 (1 C), 135.77 (1 C), 133.10 (1 C), 133.01 (1 CH), 128.95 (1 CH), 109.60 (1 CH), 107.84 (1 CH), 55.55 (1 CH_3), 55.17 (1 CH_3), 37.65 (1 CH_2).

***trans*-3-(2,5-Difluorophenyl)propenoic Acid (9).** A solution of malonic acid (3.16 g, 30.0 mmol), pyridine (0.75 mL, 9 mmol), and 2,5-difluorobenzaldehyde (3 mL, 28.0 mmol) in dry EtOH (12 mL) was prepared. The solution was heated and stirred for 18 h at reflux temperature. The mixture was poured on ice (200 g), and the formation of a crystalline white solid was observed. Because of the good solubility of **9** in EtOH, the carboxylic acid was treated with $NaHCO_3$ to give the corresponding sodium carboxylate. The basic aqueous solution was extracted with CH_2Cl_2 to remove the pyridine and the byproducts. Treating the aqueous solution with diluted HCl, a white precipitate of **9** formed. The desired product was extracted with CH_2Cl_2 (3×), and the combined organic phases were washed with water, dried, filtered, and evaporated. Crystallization of the reaction product from CH_2Cl_2/*n*-hexane yielded 76% (3.94 g) **9** as white crystals; mp 140 °C. MS: *m/e* 184 (M^+). ^1H NMR (300 MHz, ppm in CD_3OD): δ 7.73 (d, J = 16.2 Hz, 1 H), 7.51–7.44 (m, 1 H), 7.3–7.12 (m, 2 H), 6.58 (d, J = 16.2 Hz, 1 H). ^{19}F NMR (85 MHz, ppm in CD_3OD, ^1H decoupled): δ −120.51 (d, J = 18.3 Hz, 1 F), −123.80 (d, J = 18.5 Hz, 1 F). ^{13}C NMR (75 MHz, ppm in CD_3OD, ^1H decoupled): δ 169.57 (s, 1 C), 161.13 (d, J = 121.6 Hz, 1 C), 157.89 (d, J = 127.6 Hz, 1 C), 137.01 (s, 1 CH), 125.08 (dd, J = 8.3, J = 14.4 Hz, 1 C), 123.46 (d, J = 5.7 Hz, 1 CH), 119.44 (dd, J = 9.0, J = 24.8 Hz, 1 CH), 118.53 (dd, J = 8.7, J = 25.4 Hz, 1 CH), 115.70 (dd, J = 2.9, J = 25.0 Hz, 1 CH).

3-(2,5-Difluorophenyl)propanoic Acid (10). To a solution of **9** (17.56 g, 95 mmol) in EtOH (200 mL) was added PtO_2 (170 mg). The reaction vessel was set under hydrogen atmosphere and connected with a gas buret. The reaction mixture was stirred until the hydrogen takeup ceased (3 h). The catalyst was separated from the solution by filtration, and the solvent was evaporated. The reaction product was recrystallized from CH_2Cl_2/*n*-hexane, giving **10** as colorless needles with quantitative yield; mp 72 °C. MS: *m/e* 186 (M^+). Anal. Calcd for $C_9H_8F_2O$: C, 58.07; H, 4.33; F, 20.16. Found: C, 58.01; H, 4.47; F, 20.16. ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 11.91 (s, 1 H), 7.02–6.83 (m, 3 H), 2.95 (t, J = 7.6 Hz, 2 H), 2.69 (t, J = 7.6 Hz, 2 H). ^{19}F NMR (85 MHz, ppm in $CDCl_3$, ^1H decoupled): δ −119.00 (d, J = 18.7 Hz, 1 F), −124.33 (d, J = 18.5 Hz, 1 F). ^{13}C NMR (75 MHz, ppm in $CDCl_3$, ^1H decoupled): δ 179.11 (s, 1 C), 159.53 (dd, J = 112.0, J = 2.4 Hz, 1 C), 156.33 (dd, J = 111.2, J = 2.4 Hz, 1 C), 128.75 (dd, J = 18.3, J = 7.7 Hz, 1 C), 117.02 (dd, J = 24.0, J = 5.1 Hz, 1 CH), 116.36 (dd, J = 25.0, J = 8.8 Hz, 1 CH), 114.56 (dd, J = 24.0, J = 8.5 Hz, 1 CH), 33.87 (d, J = 1.6 Hz, 1 CH_2), 24.28 (q, J = 2.4, J = 1.2 Hz, 1 CH_2).

