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Electronic Effects in Ziegler–Natta Polymerization of Propylene and Ethylene Using Soluble Metallocene Catalysts

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The polymerization of ethylene was studied by using a series of $(\eta^5\text{-}5,6\text{-}X_2C_9H_5)_2ZrCl_2$ catalysts (**4a**, X = H; **4b**, X = CH_3; **4d**, X = OCH_3; **4e**, X = Cl), and the polymerization of propylene and ethylene was studied by using a number of the corresponding racemic, ethylene-bridged analogues (**5a**, X = H; **5b**, X = CH_3; **5d**, X = OCH_3). The presence of electron-withdrawing substituents on the indenyl ring in catalysts **4a–e** led to a decrease in catalytic activity for ethylene polymerization and a decrease in polymer molecular weights. Ethylene-bridged catalysts produced lower molecular weight polyethylene than their unbridged counterparts but possessed similar activities toward ethylene. Similar trends in catalytic activity toward propylene were observed by using the ethylene-bridged catalysts, but the molecular weight of polypropylene was not as sensitive to changes in electron density at the metal center. Surprisingly, the stereoselectivity of propylene insertion was sensitive to electronic effects; an increase in electron density at the metal center led to a decrease in the stereoselectivity of propylene insertion.

Introduction

The study of ligand effects on the Ziegler–Natta polymerization of olefins using soluble, chiral catalysts derived from group 4 metallocene compounds and methylaluminoxane cocatalyst has shed a great deal of light on the mechanism of this important process.[1] Much of the work in this area has been concerned with how steric hindrance at the metal center in these compounds influences the catalytic activity and stereoregulating ability of these catalysts.[1,2] In addition, some work has been directed toward the elucidation of how changes in electron density at the metal center influence catalytic activity, polymer molecular weights, and weight distributions.[3] With few exceptions, most of the work in the latter area has failed to address this issue in an unambiguous manner; most of the complexes studied differ in the degree of steric hindrance at the metal center, either by virtue of having different bridging atoms (e.g., Me_2Si versus CH_2CH_2 or CMe_2CMe_2) in these complexes or by having differing degrees of substitution on the cyclopentadienyl rings of these compounds, where the substituents were sufficiently close to the metal center so as to modify the degree of steric hindrance at the metal center.

We set out to prepare metallocene compounds of zirconium that would differ in the amount of electron density at the metal center but would be sterically very similar with respect to coordination and insertion processes occurring at the transition metal. We were interested in answering the following questions: How do changes in electron density affect catalytic activity, polymer molecular weights and weight distributions, and stereoregulating ability of chiral catalysts in propylene polymerization? This paper describes our results, which complement those recently reported by Pino and his co-workers.[4]

Results

General Approach. The target metallocene compounds were all based on the use of 5,6-disubstituted indenes as ligands (Scheme I). It seemed reasonable, especially in the case of bridged metallocenes, that these substituents would be far enough removed from the metal center so as not to introduce steric complications during polymerization.

Moreover, the effects of these substituents on the electron density at a transition-metal center were established by using a simple system—$(\eta^5\text{-}5,6\text{-}X_2\text{indenyl})Rh(I)(CO)_2$ complexes. As will be reported in detail elsewhere,[5a–c] the average CO stretching frequency observed in these complexes[5a,b] is an indirect measure of the amount of electron density at the metal center in these complexes—e.g., there is a positive correlation between the average CO stretching frequencies and the energies of occupied, metal-based orbitals in these sytems.[6] Since we are dealing with d^0 compounds in this study, it is the interaction of filled ligand orbitals with empty, metal-based orbitals that will dominate the bonding. One would expect the donor properties of the indene toward an early-transition-metal

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[1] (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. W. R. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Kaminsky, W. *Angew. Makromol. Chem.* **1986**, *145/146*, 149. (d) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (e) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (f) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *Ibid.* **1987**, *109*, 6544. (g) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 305. (h) Corradini, P.; Guerra, G.; Vacatello, M.; Villani, V. *Gazz. Chim. Ital.* **1988**, *118*, 173. (i) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (j) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzochi, R. *Macromolecules* **1988**, *21*, 617. (k) Kaminsky, W.; Ahlers, A.; Moller-Lindehof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 1216. (l) Rieger, B.; Chien, J. W. C. *Polym. Bull.* **1989**, *21*, 159. (m) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Makromol. Chem.* **1989**, *190*, 1177. (n) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. W. C. *J. Am. Chem. Soc.* **1990**, *112*, 2030.

[2] (a) Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061. (b) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (c) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853.

[3] See, for example: (a) Ewen, J. A.; Haspeslagh, L.; Elder, M. J.; Atwood, J. L. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W.; Sinn, H.; Eds.; Springer-Verlag. Berlin, Heidelberg, 1988; p 281. (b) Chien, J. C. W.; Razavi, A. *J. Polym. Sci., Part A* **1988**, *26*, 2369.

[4] Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

[5] The average CO stretching frequencies (cm^{-1}) for these Rh(I) dicarbonyl complexes are as follows: X = Cl, 2028.5; X = H, 2018.5; X = Me, 2016.0; X = OMe, 2013.0. (a) Kakkar, A. K. Ph.D. Thesis, University of Waterloo, 1990. (b) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Hallinan, N.; Shen, J. K.; Basolo, F., manuscript in preparation. (c) Kakkar, A. K.; Marder, T. B.; Taylor, N. J.; Westcott, S. A.; Ball, J. M.; Lee, I.-M.; Collins, S., manuscript in preparation.

[6] Kakkar, A. K.; Marder, T. B.; Nagy, A.; Frankcon, T. M.; Green, J. C.; manuscript in preparation.

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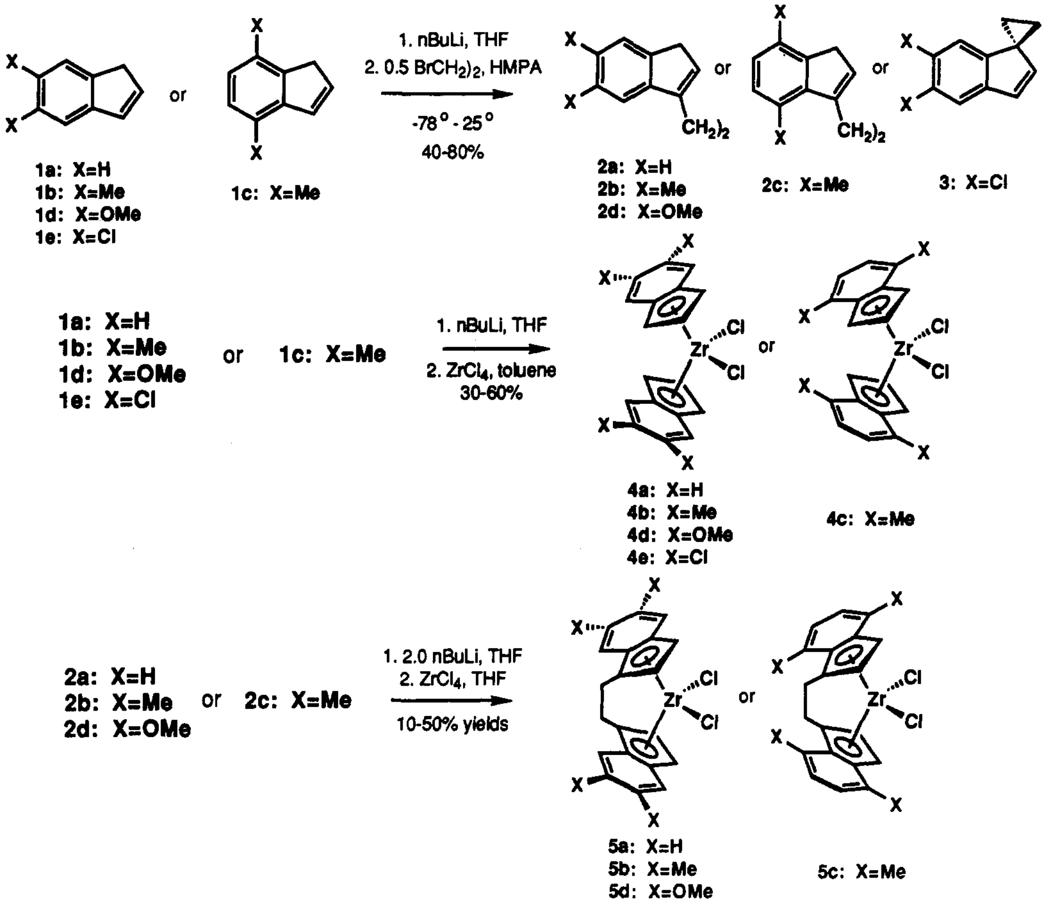
Scheme I



