

# Alkyl exchange between aluminum trialkyls and zirconocene dichloride complexes — a measure of electron densities at the Zr center <sup>1</sup>

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## Abstract

Equilibrium constants have been determined for the formation of 15 different zirconocene monomethyl monochloro complexes from the respective dichloride complexes and  $\text{Al}_2(\text{CH}_3)_6$ . The results indicate that the tendency of a particular zirconocene complex to exchange a chloride against a methyl ligand is a measure for the electron deficiency at its Zr center. The results indicate particularly low electron densities for complexes with indenyl instead of cyclopentadienyl ligands, especially for those containing a dimethylsilyl bridge. Only one methyl group is transferred to a zirconocene dichloride even by a large excess of  $\text{Al}_2(\text{CH}_3)_6$ , while the uptake of two alkyl groups, followed by alkane evolution, is observed with triethyl and triisobutyl aluminum.

**Keywords:** Zirconocenes; Electron density; Aluminum alkyls; Methyl transfer

## 1. Introduction

Homogeneous catalyst systems based on chiral rhodium phosphine complexes are very well understood today, thanks to the paradigmatic work of Halpern and his associates [1,2]. Our understanding of zirconocene-based catalysts, e.g. for the polymerization of  $\alpha$ -olefins, is however still rather fragmentary, even though some insights have recently been gained regarding the modes of interaction of zirconocene complexes with various boron- or aluminum-containing activators [3–6] as well as the origins and limitations of stereoselective polymer-chain growth in these catalyst systems [7,8].

In order to clarify which preequilibria contribute to the activation of zirconocene complexes by alkyl–aluminum compounds, we have studied alkyl exchange reactions between aluminum trialkyls and various zirconocene dichloride complexes in hydrocarbon solutions. Of particular interest in this regard are methyl exchange reactions with trimethyl aluminum, which is an ubiquitous ingredient in the frequently employed methylalumoxane activator systems [9,10]. A further study of this methyl exchange reaction for a series of

different zirconocene complexes, should help us to understand the effects of changing ligand environments on the electron density at the Zr center, which is generally thought to be a relevant factor in zirconocene-based catalyst systems [11,12]. Electronic ligand effects are frequently difficult to separate from the associated steric effects [13–15]. In the exchange of Cl against  $\text{CH}_3$ , steric effects play only a minor role; thus ligand effects on its thermodynamics can be assumed to be essentially of electronic origin.

## 2. Experimental

Preparation of zirconocene dichloride complexes:  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$  [16],  $(\text{C}_5\text{H}_4\text{Me})_2\text{ZrCl}_2$  [17],  $(1,3\text{-C}_5\text{H}_3\text{Me}_2)_2\text{ZrCl}_2$  and  $(1,2,3\text{-C}_5\text{H}_2\text{Me}_3)_2\text{ZrCl}_2$  [18,19],  $(\text{C}_5\text{HMe}_4)_2\text{ZrCl}_2$  [20],  $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$  [21],  $(\text{C}_5\text{H}_4\text{tBu})_2\text{ZrCl}_2$  [22],  $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{ZrCl}_2$  [23],  $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$  [24,25],  $\text{Me}_4\text{C}_2\text{-}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$  [26],  $(\text{C}_5\text{H}_{10})_2\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$  [27], *rac*- $\text{Me}_2\text{Si}(\text{indenyl})_2\text{ZrCl}_2$  [28,29], *rac*- $\text{C}_2\text{H}_4(\text{indenyl})_2\text{ZrCl}_2$  [30],  $\text{Me}_2\text{Si}(2\text{-NMe}_2\text{-indenyl})_2\text{ZrCl}_2$  [31],  $\text{Me}_2\text{C}(\text{Flu})\text{-}(\text{C}_5\text{H}_4)\text{ZrCl}_2$  [32]. Trimethyl aluminum was purchased from Aldrich as a 2 M toluene solution.  $\text{AlCl}_3$  was purchased from Merck and purified by sublimation in an HCl stream. Solutions of  $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$  and  $\text{Al}_2(\text{CH}_3)_5\text{Cl}$  were prepared by mixing  $\text{Al}_2\text{Cl}_6$  and  $\text{Al}_2(\text{CH}_3)_6$  in ratios of 1:2 and 1:4, respectively, in  $\text{C}_6\text{D}_6$ .