4,7-Difluoroindanone (11). The reactions were carried out under N_2 in dried vessels. To **10** (74.19 g, 0.39 mol) was added thionyl chloride (48 mL, 0.65 mol). The mixture was heated and stirred at 70 °C until gas evolution ceased (40 min). The excess $SOCl_2$ was distilled off, and the remaining yellow liquid was used for the following reaction without further purification (m/e 204 (M^+)). A solution of this compound (2.04 g, 10 mmol) in CS_2 (10 mL) was added dropwise under vigorous magnetical stirring to a solution of $AlBr_3$ (5 g, 18 mmol) in CS_2 (20 mL). The orange mixture was stirred until no more reagent could be detected by TLC (45 min). The reaction mixture was poured on ice (200 g) and extracted with Et_2O (3×). The combined organic phases were neutralized with $NaHCO_3$, dried, filtered, and evaporated. The crude product was crystallized from CH_2Cl_2/*n*-pentane, yielding 68% (1.14 g, 6.8 mmol) **11** as small white needles; mp 118 °C. MS: *m/e* 168 (M^+). Anal. Calcd for $C_9H_6F_2O$: C, 64.20; H, 3.60. Found: C, 63.87; H, 3.63. ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 7.02–6.94 (m, 2 H), 3.15 (m, J = 5.8 Hz, 2 H), 2.75 (m, J = 6.1 Hz, 2 H). ^{19}F NMR (85 MHz, ppm in $CDCl_3$): δ −120.55 (dq, J = 23.8, J = 8.1, J = 3.8 Hz, 1 F), −124.39 (dq, J = 23.8, J = 7.6, J = 3.4 Hz, 1 F). ^{13}C NMR (75 MHz, ppm in $CDCl_3$, ^1H decoupled): δ 201.49 (s, 1 C), 157.04 (dd, J = 66.6, J = 2.7 Hz, 1 C), 153.68 (dd, J = 80.3, J = 2.6 Hz, 1 C), 142.06 (dd, J = 22.0, J = 2.8 Hz, 1 C), 126.45 (dd, J = 15.4, J = 4.7 Hz, 1 C), 122.14 (dd, J = 23.2, J = 8.4 Hz, 1 CH), 115.78 (dd, J = 22.6, J = 6.7 Hz, 1 CH), 36.47 (s, 1 CH_2), 21.72 (s, 1 CH_2).

4,7-Difluoroindanol (12). The reaction was carried out under N_2 in dried vessels and solvents. A solution of 11 (5 g, 30 mmol) in *n*-hexane (200 mL)/benzene (100 mL) was prepared and cooled to −10 °C. Under magnetical stirring, 70 mL of a DIBAH solution (20% in *n*-hexane) was added dropwise via syringe over 45 min. The reaction mixture was stirred for 45 min and then hydrolyzed. After filtration, the organic phase was separated and the aqueous phase extracted with diethyl ether (2×). The combined organic phases were washed with water, dried, filtered, and evaporated. The obtained light yellow liquid was purified by chromatography on silica gel with a mixture of Et_2O and petroleum ether (5/4) as eluent. **12** was obtained in 80% (4.08 g, 24 mmol) yield. MS: *m/e* 170 (M^+). Anal. Calcd for $C_9H_8F_2O$: C, 63.53; H, 4.74. Found: C, 63.29; H, 4.85. ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 6.94–6.80 (m, 2 H), 5.47 (dd, J = 7.0, J = 3.6 Hz, 1 H), 3.18–3.07 (m, 1 H), 2.91–2.80 (m, 1 H), 2.52–2.38 (m, 2 H), 2.15–2.03 (m, 1 H). ^{19}F NMR (85 MHz, ppm in $CDCl_3$, ^1H decoupled): δ −123.53 (d, J = 22.7 Hz, 1 F), −126.34 (d, J = 22.7 Hz, 1 F). ^{13}C NMR (75 MHz, ppm in $CDCl_3$, ^1H decoupled): δ 157.03 (d, J = 24.8 Hz, 1 C), 153.80 (d, J = 23.8 Hz, 1 C), 133.58 (dd, J = 19.1, J = 5.6 Hz, 1 C), 132.56 (dd, J = 20.6, J = 4.9 Hz, 1 C), 116.44 (dd, J = 23.7, J = 7.9 Hz, 1 CH), 114.83 (dd, J = 23.1, J = 6.9 Hz, 1 CH), 73.70 (s, 1 CH), 34.93 (s, 1 CH_2), 26.75 (s, 1 CH_2).

