Tetrahedron 66 (2010) 1051–1056

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Ruthenium catalysts bearing chelating carboxylate ligands: application to metathesis reactions in water

Rafał Gawin [a], Patrycja Czarnecka [a,b], Karol Grela [a,*]

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[b] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

ARTICLE INFO

Article history:
Received 13 July 2009
Accepted 7 September 2009
Available online 10 November 2009

Keywords:
Carbene complex
Olefin metathesis
Ruthenium
Green chemistry
Aqueous media

ABSTRACT

The novel catalytic system, composed of a ruthenium alkylidene containing a surfactant fragment in the catalysts molecule, is reported. Ring closing metathesis and cross metathesis reactions proceed efficiently in neat water at room temperature, in air, without need of adding an external surfactant.

1. Introduction

Since the development of ruthenium catalyst $(PCy_3)_2Cl_2$-Ru=CHPh and $(SIMes)(PCy_3)Cl_2Ru$=CHPh (Cy=cyclohexyl, SIMes=1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) olefin metathesis became well established tool in organic synthesis.[1] Such a tremendous revolution was possible mainly by developing new catalysts, which can be used in more and more challenging reactions, under very mild conditions. Ruthenium catalysts tolerance to air and moisture is well known. Recently a lot of work was made to show that carrying out metathesis reactions is possible in water as a reaction medium.[2] Using water as a solvent for catalytic reactions is attractive from economical and ecological point of view. It also opens a route for new applications e.g., metathesis on complex biological systems sensitive to organic solvents, etc.[3] The problem of low solubility of catalyst in water can be solved by using mixed water-organic solvent reaction media.[4] Another approach is related to design of new catalysts bearing polar groups, which make them more or fully water soluble (**1**–**4**).[5] Novel approach, based on catalysts, which can act as surfactants (these molecules are sometimes called *catsurfs* for *cat*alyst and *surf*actant) (**4**–**6**, see Fig. 1) shows that solubility of catalyst is not necessary.[6] Recently it has been shown that promising results can be achieved under conditions of micellar catalysis. Water emulsions can be stabilized by various amphiphiles (e.g., **7**)[7] or supramolecular additives (**8**).[8]

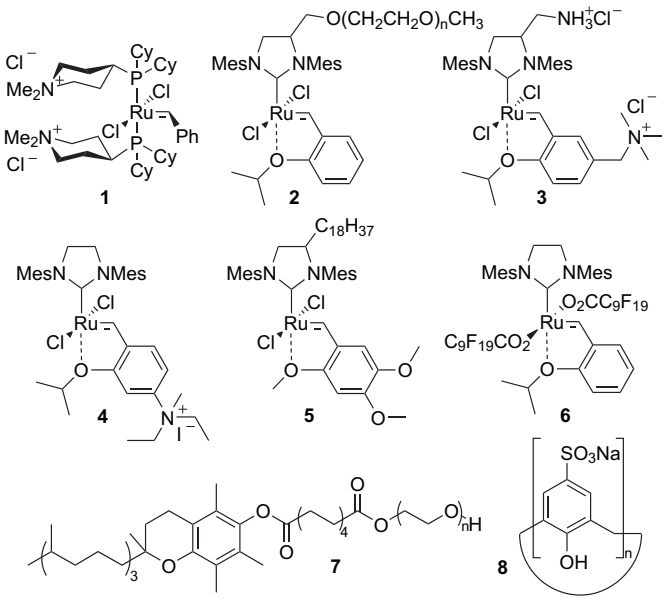
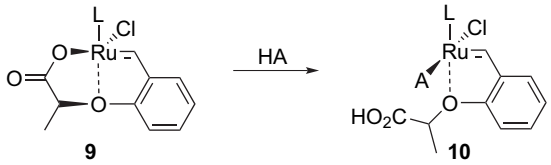


Figure 1. Selected ruthenium catalysts with polar groups (**1**–**4**), *catsurf* catalysts (**4**–**6**) and additives for metathesis in water (**7**,**8**). Mes=2,4,6-trimethylphenyl.

