

## SUPPORTING INFORMATION

### Facile Catalyst Recycling by Thermomorphic Behavior Avoiding Organic Solvents – A Reactive Ionic Liquid in the Homogeneously Pd-Catalyzed Telomerisation of the Renewable $\beta$ -Myrcene

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# 1. Autoclaves

The utilized autoclaves are shown in Figure 1.



*Figure 1: 25 mL stainless steel autoclave for screening experiments (left) and glass autoclave for recycling experiments (right)*

## 2. Analytics

**NMR-Spectroscopy:**  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR-spectra were recorded with spectrometers BRUKER DRX-500, -600 and -700 at ambient temperature with the frequency and solvent noted. Chemical shifts  $\delta$  are given in ppm relative to tetramethylsilane.

**Gaschromatography:** Conversion and yield of the reactions were determined via GC on an HEWLETT PACKARD chromatograph of the type HP6890 with a flame ionization detector (FID). A HP-5 column was used (30 m long, 0.32 mm diameter, 0.25  $\mu\text{m}$  thickness of the layer, 3 minutes at 40  $^\circ\text{C}$ , heating rate 7.5  $^\circ\text{C}/\text{min}$  to 150  $^\circ\text{C}$ , heating rate 40  $^\circ\text{C}/\text{min}$  to 320  $^\circ\text{C}$ , holding for 8 minutes). The split was set to 1:15. Dodecane was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analyzing known quantities of the substances.

**Mass Spectrometry:** The qualitative mass analysis was performed via GC as well. A HP-5MS UI 30 m long, 0.25 mm diameter, 0.25  $\mu\text{m}$  thickness of the layer) column was used. The carrier gas was Helium and the detector was of the Type 5977A MSD of AGILENT TECHNOLOGIES INC.

**ICP-OES-Analytics:** The ICP-OES analysis (Optical Emission Spectrometry with Inductively Coupled Plasma) of the palladium and phosphorus leaching into the organic product phase was performed on a Plasma Quant PQ 9000 spectrometer.

### 3. Results of initial investigations using DMF, toluene and MeOH as solvents

Table 1: initial results by using DMF, MeOH and toluene as solvents in the telomerisation of  $\beta$ -myrcene with dimcarb under reaction conditions given by BEHR et. al. [1]

#	dimcarb [eq.]	solvent	conversion [%]	Y <sub>telomerisation</sub>	Y <sub>dimerization</sub>	Y <sub>hydroamination</sub>
1.1	0.375	toluene	14	0	2	0
1.2	0.25	DMF	14	8	3	1
1.3	0.375	DMF	13	6	3	0
1.4	0.5	DMF	10	0	3	0
1.5	1	DMF	14	0	3	0
1.6	0.25	MeOH	79	46	3	18
1.7	0.313	MeOH	71	39	3	0
1.8	0.375	MeOH	47	34	4	0
1.9	0.438	MeOH	42	27	3	0
1.10	0.5	MeOH	39	30	3	0

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane (TPP); 15 mmol  $\beta$ -myrcene;  $\eta_{\text{Pd}} = 0.05$  mol%,  $\eta_{\text{TPP}} = 0.4$  mol%,  $t = 4$  h,  $T = 100$  °C, 500 rpm,  $p = 0.05$  MPa argon,  $V_{\text{solvent}} = 6$  mL

## 4. Results of first solvent-free telomerisation of myrcene with dimcarb

Table 2: results of investigation on solvent-free telomerisation of  $\beta$ -myrcene with dimcarb

#	$X_{\text{dimcarb}}$ [mol/mol]	conversion [%]	$Y_{\text{telomerisation}}$	$Y_{\text{dimerization}}$	$Y_{\text{hydroamination}}$
2.1	0.200	96	73	7	2
2.2	0.238	99	81	9	2
2.3	0.333	99	83	12	2
2.4	0.385	>99	75	12	3
2.5	0.429	66	30	7	6
2.6	0.467	45	21	5	7
2.7	0.500 <sup>[a]</sup>	51	23	6	4
2.8	0.667 <sup>[a]</sup>	43	17	4	2

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane (TPP);  $c_{\text{Pd}} = 0.1 \text{ mol\%}$ ,  $n_{\text{TPP}} = 0.4 \text{ mol\%}$ ,  $t = 4 \text{ h}$ ,  $T = 100 \text{ }^\circ\text{C}$ , 500 rpm,  $p = 0.05 \text{ MPa}$  argon,  $V_{\text{tot}} = 8.5 \text{ mL}$ , [a]: biphasic before and after reaction

## 5. Determination of Critical Solution Temperatures

The telomers for the determination of the critical solution temperatures (CST) were synthesized with the conditions of Entry 2.3 in Table 2. The telomers were isolated via distillation of the crude mixture.

The investigation was carried out in pressure tubes of the brand ACE GLASS (Figure 2).



