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Substituent effects in cyclic voltammetry of titanocene dichlorides

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Abstract

Methyl-substituted titanocene dichlorides $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n=0$–5), $[C_5Me_4(SiMe_3)]_2TiCl_2$, $(C_5Me_4Ph)_2TiCl_2$ (Ph = phenyl), $[C_5Me_4(FPh)]_2TiCl_2$ (FPh = *para*-fluorophenyl), $[C_5Me_4(CH_2Ph)]_2TiCl_2$ and *ansa*-compounds $Me_2Si(C_5H_4)_2TiCl_2$ and $Me_2Si(C_5Me_4)_2TiCl_2$ were investigated by means of cyclic voltammetry at a mercury electrode in tetrahydrofuran. The standard potential (E°_1) of the first electron uptake shifts to more negative values proportionally to the number of methyl groups in the $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n=0$–3) compounds, with an increment of 0.093 V per one methyl group. A decline from this linear dependence is observed for $(C_5HMe_4)_2TiCl_2$ and a positive shift for $(C_5Me_5)_2TiCl_2$. The $[C_5Me_4(R)]_2TiCl_2$ (R = $SiMe_3$, Ph, FPh and CH_2Ph) compounds show even larger positive shifts of E°_1. These positive shifts can be brought about by a steric strain between the cyclopentadienyl ligands which lowers the dihedral angle between cyclopentadienyl ring planes (ϕ) and thus decreases energies of bent titanocene $1a_1$ and b_2 LUMO orbitals. This opinion is corroborated by the voltammetry of *ansa*-compounds $Me_2Si(C_5H_4)_2TiCl_2$ and $Me_2Si(C_5Me_4)_2TiCl_2$, having a large and fixed angle ϕ. Their E°_1 values are close to those of $(C_5H_5)_2TiCl_2$ and $(C_5HMe_4)_2TiCl_2$, respectively. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Substituted titanocene dichlorides; Cyclic voltammetry; Substituent effects

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1. Introduction

Bent sandwich metallocene dichlorides of Group 4B elements (Ti, Zr, Hf) combined with aluminium alkyls or methylalumoxane (MAO) are frequently used homogeneous catalysts for α-olefin polymerization. Due to the outstanding steric and electronic versatility of the cyclopentadienyl-based ligands, metallocene catalysts produce polyolefins with a broad range of molecular weights, compositions and microstructures. The catalyst properties are finely tuned by electron donating/withdrawing and steric effects of the substituents attached to the cyclopentadienyl ligands [1–3]. Particularly, the effect of methyl group(s), which increases electron density at the metal center, has been investigated by various spectroscopic, physico-chemical and chemical methods with the aim to effectively design new catalyst systems. Electron spectroscopy for chemical analysis (ESCA) measurements revealed that replacement of cyclopentadienyl by permethylcyclopentadienyl ligands in the metallocene dihalide series $(C_5H_{5-n}Me_n)_2MX_2$ ($n=0$, 5) (M = Ti, Zr, Hf) (X = F, Cl, Br) results in the decrease of binding energies of the inner shell metal ($2p_{3/2}$) electrons by ca. 0.8 eV [4]. The Zr ($3d_{5/2}$) binding energies in the $(C_5H_{5-n}Me_n)_2ZrCl_2$ compounds show a linear decrease with increasing n for $n=0$–5, with the increment of 0.13 eV per one Me group [5]. A thorough study was carried out on the series of methyl-substituted hafnocene dichlorides [6]. The Hf (4f) binding energies were decreasing proportionally to the number of Me substituents and the increment per one methyl group was 0.06 eV. The parallel X-ray structural determination revealed no significant change in angles between the planes of cyclopentadienyl rings ϕ (ϕ 130.5° for $n=0$ and 129.8° for $n=5$) [6]. Similar dependences

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for valence electron energies were obtained by ultraviolet photoelectron spectroscopy (UPS) in the series of $(C_5H_{5-n}Me_n)_2TiCl_2$ [7] and $(C_5H_{5-n}Me_n)_2TiCl$ [8] ($n = 0–5$) compounds. The former compounds showed a deviation from the linear dependence for $n = 5$, whereas the less sterically congested monochlorides gave a monotonous dependence of binding energies. Chemical shifts in the ^{49}Ti- and ^{47}Ti-NMR [9,10] and ^{91}Zr-NMR spectra [11] also closely correlate with the electron density at the metal nucleus; moreover, the linewidth of signals brings information on the ligand field symmetry around the metal atom [11].

An increase in the electron density on the metal induced by Me groups is likely to be responsible for a decrease in the rate constants of the chemical reduction of $(C_5H_{5-n}Me_n)TiCl_3$ ($n = 0–5$) compounds by Et_2AlCl yielding $(C_5H_{5-n}Me_n)TiAl_2Cl_{8-x}Et_x$ ($n = 0–5$; $x = 0–4$) complexes [12]. The rate constants decrease within the whole series of compounds ($n = 0–5$). The affinity to coordinate THF in the series of $(C_5H_{5-n}Me_n)_2TiCl$ [13] and $(C_5H_{5-n}Me_n)_2Zr(Me_3SiC{\equiv}CSiMe_3)$ ($n = 0–5$) compounds decreases with the increasing n and becomes negligible for the permethylated compounds [14]. On the other hand, the steric congestion apparently plays the key role in an enzyme-like selectivity of the head-to-tail dimerization of terminal acetylenes catalyzed by permethyltitanocene derivatives [15,16].