* Corresponding author. Tel.: +48 22 632 32 21; fax: +48 22 632 66 81.
E-mail address: grela@icho.edu.pl (K. Grela).
URL: http://www.karolgrela.eu/

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.11.009



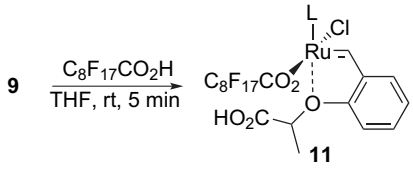
Scheme 1. Complex **9**—universal platform for straightforward anionic ligand introduction in ruthenium catalysts. L=SIMes, HA=general formula of acid.

In the present work we are reporting a *catsurf* complex, derived from the previously reported ruthenium carboxylate.[9] This novel system was applied to a number of ring closing metathesis (RCM) and cross metathesis (CM) reactions of water-insoluble substrates, using water as a only reaction medium. Reactions proceed smoothly at room temperature in air atmosphere. Using water as a reaction medium and an example of isolation of pure product by crystallization from non toxic solvent is confirmation that this system works according to green chemistry principles.[10]

2. Results and discussion

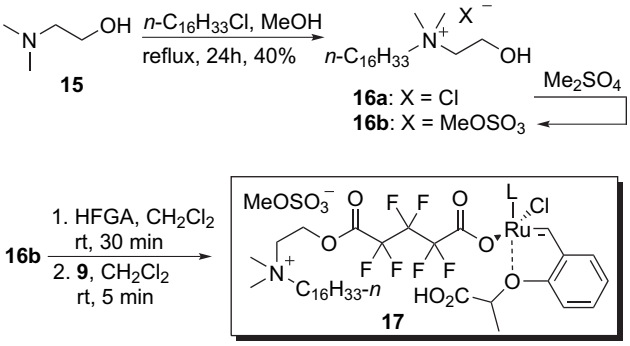
Surfactants are typically composed of a long lipophilic, nonpolar chain and a polar head. We decided to introduce a similar structural motif into a ruthenium alkylidene complex, in order to obtain a catalyst exhibiting at the same time surfactant properties. Thus, as the ruthenium platform carboxylate complex **9** (Scheme 1) was chosen.[9] While **9** itself is not very potent in olefin metathesis, it's main advantage relies in possibility of straightforward introduction of various acids residues into its structure, thus forming new complexes **10**, highly active in olefin metathesis.

As a starting point we checked surfactant properties of previously reported complex **11**, obtained from commercially available perfluorononanoic acid and **9** (Scheme 2).[9] Unfortunately, in the presence of water and organic substrates, **11** formed unstable emulsions of unsatisfactory quality.[11]



Scheme 2. Synthesis of catalyst **11**. L=SIMes.

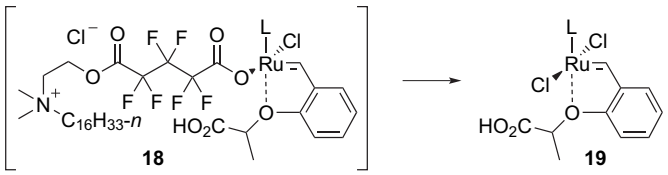
The second approach was based on tocopherol derivative. Tocopherol (**12**) was treated with hexafluoroglutaric anhydride in the presence of pyridine in dichloromethane (Scheme 3). Reaction mixture was washed with diluted hydrochloric acid and after passing trough pad of silica tocopherol derivative **13** was obtained in 71% yield. Next, complex **14** was formed by simple addition of **13** to solution of **9** in dichloromethane.



Scheme 4. Synthesis of catalyst **17**. HFGA=hexafluoroglutaric anhydride, L=SIMes.

Quantitative conversion of cyclic carboxylate **9** into it's open form **14** was clearly confirmed by ^{1}H NMR.[12] Unfortunately also in this case, the obtained results were not enough satisfactory.[11]

