Green Chemistry

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Water decontamination with hydrogen production using microwave-formed minute-made ruthenium catalysts

Supporting Information

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Contents

TABLE OF CONTENTS

EXPERIMENTAL

GENERAL

All chemicals were used as received without further purification. Aqueous formaldehyde, α-Phellandrene, 1,4-cyclohexadiene, 1-methylcyclohexa-1,4-diene, 1-methoxycyclohexa-1,4-diene and [Ru(*p*-cymene)I_2]$_2$ were purchased from *Sigma-Aldrich.* 1,3,5-Trimethylcyclohexa-1,4-diene was synthesised *via Birch*-reduction according to the literature procedure.[S1] The complex syntheses are in general based on the diene-protocol by *Bennett*.[S1] Hydrated ruthenium(III)chloride was bought from *ABCR* and hydrated ruthenium(III)bromide from *Alpha Aesar*. For reactions in aqueous media HPLC-grade water was used. Formaldehyde tests (108028 | Formaldehyde Test: Method: colorimetric with colour card and sliding comparator 0.1-1.5 mg.L^{-1} HCHO MColortest™ and 110036 | Formaldehyde Test: Method: colorimetric with test strips and reagent 0-100 mg.L^{-1} HCHO MQuant™) were purchased from *Merck Millipore* and used according to the user guideline´s manual. The *Merck Millipore* formaldehyde tests are limited to concentration ranges 0-100 ppm and 0-1.5 ppm, the given mean conversions consider the precisions of the tests in the analyses of diluted samples. Dilution factor 500 for higher concentrated samples and dilution factor 100 or 200 for lower concentrated samples has been used. All dehydrogenation reactions were carried out without precautions against moisture or oxygen unless otherwise stated. All dehydrogenation data were corrected by experimental data of empty glass reactors at the set temperature to compensate for thermal expansion. The amount of released gas was determined with a mass flow meter of the manufacturer *mks* connected via an analogue connection to a desktop computer or with an set up using a gas burette collecting the total gas volume. Microwave assisted reaction were performed with a *Monowave 300* microwave (*Anton Paar*®) using a maximum power of 850 W at 2.45 MHz to reach near-instantaneously the reaction temperature. The microwave was equipped with a ruby-thermometer and an IR-reference thermometer as well as a stirring unit. Reactions can be carried out up to a maximum pressure of 30 bar and a maximum temperature of 300 °C. Reaction mixtures were handled without precautions against water/moisture or air/oxygen in 30 ml microwave-borosilicate vials equipped with a Teflon/silicon septum and a quartz inlet for the thermometer. The synthesised complexes were identified by comparison with authentic literature data.[S1,S2]

COMPLEX-SYNTHESIS - SYNTHESIS OF [$RuCl_2$(arene)]$_2$-COMPLEXES

Experimental procedure for the formation of catalysts Entries 1-9 in Table 1. A 30 mL microwave vessel was filled with 0.96 mmol of hydrated ruthenium(III) halide, 10 equiv. of the desired cyclohexadiene and 15.5 mL ethanol. For Entries 8 & 9 in Table 1 1-methoxy-1,4,cyclohexadiene was used as the diene along with the corresponding alcohol. The reaction mixture was heated to 130 °C, except for 9 which required 90 °C, for the reaction times indicated in Table 1. Afterwards the reaction mixture was cooled down to -78 °C, the precipitated complex was filtered off and washed with pentane (20 mL) and dried in air. The yields for complexes 1-9 are 30-100%. For the catalysts formed in Entries 10 & 11; a 30 mL microwave vessel was filled with 0.2 grams of [Ru(*p*-cymene)Cl_2]$_2$, 10 wt. equiv. (2.0 grams) of the desired arene was added without solvent and the reaction mixture was heated to 200 °C for 30 minutes. Excess arenes were removed by soxhlet extraction with pentane overnight and the catalyst recovered from DCM *in vacuo* in 64-69% yield.

