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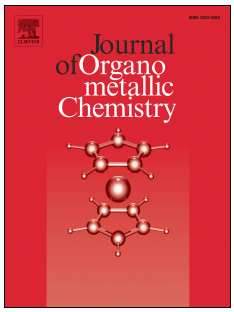

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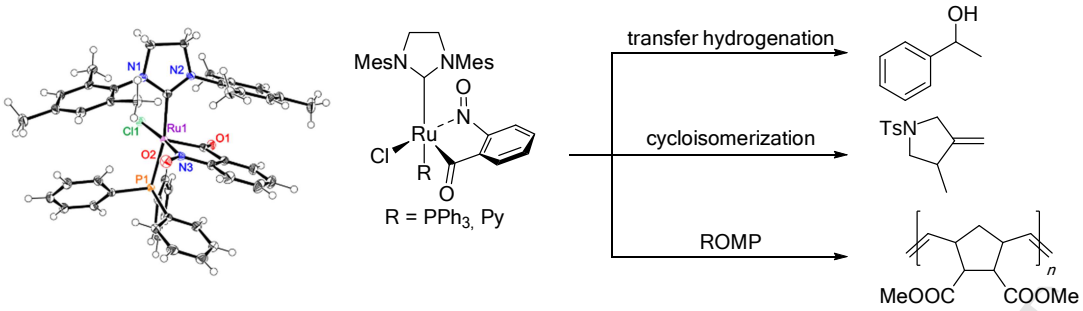

Unexpected ruthenium complexes for transfer hydrogenation, cycloisomerization, and ring opening metathesis polymerization.

Unexpected formation of nitroso-chelated cyclic η^1-acylruthenium(II) complex, an effective catalysts for transfer hydrogenation reaction

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This paper is dedicated to Professor Irina P. Beletskaya on the occasion of her 85th birthday.

ABSTRACT: Reaction of commercial ruthenium complexes M31 and M20 with 2-nitrostyrene gave a new nitroso-chelated cyclic η^1-acyl ruthenium(II) complexes **Ru-4** and **Ru-6** respectively instead of expected Hoveyda-Grubbs type (pre)catalyst **Ru-3**. New complexes were characterized by means of standard analytical techniques and their crystallographic structure has been confirmed by X-ray structural analysis. It was found that **Ru-4** and **Ru-6** do not exhibit any activity in standard metathesis reactions. However, a dramatic increase of activity was observed upon treatment with (trimethylsilyl)diazomethane, allowed for the successful application of **Ru-4** in ROMP of endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester. Moreover, such complexes can be effective catalysts of transfer hydrogenation of ketones as well as cycloisomerisation reactions.

KEYWORDS: Olefin metathesis, transfer hydrogenation, cycloisomerization, ring opening metathesis polymerisation (ROMP), racemisation, ruthenium

Introduction

Transition metal complexes have been used in plethora of chemical transformations for decades [1-4]. Particularly noteworthy are the ruthenium-based complexes which can catalyse numerous different reactions. One of the most important transformations occurring in the presence of ruthenium compounds is olefin metathesis, a reaction intensively studied for years [3, 4], especially after 2005, when Yves Chauvin, Robert H. Grubbs and Richard R. Schrock received the Nobel Prize in Chemistry [5]. One of the main development directions of this

methodology is the research conducted on obtaining new, more active and selective catalysts, often for specialized applications such as ethenolysis [6, 7], self-cross metathesis of α-olefins [8, 9], or stereoselective synthesis of products with *E* [10, 11] or *Z* [12, 13] configured double bonds.

In our previous research we studied the Hoveyda-Grubbs second generation catalyst's analogues containing nitro group in the benzylidene fragment. The most active was a complex **Ru-1** containing NO_2 substituent in *para* position to isopropoxy group (Figure 1) [14]. As this complex was highly active in the case of so-called "difficult substrates" (belonging to the olefin types II [14, 15] or III [14-17] according to the Grubbs classification [18], as well as toward substrates sensitive to harsh reaction conditions) [19] and was later used in a number of target-oriented synthesis and commercialized [20], we decided to look for its analogues. The catalyst with nitro group in *meta* position to isopropoxy group was also obtained (**Ru-2**, Figure 1) and shown similar activity to its *para* analogue, but due to more complicate synthesis it was not commercialized. In the present study, we wanted to obtain a complex **Ru-3** in which the nitro group located in the *ortho* position to the double bond in benzylidene ligand would be on one side an electron-withdrawing group and at the same time would form a chelate with a ruthenium atom (Figure 1). To our surprise we did not get the desired complex but instead we obtained ruthenium complex destitute benzylidene ligand, which demonstrated activity in transfer hydrogenation and other reactions.

