



Turn me on: The iron-centered oxidation of ferrocenyl-substituted ruthenium-based olefin metathesis precatalysts by chemical oxidants or by an

electrode at the oxidizing potential converts a latent catalyst into a catalytically active complex for ROMP reactions (see scheme).

Latent Catalysts -

R. Savka, S. Foro, M. Gallei, *M. Rehahn, H. Plenio**..... **IIII**-**IIII**

Oxidation-Triggered Ring-Opening Metathesis Polymerization



Oxidation-Triggered Ring-Opening Metathesis Polymerization

Roman Savka,^[a] Sabine Foro,^[c] Markus Gallei,^[b] Matthias Rehahn,^[b] and Herbert Plenio*^[a]

Abstract: Eight new *N*-Hoveyda-type complexes were synthesized in yields of 67–92 % through reaction of [RuCl₂-(NHC)(Ind)(py)] (NHC=1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes) or 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr), Ind= 3-phenylindenylid-1-ene, py = pyridine) with various 1- or 1,2-substituted ferrocene compounds with vinyl and amine or imine substituents. The redox potentials of the respective complexes were determined; in all complexes an iron-

centered oxidation reaction occurs at potentials close to E = +0.5 V. The crystal structures of the reduced and of the respective oxidized Hoveyda-type complexes were determined and show that the oxidation of the ferrocene unit has little effect on the ruthenium envi-

Keywords: iron • olefin metathesis • oxidation • polymerization • ringopening metathesis polymerization • ruthenium ronment. Two of the eight new complexes were found to be switchable catalysts, in that the reduced form is inactive in the ring-opening metathesis polymerization of *cis*-cyclooctene (COE), whereas the oxidized complexes produce polyCOE. The other complexes are not switchable catalysts and are either inactive or active in both reduced and oxidized states.

Introduction

Latent or switchable catalysts require physical or chemical stimuli to convert a catalytically inactive species into an active one.^[1] This principle has been put to good use in polymer chemistry since it allows spatial and temporal control over polymerization reactions.^[2,3] Various stimuli, such as light-induced catalyst activation, have been employed in ring-opening polymerization^[4] and ring-opening metathesis polymerization (ROMP) reactions (Scheme 1).^[5] Buchmeiser et al. reported a ROMP catalyst that is activated upon irradiation with UV light.^[6] Later, Grubbs et al. described an alternative approach using a pH-responsive catalyst that, in combination with a photo acid, also turns out to be a photo-

 M. Sc. R. Savka, Prof. Dr. H. Plenio Organometallic Chemistry, Technische Universität Darmstadt Petersenstrasse 18, 64287 Darmstadt (Germany) E-mail: plenio@tu-darmstadt.de

- [b] Dr. M. Gallei, Prof. Dr. M. Rehahn Ernst–Berl Institute for Chemical Engineering and Macromolecular Science Technische Universität Darmstadt Petersenstrasse 22, 64287 Darmstadt (Germany)
- [c] S. Foro Clemens–Schöpf-Institut for Organic Chemistry and Biochemistry Technische Universität Darmstadt Petersenstrasse 22, 64287 Darmstadt (Germany)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300868. It contains the general experimental details, ROMP procedures, and additional experimental data, including NMR spectra, cyclic voltammograms, SEC traces, mass spectra, and crystal structure analyses.



Scheme 1. Light- or redox-switchable polymerization catalysts (tren = tris[2-(dimethylamino)ethyl]amine).

sensitive ROMP catalyst.^[7] The same group reported a different pH-sensitive catalyst in which an NHC ligand bound to ruthenium is decomposed by protons resulting in catalyst activation.^[8] Slugovc et al. reported on pyridine/chloride-induced ROMP reactions.^[9]

The modulation of ligand donor ability by the protonation of basic groups attached to a ligand enables control over the stereochemistry of ROMP polymers because the electron density at the catalytic site has been shown to have an influence on the E/Z ratio of polynorbornenes.^[10] Alternatively, activation of olefin metathesis catalysts is also possible by utilizing ultrasound-induced shear forces.^[11] Recently, Matyjaszewski et al. demonstrated redox-controlled atom-transfer radical polymerization (ATRP) by electrochemically shuttling between a deactivated Cu²⁺ and an activated Cu⁺ state.^[12] Ferrocene-based redox switches^[13] attached to a catalytically active complex modulate the electron donation of

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FF These are not the final page numbers!

www.chemeurj.org

the respective ligand, which then oscillates between a highand low-activity polymerization catalyst state.^[14] In another example, ring-closing metathesis reactions were controlled through a redox-switched solubility change since the oxidation of a ferrocene-tagged olefin metathesis catalyst led to the precipitation of the salt from the nonpolar solvent, followed by redissolution upon reduction of the catalyst.^[15]

Herein, we demonstrate oxidation-activated catalysts for ROMP reactions employing chemical, as well as electrochemical, stimuli.

Results and Discussion

Synthesis of ligands and Hoveyda-type ruthenium complexes: The synthesis of new ferrocene-containing ligands is described in Scheme 2. The bidentate ligands are characterized by a nitrogen donor and a vinyl group bonded to a ferrocene group. The nitrogen donor is either directly attached to the ferrocene unit (5, 6, and 7) or in conjugation with the electrochemically active group (3) to allow a large change in the donor ability of this nitrogen donor upon oxidation of the ferrocene unit.^[16] The vinyl group is required for the formation of a carbene complex with a suitable ruthenium pre-

with a suitable rutheniur cursor complex.