CATALYSIS: FORMALDEHYDE DECOMPOSITION

Exemplary experiment: 4.0 µmol (0.1 mol-%) [$RuCl_2$(*p*-cymene)]$_2$ were added with 2.5 g (4 mmol) of an aqueous formaldehyde solution (5.0 wt.% formaldehyde) into a vessel. The reaction mixture was heated with stirring to 95 °C for 24 h. An aliquot (200 µL) of the reaction mixture was used to determine the residual formaldehyde content using the *Merck Millipore* formaldehyde tests.

Ionic Liquid screen for biphasic decontamination.

ESI Table 1: Biphasic Ru catalysed decomposition of aqueous formaldehyde

Entry	Ionic Liquid	Conversion
1	BMMIM NTf_2	55%
2	C_3CNMIM NTf_2	20%
3	C_3CNMMIM NTf_2	10%
4	EMIM NTf_2	60%

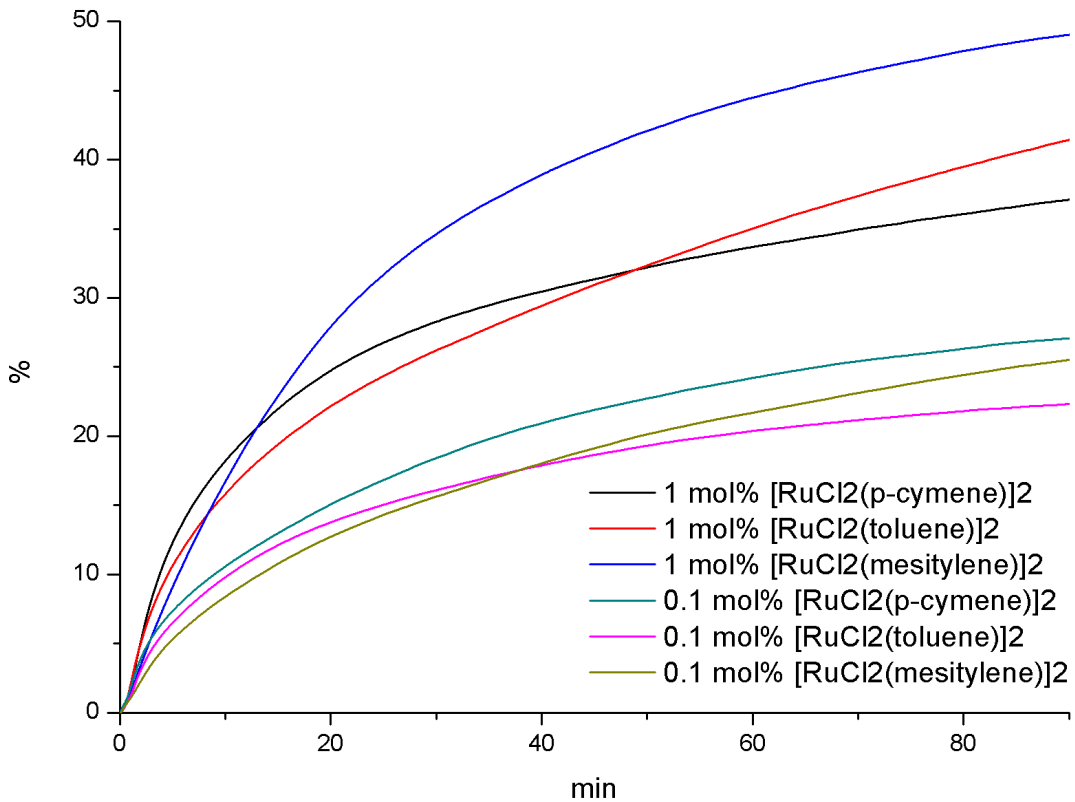
[a] Measured after 24 h at 95 °C, starting concentration: 5 wt% HCHO. Catalyst loadings of 0.25 mol% $[Ru(p\text{-cymene})Cl_2]_2$ used.

REFERENCES

[S1] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.