All materials were kept and handled in a glovebox under nitrogen. NMR tubes and other glassware were dried by heat-

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<sup>1</sup> Dedicated to Professor Jack Halpern on the occasion of his 70th birthday.

ing under vacuum.  $C_6D_6$  was dried and distilled over potassium metal, degassed, condensed onto a 4 Å molecular sieve and then stored in a glovebox. For the preparation of the NMR samples, 10 mM stock solutions of the zirconocenes (5 mM for the bis-indenyl complexes), of  $Al_2(CH_3)_6$  (40 mM),  $Al_2(CH_3)_4Cl_2$  (40 mM) and  $Al_2(CH_3)_5Cl$  (200 mM) were used. To determine the equilibrium constants, samples with initial  $Al_2(CH_3)_6$ :zirconocene ratios of 1:1, 2:1, 3:1, 4:1, 5:1, 7.5:1 and 15:1 were prepared with total zirconocene concentrations ranging from 2 mM to 8 mM (4 mM for the bisindenyl complexes). In the experiments with an excess of  $Al_2(CH_3)_6$  and  $Al_2(CH_3)_5Cl$ , zirconocene concentrations varied from 2.5 to 5 mM.  $^1H$  NMR spectra of the solutions thus prepared were measured on a Bruker WM 250 spectrometer. Concentration ratios  $Q$  were determined by evaluating the integral values of the zirconocene dichloride and monomethyl monochloride species.

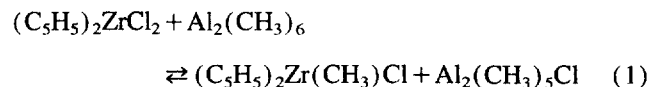
### 3. Results and discussion

When solutions of  $Al_2(CH_3)_6$  and  $(C_5H_5)_2ZrCl_2$  in  $C_6D_6$  are mixed at room temperature, the  $^1H$  NMR signals of the monomethyl complex  $(C_5H_5)_2Zr(CH_3)Cl$  appear within the time of about 5 min, required to measure the first NMR spectrum. The concentration ratio  $[(C_5H_5)_2Zr(CH_3)Cl] / [(C_5H_5)_2ZrCl_2]$  then remains constant for many hours. The fact that methyl exchange in these solutions occurs in a dynamic equilibrium was further established by the observation that exposure of  $(C_5H_5)_2Zr(CH_3)Cl$  to an excess of  $Al_2(CH_3)_4Cl_2$  leads to its partial conversion to  $(C_5H_5)_2ZrCl_2$ . While an increase in temperature to 50°C does not significantly change the final concentration ratios  $Q =$

$[(C_5H_5)_2Zr(CH_3)Cl] / [(C_5H_5)_2ZrCl_2]$ , the signals of these two species broaden noticeably at this temperature and coalesce at 115°C in a  $D_8$ -toluene solution. Furthermore, in two-dimensional NOESY experiments, we observe intense off-diagonal exchange signals which indicate an interconversion between  $(C_5H_5)_2ZrCl_2$  and  $(C_5H_5)_2Zr(CH_3)Cl$  with a rate of  $\sim 2-3 s^{-1}$  at 30°C.

When  $Al_2(CH_3)_6$  and  $(C_5H_5)_2ZrCl_2$  are mixed in a 1:1 ratio, almost equal concentrations of  $(C_5H_5)_2Zr(CH_3)Cl$  and  $(C_5H_5)_2ZrCl_2$  are present in equilibrium. The formation of  $(C_5H_5)_2Zr(CH_3)Cl$  approaches completion when  $Al_2(CH_3)_6$  is present in about a 20-fold excess (Fig. 1). Even at the highest  $Al_2(CH_3)_6$  concentrations studied, no signals assignable to the dimethyl complex  $(C_5H_5)_2Zr(CH_3)_2$  are apparent. With regard to the zirconocene species involved, an uncomplicated exchange of a single methyl group appears to occur in equilibrium with  $Al_2(CH_3)_6$ .