center to mirror those observed in the late-metal system; in fact, one might expect even more pronounced effects in the d^0 case.

Preparation of the Ligands. The indenes (**1a–e**; Scheme I) used in this study, most of which are known compounds,[7] were prepared by standard synthetic methods, which will be described in detail elsewhere.[5c] The ethylene-bridged ligands (**2a–d**) were prepared by reaction of the indenyllithium compounds with 1,2-dibromoethane in THF/HMPA solution.[8c] We were unable to prepare ethylene-bridged compound **2e** by this method or by a variety of other approaches; under all conditions studied the formation of the spiroindene **3** predominated.

Preparation of Metallocenes 4 and 5. The unbridged metallocene compounds (**4a–e**; Scheme I) were prepared by following the basic procedure of Rausch with slight modifications (see Experimental Section).[9] Analytically pure materials could be obtained by sublimation or crystallization. The ethylene-bridged systems (**5a–d**; Scheme I) were obtained in low to moderate yields by the reaction of the dilithio salt of ligands **2a–d** with $ZrCl_4 \cdot 2THF$ in THF or DME solution at room temperature, using a previously described method.[8c] A mixture of racemic and meso stereoisomers was generally produced (racemic:meso ~ 5–6:1); the racemic isomers **5** could be obtained in pure form by extracting the mixture with hot toluene, in which the meso isomers are much more soluble. We have been unable to obtain suitable crystals of compounds **5b–d** for X-ray diffraction studies; the similarity of the spectral characteristics of compounds **5b–d** to that of the parent compound **5a** argues that they can be assigned the racemic structure. Furthermore, the use of these compounds in propylene polymerization provided isotactic polymer (vide infra)—this result is only plausible if the catalyst is derived from a chiral compound.

Table I. Polymerization of Ethylene with Compounds 4a–e and 5a–c[a]

catalyst, (mg)	t, min	yield, g	R_p, kg PE/(mol of Zr × h)	M_n	M_w/M_n
4a (1.36)	20	16.2	14 000	250 000	2.28
4b (1.25)	20	23.4	25 200	278 000	2.08
4c (1.74)	20	17.9	13 800	352 000	2.55
4d (1.19)[b]	180	nil			
4d (1.11)[c]	90	0.4	122	75 000	2.77
4e (0.96)	90	5.0	1 900	127 000	2.38
5a (1.45)	20	11.5	10 000	145 000	2.32
5b (1.32)	20	20.6	22 200	125 000	2.10
5c (1.83)	20	16.8	13 000	205 000	2.34
5d (1.17)[c]	90	0.4	120	70 000	3.08

[a] Conditions: 500 mL of toluene, [Al]:[Zr] = 2000:1, 25 °C, 0.75 bar of C_2H_4 unless otherwise noted. [b] The metallocene was precontacted with MAO prior to injection into a solution of MAO in toluene, presaturated with C_2H_4 (3.0 bar) at 40 °C. [c] The metallocene was injected into a solution of MAO in toluene, presaturated with C_2H_4 (3.0 bar) at 40 °C.

Polymerization of Ethylene Using Compounds 4 and 5. The results of a series of ethylene polymerizations using compounds **4a–e** and methylaluminoxane ([Al]:[Zr] ~ 2000:1) in toluene solution at 25 °C are summarized in Table I. As can be seen from the table, there is a wide range in catalytic activity observed. Compound **4b** is about

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[7] (a) Compound **1b**: Normant-Chefnay, C. *Bull. Soc. Chim. Fr.* **1971**, 1451. (b) Compound **1c**: Herz, W. *J. Am. Chem. Soc.* **1954**, *75*, 74. (c) Compound **1d**: Cedheim, L.; Eberson, L. *Acta Chim. Scand. B* **1976**, *40*, 544 and references therein.

[8] (a) Wild, F. W. R. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Wild, F. W. R. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *Ibid.* **1985**, *288*, 63. (c) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Ibid.* **1988**, *342*, 21.

[9] Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E.; Samuel, E. *J. Organomet. Chem.* **1987**, *327*, 39.

Table II. Polymerization of Propylene with Compounds 5a–d[a]

catalyst (mg)	t, min	yield, g	R_p, kg of PP/(mol of Zr × h)	% mmmm	M_n	M_w/M_n	T_m, deg
5a (1.66)	30	53.6	27 000	89.4	15 700	2.16	131
5b (1.60)	30	53.9	32 000	79.4	16 000	2.25	115
5c (1.44)	60	23.5	7 800	92.2	5 800	2.08	130
5d (1.19)	>120	nil					
5d (1.59)[b]	120	2.1	360	87.6	15 200	2.10	130

[a] Conditions: 500 mL of toluene, [Al]:[Zr] = 2000:1, 40 °C, 3.0 bar of C_3H_6. [b] Same conditions but with direct injection of the metallocene (see Table I).

twice as active as the parent compound **4a**, whereas compound **4c** possesses the same activity as the latter. Compound **4d** is essentially inactive in ethylene polymerization. Finally, compound **4e** is much less active than compounds **4a–c**. These results differ in some important aspects from those reported recently using 4,7-disubstituted, dibenzyl analogues.[4] In that study, the 4,7-disubstituted dibenzyl analogue of compound **4d** retained some catalytic activity. Also as can be appreciated from the table, compound **4b** is much more active than **4c**, despite being very similar electronically.[10]

We also prepared the dimethyl derivative of compound **4d** in order to investigate whether alkylation of the metal center of compound **4d** might not be efficient in the presence of MAO. This compound possessed minimal activity in ethylene polymerization (i.e., <0.1 g of polymer after 24 h under the conditions in Table I).

