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Methyl-versus-Chloride Exchange as a Measure of Electron Density at the Metal Center of Ring-Substituted Zirconocene Complexes

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Methyl-versus-cloride exchange equilibria between different zirconocene complexes provide a sensitive measure of relative electron densities at the Zr centers of these complexes. As expected, methyl and trimethyl silyl substituents increase the electron density at the Zr center of a bis(cyclopentadienyl) Zr(IV) complex; the same holds for a dimethyl silyl bridge. In bis(indenyl) complexes, on the other hand, electron density at the metal center is reduced and substituent and bridge effects are different from those observed in bis(cyclopentadienyl) Zr(IV) complexes.

Introduction

Substantial efforts have been undertaken to relate the properties of different zirconocene complexes as olefin-polymerization catalysts with their molecular structures. Steric effects of various ring substituents and bridging units on the properties of zirconocene-based olefin polymerization catalysts and their polymer products have been the object of rather thorough studies.[1] Much less is known about the electronic effects that different ligand frameworks exert on relative electron densities (or deficiencies) at the Zr center,[2] although these must profoundly influence the reactivity of zirconocene-based catalyst systems.[3]

Experimental clues as to the effects of various substituted ring ligands $(Cp^x)^-$ on the electron density of a metallocene complex are provided by the electrochemical potential at which an M(+III) complex $(Cp^x)_2MCl_2^-$ is generated from the respective neutral dichloride[4] and by the extent to which the ν(CO) absorption frequencies are reduced in the respective M(+II) complex $(Cp^x)_2M(CO)_2$.[5] For oxidation state M(+IV), generally thought to be most relevant for group IV metallocene polymerization catalysts, Gassman and co-workers have introduced XPS-derived 3d-shell ionization energies as an electron density measure.[6]

Recent studies[7] on ligand exchange equilibria of the type $(Cp^x)_2ZrCl_2 + Al_2Me_6 \rightleftharpoons (Cp^x)_2ZrClMe + Al_2Me_5Cl$ have shown that the associated free enthalpy changes $\Delta G°$ parallel the XPS-derived ionization energies,[6] in line with the rule that alkyl-vs-halide exchange places the alkyl preferentially at the more electronegative metal.[8] Studies on Me-vs-Cl exchange between Al_2Me_6 and various zirconocene dichlorides are burdened, however, with uncertainties concerning adduct formation between each of the zirconocene species involved and $AlMe_3$ and/or $AlMe_2Cl$.[7,9] To avoid this problem, we have now developed a refined method that measures Me-vs-Cl exchange equilibrium constants between pairs of zirconocene dichloride and monochloride−monomethyl complexes.

Results and Discussion

When one of the substituted zirconocene dichloride derivatives $(Cp^x)_2ZrCl_2$ shown in Table 1 and Figure 1 is equilibrated with an approximately equivalent amount of $(C_5H_5)_2ZrClMe$ in C_6D_6 solution, Me-vs-Cl exchange between the Zr centers of both zirconocenes is indicated

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[9] Equilibrium studies with $(Cp)_2ZrCl_2$ and Al_2Me_6 showed that the ratio $[(Cp)_2ZrClMe]\cdot[Al_2Me_5Cl]/([(Cp)_2ZrCl_2]\cdot[Al_2Me_6])$ varies with the initial concentrations of $(Cp)_2ZrCl_2$ and Al_2Me_6, even when Al_2Me_6 was used in great excess over zirconocene dichloride in order to keep its concentration practically constant. This observation and changes in chemical shifts of the zirconocene complexes in the equilibrium mixtures with changing concentrations of Al_2Me_6 and Al_2Me_5Cl indicate that other equilibria, such as formation of adducts of the type $(Cp)_2ZrMeCl\cdot AlMe_2Cl$, have to be taken into account. Determination of the respective adduct formation constants, while possible in principle, proved impracticable due to limitations concerning suitable concentration ranges and data accuracies.

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Table 1. Equilibrium Constants for Methyl-versus-Chloride Exchange between Pairs of Zirconocene Dichloride and Methyl Chloride Complexes