The aluminum chloride species which must arise in this exchange, *prima facie* e.g.,  $Al_2(CH_3)_4Cl_2$ , does not give rise to a separate  $^1H$  NMR signal, presumably because of its association and/or rapid methyl exchange with  $Al_2(CH_3)_6$ . As aluminum alkyls are known to associate via Cl bridges rather than via alkyl bridges [33], we can assume that the dominant species arising in these equilibrium systems in the presence of excess  $Al_2(CH_3)_6$ , is  $Al_2(CH_3)_5Cl$ , i.e., a complex of  $Al(CH_3)_2Cl$  with  $Al(CH_3)_3$ . The methyl exchange equilibrium should then be formulated as in Eq. (1):



This basic equilibrium will undoubtedly be superimposed by a partial association of each of the zirconocene species,

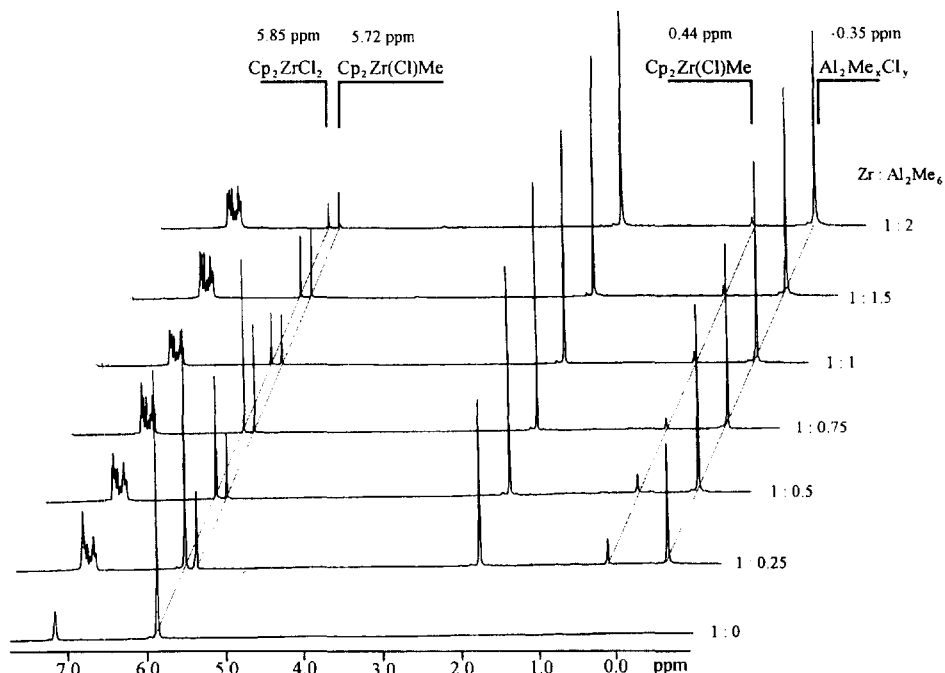
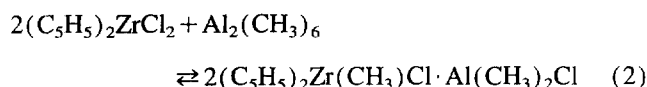


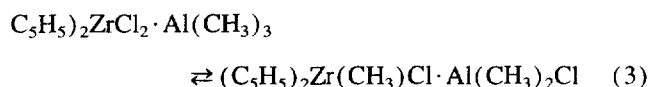
Fig. 1.  $^1H$  NMR spectra of  $C_6D_6$  solutions of  $(C_5H_5)_2ZrCl_2$  (4 mM) in the presence of increasing initial amounts of  $Al_2(CH_3)_6$  (in toluene solution).

(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl, with Al(CH<sub>3</sub>)<sub>3</sub> as well as with Al(CH<sub>3</sub>)<sub>2</sub>Cl [34,35], since the zirconocene chlorides are likely to be stronger Lewis bases than each of the aluminum methyl species. Such an association is indeed apparent from shifts in the <sup>1</sup>H and <sup>13</sup>C NMR signals of both (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl. Whereas these compounds give rise to C<sub>5</sub>H<sub>5</sub> <sup>13</sup>C NMR signals at 115.66 and 112.47 ppm, respectively, when measured as such in C<sub>6</sub>D<sub>6</sub> solution, the corresponding signals are found at 115.87 and 112.81 ppm in the equilibrium mixtures containing also Al<sub>2</sub>(CH<sub>3</sub>)<sub>5</sub>Cl and excess Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>. The occurrence of only one averaged NMR signal for each zirconocene species and its adducts precludes, in the absence of the respective limiting shift values, any determination of the degrees of association. Qualitatively, minor <sup>1</sup>H NMR shift differences of less than 0.03 ppm, compared e.g., to shift differences of ~0.3 ppm between (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and its AlCl<sub>3</sub> adduct [36], would indicate only partial association with the weaker Lewis acids Al(CH<sub>3</sub>)<sub>3</sub> and Al(CH<sub>3</sub>)<sub>2</sub>Cl.