Among electrochemical methods, the cyclic voltammetry has been largely used to study the substituent effects. Lowering of the oxidation potential upon introduction of permethylcyclopentadienyl ligand(s) into the $(C_5H_{5-n}Me_n)_2MX_2$ ($n = 0$ or 5) (M = Ti, Zr, Hf) (X = F, Cl, Br) compounds is not associated with the central atom as the electron is released from HOMO localized over the cyclopentadienyl ligands [3]. The electrochemical reduction of non-substituted parent metallocene dihalides Cp_2MX_2 (M = Ti, Zr) and their alkyl derivatives Cp_2MR_2 has been the subject of numerous works [17–22]. Series of mono- and di-substituted titanocenes and zirconocenes have been recently investigated in an attempt to correlate their electrochemical behaviour with inductive and steric properties of the substituents [23]. However, none of the studies deals with a complete series of substituted titanocenes. The electrochemical data for the bridged and non-bridged metallocene derivatives are also absent although some differences in their reactivity are known [24,25].

In this work cyclic voltammetry is used to study electronic and steric effects of methyl substituents in a complete series of methyl-substituted titanocene dichlorides. The effects of substituents R in the $(C_5Me_4R)_2TiCl_2$ (R = $SiMe_3$, CH_2Ph, Ph and FPh) compounds and the effect of the dimethylsilylene bridge in representative *ansa*-compounds are also investigated.

2. Experimental

2.1. Chemicals

Tetrahydrofuran (THF) (Fluka) as a non-aqueous solvent was employed. It was purified by standard methods, dried by refluxing over $LiAlH_4$ and stored as a solution of the dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [26]. Immediately before use it was distilled on a vacuum line and handled by a syringe technique under argon. Tetrabutylammonium hexafluorophosphate (Aldrich) was dried up under high vacuum overnight. Titanocene dichloride $(C_5H_5)_2TiCl_2$ (Fluka) was purified by recrystallization from hot toluene. All other complexes were prepared as described elsewhere: $(C_5H_4Me)_2TiCl_2$ [27], $(C_5H_3Me_2)_2TiCl_2$ (1,3-dimethyl) [28], $(C_5H_2Me_3)_2TiCl_2$ (1,2,3-trimethyl), $(C_5HMe_4)_2TiCl_2$ and $(C_5Me_5)_2TiCl_2$ [12], $[C_5Me_4(SiMe_3)]_2TiCl_2$ [29], $(C_5Me_4Ph)_2TiCl_2$ (Ph = phenyl) [30], $Me_2Si(C_5H_4)_2TiCl_2$ [31], and $Me_2Si(C_5Me_4)_2TiCl_2$ [31,32]. $[C_5Me_4(CH_2Ph)]_2TiCl_2$ and $[C_5Me_4(FPh]_2TiCl_2$ (FPh = *para*-fluorophenyl) were obtained analogously to $(C_5Me_4Ph)_2TiCl_2$ [31]. The corresponding cyclopentadienes were prepared from 2,3,4,5-tetramethylcyclopent-2-enone and *p*-fluorophenyl Grignard reagent in THF (Aldrich) or benzyl Grignard reagent which was prepared from benzyl chloride and Mg in diethyl ether. The dehydration of alcohols was induced by iodine. The cyclopentadienes were dried by Na_2SO_4 and distilled in a dynamic vacuum of oil rotary pump. Yield of $[C_5Me_4(CH_2Ph)]_2TiCl_2$ was 55%. EI-MS (direct inlet, 70 eV, 185°C): 540 ($M^{+\bullet}$; 0.6), 508(6), 507(16), 506(15), 505 ($[M–Cl]^+$; 34), 333(15), 332(18), 331(69), 330(37), 329(100), 328(23), 327(11), 296(21), 295(20), 294(53), 293(22), 292(9), 212(18), 211(64), 210(10), 197(7), 196(20), 195(13), 181(16), 180(11), 179(9), 178(7), 165(14), 133(9), 121(7), 119(20), 105(11), 91(37), 77(9), 41(11). ^{1}H-NMR: δ 1.81, 1.96 (2 × s, 6H, *Me*$_4$C$_5$); 4.03 (s, 2H, C*H*$_2$), 6.90–7.11 (m, 5H, Ph). ^{13}C-NMR: δ 12.8, 13.7 (*Me*$_4$C$_5$), 34.2 (*C*H$_2$), 126.2 (Ph, *C*H), 130.6 (Ph, C_{ipso}), 128.4, 128.7 (Ph, *C*H); 129.2, 131.5 (Me$_4$C$_5$, *C*–Me); 140.7 (Me$_4$C$_5$, *C*–CH$_2$).