exchange equilibrium	K_{EXC}
$(Me_5Cp)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons (Me_5Cp)_2ZrClMe + (Cp)_2ZrCl_2$	0.018
$(1,3\text{-}Me_2Cp)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons (1,3\text{-}Me_2Cp)_2ZrClMe + (Cp)_2ZrCl_2$	0.09
$(Me_3SiCp)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons (Me_3SiCp)_2ZrClMe + (Cp)_2ZrCl_2$	0.27
$(MeCp)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons (MeCp)_2ZrClMe + (Cp)_2ZrCl_2$	0.28
$Me_2Si(Cp)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons Me_2Si(Cp)_2ZrClMe + (Cp)_2ZrCl_2$	0.36
$(MeCp)(Cp)ZrCl_2{}^a + (Cp)_2ZrClMe \rightleftharpoons (MeCp)(Cp)ZrClMe + (Cp)_2ZrCl_2$	0.52
$Me_2Si(2\text{-}MeInd)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons Me_2Si(2\text{-}MeInd)_2ZrClMe + (Cp)_2ZrCl_2$	1.62
$Me_2Si(Ind)_2ZrCl_2 + (Cp)_2ZrClMe \rightleftharpoons Me_2Si(Ind)_2ZrClMe + (Cp)_2ZrCl_2$	2.56
$Me_2Si(Ind)_2ZrCl_2 + (Ind)_2ZrClMe \rightleftharpoons Me_2Si(Ind)_2ZrClMe + (Ind)_2ZrCl_2$	0.98

[a] Contained as an impurity in the $(MeCp)_2ZrCl_2$ sample used.

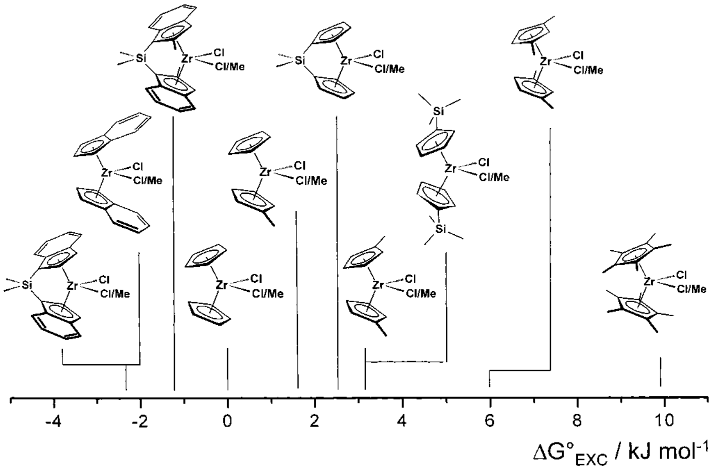

Figure 1. Standard free enthalpy changes $\Delta G°_{EXC} = -RT \ln K_{EXC}$ for methyl-versus-chloride exchange between various zirconocene dichloride/monomethyl−monochloride pairs and $Cp_2ZrCl_2/Cp_2ZrMeCl$.

by their ^1H NMR spectra. These exchange reactions were found to be very slow in the ca. 0.01 M solutions used.[10] They proceed to equilibrium within a few minutes, however, when a catalytic quantity of MAO ([Al]:[Zr] < 0.1) is added to the reaction mixture.[11] Equilibrium constants according to eq 1 (see Table 1) were determined by integration of the ^1H NMR signals of the four complex species involved (see Experimental Section) and found to be constant within 2−3% over a 5−10-fold range of the concentration ratios $[(Cp^x)_2ZrCl_2]/[(Cp^x)_2ZrClMe]$ and $[(C_5H_5)_2ZrClMe]/[(C_5H_5)_2ZrCl_2]$.

$$(Cp^x)_2ZrCl_2 + (C_5H_5)_2ZrClMe \rightleftharpoons (Cp^x)_2ZrClMe + (C_5H_5)_2ZrCl_2 \quad (1)$$

A graphical representation of the corresponding standard free enthalpy changes $\Delta G°_{EXC}$ (Figure 1) shows, in remarkable agreement with our earlier study on Me-vs-Cl exchange with Al_2Me_6,[7] that $\Delta G°_{EXC}$ is practically proportional—with ca. 1.5 kJ/mol per CH_3 group—to the number of methyl substituents at the cyclopentadienyl ligands of a zirconocene complex, except for the sterically particularly crowded $(C_5Me_5)_2Zr$ complexes, where this increment is diminished to less than 1 kJ/mol per CH_3 group.[12] For all but the most crowded zirconocene complexes, the free enthalpy change $\Delta G°_{EXC}$ for Me-vs-Cl exchange according to eq 1 can thus be considered as a measure of electron density at the Zr center of a ring-substituted complex $(Cp^x)_2ZrCl_2$, which is unaffected by its steric constraints and homologous to its XPS-derived 3d-shell ionization energy.[6]