Unfortunately, it is difficult to quantify to which degree the equilibrium in Eq. (1) is perturbed by these partial associations. In the worst case, Eq. (1) could be superseded by an essentially complete complex formation between the reaction products, i.e. between the stronger Lewis acid Al(CH<sub>3</sub>)<sub>2</sub>Cl [37] and the presumably stronger Lewis base (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl, while the initial species (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> would remain uncomplexed (Eq. (2)). This would manifest itself, however, by sizeable changes of the signal ratios of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl at any given Al:Zr ratio with total Zr concentrations, for which we cannot find any evidence.



If the initial and final species were both totally complexed, on the other hand, it is not apparent how the resulting Eq. (3) could explain the observed changes in the ratio of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> signals with excess Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>.



In the absence of sufficiently detailed information about these association equilibria and of any reasonable simplifications, we decided to resort to Eq. (1) as the simplest justifiable formulation. Apparent equilibrium constants  $K_{\text{obs}}$  were thus derived from final concentration ratios  $Q = [(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)\text{Cl}] / [(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]$ , determined at various initial concentration ratios  $I = [\text{Al}_2(\text{CH}_3)_6]_{\text{init}} / [(\text{C}_5\text{H}_5)_2\text{ZrCl}_2]_{\text{init}}$  by integration of the respective <sup>1</sup>H NMR signals. Since the use of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> as starting materials leads to equal concentrations of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl and of Al<sub>2</sub>(CH<sub>3</sub>)<sub>5</sub>Cl,  $K_{\text{obs}}$  is obtained from  $Q$  and  $I$  according to Eq. (4):

$$K_{\text{obs}} = \frac{[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)\text{Cl}] \cdot [\text{Al}_2(\text{CH}_3)_5\text{Cl}]}{[(\text{C}_5\text{H}_5)_2\text{ZrCl}_2] \cdot [\text{Al}_2(\text{CH}_3)_6]} = \frac{Q}{I \cdot (1 + 1/Q) - 1} \quad (4)$$

From concentration ratios  $Q$  of ~0.9 to 16, determined with initial ratios  $I$  ranging from 1 to 15, we obtain reasonably constant values of  $K_{\text{obs}} = 0.49 \pm 0.08$ . To check whether any perturbations of equilibrium 1 by the association of zirconocene and aluminum species will be cancelled at least in part, due to a stabilization of both sides of Eq. (1) to comparable degrees, we conducted further measurements in which (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> was exposed to a 20-fold excess of a 1:1 mixture of Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> and Al<sub>2</sub>(CH<sub>3</sub>)<sub>5</sub>Cl. Values of  $K'_{\text{obs}} = 0.74 \pm 0.06$  were obtained in this manner. Comparison with the  $K_{\text{obs}}$  values derived from the experiments described above indicates that an increasing excess of Lewis-acidic aluminum species appears to favor, to a moderate degree, the formation of the stronger Lewis base (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)Cl.

Nevertheless, we have used the basic Eq. (1) for an extension of these measurements to a series of zirconocene complexes with differently substituted and/or bridged ligand frameworks. In each case, the corresponding methyl complexes were prepared by reaction of the dichloride with one equivalent of (CH<sub>3</sub>)MgCl, to allow an unambiguous assignment of the species arising in the equilibrium mixtures. Addition of Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> always leads to a rapid, partial formation of the monomethyl complex only, which increases with increasing initial concentration ratio  $I$ .

Except for the case of the dimethylamino-substituted complex Me<sub>2</sub>Si(2NMe<sub>2</sub>-indenyl)<sub>2</sub>ZrCl<sub>2</sub>, where several days are required to reach equilibrium, methyl exchange with Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> is found again to be complete within a few minutes in all other instances. The values of  $K_{\text{obs}}$  obtained in this zirconocene series vary substantially (Table 1). Very small values ( $K_{\text{obs}} \approx 0.005$ ) are found for highly methyl-substituted complexes, [C<sub>5</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>ZrCl<sub>2</sub>, [C<sub>5</sub>H(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>ZrCl<sub>2</sub> and [C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>ZrCl<sub>2</sub>, the largest values ( $K_{\text{obs}} \approx 1$ ) for complexes with Me<sub>2</sub>Si-bridged indenyl ligands. The origins and implications of this variation in the values of  $K_{\text{obs}}$  are discussed below.