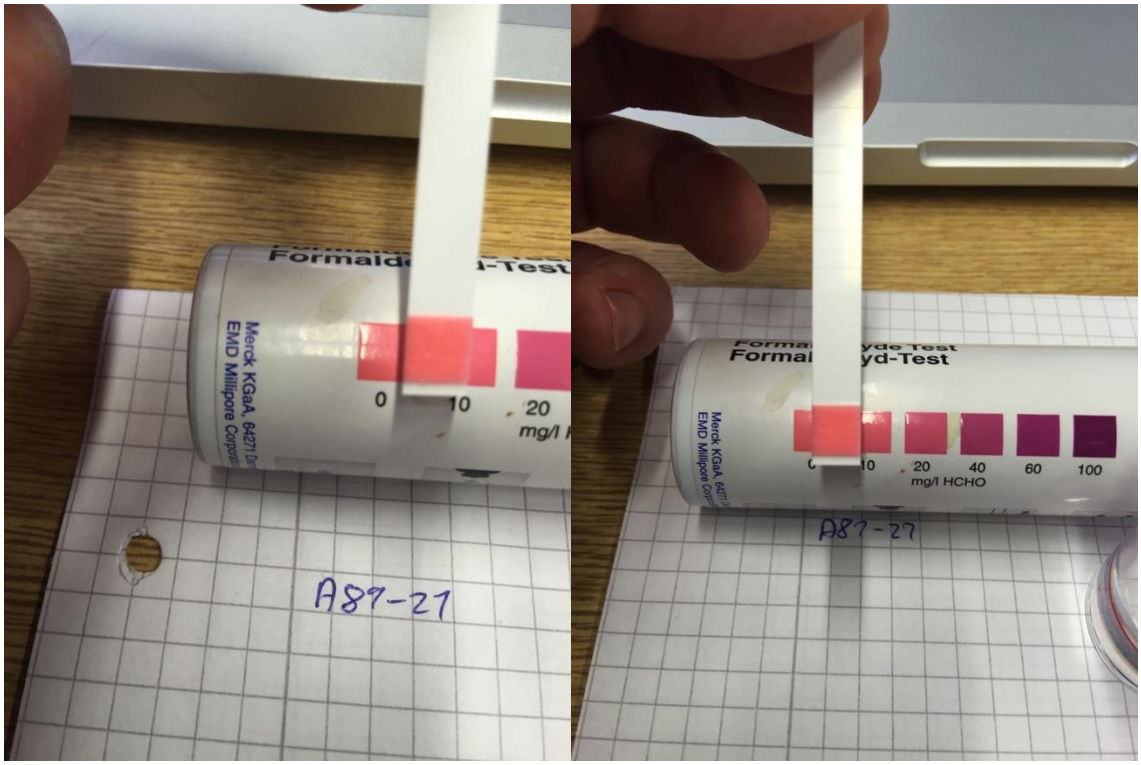
[S2] J. Soleimannejad, C. White, *Organometallics*, 2005, 2538–2541.

