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Cyclic voltammetry of methyl- and trimethylsilyl-substituted zirconocene dichlorides

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Abstract

Redox properties of the substituted zirconocene dichlorides: $(C_5H_{5-n}Me_n)_2$ $ZrCl_2$ ($n=0$–5), $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ ($n=0$–3), $[C_5Me_4(SiMe_3)](C_5HMe_4)ZrCl_2$ and two *ansa*-analogues $Me_2Si(C_5H_4)_2ZrCl_2$ and $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ were investigated by cyclic voltammetry on a mercury electrode in tetrahydrofuran. In the $(C_5H_{5-n}Me_n)_2ZrCl_2$ ($n=0$–4) compounds, standard electrode potential ($E°$) of the one-electron uptake shifts to more negative values by 0.071 V per one methyl group. A deviation from this linear dependence to a less negative $E°$ is observed for $(C_5Me_5)_2ZrCl_2$. This effect is attributed to the steric hindrance between rotating C_5Me_5 ligands which tends to decrease the angle between the cyclopentadienyl ring planes (ϕ) and consequently, the energy difference between MO frontier orbitals. In the trimethylsilylated compounds, the net effect of $SiMe_3$ is negligible, giving virtually the same value of $E°$ for $n=0$–3. In μ-$SiMe_2$-bridged *ansa*-compounds the difference in $E°$ of 147 mV corresponds to the negative shift of 37 mV per one $SiMe_3$ group. Owing to the rigid angle ϕ, this shift can be tentatively accounted for the electronic effect of the $SiMe_3$ groups. In the non-*ansa*-compounds, the negative shift due to the electronic effect of $SiMe_3$ groups is assumed to be roughly compensated by a positive shift resulting from a sterically controlled diminution of ϕ. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Substituted zirconocene dichlorides; *ansa*-Zirconocene dichlorides; Cyclic voltammetry; Methyl and trimethylsilyl substituents; Steric effect; Electronic effect

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1. Introduction

In search for versatile, highly stereospecific olefin polymerization metallocene catalysts based on early transition metals, attention has been focused on the modification of cyclopentadienyl ligands by various substituents. So far, in the most widely used Cp'_2MCl_2 (Cp′ = substituted cyclopentadienyl ligand; M = Ti, Zr and Hf)-methylalumoxane (MAO) systems, a variety of metallocene components containing simply substituted cyclopentadienyl rings (identical or different), cyclopentadienyl rings fused with aromatic or saturated cyclic substituents, and rigidly bridged *ansa*-metallocenes containing the above Cp′ ligands are synthetically accessible [1]. The Cp′ ligands influence the properties of catalytic complexes [2] through their electronic and steric effects at the metal centre [3]. The steric control of the catalyst stereospecificity lies in the shaping of co-ordination space at the metal atom whereas the catalyst activity in the polymerization reaction should be governed by the Lewis acidity of the metal [4]. Although modifications of cyclopentadienyl ligands simultaneously change both the steric and electronic effects a rational design of new catalysts requires an approach in which the electron density at the metal and the shape of a co-ordination space can be predicted.

Concerning electronic effects, that of the methyl substituent is well established: the electron density at the metal generally increases with increasing number of Me

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groups at the cyclopentadienyl ligands. In methyl-substituted zirconocene dihalides $(C_5H_{5-n}Me_n)_2ZrCl_2$ $(n = 0–5)$ such trends were observed in shifts of electrochemical oxidation potentials and shifts of binding energies of inner shell electrons (for $n = 0$ and 5) (Ref. [5]), in ^{91}Zr down-field chemical shift $(n = 0, 1, 5)$ (Ref. [6]), and in a down-field chemical shift of acetylenic carbon atoms in ^{13}C-NMR spectra of $(C_5H_{5-n}Me_n)_2Zr(Me_3SiC{\equiv}CSiMe_3)$ $(n = 0–5)$ complexes [7]. Analogous behaviour was also found in methyl-substituted hafnocene dichlorides [8] and titanocene dichlorides [9].