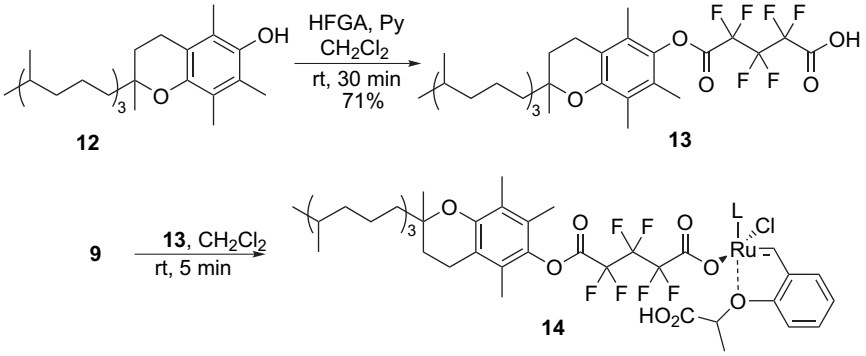
Ammonium salts with long lipophilic chain, e.g., cetyl trimethylammonium bromide (CTAB), are well known surfactants. We decided to introduce a similar structural motif to **9**. Starting from *N*,*N*-dimethylaminoethanol (**15**) 1-chlorohexadecane ammonium salt **16a** was obtained in 40% yield (Scheme 4).[13] Chloride was exchanged to methylsulfate anion in a simple and effective procedure by treatment with dimethyl sulfate.[14] Methylsulfate salt **16b** was obtained in quantitative yield as a white crystalline solid. It was next converted to the corresponding acid by treatment with hexafluoroglutaric anhydride in dichloromethane and used in situ in reaction with **9**. Quantitative conversion of **9** into **17** was clearly confirmed by ^{1}H NMR.[12]



Scheme 5. Formation of dichloride Ru complex **19** in presence of chloride anions. L=SIMes.

The lability of anionic ligands in ruthenium alkylidene complexes is well known.[15] When a chloride containing acid, derived from **16a**, was used in the formation of catalyst **18**, a complete exchange of a perfluoroglutarate anion to chloride was observed, leading to dichloride Ru complex **19** (Scheme 5).[16] Therefore, the previous replacement of chloride into methylsulfate in salt **16b** was necessary.[17]

Catalyst **17** is water insoluble, however, after the addition of organic substrates, insoluble in water, a stable emulsion was formed upon mechanical stirring (Fig. 2). We tested this new catalytic system in ring closing metathesis (RCM) and cross metathesis



Scheme 3. Synthesis of catalyst **14**. HFGA=hexafluoroglutaric anhydride, Py=pyridine, L=SIMes.

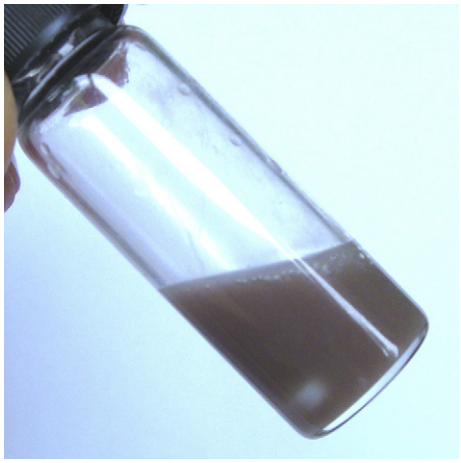
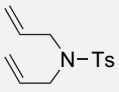
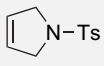
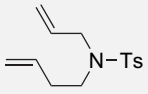
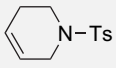
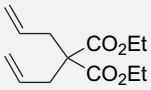
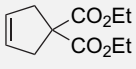
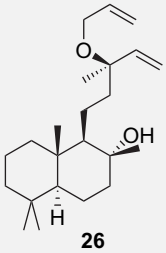
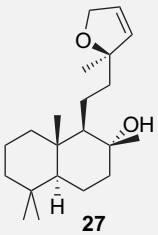
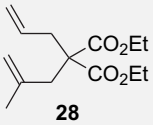
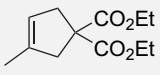
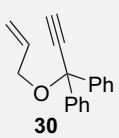
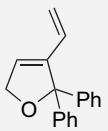


Figure 2. Emulsion formed from water, organic substrates and catalyst **17**.

Table 1
Representative RCM reactions catalyzed by **17**

Entry	Substrate	Product	Yield[a] (%)
1[b]	 **20**	 **21**	96
2[b]	 **22**	 **23**	94
3[c]	 **24**	 **25**	95
4[d]	 **26**	 **27**	72
5[d]	 **28**	 **29**	94
6[b]	 **30**	 **31**	97

[a] Isolated yield of analytically pure compounds. All RCM reactions were carried out on 0.2 mmol scale of substrate in 1 mL of water (0.2 M formal) at 30 °C in air atmosphere.
[b] With 2 mol % of **17**, 2 h.
[c] With 2 mol % of **17**, 6 h.
[d] With 5 mol % of **17**, 6 h.