4,7-Difluoroindene (13). $KHSO_4$ (670 mg, 5 mmol) and hydroquinone (10 mg) were introduced into a two-neck flask connected with a microdistillation apparatus and a dropping funnel, charged with of **12** (3.15 g, 18 mmol). The pressure in the apparatus was lowered to 120 mmHg, and the temperature rose to 120 °C. Under magnetical stirring, 20% **12** was added to the $KHSO_4$ in a few minutes, while the pressure was lowered to 30 mmHg. The mixture of **13** and H_2O was distilled under these conditions at 50–75 °C. This procedure was repeated, until the whole reagent had been consumed. Under careful temperature and pressure control, pure **13** was obtained with a yield of 50%. MS: *m/e* 152 (M^+). ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 6.98–6.88 (m, 2 H), 6.86–6.78 (m, 1 H), 6.56 (dt, J = 5.5, J = 1.9 Hz, 1 H), 3.48 (t, J = 1.8 Hz, 2 H). ^{19}F NMR (85 MHz, ppm in $CDCl_3$, ^1H decoupled): δ −124.86 (d, J = 22.3 Hz, 1 F), −127.62 (d, J = 22.3 Hz, 1 F). ^{13}C NMR (75 MHz, ppm in $CDCl_3$, ^1H decoupled): δ 155.38 (dd, J = 193.5, J = 2.2 Hz, 1 C), 152.17 (dd, J = 195.6, J = 2.2 Hz, 1 C), 134.58 (s, 1 CH), 134.22 (dd, J = 19.1, J = 6.7 Hz, 1 C), 131.01 (dd, J = 21.0, J = 6.1 Hz, 1 C), 126.84 (t, J = 1.8 Hz, 1 CH), 114.54 (dd, J = 23.2, J = 7.8 Hz, 1 CH), 112.52 (dd, J = 24.0, J = 7.4 Hz, 1 CH), 36.45 (s, 1 CH_2).

Synthesis of Unsubstituted and Substituted Bis(indenyl)zirconium(IV) Derivatives. NaInd (14). To metallic sodium in small pieces (9 g, 0.39 mol) were added freshly distilled indene (35 mL, 0.30 mol) and THF (50 mL) under magnetical stirring. The reaction mixture was heated for 18 h at reflux temperature and then cooled to room temperature. The violet solution was separated from the excess of sodium via cannula and used as soon as possible.

Na[4,7-Me_2Ind] (15). The procedure of **14** was used except that **4** (3.78 g, 26 mmol) was reacted with sodium (1.7 g, 74 mmol) in THF (25 mL). The mixture was stirred for 13 h at reflux temperature and immediately used.

Li[4,7-$(MeO)_2$Ind] (16). A hexane solution (2.8 mL) of butyllithium (1.68 M) was added dropwise via syringe to a solution of **8** (0.8 g, 4.5 mmol) in THF (8 mL). The mixture was stirred at room temperature for 18 h and immediately used.