All of the experiments summarized in Table I were conducted by precontacting the metallocene with MAO in a small volume of toluene. The resulting solution was then added to the reactor containing additional MAO in toluene, presaturated with ethylene. Quite surprisingly, however, if compound **4d** was separately dissolved in toluene and injected into the reactor containing MAO and toluene saturated with ethylene, polymerization activity is enhanced (Table I, entry 4 versus 5).

The molecular weights (M_n) and the dispersity (M_w/M_n) (Table I) of the polymers produced were determined by GPC. The molecular weights of poly(ethylene) produced by using catalysts **4a** and **4b** are rather similar, whereas significantly higher molecular weight polymer was obtained by using catalyst **4c**. Much lower molecular weight material was obtained with compounds **4d** or **4e**.

Compounds 4 are all conformationally mobile with respect to indenyl ring rotation. Since the conformation(s) adopted by these catalysts in solution may well be different (e.g., **4b** versus **4c**), this might also influence catalytic activity and polymer molecular weights.[1,2] We therefore investigated ethylene polymerization with the ethylene-bridged compounds **5a–d** for comparison purposes; the results are summarized in Table I.

By comparing entries 1–3 and 5 of Table I with entries 6–9, it is apparent that similar trends are observed with respect to catalytic activity.

The most marked difference seen when using conformationally rigid catalysts 5 compared with their unbridged analogues 4 is with respect to polymer molecular weights. In all cases, catalysts 4 produce higher molecular weight polymer, although qualitatively similar trends in the molecular weights are observed in comparing catalysts **5a–c** and **4a–c**.

Polymerization of Propylene with Compounds 5. Polymerizations of propylene were conducted with compounds **5a–d** and methylaluminoxane and the results are summarized in Table II. Similar trends in catalytic activity for propylene polymerization are observed with these catalysts as for ethylene polymerization using unbridged analogues. For example, compound **5b** is slightly more active than the well-studied system **5a**, which is in turn much more active than either **5c** or **5d**. Again, it is interesting to note compound **5b** is much more active for propylene polymerization than compound **5c** (by about a factor of 4) when compared to the corresponding difference in ethylene polymerization activity (about a factor of 2). Compound **5d** is not active for propylene polymerization when precontacted with MAO. However, as with ethylene polymerization, direct injection of the catalyst leads to significant polymer production; interestingly, under these conditions, compound **5d** produces polypropylene at a higher rate than polyethylene.

Polymer molecular weights show similar trends as those observed for ethylene polymerization with the exception that compound **5c** produces much lower molecular weight polymer than either **5a** or **5b**.

Polymer microtacticities show considerable variation. The polymer produced using catalyst **5c** is very highly stereoregular, whereas that produced by compound **5b** is significantly less stereoregular than that produced by either **5a** or **5c**. The melting temperatures of the polymers produced qualitatively reflect this trend (Table II).

Discussion

We begin our discussion with the results obtained for ethylene polymerization by both ourselves and Pino's group.[4] In both studies, electron-withdrawing groups led to a decrease in catalytic activity and polymer molecular weights. The effect of electron donors is less clear, however, since significantly lower activites were encountered with strong π donors (i.e., OMe), an effect that has been attributed to coordination of these groups to MAO leading to inductive electron withdrawal.[4]

The interesting effects observed with the dimethoxy-substituted catalysts demand explanation. We have noted that measurable activity is observed only when injecting the catalyst into *dilute* solutions of MAO presaturated with monomer. For example, essentially no activity is observed in 50 mL (as opposed to 500 mL, Tables I and II) of toluene, with the same amount of catalyst and MAO. Furthermore, under identical conditions of temperature and pressure, more propylene is polymerized than ethylene with catalyst **5d**.

These results suggest that in the case of catalyst **5d** (and **4d**) there is a competing reaction of the active species with MAO that leads to deactivation. Under conditions in which monomer concentration is much greater than [MAO], significant activity is observed. Furthermore, the higher rate of propylene polymerization is readily explained; under identical conditions of temperature and pressure, propylene is roughly 10 times more soluble in toluene than ethylene. If this is taken into account, the rates of ethylene versus propylene polymerization are in

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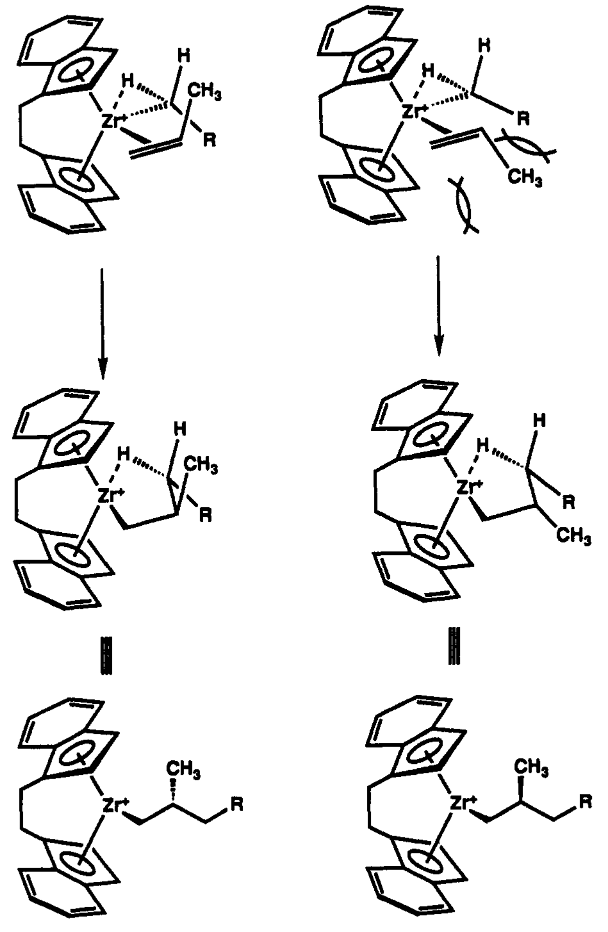
[10] The difference in average CO stretching frequencies between the Rh(I) dicarbonyl complexes of 5,6- and 4,7-dimethylindene is less than 0.5 cm^{-1}.[5]

Scheme II



the expected order (i.e., $C_2H_4 > C_3H_6$). The nature of the deactivation process is unclear; it may result from strong binding of the catalyst to MAO, facilitated by the presence of additional donor substituents,[4,11a] or it may be related to work reported by Siedle on exchange reactions of dialkyl metallocenes and MAO.[11b]

The significant difference in activity between catalysts **4b** and **4c** is unlikely to arise from differences in electronic density at the metal center.[10] It would seem reasonable to attribute this difference in activity to steric effects—e.g., steric hindrance to insertion in the case of compound **4c**.

This effect is more dramatically illustrated when analyzing the results obtained for propylene polymerization using catalysts **5a–c**. In this case, compound **5c** is much less active than compound **5b**. Also, the polymer produced by using catalyst **5c** is more highly stereoregular than that produced by using **5b**, as would be expected on steric grounds alone.[2a]

What is perhaps more surprising, however, is that the polymer produced by using catalyst **5b** is *less* stereoregular than that obtained by using catalyst **5a**. This effect must be electronic in nature—on purely steric grounds one would have expected the opposite result.[2a]

It seems reasonable to rationalize this effect in terms of models proposed for the structure of the active catalytic species.[12] For example, it has been recently demonstrated that, in the case of achiral, scandium- and chiral, zirconium-based catalysts, the transition state for monomer insertion is α-agostically stabilized.[13] According to the "modified Green–Rooney" mechanism for α-agostic insertion,[14] this interaction may be an important one in influencing the stereoselectivity of insertion. As shown in Scheme II and by using a chiral catalyst, α-agostic stabilization of the transition-metal center by *one* of the diastereotopic α-protons is expected to increase the stereoselectivity of insertion.[15] Increases in electron density at the metal center should render α-agostic stabilization of the transition state less important. Thus, the stereoselectivity of insertion might decrease with increasing electron density at the metal center for catalysts with similar steric environments.