On the other hand, effects of the $SiMe_3$ substituent at cyclopentadienyl ligands on electron density at the metal atom are not so unequivocal. Both electron-attracting and electron-donating effects have been experimentally observed in early transition metal metallocene derivatives, depending on evaluated property. For example, the reduction potential $(E^{red}_{1/2})$ of Cp'_2ZrCl_2 compounds increases in the series of substituents in the order $(SiMe_3)_2 < SiMe_3 < H < Me < Et$, thus qualifying the $SiMe_3$ group to be an electron acceptor with respect to hydrogen [10,11]. This corresponds to the ease of reduction of the $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ compounds, increasing in the order of n $0 < 1 < 2$ (Ref. [12]). In contrast, the binding energies of inner-shell electrons in the series of compounds $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ $(n = 0–3)$ and $[C_5H_{5-n}(SiMe_3)_n]_2HfCl_2$ $(n = 0$ and 3) indicated that the $SiMe_3$ group is a 1.25-times stronger electron donor than Me group [13]. This is compatible with values of free energies of ionization of ruthenocene complexes which show that the $SiMe_3$ group is an electron donor comparable with Me group [14].

The steric effect of Me groups in the bent $(C_5H_{5-n}Me_n)_2MCl_2$ $(M = Ti, Zr, Hf; n = 0–5)$ compounds controls to some extent the magnitude of the angle between the least-squares planes of cyclopentadienyl rings (ϕ), depending on the covalent radius of the metal. The angle ϕ is known from single-crystal X-ray diffraction measurements for many methyl-substituted titanocene [15–17], zirconocene [18,19] and hafnocene [8] dichlorides. In the series of titanocene dichlorides, the angle ϕ decreases by 4° on going from $(C_5HMe_4)_2TiCl_2$ to $(C_5Me_5)_2TiCl_2$, indicating an increased steric hindrance between the C_5Me_5 ligands. The data of Ti $(2p_{3/2})$ binding energies are known for only non- and permethylated titanocene dichlorides [21], which precludes any estimate for the steric effect. However, the first reduction standard potentials showed regular shifts to negative values with increasing number of Me groups for $n = 0–3$, whereas the values for $(C_5Me_5)_2TiCl_2$ and a number of persubstituted $(C_5Me_4R)_2TiCl_2$ $(R = \text{bulky substituent})$ compounds remarkably deviated to positive values [9]. This effect can account for a decrease in energy difference between the frontier orbitals, which is induced by the change in angle ϕ [20]. In the series of zirconocene chlorides a linear correlation of decreasing Zr $(3d_{5/2})$ binding energies with the increasing number of Me groups was found for $n = 0–5$ (Ref. [22]); however, the crystal structure of $(C_5Me_5)_2ZrCl_2$ is not known and hence, the effect of angle ϕ cannot be evaluated. In hafnocene dichlorides, the Hf $(4f_{7/2})$ binding energies decrease proportionally to the increasing number of Me groups; the steric effect is probably not involved since the CE-Hf-CE (CE, centroid of the cyclopentadienyl ring) angle is practically constant within the whole series of methylated compounds [8]. This does not apply for the series of the trimethylsilyl-substituted zirconocene compounds $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ $(n = 0–3)$ where the CE-Zr-CE angle increases with increasing n by 9° (Refs [18,23–25]). In contrast to the destabilizing effect on the Zr $(3d_{5/2})$ binding energy [13], the first reduction potential slightly shifts to positive values for $n = 1$ and 2 (Refs [10,11]), whereas it was not found at all for $n = 3$ [25].

In this work, cyclic voltammetry is used to investigate redox properties of the complete series of methylated $(C_5H_{5-n}Me_n)_2ZrCl_2$ $(n = 0–5)$, trimethylsilylated $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ $(n = 0–3)$ and $[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$ compounds in tetrahydrofuran. The study is also complemented by the investigation of two bridged $Me_2Si(C_5H_4)_2ZrCl_2$ and $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ derivatives.