The reactions of the new ligands, 3, 5, 6, and 7, with the commercially available [RuCl₂-(NHC)(Ind)(py)] (Ind=3-phenylindenylid-1-ene; py=pyridine; NHC=1,3-bis(2,4,6-trimethylphenylimidazolin)-2-ylidene (SIMes) or 1,3-bis(2,6-diisopropylphenylimidazolin)-2-ylidene (SIPr)) result in the facile formation of the respective Hoveyda-type complexes in yields of 67-92% (Scheme 3). All complexes were characterized by NMR spectroscopy and mass spectrometry. Complexes with organometallic fragments in the benzylidene ligand are rare, although recently a Hoveyda-type complex with a {Cr(CO)₃} unit was reported.^[17] Complexes, closely related to 8, 9, 10, and 11, with phenyl or 1,2-benzenediyl groups instead of ferrocenyl groups, have been reported in the literature before and several were shown to be latent catalysts in ROMP or ring-closing metathesis (RCM) reactions.[18]



Scheme 2. Synthesis of ferrocenyl-based ligands (Fc=ferrocenyl; Mes= mesityl). Reagents and conditions: a) 2,4,6-trimethylaniline, TsOH (Ts= tosyl), toluene, reflux, overnight; b) *n*BuLi, THF, -78 °C, 1 h then DMF, -78 °C to RT; c) MePPh₃I, KO*t*Bu, THF, -10 °C to RT, overnight; d) molecular sieves, CH₂Cl₂, RT; e) molecular sieves, toluene, 100 °C.





Scheme 3. Synthesis of the new ferrocenyl-substituted Hoveyda complexes 8a, 8b, 9a, 9b, 10a, 10b, 11a, and 11b (yields given in brackets), and the structure of the known complex 10c.

Chem. Eur. J. 2013, 00, 0-0

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

______3

The complexes 8–11 can be oxidized, thereby converting an electron-donating ferrocene into an electron-withdrawing ferrocenium unit. To better understand the properties of the oxidized species, complexes 11a and 11b were reacted with acetyl ferrocenium BF_4^- to afford 11a⁺ and 11b⁺ in good yields (Scheme 4). The oxidized complexes are stable spe-



Scheme 4. Synthesis of oxidized ferrocenyl-substituted Hoveyda complexes.

cies and single crystals of $11a^+$ were obtained without special precautions. The NMR signals of the paramagnetic complexes $11a^+$ and $11b^+$ are broadened (especially for the protons close to the paramagnetic iron), but nonetheless the benzylidene proton can be identified at $\delta = 16.2$ ($11a^+$) and 16.9 ppm ($11b^+$), which corresponds to a nearly 2 ppm shift of this resonance in comparison with the neutral complexes 11a and 11b. The identification of the oxidized complexes is based on high-resolution mass spectra and a crystal structure analysis of $11a^+$.

Determination of redox potentials: The redox potentials for the eight new complexes, **8–11**, were determined (Table 1).

radie in reedon potentialo di compienes o in	Table 1.	Redox	potentials	of c	complexes	8-11. ^[a]
--	----------	-------	------------	------	-----------	----------------------

Complex	Redox potential [V] $(E_a-E_c [mV])$
8a	0.518 (64)
8b	0.513 (64)
9a	0.483 (96)
9b	0.511 (78)
10a	0.496 (81)
10b	0.482 (68)
11a	0.501 (72)
11b	0.485 (62)
10c	$0.783 (-)^{[b]}$

[a] Solvent: CH₂Cl₂, scan rate: 100 mV s⁻¹, supporting electrolyte: 0.1 m NBu₄PF₆, potentials versus FcMe₈: $E_{1/2} = -0.01$ V. [b] Oxidation potential only, irreversible oxidation.

For all complexes a single reversible redox event is observed and all potentials are located in a narrow range of 0.48– 0.52 V. This is not surprising for the structurally closely related complexes **10a**, **10b**, **11a**, and **11b**, but is unexpected for the four complexes **8a**, **8b**, **9a** and **9b**. In principle, two redox reactions have to be considered in such complexes:

the oxidation of Ru^{II/III} and of Fe^{II/III}. The similarity of the redox potentials in the series of complexes studied raised the question of whether the observed redox events are iron or ruthenium centered. On comparing the redox potentials of iron in nitrogen-substituted ferrocenes (typically close to $E = 0.0 \text{ V}^{[19]}$ with those of ruthenium in Grubbs-Hoveydatype complexes $(E = +0.45 - +1.1 \text{ V})^{[20]}$ the redox potentials observed in the Hoveyda-type complexes 8-11 appear to be closer to the Ru^{II/III} potentials than to the typical Fe^{II/III} potentials. However, it is known that, upon coordination of metal ions to donor atoms located in the vicinity to the ferrocene unit, the Fe^{II/III} redox potentials can be shifted anodically by several hundred millivolts.[21] To firmly assign the iron- or ruthenium-centered nature of the oxidation reaction, the redox potential of the closely related and known^[18c] complex **10c**, in which the ferrocenyl group is replaced by a phenyl group, was determined. Based on the oxidation curve, the Ru^{II/III} redox potential for complex 10c was estimated as approximately 0.75 V.^[22] This is clearly higher than the Fe^{II/III} redox potentials reported for complexes 8-11, but is a typical Ru^{II/III} value for such complexes.^[20a] Based on this experiment, the redox potentials reported in Table 1 correspond to Fe^{II/III}.

X-ray crystal structure analysis of ferrocenyl-substituted Hoveyda-type complexes: The crystal structures^[23] of complexes 8a, 11a, and of the oxidized complex $11a^+$ were determined (Figures 1, 2, and 3). Selected bond lengths and



Figure 1. X-ray crystal structure of complex **8a**. Selected bond lengths [pm] and angles [°]: Ru=CH 181.3(1), Ru-C(NHC) 202.6(11), Ru-Cl 237.0(3), 237.8(3), Ru-N 217.6(8), Fe-C average 203.1; Cl-Ru-Cl 173.1(3), N-Ru-C(NHC) 168.8(3). CCDC-916243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

angles are summarized in the legend of the respective figures. In all complexes studied, ruthenium displays a nearly square-pyramidal coordination geometry, which is typical for such complexes.^[24] Complex **8a** crystallizes as a racemic mixture of the two planar chiral isomers. In the crystal of **8a**, the two chloro ligands are located *trans* to each other; there is no evidence (NOESY NMR spectroscopy) that a different structure (*cis*-chloro) occurs in solution. On com-

