

Zirconium enolate radical cations in solution—characterisation and kinetics of their mesolytic Zr–O bond cleavage†

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Six zirconocene enolate radical cations and one hydroquinone biszirconocene radical cation have been generated and characterised in solution by standard and fast scan cyclic voltammetry. The electroanalytical results along with those from product analysis of preparative one-electron oxidations indicate that the sterically congested radical cations undergo a mesolytic Zr–O bond cleavage process. The kinetics of the mesolytic Zr–O bond cleavage yielding zirconocene cations and the lifetime (t_1) of the zirconium enolate radical cations in dichloromethane at room temperature are determined.

Introduction

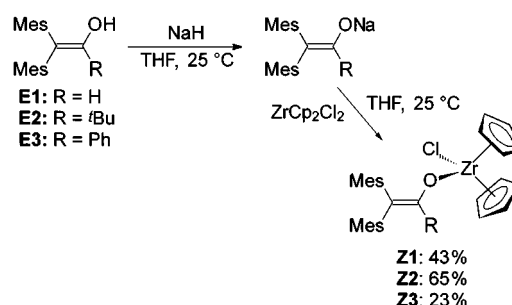
Over the last 15 years the use of early transition metals (titanium, zirconium) has become an established method¹ in modern organic synthesis to control enolate reactivity, allowing for example the improvement of the regioselectivity and diastereoselectivity of aldol additions.² Furthermore, highly enantioselective aldol reactions (with chiral ligands at the metal atom) have become part of the synthetic repertoire.³ Despite the importance of these metal enolates little is known about structure–reactivity relationships. In general, these highly reactive compounds exhibit a pronounced sensitivity towards hydrolysis which is reflected in the fact that in synthetic applications they are generated and converted without isolation. Therefore, only a small number of titanium^{4,5} and zirconium enolates⁶ have been isolated and investigated with regard to spectroscopic and/or structural data. To some extent, the hydrolytic stability of these compounds can be increased by using a kinetically non-labile and coordinatively saturated metallocene fragment as a stabilising motif. More importantly, however, by choosing sterically shielded enolate systems the hydrolytic stability of the corresponding titanium enolates⁵ can be increased immensely, thus facilitating investigations on structure and reactivity.

Although early transition metal enolates are rather electron-rich compounds their one-electron oxidation chemistry has been overlooked for a long time. Actually, the first reports on titanium enolate radical cations in solution generated by one-electron oxidation from their neutral precursors have become available just recently from our laboratory.⁷ In the present investigation⁸ we make use again of sterically shielded enolates in order to prepare isolable zirconium enolates and to examine for the first time the properties and reactions of zirconium enolate radical cations. In addition, a hydroquinone biszirconocene was synthesised and subjected to one-electron oxidation.

Results

We started our investigation with the preparation of sterically shielded zirconium enolates. The first strategy leading to the chlorine substituted zirconocene enolates started from simple stable β,β -dimesitylenols which were deprotonated quanti-

tatively by sodium hydride in THF at room temperature. The generated sodium enolates were subsequently converted into the corresponding zirconocene enolates by transmetalation with stoichiometric amounts of zirconocene dichloride (Scheme 1). All chlorine substituted zirconocene enolates



Scheme 1

Z1–Z3 were obtained in an analytically pure form as bright yellow crystals after recrystallisation from *n*-hexane and a *n*-hexane–toluene mixture, respectively.

A second route leading to methyl substituted zirconocene enolates was realised by treating the corresponding β,β -dimesitylenols with dimethyl zirconocene⁹ that was prepared from zirconocene dichloride with methylmagnesium chloride in diethyl ether at room temperature (Scheme 2). The methylated zirconocene enolates **ZM1–ZM3** could be obtained in analytically pure form as pale yellow solids. The analogous reaction was used for the preparation of the hydroquinone based methyl substituted biszirconocene **ZM4**.

The preparative scale one-electron oxidations of the zirconium enolates were performed in an acetonitrile–dichloromethane mixture by using the one-electron oxidant tris(1,10-phenanthroline)iron(III) hexafluorophosphate (**Fephen**, $E_1 = +0.69$ V_{Fe}) in the case of the chlorine substituted zirconocene enolates **Z1–Z3** and nitrosonium hexafluoroantimonate (NOSbF₆, $E_1 = +0.89$ V_{Fe}) in the case of the methyl zirconocene enolates **ZM1–ZM3**. For all compounds the corresponding benzofuran derivatives **B1–B3** were formed in good to excellent yields (*cf.* Scheme 3).

We started the electroanalytical investigation with the determination of the oxidation potentials of these compounds. All zirconocene enolates exhibit irreversible oxidation waves (E_{pa} ; *cf.* Table 1) in acetonitrile at 100 mV s^{−1} in cyclic voltam-

† Electroactive Protecting Groups and Reaction Units. Part 8. For Part 7 see ref. 7c.