In order to compare a few related alkyl exchange reactions, we also briefly studied also reactions of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> with triethyl or with tri-isobutyl aluminum (AlEt<sub>3</sub> or Al<sup>t</sup>Bu<sub>3</sub>). In a 1:1 mixture of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrCl<sub>2</sub> and AlEt<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> solution, we observed only the monoethyl complex (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr-(CH<sub>2</sub>CH<sub>3</sub>)Cl. Analysis in analogy to Eq. (1) yields an equilibrium constant  $K_{\text{obs}} \approx 5$ . An ethyl group is thus transferred to the zirconocene about ten times more efficiently by AlEt<sub>3</sub> than a methyl group is by Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>. The less favorable stabilization of AlEt<sub>3</sub> by ethyl rather than methyl bridges, and the associated increased energy gain by formation of a Cl-bridged product Al<sub>2</sub>Et<sub>5</sub>Cl probably contribute to this observation. At higher Al:Zr ratios of 2:1 and 4:1, the <sup>1</sup>H NMR spectra of the reaction mixtures indicate the evolution of

Table 1

Equilibrium constants  $K_{\text{obs}}$  for transfer of a methyl group from  $\text{Al}_2(\text{CH}_3)_6$  to different zirconocene dichloride complexes according to Eq. (1)

	$K_{\text{obs}}$		$K_{\text{obs}}$
$(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$	0.0054(3)	$(\text{C}_5\text{H}_4^t\text{Bu})_2\text{ZrCl}_2$	0.16(2)
$(\text{C}_5\text{HMe}_4)_2\text{ZrCl}_2$	0.0056(2)	$(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{ZrCl}_2$	0.19(2)
$(\text{C}_5\text{H}_2\text{Me}_3)_2\text{ZrCl}_2$	0.0059(7)	$\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$	0.22(3)
$(\text{C}_5\text{H}_3\text{Me}_2)_2\text{ZrCl}_2$	0.041(7)	$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	0.49(4)
$(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$	0.076(9)	$\text{Me}_2\text{C}(\text{Flu})(\text{C}_5\text{H}_4)\text{ZrCl}_2$	0.66(5)
$(\text{C}_5\text{H}_{10})_2\text{C}_2(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$	0.10(1)	$\text{rac-Me}_2\text{Si}(2\text{-NMe}_2\text{-ind})_2\text{ZrCl}_2$	0.72(3)
$(\text{C}_5\text{H}_4\text{Me})_2\text{ZrCl}_2$	0.13(3)	$\text{rac-C}_2\text{H}_4(\text{ind})_2\text{ZrCl}_2$	1.0(2)
		$\text{rac-Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2$	1.2(3)

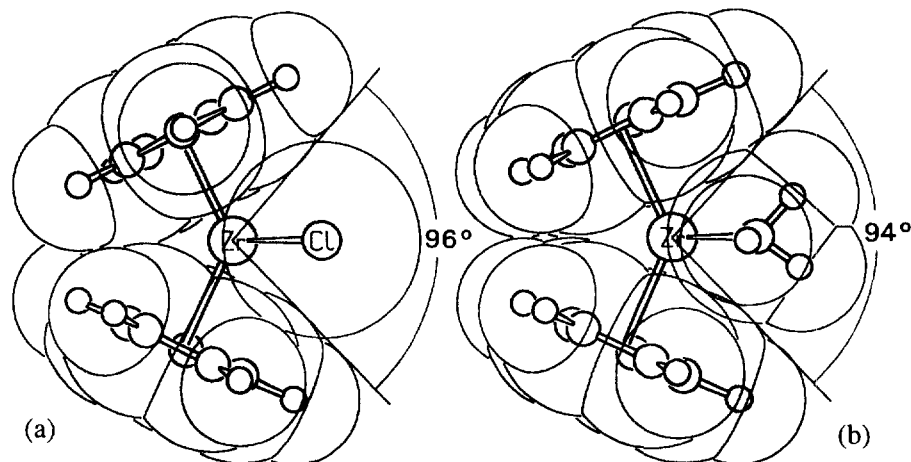


Fig. 2. Molecular structures and van der Waals outlines for  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$  ((a), Ref. [41]) and for  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$  ((b), Ref. [42]). Coordination gap apertures of 96 and 94°, respectively, indicate a slightly smaller effective size for  $\text{CH}_3$  than for Cl ligands.