*Figure 2: pressure tubes for investigations on critical solution temperatures.*

Dimcarb and the corresponding myrcene or telomers were filled into the tube and it was sealed. The mixtures were heated and stirred. If two phases were present, the mixture became blurry and when the critical temperature was reached, a clear mixture became apparent. The temperature at which a switch was recognizable was determined several times by cooling and heating again to obtain a representative result.

Table 3: critical solution temperatures of different  $\beta$ -myrcene/dimcarb mixtures and of different telomer/dimcarb mixtures with regard to a 100% selective telomerisation reaction towards the telomers (total volume ~ 4 mL)

#	before reaction			after reaction (100% conversion of myrcene)		
	X <sub>dimcarb</sub> [mol/mol]	X <sub><math>\beta</math>-myrcene</sub> [mol/mol]	CST [°C]	X <sub>dimcarb</sub> [mol/mol]	X <sub>telomers</sub> [mol/mol]	CST [°C]
3.1	0.30	0.70	55	0.26	0.74	85
3.2	0.40	0.60	58	0.45	0.55	104
3.3	0.50	0.50	70	0.60	0.40	116
3.4	0.60	0.40	73	0.71	0.29	121
3.5	0.67	0.33	75	0.78	0.22	124
3.6	0.71	0.29	77	0.81	0.19	125
3.7	0.75	0.25	78	0.85	0.15	127
3.8	0.80	0.20	63	0.88	0.12	109
3.9	0.90	0.10	43	0.94	0.06	95

At an elevated molar dimcarb fraction of 0.66 an investigation with regard to the myrcene conversion was carried out as well.

Table 4: critical solution temperatures of different  $\beta$ -myrcene/telomer/dimcarb mixtures representing a simulated telomerisation reaction with 100% selectivity towards the telomers (total volume ~ 4 mL)

#	simulated conversion level [% of myrcene]	X <sub>dimcarb</sub> [mol/mol]	X <sub><math>\beta</math>-myrcene</sub> [mol/mol]	X <sub>telomers</sub> [mol/mol]	CST [°C]
4.1	0	0.67	0.33	0	75
4.2	25	0.70	0.24	0.06	95
4.3	50	0.73	0.16	0.11	109
4.4	75	0.76	0.08	0.16	118
4.5	100	0.78	0	0.22	124

## 6. Determination of ligand solubilities

The solubility of the ligands has been determined by creation of a saturated solution of the ligand in dimcarb,  $\beta$ -myrcene or the telomers. Then the mixture was tempered and three samples are taken of each ligand/compound mixture and the liquid compound is evaporated to leave back the ligand residue that is weighed and thus the solubility is determined.

Table 5: solubilities of TPP, TPPMS and TPPTS in dimcarb and solubilities of TPPMS and TPPTS in  $\beta$ -myrcene and the telomers

#	ligand	solubility <sub>dimcarb</sub> at 25 °C [mmol/g]	solubility <sub>dimcarb</sub> at 0°C [mmol/g]	solubility <sub><math>\beta</math>-myrcene</sub> at 25 °C [mmol/g]	solubility <sub>telomers</sub> at 25 °C [mmol/g]
5.1	TPP	0.385 $\pm$ 0.008	0.381 $\pm$ 0.008	-	-
5.2	TPPMS	0.821 $\pm$ 0.012	0.716 $\pm$ 0.012	0.0018 $\pm$ 0.0001	0.040 $\pm$ 0.008
5.3	TPPTS	0.301 $\pm$ 0.013	0.289 $\pm$ 0.002	0.0011 $\pm$ 0.0002	0.023 $\pm$ 0.002



## 7. Optimization of neat telomerisation reaction of myrcene with dimcarb

### Pressure Screening:

Table 6: Influence of different argon-pressures on the telomerisation of  $\beta$ -myrcene with dimcarb

#	p (Ar) [MPa]	conversion [%]	Y <sub>telom.</sub> [%]	Y <sub>dim.</sub> [%]	Y <sub>hydroam.</sub> [%]	S <sub>telomers</sub> [%]
6.1	1	>99	73	5	18	77
6.2	3	>99	74	5	19	76
6.3	7	>99	70	5	18	75
6.4	10	>99	71	5	17	76
6.5	15	>99	68	5	19	74

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane monosulfonate (TPPMS); 20 mmol  $\beta$ -myrcene,  $\text{C}_{\text{Pd}} = 0.05$  mol%,  $\text{n}_{\text{TPPMS}} = 0.2$  mol%,  $\text{X}_{\text{dimcarb}} = 0.66$  (mol/mol); t = 4 h, T = 100 °C, 500 rpm,

### Temperature Screening:

Table 7: Influence of different temperatures on the telomerisation of  $\beta$ -myrcene with dimcarb

#	T [°C]	t [h]	conversion [%]	Y <sub>telom.</sub> [%]	Y <sub>dim.</sub> [%]	Y <sub>hydroam.</sub> [%]	S <sub>telomers</sub> [%]
7.1	120	2	>99	76	9	18	74
7.2	100	2	>99	72	4	15	79
7.3	80	5	81	49	2	15	74
7.4	60	16	95	68	4	14	79

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane monosulfonate (TPPMS); 20 mmol  $\beta$ -myrcene,  $\text{C}_{\text{Pd}} = 0.05$  mol%,  $\text{n}_{\text{TPPMS}} = 0.2$  mol%,  $\text{X}_{\text{dimcarb}} = 0.66$  (mol/mol); p = 0.01 MPa, 500 rpm,

### Influence of Catalyst Preforming:

Table 8: Influence of different preforming conditions on the telomerisation of  $\beta$ -myrcene with dimcarb (Reaction time = 2 h)

#	Preforming		conversion [%]	Y <sub>telom.</sub> [%]	Y <sub>dim.</sub> [%]	Y <sub>hydroam.</sub> [%]	S <sub>telomers</sub> [%]
	T [°C]	p (Ar) [MPa]					
8.1	-	-	>99	72	4	15	79
8.2	20	1	>99	71	5	15	78
8.3	100	1	>99	73	5	14	79
8.4	20	5	>99	74	6	15	79
8.5	100	5	>99	75	6	13	80

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane monosulfonate (TPPMS); 20 mmol  $\beta$ -myrcene,  $\text{C}_{\text{Pd}} = 0.05$  mol%,  $\text{n}_{\text{TPPMS}} = 0.2$  mol%,  $\text{X}_{\text{dimcarb}} = 0.66$  (mol/mol); t = 2 h, T = 100 °C, p = 0.01 MPa, 500 rpm,

Table 9: Influence of different preforming conditions on the telomerisation of  $\beta$ -myrcene with dimcarb (Reaction time = 0.5 h)

#	Preforming		conversion [%]	$Y_{\text{telom.}}$ [%]	$Y_{\text{dim.}}$ [%]	$Y_{\text{hydroam.}}$ [%]	$S_{\text{telomers}}$ [%]
	T [°C]	p (Ar) [MPa]					
9.1	20	1	32	21	3	1	84
9.2	20	1	36	20	3	2	80
9.3	100	1	29	20	3	1	84
9.4	20	5	35	23	3	2	83
9.5	100	5	41	29	3	3	85

**conditions:** precursor:  $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ ; ligand: triphenylphosphane monosulfonate (TPPMS); 20 mmol  $\beta$ -myrcene,  $C_{\text{Pd}} = 0.05$  mol%,  $n_{\text{TPPMS}} = 0.2$  mol%,  $X_{\text{dimcarb}} = 0.66$  (mol/mol);  $t = 0.5$  h,  $T = 100$  °C,  $p = 0.01$  MPa, 500 rpm,

### Precursor Screening:

Table 10: Influence of different precursors on the telomerisation of  $\beta$ -myrcene with dimcarb

#	Precursor	conversion [%]	$Y_{\text{telom.}}$ [%]	$Y_{\text{dim.}}$ [%]	$Y_{\text{hydroam.}}$ [%]	$S_{\text{telomers}}$ [%]
10.2	$\text{Pd}(\text{acac})_2$	96	72	5	16	77
10.3	$\text{Pd}(\text{CF}_3\text{CO}_2)_2$	85	62	5	15	76

**conditions:** ligand: triphenylphosphane monosulfonate (TPPMS); Preforming: 1 h (100 °C, 0.05 MPa (Ar)) in dimcarb; 20 mmol  $\beta$ -myrcene,  $C_{\text{Pd}} = 0.05$  mol%,  $n_{\text{TPPMS}} = 0.2$  mol%,  $X_{\text{dimcarb}} = 0.66$  (mol/mol);  $t = 2$  h,  $T = 100$  °C,  $p = 0.01$  MPa, 500 rpm,

### Screening of catalyst concentration:

Table 11: Influence of different Pd-concentrations on the telomerisation of  $\beta$ -myrcene with dimcarb

#	Pd-conc. [mol%]	TPPMS-conc. [mol%]	conversion [%]	$Y_{\text{telom.}}$ [%]	$Y_{\text{dim.}}$ [%]	$Y_{\text{hydroam.}}$ [%]	$S_{\text{telomers}}$ [%]
11.2	0.050	0.20	82	59	5	16	75
11.3	0.035	0.14	73	58	5	7	83
11.4	0.025	0.10	22	11	3	2	68

**conditions:** precursor:  $\text{Pd}(\text{acac})_2$ ; ligand: triphenylphosphane monosulfonate (TPPMS); Preforming: 1 h (100 °C, 0.05 MPa (Ar)) in dimcarb; 20 mmol  $\beta$ -myrcene,  $X_{\text{dimcarb}} = 0.66$  (mol/mol);  $t = 2$  h,  $T = 100$  °C,  $p = 0.01$  MPa, 500 rpm,

## Influence of different dimcarb/myrcene ratios

Table 12: Influence of different dimcarb/myrcene-concentrations on the telomerisation of  $\beta$ -myrcene with dimcarb

#	X <sub>dimcarb</sub> [mol/mol]	conversion [%]	Y <sub>telom.</sub> [%]	Y <sub>dim.</sub> [%]	Y <sub>hydroam.</sub> [%]	S <sub>telomers</sub> [%]
12.1	0.250	55	38	5	4	79
12.2	0.500	89	65	5	12	79
12.3	0.666	84	63	5	10	81
12.4	0.750	87	56	4	17	73
12.5	0.800	65	48	4	13	73

**conditions:** precursor: Pd(acac)<sub>2</sub>; ligand: triphenylphosphane monosulfonate (TPPMS); Preforming: 1 h (100 °C, 0.05 MPa (Ar)) in dimcarb; 20 mmol  $\beta$ -myrcene, C<sub>Pd</sub> = 0.035 mol%, C<sub>TPPMS</sub> = 0.14 mol%, t = 2 h, T = 100 °C, p = 0.01 MPa, 500 rpm,

## Screening of Pd/P Ratio:

Table 13: Influence of different dimcarb/myrcene-concentrations on the telomerisation of  $\beta$ -myrcene with dimcarb

#	TPPMS-conc. [mol%]	conversion [%]	Y <sub>telom.</sub> [%]	Y <sub>dim.</sub> [%]	Y <sub>hydroam.</sub> [%]	S <sub>telomers</sub> [%]
13.1	-	10	0	2	1	0
13.2	0.035	35	23	3	3	78
13.3	0.070	56	45	5	2	86
13.4	0.105	66	53	5	4	85
13.5	0.140	84	63	5	10	81
13.6	0.175	82	57	5	15	75
13.7	0.210	79	47	3	13	74

**conditions:** precursor: Pd(acac)<sub>2</sub>; ligand: triphenylphosphane monosulfonate (TPPMS); Preforming: 1 h (100 °C, 0.05 MPa (Ar)) in dimcarb; 20 mmol  $\beta$ -myrcene, C<sub>Pd</sub> = 0.035 mol%, t = 2 h, T = 100 °C, p = 0.01 MPa, 500 rpm,

## 8. Reaction profile:

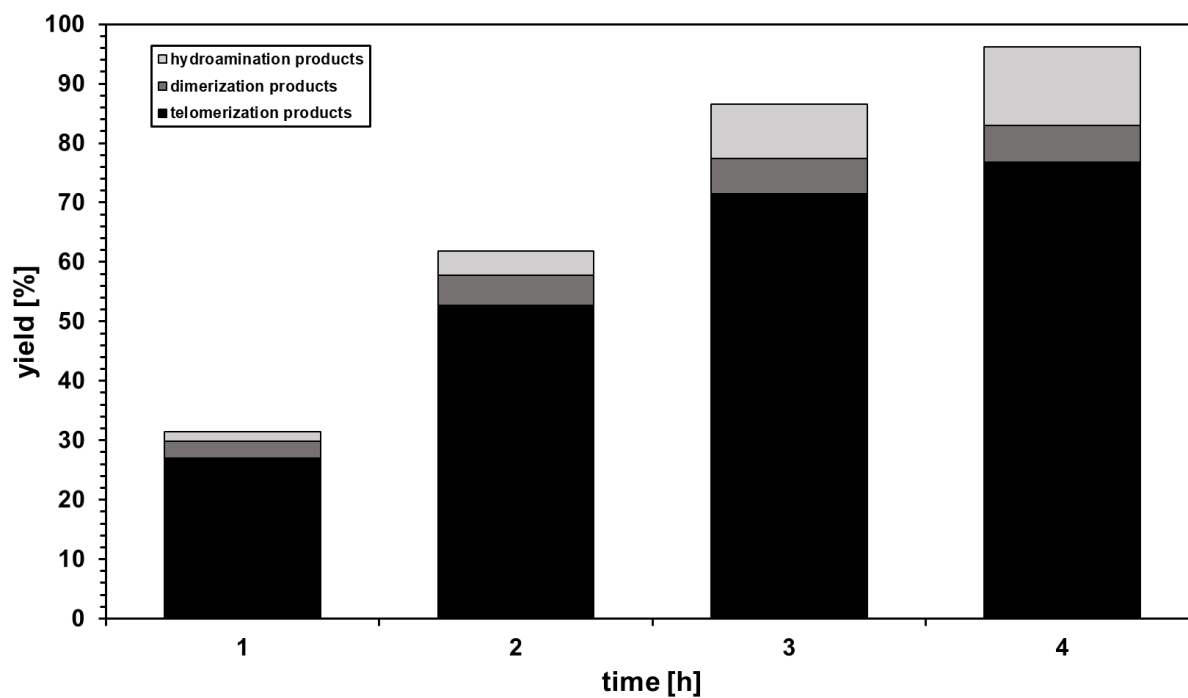


Figure 3: reaction profile of telomerisation of myrcene with dimcarb under optimized conditions

**conditions:** precursor: Pd(acac)<sub>2</sub>; ligand: triphenylphosphane monosulfonate (TPPMS); Preforming: 1 h (100 °C, 0.05 MPa (Ar)) in dimcarb; 20 mmol β-myrcene, C<sub>Pd</sub> = 0.035 mol%, C<sub>TPPMS</sub> = 0.14 mol%  
T = 100 °C, p = 0.01 MPa, 500 rpm,

## 9. Leaching results of recycling experiments

Table 14: Leaching results of first recycling experiments with Pd(acac)<sub>2</sub> and TPPMS / TPPTS at a Pd/Ligand ratio of 1/3 (consistent with Figure 4)

#	recycle run	ligand	Pd-Leaching [%]	P-Leaching [%]
14.1	initial		13	2
14.2	1	TPPMS	21	3
14.3	2		22	3
14.4	3		17	2
14.5	initial		4	0.9
14.6	1	TPPTS	6	1.1
14.7	2		8	1.2
14.8	3		4	1.2

Table 15: Leaching results of recycling experiment Pd(acac)<sub>2</sub> and TPPTS at a Pd/Ligand ratio of 1/8 (consistent with Figure 6)

#	recycle run	Pd-Leaching [%]	P-Leaching [%]
15.1	Initial	0.5	0.1
15.2	1	1.5	0.2
15.3	2	0.9	0.2
15.4	3	0.7	0.2
15.5	4	0.8	0.2
15.6	5	0.8	0.2
15.7	6	0.8	0.2
15.8	7	0.7	0.2
15.9	8	0.7	0.7
15.10	9	0.7	0.6
15.11	10	0.7	0.6
15.12	11	0.7	0.5
15.13	12	0.6	0.5
15.14	13	0.7	0.5

## 10. NMR-analysis of telomer products

The evaluation of the  $^1\text{H-NMR}$  was analogous to that performed by VOGELANG et al. 2018 in the telomerisation of  $\beta$ -farnesene with different N-nucleophiles.<sup>[2]</sup>

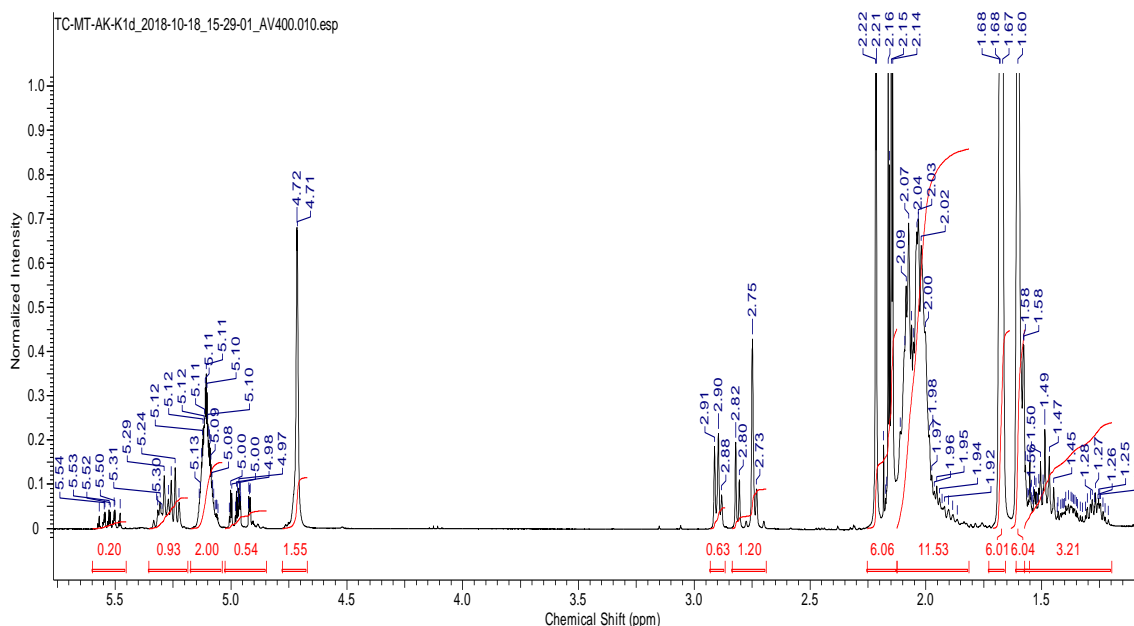


Figure 4:  $^1\text{H-NMR}$  of the isolated telomer mixture.

The head-tail nomenclature is usually used for the classification of products in which two terpene units are linked together, which is also the case in this telomerisation.

How far x-head and x-tail isomers have formed during the telomerisation of  $\beta$ -myrcene can be determined by the number of protons bound to  $\text{sp}^2$ -hybridized carbon atoms. Due to their chemical shift, which is at  $\delta = 4.5 - 5.5$  ppm, these protons can easily be distinguished from the other protons which are not bound to C-C double bonds. Figure 5 shows the two possible x-links, whereby the protons bound to  $\text{sp}^2$ -hybridized carbons are marked in red.

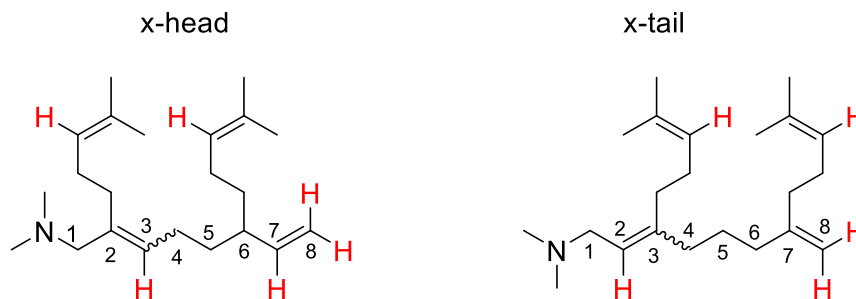


Figure 5: x-head and x-tail telomers

Here it can be seen that in an x-head linkage a total of six protons, four of them in the octadienyl part of the molecule, are bound to  $\text{sp}^2$ -hybridized carbon atoms. In contrast, only three protons are bound to  $\text{sp}^2$ -hybridized carbon atoms in the octadienyl part and thus a total of six protons are bound to  $\text{sp}^2$ -hybridized carbon atoms. The linkage of the first  $\beta$ -myrcenes, whether head-y or

tail-y, is not important, since it has no influence on the number of protons bound to double bonds. The integration of these proton signals in the range of  $\delta = 4.5 - 5.5$  ppm leads to a number between five and six, which thus indicates the distribution between these two isomers.

The investigation of the chemical shift of the protons at the C1 atom of the octadienyl skeleton, which exhibit a chemical shift in the range of  $\delta = 2.5 - 3.0$  ppm, provides information about the distribution of the head-y and tail-y isomers. Figure 6 shows the two types of linkage with the relevant protons in red.

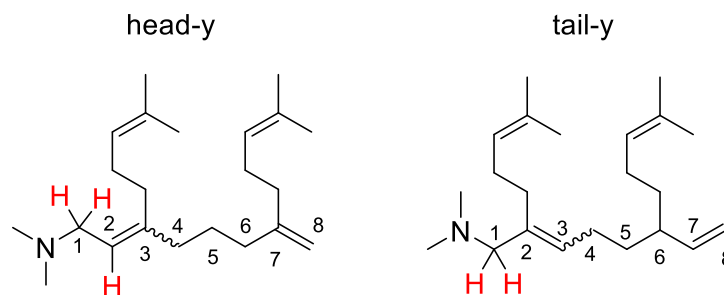


Figure 6: head-y and tail-y telomer

In a head-y linkage in  $^1\text{H-NMR}$ , the two protons at the C1 atom are split into a multiplet. Since a proton is also bound to the C2 atom in the head-y isomer, it couples directly to the two protons at the C1 atom, resulting in a multiplet as a splitting pattern. In the case of the tail-y isomer, the remaining part is bound to the C2 atom of the octadienyl skeleton. Therefore there is no direct coupling of a proton with the C1 protons and a simple triplet results as a splitting pattern.

Figure 4 shows the obtained  $^1\text{H-NMR}$  spectrum of the telomer products, which have been distillatively separated from the by-products and the unreacted  $\beta$ -myrcene. The integration of the signals of the protons bound to  $\text{sp}^2$ -hybridized carbon atoms and having a chemical shift in the range of  $= 4.5 - 5.5$  ppm results in a sum of 5.21, which suggests a distribution of 79:21 from x-tail to x-head isomer. The proton signals in the range of  $= 2.5 - 3.0$  ppm are used to determine the ratio of head-y-to tail-y linkage. The integration sums result in a ratio of approx. 66:34 to the head-y isomer. Due to these ratios obtained during the telomerisation of  $\beta$ -myrcene with dimcarb, the isomer mixture of the head-tail product (Figure 7) is statistically the main product.

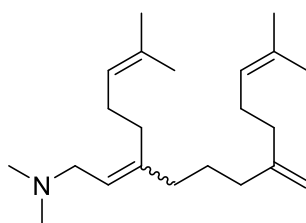


Figure 7: main product of telomerisation of  $\beta$ -myrcene with dimcarb (head-tail isomer)

## 11. $^{31}\text{P}$ -NMR Measurements of catalyst phase after recycling

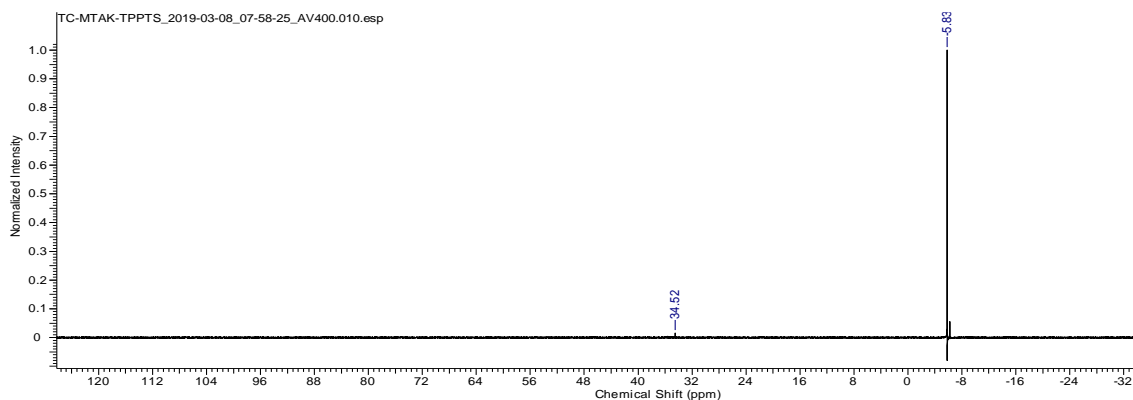


Figure 8:  $^{31}\text{P}$ -NMR of pure TPPTS

Two signals are seen in the  $^{31}\text{P}$ -NMR of pure TPPTS. One between -5 and -7 ppm and one between 34 and 35 ppm which represents oxidized TPPTS.

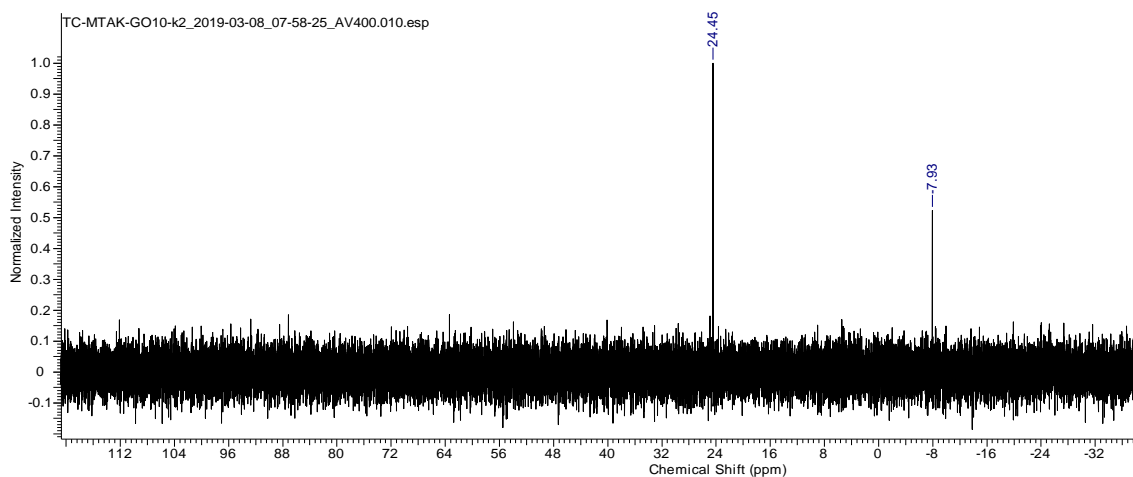


Figure 9:  $^{31}\text{P}$ -NMR of catalyst phase after recycling

Two signals are seen in the  $^{31}\text{P}$ -NMR of the catalyst phase after recycling. One between -5 and -7 ppm and one between 24 and 25 ppm which represents a coordinated TPPTS-Pd-species.<sup>[3]</sup>



## 12. EDX-Measurements of black particles after recycling

The black residues that became apparent during the recycling were isolated and purified under 5 mbar at 200 °C. The products of the telomerisation were pyrolyzed under this conditions. The black residues were analyzed via EDX experiments and carbon, calcium and palladium could be determined

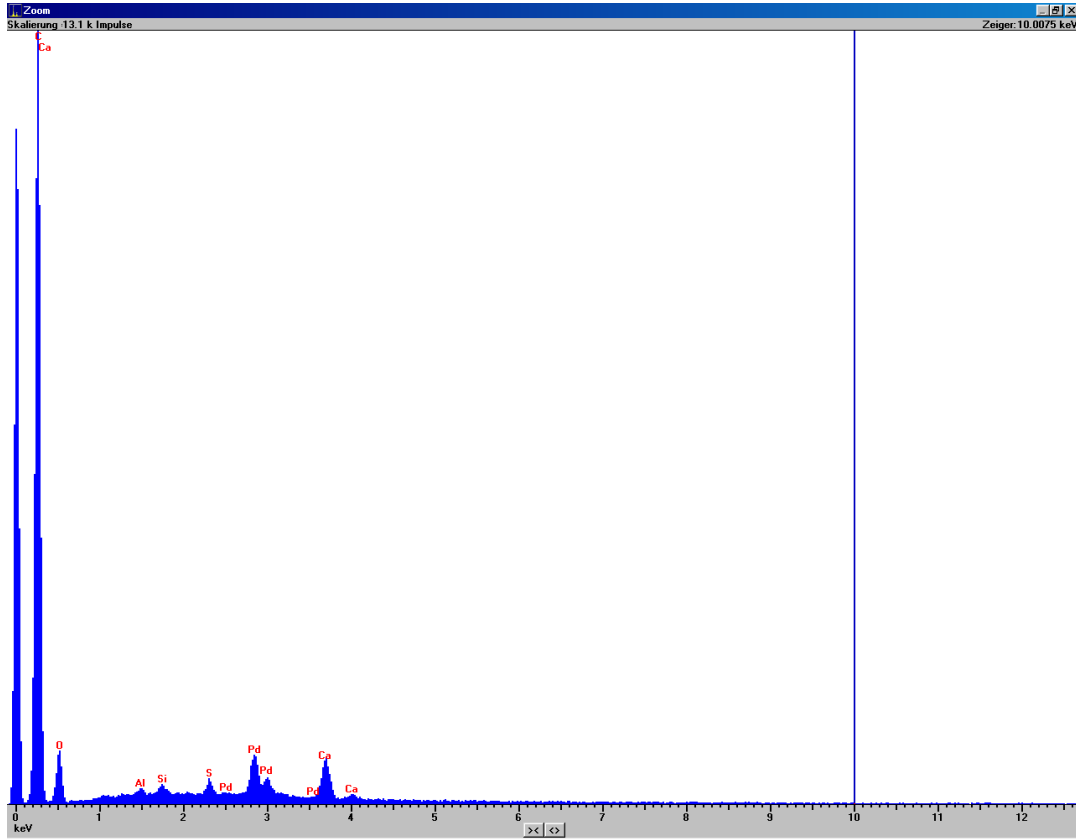


Figure 10: results of the EDX-analysis of the black residues.

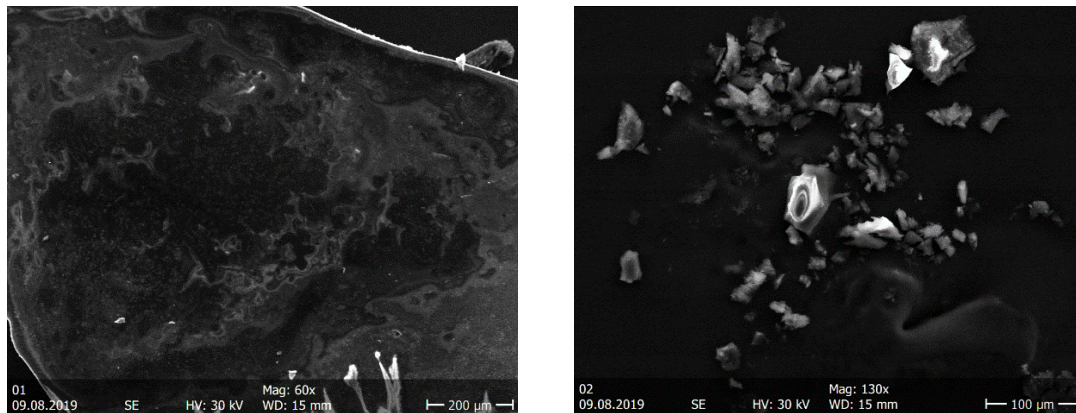


Figure 11: REM images of the black residue with 200 µm and 100 µm scale.

## 13. Additional Literature

- [1] A. Behr, L. Johnen, A. J. Vorholt, *ChemCatChem* **2010**, 2, 1271–1277.
- [2] D. Vogelsang, T. A. Faßbach, P. P. Kossmann, A. J. Vorholt, *Adv. Synth. Catal.* **2018**, 360, 1984–1991.
- [3] B. Driessen-Hölscher, T. Prinz, *Chem. Eur. J.* **1999**, 5, 2069–2076.