(CM) reactions. All reactions were performed in glass vials (2 mL of capacity, Fig. 2) containing a Teflon-coated stir bar.

Typical procedure of RCM is as follow: to a vial containing catalyst **17** (2–5 mol %), distilled water (which was non degassed) was added and mixture was stirred for 1 h in the atmosphere of air. Then, a substrate was added, which forms an oily layer on top of the aqueous layer. Next, the content of the vial was stirred for 2–6 h.[18] After the reaction was completed, to the vial vinyl ethyl ether was added to quench the reaction.[19] The reaction mixture was poured onto a silica gel column and the desired product was eluted from the column. In the cases where complete conversions were achieved, pure products were obtained by passing the reaction mixture through a short pad of silica and evaporation of the eluent. Due to high affinity of the polar catalyst to silica gel, the products were obtained as colorless oils or solids and were not colored of ruthenium. Representative examples of RCM reactions are shown in Table 1. RCM of simple not substituted substrates proceed smoothly with low catalyst loading (2 mol % of **17**) within 2–6 h (entry 1–3). More substituted substrates undergo RCM reaction with high yield, although higher catalyst loading (5 mol %) was needed (entry 5). Enyne cycloisomerisation (entry 6) gave the expected product in almost quantitative yield.

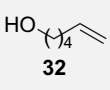
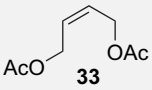
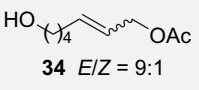
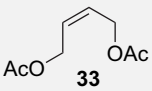
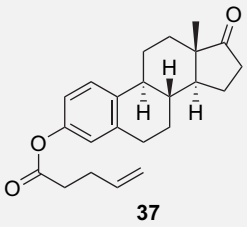
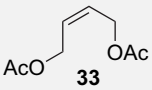
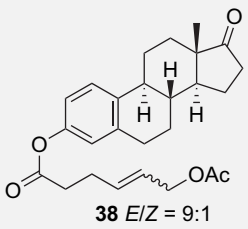
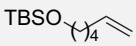
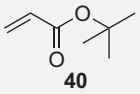
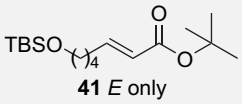
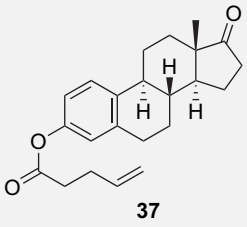
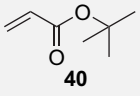
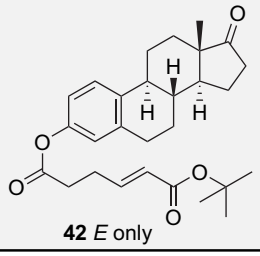
Encouraged by good results of RCM reactions we decided to try our catalytic system in CM reactions. Typical procedure of CM reaction and the workup was the same as RCM, however higher catalyst loadings (5 mol %) and reactions time (12 h) were necessary. Emulsions formed have even better quality than in the case of RCM reactions (due to excess of the liquid cross partner). Representative examples of CM reactions are shown in Table 2. Products were obtained in lower but still satisfactory yield. Also challenging CM with electron deficient *tert*-butyl acrylate gave expected product with high yield (entries 4 and 5). It is worthy of mention that solid substrates also undergo cross metathesis (entries 3 and 5). Moreover in case of CM of solid steroid substrate **37** (entry 5) was not dissolved in small excess of *tert*-butyl acrylate and after repeating reaction with high excess of *tert*-butyl acrylate no better results was obtained. In some cases, the emulsion formed was so stable that the reaction mixture do not form two phases even long after stirring was stopped. In this case sodium chloride was added and after ca. 10 min two phases were formed. It is important because in a bigger scale crude products can be isolated by simple decantation (in case of oil) or by filtration (in case of solid material) followed by distillation or crystallization to separate from catalyst. In order to demonstrate that toxic organic solvents can be completely avoided in the synthesis of metathesis products, we have run RCM of **20** on a gram-scale. To biphasic mixture of 1 g of **20** and 8 mL of water catalyst **17** was added (2 mol %) and after shaking an emulsion was formed (Fig. 3). Rapid evolution of ethylene was observed and after stirring at room temperature for 2 h the reaction was complete.