Table III. Rates of Polymerization of Ethylene and Propylene Using Catalysts 4 and 5[a]

entry	catalyst	monomer	R_p, 10^{-4} mol s^{-1} [b]	DP_n, 10^3 [c]	R_{tr}, 10^{-8} mol s^{-1} [d]
1	**4b**	C_2H_4	6.96	9.91	7.02
2	**4a**	C_2H_4	3.93	8.91	4.41
3	**4e**	C_2H_4	0.681	4.53	1.51
4	**4c**	C_2H_4	5.40	12.54	4.31
5	**5b**	C_2H_4	6.23	4.45	14.0
6	**5a**	C_2H_4	3.48	5.17	6.73
7	**5c**	C_2H_4	3.85	7.30	5.27
8	**5b**	C_3H_6	12.0	0.380	315.8
9	**5a**	C_3H_6	10.9	0.374	291.4
10	**5d**	C_3H_6	0.451	0.362	12.4
11	**5c**	C_3H_6	2.96	0.137	216.1

[a] Ethylene polymerization data for compounds **4d** and **5d** are not included as the steady-state rate of ethylene consumption could not be accurately measured. [b] Rate of monomer consumption at steady-state measured by calibrated mass flow meters. [c] Number average degree of polymerization = M_n/M_o. [d] Rate of chain transfer = R_p/DP_n.

The effect of electron density at the metal center on polymer molecular weights is not straightforward. A decrease in molecular weight of polyethylene is seen by using catalyst **4e** (and in Pino's work using $(\eta^5\text{-}4,7\text{-}F_2C_9H_5)_2Zr(CH_2Ph)_2$).[4] Similar results are observed with catalysts **4d** and **5d** as well as in earlier work and this has been attributed to coordination of donor methoxy groups to MAO, leading to inductive electron withdrawal.[4]

While one might be tempted to relate this to, e.g., acceleration of the chain-transfer processes, it should be borne in mind that the molecular weights of the polyethylene produced should be considered in light of the reduced activity observed for these catalyst systems. Perusal of the results shown in Table I indicates that the decrease in the degree of polymerization is certainly not as pronounced as the decrease in polymerization activity.

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(11) (a) A referee has pointed out that these catalysts may deactivate via a process that is bimolecular in [Zr] and could involve, e.g., coordination of the methoxy groups on one molecule with the metal center of another. While we cannot eliminate this possibility, we do note that catalysts such as **5a** cannot be "poisoned" with 1–2 equiv of, e.g., anisole in the presence of excess aluminoxane: Collins, S.; Poulton, L., unpublished results. (b) Siedle, A. R.; Newmark, R. A.; Lamana, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.

(12) (a) Eisch, J. J.; Piotrowski, A. M.; Browstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219 and references therein. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *Ibid.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *Ibid.* **1987**, *109*, 4111. (d) Gassman, P. G.; Callstrom, M. R. *Ibid.* **1987**, *109*, 7875. (e) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148 and references therein. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. F.; *J. Am. Chem. Soc.* **1990**, *112*, 1289. (h) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *Ibid.* **1990**, *112*, 1566 and references therein.

(13) (a) Kraudelat, H.; Brintzinger, H.-H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (b) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. See also: (c) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *Ibid.* **1985**, *107*, 3377.

(14) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(15) The other possible, α-agostic structure places the R group in the region of space occupied by the six-membered ring of the indenyl ligand.

From the steady-state rate of polymerization and the degree of polymerization, one can estimate the rate of chain-transfer processes using these catalysts. These data are summarized in Table III for both ethylene and propylene polymerization. There is a dramatic decrease in the steady-state rate of polymerization and a less pronounced drop in the rate of chain transfer with *decreasing* electron density at the metal center in ethylene polymerization (entries 1–3). The data for compound **4c** (entry 4) do not fit this trend, an effect that may be steric in origin (vide supra). The ethylene-bridged catalysts **5a–c** have similar rates of polymerization but higher rates of chain transfer (entries 5–7) than their unbridged counterparts. This is partly consistent with the notion that increasing electron density at the metal center facilitates chain transfer; the ethylene bridge is an electron-donating substituent and substitution of donors at the 1-position of the indenyl ring has a more pronounced effect than at the 5,6- or 4,7-positions.[5,6]

Part of these trends is undoubtedly due to differences in the steady-state concentration of active centers when using the different catalysts; both propagation and transfer are first order in [Zr*][16] and it might be expected that ionization of the neutral metallocene precursor would be facilitated by an increase in electron density at the metal center in these systems. Future work will address this important point. However, on the basis of the data reported in Table III, one can conclude, that this effect is not solely responsible for the trends seen. For example, differences in the active site concentration should have equal effects on both propagation and chain-transfer rates. This is clearly not the case. Also, the propagation rate for catalyst **5b** is nearly double that of **5a** in ethylene polymerization, whereas there is not much of a difference in propylene polymerization. This observation is not consistent with differences due solely to, e.g., higher active site concentration for catalyst **5b**.

The dramatic decrease in propagation rates with decreasing electron density at the metal center in these systems can be explained from several viewpoints. One simple explanation is that the degree of association (i.e., coordination) with the aluminoxane counterion is much greater with an electron-deficient metallocene. This would be expected to reduce activity by analogy to work with model cationic systems.[12] Alternatively, the changes observed may be related to changes in metal–carbon bond strengths with changes in electron density at the metal center. For example, with decreasing electron density at the metal center, the frontier molecular orbitals on a Cp_2Zr moiety[17] are expected to decrease in energy. This should lead to stronger bonding between zirconium and σ-bonded ligands. In the transition state for olefin insertion, the Zr–C bond must be broken, so that one is looking at an effect on reaction rates due to ground-state stabilization.

As to the less dramatic effects seen on chain transfer, several explanations are possible. In propylene polymerization, chain transfer by β-hydride elimination is most important at conventional temperatures.[1,2] While our data are less complete for propylene polymerization, the results of Table III do not indicate a strong influence of electron density on rates of β-hydride elimination. While catalyst **5c** has a reduced rate of chain transfer when compared with **5b**, this effect is likely steric in origin; the transition state for this process places the methyl group of the last inserted monomer (or the polymer chain) close to the six-membered ring of the indenyl ligand. The rate of chain transfer for catalyst **5d** is considerably slower than that for, e.g., **5a**. As we do not have comparable data using the ethylene bridged analogue of compound **4e**, it is not clear that this result is due to a decrease in electron density at the metal center in **5d**.