GAS MEASUREMENT

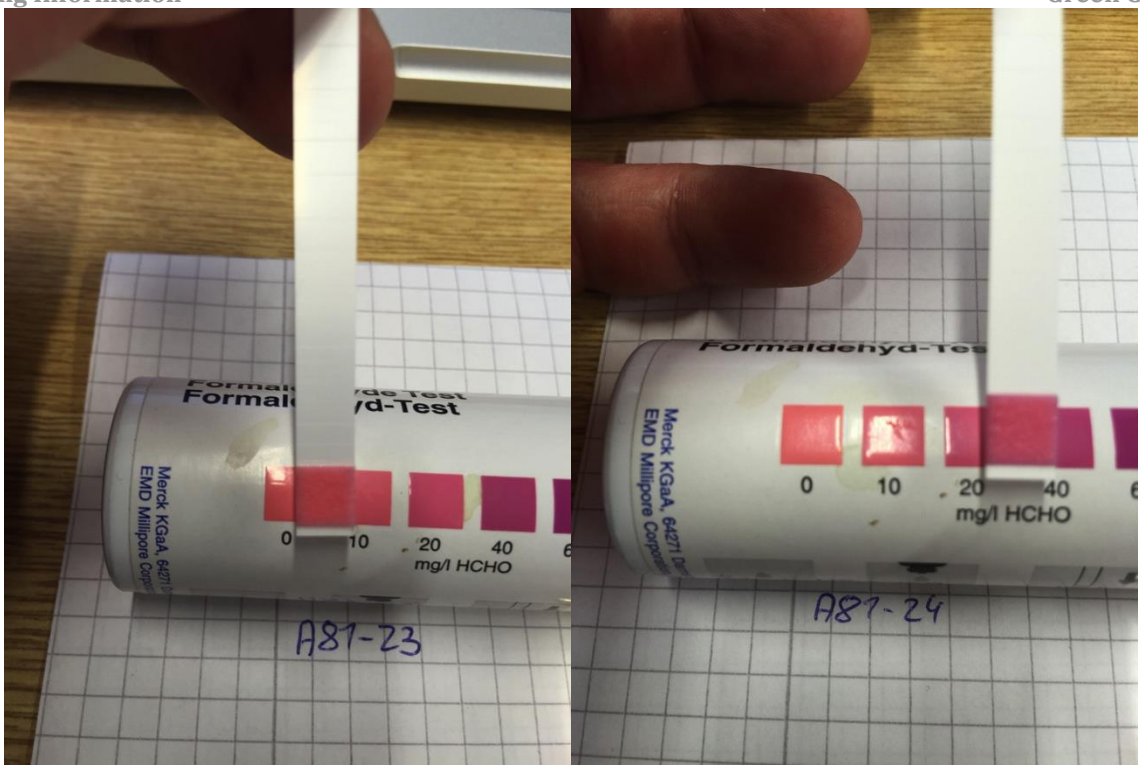


SI-Figure 1: Time-conversion plots based on gas evolution over the initial 2 h. Reaction conditions: 95 °C, 5 wt% aqueous Formaldehyde. The gas evolution is only in the beginning of the reaction soley dependant from the formaldehyde concentration. In the later stage of the reaction CO_2 and H_2 evolution from formic acid make up a increasing percentage of the gas stream.