Na[4,7-F_2Ind] (17). The procedure of **14** was used except that **13** (8.3 g, 55 mmol) was reacted with sodium (2 g, 87 mmol) in DMOE (10 mL). The mixture was stirred at room temperature for 2 h, and the solution was removed from the excess of Na via cannula and immediately used.

(η^5-Ind)$_2$ZrCl$_2$ (18).[19] To freshly sublimed $ZrCl_4$ (14.5 g, 62 mmol) was added precooled THF (100 mL) dropwise at −78 °C via a cannula. Under magnetical stirring, the mixture was allowed to warm to room temperature and stirred for 1 h. The gray suspension of $ZrCl_4$/THF adduct was treated dropwise with a solution of **14** (17 g, 0.12 mol) in THF (30 mL). The temperature was controlled with a water bath. On addition of the second equivalent of **14**, the formation of a yellow precipitate was observed. After 1 h of stirring at room temperature, the mixture was cooled to 0 °C, and for 2 min HCl gas, dried over H_2SO_4, was bubbled into the suspension. Subsequently two-thirds of the solvent was removed by evaporation, and the precipitation of the complex was completed by addition of Et_2O (200 mL). The fine yellow precipitate was separated quickly from the solution by centrifugation and dried under vacuum. The crude product was sublimed at 200–220 °C at 0.03 mmHg. **18** could be obtained as fine yellow needles with 35% yield (8.53 g). MS: *m/e* 390 (M^+). Anal. Calcd for $C_{18}H_{14}Cl_2Zr$: C, 55.09; H, 3.60; Cl, 18.07. Found: C, 54.61; H, 3.33; Cl, 17.78. ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 7.6 (m, 4 H), 7.4–7.15 (m, 4 H), 6.45 (t, J = 3 Hz, 2 H), 6.2 (d, J = 3 Hz, 4 H).

[η^5-4,7-Me_2Ind]$_2$ZrCl$_2$ (19). Following the procedure of **18**, the $ZrCl_4$/ether adduct was prepared with freshly sublimed $ZrCl_4$ (3.03 g, 13 mmol) and THF (100 mL). To the vigorously stirred suspension was added a solution of **15** (4.32 g, 26 mmol) in THF (30 mL) dropwise over 20 min. The formation of a yellow precipitate was observed. The mixture was stirred for 2 h at room temperature and then concentrated to one-fourth of the volume. The precipitation of the complex was completed by addition of Et_2O, and the solid was separated from the solution by centrifugation. The crude product was washed quickly with small volumes of H_2O/HCl, EtOH, and Et_2O. The crystallization from CH_2Cl_2/*n*-hexane at −25 °C yielded **19** as small yellow needles (3.8 g, 65%). MS: *m/e* 446 (M^+). Anal. Calcd for $C_{22}H_{22}Cl_2Zr$: C, 58.91; H, 4.94; Cl, 15.81. Found: C, 58.17; H, 4.78; Cl, 15.58. ^1H NMR (300 MHz, ppm in $CDCl_3$): δ 6.97 (s, 4 H), 6.49 (t, J = 3 Hz, 2 H), 6.25 (d, J = 3 Hz, 4 H), 2.44 (s, 12 H). ^{13}C NMR (75 MHz, ppm in $CDCl_3$, ^1H decoupled): δ 132.4 (4 C), 128.4 (4 C), 126.2 (4 CH), 119.0 (2 CH), 103.7 (4 CH), 19.1 (4 CH_3).