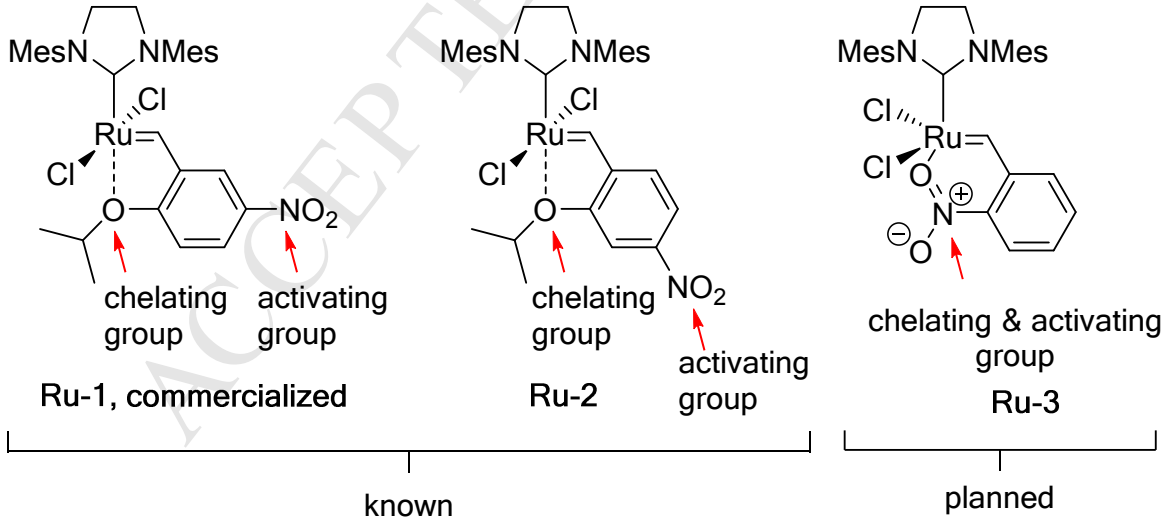
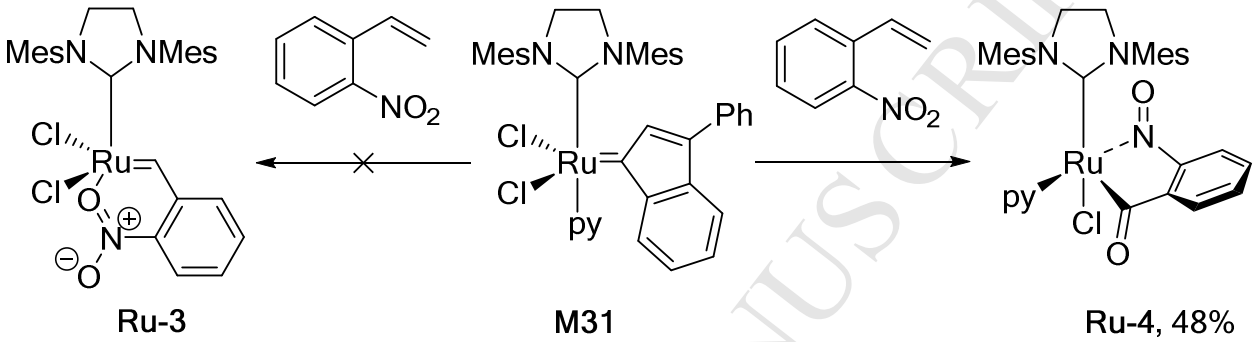


Figure 1. Known and planed complexes bearing NO_2 group in different positions in benzylidene ligand (Mes = mesityl group).

Results and discussion

Reaction of indenylidene ruthenium complexes M31 and M20 with 2-nitrostyrene

We attempted to synthesize the catalysts **Ru-3** according to well established methodology, previously used for synthesis of its analogues bearing NO_2 group in different positions in benzylidene ligand (Scheme 1) [14].



Scheme 1. Synthesis of complex **Ru-4**. Conditions: toluene, 80°C, 5 min.

To do so, we mixed 2-nitrostyrene with the third generation indenylidene catalyst (Umicore M31) in toluene at 80°C and stirred the mixture until the substrate disappeared completely. To our surprise instead of expected product **Ru-3** we obtained a new benzylidene-deprived ruthenium complex **Ru-4**. Spectroscopic techniques and X-ray crystallographic analysis showed that the major product obtained in 48% yield is a nitroso-chelated cyclic η^1-acylruthenium(II) complex **Ru-4** (Figure 2), however single crystals of this compound were of low quality and they were diffracting X-ray radiation very poorly. In consequence the quality of the structure **Ru-4** is not too high. The obtained thermal parameters are accompanied by a quite high residual peak at the centre of the *N*-heterocyclic ring indicating possible twining for the single crystal used for data collection. Unfortunately, the quality of data was too poor to resolve twinning. The presented structure was solved and refined against reflection data of the main component which consists of ca. 82% of all collected reflections.