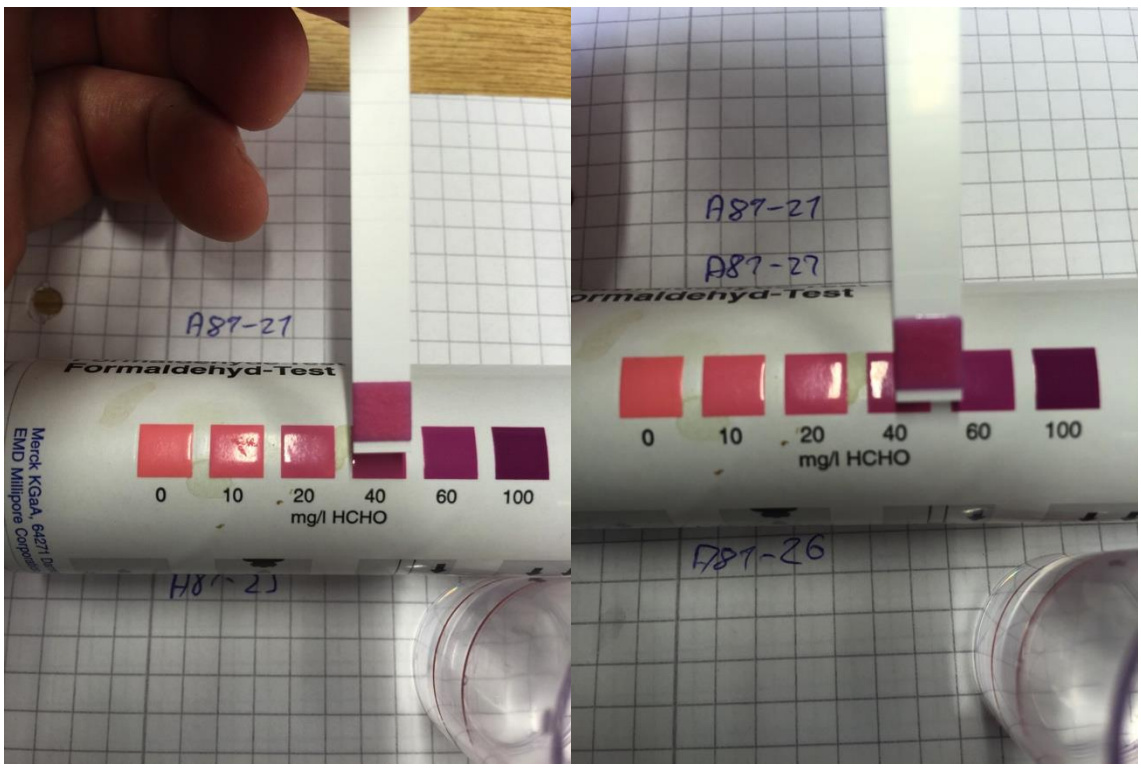
EXEMPLARY PHOTOS OF FORMALDEHYDE TESTS



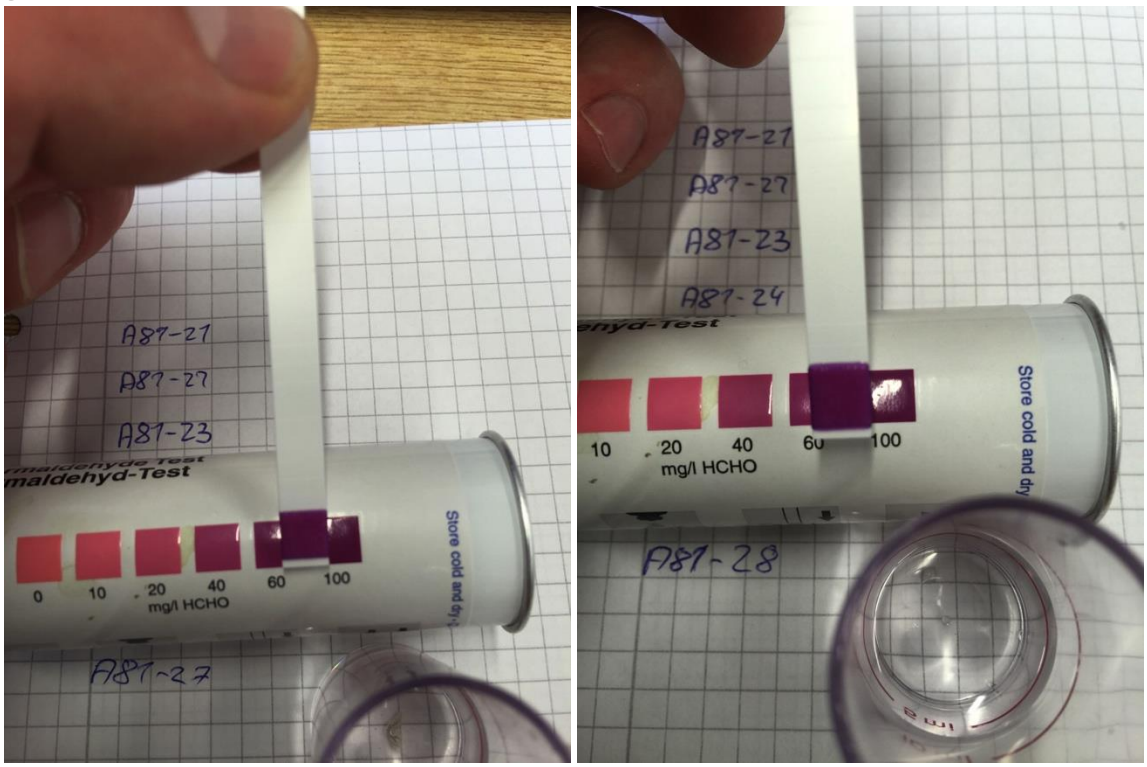
SI-Figure 2: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuCl_2(p\text{-Cymene})]_2$ at 95 °C.