For the trimethylsilyl-substituted pair $(Me_3SiC_5H_4)_2ZrCl_2/ClMe$ we find practically the same value of $\Delta G°_{EXC}$ as for the methyl-substituted analogue $(MeC_5H_4)_2ZrCl_2/ClMe$. This indicates, in accord with XPS data,[6] similar properties of methyl and trimethylsilyl ring substituents with regard to electron donation to the metal center. This similarity is to be expected if electron densities at the metal center and at the aromatic ring ligands are correlated, since rather similar Hammett parameters ($\sigma_m = -0.06$, $\sigma_p = -0.14$ and $\sigma_m = -0.04$, $\sigma_p = -0.07$) have been reported for Me and Me_3Si substituents, respectively.[13] Interestingly, an interannular Me_2Si bridge appears to increase the value of $\Delta G°_{EXC}$, and hence the electron density at the Zr center, to a similar extent as one trimethylsilyl substituent at each of two unbridged cyclopentadienyl rings does. This indicates that the

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(10) Similarly slow exchange reactions have been observed by: Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(11) Even then, exchange reactions involving the sterically hindered complexes required periods of 12−48 h to reach equilibrium under these conditions.

(12) Since interligand angles in zirconocene complexes are controlled by mutual repulsion between the Cp ligands and between Cp and Cl or CH_3 ligands (Brintzinger, H. H.; Prosenc, M. H.; Schaper, F.; Weeber, A.; Wieser, U. *J. Mol. Struct.* **1999**, 409), centroid−metal−centroid angles provide a reliable measure of effective van der Waals radii. Values of 130.5° and 132.5° for Cp_2ZrCl_2 and for Cp_2ZrMe_2, respectively (Corey, J. Y.; Zhu, X. H.; Brammer, L.; Rath, N. P. *Acta Crystallogr.* (*C*) **1995**, *51*, 565; Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750) indicate an almost equal size of the Cl and Me ligands. A slight steric advantage of the marginally less space-demanding CH_3 over a Cl ligand might partially offset its electronic disadvantage in the highly crowded $(C_5Me_5)_2Zr(IV)$ complexes.

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Table 2. Values of $\Delta G°_{EXC}$ for Methyl-versus-Chloride Exchange between Zirconocene Dichloride and Monochloride Monomethyl Complexes (Eq 1), Ionization Energies IE(XPS) for $3d_{5/2}$ States of Zirconocene Dichlorides,[6] ν(CO) Frequencies for Dicarbonyl Complexes,[5] Standard Reduction Potentials $E°$ for Reduction of Dichloride Complexes to the Zr(III) Oxidation State,[4] and Chemical Shifts $\delta(CH_3)$ for Zr-Bound Methyl Groups in the Respective Zirconocene Monochloride Monomethyl Complexes

complex	$\Delta G°_{EXC}$ [kJ/mol]	IE(XPS) [eV]	ν(CO)[a] [cm^{-1}]	$E°$ [V]	$\delta(CH_3)$[b] [ppm]
$(Me_5Cp)_2ZrCl_2$	9.96	181.0	1945	−2.418	0.29
$(1,3\text{-}Me_2Cp)_2ZrCl_2$	5.97			−2.298	0.36
$((Me_3Si)_2Cp)_2ZrCl_2$		181.4	1962	−2.163	
$(Me_3SiCp)_2ZrCl_2$	3.25	181.5	1970	−2.163	0.51
$(MeCp)_2ZrCl_2$	3.16			−2.228	0.39
$Me_2Si(Cp)_2ZrCl_2$	2.53			−2.068	0.49
$(MeCp)(Cp)ZrCl_2$	1.62				0.41
Cp_2ZrCl_2	0.00	181.7	1975	−2.158	0.44
$Me_2Si(2\text{-}MeInd)_2ZrCl_2$	−1.20				−0.42
$Me_2Si(Ind)_2ZrCl_2$	−2.33				−0.55
$(Ind)_2ZrCl_2$	−2.33		1985		−0.35

[a] For the $Cp^x{}_2Zr(CO)_2$ analogues. [b] For the $Cp^x{}_2ZrClMe$ analogues.

effects of a Me_2Si bridge on electronic density at the Zr center originate mainly from its inductive and mesomeric influence on the electron density of the aromatic ring ligands and not from any changes in geometry such as ligand tilt or inclination angles.