Yield of $[C_5Me_4(FPh)]_2TiCl_2$ was 43%. EI-MS (direct inlet, 70 eV, 190°C): 548($M^{+\bullet}$; 1.7), 515(12), 514(11), 513($[M–Cl]^+$; 26), 335(15), 334(7), 333(22), 300(9), 299(11), 298(24), 297(18), 296(5), 216(22), 215(100), 200(8), 199(7), 185(8), 184(7), 183(9), 165(7), 109(6), 91(7), 55(9), 41(8). ^{1}H-NMR: δ 1.72, 1.95 (2 × s, 6H, *Me*$_4$C$_5$); 6.70–6.85 (m, 4H, C$_6$*H*$_4$). ^{13}C-NMR: δ 13.6, 14.1 (*Me*$_4$C$_5$); 115.0 (d, $^2J_{FH} = 21$ Hz, C$_6$H$_4$F γ-*C*H), 122.6 (Me$_4$C$_5$, *C*–Me), 130.6 (d, $^4J_{FH} = 4$ Hz, C$_6$H$_4$F α-*C*H), 130.9 (Me$_4$C$_5$, *C*–Me), 132.3 (d, $^3J_{FH} = 8$ Hz, C$_6$H$_4$F β-*C*H), 162.0 (d, $^1J_{FH} = 247$ Hz, C$_6$H$_4$F δ-*C*F); *C*–C$_6$H$_4$F not found.

2.2. Cyclic voltammetry

The electrochemical instrumentation consisted of an EG&G PAR potentiostat/galvanostat model 273A equipped with the M270 software. The cell was a three-electrode type with a saturated silver chloride reference electrode separated from the solution by a salt double bridge. Potentials were related to the standard redox potential of ferricenium/ferrocene couple (0.203 V against sat. Ag/AgCl in water), which was taken as a reference zero potential. A Pt spiral served as a counter electrode. A static mercury drop electrode SMDE model 1 (Laboratory Instruments, Prague) with surface area 0.009 cm^2 was used as a working electrode. The EG&G PAR Condecon 710 software and the developmental simulation software [33] were used for the simulation of electrochemical reduction mechanism. Tetrabutylammonium hexafluorophosphate (Aldrich) was used as an electrolyte in THF at 10^{-1} mol dm^{-3} concentration. Stock solutions of the titanocene dichlorides at the 1.5×10^{-2} mol dm^{-3} concentration were prepared by dissolving the appropriate amounts of dried compounds in 5 cm^3 of the solvent. They were syringed into the cell containing 15 cm^3 of the electrolyte to give a required concentration in the range of 5×10^{-5}–2×10^{-4} mol dm^{-3}. Each complex was voltammetrically investigated within the potential window from −0.835 V to −3.335 V. The potential scan rates were varied from 20 mV s^{-1} to 50 V s^{-1}. All experiments were carried out at 25°C in the absence of oxygen. A dry argon was bubbled through the solution in the cell before measurements and passed through the cell during measurements.

3. Results and discussion

3.1. Reduction of $(C_5H_5)_2TiCl_2$

In accordance with electrochemical data obtained at the dropping mercury [17,23], platinum [17,25], and glassy carbon [17,19] electrodes in THF, three reduction peaks are observed at −1.325, −2.533 and −2.932 V (see Table 1 and Fig. 1). The height of the first peak is proportional to the titanocene concentration and to the square root of the scan rate. With the increasing scan rate, the peak potential shifts negatively and the peak potential difference increases, cf. Fig. 1. Such a behaviour points to the quasi-reversible electrode process, which is controlled by both the linear diffusion and electron transfer kinetics. At low scan rates, the second electron transfer gives rise to a wave, which is typical for a catalytic reaction. However, the wave is distorted by a current drop at more negative potentials, probably due to a passivation of the electrode surface by a reduction product. Towards higher scan rates, both catalytic and passivation effects cease and a quasi-reversible behaviour is recovered, cf. Fig. 1. The third voltammetric peak exhibits similar features.

Table 1
Experimental data taken from cyclic voltammograms of titanocenes in THF[a]

Compound	E_{PR1}[b] (V)	E_{PR2} (V)	E_{PR3} (V)
$(C_5H_5)_2TiCl_2$	−1.325	−2.533	−2.935
$(C_5H_4Me)_2TiCl_2$	−1.421	−2.581	−2.977
$(C_5H_3Me_2)_2TiCl_2$	−1.499	−2.635	−3.059
$(C_5H_2Me_3)_2TiCl_2$	−1.609	−2.703	−3.113
$(C_5HMe_4)_2TiCl_2$	−1.639	−2.727	−3.177
$(C_5Me_5)_2TiCl_2$	−1.621	−2.663	−3.279
$[C_5Me_4(SiMe_3)]_2TiCl_2$	−1.515	−2.517	−3.151
$(C_5Me_4Ph)_2TiCl_2$	−1.468	−2.461	−3.169
$[C_5Me_4(PhF)]_2TiCl_2$	−1.464	−2.436	−3.116
$[C_5Me_4(CH_2Ph)]_2TiCl_2$	−1.519	−2.546	−3.180
$Me_2Si(C_5H_4)_2TiCl_2$	−1.295	−2.519	—[c]
$Me_2Si(C_5Me_4)_2TiCl_2$	−1.641	−2.599	−2.879

[a] Concentration, 2×10^{-4} mol dm^{-3}; scan rate, 500 mV s^{-1}.