4 ____

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 2. X-ray crystal structure of complex **11 a**. Selected bond lengths [pm] and angles [°]: Ru=CH 182.6(3), Ru-C(NHC) 207.0(3), Ru-Cl 237.1(1), 237.5(1), Ru-N 213.1(3), Fe-C average 204.6; Cl-Ru-Cl 168.2(3), N-Ru-C(NHC) 170.1(1). CCDC-916235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Figure 3. X-ray crystal structure of oxidized complex **11** a^+ (cation only, BF₄⁻ omitted). Selected bond lengths [pm] and angles [°]: Ru=CH 182.8(8), Ru-C(NHC) 206.6(7), Ru-Cl 235.6(3), 233.1(3), Ru-N 213.2(6), Fe-C average 207.5; Cl-Ru-Cl 161.5(1), N-Ru-C(NHC) 170.8(1). CCDC-916218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

paring the bond parameters of **8a** to those of the related complex by Slugovc et al.,^[18a] which has a 1,2-phenylendiyl group instead of the ferrocene group, only two significant differences are found: the Ru–N bond in **8a** is almost 10 pm longer, and the Ru=CH bond in **8a** is approximately 5 pm shorter. The crystal structures of **11a** and **11a**⁺ were of particular interest in order to determine whether oxidation leads to characteristic changes in the structure of the oxidized complex compared to the neutral species (**11a**). On comparing the geometric parameters around ruthenium, only minor changes are seen; the iron-centered oxidation appears to have little influence. The Fe–C bond lengths in **11a**⁺ show modest elongation (**11a** Fe–C average = 204.6 pm and **11a**⁺ Fe–C average = 207.5 pm), which is indicative of iron-centered oxidation of the bimetallic complexes. The eclipsed orientation of the two cyclopentadienyl rings in $11a^+$ is as normal as the staggered orientation of those rings in the neutral complex $11a^{[25]}$ These structural changes reconfirm the iron-centered nature of the electrochemical redox processes.

Redox-switched ring-opening metathesis polymerization: The five complexes **8a**, **9a**, **9b**, **10a**, and **11a** were evaluated in the ROMP of *cis*-cyclooctene, which is a popular monomer in ROMP reactions (Scheme 5).^[26] To be useful as



Scheme 5. ROMP reaction of cis-cyclooctene.

switched catalysts, the complexes need to be latent catalysts in the reduced state and display sufficient polymerization activity in the oxidized state.

Complexes **9a** and **10a** were found to rapidly polymerize *cis*-cyclooctene at room temperature and cannot be considered to be latent. The respective SIPr-based complexes **9b** and **10b** initiate the reaction more slowly, but still show significant ROMP activity with *cis*-cyclooctene under the same reaction conditions and thus are not suitable for switched ROMP reactions (Figure 4). The nonlatent behavior of com-



Figure 4. Conversion-time data for the ROMP reaction of *cis*-cyclooctene $(0.2 \text{ mol } L^{-1})$ at 20 °C in toluene/CH₂Cl₂ with complexes **9a** (\bullet ; 0.1 mol%) and **10a** (\bullet ; 0.1 mol%).

plex **10a** is closely related to that of **10c** (Ph instead of Fc), which displays room temperature activity in the ROMP of dicyclopentadiene.^[18c] The nonlatency of complexes **9** reconfirms the previous observation that five-membered-ring Hoveyda-type chelates initiate reactions much faster than six-membered-ring chelates.^[18a] In this vain, complex **11a** shows negligible ROMP activity at room temperature; unfortunately the same holds true for the oxidized complex **11a**⁺. This is in line with the behavior of the related com-

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

GaA, Weinheim www.chemeurj.org _____5 These are not the final page numbers!





Figure 5. Conversion-time data for the ROMP reaction of *cis*-cyclooctene $(0.2 \text{ mol } L^{-1})$ at 20°C in toluene/CH₂Cl₂ (12:1) with the complexes **8a** (\blacksquare , \Box ; 0.1 mol%) and **8b** (\bullet , \odot ; 0.2 mol%) with (\blacksquare , \bullet) or without (\Box , \odot) added oxidizer (acetylferrocenium tetrafluoroborate).

plex with Ph instead of Fc, which was previously found to be a very reluctant ROMP catalyst.^[18a]

In contrast, complexes 8a and 8b appear to be useful in redox-switched ROMP (Figure 5). The reaction of *cis*-cyclooctene with 8a gives only 4% conversion after 5 h. Adding an oxidizer (acetylferrocenium tetrafluoroborate) to complex 8a immediately generates $8a^+$, which is a much more active catalyst in ROMP reactions. Even better results are obtained with the more slowly initiating complex 8b in the same reaction; with 8b, after 24 h, less than 1% of the monomer is consumed, whereas $8b^+$ converts 96% of the monomer into a polymer during the same period of time (Figure 5).

We do not know with certainty, why complexes 11 are inactive following oxidation and why complexes 8 are switchable catalysts. The main difference between the two complexes is that the oxidation of the ferrocene unit in complexes 11 has a smaller influence on the electron density at the ruthenium atom than in complexes 8. This becomes apparent when comparing the redox potentials of related Hoveyda-type complexes bearing substituents on the 2-OPh or on the 1,2-benzenediyl unit.^[20b,c] In complexes 8, oxidation of the ferrocene unit acts on the nitrogen donor and on the ruthenium. In complexes 11, the oxidation of the ferrocenyl unit weakens nitrogen donation, but has little influence on the ruthenium atom. It is known that weak donors trans to the NHC ligand and electron deficiency at the ruthenium center both enhance precatalyst activation.^[20b] Both of these effects are active in complexes 8^+ and this likely contributes to their better switchability in comparison with 11.