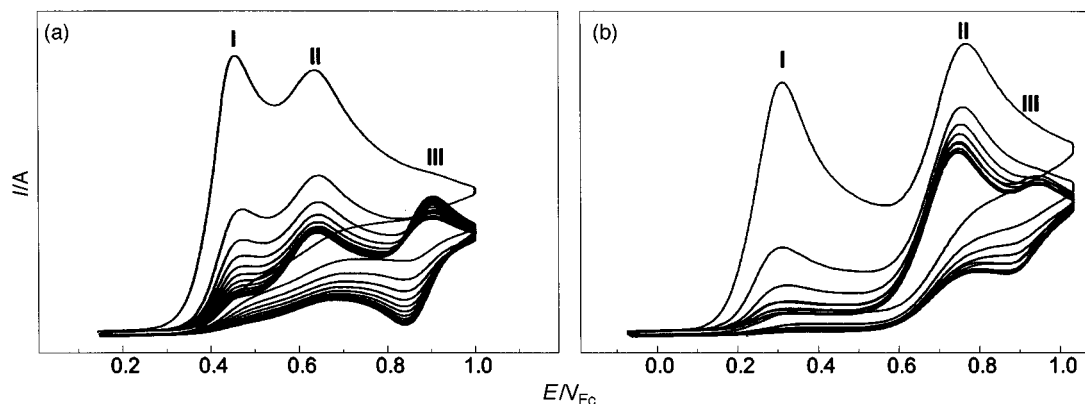
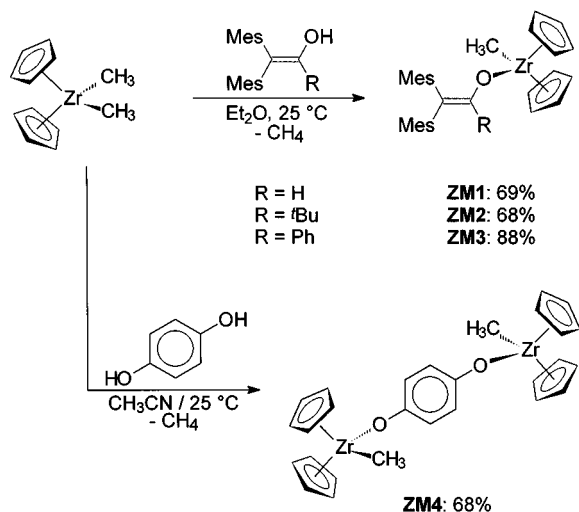
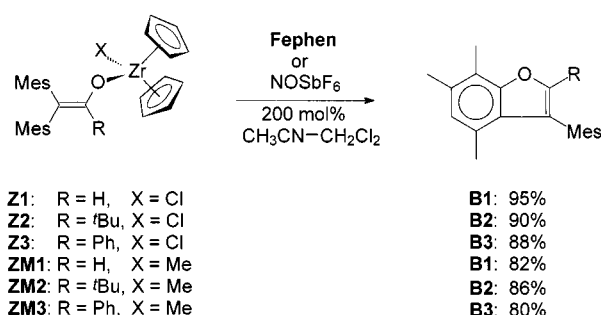


Fig. 1 a) Multisweep CV of **Z3** in CH_3CN at $\nu = 500 \text{ mV s}^{-1}$; b) multisweep CV of **ZM2** in CH_2Cl_2 at $\nu = 500 \text{ mV s}^{-1}$.



Scheme 2



Scheme 3

metry (CV) experiments. Likewise in dichloromethane, irreversible waves were obtained at the usual scan rates. However, upon increase of the scan rates by using fast scan cyclic voltammetry at ultramicroelectrodes, fully or at least partially reversible waves were recorded: partially reversible waves showed up for **Z1–Z3** at scan rates $\nu \geq 100 \text{ V s}^{-1}$, for **ZM1** at $\nu \geq 200 \text{ V s}^{-1}$, for **ZM2** at $\nu \geq 100 \text{ V s}^{-1}$, for **ZM3** at $\nu \geq 20 \text{ V s}^{-1}$ and for **ZM4** at $\nu \geq 100 \text{ V s}^{-1}$. As a consequence, the above electroanalytical investigations constitute the first evidence for the existence of zirconium enolate and zirconium phenolate radical cations in solution. These measurements allowed us to determine the thermodynamically relevant redox potentials E_1^{ox} (cf. Table 1), which range between +0.30 to +0.57 V vs. ferrocene/ferrocenium (V_{Fc}). The E_2^{ox} values are about 100 mV more anodic than those of the structurally analogous titanium enolates,⁷ an effect which is already known for other titanocene and zirconocene compounds.¹¹ Despite this fact the redox potentials of **Z1–Z3**, **ZM1–ZM4** are still sufficiently low so that their

Table 1 Oxidation potentials of zirconocene enolates determined by CV

Zirconocene enolate	$E_{\text{pa}}/V_{\text{Fc}}$	$E_2^{\text{ox}}/V_{\text{Fc}}$
Z1	+0.45 ^a	+0.57 ^b
Z2	+0.32 ^a	+0.43 ^b
Z3	+0.41 ^a	+0.44 ^b
ZM1	+0.51 ^a	+0.46 ^b
ZM2	+0.30 ^a	+0.35 ^b
ZM3	+0.35 ^a	+0.36 ^b
ZM4	+0.30 ^c	+0.30 ^b

^a In acetonitrile at $\nu = 100 \text{ mV s}^{-1}$. ^b In dichloromethane at $\nu = 1000 \text{ V s}^{-1}$. ^c In dichloromethane at $\nu = 100 \text{ mV s}^{-1}$.