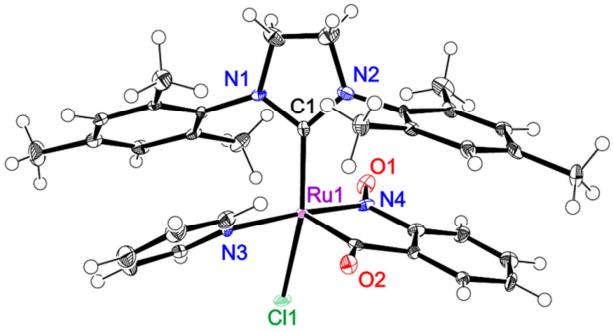
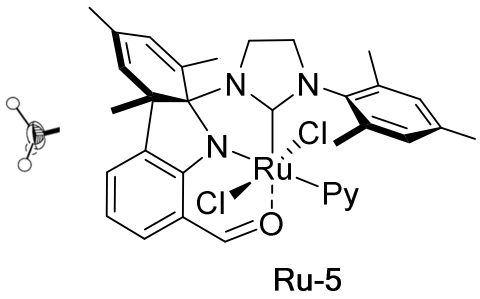


Figure 2. Crystallographic structure of the complex **Ru-4** (one of two molecules in the asymmetric part of the unit cell). Selected bond lengths in angstroms [the corresponding bond lengths in the second molecule in brackets]: Ru1-Cl1 2.421(2) [2.418(2)], Ru1-C1 2.042(6) [2.013(7)], Ru1-N3 2.165(6) [2.175(6)], Ru1-N4 1.915(6) [1.900(6)], Ru1-$C27_{\text{carbonyl group}}$ 1.950(7) [1.945(7)].

Interestingly, during preparation of **Ru-4**, a very small amount (yield < 1%) of other compound crystallized out of the reaction mixture. On the base of X-ray measurement, the structure of this side product **Ru-5** has been solved and refined (Figure 3).

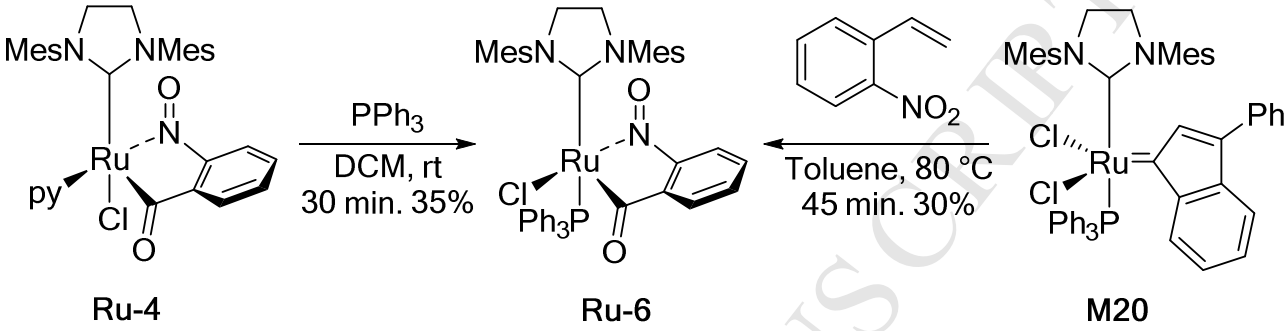


Ru-5

Figure 3. Structure and crystallographic structure of unexpected by-product **Ru-5**. Selected bond lengths in angstroms: Ru1-Cl1 2.3714(5), Ru1-Cl2 2.3522(6), Ru1-C1 1.983(2), Ru1-O1 2.175(2), Ru1-N3 2.187(2), Ru1-N4 1.938(2).

Due to some rearrangement within the molecule of the complex **Ru-4**, a product where mesitylene group was bridged to the phenyl ring and nitrogen atom of a neighbouring moiety has been established. As a result of this double bridging, six combined rings were created.

In order to confirm that the complex **Ru-4** contains the nitroso-acyl moiety, we have decided to transform compound **Ru-4** into its derivative containing PPh_3 ligand. To achieve this goal, triphenylphosphine was added to the DCM solution of the previously obtained compound **Ru-4** and a new compound **Ru-6** was afforded in 35% yield (Scheme 2).