[η^5-4,7-$(MeO)_2$Ind]$_2$ZrCl$_2$ (20). Following the procedure of **18**, the $ZrCl_4$/ether adduct was prepared with freshly sublimed $ZrCl_4$ (510 mg, 2.2 mmol) in THF (20 mL). To the vigorously stirred suspension was added a solution of **16** (4.5 mmol) in THF (8 mL) dropwise. The color of the mixture turned immediately to intense yellow, and after 10 min, the formation of a fine precipitate was observed. The reaction mixture was stirred at room temperature for 3 h, and subsequently, the solvent was evaporated. The crystallization of the yellow–orange residue from toluene/*n*-hexane yielded **20** (40%, 430 mg) as fine yellow needles. Through ^1H NMR spectroscopy with 1,2-dibromoethane as the internal standard, a chemical purity of 97% was established. Anal. Calcd for $C_{22}H_{22}Cl_2O_4Zr$: C, 51.56; H, 4.33; Cl, 13.83. Found: C, 51.28; H, 4.35; Cl, 14.61. ^1H NMR (300 MHz, ppm in C_6D_6): δ 6.49 (d, J = 3.3 Hz, 4 H), 6.30 (t, J = 3.3 Hz, 2 H), 6.11 (s, 4 H), 3.51 (s, 12 H). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): δ 149.7 (4 C), 122.3 (4 C), 118.9 (2 CH), 103.4 (4 CH), 101.8 (4 CH), 55.1 (4 CH_3).

[η^5-4,7-F_2Ind]$_2$ZrCl$_2$ (21). Following the procedure of **18**, the $ZrCl_4$/ether adduct was prepared with freshly sublimed $ZrCl_4$ (6.00 g, 26 mmol) and DMOE (100 mL). To the resulting homogeneous solution was added **17** (9.57 g, 55 mmol) in DMOE (30 mL) dropwise over 30 min. The formation of a yellow precipitate was observed. The suspension was stirred for 2 h at room temperature and then filtered, washed with 20 mL of cold DMOE, and dried under vacuum. The crude product could not be successfully purified by crystallization or sublimation. By ^1H NMR spectroscopy with 1,2-dibromoethane as the internal standard, a yield of at least 45% could be established for the reaction. MS: *m/e* 462 (M^+). ^1H NMR (300 MHz, ppm in C_6D_6): δ 6.21 (t, J = 7 Hz, 4 H), 6.03 (t, J = 4 Hz, 2 H), 5.92 (m, 4 H). ^{19}F NMR (85 MHz, ppm in C_6D_6, ^1H decoupled): δ −118.41 (s, 4 F).

[η^5-Ind]$_2$ZrBz$_2$ (22).[20] To a suspension of **18** (500 mg, 1.3 mmol) in Et_2O (40 mL) was added a 0.72 M solution of benzylmagnesium chloride (8 mL) in Et_2O dropwise at room temperature via syringe. The mixture was stirred for 2 days, and subsequently, the solvent was evaporated. The crystallization of the remaining oil from toluene/*n*-hexane at −25 °C yielded **22** (50%, 320 mg) as fine yellow needles. Anal. Calcd for $C_{32}H_{28}Zr$: C, 76.29; H, 5.60. Found: C, 76.06; H, 5.62. ^1H NMR (300 MHz, ppm in C_6D_6): δ 7.24 (t, 4 H), 7.03 (m, 4 H), 6.94 (t, 2 H), 6.9–6.8 (m, 8 H), 5.63 (d, J = 3.4 Hz, 4 H), 5.52 (t, J = 3.4 Hz, 2 H), 0.99 (s, 4 H). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): δ 152.0 (4 C), 128.5 (4 CH), 126.4 (4 CH), 125.3 (4 CH), 152.2 (4 CH), 125.1 (2 C), 121.4 (2 CH), 119.1 (2 CH), 103.2 (4 CH), 66.0 (2 CH_2).

[η^5-4,7-Me_2Ind]$_2$ZrBz$_2$ (23). To a suspension of **19** (1.5 g, 3.34 mmol) in Et_2O (120 mL) was added 23 mL of a 0.72 M solution