Table 2 Kinetics of the mesolytic Zr–O bond cleavage (k_f) and the lifetime (t_f) of the zirconium enolate radical cations in dichloromethane at room temperature

	Z2	Z3	ZM1	ZM2	ZM4
k_f/s^{-1}	3.3×10^2	3.1×10^2	8.3×10^2	5.0×10^2	3.2×10^2
t_f/s	2.1×10^{-3}	2.2×10^{-3}	8.4×10^{-4}	1.4×10^{-3}	2.2×10^{-3}

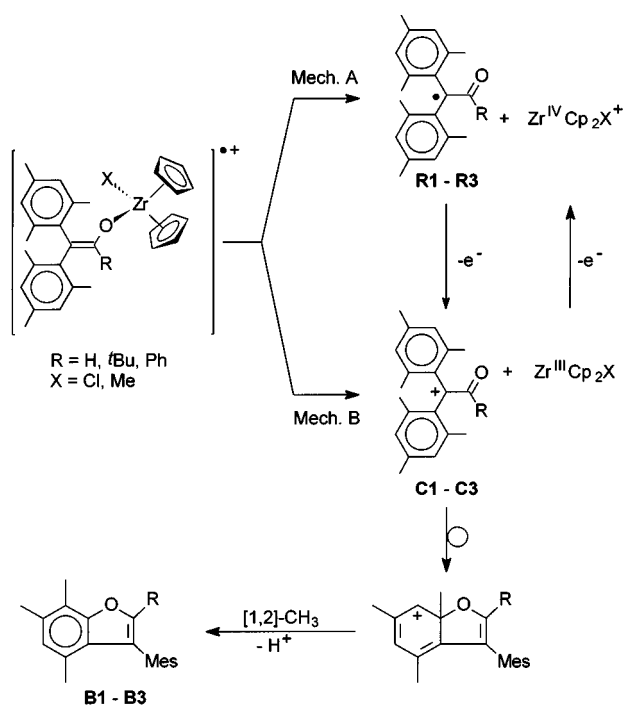
chemical and/or anodic oxidation is possible in the presence of many other common functional groups.

At higher anodic potentials all zirconium enolates exhibit two additional oxidation waves in standard CV investigations in acetonitrile as well as in dichloromethane (Fig. 1). These waves can readily be ascribed to the oxidation of the corresponding enols (wave II) and benzofurans (wave III) by comparison of the observed oxidation potentials with data obtained from authentic samples.^{26b} In multisweep CV experiments the current for wave I decreases rapidly with an increasing number of cycles whereas the currents for waves II and III increase relative to that for wave I. These findings reveal that on the time scale of the CV experiment zirconium enolates **Z1–Z3** and **ZM1–ZM3** are converted into the corresponding enols and into the benzofuran derivatives **B1–B3**.

As already mentioned above, partially reversible waves of all compounds could be recorded by using fast scan cyclic voltammetry, which allowed determination of the kinetics of the follow-up reaction (mesolytic¹² Zr–O bond scission) of some of the investigated zirconocene enolate radical cations. The kinetic analysis was undertaken by relating the ratio of the cathodic to anodic peak current $I_{\text{pc}}/I_{\text{pa}}$ to the kinetic parameter kt according to the method of Nicholson and Shain¹³ by applying a working curve¹⁴ for an $\text{EC}_{\text{irr}}\text{E}$ mechanism (electron transfer/irreversible chemical reaction/electron transfer). The rate constants for the Zr–O bond cleavage process and the related lifetimes of the corresponding radical cations are depicted in Table 2.

Discussion

The key intermediate in oxidative benzofuran formation starting from simple stable enols¹⁵ and various enol derivatives¹⁶ (including titanium enolates⁷) is the α -carbonyl cation **C1–C3** which undergoes a Nazarov type cyclisation, [1,2]-methyl shift and deprotonation to **B1–B3**. This species is generated from the

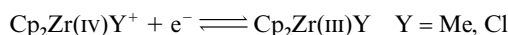
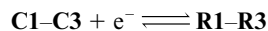


above mentioned enol radical cations $C=C-OX^{++}$ by mesolytic¹² bond cleavage of the O–X bond.

In the case of the investigated zirconocene enolates the Zr–O bond must have been broken somewhere during this reaction. A dissociative electron transfer process can be ruled out because reversible (or at least partially reversible) waves were obtained for all compounds in cyclic voltammetric experiments. As direct cyclisation at the stage of the radical cation is highly unlikely because of steric reasons for all investigated β,β -dimethyl zirconium enolates **Z1–Z3**, **ZM1–ZM3**, this mechanistic pathway can be excluded as well. Hence, mechanistic considerations suggest that in fact the Zr–O bond is cleaved in a mesolytic fragmentation process which is the primary follow-up reaction of the radical cations **Z1–Z3**⁺ and **ZM1–ZM3**⁺.

As a matter of fact there are two possibilities for how the mesolytic bond cleavage may take place: on the one hand a Zr–O bond scission of the radical cation providing an α -carbonyl radical **R1–R3** and a zirconocene(IV) cation according to Mechanism A (heterolytic variant¹²) whereas on the other hand a bond cleavage leading to an α -carbonyl cation **C1–C3** and a zirconocene(III) species (Mechanism B, homolytic variant¹²) is conceivable. Both cleavage selectivities are realised in radical cations of structural analogous enols and their derivatives: homolytic cleavage can be observed for radical cations of enol esters,^{16a} enol carbonates and enol carbamates^{16d} whereas the radical cations of enols,^{15b} silyl enol ethers,^{16b} enol phosphites and enol phosphinates^{16c} and of the structurally very closely related titanocene enolates⁷ follow the heterolytic variant.