Next, we were interested in whether the ROMP activity can also be switched electrochemically. Analogous experiments by using complex **8a** were done in CH_2Cl_2 as the solvent and in the presence of a supporting electrolyte, Bu_4NPF_6 (Figure 6). Again, complex **8a** was found to be a latent catalyst and, over 5 h, only about 1 % of the monomer underwent a ROMP reaction. In the next experiment, a solution of complex **8a** with *cis*-cyclooctene in CH_2Cl_2 was oxidized electrochemically on a platinum mesh electrode. A constant current of 1 mA was applied to the cell until



Figure 6. Conversion–time data for the ROMP reaction of *cis*-cyclooctene $(0.2 \text{ mol } L^{-1})$ at 20 °C in CH₂Cl₂ with the complex **8a** (\bullet ; 0.1 mol%) and electrochemically oxidized **8a** (\blacksquare ; 0.1 mol%).

0.385 C of charge had been passed through the solution. The electrochemical oxidation of 8a generates a catalytically active species that converts 95% of the monomer into a polymer over the following 5 h. To make sure that the polymerization of the monomer is induced by oxidation of the ruthenium complex, the experiment was repeated in the absence of ruthenium complex 8a, under otherwise identical conditions. Polymerization of *cis*-cyclooctene was not observed. This clearly shows that the oxidation of precatalyst 8a to form $8a^+$ is responsible for the redox-switched catalysis.

The molar masses of the polycyclooctene (polyCOE) compounds produced with complexes 9a and 10a were determined by using size-exclusion chromatography (SEC) against polystyrene standards (Table 1). Unfortunately, the polymer obtained from the switchable catalysts 8a and 8b was insoluble in THF^[27] and SEC data could not be obtained.^[28] This insolubility of polyCOE in various solvents is not uncommon and has been reported previously.^[29] Nonetheless, the question remains, whether the insolubility of polyCOE is due to very long polymer chains or whether an unknown (oxidation-induced) process leads to significant cross-linking. To clarify this, the oxidation-triggered polymerization of 8b was repeated for a much higher ratio of COE/Ru (100:1) to obtain shorter polymer chains. The polymer formed in this experiment is soluble and (according to NMR spectroscopy) is a normal linear polyCOE. SEC data (Figure SI42 in the Supporting Information) reveal the formation of a polymer with $M_{\rm n} = 88\,000 \,{\rm g\,mol^{-1}}$ and $M_{\rm w} =$ 129000 gmol⁻¹, indicative of a relatively low initiation efficiency of the switched catalyst. The insolubility of the ("switched") polymer at COE/Ru=1000 appears to be due to the length of the (linear) polymer chains.

The ¹H NMR spectra of the various polyCOE compounds obtained (or the CDCl₃ soluble fraction) display two peaks, at $\delta = 5.34$ and 5.38 ppm, which can be integrated to provide the *trans/cis* ratio (data are listed in Table 2). This parameter depends very much on catalyst design and has an influence on $T_{\rm m}$.

⁶ www.chemeurj.org © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Table 2. Data for polyCOE synthesis obtained with complexes 8a, 9a, and 10a.

Catalyst	Ratio COE/Ru	$M_{\rm n}$ [g mol ⁻¹] ^[c]	PDI	<i>trans/cis</i> ratio ^[e]	Time	Conversion [%]
8a ^{+[a]}	1000	_[d]	-	3.2:1	5 h	96
8a ^{+[b]}	1000	_[d]	_	3.1:1	5 h	95
8b+[a]	500	_[d]	_	$2.8:1^{[f]}$	24 h	96
9a	1000	55760	1.16	4.3:1	10 min	99
10 a	1000	66 990	1.22	4.3:1	30 min	99

[a] Chemical oxidation. [b] Electrochemical oxidation. [c] Solvent: THF. [d] Insoluble in THF. [e] Determined by NMR spectroscopy in $CDCl_3$. [f] Same ratio observed for the soluble polyCOE obtained at COE/Ru = 100.

Conclusion

Eight new Hoveyda-type complexes with ferrocenyl substituents were synthesized. Two of these complexes (**8a** and **8b**) were found to be latent catalysts for ROMP reactions in the reduced state, but are able to polymerize *cis*-cyclooctene following chemical or electrochemical oxidation of the ferrocenyl group. The oxidative stimulus by using mild chemical oxidizers is orthogonal to most organic functional groups. The electrochemical initiation of the polymerization through electrodes adjusted to an oxidative potential is unprecedented for ROMP reactions and could enable microstructure control of the polymerization process. Furthermore, control over the cross-linking process, might provide access to thermally triggered shape-memory polymers.

Experimental Section

Synthesis of complexes 8a and 8b: A Schlenk flask containing [RuCl₂-(SIMes)(Ind)(py)] (200 mg, 0.26 mmol) or [RuCl₂(SIPr)(Ind)(py)] (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Next, a stock solution of **3** (0.1 m, 3.1 mL) in dry and degassed toluene was added under an atmosphere of nitrogen. The resulting solution was heated for 1.5 h at 65 °C. The volatile compounds were removed in vacuo and the residue purified by column chromatography (cyclohexane/acetone/NEt₃, 100:20:1 v/v/v). After evaporation of the volatile compounds, *n*-pentane (5 mL) was added to the remaining solid, and the mixture was sonicated and kept in a fridge at -35 °C for 2 h. The precipitate was collected by filtration and dried in vacuo.