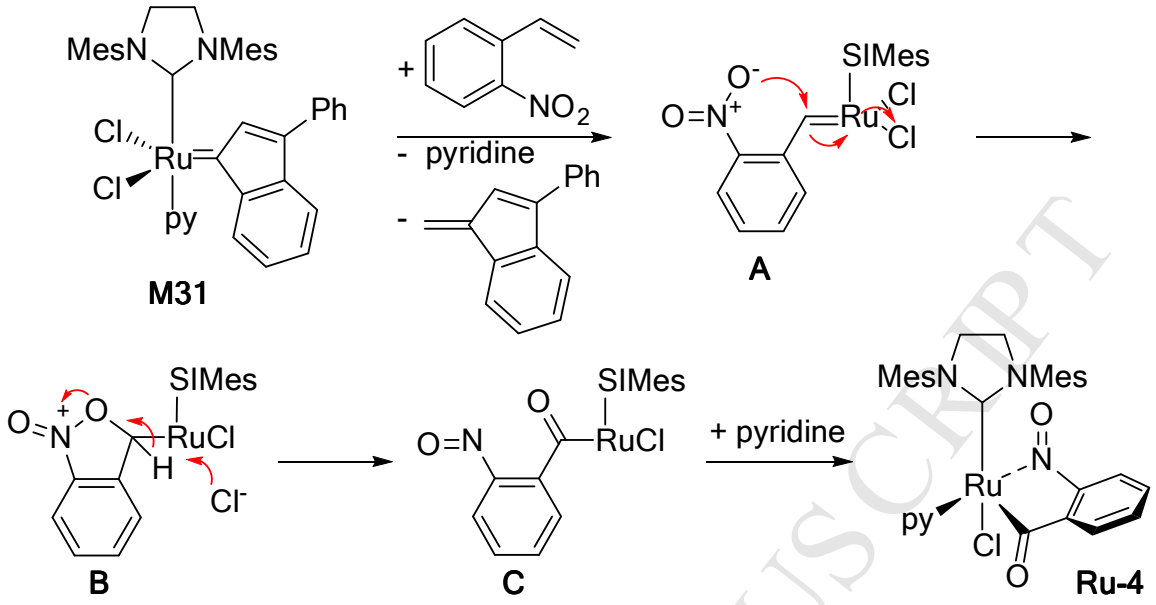


Ru-4 Ru-6 M20

Scheme 2. Synthesis of complex **Ru-6**.

Alternatively, compound **Ru-6** can be obtained by the reaction between the commercially available indenylidene complex containing PPh_3 as a ligand (Umicore M20) and 2-nitrostyrene, but also in this case the yield was low and reached only 30%. Fortunately in this case a crystal of **Ru-6** of good quality was obtained by crystallization from DCM/*n*-hexane mixture (Figure 4) which allowed us to confirm the structure of the isolated compound. Unfortunately any attempts to increase the yield of the desired catalysts **Ru-4** and **Ru-6** crashed and burned. Although a complete conversion of both substrates was observed, due to the low stability of complexes during the column chromatography it was impossible to obtain high yield even when silica gel was replaced by aluminium oxide or Florisil.

On Scheme 3 a hypothetical mechanism of formation of complex **Ru-4** is presented.



Scheme 3. Proposed mechanism of formation of a **Ru-4** (SIMes = 1,3-dimesitylimidazolin-2-ylidene).

In the first step, alkylidene ligands are exchanged with a subsequent elimination of the pyridine moiety leading to compound **A**. Next, a rearrangement of the molecule takes place, which results in the formation of a bicyclic system **B**, which, as a result of the chloride ion attack, is then transformed into complex **C**. In the final stage, the resulting compound in reaction with pyridine is converted into a catalyst **Ru-4**.

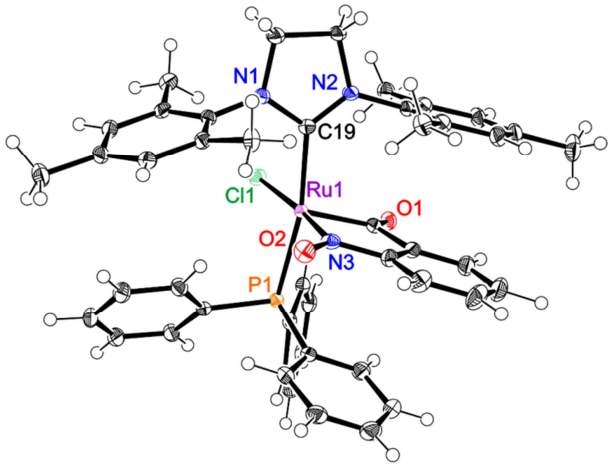


Figure 4. Crystallographic structure of the complex **Ru-6**. Selected bond lengths in angstroms: Ru1-Cl1 2.4043(5), Ru1-P1 2.3861(5), Ru1-N3 1.911(2), Ru1-C19 2.142(2), Ru1-C47 $_{\text{carbonyl group}}$ 1.970(2).

Here, we report the first structure of the nitroso-chelated ruthenium atom. The catalyst molecules **Ru-4** and **Ru-6** crystallize in the C2/c and P-1 space groups of the monoclinic and triclinic crystal systems, respectively. The crystal structure of the complex **Ru-4** contains two molecules of catalyst and two molecules of solvent (DCM) in the asymmetric unit. The molecules of catalyst are not identical as they are differentiated by the N4 atom located in the five-membered heterocyclic ring. This particular N4 atom is a part of nitroso group. This group is always on the opposite site of the carbonyl group in this ring. In the first molecule, the nitroso group is on the one side of the five-membered heterocyclic ring (molecule) and in the second molecule it is on the other side of the ring (molecule). The position of the carbonyl group is changing respectively. Different positions of nitroso and carbonyl groups are confirmed by of the N=O and C=O bond lengths. The crystal structure of the complex **Ru-6** contains only one molecule of catalyst and one solvent molecule (DCM) in the asymmetric unit. Based on these two X-ray structures, one should note that while in the complex **Ru-4,** the pyridine ligand occupies the *cis* position relative to the NHC ligand, in **Ru-6** the PPh_3 ligand occupies the *trans* position. However, both of conformations show the X-Ru-N angle (X=N3 for **Ru-4** and Cl1 for **Ru-6**) close to 180 degrees. Introduction of the pyridine ligand also changes the conformation of the phenyl ring in the NHC ligand that rotates out of the ruthenium centre. Solution of crystal structure of complex **Ru-4** has revealed that there are two types of assignment of the nitrogen atom position in the cyclic η1-acyl group (as a consequence, two different molecules are observed in the asymmetric unit). Nevertheless, in both structures the N-O and C-O bonds are distinguishable. The length of the N-O bond is: 1.249(7)Å (molecule 1) and 1.267(7)Å (molecule 2) for the complex **Ru-4** and 1.255(3)Å for **Ru-6**. The length of the C-O bond is: 1.209(9)Å in the molecule 1 and 1.226(8)Å in the second molecule of the complex **Ru-4** and 1.219(3)Å in the complex **Ru-6**.