[b] $E_{PR1,2,3}$, first, second and third reduction peak potentials.

[c] Third peak behind the potential window limit.

The above observations suggest that a simple reaction scheme involving three successive one-electron transfer steps [17] can be modified by considering the chemical oxidation of the electrochemically reduced species by a mediator $M_{1,2,3}$ (a catalytic reaction) and their chemical deactivation (a successive reaction) yielding the product $P_{1,2,3}$, which both follow each electron transfer step (Scheme 1). Unfortunately, the nature of species involved in these chemical steps is mostly a matter of speculation. They can comprise the traces of oxygen and water present in the solvent or the electrolyte, or their decomposition products. So far, only the species $(C_5H_5)_2TiCl(THF)$ [21] and $[(C_5H_5)_2TiCl]^-$ [17] have been identified as the products P_1 and P_2, both of which are connected with the halogen cleavage.

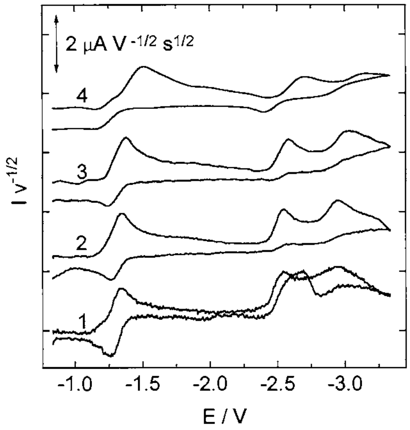
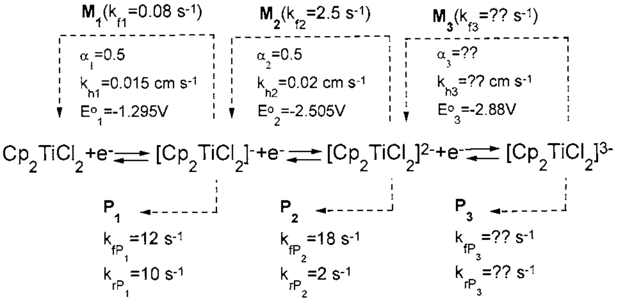


Fig. 1. Cyclic voltammograms of $(C_5H_5)_2TiCl_2$ corrected for the background current and normalized to unit scan rate. Curve numbers denote original scan rate: 1, 50 mV s^{-1}; 2, 500 mV s^{-1}; 3, 5 V s^{-1}; and 4, 50 V s^{-1}. Concentration, 2×10^{-4} mol dm^{-3}.



Scheme 1. Reaction scheme of titanocenes reduction. Symbols denote: α_n, electron transfer coefficient; k_{h_n}, heterogeneous rate constant; E°_n, standard redox potential; M_n, catalytic mediator; k_{f_n}, catalytic forward rate constant; P_n, coupled chemical reaction product; k_{fP_n} and k_{rP_n}, coupled chemical reaction forward and reverse rate constant. Subscript n stands for the first, second and third electron transfer, respectively. Numerical values represent simulated data obtained for $(C_5H_5)_2TiCl_2$.

This reaction scheme is corroborated by numerical simulation of cyclic voltammograms. Both the catalytic and successive chemical reactions were considered to be the pseudo-first order reactions. Some of the parameters involved were known, namely the titanocene 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 standard redox potential E°, the rate constant of the heterogeneous electron transfer k_h, the catalytic forward rate constant k_f and chemical forward and reverse rate constants k_{fP} and k_{rP} were varied until a reasonable agreement between the simulated and experimental voltammograms was achieved. Only the first, or the first and second reduction peaks were simulated, because simulations comprising the third electron transfer step would involve too many variables. The experimental and simulated curves at different scan rates normalized to unit scan rate are shown in Fig. 2. The optimized kinetic parameters for the first two electron transfers are given in Scheme 1. Owing to the possible strong effects of impurities, the simulated kinetic data should be considered as the estimates having mainly comparative validity. For instance, the data prove that products of subsequent uptake of electrons are more reactive since the rate of coupled chemical reactions increases with the number of accepted electrons. Besides, the proposed reaction scheme enables additional comparative description of the other substituted titanocene derivatives.