2. Experimental

2.1. Chemicals

Zirconocene dichloride $(C_5H_5)_2ZrCl_2$ (Fluka) was purified by recrystallization from hot toluene. Methylated zirconocene dichlorides $(C_5H_{5-n}Me_n)_2ZrCl_2$ $(n = 1–5)$ were identical with those recently described [7]. $[C_5Me_4(SiMe_3)](C_5HMe_4)ZrCl_2$ was obtained accidentally using the cyclopentadiene consisting of a mixture of $C_5Me_4H_2$ and $C_5Me_4(SiMe_3)H$. Its composition was proved by EI-MS (VG-7070E, direct inlet) and ^1H- and ^{13}C-NMR spectra. Compounds $[C_5H_4(SiMe_3)]_2ZrCl_2$ [23], $[C_5H_3(SiMe_3)_2]_2ZrCl_2$ [24] and $[C_5H_2(Si\text{-}Me_3)_3]_2ZrCl_2$ [25] were obtained by known procedures and their purity was proved by EI-MS and ^1H- and ^{13}C-NMR spectra. *Ansa*-compound $Me_2Si(C_5H_4)_2ZrCl_2$ was obtained by the reported procedure [26]. Compound $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ was obtained as follows. Deprotonation of $C_5H_4(SiMe_3)_2$ [23] with BuLi followed by addition of 0.5 equivalents of Me_2SiCl_2 gave after workup $Me_2Si[C_5H_3(SiMe_3)_2]$ as a colourless liquid (b.p. 110°C/0.001 mmHg). Anal. Calc. for $C_{24}H_{48}Si_5$: C, 60.44; H, 10.07. Found: C, 60.10; H, 10.15. This was reacted with two equivalents of KO*t*-Bu in THF to give after workup with diethyl ether the potassium salt $Me_2Si[C_5H_2(SiMe_3)_2]K_2$. Anal. Calc. for $C_{24}H_{46}Si_5K_2$: C, 52.11; H, 8.32. Found: C, 52.0; H, 8.35. The potassium salt (6.46 g, 11.7 mmol) was refluxed with $ZrCl_4$ (2.7 g, 11.6 mmol) in toluene for 12 h under a nitrogen atmosphere. The reaction mixture was filtered, the clear solution was evaporated to dryness under vacuum and the residue was extracted with pentane. Cooling of the concentrated solution afforded $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ as white fine crystals. Yield 1.6 g (22%). Anal. Calc. for $C_{24}H_{46}Si_5ZrCl_2$: C, 45.23; H, 7.22. Found: C, 44.9; H, 7.10. EI MS (70 eV, direct inlet, 180°C; *m*/*z* (%)): 634 ($M^{\cdot +}$; 4), 627(8), 626(11), 625(26), 624(24), 623(51), 622(38), 621(67), 620(36), 619($[M-Me]^+$; 48), 305(9), 304.5(9), 304(18), 303.5(13), 303(22), 302.5(12), 302(17), 74(8), 73(100), 45(8). ^{1}H-NMR (toluene-d_8, 200 MHz, Bruker): 6.37 (4H, C_5H_2); 0.47 (36 H, $SiMe_3$); 0.29 (6H, Me_2Si).

Tetrahydrofuran (THF, Fluka) was purified by standard methods, dried by refluxing over $LiAlH_4$ and stored as a solution of dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [27]. Prior to use, THF was distilled from this solution on a vacuum line and handled by a syringe technique under argon. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Aldrich) was dried under vacuum overnight and used without further purification.

2.2. Apparatus

Voltammetric measurements were carried out in a three-electrode cell by using the EG&G PAR potentiostat/galvanostat model 273A equipped with the M270 software. The static mercury drop electrode SMDE model 1 (Laboratory Instruments, Prague) with surface area of 0.009 cm^2, the saturated silver chloride electrode separated from the solution by a salt double bridge and a platinum spiral were used as working, reference and counter electrode, respectively. All potentials in this work are referred to the standard redox potential of the ferricenium/ferrocene redox couple (0.203 V vs. saturated silver chloride electrode in water). Stock solution of 0.015 M zirconocene dichlorides was prepared by dissolving the appropriate amounts of the dried compounds in 5 cm^3 of THF. The solution was syringed into the cell containing 15 cm^3 of 0.1 M $TBAPF_6$ in THF as the base electrolyte, so that the zirconocene concentration was between 5×10^{-5} and 2×10^{-4} mol dm^{-3}.

Oxygen was removed from solutions by purging argon through the cell. All experiments were carried out at the ambient temperature of 25 ± 2°C.