In the case of ethylene polymerization, transfer to aluminum and β-hydride elimination are believed to be kinetically significant chain-transfer processes.[18] At higher temperatures (i.e., 70 °C), the latter process is dominant.[18] Under the conditions reported here, both processes are expected to be competitive. The fact that there are more dramatic differences in the rate of transfer by using the same catalysts for ethylene versus propylene suggests that chain transfer to aluminum may dominate under these conditions (e.g., compare entries 5 and 6 versus 8 and 9, Table III). An increase in electron density at the metal center appears to facilitate this process.

A plausible explanation for this effect is outlined in Scheme III. Chain transfer to aluminum may occur in two distinct steps; methyl transfer from anionic aluminum sites (generated during active site formation) to the cationic metallocene followed by back transfer of the polymer chain to aluminum. The second step in this process is expected to be rate limiting as far as transfer is concerned and will be facilitated by an *increase* in electron density at the metal center. One can see that this process may also relate to the efficiency of active site formation with these catalysts.[16] The best evidence for this hypothesis is found in the work of Siedle[11b] who demonstrated that the barrier to methyl exchange between dimethylzirconocene compounds and (methyl)aluminum acceptors (including MAO) was *reduced* when electron density at the metal center increased.

Conclusions

Decreasing electron density at the metal center in these catalysts elicits two effects in ethylene polymerization: reduced propagation and chain-transfer rates. The effect on the former is more pronounced and thus accounts for the decrease in polymer molecular weights with electron-deficient catalysts. In propylene polymerization less dramatic effects are seen with respect to both processes. The result that stereoselectivity is remarkably sensitive to electronic effects at the metal center is unexpected. While this may be related to the degree of α-agostic assistance during olefin insertion, one cannot ignore association effects of the cationic catalyst with the aluminoxane counterion. In view of this uncertainty, it would be most interesting to investigate this effect by using well-defined, single-component catalyst systems analogous to one that has recently been discovered.[19]

Experimental Section

All chemicals were reagent grade and purified as required. Tetrahydrofuran, glyme, hexanes, diethyl ether, and toluene were all dried and deoxygenated by distillation from sodium–benzophenone ketyl. Dichloromethane was dried by distillation from calcium hydride. Methylaluminoxane was purchased as a solution in toluene from Ethyl Corp. and the solution pumped to dryness in vacuo (10^{-3} mmHg) to provide solid methylaluminoxane, which was then used without further characterization (quoted M_n = 1200). NMR spectra were obtained on a Bruker AM-250 or AC-200 spectrometer. Chemical shifts are referenced to residual undeuterated solvent. IR spectra were recorded on a Perkin-Elmer 984 or a Nicolet 510P FT-IR instrument. Spectra were calibrated

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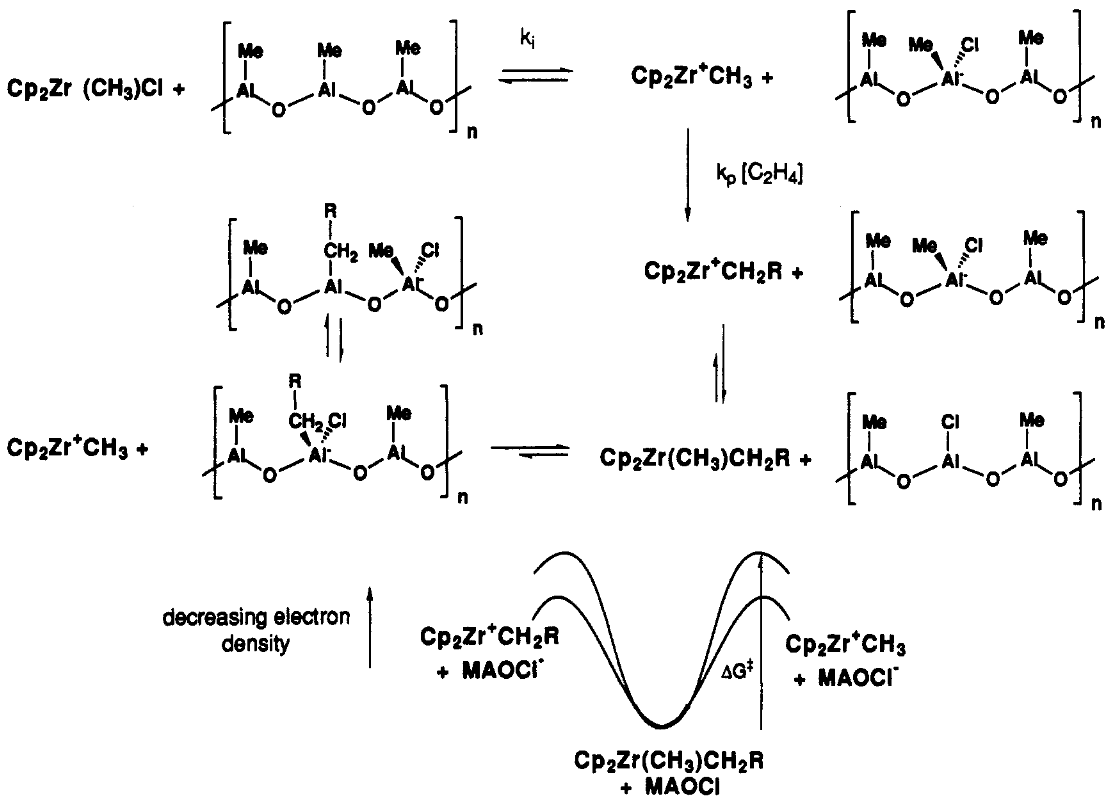
[16] See, for example: Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci., Part A* **1991**, *29*, 459 and references therein.

[17] Lauher, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[18] See, for example: Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Part A* **1990**, *28*, 15.

[19] Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

Scheme III



with poly(styrene) film. Mass spectra were measured on a KRATOS MSX-90 instrument at the University of Guelph. Elemental analyses were performed by M.H.W. Laboratories of Phoenix, AZ.

Polymerization Procedure. Polymerizations were conducted in a 1-L, Autoclave Engineers Zipperclave reactor equipped as previously described.[2a] Ethylene polymerizations were performed in a 500-mL toluene solution at 25 °C, under 0.75 bar of ethylene, that was purified by passage through columns of BASF R3-11 catalyst and 4A molecular sieves, whereas propylene polymerizations were conducted in a 500-mL toluene solution at 40 °C, under 3.0 bar of propylene, that was similarly purified. The ratio of methylaluminoxane to catalyst was 2000:1 for all polymerizations conducted. Polymerizations were initiated by injecting a solution of the catalyst and one-half of the MAO in 5.0 mL of toluene into the reactor that contained the remaining MAO and was presaturated with the monomer. The polymerizations were conducted for the times indicated in Tables I and II. Propylene polymerizations were stopped by venting the monomer and rapidly draining the polymer slurry into a small volume of methanol. Ethylene polymerizations were stopped by venting the monomer and quenching with a small volume of methanol. Polyethylene was recovered by filtration and by scraping the reactor walls and stirrer assembly. In the case of poly(propylene), the solvent was removed in vacuo, the polymer suspended in methanol, and the methanol removed in vacuo to remove residual toluene by azeotropic distillation. The polymer was then agitated with methanol/3 M aqueous HCl 1:1 in a blender for several minutes. The polymer was filtered, washed with methanol, and then dried in vacuo at 60 °C and 10^{-2} mmHg overnight.