3.2. Reduction of methyl-substituted titanocene dichlorides

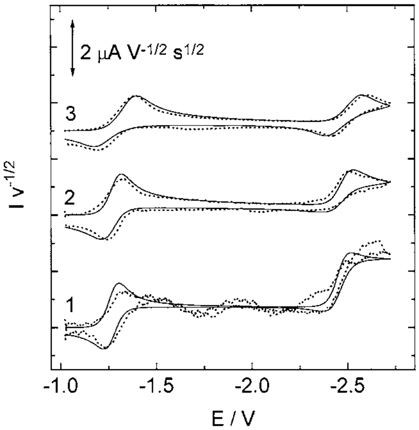


Fig. 2. Simulated (solid line) and real (dotted line) voltammograms of $(C_5H_5)_2TiCl_2$ within the two electron transfer potential range obtained at scan rates 20 mV s^{-1} (curve 1), 200 mV s^{-1} (curve 2) and 20 V s^{-1} (curve 3). Curves are normalized to unit scan rate. Concentration, 2×10^{-4} mol dm^{-3}.

The series of methylated titanocene dichlorides $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n = 0$–5) was investigated voltammetrically in the same way as described for $(C_5H_5)_2TiCl_2$. A comparative set of voltammograms measured at moderately slow scan rate of 500 mV s^{-1} is shown in Fig. 3. The corresponding potentials of the three reduction peaks are listed in Table 1, and plotted against the number of methyl substituents in cyclopentadienyl ligands in Fig. 4. As the number of methyl groups increases, all three peaks shift to more negative potentials. For $n = 0$–3, the average increments for the reduction peaks are $\Delta E_{PR1} = -0.095$ V, $\Delta E_{PR2} = -0.057$ V and $\Delta E_{PR3} = -0.060$ V per one methyl group. However, for $n > 3$, this tendency is maintained only for the third reduction peak. The first two reduction peaks are only slightly shifted to negative side for $n = 4$, and shifted to more positive values for $n = 5$. The values of thermodynamic and kinetic parameters

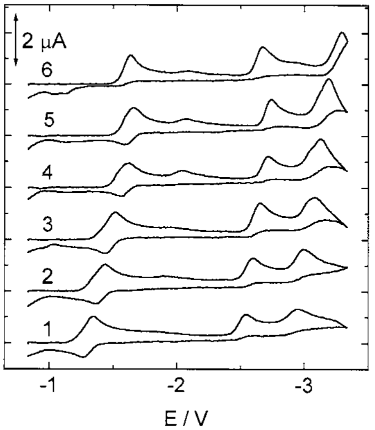


Fig. 3. Cyclic voltammograms of methylated titanocene dichlorides. Curves are corrected for the background current. Numbers denote: 1, $(C_5H_5)_2TiCl_2$; 2, $(C_5H_4Me)_2TiCl_2$; 3, $(C_5H_3Me_2)_2TiCl_2$; 4, $(C_5H_2Me_3)_2TiCl_2$; 5, $(C_5HMe_4)_2TiCl_2$; and 6, $(C_5Me_5)_2TiCl_2$. Concentration, 2×10^{-4} mol dm^{-3}; scan rate, 500 mV s^{-1}.

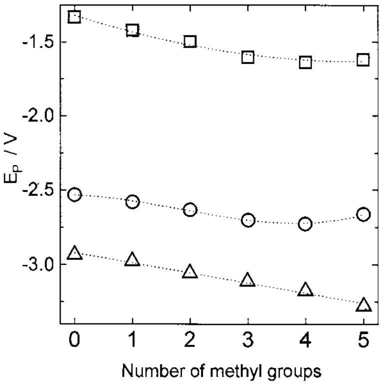


Fig. 4. Peak potential dependence on the number of methyl substituents attached to cyclopentadienyl ligand. Symbols □, ○ and △ denote peak potentials for the first, second and third electron transfer. Concentration, 2×10^{-4} mol dm^{-3}; scan rate, 500 mV s^{-1}.

derived from the first reduction peak records are listed in Table 2. Small differences between E_{PR1} and E_1° indicate that the kinetic effects are small, i.e. the heterogeneous electron transfer is rather fast, while the chemical reactions succeeding the electron transfer are rather slow. The heterogeneous rate constants k_{h1} are of order of 10^{-2} cm s^{-1} and decrease only slightly with the increasing number of Me substituents. The simulations further showed that the homogeneous pseudo-first order rate constants fall in the range 0.1–10 s^{-1}, and tend to increase with the increasing number of substituents. Then, the rate constants of the successive reactions of the $[(C_5H_{5-n}Me_n)_2TiCl_2]^-$ particles $k_{fP1}\approx 12$ s^{-1} for $n=0$–3, and $k_{fP1}=250$ s^{-1} for $n=5$. This is compatible with the expected increasing rate of the halogen cleavage from the highly methyl-substituted primary radical anions.

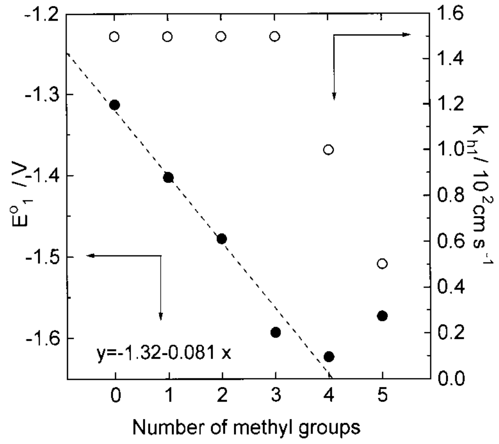


Fig. 5. Standard redox potentials E_1° (full circle) and heterogenous rate constants k_{h1} (open circle) of individual methyl substituted titanocene derivatives vs. number of methyl substituents attached to cyclopentadienyl ligand.