3. Results and discussion

3.1. Cyclic voltammetry of $(C_5H_5)_2ZrCl_2$ and methyl-substituted zirconocene dichlorides

Fig. 1 shows the voltammetric behaviour of the complete series of methylated zirconocene dichlorides $(C_5H_{5-n}Me_n)_2ZrCl_2$ ($n = 0$–5) at the scan rate of 500 mV s^{-1}. In agreement with the literature data for Pt [10,11,28,29], mercury [29,30] and glassy carbon [31] electrodes, $(C_5H_5)_2ZrCl_2$ exhibits a single voltammetric peak. The cathodic peak current $I_{p,c}$ was found to be proportional to the $(C_5H_5)_2ZrCl_2$ concentration and to the square root of the scan rate (0.02–50 V s^{-1}). With increasing scan rate, the cathodic peak potential shifts negatively and the difference E_p between the cathodic and anodic peak potentials increases, $|E_p| = |E_{p,c} - E_{p,a}| \gtrsim 0.059$ V. Such a behaviour points to the quasi-reversible one-electron reduction of $(C_5H_5)_2ZrCl_2$ to the radical anion $[(C_5H_5)_2ZrCl_2]^-$, which is controlled by both the linear diffusion and electron transfer kinetics.

As it can be seen from Fig. 1, the methylated derivatives exhibit a similar behaviour. The corresponding cathodic peak potential $E_{p,c}$ shifts negatively with the increasing number of substituents *n*, cf. the voltammetric data summarized in Table 1. The reverse scans reveal that the stability of the reduction product $[(C_5H_{5-n}Me_n)_2ZrCl_2]^-$ decreases with increasing *n* (cf. the decreasing ratio of the anodic to cathodic peak current in Fig. 1). These changes apparently reflect the increasing rate of the chemical reaction following the electron uptake. As compared with the analogous series of titanocene dichlorides [9], the first electron uptake occurs at a potential that is about 0.9 V more negative.

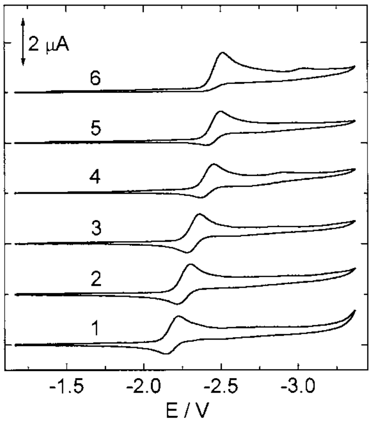

Fig. 1. Cyclic voltammograms of 2×10^{-4} mol dm^{-3} methylated zirconocene dichlorides. Curves are corrected for the background current. Curve numbers denote: 1, $(C_5H_5)_2ZrCl_2$; 2, $(C_5H_4Me)_2ZrCl_2$; 3, $(C_5H_3Me_2)_2ZrCl_2$; 4, $(C_5H_2Me_3)_2ZrCl_2$; 5, $(C_5HMe_4)_2ZrCl_2$ and 6, $(C_5Me_5)_2ZrCl_2$. Concentration 2×10^{-4} mol dm^{-3}, scan rate 500 mV s^{-1}.

Table 1
Cyclic voltammetry of zirconocenes in THF-experimental and simulated data[a]

Compound	E_P (V)	ΔE_p (V)	$I_{p,a}/I_{p,c}$	$E°$ (V)
$(C_5H_5)_2ZrCl_2$	−2.214	−0.078	−0.871	−2.158
$(C_5H_4Me)_2ZrCl_2$	−2.296	−0.085	−0.756	−2.228
$(C_5H_3Me_2)_2ZrCl_2$	−2.350	−0.114	−0.802	−2.298
$(C_5H_2Me_3)_2ZrCl_2$	−2.442	−0.114	−0.698	−2.378
$(C_5HMe_4)_2ZrCl_2$	−2.492	–[b]	–[b]	−2.438
$(C_5Me_5)_2ZrCl_2$	−2.485	–[b]	–[b]	−2.418
$[C_5H_4(SiMe_3)]_2ZrCl_2$	−2.223	−0.071	−1.000	−2.163
$[C_5H_3(SiMe_3)_2]_2ZrCl_2$	−2.208	−0.070	−0.982	−2.163
$[C_5H_2(SiMe_3)_3]_2ZrCl_2$	−2.208	−0.065	−0.931	−2.163
$[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$	−2.424	–[b]	–[b]	−2.348
$Me_2Si(C_5H_4)_2ZrCl_2$	−2.122	−0.078	−0.905	−2.068
$Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$	−2.288	−0.068	−0.946	−2.215

[a] Concentration 2×10^{-4} mol dm^{-3}; scan rate 50 mV s^{-1}; E_P, reduction peak potential; ΔE_p, difference between oxidation and reduction peak potentials; $I_{p,a}/I_{p,c}$, reduction and oxidation peak currents ratio; $E°$, standard redox potential.