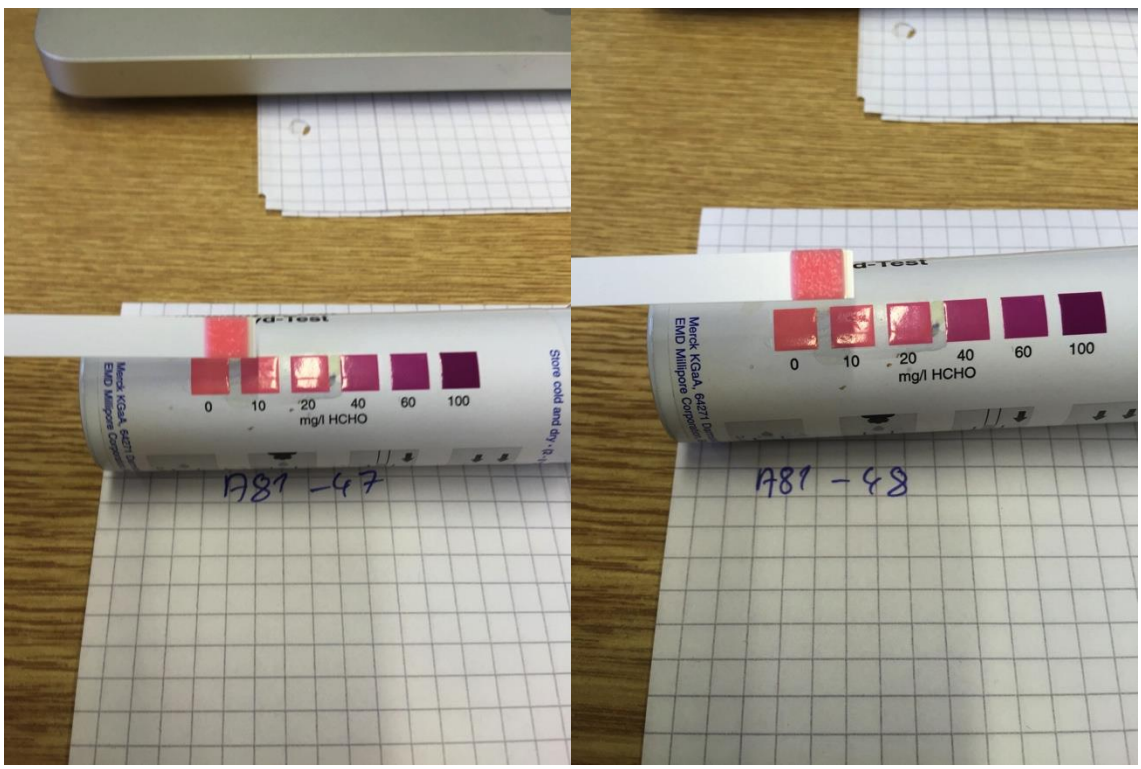
SI-Figure 3: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuCl_2(p\text{-Cymene})]_2$ at 70 °C.