The plot of E_1° versus number of Me groups (n) (Fig. 5) is approximately linear for $n=0$–3 and gives virtually the same increment of -0.093 V per one methyl group as that obtained from the peak potentials. The negative shift can be attributed to an increase in the electron density at the central Ti atom induced by the electron releasing effect of Me groups [4–9]. A similar argument can also apply to negative shifts of the second and the third peak potentials. On the other hand, the decline from the linear dependence for $n=4$ and even the reverse, positive shift for $n=5$, as it is seen in the peak potential of the first and the second electron transfer (Figs. 4 and 5), indicate that the electronic effect of Me substituents has to be accompanied by a steric effect. This should become dominant for the $[C_5Me_4(R)]_2TiCl_2$ compounds containing bulky ligands R (vide infra).

Table 2
Experimental data for the first reduction taken from cyclic voltammograms of titanocenes in THF[a]

Compound	E_{PR1}[b] (V)	I_{PR1}/I_{PO1}	ΔE_{P1} (V)	E_1° (V)	k_{h1} (cm s^{-1})
$(C_5H_5)_2TiCl_2$	−1.326	−0.914	0.090	−1.313	0.015
$(C_5H_4Me)_2TiCl_2$	−1.419	−1.011	0.083	−1.403	0.015
$(C_5H_3Me_2)_2TiCl_2$	−1.497	−0.984	0.093	−1.478	0.015
$(C_5H_2Me_3)_2TiCl_2$	−1.605	−1.213	0.079	−1.593	0.015
$(C_5HMe_4)_2TiCl_2$	−1.640	−1.140	0.081	−1.623	0.010
$(C_5Me_5)_2TiCl_2$	−1.588	—[c]	—[c]	−1.573	0.005
$[C_5Me_4(SiMe_3)]_2TiCl_2$	−1.486	—[c]	—[c]	−1.453	0.003
$(C_5Me_4Ph)_2TiCl_2$	−1.440	—[c]	—[c]	−1.392	0.004
$[C_5Me_4(PhF)]_2TiCl_2$	−1.447	—[c]	—[c]	−1.392	0.005
$[C_5Me_4(CH_2Ph)]_2TiCl_2$	−1.497	—[c]	—[c]	−1.447	0.005
$Me_2Si(C_5H_4)_2TiCl_2$	−1.297	−1.025	0.079	−1.283	0.010
$Me_2Si(C_5Me_4)_2TiCl_2$	−1.640	−0.970	0.091	−1.623	0.010

[a] Concentration, 2×10^{-4} mol dm^{-3}; scan rate, 50 mV s^{-1}.

[b] E_{PR1}, reduction peak potential; E_{PO1}, oxidation peak potential; $\Delta E_{P1}=E_{PR1}-E_{PO1}$; I_{PR1}, reduction peak current; I_{PO1}, oxidation peak current.

[c] Without any sign of reoxidation.

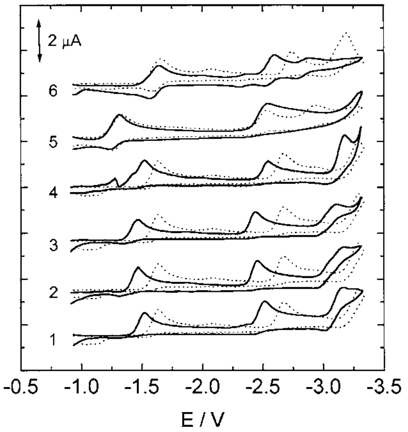


Fig. 6. Cyclic voltammograms of some persubstituted and *ansa*-titanocene dichlorides (full lines) and reference compounds (dotted lines). Full lines: 1, $[C_5Me_4(SiMe_3)]_2TiCl_2$; 2, $(C_5Me_4Ph)_2TiCl_2$; 3, $[C_5Me_4(FPh)]_2TiCl_2$; 4, $[C_5Me_4(CH_2Ph)]_2TiCl_2$; 5, $Me_2Si(C_5H_4)_2TiCl_2$; and 6, $Me_2Si(C_5Me_4)_2TiCl_2$. Dotted lines: 1–4, $(C_5Me_5)_2TiCl_2$; 5, $(C_5H_5)_2TiCl_2$; and 6, $(C_5HMe_4)_2TiCl_2$. Voltammograms are corrected for the backround current; concentration, 2×10^{-4} mol dm^{-3}; scan rate, 500 mV s^{-1}.