Stirring was stopped and crude solid product **21** contaminated with ruthenium was collected on the bottom of the vial. Water was removed by decantation and crude product was washed with ethanol. After crystallization from ethanol and drying analytically pure product **21** was obtained with yield 91%.

3. Conclusions

In summary, a novel *catsurf* catalytic system for metathesis in aqueous emulsion is reported. RCM and CM reactions proceed smoothly at room temperature in water as a only reaction medium in air atmosphere providing products with high yield. Additionally, products can be isolated without need of toxic solvents fulfilling green chemistry principles.

Table 2
Representative CM reactions catalyzed by **17**

Entry	Substrates		Product	Yield[a] (%)
1[b]	 **32**	 **33**	 **34** *E*/*Z* = 9:1	76
2[b]	 **35**	 **33**	 **36** *E*/*Z* = 9:1	68
3[c]	 **37**	 **33**	 **38** *E*/*Z* = 9:1	75
4[d]	 **39**	 **40**	 **41** *E* only	78
5[d]	 **37**	 **40**	 **42** *E* only	74

[a] Isolated yield of analytically pure compounds. All CM reactions were carried out on 0.2 mmol scale of substrate with 5 mol % of **17** in 1 mL of water (0.2 M formal), 12 h at 30 °C.
[b] With 2 equiv of **33**.
[c] With 10 equiv of **33**.
[d] With 4 equiv of **40** TBS=*tert*-butyldimethylsilyl. *E*/*Z* ratio determined by ^{1}H NMR.

4. Experimental section

4.1. General

All reactions were preformed in 2 mL glass vials (Fig. 1) containing a Teflon-coated stir bar. Column chromatography was preformed using Merck silica gel 60 (230–400 mesh). Thin-Layer-Chromatography analysis was conducted using commercially available Merck silica gel 60 F_{254} plates. Nuclear Magnetic Resonance spectra were obtained Varian Gemini 200 and 400 spectrometers in $CDCl_3$, with proton and carbon resonances at 200 and 50 MHz, respectively, and are referenced to the residual solvent signal at δ 7.27 ppm for ^{1}H and δ 77.23 ppm for ^{13}C. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, sep=septet), coupling constant (J Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift. IR: Perkin–Elmer Spectrum 2000 FTIR. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner PerSeptive Biosystems, Inc. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. All commercially available substrates were used as received. All other chemicals or reagents were prepared according to literature procedures.

4.2. General procedure for metathesis reactions

To glass vial (2 mL of capacity) containing Teflon-coated stir bar, catalyst **17** (2–5 mol %) and 1 mL (0.2 M formal) of distilled water were added and mixture was stirred for 1 h. Then substrate(s) were added (0.2 mmol) and mixture (emulsion) was stirred for 2–12 h at 30 °C in air atmosphere. Ethyl vinyl ether was added (1 mL). Mixture was poured onto a silica gel column and desired product was eluted from the column with ethyl acetate/cyclohexane mixture.

4.3. RCM reaction of compound 20 in a one gram-scale

To vial (10 mL of capacity) compound **20** was added (1.01 g, 4 mmol) and 8 mL (0.5 M formal) of distilled water. Then catalyst **17** was added (101 mg, 0.08 mmol, 2 mol %) and mixture was vigorously stirred at 30 °C for 2 h. Greenish emulsion was formed and rapid evolution of ethylene was observed. After 2 h stirring was stopped and precipitated crude brownish product **21** was collected on the bottom of the vial. Water was decanted and solid residue was washed with ethanol (3 mL) to give almost white product **21**. After additional crystallization from ethanol (3 mL) analytically pure product **21** was obtained as white crystalline solid (812 mg, 91% yield).