Table V. Crystal Data for $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$[a]

formula	$C_{32}H_{24}F_4Zr$
fw, amu	575.8
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	10.786 (1)
b, Å	11.084 (2)
c, Å	21.602 (2)
β, deg	98.30 (1)
V, Å^3	2555.5
Z, ρ(calc), g cm^{-3}	4, 1.496
$F(000)$	1168
radiation (graphite monochrator)	Mo Kα (λ = 0.71073 Å)
diffractometer	CAD4 Enraf-Nonius
μ(Mo Kα), cm^{-1}	4.69
2θ range, deg	$6 < 2\theta \leq 50$
scan method	ω
scan interval, deg	$1.1 + 0.347 \tan \theta$
scan speed, deg min^{-1}	1.6
max time for 1 refln measr, s	60
collected octants	$\pm hkl$
no. of data collected (at room temp.)	4460
no. of data used ($I > 3\sigma(I)$)	3679
no. of variable parameters	431
crystal decay	no
no. azimut reflns for abs corr	3
max–min transmission factor	1.00–0.98
crystal size, mm	0.28 × 0.35 × 0.44
weighting fudge p factor	0.035
ESD	1.39
R	0.0220
R_w	0.0295
max peak in final diff Fourier, e Å^{-3}	0.39

[a] ESD = $(\sum w(|F_o| - k|F_c|)^2/(N_{obs} - N_{var}))^{1/2}$. $w = 4|F_o|^2/\sigma^2(|F_o|^2)$ where $\sigma(|F_o|^2) = (\sigma^2(I) + (pI)^2)^{1/2}/L_p$. $R = \sum||F_o| - k|F_c||/\sum|F_o|$. $R_w = (\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2)^{1/2}$.

of benzylmagnesium chloride in Et_2O (23 mL) dropwise at room temperature via syringe. The mixture was stirred for 3 days, and subsequently, two-thirds of the solvent was evaporated. The yellow–orange solid was separated from the mother liquids by filtration and recrystallized from toluene/hexane at −25 °C, yielding **23** (64%, 1.2 g, 2.1 mmol) as small yellow crystals. Anal. Calcd for $C_{36}H_{38}Zr$: C, 77.23; H, 6.48. Found: C, 77.12; H, 6.54. ^1H NMR (300 MHz, ppm in C_6D_6): δ 7.30–7.20 (m, 4 H), 6.94–6.90 (m, 6 H), 6.66 (s, 4 H), 5.71 (d, J = 3.0 Hz, 4 H), 5.67 (t, J = 3 Hz, 2 H), 2.11 (s, 12 H), 1.11 (s, 4 H). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): δ 152.21 (C), 131.79 (C), 128.56 (CH), 126.46 (C), 126.31 (CH), 124.97 (CH), 121.54 (CH), 116.64 (CH), 103.83 (CH), 65.02 (CH_2), 19.10 (CH_3).

$[\eta^5\text{-}4,7\text{-}(MeO)_2Ind]_2ZrBz_2$ (24). To a suspension of **20** (600 mg, 1.17 mmol) in Et_2O (70 mL) was added a 0.72 M solution of benzylmagnesium chloride in Et_2O (8 mL) dropwise via syringe. The mixture was stirred 3 days at room temperature. During this time, the color changed from yellow to orange. Subsequently two-thirds of the solvent was removed by distillation, and the solid was separated from the mother liquid by filtration. The crude product was recrystallized from toluene/n-hexane at −25 °C, yielding **24** (68%, 500 mg, 0.8 mmol) as fine orange crystals. ^1H NMR (300 MHz, ppm in C_6D_6): δ 7.29–7.23 (m, 4 H), 7.17–7.15 (m, 4 H), 6.93–6.88 (m, 2 H), 6.12 (d, J = 3.3 Hz, 4 H), 6.04 (s, 4 H), 6.00 (t, J = 3.3 Hz, 2 H), 3.40 (s, 12 H), 1.25 (s, 4 H). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): δ 152.44 (2 C), 150.35 (2 C), 128.00 (4 CH), 127.00 (4 CH), 126.42 (4 C), 121.37 (2 CH), 119.69 (2 CH), 116.88 (2 C), 101.93 (4 CH), 101.72 (4 CH), 65.67 (2 CH_2), 54.89 (4 CH_3). NMR analysis indicates a high purity of this material. However, elemental analysis determinations of different laboratories gave erratic results.