ethane and the formation of an additional zirconocene species, presumably the ethene complex  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{C}_2\text{H}_4)$  [38]. With  $\text{Al}^i\text{Bu}_3$ , uptake of two alkyl groups and formation of a decomposition product are observed, together with some monoalkyl complex, already at an Al:Zr ratio of 1:1. In these systems, the occurrence of irreversible reactions precludes the determination of any equilibrium constants.

#### 4. Conclusions

Alkyl exchange equilibria between aluminum alkyls and zirconocene complexes are clearly quite sensitive to the structure of either reactant [39,40]. In general, steric and electronic contributions will affect the position of such an exchange equilibrium. For the methyl transfer from  $\text{Al}_2(\text{CH}_3)_6$  to the zirconocene dichloride complexes studied here, steric ligand effects on the values of  $K_{\text{obs}}$  given in Table 1 can be assessed from the relative steric demands of Cl and  $\text{CH}_3$  ligands bound to a  $(\text{C}_5\text{H}_5)_2\text{Zr}$  unit. From the crystal structures of  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$  [41] and  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$  [42] (Fig. 2), it is apparent that the  $\text{C}_5\text{H}_5$  rings are in close repulsive contact with each other, and with the Cl and  $\text{CH}_3$  ligands in both complexes. The relative spatial requirements of these ligands will thus be manifested by the 'openness' of the  $(\text{C}_5\text{H}_5)_2\text{Zr}$  wedge. Coordination gap apertures

[43] of 96 and 94°, measured for  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$  and  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$ , respectively (Fig. 2), indicate that a  $\text{CH}_3$  ligand has a slightly smaller effective size than a Cl ligand. However, compared to changes in coordination gap apertures of other zirconocene complexes [43], the difference between 96 and 94° is rather minute. We can thus assume that steric contributions to the ligand effects considered here are of minor significance and that these ligand effects are primarily of electronic origin.

A synopsis of free enthalpy changes,  $\Delta G_{\text{obs}}^\circ = -RT \ln K_{\text{obs}}$ , associated with methyl transfer from  $\text{Al}_2(\text{CH}_3)_6$  to different zirconocene complexes according to Eq. (1) (Fig. 3) reveals an increase of  $\Delta G_{\text{obs}}^\circ$  with increasing numbers of alkyl or silyl substituents at the  $\text{C}_5$ -ring ligands, which are known, from electron microscopy for chemical analysis (ESCA) data of substituted zirconocenes [44,45], to increase the electron density at the Zr center. Decreased electron density at the Zr center of a zirconocene dichloride complex thus appears to favor uptake of a methyl group. This notion is in line with the general rule that the more electronegative metal is the favored alkyl recipient in halide/alkyl exchange between two metal centers [46,47]. Related electronic ligand effects have been briefly noted also for reactions of  $\text{AlMe}_3$  with some titanocene dichloride complexes [48]. Our data indicate that for substituted zirconocene complexes, changes in the methyl exchange equilibrium constant  $K_{\text{obs}}$  measure, in essence, the