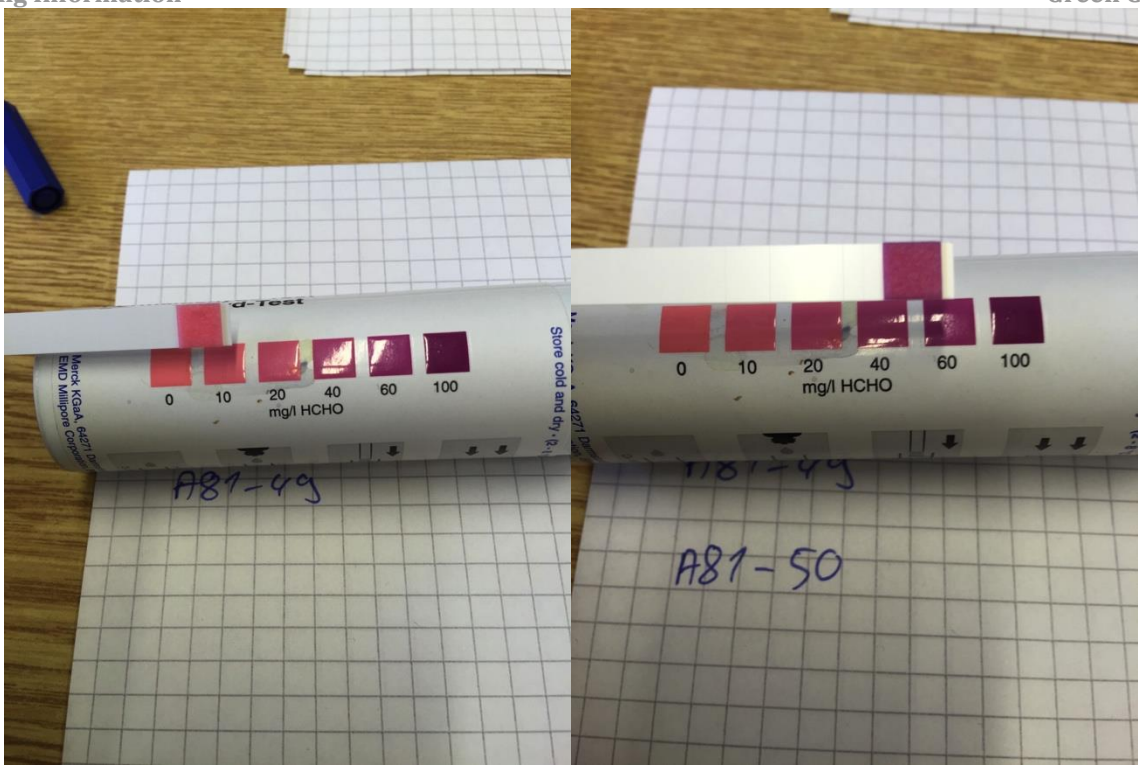
SI-Figure 4: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuI_2(p\text{-Cymene})]_2$ at 95 °C.



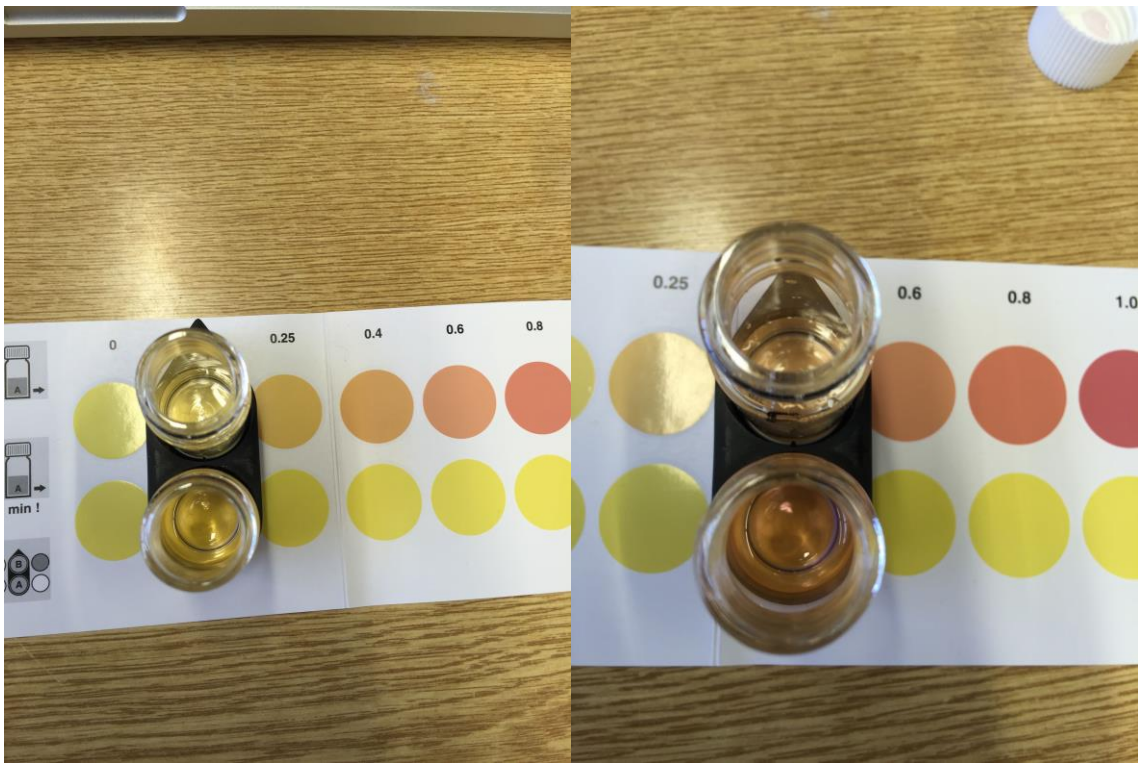
SI-Figure 5: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuI_2(p\text{-Cymene})]_2$ at 70 °C.