For the bis(indenyl) Zr(IV) complexes represented in Table 1 and Figure 1, lower Zr electron densities than for bis(cyclopentadienyl) complexes are indicated by their $\Delta G°_{EXC}$ data, in accord with a smaller ν(CO) shift found for $(Ind)_2Zr(CO)_2$.[5] In addition, bis(indenyl) complexes deviate in several respects from their bis(cyclopentadienyl) counterparts. Introduction of a Me_2Si bridge does not affect electron densities in these complexes to any noticeable degree: An equilibrium constant equal to unity is found for the reaction $Me_2Si(Ind)_2ZrCl_2 + (Ind)_2ZrClMe \rightleftharpoons Me_2Si(Ind)_2ZrClMe + (Ind)_2ZrCl_2$. In addition, the increase of electron density at the Zr center of the Me_2Si-bridged bis(indenyl) complex by 2,2′-positioned Me substituents is much smaller (only about one-third) than that caused by Me substituents in the typical bis(cyclopentadienyl) complexes discussed above. These anomalies are to be analyzed, together with spectral observations on these complexes, in an accompanying publication.[14]

The scale of increasing electron donation by various zirconocene ring substituents derived from their $\Delta G°_{EXC}$ values can be compared with related scales derived from other experimental data (Table 2). Shifts of the ν(CO) absorption bands of Me- and Me_3Si-substituted zirconocene dicarbonyl complexes to lower wavenumbers,[5] which measure the propensity of the respective Zr(+II) center for electron back-donation into CO π^* orbitals, follow the same sequence as the respective $\Delta G°_{EXC}$ values. The increments of 2−3 cm^{-1} observed per Me or Me_3Si group are rather small, however.

Electrochemical potentials for the reduction $(Cp^x)_2ZrCl_2 + e^- \rightleftharpoons (Cp^x)_2ZrCl_2^-$ in THF solution have been found by Mach and co-workers to become more negative, by about 35 mV per Me group, with increasing numbers of Me substituents.[4] Surprisingly, however, these reduction potentials are practically unaffected by the presence of up to three Me_3Si groups at each C_5 ring. Apparently, Me_3Si substituents have much smaller effects on the energy of the SOMO, which accommodates the extra electron in $(Cp^x)_2ZrCl_2^-$, than on that of the binding orbitals involved in Me-vs-Cl exchange.

Chemical shifts of the ^1H NMR signals of Zr-bound methyl groups in monomethyl monochloride complexes $(Cp^x)_2ZrClMe$, also listed in Table 2, change to higher fields with increasing numbers of Me substituents at the C_5 ring ligands. Low-field shifts of comparable size are associated, however, with the presence of Me_3Si groups or a Me_2Si bridge. This observation as well as substantial high-field shifts of the Zr-Me signals in unbridged and Me_2Si-bridged bis(indenyl) complexes indicate that Zr-Me shifts are not so much related to electron densities as to anisotropic magnetic susceptibilities caused by Si−C bonds and/or additional aromatic rings present in these complexes.

In view of these divergencies it appears all the more remarkable that the electron density scale based on $\Delta G°_{EXC}$ values for Me-vs-Cl exchange closely parallels that based on XPS-derived inner-shell ionization data. We take this as an indication that the energy gain associated with the formation of a more covalent Zr−Me bond at the expense of a more polar Zr−Cl bond is indeed highly sensitive to changes in the electronegativity of the Zr center. Since equilibrium constants for the exchange reactions represented in eq 1 are easily and accurately measured, this method provides, in our opinion, a convenient and reliable opportunity to characterize electronic properties of bis(cyclopentadienyl) and bis(indenyl) zirconium(IV) dichloride or methyl chloride derivatives.

Similar electronic effects of ring substituents and bridging units are to be expected also for the cationic zirconocene alkyl derivatives thought to be direct participants in olefin polymerization catalysis.[1,15] It would thus appear rewarding to investigate these electronic effects by similar exchange equilibria involving alkyl zirconocene cations and to clarify how electron densities at the Zr centers of these cationic complexes affect the rates of the elementary reaction steps that control the properties of these polymerization catalysts.[16]

Experimental Section

Zirconocene dichloride complexes were obtained commercially or as gifts or else prepared according to previous reports.[17−27] Zirconocene dimethyl derivatives were prepared

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by methods described by Samuel and Rausch.[28] $Cp_2ZrClMe$[29] and solid MAO[30] were prepared according to literature. All manipulations were performed under argon by the use of Schlenk techniques or in a N_2-filled glovebox with vacuum antechamber.

^{1}H NMR Studies of Exchange Equilibria. Samples were prepared, in a N_2-filled glovebox, by mixing a few milligrams of a solid zirconocene dichloride complex with less than 1 equiv of the dimethyl derivative of another zirconocene complex or with approximately 1 equiv of $(Cp)_2ZrClMe$. After dissolving the solids in ca. 0.6 mL of deuteriobenzene, a minute quantity of solid methylaluminoxane (MAO) was added to speed up the ligand exchange reaction; ligand exchange reached equilibrium within several minutes after addition of a trace of MAO.[11] As expected from the initial stoichiometry, only the dichloride and methyl-chloride forms of both zirconocenes were found to be present as the products of the exchange reaction.