It is worth to mention that the Cambridge Structural Database does not contain similar compounds as these studied in this work. The ruthenium atom connected directly with the nitroso and carbonyl group is a unique molecular fragment (synthon).

All the relevant experimental details concerning the X-ray data collection for the complexes **Ru-4**, **Ru-5** and **Ru-6** as well as selected geometrical parameters are presented in the ESI (see Tables S1, S2, S3 and S4). CCDC 1584777-1584779 entries contain the supplementary crystallographic data (CIF files) for this paper.

Catalytic Performance Tests

As expected, due to the lack of benzylidene ligand, the newly obtained complexes **Ru-4** and **Ru-6** were found to be inactive in model olefin metathesis reactions such as RCM of diethyl 2,2-diallylmalonate and N,N-diallyl-4-methylbenzenesulfonamide, or CM between allyl benzene and 1,4-diacetoxy but-2-ene. Therefore, it was decided to explore other non-metathetical activities of compounds **Ru-4** and **Ru-6**, because such unusual compounds obtained "by accident" often exhibited intriguing reactivity, inaccessible to standard catalysts. A good example of such situation was the discovery of the decomposition of the ruthenium-based complexes in the environment of primary alcohols [21-24], Mol [21], and Fogg [22] investigated the mechanistic aspect of the influence of alcohols on the decomposition of Hoveyda-Grubbs type olefin metathesis catalysts. In other studies Fogg discovered also that Grubbs first generation catalyst in alcoholic solution in presence of Et_3N decompose to hydridocarbonyl complex **Ru-8** [23]. On the other hand, Nolan while working on decomposition of indenylidene metathesis catalysts in conditions similar to those used by Fogg and Mol obtained compound **Ru-9** [24-26]. Complexes **Ru-8** and **Ru-9** exhibited activity in many types of reactions including racemization of chiral alcohols [24] or transfer hydrogenation [27-40]. In this context it is also worth mentioning popular ruthenium-based transfer hydrogenation catalyst **Ru-7** (see Figure 6) reported by Shvo [41].

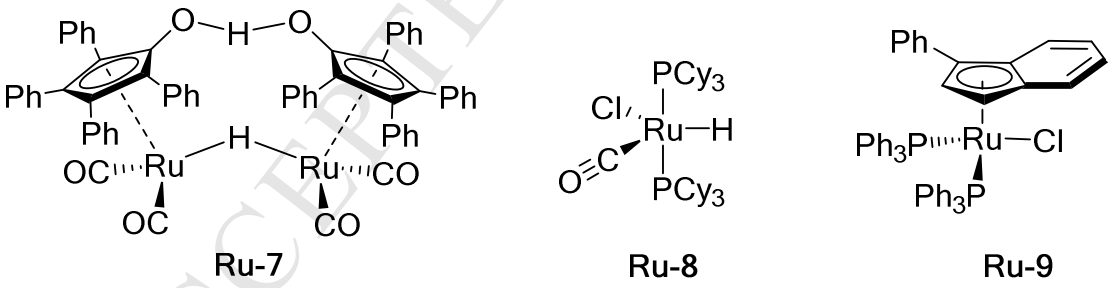
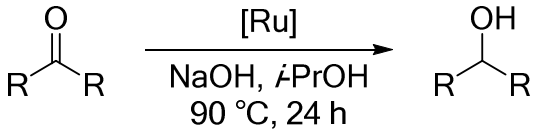


Figure 6. Selected transfer hydrogenation ruthenium-based catalysts.