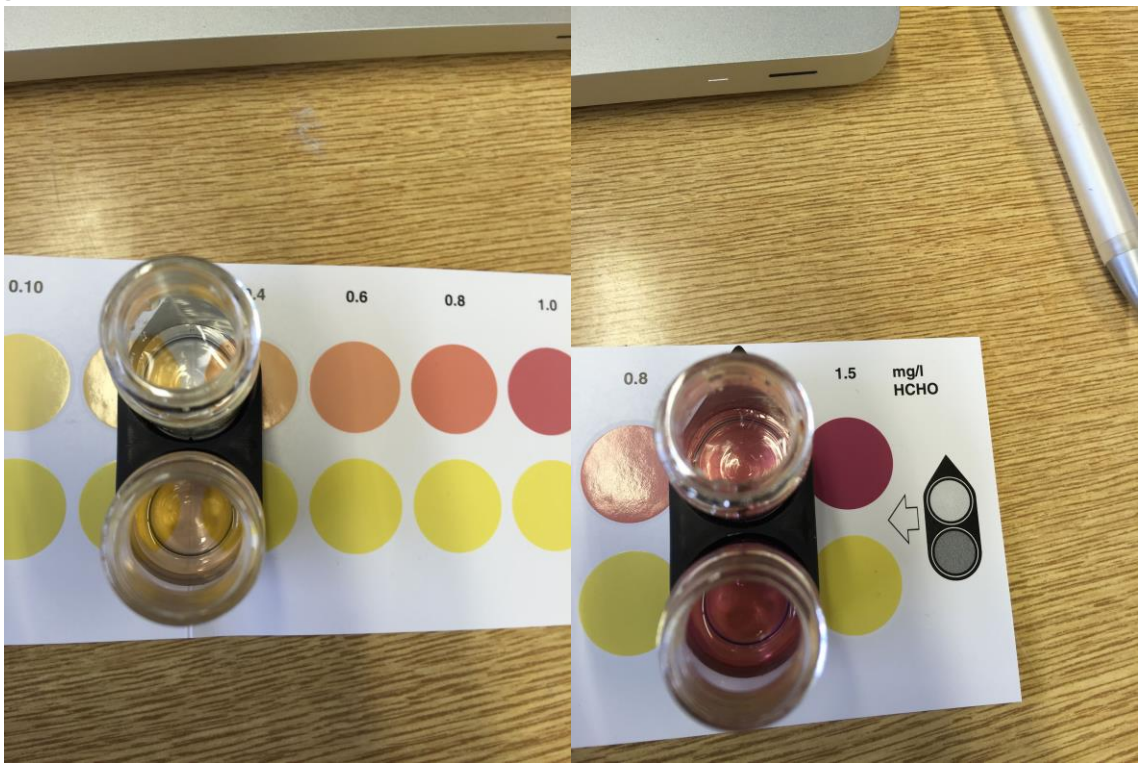
SI-Figure 6: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuCl_2(mesitylene)]_2$ at 95 °C.



SI-Figure 7: Colorimetric determination of the residual formaldehyde content after 24 h of a decontamination experiments with 1 mol% (left) and 0.1 mol% (right) $[RuCl_2(mesitylene)]_2$ at 70 °C.



SI-Figure 8: Colorimetric determination of the residual formaldehyde content after 24 h of decontamination experiments with 0.1 mol% $[RuCl_2(p\text{-cymene})]_2$ at 95 °C at pH=10 (left) and pH=7 (right).



SI-Figure 9: Colorimetric determination of the residual formaldehyde content after 24 h of decontamination experiments with 0.1 mol% $[RuCl_2(p\text{-cymene})]_2$ at 95 °C at pH=4-5 (left) and pH=3 (right).