[b] Without mark of oxidation.

The uptake of the second and third electrons [9] apparently remains hidden behind the negative potential limit.

Available software [32] was used to simulate the observed voltammetric behaviour by assuming an EC mechanism, similar to the reduction of substituted titanocene dichlorides [9]. The mechanistic parameters are represented by the standard potential $E°$ and the standard rate constant k_h of the electron transfer reaction, and by the rate constant k_c of the following pseudofirst-order chemical reaction. Other parameters involved were known, i.e. the zirconocene concentrations, the electrode surface area and the scan rate. The charge transfer coefficient α and the diffusion coefficient D were supposed to have their usual values of 0.5 and 10^{-5} cm^2 s^{-1}, respectively. The parameters $E°$, k_h and k_c were varied until a reasonable agreement between the simulated and experimental voltammograms was achieved. Values of the standard potentials $E°$ are summarized in Table 1.

Fig. 2 shows the effect of the number n of methyl groups in the cyclopentadienyl ligands on the standard potential $E°$. For $n=0$–4, the plot is linear with an increment of −71 mV per methyl group. The $E°$ value for $(C_5Me_5)_2ZrCl_2$ falls out of the dependence, being more positive than the value for $(C_5HMe_4)_2ZrCl_2$. The cathodic peak potential E_p measured at a low scan rate (Table 1) follows exactly the same trend as the $E°$ value. Such a behaviour resembles that of the analogous series of the methyl substituted titanocenes $(C_5H_{5-n}Me_n)_2TiCl_2$ [9]. In the latter case, the plot of $E°$ vs. n was found to be linear for $n=0$–3 with an increment of −81 mV per methyl group, and the positive deviations from this plot were observed for $n=4$ and 5, as is illustrated in Fig. 2. These deviations were ascribed to the decreasing angle between the cyclopentadienyl ring planes (ϕ), whose diminution results in lowering the energy difference between frontier orbitals [20]. Since the structural features of titanocene and zirconocene complexes are very similar, differing mainly in bond lengths to Zr and Ti atoms, e.g. Zr-CE 2.24 ± 0.05 Å, Ti-CE 2.05 ± 0.06 Å, we can assume that the steric congestion in the highly methylated zirconocene dichlorides is lower than in their titanocene analogues. It has to be noted that even highly substituted cyclopentadienyl ligands exert some rotational movement in solution, which further decreases the values of angle ϕ observed in the crystalline state. The dependences of $E°$ vs. n (Fig. 2) show that only $(C_5Me_5)_2ZrCl_2$ has its $E°$ value affected by the steric congestion, whereas in the titanocene series also $(C_5HMe_4)_2TiCl_2$ exerts some positive shift of $E°$ (cf. [9]). This explanation is corroborated by the $E°$ value for $[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$ (Table 1, Fig. 3), which falls between the $E°$ values of the methylated complexes for $n=2$ and 3. The bulky $SiMe_3$ group apparently largely lowers angle ϕ, positively shifting $E°$ by 90 mV relative to $(C_5HMe_4)_2ZrCl_2$.