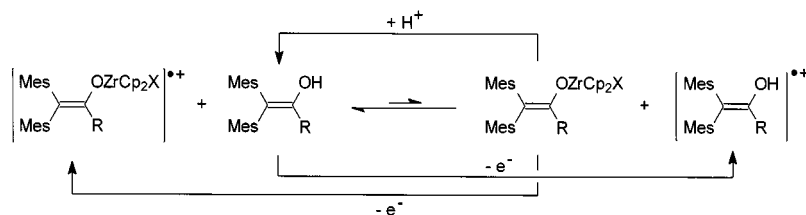
The thermodynamic preference for either Mechanism A or B could be predicted if the oxidation potentials of the fragments concerned [α -carbonyl radicals and zirconocene(III) species] or alternatively the reduction potentials of the α -carbonyl cations and $Cp_2Zr(IV)Y$ (with $Y = Me, Cl$) were known.



The potentials of the corresponding α -carbonyl radicals **R1–R3** are known to be in the range $E_{pa} = +0.15$ to $+0.36$ V_{Fe}.^{15a} Unfortunately, the oxidation potentials of the zirconocene(III) species $Cp_2Zr(III)Me$ and $Cp_2Zr(III)Cl$ have not been determined yet. Therefore, we prepared the zirconocene cation $[Cp_2Zr(IV)Me(MeCN)_2][BPh_4]$ ¹⁷ which reveals a reduction potential of $E_{pc} = -1.94$ V_{Fe} (at $\nu = 100$ mV s^{−1} in CH₃CN, supporting electrolyte: NaBPh₄). Although this is an irreversible peak potential this value should be a sufficiently good approximation for the oxidation potential of $Cp_2Zr(III)Me$. As the anodic peak potentials of the α -carbonyl radicals are about 2 V more anodic it is a safe statement that methyl zirconocene enolate radical cations cleave according to the heterolytic pathway since that pathway is by about 110 kJ mol^{−1} (derived from the difference of the oxidation potentials between the concerned redox active species) more favorable than the homolytic variant. This finding is in agreement with results by Jordan, who carried out one-electron oxidations of dimethyl zirconocene and other dialkyl zirconocenes with stoichiometric amounts of ferrocenium and isolated the cationic alkyl zirconocene complexes $[Cp_2ZrR]^+$.¹⁸ The oxidation potential of $Cp_2Zr(III)Cl$, which is not known yet, was estimated as follows: the difference between the thermodynamic E_i of $Cp_2Zr(IV)Me^+$ and $Cp_2Zr(IV)Cl^+$ should be smaller¹⁹ than the difference between the half-wave potentials of $Cp_2Zr(IV)Me_2$ ($E_i = -3.06$ V_{Fe}) and $Cp_2Zr(IV)Cl_2$ ($E_i = -2.04$ V_{Fe}). As we could determine the cathodic peak potential of $Cp_2Zr(IV)Me^+$ to $E_{pc} = -1.94$ V_{Fe} a rough approximation for the reduction potential E_{pc} of $Cp_2Zr(IV)Cl^+$ provides a value more cathodic than -0.9 V_{Fe}. As a consequence, oxidation of $Cp_2Zr(III)Cl$ occurs at a significantly more cathodic potential (>1 V) than that of the α -carbonyl radicals. Therefore, we suppose that equally the mesolytic bond cleavage of the chloro zirconocene enolate radical cations follows the heterolytic fragmentation pathway (according to Mechanism A).

If the exact mechanism of the mesolytic bond cleavage is known, the kinetics of this process can be determined using CV investigations. However, the mechanistic situation is much more complicated than displayed in Scheme 4. The proton split off during benzofuran formation is able to hydrolyse the neutral zirconium enolate on the time scale of the CV experiment. Accordingly, the oxidation waves of the corresponding enols can always be observed besides the waves of the zirconium enolate radical cation, which is endergonic electron transfer reduction of the zirconium enolate radical cation by the neutral enol **E1–E3** ($E_{pa} = 0.61 - 0.67$ V_{Fe}).^{15a} As enol radical cations are known to deprotonate fairly rapidly, however, the endergonic equilibrium can be driven to the right hand side (see Scheme 5).

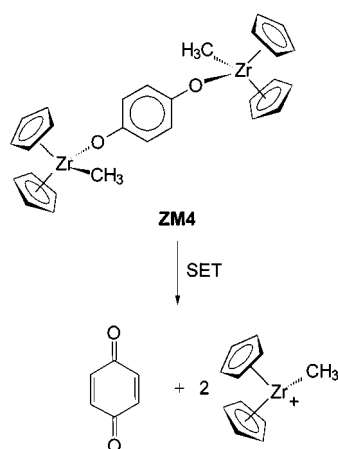
For this reason we investigated the effect of the electron transfer equilibrium on the kinetics obtained from cyclic voltammetry experiments. We chose zirconium enolate **Z1** as a model compound because the difference of the oxidation potentials between **Z1** and **E1** is the smallest of all the compounds examined. Thus, the effect of the electron transfer equilibrium should be the largest of all the zirconium enolates **Z1–Z3**, **ZM1–ZM3**. For a detailed understanding, partially reversible oxidation waves for **Z1** were digitally simulated²⁰ based on the mechanistic scenario as shown in Scheme 5. In addition, oxidation waves for **Z1** were simulated according to a simple EC_{irr}E mechanism (no effect of the electron transfer equilibrium). The waves thus obtained were compared directly with each other. Notably, the differences in reversibility of the waves



Scheme 5 Electron transfer equilibrium between zirconium enolate radical cations and neutral enols.

are extremely small indicating that the influence of the electron transfer equilibrium on the shape of the oxidation waves of the zirconium enolate and thus the kinetics of the mesolytic Zr–O bond cleavage is negligible. Thus, the kinetics of the mesolytic bond cleavage can be evaluated according to an $\text{EC}_{\text{irr}}\text{E}$ -mechanism (Table 2).