Complex 8a: Complex 8a was obtained as a brown-orange powder (156 mg, 73 % yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 17.45$ (s, 1 H; Ru= CH), 8.06 (s, 1H; N=CH), 7.12 (s, 1H; aromatic H^{SIMes}), 7.01 (s, 1H; aromatic H^{SIMes}), 6.84 (s, 1 H; aromatic H^{SIMes}), 6.75 (s, 1 H; aromatic H^{SIMes}), 6.56 (s, 2H; aromatic H^{Mes}), 4.80–4.77 (m, 1H; H^{Fc}), 4.47 (t, J=2.5 Hz, 1H; H^{Fc}), 4.40–4.37 (m, 1H; H^{Fc}), 4.16 (s, 5H; H^{Fc}), 4.09–4.02 (m, 2H; NCH₂), 3.91–3.84 (m, 2H; NCH₂), 2.68 (s, 3H; o-Me^{SIMes}), 2.50 (s, 3H; o-Me^{SIMes}), 2.45 (s, 3H; p-Me), 2.27 (s, 3H; p-Me), 2.18 (s, 3H; o-Me^{SIMes}), 2.15 (s, 3H; p-Me), 1.99 (s, 3H; o-Me^{SIMes}), 1.87 (s, 3H; o-Me^{Mes}), 1.81 ppm (s, 3H; o-Me^{Mes}); ¹³C NMR (126 MHz, CDCl₃): δ = 314.13, 217.03, 169.40, 146.80, 139.30, 139.17, 138.75, 138.71, 138.62, 138.13, 137.92, 134.76, 134.46, 132.01, 129.51, 129.14, 128.62, 99.30, 76.65, 75.15, 72.77, 70.22, 65.00, 51.92, 50.98, 21.39, 21.23, 20.90, 20.76, 20.35, 20.03, 19.19, 18.33 ppm; HRMS (EI): m/z calcd for C₄₂H₄₇N₃Cl₂FeRu: 821.1531 $[M]^+$; found: 821.1511. Single crystals of **8a** were obtained by slow evaporation of CH₂Cl₂/cyclohexane at ambient temperature under air.

FULL PAPER

Complex 8b: Complex 8b was obtained as a brown powder (158 mg, 67% yield). ¹H NMR (500 MHz, CDCl₃): δ=17.49 (s, 1 H; Ru=CH), 8.12 (s, 1H; N=CH), 7.63 (t, J = 7.7 Hz, 1H; aromatic p-H^{SIPr}), 7.52 (d, J =7.1 Hz, 1 H; aromatic *m*-H^{SIPr}), 7.43–7.37 (m, 2 H; aromatic H^{SIPr}), 7.16 (t, J = 7.8 Hz, 2 H; aromatic H^{SIPr}), 6.65 (s, 2 H; aromatic H^{Mes}), 4.81–4.79 (m, 1H; H^{Fc}), 4.47 (t, J = 2.6 Hz, 1H; H^{Fc}), 4.44–4.36 (m, 1H; NCH_xH_y), 4.34–4.32 (m, 1H; H^{Fc}), 4.23–4.10 (m, 8H; 5 H^{Fc} , 2CH(Me)₂, NCH_xCH_y), 4.09-3.97 (m, 2H; NCH₂), 3.05 (sep, J=6.8 Hz, 1H; CH(Me)₂), 3.00 (sep, J = 6.8 Hz, 1H; CH(Me)₂), 2.22 (s, 3H; p-Me^{Mes}), 1.93 (s, 3H; o-Me^{Mes}), 1.75 (s, 3H; o-Me^{Mes}), 1.38 (d, J = 7.0 Hz, 3H; Me^{iPr}), 1.36 (d, J = 6.6 Hz, 3H; Me^{*i*Pr}), 1.32 (d, *J*=6.5 Hz, 3H; Me^{*i*Pr}), 1.17 (d, *J*=6.9 Hz, 3H; Me^{*i*Pr}), 1.14 (d, J = 6.8 Hz, 3H; Me^{iPr}), 1.09 (d, J = 6.8 Hz, 3H; Me^{iPr}), 0.92 (d, J =6.6 Hz, 3H; Me^{Pr}), 0.58 ppm (d, J=6.5 Hz, 3H; Me^{Pr}); ¹³C NMR $(126 \text{ MHz}, \text{ CDCl}_3): \delta = 309.77, 220.16, 169.42, 150.34, 149.55, 149.18,$ 148.62, 147.32, 138.69, 135.23, 134.90, 132.47, 130.42, 129.83, 129.18, $129.08,\ 128.47,\ 124.83,\ 124.41,\ 123.75,\ 97.38,\ 76.53,\ 75.47,\ 72.71,\ 70.27,$ 66.43, 55.09, 53.66, 29.54, 28.72, 28.41, 28.23, 28.02, 27.05, 26.38, 26.34, 24.59, 23.90, 22.72, 22.36, 21.16, 20.97, 20.72 ppm; HRMS (EI): m/z calcd for C₄₈H₅₉N₃Cl₂FeRu: 905.2470 [M]⁺; found: 905.2472.

Synthesis of complexes 9a and 9b: A Schlenk flask containing $[RuCl_2-(SIMes)(Ind)(py)]$ (200 mg, 0.26 mmol) or $[RuCl_2(SIPr)(Ind)(py)]$ (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Toluene (3 mL) and 5 (75 μ L, 0.29 mmol) were added under an atmosphere of nitrogen and the resulting mixture was heated for 1.5 h at 65 °C. After evaporation of the volatile compounds, methanol (5 mL) was added to the remaining solid, and the mixture sonicated and kept in the fridge at -35 °C for 2 h. The precipitate was collected by filtration, washed with cold methanol, and dried in vacuo.

Complex **9***a*: Complex **9***a* was obtained as a pink powder (131 mg, 70% yield). ¹H NMR (500 MHz, C_6D_6): δ =16.43 (d, J=0.8 Hz, 1H), 6.94 (s, 2H), 6.91 (s, 2H), 4.26 (s, 5H), 4.02–4.00 (m, 1H), 3.86 (t, J=2.6 Hz, 1H), 3.74 (dd, J=2.7, 1.1 Hz, 1H), 3.45 (s, 4H), 2.68 (s, 9H), 2.64 (s, 9H), 2.19 ppm (s, 6H); ¹³C NMR (126 MHz, C_6D_6): δ =291.81, 212.61, 129.79, 129.67, 115.15, 101.18, 69.91, 68.87, 61.11, 57.58, 51.72, 21.15, 19.99 ppm (brs); HRMS (EI): m/z calcd for $C_{34}H_{41}N_3Cl_2FeRu$: 719.1061 [M]⁺; found: 719.1056.