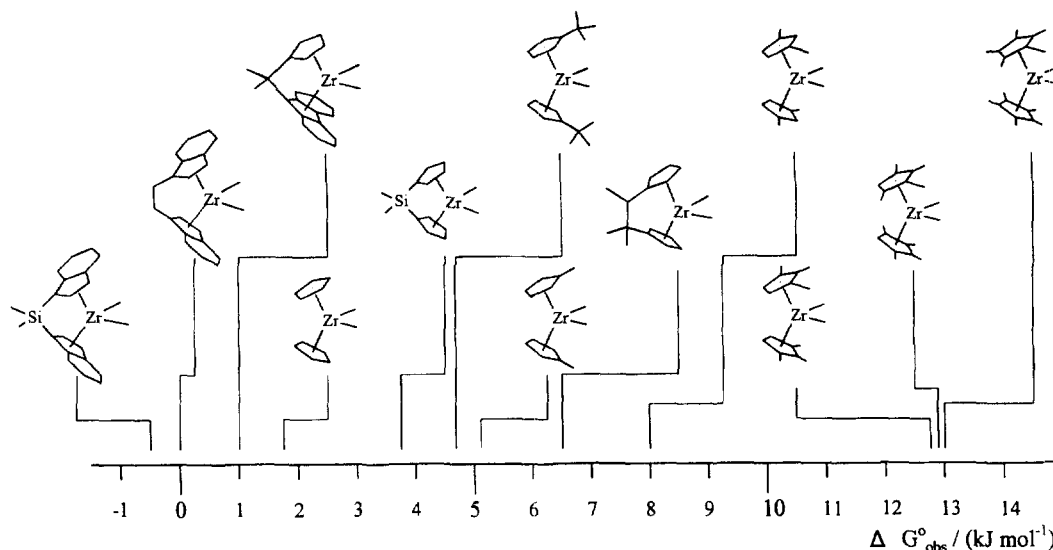


Fig. 3. Free enthalpy changes  $\Delta G_{\text{obs}}^{\circ} = -RT \ln K_{\text{obs}}$  for methyl transfer from  $\text{Al}_2(\text{CH}_3)_6$  to different zirconocene dichloride complexes according to Eq. (1).

electron density at the Zr center, induced by different ligand structures.

Some deviations of the data in Fig. 3 from the expected electron density trends might be explained by steric effects. Indeed, upon introduction of up to three methyl substituents at each  $\text{C}_5$  ring,  $\Delta G_{\text{obs}}^{\circ}$  values increase in the expected manner, by increments of  $\sim 3\text{--}5 \text{ kJ mol}^{-1}$  for each methyl group. However, for the last three members in this series —  $(\text{C}_5\text{H}_2\text{Me}_3)_2\text{ZrCl}_2$ ,  $(\text{C}_5\text{HMe}_4)_2\text{ZrCl}_2$  and  $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$  — we find  $\Delta G_{\text{obs}}^{\circ}$  values which are practically identical within limits of error. Apparently, the tightening of the zirconocene wedge, which manifests itself by a reduction of the coordination gap aperture to only  $55^\circ$  in  $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$  [43], favors the introduction of the slightly smaller ligand,  $\text{CH}_3$ , to a degree sufficient to offset the disfavoring electronic effects of the additional methyl substituents. Additional (though presumably minor) contributions might also be due to different degrees of steric shielding of the  $\text{Zr}(\text{CH}_3)\text{Cl}$  fragment vis-à-vis a stabilizing association with excess aluminum Lewis acid, caused by different ligand structures.

At any rate, the data in Fig. 3 indicate relatively low electron densities for zirconocene complexes with bridged indenyl ligands. This assessment is in line with the general notion that indenyl ligands have a tendency to donate  $\pi$  electrons to the metal less efficiently than cyclopentadienyl ligands, as manifested by the increased tendency of indenyl ligands to slip toward  $\eta^3$  coordination [49]. Among the ring-bridged representatives of this class of complexes, a dimethyl silanediyl bridge appears to induce a lower electron density than an ethanediyl bridge. This observation, which is not in line with electronegativity considerations, might be the cause of the stronger interference of the short  $\text{Me}_2\text{Si}$  bridge with a placement of the indenyl ligands. This would allow for optimal overlap of their  $\pi$  orbitals with suitable metal acceptor orbitals.

It is tempting to speculate that this high electron deficiency of zirconocene complexes with  $\text{Me}_2\text{Si}$ -bridged indenyl

ligands might be associated with their exceptional activity as catalysts for the polymerization of  $\alpha$ -olefins [50]. These catalyst systems must be activated by methylalumoxane (MAO) or other Lewis-acidic activators, however. A different type of ligand exchange — the replacement of a suitably sequestered alkyl anion for a neutral olefin ligand — thus appears to govern catalyst activities. To which degree such a pre-equilibrium follows similar trends as that represented by Eq. (1), and in which way, different  $\sigma$  and  $\pi$  contributions affect the affinity of a particular ligand for the Zr center of a given zirconocene complex, and, finally, which steric effects are superimposed to these electronic considerations in the case of large MAO- or borane-sequestered anions, remains to be investigated by similar studies on appropriate zirconocene model reactions.

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