In a typical series of experiments using catalyst **5a** and propylene monomer (500 mL of toluene, 40 °C, 3.0 bar, 0.5 h), the following results were obtained:

[**5a**], μM	[MAO], mM	yield, g	R_p[a]	% mmmm
5.9	10.2	40.2	27 200	87.9
5.9	10.2	38.0	25 800	86.1
5.9	10.2	39.2	26 600	89.5

[a] Rate of polymerization in kg of polymer/(mol of Zr x h).

Polymer Characterization. Carbon-13 NMR spectra of isotactic poly(propylene) were obtained in 1,2,4-trichlorobenzene solution (~10 wt %) that contained 0.1 wt % Irganox 1110 and 10% v/v DMSO-d_6 for field-frequency locking, at 120 °C. A pulse width of 30° was employed with inverse-gated decoupling. A spectral width of 160 ppm was employed for a total repetition time of 3.2 s. Typically, about 10 000 transients were accumulated for each sample. The spectra were integrated to determined the percentage of the main mmmm pentad at 19.7_1 ppm to the total pentad intensity, corrected for the presence of signals due to end groups or regioirregularities.

Gel permeation chromatography was conducted on a Waters 150C chromatograph equipped with a differential refractive index, a Viscotek Model 100 continuous differential viscometer, and LDC/Milton Roy KMX-6 low angle, laser light scattering detectors. Jordi mixed-bed and 1000 A linear columns (1000–25 000 and 25 000–1 000 000) were employed and samples (1% by weight in 1,2,4-TCB containing 0.1 % Irganox 1110) were eluted with 1,2,4-TCB at 135 °C at a flow rate of 1.5 mL/min. In the case of poly(ethylene) several days at 135 °C were required to "dissolve" the polymer.

DSC measurements were conducted by using a Dupont Instruments Series 99 thermal analyzer (previously calibrated with indium metal) at a heating rate of 10 °C/min from 40 to 170 °C. Repetitive runs were conducted until three constant-melting endotherms were obtained.

Indene Preparation. 5,6-Dimethylindene,[7a] 4,7-dimethylindene,[7b] and 5,6-dimethoxyindene[7c] were prepared by literature methods. 5,6-Dichloroindene was prepared by a method that will be described fully elsewhere.[5] Some spectral data for these compounds are summarized below.

5,6-Dimethylindene (1b).[7a] ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.14 (s, 1 H), 7.08 (s, 1 H), 6.68 (m, 1 H), 6.44 (m, 1 H), 3.21 (br s, 2 H), 2.21 (s, 4 H), 2.18 (s, 4 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 142.9, 141.5, 134.4, 133.1, 132.8, 131.8, 125.1, 122.2, 38.7, 20.0 (2).

4,7-Dimethylindene (1c).[7d] ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.15–7.0 (AB multiplet, 2 H), 6.80 (m, 1 H), 6.70 (m, 1 H), 3.31 (br s, 2 H), 2.58 (s, 4 H), 2.48 (s, 4 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 144.2, 142.1, 134.0, 130.5, 130.0, 127.6, 125.8, 38.2, 18.4, 18.2.

5,6-Dimethoxyindene (1d).[7c] ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.08 (s, 1 H), 6.98 (s, 1 H), 6.85 (m, 1 H), 6.36 (m, 1 H), 3.92 (s, 4 H), 3.91 (s, 4 H), 3.45 (br s, 2 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 148.4, 147.2, 137.6, 136.1, 126.1, 121.6, 108.1, 104.6, 56.6, 56.2, 39.0.

5,6-Dichloroindene (1e). IR (CHCl$_3$) 3085, 2895, 1518, 1475, 1451, 1424, 1390, 1340, 1281, 951, 928, 850 cm^{-1}; ^{H} NMR (200 MHz, CDCl$_3$) δ 7.54 (s, 1 H), 7.47 (s, 1 H), 6.80 (m, 1 H), 6.64 (m, 1 H), 3.40 (br s, 2 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 144.9, 144.4, 136.4, 130.9, 130.5, 128.6, 125.6, 122.4, 48.9; MS (EI) 148 (M$^+$, ^{35}Cl$_2$). Anal. Calcd for C$_9$H$_6$Cl$_2$: C, 58.42; H, 3.27. Found: C, 58.24; H, 3.60.

Preparation of Ethylene-Bridged Bis(indenes). The preparation of compounds **2b–d** was accomplished by the same method and conditions previously reported for the preparation of the parent compound **2a**.[8] The synthetic yields are as follows (**2a**, 75–80%; **2b**, 72%; **2c**, 55%; **2d**, 56%). The spectral data for these compounds are summarized below.

1,2-Bis[4-(5,6-dimethyl)indenyl]ethane (2b). Mp 141–142 °C; (KBr) 3007, 2965, 2795, 2771, 2719, 1602, 1493, 1470, 1394, 1378, 1360, 1302, 1263, 1234, 1217, 1168, 1138, 1123, 1110, 1022, 998, 965, 928, 863, 840, 794, 743, 714, 629, 566, 425 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.27 (s, 2 H), 7.19 (s, 2 H), 6.21 (br s, 2 H), 3.40 (br s, 4 H), 2.92 (br s, 4 H), 2.34 (br s, 12 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 144.0, 143.4, 142.2, 134.0, 132.7, 126.9, 125.1, 120.1, 37.3, 26.5, 20.1, 19.9; MS (EI) 314 (M$^+$). Anal. Calcd for C$_{24}$H$_{26}$: C, 91.67; H, 8.33. Found: C, 91.86; H, 8.11.

1,2-Bis[4-(4,7-dimethyl)indenyl]ethane (2c). Mp 180–183 °C; IR (KBr) 3061, 3028, 3010, 2942, 2937, 2917, 2863, 1589, 1491, 1454, 1435, 1379, 1360, 1318, 1254, 1229, 1174, 1158, 1148, 1119, 1060, 1034, 937, 908, 895, 838, 826, 803, 768, 732, 712, 641, 565, 549, 514, 499 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.98 (d, J = 8.0 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 6.30 (br s, 2 H), 3.20 (br s, 4 H), 3.11 (br s, 2 H), 2.57 (s, 6 H), 2.33 (s, 6 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 146.2, 128.5, 128.2, 125.8, 36.5, 30.5, 20.1, 18.4; MS (EI) 314 (M$^+$). Anal. Calcd for C$_{24}$H$_{26}$: C, 91.67; H, 8.33. Found: C, 91.76; H, 8.19.

1,2-Bis[4-(5,6-dimethoxy)indenyl]ethane (2d). Mp 152–153 °C; IR (KBr) 2993, 2926, 2835, 1604, 1574, 1491, 1464, 1415, 1357, 1320, 1285, 1257, 1228, 1203, 1173, 1125, 1046, 969, 850, 834, 791, 669, 443 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.07 (s, 2 H), 6.89 (s, 2 H), 6.19 (br s, 2 H), 3.90 (s, 6 H), 3.87 (s, 6 H), 3.27 (br s, 4 H), 2.90 (br s, 4 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 148.2, 147.4, 144.9, 138.4, 136.8, 126.5, 108.2, 102.8, 56.4, 56.2, 37.6, 26.5; MS (EI) 378 (M$^+$). Anal. Calcd for C$_{24}$H$_{26}$O$_4$: C, 76.17; H, 6.92. Found: C, 75.94; H, 7.00.