Complex **9***b*: Complex **9***b* was obtained as a pink powder (182 mg, 87% yield). ¹H NMR (300 MHz, CDCl₃): δ =16.45 (d, *J*=0.8 Hz, 1H), 7.47 (t, *J*=7.7 Hz, 2H), 7.39–7.27 (m, 4H), 4.50 (dt, *J*=2.5, 0.8 Hz, 1H), 4.23 (t, *J*=2.7 Hz, 1H), 4.20 (s, 5H), 4.09 (s, 4H), 3.80 (dd, *J*=2.6, 1.1 Hz, 1H), 3.75 (sep, *J*=6.8 Hz, 4H), 2.80 (brs, 3H), 2.63 (brs, 3H), 1.40 (d, *J*=6.6 Hz, 6H), 1.28 ppm (t, *J*=6.9 Hz, 18H); ¹³C NMR (75 MHz, CDCl₃): δ =294.43, 214.13, 148.65, 137.78, 129.32, 124.43, 124.35, 114.01, 100.96, 69.82, 69.17, 62.09, 57.33, 54.72, 53.65 (brs), 28.70, 28.59, 26.65, 26.56, 24.38, 24.19 ppm; HRMS (EI): *m*/*z* calcd for C₄₀H₅₃N₃Cl₂FeRu: 803.2000 [*M*]⁺; found: 803.1999.

Synthesis of complexes 10 a and 10b: A Schlenk flask containing $[RuCl_2-(SIMes)(Ind)(py)]$ (200 mg, 0.26 mmol) or $[RuCl_2(SIPr)(Ind)(py)]$ (216 mg, 0.26 mmol) was evacuated and back-filled with nitrogen three times. Next, a solution of **6** (92 mg, 0.31 mmol) in dry and degassed toluene (3 mL) was added under an atmosphere of nitrogen. The resulting mixture was heated for 1 h at 60 °C. After evaporation of the volatile compounds, methanol (10 mL) was added to the remaining solid, and the mixture was sonicated. The precipitate was collected by filtration, washed with methanol, and dried in vacuo.

Complex **10***a*: Complex **10***a* was obtained as a brownish powder (156 mg, 79% yield). ¹H NMR (500 MHz, CDCl₃): δ =18.72 (t, *J*= 5.2 Hz, 1H), 8.08 (s, 1H), 7.03 (s, 4H), 4.04 (s, 9H), 3.92 (t, *J*=1.9 Hz, 2H), 3.90 (t, *J*=1.9 Hz, 2H), 2.96 (d, *J*=5.2 Hz, 2H), 2.71–2.23 (m, 18H), 1.05 ppm (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ =343.65, 218.31, 173.29, 140.10, 138.39, 129.57, 103.11, 70.29, 66.40, 63.74, 51.59 (brs), 42.10, 26.85, 21.39, 20.28 (brs), 18.42 ppm (brs); HRMS (EI): *m/z* calcd for C₃₇H₄₅N₃Cl₂FeRu: 759.1374 [*M*]⁺; found: 759.1414.

Complex **10***b*: Complex **10***b* was obtained as a brownish powder (202 mg, 92% yield). ¹H NMR (500 MHz, CDCl₃): δ =18.80 (t, *J*= 4.8 Hz, 1H), 8.21 (s, 1H), 7.47 (t, *J*=7.7 Hz, 2H), 7.32 (d, *J*=7.7 Hz, 4H), 4.10 (s, 4H), 3.97 (d, *J*=2.9 Hz, 7H), 3.88 (t, *J*=1.9 Hz, 2H), 3.60 (d, *J*=12.6 Hz, 4H), 2.70 (d, *J*=4.8 Hz, 2H), 1.22 (d, *J*=6.8 Hz, 24H),

Chem. Eur. J. **2013**, 00, 0–0

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



These are not the final page numbers! **77**

CHEMISTRY

A EUROPEAN JOURNAL

1.02 ppm (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ =220.03, 175.24, 165.53, 149.33 (brs), 129.32, 124.55, 104.13, 70.14, 66.70, 64.80, 63.00, 54.43, 41.31, 28.77, 26.71, 26.63, 23.64 ppm; HRMS (EI): *m/z* calcd for C₄₃H₅₇N₃Cl₂FeRu: 843.2313 [*M*]⁺; found: 843.2331.

Synthesis of complexes 11 a and 11b: A Schlenk flask containing $[RuCl_2-(SIMes)(Ind)(py)]$ (200 mg, 0.26 mmol) or $[RuCl_2(SIPr)(Ind)(py)]$ (216 mg,0. 26 mmol) was evacuated and back-filled with nitrogen three times. A stock solution of 7 (3.1 mL, 0.1 M) in dry and degassed toluene was added under an atmosphere of nitrogen. The resulting mixture was heated for 1 h at 60 °C. After evaporation of the volatile compounds, methanol (5 mL) was added to the remaining solid, the mixture was sonicated and cooled to -40 °C. The precipitate was collected by filtration, washed with methanol, and dried in vacuo.

Complex **11***a*: Complex **11***a* was obtained as a dark-green powder (180 mg, 89% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 18.65$ (s, 1H), 9.10 (s, 1H), 7.67 (td, J = 7.5, 1.3 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.45 (td, J = 7.5, 1.3 Hz, 1H), 7.15 (s, 4H), 6.71 (d, J = 7.7 Hz, 1H), 4.21 (t, J = 1.9 Hz, 2H), 4.20 (s, 5H), 4.14 (s, 4H), 4.07 (t, J = 1.9 Hz, 2H), 2.74–2.31 ppm (m, 18H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 310.84$, 310.75, 214.52, 164.58, 150.13, 141.62, 140.43 (brs), 138.72 (brs), 134.65, 133.06, 129.81, 128.56, 127.92 (brs), 127.07, 126.37 (brs), 123.62, 104.04, 70.68, 67.24, 64.72, 53.57, 52.46 (brs), 51.07 (brs), 21.46, 20.53 (brs), 18.53 ppm (brs); HRMS (EI): m/z calcd for $C_{39}H_{41}N_3Cl_2FeRu$: 779.1061 $[M]^+$; found: 779.1072. Single crystals of **11a** were obtained by slow evaporation of CH₂Cl₂/cyclohexane at ambient temperature under air.