The relative concentrations of these four complexes were evaluated independently by integration of their respective NMR signals. Comparison of the integrals showed that less than 10% of all Zr-Me groups originate from exchange with added MAO. ^{1}H NMR spectra were recorded at 293 K using a Bruker AC-250 spectrometer. The following spectrometer settings were used: radio frequency pulse duration 8 μs (70 deg pulse), sweep width 4 kHz, 40−400 scans with a relaxation delay of 60−120 s, to ensure that relaxation was sufficient for quantitative measurements. The signal of C_6D_5H was taken as reference with chemical shift δ 7.15 ppm.

Equilibrium constants K_{EXC}, evaluated from several experiments at various times after mixing the reagents, were reproducible within 2−3%, irrespective of the concentration of the zirconocene complexes used and of which of the two was initially in the dichloride form. Chemical shifts δ (in ppm) of the signals used for integration were the following: $(Cp)_2ZrCl_2$ 5.86 (s, 10H, Cp); $(Cp)_2ZrClMe$ 5.73 (s, 10H, Cp), 0.44 (s, 3H, ZrMe); $(MeCp)(Cp)ZrCl_2$ 5.90 (s, 5H, Cp); $(MeCp)(Cp)ZrClMe$ 0.41 (s, 3H, ZrMe); $(MeCp)_2ZrCl_2$ 2.09 (unres. t, 6H, Me-C); $(MeCp)_2ZrClMe$ 5.46−5.42 (m, 4H, Cp′), 2.05 (unres. t, 6H, Me-Cp), 0.39 (s, 3H, Zr-Me); $(Me_3SiCp)_2ZrCl_2$ 0.32 (s, 18H, Me-Si), 5.91 (t, 4H, Cp), 6.38 (t, 4H, Cp); $(Me_3SiCp)_2ZrClMe$ 0.28 (s, 18H, Me-Si), 0.51 (s, 3H, Zr-Me); $(1,3\text{-}Me_2Cp)_2ZrCl_2$ 1.98 (s, 12H, Me-Cp); $(1,3\text{-}Me_2Cp)_2ZrClMe$ 1.98 (s, 6H, Me-Cp, overlaps with the corresponding signal of the dichloride), 1.86 (s, 6H, Me-Cp), 0.36 (s, 3H, Zr-Me); $(Me_5Cp)_2ZrCl_2$ 1.84 (s, 30H, Me-Cp); $(Me_5Cp)_2ZrClMe$ 0.00 (s, 3H, Zr-Me), 1.79 (s, 30H, Me-Cp); $Me_2Si(Ind)_2ZrCl_2$ 5.75 (d, 2H, −Ind), 0.53 (s, 6H, Me-Si); $Me_2Si(Ind)_2ZrClMe$ 6.70 (dd, 1H, Ind), 6.64 (dd, 1H, Ind), 5.98 (d, 1H,Ind), 5.51 (d, 1H, Ind), 0.56 (s, 3H, Me-Si), 0.46 (s, 3H, Me-Si), −0.56 (s, 3H, ZrMe); $Me_2Si(Cp)_2ZrCl_2$ 6.76 (t, 4H, −Cp), 5.47 (t, 4H, −Cp), 0.07 (s, 6H, Me-Si); $Me_2Si(Cp)_2ZrClMe$ 6.67 (m, 2H, Cp), 6.58 (m, 2H, Cp), 5.63 (m, 2H, Cp), 5.29 (m, 2H, Cp), 0.49 (s, 3H, Zr-Me), 0.13 (s, 3H, Me-Si), 0.01(s,3H, Me-Si); $(Ind)_2ZrCl_2$ 6.07 (t, 2H, Ind); $(Ind)_2ZrClMe$ −0.35 (s, 3H, Zr-Me);[31] $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ 2.00 (s, 6H, Me-Si), 0.74 (s, 6H, Me-Ind); $Me_2Si(2\text{-}MeInd)_2ZrClMe$ 2.08 (s, 3H, Me-Ind), 1.82 (s, 3H, Me-Ind), 0.76 (s, 3H, Me-Si), 0.70 (s, 3H, Me-Si), −0.42 (s, 3H, Me-Zr). Other signals of these complexes overlapped in the corresponding spectra; the respective integral sums were used for additional checks of the results obtained in the manner described above.

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(31) The ^{1}H signal of $(Cp)_2ZrCl_2$ overlaps with aromatic signals of $(Ind)_2ZrClMe$. Therefore, the latter complex was equilibrized with $Me_2Si(Ind)_2ZrCl_2$ rather than with $(Cp)_2ZrCl_2$.