Preparation of Bis(η^5-indenyl)zirconium Dichlorides 4a–e. The following procedures were employed for the preparation of these compounds.

Method A (Compounds 4a–d). A solution of the indenyllithium compound was prepared from the indene (10 mmol) by treatment of a 20-mL THF solution of this compound with *n*-butyllithium in hexanes (2.45 M, 4.1 mL, 10.05 mmol) at −78 °C. After warming to room temperature and stirring for 1 h at room temperature, the solution of the indenyllithium compound was cannulated into a suspension of ZrCl$_4$·2THF (1.89 g, 5.0 mmol) in toluene (20 mL) at 0 °C over a period of 15 min. The mixture was then warmed to room temperature, and, after 3 h at room temperature, the yellow precipitate was filtered off and washed with THF/toluene 1:2. The bis(indenyl)zirconium dichlorides were purified by sublimation under high vacuum (**4a,c,e**) or by crystallization (**4b,d** from hot toluene).

Method B [Bis(η^5-5,6-dichloroindenyl)zirconium Dichloride (4e)]. A solution of 5,6-dichloroindene (1.850 g, 10.0 mmol) in glyme (20 mL) was stirred with excess sodium hydride (360.4 mg, 15.0 mmol) at room temperature for 1 h at which time gas evolution had effectively ceased. The excess sodium hydride was allowed to settle, and the supernatant solution was added dropwise by syringe to a solution of ZrCl$_4$ (1.165 g, 5.0 mmol) in glyme (20 mL) at 0 °C over 20 min. The mixture was then warmed to room temperature, and, after 3 h, the mixture was filtered and the yellow precipitate washed with additional glyme, 6 N HCl, and then water. The yellow solid was then dried in vacuo. The title compound was purified by sublimation at 8.0 × 10^{-5} mmHg and 185 °C. Yield 0.765 g (14%); IR (KBr) 3105, 1632, 1511, 1438, 1388, 1343, 1285, 1257, 1245, 1211, 1096, 1057, 951, 877, 863, 833, 810, 775, 692, 655 cm^{-1}; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, 1000 scans!!) δ 7.78 (br s, 2 H), 6.68 (t, J = 3.4 Hz, 1 H), 6.39 (d, J = 3.4 Hz, 2 H). Due to this compound's *extremely* low solubility (or instability) in common deuterated solvents a satisfactory ^{13}C NMR spectrum was not obtained. Anal. Calcd for C$_{18}$H$_{10}$Cl$_6$Zr: C, 40.78; H, 1.90. Found: C, 40.82; H, 2.05. High-resolution mass spectrum calculated for C$_{18}$H$_{10}$^{35}Cl$_6$^{90}Zr: 525.79566. Found: 525.79543.

Bis(η^5-indenyl)zirconium Dichloride (4a). Prepared using method A in 54% yield and purified by sublimation at 10^{-4} mmHg and 220 °C. Spectral data were consistent with those reported in the literature for this compound.[9]

Bis(η^5-5,6-dimethylindenyl)zirconium Dichloride (4b). Prepared using method A in 54% yield and purified by crystallization from hot toluene. IR (KBr) 3100, 3017, 2971, 2943, 2921, 1622, 1523, 1465, 1446, 1384, 1370, 1349, 1275, 1218, 1166, 1090, 1028, 1002, 853s, 838, 815, 624 cm^{-1}; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 7.34 (s, 4 H), 6.32 (t, J = 3.4 Hz, 2 H), 6.05 (d, J = 3.4 Hz, 4 H), 2.37 (s, 12 H). A satisfactory ^{13}C NMR spectrum of this material could not be obtained because of its very low solubility in common deuterated solvents. MS (EI) 446 (M$^+$, ^{90}Zr^{35}Cl$_2$). Anal. Calcd for C$_{22}$H$_{22}$Cl$_2$Zr: C, 58.91; H, 4.94. Found: C, 58.88; H, 5.09.

Bis(η^5-4,7-dimethylindenyl)zirconium Dichloride (4c). Prepared by method A in 42% yield and purified by sublimation at 5 × 10^{-5} mmHg and 170 °C. The spectral data were identical with that reported in the literature.[4]

Bis(η^5-5,6-dimethoxyindenyl)zirconium Dichloride (4d). Prepared by method A in 35% yield and purified by crystallization from hot toluene. IR (KBr) 3100, 3082, 3075, 3005, 2962, 2955, 2938, 2833, 1624, 1540, 1495, 1465, 1455, 1440, 1306, 1235, 1215, 1200, 1186, 1175, 1132, 1042, 1037, 1029, 1003, 839, 832, 823, 492, 450, 346, 310 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 6.53 (s, 4 H), 6.15 (t, J = 3.3 Hz, 2 H), 5.91 (d, J = 3.3 Hz, 4 H), 3.36 (s, 12 H); ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 152.7, 123.3, 118.1, 102.8, 102.5, 55.4; MS (EI) 510 (M$^+$, ^{90}Zr^{35}Cl$_2$). Anal. Calcd for C$_{22}$H$_{22}$Cl$_2$O$_4$Zr: C, 51.56; H, 4.33. Found: C, 51.89; H, 4.31.

Preparation of [Ethylenebis(η^5-indenyl)]zirconium Dichlorides 5a–d. The following procedure was employed for the preparation of these compounds, except **5c** (vide infra).

Preparation of Racemic [Ethylenebis(η^5-indenyl)]zirconium Dichloride (5a). A degassed solution of diindenylethane (2.584 g, 10.0 mmol) in 100 mL of dry THF was treated with a solution of *n*-butyllithium in hexanes (8.44 mL of 2.4 M, 20.0 mmol) at −78 °C. The mixture was warmed to room temperature and after 1 h at room temperature an orange-red solution of the dianion was obtained. During this time a solution containing ZrCl$_4$·2THF (4.77 g, 10.0 mmol) dissolved in 100 mL of THF was prepared in a separate flask. The contents of both flasks were simultaneously added at the same rate to a third flask, containing ~50 mL of THF, by two cannulae with vigorous stirring. It is important that (a) a local excess of the dianion does not build up during the addition and that (b) relatively long addition times are employed (6–7 h). After the addition was completed, the orange-yellow solution (sometimes bright yellow) was stirred overnight at room temperature. The following day, the solution was cooled to 0 °C and HCl gas passed through the mixture for about 40 s with stirring. A bright, canary yellow solution was obtained. The solvent was concentrated in vacuo on a rotary evaporator (do not heat) until a considerable amount of a yellow precipitate had separated (usually less than 25 mL of solvent remains on this scale). The mixture was diluted with an equal volume of ether and filtered to give a bright yellow precipitate [additional material could be obtained by concentration of the filtrate to near dryness, suspension of the residue in a minimal volume of THF (to dissolve polymeric byproducts), and addition of ether to precipitate additional metallocene]. The crude product was then washed with ether (4 × 20 mL) and then *rapidly* washed in succession with 6 N HCl (10 mL), water (10 mL), ethanol (20 mL), and then ether (2 × 20 mL). The product was then dried in vacuo overnight at 10^{-2} mmHg and 60 °C. Yield (2.18 g, 52%). For spectral data, see ref 8.