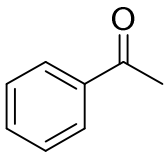
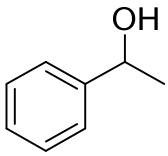
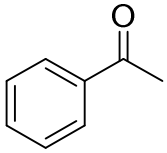
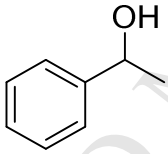
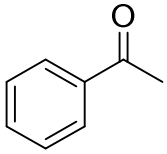
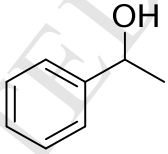
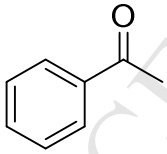
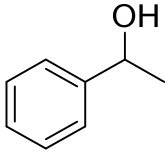
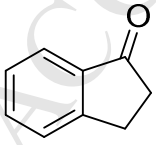
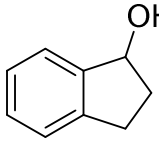
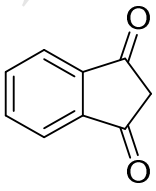
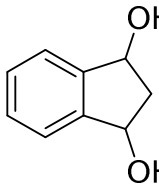
Initially, our attention was focused on the reaction of transfer hydrogenation to obtain secondary alcohols from ketones [25, 26]. The base, sodium hydroxide, has been chosen based on previous literature reports since the effect of such reactant on transfer hydrogenation is well known [42]. Solution of NaOH in isopropanol was added to given ketone and the reaction was

carried out at 90 °C in a sealed vial for 24 hours (Scheme 4). The conversion was determined by GC. Table 1 shows results of the reduction of different ketones.



Scheme 4. Transfer hydrogenations of ketones.

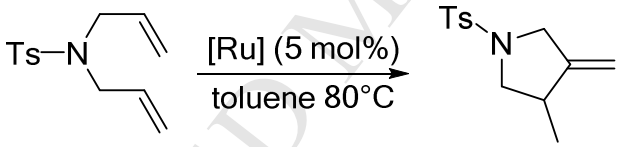
Table 1. Transfer hydrogenations of ketones.[a]

Entry	Substrate	Product	[Ru]	Conversion [%][b]
1			**Ru-6**	96
2			**Ru-4**	14
3			**Ru-6**	<5[c]
4			**Ru-6**	95[d]
5			**Ru-6**	96
6			**Ru-6**	96

[a] Reaction conditions: 0.5 mol% of [Ru], 2.5 mol% of NaOH, isopropanol, 90 °C in a sealed vial 24 h. [b] Conversion was determined by GC using durene as an internal standard. [c] Reaction carried out without NaOH. [d] 0.25 mol% of **Ru-6** was used.

Entries 1-4 showed reduction of acetophenone under different conditions. When 0.5 mol% of Ru complex **Ru-6** and 2.5 mol% of NaOH was used 96% conversion was reached (Entry 1) and the same reaction conducted in the presence of 0.5 mol% of **Ru-4** with the other conditions unchanged gave only 14% yield (Entry 2). The absence of NaOH caused a drop of conversion to less than 5% (Entry 3), while decreasing of Ru loading to 0.25 mol% had no significant influence on the degree of conversion, 95% of the desired product was obtained (Entry 4). In entries 5 and 6 the reduction of 1-indanone and 1,3-indandione is presented. Also here, in both cases, almost quantitative conversion was observed in the presence of **Ru-6**.

The next attempt to evaluate the applications of nitroso complexes was cycloisomerization reaction. On the Scheme 5 an example of such a reaction, cycloisomerisation of *N*,*N*-diallyl-4-methylbenzenesulfonamide is presented. The transformation was performed in dry toluene at 80 °C for a given time (Table 2). Progress of reaction was monitored by GC.



Scheme 5. Cycloisomerization reaction N,N-diallyl-4-methylbenzenesulfonamide.[a]

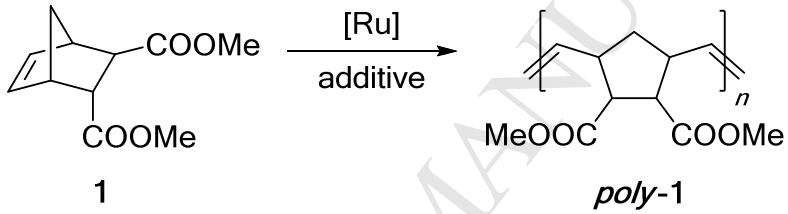
Table 2. Cycloisomerization reaction of N,N-diallyl-4-methylbenzenesulfonamide.[a]

Entry	[Ru]	Time [h]	Conversion [%][b]
1	**Ru-4**	24	76
2	**Ru-4**	48	84
3	**Ru-4**	72	90
4	**Ru-6**	24	27
5	**Ru-6**	48	28
6	**Ru-6**	72	30

[a] Reaction conditions: 5 mol% of [Ru], toluene 80 °C. [b] Conversion was determined by GC using durene as an internal standard.

In this case the reaction performed in the presence of ruthenium complex **Ru-4** containing pyridine as a ligand gave better result. In cycloisomerization reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide catalysed by **Ru-4** the slow increase of conversion (from 76% to 90%) during 72 h was observed. When **Ru-6** was applied after 24 hours the reaction reached *plateau* around 30% and an increase of the reaction time by a further two days did not result in almost any improvement in the conversion.

Next the investigation of activity of complexes **Ru-4** and **Ru-6** in ring opening metathesis polymerization (ROMP) was performed. As a model substrate endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**) was chosen (Scheme 6). We selected this reaction for benchmarking a novel initiator system [43-48]. Conversion of this transformation was determined by ^{1}H NMR spectroscopy.