Complex **11***b*: Complex **11***b* was obtained as a dark-green powder (175 mg, 78 % yield). ¹H NMR (500 MHz, CDCl₃): δ = 18.65 (s, 1H), 9.16 (s, 1H), 7.64 (td, *J* = 7.5, 1.3 Hz, 1H), 7.60 (brs, 2H), 7.50–7.45 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 4H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.30 (t, *J* = 1.9 Hz, 2H), 4.19 (brs, 4H), 4.10 (s, 5H), 4.05 (t, *J* = 1.9 Hz, 2H), 3.86–3.45 (brm, 4H), 1.45–1.20 (brm, 18H), 1.02 ppm (brs, 6H); ¹³C NMR (126 MHz, CDCl₃): δ = 303.56, 215.75, 164.64, 139.23, 133.87, 132.39, 128.34, 128.00, 127.19, 126.77, 125.55, 123.76 (brs), 123.39, 104.04, 69.27, 67.52, 66.12, 65.95, 64.41, 28.42–25.57 ppm (several broad signals); HRMS (EI): *m/z* calcd for C₄₅H₅₃N₃Cl₂FeRu: 863.2000 [*M*]⁺; found: 863.2000.

Synthesis of oxidized complexes $11a^+$ and $11b^+$; A Schlenk flask containing complex 11a (40 mg, 0.051 mmol) or 11b (44 mg, 0.051 mmol) and acetylferrocenium tetrafluoroborate (13.9 mg, 0.051 mmol) was evacuated and back-filled with nitrogen three times. CH₂Cl₂ (2 mL) was added under an atmosphere of nitrogen and the resulting solution was stirred for 20 min at room temperature. The solution was filtered and the filtrate was concentrated in vacuo. Next, diethyl ether (50 mL) was added and the precipitate was collected by filtration. The precipitate was washed with diethyl ether and toluene and dried in vacuo.

Complex 11 a⁺: Paramagnetic complex 11 a⁺ was obtained as a brownish powder (31 mg, 71 % yield). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 16.21$ ppm (s, 1H; Ru=CH); HRMS (EI): m/z calcd for C₃₉H₄₁N₃Cl₂FeRu: 779.1061 $[M-BF_4]^+$; found: 779.1060. Single crystals of 11 a⁺ were obtained by slow evaporation of CH₂Cl₂/benzene at ambient temperature under air. *Complex* 11 b⁺: Paramagnetic complex 11 b⁺ was obtained as a brown powder (33 mg, 69 % yield). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 16.86$ ppm (s, 1H; Ru=CH); HRMS (EI): m/z calcd for C₄₅H₅₃N₃Cl₂FeRu: 863.2000

 $[M-BF_4]^+$; found: 863.1959.

General procedure for the ROMP reaction of *cis*-cyclooctene by utilizing the oxidized complexes: A Schlenk tube (10 mL) charged with complexes **8**, **9**, **10**, or **11** (0.0025 mmol) and acetylferrocenium tetrafluoroborate (0.8 mg, 0.0025 mmol) was evacuated and back-filled with argon three times. CH_2Cl_2 (500 µL) was added under a stream of argon and the mixture was stirred for 10 min at room temperature. Next, a stock solution of *cis*-cyclooctene in toluene (6.0 mL (corresponding to a catalyst loading of 0.10 mol%) or 3.0 mL (catalyst loading of 0.2 mol%)) was added to the mixture. For the determination of substrate conversion, samples (60 µL) were taken after the specified times under a stream of argon and injected into vials containing ethyl vinyl ether (50 µL) and methanol (500 µL). The mixture was filtered through a clean pad of cotton to remove the insoluble polymer and the solution was analyzed by GC. The same procedure was applied for polymerization reactions utilizing complexes **8a**, **8b**, **9a**, **10a**, and **11a**.

General procedure for the ROMP reaction of *cis*-cyclooctene utilizing oxidized complex 8a and electrolysis at constant current: A three-necked electrochemical cell equipped with a magnetic stirring bar, argon inlet, platinum mesh anode, and silver spiral cathode was evacuated and backfilled with argon three times. Next, a stock solution of *cis*-cyclooctene in CH₂Cl₂ (20 mL) and complex 8a (3.3 mg, 4.0 µmol) dissolved in CH₂Cl₂ (300 µL) were added under a stream of argon. A constant current of 1 mA was applied to the cell until 0.385 C of charge had been passed through the solution (t=385 s). For the determination of substrate conversion, samples (60 µL) were taken after the specified times under a stream of argon and injected into vials containing ethyl vinyl ether (50 µL) and methanol (500 µL). The mixture was filtered through a clean pad of cotton to remove insoluble polymer and the solution analyzed by GC.

Acknowledgements

The authors would like to thank the Landesoffensive zur Entwicklung wissenschaftlich-ökonomischer Exzellenz (LOEWE Soft Control) for financial support of this work. Umicore AG & Co KG is thanked for the generous donation of ruthenium complexes.