Racemic [Ethylenebis(η^5-5,6-dimethylindenyl)]zirconium Dichloride (5b). This compound was prepared in 44% yield and was obtained free of a minor amount of its meso isomer by washing the final product with hot toluene. IR (KBr) 3062, 3055, 2947, 2940, 2925, 2863, 1488, 1471, 1446, 1372, 1212, 1043, 1026, 1010, 981, 852, 807, 787, 452, 328, 313 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.37 (s, 2 H), 7.25 (s, 2 H), 6.43 (d, J = 3.2 Hz, 2 H), 6.07 (d, J = 3.2 Hz, 2 H), 3.69 (br s, 4 H), 2.38 (s, 6 H), 2.36 (s, 6 H); ^{13}C NMR (50 MHz, CD$_2$Cl$_2$) δ 138.1, 137.7, 129.4, 124.4, 123.3, 121.4, 120.6, 113.5, 109.9, 29.5, 21.0, 20.7; MS (EI) 472 (M$^+$, ^{90}Zr^{35}Cl$_2$).

Anal. Calcd for $C_{24}H_{24}Cl_2Zr$: C, 60.74; H, 5.10. Found: C, 60.35; H, 4.98.

Racemic [Ethylenebis(η^5-4,7-dimethylindenyl)]zirconium Dichloride (5c). This compound was prepared under different conditions than that reported above: A suspension of compound **2c** (166.3 mg, 0.53 mmol) in dry DME (10 mL) was cooled to 0 °C under argon. A solution of *n*-butyllithium in hexane (0.47 mL, 2.5 M, 2.2 equiv) was added dropwise, via syringe, over 10 min. The mixture was warmed to room temperature; the indene dissolved with formation of a yellow solution, and, after 45 min at room temperature, a colorless precipitate separated. In a separate flask, $ZrCl_4$ (123.0 mg, 0.53 mmol) was treated with 5 mL of DME at −78 °C. The solution was then warmed to room temperature and then added dropwise, using a syringe pump, to the suspension of the dianion in DME over a period of 1.5 h. The dianion gradually dissolved and a yellow solution with some precipitate was obtained. The mixture was stirred overnight at 25 °C. Ethereal HCl was added via syringe (1.0 mL of 0.3 M) and the mixture concentrated in vacuo. The residue was taken up in ether and filtered, washing with small volumes of ether. The yellow solid was washed with 6 M HCl, water, ethanol, and then ether as described above and dried in vacuo (63 mg, 25% yield). The crude product was obtained as a single stereoisomer and could be purified by crystallization from hexanes–toluene. IR (KBr) 3080, 3027, 2934, 2888, 2854, 1601, 1495, 1451 s, 1379, 1328, 1096, 1068, 1005, 926, 816 s, 745, 663, 634 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.81–6.75 (two overlapping d, J = 3.5, 7.8 Hz, total 4 H), 6.62 (d, J = 7.8 Hz, 2 H), 5.90 (d, J = 3.5 Hz, 2 H), 3.5 (AA′ multiplet, 2 H), 3.0 (BB′ multiplet, 2 H), 2.34 (s, 6 H), 2.24 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.9, 130.1, 128.7, 128.4, 125.4, 125.2, 121.5, 113.3, 112.7, 30.3, 21.4, 18.6; MS (EI) 472 (M^+, $^{90}Zr^{35}Cl_2$). Anal. Calcd for $C_{24}H_{24}Cl_2Zr$: C, 60.74; H, 5.10. Found: C, 60.41; H, 5.32.

Racemic [Ethylenebis(η^5-5,6-dimethoxyindenyl)]zirconium Dichloride (5d). This compound was prepared in 24% yield and was obtained free of a minor amount of its meso isomer by washing the final product with hot toluene. IR (KBr) 3079, 3061, 2993, 2958, 2931, 2898, 2830, 1621, 1528, 1493, 1458, 1428, 1384, 1370, 1314, 1239, 1224, 1207, 1185, 1147, 1054, 1028, 1017, 997, 977, 901, 875, 851, 839, 827, 798, 728, 530, 454, 420 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.73 (s, 2 H), 6.71 (s, 2 H), 6.45 (d, J = 3.3 Hz, 2 H), 5.98 (d, J = 3.3 Hz, 2 H), 3.96 (s, 6 H) 3.93 (s, 6 H), 3.64 (AA′BB′ m, 4 H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 154.4, 152.5, 125.9, 121.0, 119.5, 110.4, 109.8, 102.6, 98.9, 56.4, 56.4, 29.0; MS (EI) 536 (M^+, $^{90}Zr^{35}Cl_2$). Anal. Calcd for $C_{24}H_{24}Cl_2O_4Zr$: C, 54.54; H, 4.49. Found: C, 54.62; H, 4.90.

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Photochemical Reactions of $Cp_2Fe_2(CO)_4$ with $HSnBu_3$

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The photochemical reactions of $Cp_2Fe_2(CO)_4$ with $HSnBu_3$ in hexane solutions have been studied by employing continuous or flash photolysis methods. The primary reaction products, $Cp(CO)_2FeH$, $Cp(CO)_2FeSnBu_3$, and $Cp(CO)Fe(H)(SnBu_3)_2$, have been independently synthesized and characterized by elemental analysis and NMR or IR spectroscopy. Under an Ar or CO atmosphere, the amount of $Cp(CO)_2FeH$ formed in the early stage of the reaction is always in a 1:1 molar ratio with the total amount of $Cp(CO)_2FeSnBu_3$ and $Cp(CO)Fe(H)(SnBu_3)_2$, and in a 1:1 molar ratio with the loss of $Cp_2Fe_2(CO)_4$. The rate for the continuous photolysis reaction is inversely related to CO partial pressure. The results rule out pathways involving the intermediacy of the $Cp(CO)_2Fe^\bullet$ radical. The behavior of the system is consistent with a reaction pathway that involves oxidative addition of $HSnBu_3$ to the CO-loss intermediate, $Cp_2Fe_2(\mu\text{-}CO)_3$. The second-order rate constant for oxidative addition of $HSnBu_3$ to $Cp_2Fe_2(\mu\text{-}CO)_3$ is $1.26 \times 10^5\ M^{-1}\ s^{-1}$ at 25 °C. The subsequent elimination of $Cp(CO)_2FeH$ obeys a first-order rate law with an apparent rate constant of $\sim 2 \times 10^{-2}\ s^{-1}$.

Introduction

It has been well established that the photochemistry of metal–metal-bonded carbonyls involves both homolysis of the metal–metal bond, which generates 17-electron radicals, and cleavage of the metal–CO bond, which produces a CO-loss intermediate.[1,2] The reactions of the 17-electron radicals,[3-7] e.g., electron and atom transfer, recombination, ligand addition, and substitution, have been the focus of studies for some years. More recently there has been increased awareness of the importance of the dinuclear intermediates resulting from CO loss.

$Cp_2Fe_2(CO)_4$ has a very diverse photochemistry.[1,2] Photochemical generation of the radical $Cp(CO)_2Fe^\bullet$ and the CO-loss species $Cp_2Fe_2(CO)_3$ has been established.[1,2,8-11] Two isomers of the CO-loss species have been identified;

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