Scheme 6. ROMP of endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**).

At the beginning polymerization was carried out in refluxing DCM without using any additives (Table 3, Entry 1-2) and neither of the two complexes (**Ru-4** and **Ru-6**) transformed **1** into the desired ***poly*-1** product. However, when under the same conditions (trimethylsilyl)diazomethane was added (1 equiv. related to ruthenium complex) ^{1}H NMR analysis showed conversion 38% and 47% for complexes **Ru-4** and **Ru-6** respectively (Entry 3-4). In entry 5 the solvent was changed from dichloromethane to toluene and the temperature of reaction was raised to 80°C and as a result almost full conversion was obtained.

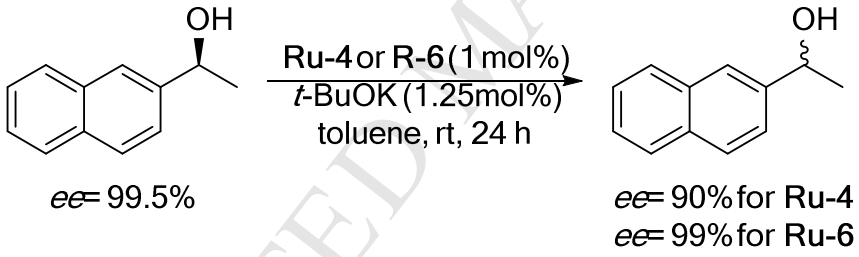
Table 3. ROMP of endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**).[a]

Entry	[Ru]	Additive	Conditions	Conv. (%)[b]
1	**Ru-4**	-	DCM, 40°C	0
2	**Ru-6**	-	DCM, 40°C	0
3	**Ru-4**	TMS-CHN_2	DCM, 40°C	38
4	**Ru-6**	TMS-CHN_2	DCM, 40°C	47
5	**Ru-4**	TMS-CHN_2	Toluene, 80°C	>98

[a] Reaction conditions: [Ru]/**1** = 1:300; Reaction time = 24 h; [Ru]/Additive = 1:1. [b] Conversion was determined by ^{1}H NMR.

As stated above, the reactions of endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**1**) catalysed by **Ru-4** and **Ru-6** in the presence of (trimethylsilyl)diazomethane were carried out in NMR tube. A detailed analysis of the spectrum should enable active species to be identified, if such would appear during the reaction. However in ^{1}H NMR spectra in region 22-14 ppm, no characteristic signal from alkylidene proton were observed.

In the last stage of research, inspired by Nolan's works [24]. we decided to check whether **Ru-4** and **Ru-6** complexes could be utilized for racemisation of chiral alcohols. For this purpose, we stirred an optically pure (99.5% ee) substrate (S)-1-(naphthalen-2-yl)ethan-1-ol in the presence of one of above mentioned catalysts and potassium tert-butanolate in toluene. After 24 hours the optical purity of alcohol was examined using HPLC (Chiralcel® OJ; HEX:IPA 95:5; 1 mL/min; 254 nm).



Scheme 7. Racemisation of (*S*)-1-(naphthalen-2-yl)ethan-1-ol.

When racemization was carried out in the presence of **Ru-4**, only a slight decrease in optical purity of 1-(naphthalen-2-yl)ethane-1-ol was observed (it dropped down from 99.5 to 90%). In the same process conducted in the presence of **Ru-6** no racemisation was observed and the optical purity of alcohol remained at the same high level, 99%.

Conclusions

During the reaction between third generation indenylidene catalyst M31 and 2-nitrostyrene, a new nitroso-chelated cyclic η1-acylruthenium(II) complexes **Ru-4** and **Ru-6** were unexpectedly obtained. Their structures were confirmed by spectroscopic techniques as well as, after transformation into a derivative containing triphenylphosphine ligand, by X-Ray crystallography.

Due to the lack of benzylidene ligand the new complexes did not show any activity in standard metathesis reactions, however in the presence of (trimethylsilyl)diazomethane they led to good results in ROMP of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester **1**. Despite both of studied complexes were not active in a base-promoted racemisation of chiral alcohols [24], complex **Ru-4** exhibited high activity in cycloisomerization of *N*,*N*-diallyl-4-methylbenzenesulfonamide, while complex **Ru-6** provided good results in transfer hydrogenation reactions leading to secondary alcohols.

Experimental section

General conditions. The catalyst preparation was carried out under argon in pre-dried glassware using Schlenk techniques or in a glove box. The anhydrous DCM was dried by distillation over CaH_2 and was transferred under argon. For polymerization toluene without styrene stabilizer from Sigma Aldrich (Chromasolv for HPLC, 99.9%) was used. Column chromatography was performed using Sigma Aldrich silica gel 60 (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated plates (0.25 mm thickness) with a fluorescent indicator. NMR spectra were recorded on Varian; Mercury 400 MHz, in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants are (*J*) in Hz. MS (ESI) spectra were recorded by Quattro LC (triple quadrupole mass spectrometer). GC measurements were done on PE Clarus 580 with InertCap 5MS-Sil column and GC/MS on PE Clarus 680/600S with InertCap 5 column. All other commercially available chemicals were used as received.