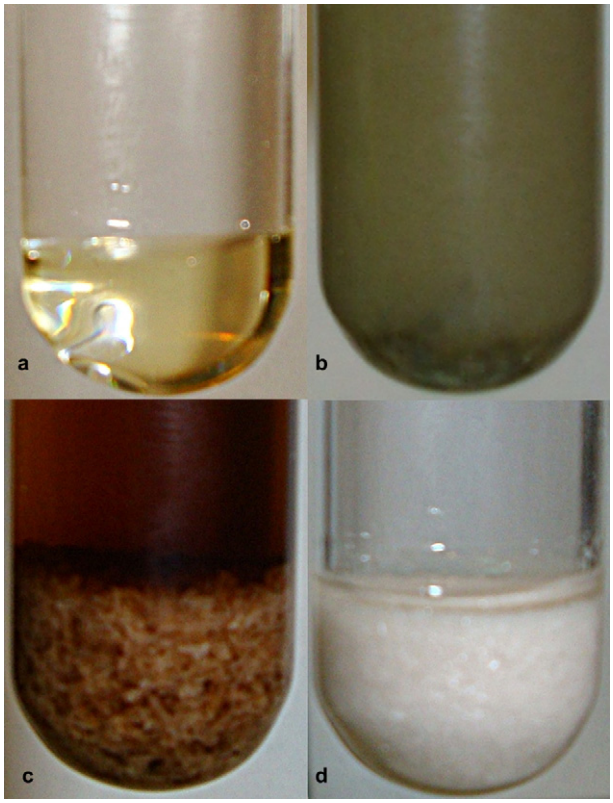


Figure 3. Different stages of RCM of **20**. a): substrate **20** under water; b) greenish emulsion formed after adding catalyst **17** and stirring; c) product **21** after removing of water and washing with ethanol; d) product **21** crystallized from ethanol.

4.4. Mono-(2,5,7,8-tetramethyl-2-(4,8,12-trimethyl-tridecyl)-chroman-6-yl) 2,2,3,3,4,4-hexafluoroglutarate (13)

In a Schlenk tocopherol (**12**, 861.4 mg, 2.0 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under argon flow in dark room. Freshly distilled pyridine was added (0.17 mL, 2.0 mmol). Then hexafluoroglutaric anhydride (0.27 mL, 2.0 mmol) in dry CH_2Cl_2 (5 mL) was added in portions and mixture was stirred for 30 min. Next mixture was washed with diluted hydrochloric acid and water. Organic layer was dried over $MgSO_4$ and passed trough pad of silica, which was additionally washed with acetone. After evaporation of solvent title product was obtained as orange oil (933 mg, 71%).^{1}H NMR (400 MHz, $CDCl_3$): δ=6.75 (br s), 2.60 (t, 2H, J=6.7), 2.10 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.79 (m), 1.52 (m), 1.32–1.44 (m), 1.27 (s, 3H), 1.20–1.25 (m), 1.00–1.23 (m, 6H), 0.83–0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.68, 11.80, 12.52, 19.56, 19.59, 19.63, 19.66, 19.72, 20.56, 20.99, 22.61, 22.71, 23.80, 24.43, 24.79, 24.81, 27.97, 29.70, 30.87, 30.93, 32.66, 32.76, 32.78, 37.27, 37.31, 37.38, 37.43, 37.47, 37.50, 39.35, 39.94, 75.46, 105–111(m), 117.93, 123.70, 124.44, 126.05, 139.66, 150.26, 157.49 (t, J=30.2), 160.73 (t, J=29.3); IR (CH_2Cl_2): ν=3550, 2952, 2928, 2869,1790, 854, 836, 781, 727, 673 cm^{-1}; HRMS (EI): calcd for $C_{34}H_{50}F_6O_5$: 652.3562; found: 652.3545.

4.5. Compound 14

To a solution of **13** (131 mg, 0.2 mmol) in dry CH_2Cl_2 (5 mL) **9** was added (124 mg, 0.2 mmol) and mixture was stirred for 5 min. Next *n*-hexane (5 mL) was added in portions. CH_2Cl_2 was evaporated and precipitated green microcrystalline solid was filtered and dried (251 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=16.63 (s, 1H), 10.57 (s, 1H), 7.56–7.58 (m, 1H), 7.08 (s, 4H), 7.06–7.02 (m, 2H), 6.82 (d, 1H, J=8.12), 6.78 (br s), 4.96 (q, 1H, J=6.82), 4.22 (s, 4H), 2.68 (t, 2H, J=6.7), 2.48 (br s, 6H), 2.45(s, 6H), 2.44 (br s, 6H), 2.42 (s, 6H), 2.07 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.82 (m), 1.51 (m), 1.30–1.48 (m), 1.24 (s, 3H), 1.17–1.21 (m), 1.08–1.20 (m, 6H), 0.86–0.82 (m, 12H); ^{13}C NMR (200 Hz, $CDCl_3$): δ=11.87, 12.36, 16.58, 19.57, 19.59, 19.64, 19.65, 19.87, 20.38, 20.92, 22.08, 23.11, 23.12, 24.66, 24.79, 24.89, 25.53, 29.81, 30.85, 30.87, 32.01 32.75, 32.77, 35.34, 37.33, 37.39, 37.41, 37.45, 37.55, 38.32, 38.86, 79.09, 101–115(m), 116.43, 122.70, 123.16, 123.56, 124.50, 124.67, 125.05, 126.11, 127.00, 129.56, 129.64, 130.64, 134.45, 138.54, 146.60, 150.19, 151.22, 156.16, 159.39 (t, J=30.1), 160.75 (t, J=29,2), 170.35, 184.19; IR (CH_2Cl_2): ν=2926, 1788, 1484, 1298, 940 cm^{-1}.