$[\eta^5\text{-}4,7\text{-}F_2Ind]_2ZrBz_2$ (25). To a suspension of 3.5 g of crude reaction product containing approximately 1.82 g of **21** (4 mmol) in Et_2O (100 mL) was added a 0.72 M solution of benzylmagnesium chloride in Et_2O (30 mL) dropwise. Immediately a color change from yellow to orange was observed, and after 30 min at room temperature, the mixture was cooled to −5 °C and stirred for 2 days. Subsequently, two-thirds of the solvent was removed by vacuum distillation, and the solid was separated from the mother liquid by filtration. The crystallization of the crude product from toluene/n-hexane yielded **25** (77%) as orange plates. Anal. Calc for $C_{32}H_{24}F_4Zr$: C, 66.76; H, 4.20; F, 13.20. Found: C, 66.68; H, 4.24; F, 13.18. ^1H NMR (300 MHz, ppm in C_6D_6): δ 7.20–7.13 (m, 4 H), 6.89–6.82 (m, 6 H), 6.79–6.76 (m, 4 H), 5.98–5.96 (m, 4 H), 5.91 (t, 2 H), 0.97 (s, 4 H). ^{19}F NMR (85 MHz, ppm in C_6D_6, ^1H decoupled): δ −120.14 (s, 4 F). ^{13}C NMR (75 MHz, ppm in C_6D_6, ^1H decoupled): δ 154.5, (1 C), 150.29 (1 C), 128.5 (1 CH), 126.39 (1 CH), 122.50 (1 CH), 118.67 (1 CH), 117.80 (dd, 1 C), 107.96 (dd, 1 CH), 100.43 (1 CH), 68.8 (1 CH_2).

Ethylene Polymerization. The polymerization reactions were carried out under inert gas in a 2-L glas autoclave equipped with a continuous monomer feed system. The equipment was dried by washing it with a solution of $Al(i\text{-}C_4H_9)_3$ in n-hexane. The toluene was refluxed and distilled first from Na/K alloy and successively from heterogeneous Ziegler–Natta catalyst.

The poly(methylaluminoxanes) were prepared according to literature methods.[28]

Reaction conditions: 510 mL of toluene, [Zr] = 3.1 × 10^{-5}, [Al]/[Zr] = 460–520, [C_2H_4] = 0.032 ± 0.002 mol/L (0.28 ± 0.01 bar), T = 33.5 ± 0.5 °C, t = 60 min. The reaction was stopped by addition of MeOH. Concentrated HCl (2 mL) was added, and the suspension was stirred overnight. After filtration, the polymer was dried under vacuum at 80 °C. The viscosity was measured in tetrahydronaphthalene at 135 °C. The molecular weight distribution was measured by GPC on Lichrosphere columns at 135 °C with 1,2,3-trichlorobenzene.

X-ray Crystal Structure of the Compound $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2C_6H_5)_2$. Crystal data and experimental conditions for compound **25** are reported in Table V. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer at room temperature. A least-squares fit of 25 reflections representative of the entire sphere with θ ranging from 10 to 14° provided the unit cell parameters. Three standard reflections were monitored at regular intervals during the data collection, and no decay was observed. The intensities were collected by using a variable scan range technique with a 25% extension at each end for background determination. Corrections for Lorentz and polarization effects were applied. An empirical absorption correction was performed based on ψ scans (ψ 0–360°, every 10°) of three suitable reflections with χ values close to 90°. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares with the Enraf-Nonius structure determination package (SDP)[30] on a 11/73 PDP computer. After the location of all non-hydrogen atoms, anisotropic thermal factors were assigned to all atoms. The hydrogen atoms were located by difference Fourier maps and subsequently isotropically refined. The refined positional parameters are reported in Table I, and the final values of the conventional agreement indices are given in Table V. The final difference Fourier map showed only small residual peaks (less than 0.4 e Å^{-3}), close to the Zr atom.

Supplementary Material Available: Table 6, listing relevant stereochemical parameters for η^5-indenyl complexes with $\sigma(d_{C-C}) \leq 0.005$ Å (data retrieved from the Cambridge Structural Database), and tables of anisotropic thermal parameters and bond distances and angles (3 pages); a table listing observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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