The effect of the number of the methyl groups on the kinetic data is rather small yet unambiguous. Standard rate constant k_h remains approximately constant and equal to 0.008 cm s^{-1} up to $n=4$ and drops down to 0.003 cm s^{-1} for $n=5$. As indicated by the change in the peak current ratio $I_{p,a}/I_{p,c}$ (Table 1), the rate of the following chemical reaction increases with increasing n. However, the simulated voltammograms were not very sensitive to the variations in the rate constant k_c and, hence, only a rough estimate of k_c was possible. Thus,

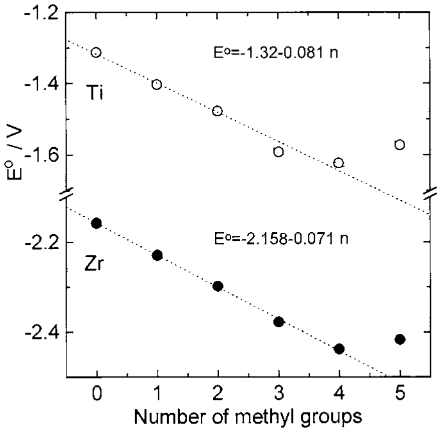

Fig. 2. Dependencies of the standard redox potential ($E°$) on the number of methyl group at the cyclopentadienyl ligands in $(C_5H_{5-n}Me_n)_2ZrCl_2$ (full circles) and $(C_5H_{5-n}Me_n)_2TiCl_2$ (open circles) compounds. Concentration 2×10^{-4} mol dm^{-3}, scan rate 50 mV s^{-1}.

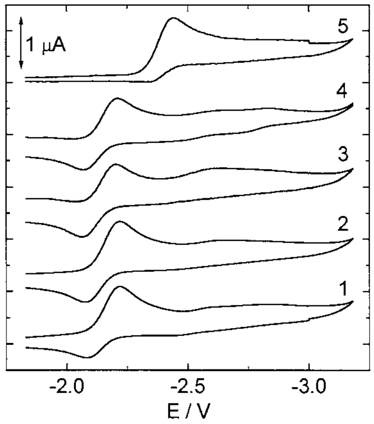

Fig. 3. Cyclic voltammograms of trimethylsilyl substituted zirconocene dichlorides. Curves numbers denote: 1, $(C_5H_5)_2ZrCl_2$; 2, $[C_5H_4(SiMe_3)]_2ZrCl_2$; 3, $[C_5H_3(SiMe_3)_2]_2ZrCl_2$; 4, $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ and 5, $[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$. Concentration 2×10^{-4} mol dm^{-3}, scan rate 500 mV s^{-1}.

hence, only a rough estimate of k_c was possible. Thus, k_c was estimated to be about 10 s^{-1} for $n = 0$–3, $k_c < 200$ s^{-1} for $n = 4$ and $k_c > 200$ s^{-1} for $n = 5$.

3.2. Cyclic voltammetry of trimethylsilyl-substituted and bridged zirconocene dichlorides

Voltammetric curves of the trimethylsilyl derivatives $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ ($n = 0$–3) are shown in Fig. 3. At high scan rates, the voltammograms resemble the curve measured for $(C_5H_5)_2ZrCl_2$. The values of E_p, $E°$, $I_{p,a}/I_{p,c}$ and k_h are listed in Table 1. Surprisingly, these compounds are reduced at the same potential, marginally more negative than $E°$ of $(C_5H_5)_2ZrCl_2$. This is in good agreement with the literature data for $[C_5H_4(SiMe_3)]_2ZrCl_2$ and $[C_5H_3(SiMe_3)_2]_2ZrCl_2$ [11], however, at variance with the report [25] that $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ is resistant toward electrochemical reduction.

