First characterisation of zirconium enolate radical cations in solution and their mesolytic bond cleavage to zirconocene cations

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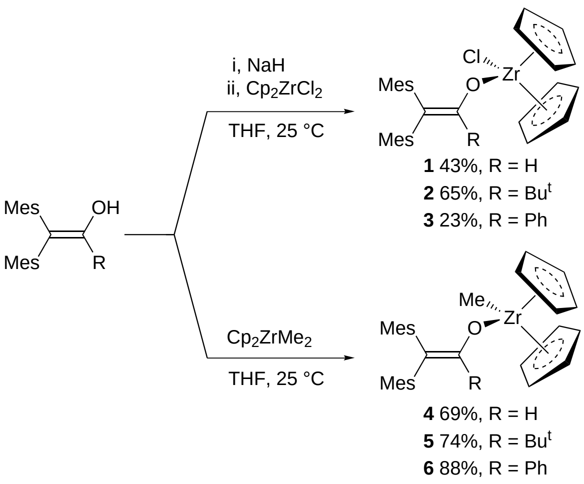
Zirconocene enolate radical cations are generated and characterised in solution for the first time; the sterically congested radical cations undergo a mesolytic Zr–O bond cleavage process yielding zirconocene cations, the kinetics of which are determined.

In light of the importance of transition metal enolates for organic synthesis[1] we have recently become interested in the redox umpolung of these nucleophilic species.[2] We were able to show that titanium enolate radical cations can undergo carbon–carbon bond formation to 1,4-diketones, a reaction which can even be conducted in a diastereoselective fashion.[3] In the present paper we describe for the first time the properties and reactions of zirconium enolate radical cations and their clean mesolytic† bond cleavage to zirconocene cations. The latter are well known as the catalytic active species in the Ziegler–Natta polymerization of α-alkenes.[4]

Since zirconium enolates constitute highly reactive compounds with a high sensitivity towards hydrolysis, only a small number of zirconium enolates[5] has been isolated and investigated. The kinetic stability of zirconium enolates should be largely increased by starting from sterically bulky β,β-dimesitylenols.[6] These were deprotonated quantitatively with sodium hydride in THF at room temperature and subsequentially reacted with stoichiometric amounts of zirconocene dichloride. All chloro zirconocene enolates could be obtained as bright yellow crystals by crystallisation from *n*-hexane or *n*-hexane–toluene.

A route leading to the methyl zirconocene enolates was realised by reacting dimethyl zirconocene with the corresponding β,β-dimesitylenols accompanied by elimination of methane. The zirconocene enolates **4–6** could be obtained in analytically pure form as pale yellow solids by crystallization from acetonitrile–dichloromethane mixtures (Scheme 1).

In standard cyclic voltammetry (CV) experiments all zirconocene enolates showed irreversible oxidation waves (E_{pa}; Table 1) in acetonitrile at 100 mV s^{-1}. By changing the solvent to dichloromethane and increasing the scan rates up to 1000 V s^{-1} reversible waves could be obtained. We observed partially reversible waves for **1–3** and **5** already at scan rates $\nu \geqslant 100$ V s^{-1}, for **4** at $\nu \geqslant 200$ V s^{-1}, and for **6** at $\nu \geqslant 50$ V s^{-1}. This represents the first direct observation of zirconium enolate radical cations in solution, allowing for the determination of their thermodynamically relevant redox potentials $E_{\frac{1}{2}}^{Ox}$ (Table 1). The oxidation potentials fall in the range +0.35 to +0.57 V *vs.* ferrocene–ferrocenium† and are *ca.* 100 mV more anodic than those of structurally analogous titanocene enolates,[2] an effect which is already known from simple titanocene and zirconocene compounds.[7]



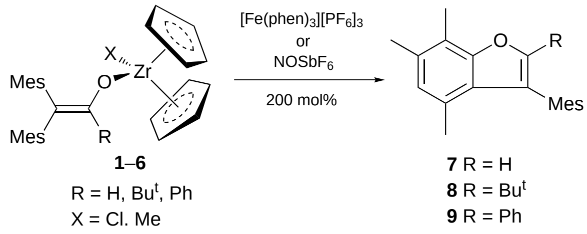
Scheme 1

Table 1 Oxidation potentials of zirconocene enolates determined by CV

Zirconocene enolate	$E_{pa}^{a,b}$/V	$E_{\frac{1}{2}}^{Ox\,a,c}$/V	Yield of benzofuran
1	+0.45	+0.57	95% of **7**
2	+0.32	+0.43	90% of **8**
3	+0.41	+0.44	88% of **9**
4	+0.51	+0.46	82% of **7**
5	+0.30	+0.35	86% of **8**
6	+0.35	+0.36	80% of **9**

[a] *vs.* Fc–Fc†. [b] In acetonitrile at ν = 100 mV s^{-1}. [c] In dichloromethane at ν = 1000 V s^{-1}.

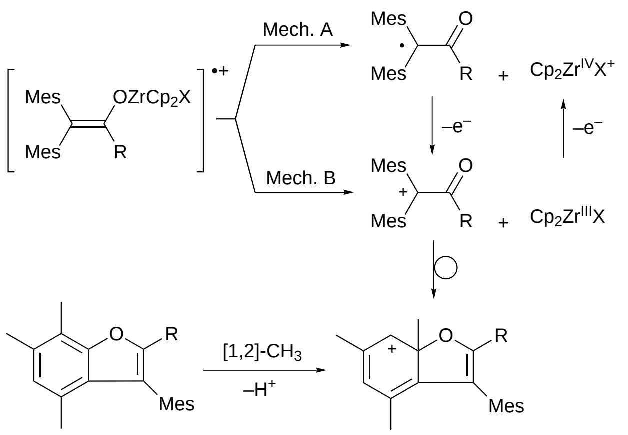
The chemical one-electron oxidations of the zirconium enolates **1–6** which were performed on a preparative scale using tris(1,10-phenanthroline)iron(III) hexafluorophosphate ($E_{\frac{1}{2}}$ = +0.69 V), as a well-defined outer-sphere one-electron oxidant, or nitrosonium hexafluorophosphate ($E_{\frac{1}{2}}$ = +0.89 V) in acetonitrile–dichloromethane afforded the benzofuran derivatives **7–9** in good yields (Scheme 2, Table 1).



Scheme 2

Formation of benzofurans by one-electron oxidation of stable enols[8] and various enol derivatives[9] (including titanium enolates[2]) is known to be initiated by a mesolytic bond cleavage of the O–X bond followed by several reaction steps that are well established (Scheme 3).

For the zirconocenes the Zr–O bond must have been broken at the stage of the enolate radical cation since the direct cyclization is highly unfavourable because of steric reasons. Equally, a dissociative electron transfer process can be ruled out since all the radical cations could be characterised at high scan rates in the CV experiment. Hence, we conclude that mesolytic Zr–O bond cleavage is the primary follow-up reaction of the



Scheme 3

radical cations $1^{\bullet+}$–$6^{\bullet+}$ which can follow two distinct mechanistic pathways:[9d] the heterolytic scission (Mech. A) would result in the formation of an α-carbonyl radical and a zirconocene cation, the homolytic variant (Mech. B) would lead to an α-carbonyl cation and a zirconocene(III) species. Both cleavage selectivities are known for enol radical cations: homolytic cleavage can be observed for radical cations of enol esters,[9a] enol carbonates and enol carbamates[9d] whereas the radical cations of enols, silyl enol ethers,[9b] enol phosphites and enol phosphinates[9c] and of the structurally very closely related titanium enolates[2] follow the heterolytic variant.

When the oxidation potentials of the homolytic cleavage fragments (α-carbonyl radicals and $Cp_2Zr^{III}X$) are known then the selectivity of such fragmentation processes can be determined by using a simple thermochemical cycle calculation. The fragments which are split off in a cationic form must have the lower redox potential. We hence measured the oxidation potential of $Cp_2Zr^{III}Me$ to $E_{pa} = -1.9$ V§ and compared it with those of the relevant α-carbonyl radicals. Since the latter are much more positive (0.15–0.36 V)[8a] it is clear that mesolytic bond cleavage of the methyl zirconocene enolates **4**–**6** takes place according to the heterolytic pathway (Mech. A). This result is in analogy to Jordan's findings, who performed one-electron oxidations of dimethyl zirconocene and other dialkyl zirconocenes with equimolar amounts of ferrocenium and isolated the cationic complexes $[Cp_2ZrR]^+$ after Zr–C bond cleavage.[10] Owing to the much larger differences of the oxidation potentials between oxidant and substrate the desired reaction time of this conversion is much longer (10 h) than in our experiments (1 min). In case of the chlorine substituted model compounds **1**–**3** simple considerations¶ propose that their fragmentation should follow the same pathway.

The knowledge of the exact mechanism of this process enabled us to determine the lifetime of zirconocene enolate radical cations by following the kinetics of the mesolytic bond cleavage through fast scan cyclic voltammetry at ultramicro electrodes in dichloromethane. From the ratio of cathodic to anodic peak current I_{pc}/I_{pa} the kinetic parameter kt was evaluated according to the method of Nicholson and Shain[11] applying a working curve for an $EC_{irr}E$ mechanism (electron transfer–chemical reaction–electron transfer). The working curve had been obtained from digital simulation of cyclic voltammograms using the implicit Crank–Nicholson technique.[12] This kinetic analysis at room temperature provided a first order-rate constant of $k_f = 3.3 \times 10^2\ s^{-1}$ ($t_{\frac{1}{2}} = 2.1 \times 10^{-3}$ s) for the mesolytic bond cleavage of $\mathbf{2}^{\bullet+}$, $k_f = 3.1 \times 10^2\ s^{-1}$ ($t_{\frac{1}{2}} = 2.2 \times 10^{-3}$ s) for that of $\mathbf{3}^{\bullet+}$, $k_f = 8.3 \times 10^2\ s^{-1}$ ($t_{\frac{1}{2}} = 8.4 \times 10^{-4}$ s) for that of $\mathbf{4}^{\bullet+}$ and $k_f = 5.0 \times 10^2\ s^{-1}$ ($t_{\frac{1}{2}} = 1.4 \times 10^{-3}$ s) for that of $\mathbf{5}^{\bullet+}$.

In conclusion, we have characterised for the first time zirconium enolate radical cations in solution and identified them as rapidly cleaving precursors for zirconocene cations. Work is in progress to use this mesolytic cleavage reaction in photo-induced electron transfer reactions for triggering polymerisation.

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Notes and References

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† The expression mesolytic was coined by Maslak to describe bond cleavage of radical ions to yield radical and ionic products: P. Maslak and J. N. Narvaez, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 283.

‡ All potentials are referenced to the ferrocene–ferrocenium (Fc) redox couple unless otherwise noted. To obtain values *vs.* SCE, simply add +0.39 V.

§ We determined the reduction potential of the corresponding cation $[Cp_2Zr^{IV}Me(MeCN)_2]BPh_4$ to $E_{pc} = -1.94$ V (in acetonitrile at 100 mV s^{-1}; supporting electrolyte: $NaBPh_4$). The preparation of this cation is described in: R. F. Jordan, C. S. Bajgur, W. E. Dasher and A. L. Rheingold, *Organometallics*, 1987, **6**, 1041.

¶ The difference between the oxidation potentials of $Cp_2Zr^{III}Me$ and $Cp_2Zr^{III}Cl$ can be approximated by the difference between the half-wave potentials of Cp_2ZrMe_2 ($E_{\frac{1}{2}} = -3.06$ V) and Cp_2ZrCl_2 ($E_{\frac{1}{2}} = -2.04$ V). As the potential of $Cp_2Zr^{III}Me$ is $E_{pa} \approx -1.9$ V we assume that that of $Cp_2Zr^{III}Cl$ is $E_{pa} \approx -0.9\ V_{Fc}$ being distinctly lower than those of the α-carbonyl radicals.

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