4.6. *N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-1-hexadecanaminium methylsulfate (16b)

To a solution of *N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-1-hexadecanaminium chloride (**16a**, 700.1 mg, 2.0 mmol)[12] in CH_2Cl_2 (1 mL) dimethyl sulfate (252.3 mg, 2.0 mmol) was added. Mixture was stirred for 30 min. and evaporated to give white crystalline solid (845 mg, 99%). ^{1}H NMR (200 MHz, $CDCl_3$): δ=4.06 (br s, 2H), 3.70 (m, 2H), 3.60 (m, 2H), 3.39 (s, 6H), 3.23, 1.72 (m, 2H), 1.32–1.24 (comp, 26H), 0.85 (t, 3H, J=7.0); ^{13}C NMR (50 MHz, $CDCl_3$): δ=65.94, 65.59, 56.25, 54.60, 53.43, 51.62, 31.92, 29.70, 29.67, 29.52, 29.45, 29.37, 29.22, 26.29, 22.79, 22.70, 14.13; HRMS (ESI): calcd for m/z calcd for $C_{20}H_{44}NO$: 314.3417; found: 314.3409; IR (thin-film): ν=3437, 2922, 2852, 1640, 1468, 1249, 1225, 1061, 1006, 766 cm^{-1}.

4.7. Compound 17

In a Schlenk **16b** (85 mg, 0.2 mmol) was dissolved in dry CH_2Cl_2 (3 mL) under argon flow. Next hexafluoroglutaric anhydride (27 μL, 0.2 mmol) in dry CH_2Cl_2 (2 mL) was added in portions and mixture was stirred for 30 min. Then **9** (124 mg, 0.2 mmol) was added and mixture was stirred for 5 min. Next *n*-hexane (5 mL) was added. CH_2Cl_2 was evaporated and precipitated green microcrystalline solid was filtered and dried (250 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=16.63 (s, 1H), 10.56 (s, 1H), 7.54–7.58 (m, 1H), 7.05 (s, 4H), 6.98–7.03 (m, 2H), 6.87 (d, J=8.12 Hz, 1H), 4.99 (q, J=6.85 Hz, 1H), 4.21 (s, 2H), 4.18 (s, 4H), 2.44–2.47 (m, 2H), 2.43 (br s, 6H), 2.41 (s, 6H), 2.38 (s, 6H), 2.36 (s, 2H), 2.34 (s, 3H), 2.27 (s, 3H), 1.36 (d, J=6.84 Hz, 3H), 1.16–1.25 (m, 12H), 0.90 (t, J=12.4, 5.4 Hz, 3H); ^{13}C NMR (200 Hz, $CDCl_3$): δ=209.62, 182.77, 154.42, 146.63, 139.34, 130.34, 129.61, 129.50, 126.85, 122.36, 119.16, 112.90, 96.96, 83.93, 77.66, 77.02, 77.39, 54.88, 51.32;IR (CH_2Cl_2): ν=2986, 1756, 1484, 1298, 941 cm^{-1}.

Acknowledgements

K.G. thanks Foundation for Polish Science for the Mistrz professorship. R.G. thanks for KBN for grant (N N204 155436).