The kinetics of the follow-up reaction of $\text{ZM4}^{\bullet+}$ were analogously determined according to an $\text{EC}_{\text{irr}}\text{E}$ -mechanism. The analysis provides a first-order rate constant (k_f) for this process similar to those of the zirconocene enolate radical cations (Table 2), suggesting a reaction as depicted in Scheme 6



Scheme 6

initiated by mesolytic Zr–O bond cleavage. We are currently validating the generality of such fragmentation reactions as an entry to the facile generation of zirconocene cations using other hydroquinone biszirconocenes.

In summary, we have synthesised six zirconium enolates **Z1**–**Z3**, **ZM1**–**ZM3** and one hydroquinone biszirconocene **ZM4**. The radical cations generated thereof by one-electron oxidation were characterised by cyclic voltammetry and fast scan cyclic voltammetry, which represents the first characterisation of zirconium enolate and phenolate radical cations in solution. The sterically congested zirconocene enolate radical cations undergo a clean mesolytic Zr–O bond scission according to the heterolytic pathway (Mechanism A) yielding α -carbonyl radicals and zirconocene(IV) cations. The kinetics of this process could be determined. Investigations are under way to probe whether such electron transfer induced bond cleavage reactions resulting in the formation of zirconocene(IV) cations can be used to trigger polymerisation of propene and other alkenes.²¹

Experimental

All reactions were carried out under an atmosphere of dry argon by using standard Schlenk tube techniques. Solvents were purified by standard literature methods and distilled directly from their drying agents under nitrogen: THF–potassium, Et_2O –sodium, *n*-hexane–potassium, toluene–sodium, CH_2Cl_2 – P_4O_{10} . Solvents for CV measurements and one-electron oxidation experiments: CH_3CN was purchased in HPLC quality from Riedel-de Haën, distilled from CaH_2 and filtered through

basic alumina (ICN); CH_2Cl_2 was purchased in HPLC quality from Riedel-de Haën, distilled from P_4O_{10} and filtered through basic alumina (ICN). Zirconocene dichloride,²² 2,2-dimesityl-ethanol,²³ 2,2-dimesityl-1-phenylethanol²⁴ and 1,1-dimesityl-3,3-dimethylbuten-2-ol²⁵ were prepared according to literature procedures. The supporting electrolyte tetra(*n*-butyl)-ammonium hexafluorophosphate (Fluka) was of electrochemical grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 200 spectrometer; chemical shifts (in ppm) refer to tetramethylsilane; owing to the nature of the β,β -dimesityl moiety signals in the ^{13}C NMR spectra are often superimposed. IR spectra were recorded on a Perkin-Elmer FT-IR 1605. Elemental analyses were carried out on a Carlo Erba Elemental Analyzer 1106. Melting points were determined by using a Dupont 910 differential scanning calorimeter.

Preparation of (2,2-dimesitylethenoxy)zirconocene chloride (**Z1**)

2,2-Dimesitylethanol (841 mg, 3.00 mmol) was added in small portions at room temperature to a suspension of sodium hydride (636 mg, 26.5 mmol) in THF (50 cm^3). After stirring for 1 h the excess NaH was filtered off and the filtrate was added slowly to a solution of zirconocene dichloride (877 mg, 3.00 mmol) in THF (50 cm^3) at room temperature. The mixture was stirred for 12 h then the solvent was evaporated *in vacuo*. The residue was extracted with Et_2O (100 cm^3) and then the extract was filtered. The filtrate was concentrated to about 10 cm^3 and *n*-hexane (90 cm^3) was added. The mixture was kept for 3 days at -40°C affording the crude product which was recrystallised from *n*-hexane. **Z1** could be obtained as bright yellow crystals (953 mg, 1.78 mmol, 59%). Mp 118°C (Found: C, 67.03; H, 6.48. $\text{C}_{30}\text{H}_{33}\text{ClOZr}$ requires: C, 67.19; H, 6.20%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3092, 2955, 2917, 2849, 1609, 1586, 1555, 1472, 1438, 1374, 1228, 1177, 1092, 1017, 904, 867, 857, 808, 674, 629, 568, 487; δ_{H} (200 MHz; CDCl_3) 1.6–2.7 (coalescence, 18 H, Mes- CH_3), 6.14 (s, 10 H, C_5H_5), 6.73 (s, 1 H, C=CH), 6.83 (br s, 4 H, Mes-H); δ_{C} (50 MHz; CDCl_3) 20.5 (Mes- CH_3), 20.7 (Mes- CH_3), 20.8 (Mes- CH_3), 21.0 (Mes- CH_3), 112.8 (C2), 114.1 (C_5H_5), 129.9 (Mes), 128.7 (Mes), 129.5 (Mes), 130.9 (Mes), 132.3 (Mes), 134.4 (Mes), 136.8 (Mes), 137.7 (Mes), 154.0 (C1).

Preparation of (1,1-dimesityl-3,3-dimethylbut-1-en-2-oxy)-zirconocene chloride (**Z2**)

To a suspension of sodium hydride (427 mg, 17.8 mmol) in THF (30 cm^3), solid 1,1-dimesityl-3,3-dimethylbut-1-en-2-ol (1.01 g, 3.00 mmol) was added in small portions at room temperature. The mixture was stirred for 1 h and the excess NaH was filtered off. The filtrate was added slowly to a solution of zirconocene dichloride (877 mg, 3.00 mmol) in THF (30 cm^3) and stirred for 1 h. The solvent was removed under reduced pressure and the residue extracted twice with boiling *n*-hexane (200 cm^3). After storing the filtrate at -40°C **Z2** was obtained as bright yellow crystals (1.15 g, 1.94 mmol, 65%). Mp 127°C (Found: C, 68.68; H, 7.25. $\text{C}_{34}\text{H}_{41}\text{ClOZr}$ requires C, 68.94; H, 6.98%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2990, 2950, 2920, 2861, 1608, 1546, 1477, 1442, 1393, 1374, 1265, 1244, 1233, 1197, 1168, 1154, 1099, 1072, 1023, 1010, 968, 937, 914, 853, 832, 814, 801, 733, 675; δ_{H} (200 MHz; CDCl_3) 1.02 (s, 9 H, $-\text{C}(\text{CH}_3)_3$), 2.1–2.3

(coalescence, 18 H, Mes-CH₃), 6.16 (s, 10 H, C₅H₅), 6.73 (br s, 2 H, Mes-H), 6.83 (br s, 2 H, Mes-H); δ_{C} (50 MHz; CDCl₃) 20.7 (Mes-CH₃), 20.8 (Mes-CH₃), 22.5 (Mes-CH₃), 29.3 (CMe₃), 40.9 (C3) 111.4 (C1), 114.2 (C₅H₅), 128.2 (Mes), 128.6 (Mes), 129.6 (Mes), 135.0 (Mes), 135.1 (Mes), 137.2 (Mes), 137.8 (Mes), 138.6 (Mes), 167.6 (C2).

Preparation of (2,2-dimesityl-1-phenylethenoxy)zirconocene chloride (Z3)

To a suspension of sodium hydride (436 mg, 18.2 mmol) in THF (50 cm³), solid 2,2-dimesityl-1-phenylethanol (713 mg, 2.00 mmol) was added in small portions at room temperature. The mixture was stirred for 1 h and the surplus sodium hydride was removed by filtration. The filtrate was added slowly to a solution of zirconocene dichloride (585 mg, 2.00 mmol) in THF (50 cm³) at room temperature. After stirring the mixture for 12 h the solvent was removed under reduced pressure. The residue was extracted with boiling *n*-hexane (100 cm³) and after filtration the solution was stored at -40 °C for 3 days affording a yellow solid. The crude product was recrystallised from *n*-hexane-toluene. **Z3** was obtained as bright yellow crystals (284 mg, 464 μ mol, 23%). Mp 119 °C (Found: C, 70.59; H, 6.34. C₃₆H₃₇ClOZr requires C, 70.61; H, 6.09%); ν_{max} (KBr)/cm⁻¹ 2990, 2955, 2915, 2855, 1610, 1587, 1560, 1491, 1438, 1370, 1292, 1278, 1245, 1204, 1158, 1082, 1012, 969, 922, 850, 807, 779, 748, 702, 670, 638; δ_{H} (200 MHz; CDCl₃) 1.9–2.3 (coalescence, 18 H, Mes-CH₃), 6.04 (s, 10 H, C₅H₅), 6.59 (s, 2 H, Mes-H), 6.86 (br s, 2 H, Mes-H), 7.10–7.22 (m, 3 H, Ph-H), 7.24–7.35 (m, 2 H, Ph-H); δ_{C} (50 MHz; CDCl₃) 20.7 (Mes-CH₃), 20.9 (Mes-CH₃), 21.2 (Mes-CH₃), 21.6 (Mes-CH₃), 114.4 (C₅H₅), 115.2 (C2), 127.2 (Ar), 127.6 (Ar), 129.0 (Ar), 129.2 (Ar), 129.8 (Ar), 135.2 (Ar), 135.5 (Ar), 135.9 (Ar), 137.9 (Ar), 138.2 (Ar), 160.1 (C1).

Preparation of (2,2-dimesitylethenoxy)methylzirconocene (ZM1)