- a) U. Lüning, Angew. Chem. 2012, 124, 8285–8287; Angew. Chem. Int. Ed. 2012, 51, 8163–8165; b) D. Díaz Díaz, D. Kühbeck, R. J. Koopmans, Chem. Soc. Rev. 2011, 40, 427; c) A. M. Allgeier, C. A. Mirkin, Angew. Chem. 1998, 110, 936–952; Angew. Chem. Int. Ed. 1998, 37, 894–908.
- [2] a) F. A. Leibfarth, K. M. Mattson, B. P. Fors, H. A. Collins, C. J. Hawker, *Angew. Chem.* 2013, 125, 210–222; *Angew. Chem. Int. Ed.* 2013, 52, 199–210; b) S. Monsaert, A. L. Vila, R. Drozdzak, P. V. D. Voort, F. Verpoort, *Chem. Soc. Rev.* 2009, 38, 3360–3372.
- [3] The term "latent catalyst" is not rigorously defined in the literature, but is often understood to mean that the catalyst is inactive under ambient conditions and needs to be activated (converted into a catalytically active state) by some chemical or physical stimulus to enable a catalytic transformation.
- [4] M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider, I. Manners, *Nat. Mater.* 2006, 5, 467–470.
- [5] a) Y. Vidavsky, N. G. Lemcoff, *Beilstein J. Org. Chem.* **2010**, *6*, 1106–1119; b) Y. Vidavsky, A. Anaby, N. G. Lemcoff, *Dalton Trans.* **2012**, *41*, 32–43.
- [6] D. Wang, K. Wurst, W. Knolle, U. Decker, L. Prager, S. Naumov, M. R. Buchmeiser, *Angew. Chem.* **2008**, *120*, 3311–3314; *Angew. Chem. Int. Ed.* **2008**, *47*, 3267–3270.
- [7] B. K. Keitz, R. H. Grubbs, J. Am. Chem. Soc. 2009, 131, 2038-2039.
- [8] B. K. Keitz, J. Bouffard, G. Bertrand, R. H. Grubbs, J. Am. Chem. Soc. 2011, 133, 8498–8501.
- [9] M. Zirngast, E. Pump, A. Leitgeb, J. H. Albering, C. Slugovc, *Chem. Commun.* 2011, 47, 2261–2263.
- [10] L. H. Peeck, S. Leuthäußer, H. Plenio, Organometallics 2010, 29, 4339–4345.
- [11] A. Piermattei, S. Karthikeyan, R. P. Sijbesma, Nat. Chem. 2009, 1, 133–137.
- [12] A. J. D. Magenau, N. C. Strandwitz, A. Gennaro, K. Matyjaszewski, *Science* 2011, 332, 81–84.
- [13] a) H. Plenio, C. Aberle, Y. A. Shihadeh, J. M. Lloris, R. Martinez-Manez, T. Pardo, J. Soto, *Chem. Eur. J.* 2001, 7, 2848–2861; b) H. Plenio, R. Diodone, *J. Organomet. Chem.* 1995, 492, 73–80.
- [14] a) C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, *J. Am. Chem. Soc.* 2006, *128*, 7410–7411;
 b) E. M. Broderick, N. Guo, T. Wu, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, T. Cantat, P. L. Diaconescu, *Chem. Commun.* 2011, *47*, 9897–9899.
- [15] H. Plenio, C. Aberle, Angew. Chem. 1998, 110, 1467–1470; Angew. Chem. Int. Ed. 1998, 37, 1397–1399.
- [16] H. Plenio, C. Aberle, Chem. Eur. J. 2001, 7, 4438-4446.

www.chemeurj.org © 2013 Wiley-V

@ 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 0000, 00, 0-0

- [17] N. Vinokurov, J. R. Garabatos-Perera, Z. Zhao Karger, M. Wiebcke, H. Butenschön, Organometallics 2008, 27, 1878-1886.
- [18] a) C. Slugovc, D. Burtscher, F. Stelzer, K. Mereiter, Organometallics 2005, 24, 2255-2258; b) Y. Schrodi, T. Ung, A. Vargas, G. Mkrtumyan, C. Lee, T. M. Champagne, R. L. Pederson, S. H. Hong, Clean 2008, 36, 669-673; c) A. Hejl, M. W. Day, R. H. Grubbs, Organometallics 2006, 25, 6149-6154.
- [19] W. E. Britton, R. Kashyap, M. El-Hashash, M. El-Kady, M. Herberhold, Organometallics 1986, 5, 1029-1031.
- [20] a) L. H. Peeck, R. Savka, H. Plenio, Chem. Eur. J. 2012, 18, 12845-12853; b) V. Thiel, M. Hendann, K. J. Wannowius, H. Plenio, J. Am. Chem. Soc. 2012, 134, 1104-1114; c) P. Kos, R. Savka, H. Plenio, Adv. Synth. Catal. 2013, 355, 439-447.
- [21] a) H. Plenio, R. Diodone, Inorg. Chem. 1995, 34, 3964-3972; b) H. Plenio, H. El-Desoky, J. Heinze, Chem. Ber. 1993, 126, 2403-2408.
- [22] In the cyclic voltammogram only the oxidation peak and no reduction wave was observed. The estimate of the redox potential given here is based on the potential of the oxidation wave at 0.78 V from which 30 mV (ca. 57/2 mV) were substracted.

- [23] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [24] C. Samojłowicz, M. Bieniek, K. Grela, Chem. Rev. 2009, 109, 3708-3742.
- [25] M. R. Churchill, A. G. Landers, A. L. Rheingold, Inorg. Chem. 1981, 20, 849-853.
- [26] a) A. M. Alb, P. Enohnyaket, J. F. Craymer, T. Eren, E. B. Coughlin, W. F. Reed, Macromolecules 2007, 40, 444-451; b) A. Leitgeb, J. Wappel, C. Slugovc, Polymer 2010, 51, 2927-2946.
- [27] Sometimes, polyCOE can be dissolved in THF when the freshly generated polymer is not dried rigorously following its isolation. However, in our case this approach did not help.
- [28] Attempts to obtain high temperature GPC data with 1,2,4-trichlorobenzene as the solvent were also unsuccessful.
- [29] J. Alonso-Villanueva, J. M. Cuevas, J. M. Laza, J. L. Vilas, L. M. León, J. Appl. Polym. Sci. 2010, 115, 2440-2447.

Received: March 6, 2013 Revised: May 15, 2013 Published online:

