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Novel Initiators for Thermally and UV-Triggered ROMP

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Summary: Novel ruthenium-based photoactive transition metal catalysts, i.e. [Ru(CF_3CO_2)$_2$(*p*-cymene)(IMes)] (**2**), [Ru(CF_3CO_2)$_2$(PhNC)$_3$(IMes)] (**3**), [Ru(CF_3CO_2)$_2$(*p*-cymene)($IMesH_2$)] (**4**), [Ru(CF_3CO_2)$_2$(PhNC))$_3$($IMesH_2$)] (**5**), have been prepared and investigated for their use as initiators for the thermally and photo-initiated ring-opening metathesis polymerization (photo-ROMP). The polymerization behavior of the novel systems for both norborn-2-ene and functional monomers, such as norborn-5-ene-2-ylmethanol, has been investigated.

Keywords: coatings; organometallic catalysts; photopolymerization; ring-opening metathesis polymerization (ROMP)

Introduction

Among those polymerizations, which allow for the manufacture of highly functional materials, metathesis-based polymerization techniques such as ring-opening metathesis polymerization (ROMP), 1-alkyne polymerization and the cyclopolymerization of 1,6-heptadiynes have gained a strong position.[1–3] This fact and the prerequisite to that, *i.e.* the development of well-defined, highly active and functionality tolerant polymerization catalysts,[4–8] have been recognized by awarding the Nobel Prize in Chemistry 2005 to the protagonists of this Chemistry.[9] So far, the vast majority of metathesis-based reactions is initiated thermally and comparably few reports exist on the chemistry of photo-active initiators for metathesis polymerization.[10–28] In addition, the few systems available so far may be activated either thermally or by visible light and show significant metathesis efficiency for any norborn-2-ene-based monomer even at room temperature and below. This significantly reduces the stability and aggravates their applicability to photopolymerization. In addition, the storage of preformed monomer-catalyst mixtures as used in photochemically triggered radical or cationic polymerization is impossible. Consequently, *photochemically* triggered initiators derived from *inactive pre-catalysts* would significantly contribute to this area of research since they would allow for the *in situ* manufacture of (surface-immobilized) ring-opening metathesis polymerization- (ROMP) derived structures. Here, we describe novel Ru-based, N-heterocyclic carbene-derived initiators and their use as photo-active ROMP catalysts. The new catalysts allow for the manufacture of monomer/catalyst mixtures that are stable at room temperature and towards exposure to visible light, yet may be initiated by high energy 172 nm excimer generated light.

Experimental

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further

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purification. Tetrahydrofurane (THF) and dichloroethane were distilled from sodium benzophenone ketyl and calcium hydride under nitrogen respectively. Pentane, diethyl ether, toluene and methylene chloride were dried and deoxygenated by means of an MBraun SDS drying system. NMR data were obtained at 250.13 MHz for proton and 62.90 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. Elemental analyses were carried out at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by GPC at 30 °C on Polymer Laboratories columns (PLgel 10 μm MIXED-B, 7.5 × 300 mm) in THF at 25 °C using a Waters Autosampler, a Waters 484 UV spectrometer detector (254 nm), an Optilab Rex refractive index detector (Wyatt) and a MiniDawn light scattering detector (Wyatt). [$RuCl_2$(*p*-cymene)(IMes)] (**1**, IMes = 1,3-dimesitylimidazol-2-ylidene)[27] was prepared according to the literature. Phenyl isonitrile was prepared according to published procedures[29] and stored at 4 °C. A Xe_2^*-excimer source (172 nm, XERADEX-System, 20W, 120 mm, Radium Lampenwerk Wipperfürth, Germany) was used for irradiation experiments. Infrared spectra were recorded in real time with a Digilab FTS 6000 FTIR spectrometer or on a Bruker Vector 22 using ATR technology. The real time FT-IR spectrometer equipped with a MCT detector reaches a maximum temporal resolution of 40 and 340 msec, respectively, at a spectral resolution of 16 cm^{-1}. A heatable single reflection diamond ATR module (''Golden Gate''; Graseby Specac) was used for sampling. The monomer film was coated on a diamond with a thickness of about 1 μm. UV irradiation was performed with an Osram Xe_2^* excimer lamp with an emission at 172 nm. The lamp head was directly affixed to the top plate of the ATR device. It was sealed against the surrounding and flushed with nitrogen to avoid absorption of the short-wavelength radiation by the atmospheric oxygen. Water contact angles were measured on a System 2 (Krüss, Germany).

[$Ru(CF_3CO_2)_2$(*p*-cymene)(IMes)] (2)

Complex **1** (61.0 mg, 0.10 mmol) was dissolved in THF and added to a solution of silver trifluoroacetate (44.2 mg, 0.20 mmol) in THF, both cooled to −36 °C. After mixing, the solution was stirred for another 4 hours, allowing it to reach room temperature. During that time a white precipitate of AgCl formed. The mixture was filtered through a short bed of celite and the THF was removed *in vacuo*. Methylene chloride was added to dissolve the residue and the solution was filtered through glass-fiber paper and concentrated in vacuo. Diethyl ether and *n*-pentane was layered over the red, saturated solution. Red crystal formed at −36 °C. Yield: 66.5 mg, 87%. FTIR: 3120, 2967, 2916, 1687, 1477, 1397, 1262, 1194, 1175, 1122, 838, 740, 724 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.02 (s, 2H, *H*C=C*H*), 6.95 (s, 4H, mesityl), 5.34 (d, 2H, $J = 6.0$ Hz, *p*-cymene), 5.14 (d, 2H, $J = 6.0$ Hz, *p*-cymene), 2.50 (pent, 1H, $J = 6.9$ Hz, C*H*), 2.33 (s, 6H, mesityl-*p*-CH_3), 2.14 (s, 12H, mesityl-*o*-CH_3), 1.90 (s, 3H, CH_3), 0.94 (d, 6H, $J = 6.9$ Hz, $2CH_3$); ^{13}C NMR ($CDCl_3$): δ 173.1 (s, NCN), 162.9 [q, CO, $^2J(^{19}F, ^{13}C) = 35.8$ Hz], 139.2, 137.0, 135.5, 128.9, 125.6 (mesityl and *C*=*C*), 114.5 [q, CF_3, $^1J(^{19}F, ^{13}C) = 292.2$ Hz], 107.6, 93.8, 84.9, 80.3 (*p*-cymene), 30.7 (CH), 22.4, 21.0, 18.8, 18.0 (CH_3); Elemental analysis (%) calcd. for $C_{35}H_{38}F_6N_2O_4Ru$ ($M_r = 766.18$ g/mol): C, 54.90; H, 5.00; F, 14.89; N, 3.66; found: C, 54.91; H, 5.14; N, 3.48.

[$Ru(CF_3CO_2)_2$(PhNC)$_3$(IMes)] (3)

Compound **1** (53.7 mg, 70.0 μmol) was dissolved in 5 mL of CH_2Cl_2 in a Schlenk tube. Excess of phenyl isonitrile (43.3 mg, 0.42 mmol) was added at room temperature under argon and the red solution became yellow. The mixture was refluxed for 2 hour at 42 °C, then the dichloromethane and phenyl isonitrile were removed in vacuo.

A yellow powder was obtained which was washed with *n*-pentane and diethyl ether. Recrystallization was accomplished at −36 °C by layering diethyl ether and *n*-pentane over a saturated dichloromethane solution. Yield: 41.0 mg, 78%. FTIR: 2920, 2168, 2101, 1682, 1593, 1485, 1398, 1308, 1182, 1129, 842, 753, 684 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.37–7.10 (m, 15H, Ph), 7.05 (s, 2H, *H*C=C*H*), 6.80 (s, 4H, mesityl), 2.12 (s, 12H, mesityl-*o*-CH_3), 1.72 (s, 6H, mesityl-*p*-CH_3). ^{13}C NMR ($CDCl_3$): δ 186.6 (NCN), 163.1 [q, CO, $^2J(^{19}F, ^{13}C) = 35.0$ Hz], 160.3, 158.4 (NC), 139.9, 138.1, 137.4, 129.1, 129.0, 128.8, 127.8, 127.7, 126.6, 126.3, 123.5 (mesityl, *C*=*C* and Ph), 113.9 [q, CF_3, $^1J(^{19}F, ^{13}C) = 291.1$ Hz], 20.6, 17.0 (mesityl *C*H_3); Elemental analysis (%) calcd. for $C_{46}H_{39}F_6N_5O_4Ru$ ($M_r = 941.19$ g/mol): C, 58.72; H, 4.18; N, 7.44; found: C, 58.40; H, 4.39; N, 7.24.

[Ru(CF_3CO_2)$_2$(*p*-cymene)(IMesH$_2$)] (4)

[$RuCl_2$(*p*-cymene)$_2$]$_2$ (**6**) (61.2 mg, 0.10 mmol) was suspended in THF and the solution of 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene (**7**)[4] (61.6 mg, 0.20 mmol) in THF was added dropwise. The mixture was stirred for 2 hours at room temperature and cooled to −36 °C. A chilled solution of silver trifluoroactate (88.4 mg, 0.40 mmol) in THF was added dropwise. The solution was stirred for another 2 hours, allowing it to reach room temperature. During that time a white precipitate of AgCl formed. The mixture was filtered through a short bed of celite and the THF was removed in vacuo. Methylene chloride was added to dissolve the residue and the solution was filtered through glass-fiber paper and concentrated in vacuo. Diethyl ether and *n*-pentane were layered over the red, saturated solution. Red crystals formed at −36 °C. Yield: 119.8 mg, 78%. FTIR: 3095, 2959, 2915, 1690, 1414, 1403, 1263, 1177, 1123, 834, 799 724 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.91 (s, 4H, mesityl), 5.32 (d, 2H, $J = 6.0$Hz, ArH), 5.14 (d, 2H, $J = 6.1$Hz, ArH), 3.94 (s, 4H, CH_2–CH_2), 2.36–3.28 (m, 19H, mesityl-CH_3+ C*H*(CH_3)$_2$), 1.86 (s, 3H, CH_3), 0.92 (d, $J = 6.9$Hz, 2CH_3); ^{13}C NMR ($CDCl_3$): δ 203.2 (s, NCN), 162.8 [q, CO, $^2J(^{19}F, ^{13}C) = 36.3$ Hz], 138.3, 137.2, 136.0, 129.3 (mesityl), 114.5 [q, CF_3, $^1J(^{19}F, ^{13}C) = 292.4$ Hz], 107.2, 94.4, 85.2, 81.0 (*p*-cymene), 52.5 (CH), 30.6, 22.4, 20.9, 18.1 (CH_3). Elemental analysis (%) calcd. for $C_{35}H_{40}F_6N_2O_4Ru$ ($M_r = 768.19$ g/mol): C, 54.75; H, 5.25; F, 14.85; N, 3.65; found: C, 54.87; H, 5.19; N, 3.48.

[Ru(CF_3CO_2)$_2$(PhNC))$_3$(IMesH$_2$)] (5)

Compound **4** (53.7 mg, 70 μmol) was dissolved in 5 mL of CH_2Cl_2 and then removed from the dry box. Excessive phenyl isonitrile (43.3 mg, 0.42 mmol) was added dropwise at room temperature under argon. The red solution immediately became yellow. The mixture was stirred at room temperature for 3 hours, then dichloromethane and phenyl isonitrile was removed in vacuo. The remaining pale yellow powder was washed by *n*-pentane and diethyl ether, and then recrystallized by layering diethyl ether and *n*-pentane over a saturated dichloromethane solution. Pale yellow crystals were obtained at −36 °C in 78% yield. FTIR: 2918, 2170, 2104, 1683, 1594, 1484, 1455, 1266, 1189, 1130, 843, 787, 753, 726, 686 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.34–7.10 (m, 15H, Ph), 6.78 (s, 4H, mesityl), 3.97 (s, 4H, CH_2–CH_2), 2.34 (s, 12H, mesityl-*o*-CH_3), 1.70 (s, 6H, mesityl-*p*-CH_3). ^{13}C NMR ($CDCl_3$): δ 213.4 (NCN), 163.1 [q, CO, $^2J(^{19}F, ^{13}C) = 35.1$ Hz], 159.8, 158.0 (NC), 139.0, 138.6, 138.0 (mesityl), 129.6, 128.9, 128.8, 127.8, 127.6, 126.6, 126.2 (Ph), 114.0 [q, CF_3, $^1J(^{19}F, ^{13}C) = 289.4$ Hz], 51.5 (*C*H_2–*C*H_2), 20.6, 17.2 (mesityl *C*H_3); Elemental analysis (%) calcd. for $C_{46}H_{41}F_6N_5O_4Ru$ ($M_r = 943.21$ g/mol): C, 58.59; H, 4.38; F; N, 7.43; found: C, 58.77; H, 4.60; N, 7.27.

Solution Polymerization of Norborn-2-ene and Norborn-5-ene-2-ylmethanol, Respectively

A) Thermal Initiation

The monomer (80 mg) was dissolved in dichloromethane, the catalyst (1 mol-%) was added and the mixture was heated to

40 °C. After the indicated time, the polymer was collected by means of precipitation from methanol. In the case of norborn-5-ene-2-ylmethanol, an insoluble polymeric precipitate formed.

B) UV Initiation

Alternative to heating, solutions weres irradiated for 30 minutes (UV, 172 nm). Work up was identical to A).

Poly(norborn-2-ene) Obtained via Thermal Treatment of Norborn-2-ene with 4

^{1}H-NMR ($CDCl_3$) δ 5.33 (d, J = 2.5*Hz*, 1H, C*H*=C*H*$_{cis}$), 5.20 (d, J = 19*Hz*, 1H, C*H*=C*H*$_{trans}$), 2.78 (bs, 1H), 2.43 (bs, 1H), 1.80 (bs, 3H), 1.35 (bs, 2H), 1.01 (bs, 1H).

Poly(norborn-5-ene-2-ylmethanol) Obtained via Thermal Treatment of Norborn-5-ene-2-ylmethanol with 4

THF and chloroform insoluble polymer. FT-IR: cm^{-1}: 3315 (b), 2930 (s), 2861 (s), 1448 (w), 1016 (vs), 973 (s), 744 (m).

X-ray Measurement and Structure Determination of 2

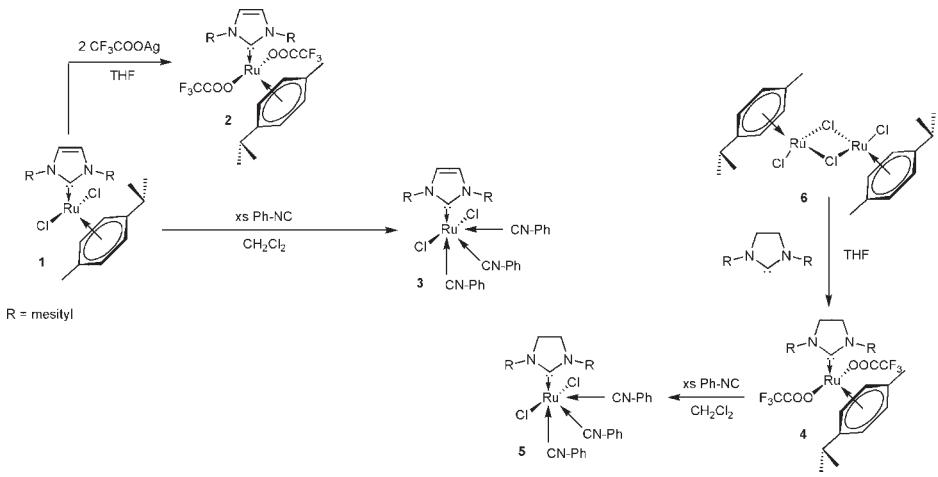
Data collection was performed at 180(2) K on a Stoe-IPDS-2 imaging plate diffractometer using ω scan mode and Mo-K$_\alpha$-radiation (λ = 0.71073 Å), numerical absorption correction with XRED[30]; min. / max. transmission: 0.8708 / 0.9290, 76778 reflections collected, 11791 independent reflections (R(int) = 0.0510). The structures were solved by direct methods (SHELXS97) and refined with SHELXL97 using all reflections.[31]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were calculated on idealized positions.

Supporting Information Available

Crystallographic data for **2** have been deposited with the CCDC-No. 293339 on the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

In view of the existing knowledge on Ru-based catalysts for photo-ROMP of the general formula $[RuCl_2(p\text{-cymene})]_2$ and $RuCl_2(L_1)(L_2)$ (L_1 = IMes, L_2 = *p*-cymene; L_1 = *p*-cymene, $L_2 = PR_3$), respectively, it was quite clear that the existing set of ligands was inadequate. Thus, even at room temperature, moderate polymerization activity for norborn-2-ene-derived monomers is observed with all pre-catalysts. This is indicative for an uncontrolled, untriggered loss of ligand in the presence of monomer and may be well attributed to the comparably weak binding of the p-cymene ligand in these systems. However, in order to become suitable for real technical applications, such a pre-catalyst needs to be stable in the presence of monomer. Only such behavior allows for the premixing of all reactants prior to use. Initiation is then accomplished either via heating above 60 °C or UV irradiation. Keeping our latest results in terms of catalyst activity in mind,[32–38] we performed the following modifications: First, all pre-catalysts were synthesized on the base of Ru-N-heterocyclic carbene (NHC) complexes. Both the 1,3-dimestylimidazol-2-ylidene and the 1,3-dimestyl-4,5-dihydroimidazolin-2-ylidene ligand were used for this purpose. Second, we performed variations in the ligand sphere, *i.e.* exchanged the *p*-cymene ligand by phenyl isonitrile as well as the chlorine ligand by trifluroacetate groups. These transformations were expected to generate pre-catalysts which, upon loss of the auxiliary ligand, i.e. the *p*-cymene and phenyl isonitrile groups, respectively, would form a highly active species. However, exchanging the chlorines by trifluoroacetate groups was believed to stabilize the parent complexes to an extent that would render them stable in the presence of



Scheme 1.
Synthesis of catalysts **1**–**5**.

monomer, thus requiring an external trigger to initiate the dissociation of the auxiliary ligands. Scheme 1 summarizes the synthesis of the complexes, $[Ru(CF_3CO_2)_2(p\text{-cymene})(IMes)]$ (**2**), $[Ru(CF_3CO_2)_2(PhNC)_3(IMes)]$ (**3**), $[Ru(CF_3CO_2)_2(p\text{-cymene})(IMesH_2)]$ (**4**), $[Ru(CF_3CO_2)_2(PhNC))_3(IMesH_2)]$ (**5**), that have been prepared. As can be seen, 18 electron complexes were formed throughout as evidenced by NMR and elemental analysis. In addition, the x-ray structure of **2** was determined. **2** crystallizes in the monoclinic space group P2(1)/c, $a = 1454.08(4)$ pm, $b = 1124.65(4)$ pm, $c = 2205.46(8)$ pm, $\alpha = 90^\circ$, $\beta = 108.177(3)^\circ$, $\gamma = 90^\circ$, $Z = 4$. Upon irradiation or thermal treatment, the cymene ligand in **2** or **4** must dissociate in order to generate free coordination sites for the monomer. Similarly, at least two of the three phenyl isonitrile groups must dissociate in **3** or **5**, resulting in a reactive 14 electron species.

The x-ray structure of catalyst **1** is shown in Figure 1. A summary on the crystal data is given in Table 1, selected bond distances and angles are summarized in Table 2. As can be seen, the distance Ru – NHC (i.e. Ru1-C31) is 210.52 (14) pm, a value which is comparable to other Ru-NHC complexes.[38] Similarly, the distances to either of the two trifluroacetate groups (i.e. Ru1-O1

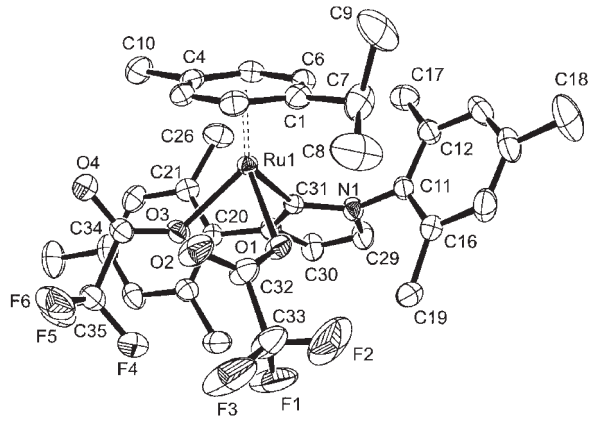


Figure 1.
X-ray crystallographic structure of compound **2**.

Table 1.
Crystal data and structure refinement for **2**.

1	**2**
mol formula	$C_{35}H_{38}F_6N_2O_4Ru$
fw	765.74
cryst syst	monoclinic
space group	P2(1)/c
a (pm)	1454.08(4)
b (pm)	1124.65(4)
c (pm)	2205.46(8)
α (deg)	90
β (deg)	108.177(3)
γ (deg)	90
vol (nm^3)	3426.7(2)
Z	4
density (calcd) (mg/m^3)	1.484
goodness-of-fit on F^2	0.999
R indices $I > 2\sigma(I)$	$R_1 = 0.0311$
	$\omega R^2 = 0.0704$

and Ru1-O3, respectively) are basically the same and within the expected range. The cymene ligand, defined by C1-C6, is attached to the Ru center in an almost symmetrical manner, resulting in only slightly different distances between the Ru center and the corresponding carbons.

In a first set of reactions, catalysts **2–5** were used in the solution polymerization of norborn-2-ene (NBE) at room temperature. The results are summarized in Table 3. As can be seen, all initiators rapidly polymerize NBE at room temperature and are therefore not suitable as UV-catalysts for this monomer. Using 1 mol-% of catalyst the theoretical number average molecular weight M_n is 9,400 g/mol. With the exception of **3**, all catalysts showed significantly increased values for M_n, indicative for non quantitative initiation.

A representative ^{1}H-NMR spectrum of poly-NBE prepared by the action of **2** revealed the existence of 52% *cis*-configured and 48% *trans*-configured double bonds. This is in contrast to poly-NBE prepared by other Ru-based initiators, which usually give raise to the formation of norborn-2-ene-derived polymers with a trans content of 70–80%.[39] Switching from unsubstituted norborn-2-ene to norborn-5-ene-2-ylmethanol, **no polymerization activity was observed at room temperature with either of the new catalysts**. However, polymerizations commenced, when heating the corresponding reaction mixtures to 40 °C, yielding insoluble poly(norborn-5-ene-2-ylmethanol). This makes catalysts **2–5** in principle suitable for UV initiation of this functional monomer. When a mixture of **4** (1 mol-% with respect to the monomer) and norborn-5-ene-5-ylmethanol was cast on clean yet untreated glass plates to form layers of approximately 1 μm thickness and was subject to irradiation @ 172 nm using an excimer lamp, polymerization occurred, resulting in a strongly adjacent cured layers of (insoluble) poly(norborn-5-ene-2-ylmethanol) which could only be removed by extensive scratching. The conversion of the monomer into the corresponding polymer was monitored by FT-IR. Complete disappearance of the C=C stretching band ($\nu_{C=C\text{-st}}$) at 1571 cm^{-1} as well as of the $\delta_{C=C\ oop}$ band at 717 cm^{-1} ($\delta_{C=C\ oop,\ cis,\ monomer}$) and formation of new bands at 973 cm^{-1} ($\delta_{C=C\ oop,\ trans}$) and 747 cm^{-1} ($\delta_{C=C\ oop,\ cis}$) were indicative for the polymerization reaction. As a consequence of their chemical nature, poly(norborn-5-ene-2-ylmethanol) films gave raise to water contact angles of up to 79.0° compared to the native glass substrate (63.1°).

Further experiments that shall determine the scopes and limitations of these

Table 2.
Selected bond lengths (pm) and angles (°) of **2**.

Ru1-C31	210.52(14)
Ru1-O1	211.07(11)
Ru1-O3	211.42(11)
Ru1- C6	216.81(16)
Ru1-C5	218.58(16)
Ru1-C1	220.37(16)
Ru1-C4	222.05(15)
Ru1-C2	224.00(16)
Ru1-C3	224.26(15)
C31 Ru1 O3	86.81(5)

Table 3.
Summary of polymerization results for norborn-2-ene.

#	catalyst	yield (%)	time (h)	PDI	M_n(g/mol)
1	**2**	99	2	3.87	42,000
2	**3**	35	2	2.80	94,000
3	**4**	99	2	3.19	10,000
4	**5**	99	14	2.09	92,000

Polymerizations were carried out in dichloromethane at room temperature. 1 mol-% of initiator was used.

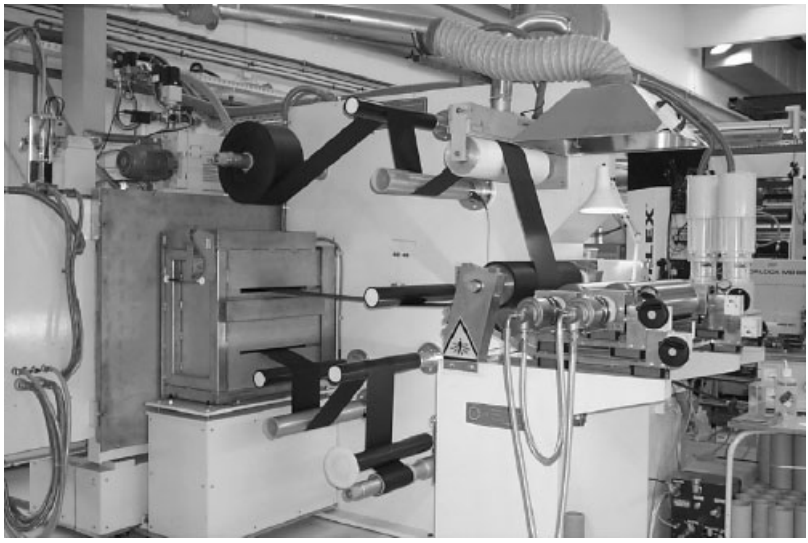


Figure 2.
Lab-coater applicable to roll-to-roll coating purposes.

catalysts in terms of reactivity towards other functional monomers and substrates are under way. Particular attention will be devoted to the development of fast, continuous, roll-to-roll applications applicable to lab coaters as shown in Figure 2.

Conclusion

In summary, novel photo-active Ru-based pre-catalysts for ROMP have been prepared. They may either be activated by UV-light or at elevated temperatures and effectively catalyze the ROMP of norborn-2-ene and norborn-5-ene-2-ylmethanol. Further investigations will focus on theoretical calculation-based synthesis of thermally stable pre-catalysts that allow for a quantitative and fast initiation of monomers at wavelengths in the range of 200–230 nm. This will allow for the UV-based curing of formulations up to a few μm in thickness and thus contribute to relevant technical applications.

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