A suspension of zirconocene dichloride (877 mg, 3.00 mmol) in Et₂O (40 cm³) was treated with a solution of methylmagnesium chloride (2.0 cm³, 3.0 M solution in THF, 6.0 mmol) at room temperature. The mixture from which a white solid precipitated was stirred at this temperature for 3 h. Now a solution of 2,2-dimesitylethanol (841 mg, 3.00 mmol) in Et₂O (60 cm³) was added slowly over a period of 2 h. The mixture was stirred for an additional 3 h, then the precipitate was removed by filtration. The filtrate was concentrated to a volume of about 10 cm³ and *n*-hexane (40 cm³) was added. After storing the solution overnight at -40 °C a colorless solid could be removed by filtration. The filtrate was evaporated to dryness affording **ZM1** as a pale yellow solid (1.07 g, 2.07 mmol, 69%). Mp 45 °C (Found: C, 71.98; H, 6.70. C₃₁H₃₆OZr requires C, 72.18; H, 7.03%); ν_{max} (KBr)/cm⁻¹ 2982, 2951, 2918, 2870, 2855, 1591, 1560, 1476, 1458, 1439, 1373, 1248, 1230, 1175, 1092, 1014, 905, 851, 800, 741, 676, 629, 485; δ_{H} (200 MHz; CDCl₃) 0.10 (s, 3 H, Zr-CH₃), 1.7–3.0 (coalescence, 18 H, Mes-CH₃), 5.99 (s, 10 H, C₅H₅), 6.68 (s, 1 H, C=CH), 6.89 (br s, 4 H, Mes-H); δ_{C} (50 MHz; CDCl₃) 20.7 (Mes-CH₃), 20.8 (Mes-CH₃), 20.9 (Mes-CH₃), 21.1 (Mes-CH₃), 23.1 (Zr-CH₃), 110.8 (C₅H₅), 112.7 (C2), 128.5 (Mes), 129.4 (Mes), 130.4 (Mes), 134.8 (Mes), 134.9 (Mes), 136.0 (Mes), 137.5 (Mes), 153.5 (C1).

Preparation of (1,1-dimesityl-3,3-dimethylbut-1-en-2-oxo)-methylzirconocene (ZM2)

A suspension of zirconocene dichloride (877 mg, 3.00 mmol) in Et₂O (50 cm³) was treated with a solution of methylmagnesium chloride (2.0 cm³, 3.0 M solution in THF, 6.0 mmol) at room temperature. The mixture was stirred at this temperature for 3 h. Now a solution of 1,1-dimesityl-3,3-dimethylbut-1-en-2-ol (1.01 g, 3.00 mmol) in Et₂O (50 cm³) was added slowly over a period of 2 h. The mixture was stirred for an additional 3 h,

then the precipitated magnesium chloride was removed by filtration. The filtrate was concentrated to a volume of about 10 cm³ and *n*-hexane (40 cm³) was added. After storing this solution overnight at -40 °C a colorless solid could be removed by filtration. The filtrate was evaporated to dryness affording **ZM2** as a pale yellow solid (1.16 g, 2.07 mmol, 68%). Mp 222 °C (Found: C, 73.41; H, 7.83. C₃₅H₄₄OZr requires C, 73.50; H, 7.75%); ν_{max} (KBr)/cm⁻¹ 3000, 2952, 2924, 2873, 2855, 1608, 1542, 1474, 1459, 1442, 1392, 1370, 1352, 1266, 1235, 1198, 1169, 1158, 1104, 1015, 967, 940, 916, 850, 800, 788, 734, 669, 568; δ_{H} (200 MHz; CDCl₃) -0.22 (s, 3 H, Zr-CH₃), 0.96 (s, 9H, -C(CH₃)₃), 2.0–2.3 (coalescence, 18 H, Mes-CH₃), 5.94 (s, 10 H, C₅H₅), 6.71 (br s, 2 H, Mes-H), 6.76 (br s, 2 H, Mes-H); δ_{C} (50 MHz; CDCl₃) 20.7 (Mes-CH₃), 22.0 (Mes-CH₃), 22.2 (Mes-CH₃), 25.2 (Zr-CH₃), 29.4 (CMe₃), 39.9 (C3), 110.5 (C1), 110.8 (C₅H₅), 128.3 (Mes), 129.5 (Mes), 134.3 (Mes), 134.8 (Mes), 138.2 (Mes), 138.6 (Mes), 138.7 (Mes), 169.1 (C2).

Preparation of (2,2-dimesityl-1-phenylethenoxy)methylzirconocene (ZM3)

To a suspension of zirconocene chloride (877 mg, 3.00 mmol) in Et₂O (50 cm³) a solution of methylmagnesium chloride (2.0 cm³, 3.0 M solution in THF, 6.0 mmol) was added at room temperature. The mixture was stirred for 3 h then a solution of 2,2-dimesityl-1-phenylethanol (1.07 g, 3.00 mmol) in Et₂O (50 cm³) was added dropwise. After stirring at room temperature for an additional 3 h the precipitate was removed by filtration. The solution was concentrated to a volume of about 10 cm³ and *n*-hexane (40 cm³) was added. After storing the mixture at -40 °C for 24 h the colorless precipitate was removed and the filtrate was evaporated to dryness affording **ZM3** as a pale yellow solid (1.56 g, 2.64 mmol, 88%). The product could be obtained in crystalline form by recrystallisation from an CH₃CN-CH₂Cl₂ mixture. Mp 218 °C; ν_{max} (KBr)/cm⁻¹ 2989, 2953, 2930, 2917, 2876, 2854, 1609, 1586, 1558, 1490, 1475, 1443, 1371, 1299, 1280, 1248, 1205, 1160, 1083, 1018, 969, 938, 922, 852, 801, 778, 749, 740, 701, 669, 638, 594, 558; δ_{H} (200 MHz; CDCl₃) -0.10 (s, 3 H, Zr-CH₃), 1.9–2.3 (coalescence, 18 H, Mes-CH₃), 5.89 (s, 10 H, C₅H₅), 6.62 (br s, 2 H, Mes-H), 6.81 (br s, 2 H, Mes-H), 7.0–7.2 (m, 5 H, Ph-H); δ_{C} (50 MHz; CDCl₃) 20.7 (Mes-CH₃), 20.9 (Mes-CH₃), 21.1 (Mes-CH₃), 21.7 (Mes-CH₃), 24.9 (Zr-CH₃), 111.0 (C₅H₅), 113.9 (C2), 127.1 (Ar), 127.3 (Ar), 127.6 (Ar), 128.7 (Ar), 129.0 (Ar), 129.1 (Ar), 129.2 (Ar), 134.8 (Ar), 135.0 (Ar), 137.0 (Ar), 137.9 (Ar), 140.4 (Ar), 159.0 (C1); *m/z* (EI) 575.1896. C₃₇H₄₀OZr requires 575.1891.