References and notes

1. (a) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Viley-VCH: Weinheim, 2003; (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29; (c) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900–1923; (d) Astruc, D. *New J. Chem.* **2005**, *29*, 42–56; (e) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490–4527; (f) Boeda, F.; Clavier, H.; Nolan, S. P. *Chem. Commun.* **2008**, 2726–2740.
2. Burtscher, D.; Grela, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 442–454.
3. (a) Binder, J. B.; Raines, R. T. *Curr. Opin. Chem. Biol.* **2008**, *12*, 767–773; (b) Lin, Y. A.; Chalker, J. M.; Floyd, N.; Bernardes, G. J. L.; Davis, B. G. *J. Am. Chem. Soc.* **2008**, *130*, 9642–9643.
4. Binder, J. B.; Blank, J. J.; Raines, R. T. *Org. Lett.* **2007**, *9*, 4885–4888.
5. (a) Complex **1**: Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627–1628; (b) Complex **2**: Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508–3509; (c) Complex **3**: Jordan, J. P.; Grubbs, R. H. *Angew. Chem., Int. Ed.*

2007, *46*, 5152–5155; (d) Complex **4** Gułajski, L.; Michrowska, A.; Narożnik, J.; Kaczmarska, Z.; Rupnicki, L.; Grela, K. *ChemSusChem* **2008**, *1*, 103–109.
6. (a) Mingotaud, A. F.; Krämer, M.; Mingotaud, C. *J. Mol. Catal. A Chem.* **2007**, *263*, 39–47; (b) Lipshutz, B. H.; Ghorai, S. *Org. Lett.* **2009**, *11*, 705–708.
7. (a) Lipshutz, B. H.; Ghorai, S.; Aguinaldo, G. T. *Adv. Synth. Catal.* **2008**, *350*, 953–956; (b) Lipshutz, B. H.; Aguinaldo, G. T.; Ghorai, S.; Voigtritter, K. *Org. Lett.* **2008**, *10*, 1325–1328.
8. Brendgen, T.; Fahlbusch, T.; Frank, M.; Schühle, D. T.; Seßler, M.; Schatz, J. *Adv. Synth. Catal.* **2009**, *351*, 303–307.
9. Gawin, R.; Makal, A.; Woźniak, K.; Mauduit, M.; Grela, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7206–7209.
10. (a) Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686–694; (b) Horváth, I. T.; Anastas, P. T. *Chem. Rev.* **2007**, *107*, 2169–2173.
11. In case of catalysts **11** and **14**, carboxylic acid function seems to be not enough polar to play a role of polar 'head' of surfactant. Thus these catalysts were bad surfactants and emulsions (if formed, depend of substrate) rapidly formed two phases. Model reactions with **20** (repeated several times) shows different results varying from low to high conversion.
12. Formation of complex **14** and **17** was determined by ^{1}H NMR spectroscopy—characteristic benzylidene proton shift ($CDCl_3$): 16.52 ppm for complex **9** and 16.63 ppm for complex **14** and **17**, same as benzylidene proton shift of complex **11** (see Ref. 9).
13. Wong, Y.; Hubieki, M. P.; Curfman, C. L.; Doncel, G. F.; Dudding, T. C.; Savle, P. S.; Gandour, R. D. *Bioorg. Med. Chem.* **2002**, *10*, 3599–3608.
14. Vu, P. D.; Boydston, A. J.; Bielawski, C. W. *Green. Chem.* **2007**, *9*, 1158–1159.
15. Tanaka, K.; Böhm, V. P. W.; Chadwick, D.; Roeper, M.; Braddock, C. D. *Organometallics* **2006**, *25*, 5696–5698.
16. Complex **19** was previously reported (see Ref. 9). Formation of complex **19** was determined by ^{1}H NMR spectroscopy—characteristic benzylidene proton shift ($CDCl_3$): 16.72 ppm.
17. Even if ammonium salt **16b** (without chloride) was used in synthesis, in ^{1}H NMR spectra of **17** complex **19** was visible. However, the major product of the reaction was the expected complex **17**. Complex **19** is also visible in ^{1}H NMR spectra of **11** and **14**. Formation of complex **19** is due to anionic ligand exchange (see Ref. 15).
18. Adding catalyst and substrates to vial simply starts the reaction before addition of water. We observed, that in the case of reactive substrates mixed with a catalyst, the reaction is already in advanced stage before water was added. This protocol can lead to false positive results and therefore should be avoided.
19. Addition of a vinyl ether, which quench the reaction, assures that the metathesis occurred only in water emulsion, and not in an organic solvent used during workup. Indeed, in numerous cases when the quenching agent was not added, we observed higher (but false) conversions.