3.3. Reduction of the $[C_5Me_4(R)]_2TiCl_2$ ($R = SiMe_3$, Ph, FPh and CH_2Ph) compounds, $Me_2Si(C_5Me_4)_2TiCl_2$ and $Me_2Si(C_5H_4)_2TiCl_2$

Replacement of one methyl group in $(C_5Me_5)_2TiCl_2$ by the trimethylsilyl, phenyl, *para*-fluorophenyl or benzyl group in $[C_5Me_4(SiMe_3)]_2TiCl_2$, $(C_5Me_4Ph)_2TiCl_2$, $[C_5Me_4(FPh)]_2TiCl_2$ and $[C_5Me_4(CH_2Ph)]_2TiCl_2$ results in positive shifts of all three peak potentials (Table 1 and Fig. 6, curves 1–4). Standard potentials of the first electron transfer move positively in the order of the substituents $Me < SiMe_3 \sim CH_2Ph < Ph = FPh$ (Table 2, Fig. 7). The shifts as large as 120–180 mV cannot be due to an electron attracting behaviour of the R substituents. For example, the $SiMe_3$ group showed no shift of E_1° in $[C_5H_4(SiMe_3)]_2TiCl_2$ and $[C_5H_3(SiMe_3)_2]_2TiCl_2$ with respect to $(C_5H_5)_2TiCl_2$ [23]. The value of E_1° for $[C_5Me_4(SiMe_3)]_2TiCl_2$ which is close to that of $(C_5H_3Me_2)_2TiCl_2$ shows that the positive shift of E_1° has to be attributed to steric effects of the persubstituted cyclopentadienyl ligands. Equal values of E_1° for the $(C_5Me_4Ph)_2TiCl_2$ and $[C_5Me_4(FPh)]_2TiCl_2$ compounds also indicate that a well-known electron attracting effect of the *para*-fluoro substituent on the phenyl ring is small compared with a steric effect.

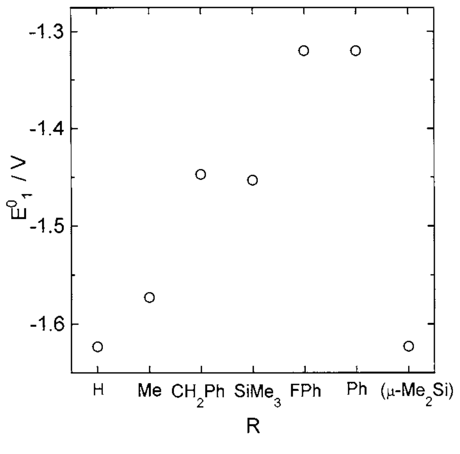


Fig. 7. Plot of standard potentials E_1° for the series of $(C_5Me_4R)_2TiCl_2$ compounds.

It is noteworthy that the increase in the pseudo-first-order rate constant k_{fP1} of the successive chemical reaction cannot account for shifts in the first peak potential by several hundred millivolts, because this would require the increase in k_{fP1} by the factor of 10^5–10^7 [34]. Also, the coordination of solvent molecules can affect the standard redox potential via the stabilization of the initial complex or the product. In the present case, the tetrahedrally coordinated $(C_5H_{5-n}Me_n)_2TiCl_2$ compounds do not coordinate THF and the same behaviour is expected for the short-lived reduction products $[(C_5H_{5-n}Me_n)_2TiCl_2]^-$. The final reduced products, the trigonal $(C_5H_{5-n}Me_n)_2TiCl$ compounds loose their Lewis acidity with increasing n. For $n = 0$–2, they dimerize to halogen-bridged $[(C_5H_{5-n}Me_n)_2Ti(\mu\text{-}Cl)]_2$ compounds or coordinate one molecule of THF to give the tetrahedral $(C_5H_{5-n}Me_n)_2TiCl(THF)$ compounds [35,36]. However, for $n =$ 3–5 they loose this property with increasing n and remain uncoordinated in THF at room temperature for $n = 4$ and 5 [13]. Hence, the solvation effect should add a positive increment to the standard redox potential for $n = 0$–3, however, this is vastly overbalanced by the negative shift due to electron donation of methyl groups. For $n = 3$ the solvation effect should approach zero.

The voltammograms of *ansa*-dimethylsilylene-bridged compounds show interesting new features (Fig. 6). Compound $Me_2Si(C_5H_4)_2TiCl_2$ gives potentials of the first and the second electron uptake at slightly more positive values compared with $(C_5H_5)_2TiCl_2$ whereas the third peak potential shifts to negative potential, outside the potential window. Similar behaviour has been reported for tetramethylethylene-bridged $Me_4C_2(C_5H_4)_2TiCl_2$ [25]. In $Me_2Si(C_5Me_4)_2TiCl_2$, the first electron transfer occurs at virtually the same potential as in $(C_5HMe_4)_2TiCl_2$, however, the second and the third peak potentials shift to positive values (Table 1).