Preparation of 1,4-bis(methylzirconocenoxy)benzene (ZM4)

A solution of dimethylzirconocene (251 mg, 1.00 mmol) in CH₃CN (4 cm³) was treated dropwise with a solution of hydroquinone (55.0 mg, 500 μ mol) in CH₃CN (3 cm³) at room temperature. After stirring for 3 h the precipitate was collected and dried under reduced pressure affording **ZM4** as a colorless powder (197 mg, 339 μ mol, 68%). Mp 147 °C (Found: C, 57.66; H, 5.34. C₂₈H₃₀O₂Zr₂ requires C, 57.89; H, 5.20%); ν_{max} (KBr)/cm⁻¹ 3101, 3019, 2923, 2870, 1489, 1441, 1245, 1082, 1016, 862, 802; δ_{H} (200 MHz; CDCl₃) 0.20 (s, 6 H, Zr-CH₃), 6.10 (s, 20 H, C₅H₅), 6.30 (s, 4 H, Ph-H); δ_{C} (50 MHz; CDCl₃) 21.2 (Zr-CH₃), 110.9 (C₅H₅), 117.5 (*o*-Ph), 158.1 (quart.-Ph).

General procedure for one-electron oxidations

In an argon filled glovebox the desired amounts of the one-electron oxidant (**Fephen** or NOSbF₆) and the zirconium enolates were placed into two separate test tubes equipped with stirring rods. At a high purity argon line, 3 cm³ of the appropriate solvent (CH₃CN or CH₂Cl₂) were added to each test tube to dissolve the reactants. When the blue solution of the one-electron oxidant **Fephen** was added through a syringe to the solution of the zirconium enolate, the color of the mixture

immediately turned to a bright red. The resulting mixture was stirred at room temperature for 1 min, quenched with saturated aqueous NaHCO_3 (10 cm^3) and diluted with CH_2Cl_2 (10 cm^3). The aqueous layer was extracted three times with CH_2Cl_2 , the combined organic layers were washed with water and dried with Na_2SO_4 . The solution was filtered through silica gel in order to remove the red $\text{Fe}(\text{phen})_3(\text{PF}_6)_2$ as well as zirconium fragments split off in the course of the reaction. Removal of the solvent afforded the crude product. Product analysis was performed by ^1H NMR spectroscopy. All products were identified by comparison with data of authentic samples. For 3-mesityl-4,6,7-trimethylbenzofuran (**B1**) see ref. 26a, for 2-*tert*-butyl-3-mesityl-4,6,7-trimethylbenzofuran (**B2**) see ref. 26a and for 3-mesityl-2-phenyl-4,6,7-trimethylbenzofuran (**B3**) see ref. 26b. The yields were determined by adding *m*-nitroacetophenone as an internal ^1H NMR standard.

Cyclic voltammetry

In a glove box tetra(*n*-butyl)ammonium hexafluorophosphate (232 mg, 600 μmol) and the electroactive species (6 μmol) were placed into a thoroughly dried CV cell. At a high purity argon line CH_3CN or CH_2Cl_2 (6.0 cm^3) was added through a gastight syringe. Then a platinum disc working electrode ($d = 1$ mm), a platinum wire counter electrode and a silver wire as pseudo reference electrode were placed into the solution. The cyclic voltammograms were recorded at various scan rates using different starting and switching potentials. For determination of the oxidation potentials, ferrocene ($E^\circ = +0.39$ V vs. SCE) was added as the internal standard. Cyclic voltammograms were recorded using a Princeton Applied Research Model 362 potentiostat with a Philips model PM 8271 XYt-recorder for scan rates $\nu < 1$ V s^{-1} . For fast scan cyclic voltammetry, a Hewlett Packard model 3314A function generator was used connected to a three-electrode potentiostat developed by C. Amatore.²⁷ The employed working electrodes were laboratory-made gold (diameter: 25 μm) and platinum (diameter: 10 μm) ultramicro-electrodes. The ratios $I_{\text{pc}}/I_{\text{pa}}$ were determined according to the procedure of Nicholson.²⁸

Digital simulation of the cyclic voltammograms

The computer simulation of the redox chemistry concerning the two mechanistic scenarios was carried out on a P166+ Computer using the Crank–Nicholson technique²⁰ and Digi-Sim 2.0 for Windows.²⁹ All chemical reactions were assumed to be irreversible first-order processes except the ET-equilibrium. The cyclic voltammograms were simulated using a standard heterogeneous electron transfer rate constant $k^0_{\text{hetero}} = 0.5$ cm^{-1} and standard diffusion coefficients of $D = 5 \times 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$.

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