Cyclic voltammograms of the bridged compounds $Me_2Si(C_5H_4)_2ZrCl_2$ and $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ are shown in Fig. 4. The former compound is reduced at a less negative potential (by 0.1 V) than $(C_5H_5)_2ZrCl_2$. This allows us to observe the second reduction peak even at high scan rates. In contrast, the value of $E°$ for $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ is slightly more negative than $E°$ of the unbridged analogue $[C_5H_3(SiMe_3)_2]_2ZrCl_2$. Similar effects of the μ-$SiMe_2$ group were observed for the *ansa*-titanocene compounds $Me_2Si(C_5H_4)_2TiCl_2$ and $Me_2Si(C_5Me_4)_2TiCl_2$ which gave the most positive and most negative values of $E°$ within the series of the methylated compounds [9]. The difference of 0.340 V between the *ansa*-titanocene compounds can be roughly assigned to a pure electronic effect of the total of eight Me substituents, giving an increment of 42 mV per Me group. In the present case, the difference of 0.147 V between $E°$ for $Me_2Si(C_5H_4)_2ZrCl_2$ and $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ can similarly be attributed to the electronic effect of four $SiMe_3$ substituents because the CE-Zr-CE angles differ negligibly (125.4° [26] against 124.7° [33]). The increment of 37 mV per $SiMe_3$ group identifies the electronic effect of the $SiMe_3$ group to be similar to the effect of the methyl group. The increments are probably even closer to each other when we take into account that the slope of linear dependences of $E°$ on the number of Me groups in the titanocene and zirconocene dichlorides (Fig. 2) is steeper by the factor 1.1 for the titanocene series. In light of these results, the equal values of $E°$ for the $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ ($n = 1$–3) compounds imply that the electronic effect of $SiMe_3$ groups is fully compensated by their steric effect arising from the diminution of angle ϕ. Although angles between rotating cyclopentadienyl rings are not known, the magnitudes of the CE-Zr-CE angles for $(C_5H_5)_2ZrCl_2$ 129.5° [34], $[C_5H_4(SiMe_3)]_2ZrCl_2$ 129.1° [23], $[C_5H_3(SiMe_3)_2]_2ZrCl_2$ 131.4° [24] and $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ 135.4° [25] indicate that angle ϕ may regularly increase with the increasing number of $SiMe_3$ groups. Apparently, the bulkiness of $SiMe_3$ group induces the steric congestion between the rotating cyclopentadienyl rings at low numbers n, whereas the effect of Me groups is remarkable only for $n = 5$ in the case of Zr and for $n = 4$ and 5 in the case of Ti [9]. It also precludes the formation of highly trimethylsilylated zirconocene [25] and titanocene [35] dichlorides ($n = 4$ and 5).

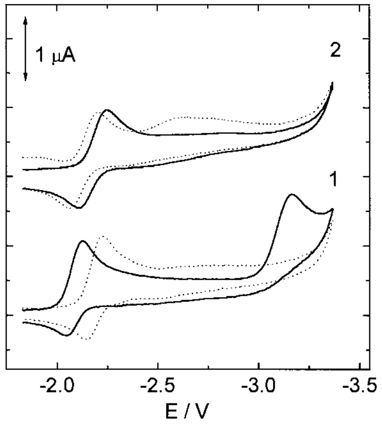

Fig. 4. Cyclic voltammograms of *ansa*-zirconocenes (full lines) and their unbridged analogues (dotted lines). Full lines: 1, $Me_2Si(C_5H_4)_2ZrCl_2$ and 2, $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$; dotted lines: 1, $(C_5H_5)_2ZrCl_2$ and 2, $[C_5H_3(SiMe_3)_2]_2ZrCl_2$. Concentration 2×10^{-4} mol dm^{-3}, scan rate 500 mV s^{-1}.

4. Conclusions

Standard reduction potentials for the $(C_5H_{5-n}Me_n)_2ZrCl_2$ ($n = 0–5$) compounds and $[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$ corroborate the recent proposal made for analogous titanocene compounds that diminution of the dihedral angle between the rotating cyclopentadienyl rings. induces shifts of first reduction standard potentials to the positive side. The positive shifts of $E°$ occur for $(C_5Me_5)_2ZrCl_2$ and $[C_5Me_4(SiMe_3)][C_5HMe_4]ZrCl_2$ where angle ϕ is expected to be diminished due to steric congestion in the bent zirconocene structure. The electronic and steric effects on $E°$ values have been identified in the $[C_5H_{5-n}(SiMe_3)_n]_2ZrCl_2$ ($n = 1–3$) compounds, their magnitudes being roughly equal and oppositely directed. The electronic effect of $SiMe_3$ groups was established using a pair of *ansa*-compounds $Me_2Si(C_5H_4)_2ZrCl_2$ and $Me_2Si[C_5H_2(SiMe_3)_2]_2ZrCl_2$ where virtually equal fixed angles ϕ eliminate the presence of the steric effect. The explanation of voltammetric behaviour of the above bent metallocene dichlorides is only tentative as neither the values of angle ϕ are experimentally accessible nor the dependencies of frontier orbital energies on ϕ are reliable and accurate enough. The results can, however, serve as a clue to understanding the controversial results of various physico–chemical measurements on bent metallocene compounds where steric effects may interfere with electronic effects.

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