3.4. The nature of the steric effect

The presence of steric strain in highly substituted titanocene dichlorides can be estimated from the value of the dihedral angle (ϕ) formed by the least-squares planes of the cyclopentadienyl rings. The X-ray crystal data afforded low values of ϕ for $(C_5Me_5)_2TiCl_2$ (44.6°)

[32,37], $[(C_5Me_4(SiMe_3)]_2TiCl_2$ (39.8°) [29], and $(C_5Me_4Ph)_2TiCl_2$ (45.6°) [30] and a remarkably higher value (54.4°) for $(C_5HMe_4)_2TiCl_2$ [38]. The strain in $(C_5Me_5)_2TiCl_2$ arises from the mutual interaction of methyl groups that are situated close to the top of the dihedral angle ϕ. A low value of ϕ then induces some steric congestion between the methyl groups on the other side of the C_5Me_5 ligands and the chlorine atoms [37]. The strain brings about a large deviation of carbon atoms of the pertinent methyl groups away from the least-squares plane (up to ca. 0.3 Å). The same effects are observed in the $(C_5Me_4R)_2TiCl_2$ compounds where bulky substituents R = $SiMe_3$ or Ph occupy the antipodal side positions and, hence, do not affect the intramolecular strain in the solid state. This strain is absent in $(C_5HMe_4)_2TiCl_2$ because the hinge positions of the C_5HMe_4 ligands are occupied by hydrogen atoms [38]. Correspondingly, the angle ϕ (54.4°) is by ca. 10° larger than in the above-mentioned persubstituted compounds. The hinge positions are occupied by hydrogen atoms also in other less-methylated titanocene dichlorides and the angle ϕ remains approximately constant [39]. It is noteworthy, that the CE–Ti–CE (CE is the centroid of the cyclopentadienyl ring) angle, which is commonly used in crystallographic descriptions, does not reflect the congestion properly due to a ring slippage effect (the CE–Ti interconnection differs from the normal from Ti to the plane). The cyclopentadienyl rings in titanocene chlorides have been always found slipped towards the open side of angle. [32]. Moreover, it is the angle ϕ whose magnitude is related, according to Extended Hückel MO [40] as well as recent density functional calculations [41], to energies of LUMO orbitals $1a_1$ or b_2 in titanocene derivatives. Qualitatively, a decrease in ϕ leads to a decrease in energy of the LUMO $1a_1$ or b_2 orbitals and hence, to a decrease of the absolute value of the reduction potential.

The observed positive shifts of the reduction potential in the $(C_5Me_4R)_2TiCl_2$ compounds with respect to the reduction potential of $(C_5Me_5)_2TiCl_2$ are not, however, compatible with approximately constant value of the angle ϕ in all these compounds. This enigma can be solved by realizing that angle ϕ has to differ in the solid state and in solution. In solution, the cyclopentadienyl ligands rotate [42] and the groups larger than the methyl group induce an additional hindrance to the rotation. We assume that the rotating ligands tend to further decrease angle ϕ in order to lower the barrier to rotation. This assumption is in line with large positive shifts of E_1° of $(C_5Me_4R)_2TiCl_2$ compounds with respect to E_1° of $(C_5Me_5)_2TiCl_2$ although their solid state ϕ angles differ only marginally. It also accounts for a positive deviation of E_1° for $(C_5HMe_4)_2TiCl_2$ from the linear dependence of E_1° on n (Fig. 5, cf. Table 2) although its solid state angle ϕ is large, and does not differ from the ϕ angles of lower methyl homologues. This suggestion is corroborated by the results for *ansa*-complexes with the large fixed angles ϕ. Since the combined electronic and steric effect of μ-$SiMe_2$ bridge in $Me_2Si(C_5H_4)_2TiCl_2$ ($\phi = 51.2°$ [24]) shifts E_1° of $(C_5H_5)_2TiCl_2$ to a more positive value (-1.283 V against -1.313 V, Table 2) the equal values of E_1° for $(C_5HMe_4)_2TiCl_2$ and $Me_2Si(C_5Me_4)_2TiCl_2$ ($\phi = 59.3°$ [32]) (see Fig. 7 and Table 2) are compatible with a slight positive declination of E_1° for $(C_5HMe_4)_2TiCl_2$ from the linear dependence of standard potentials on the number of methyl groups (Fig. 5). In its absence, E_1° of $(C_5HMe_4)_2TiCl_2$ would be more negative with respect to that of $Me_2Si(C_5Me_4)_2TiCl_2$, as for the non-methylated analogues. The both extreme negative E_1° values clearly point to an approximately equal electronic effect of four methyl susbtituents at the cyclopentadienyl ligands, whereas the steric effects at large ϕ angles (54.4° resp. 59.3°) seem to play a minor role.

The above experimental evidence for the correlation between ϕ and E_1° would require an insight by means of quantum chemistry. Unfortunately, reliable energies of frontier orbitals would require the knowledge of molecular parameters, which is not available for molecules in solution. A computational approach to these effects is behind the scope of this study.

4. Conclusions

The present dependence of E_1° on ϕ shows how the Lewis acidity at the central Ti atom can be controlled by the steric strain in titanocene dichlorides. It may afford a basis for explanation of various unexpected results in the design of metallocene catalysts for olefin polymerization.

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