Synthesis of Compound Ru-4.

To 748.0 mg (1 mmol) of [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(pyridyl) ruthenium(II) (**M31**) in toluene (13 mL) 2-nitrostyrene (298.0 mg, 2 mmol) in toluene (2 mL) was added at 80°C. After 5 min the mixture was cooled to room temperature and solvent was evaporated. Residue was purified by silica gel column chromatography (eluent: ethyl acetate/cyclohexane 10% v/v → ethyl acetate). Violet fraction was collected. After evaporation residue was recrystallized twice from CH_2Cl_2/*n*-hexane to give 310.0 mg of dark violet crystalline solid (48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47–8.37 (m, 1H), 8.07 (s, 1H), 7.60–7.38 (m, 2H), 7.25–7.12 (m, 1H), 7.07–6.95 (m, 3H), 6.85–6.75 (m, 3H), 6.60–6.42 (m, 1H), 6.17 (s, 1H), 4.00–3.75 (m, 4H), 2.50–2.05 (m, 15H), 1.76 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ: 238.0, 209.1, 171.4, 153.1, 149.6, 148.3, 138.0, 135.9, 135.8, 135.6, 135.2, 130.2, 129.6, 129.0, 128.2, 122.8, 118.6, 107.8, 53.4, 51.8, 31.4, 22.5, 20.7, 18.3, 17.5, 14.0 ppm.

IR: ν = 3495, 2913, 1617, 1605, 1483, 1445, 1354, 1263, 898, 850, 756, 690, 575, 521 cm^{-1}.

HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{35}N_4O_2Ru$: [M-Cl^-] 621.1804, found 621.1797.

Synthesis of compound Ru-6.

Method A: To a solution of complex **Ru-4** (87.8 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) triphenylphosphine (68.2 mg, 0.26 mmol) was added. The mixture was stirred at room temperature for 30 min and then evaporated. Residue was purified by silica gel column chromatography (eluent: ethyl acetate/cyclohexane 3:7 v/v). Violet fraction was collected and evaporated. Residue was recrystallized twice from CH_2Cl_2/*n*-hexane to give 40 mg of violet crystalline solid (35%).

Method B: To a solution of 93.2 mg (0.1 mmol) [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(triphenylphosphine)ruthenium(II) (**M20**) in toluene (1 mL) 2-nitrostyrene (29.8 mg, 0.2 mmol) in toluene (1 mL) was added at 80°C. The mixture was stirred for 45 min and then cooled to room temperature and evaporated. Residue was purified by silica gel column chromatography (eluent: ethyl acetate/cyclohexane 1:9 → 3:7 v/v). Violet fraction was collected and evaporated. Residue was recrystallized twice from CH_2Cl_2/*n*-hexane to give 25 mg of violet crystalline solid (30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15–7.09 (m, 3H), 7.06–6.97 (m, 14H), 6.94–6.91 (m, 1H), 6.89–6.85 (m, 2H), 6.75–6.70 (m, 1H), 6.50–6.33 (m, 2H), 3.95–3.80 (m, 4H), 2.46 (s, 6H), 2.30–1.90 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ: 234.0, 233.9, 207.0, 205.8, 170.8, 144.5, 137.6, 135.2, 134.1, 134.0, 130.4, 130.3, 130.0, 129.3, 129.2, 128.0, 127.6, 127.5, 118.9, 109.8, 51.8, 21.0, 18.8 ppm.

^{31}P NMR (160 MHz, $CDCl_3$) δ: 21.4 ppm.

IR: ν = 3053, 2913, 1623, 1479, 1433, 1349, 1266, 1137, 1091, 1027, 997, 898, 849, 756, 695, 650, 512 cm^{-1}.

HRMS (ESI): *m*/*z* calcd. for $C_{46}H_{45}N_3O_2PRu$: [M-Cl^-] 804.2293, found 804.2289.

X-ray Analysis

The single crystal diffraction data collection for complex **Ru-4** and complex **Ru-6** was performed on a single crystal Oxford Diffraction diffractometers with graphite-monochromated MoKα radiation. The diffractometers were equipped with an Oxford Cryosystems nitrogen gas-flow apparatus and measurements were conducted at 100K. In the case of the complex **Ru-5**, data collection was performed on a SuperNova diffractometer with mirror-monochromated CuKα radiation. For all measurements multi-scan absorption correction was applied. The CrysAlis PRO program was used for the data collection and its further reduction [49]. The structures were solved by direct methods and refined using SHELXL [50] program in cooperation with the Olex2 program [51]. The refinements were based on F^2. Some geometric and ADP restrains were required during refinement of the complex **Ru-4**.

The lattice parameters and the final *R*-indices obtained for the refinement of the structures of complexes **Ru-4**, **Ru-5** and **Ru-6** are presented in Table S1. Selected geometrical parameters for these structures are shown in Table S2, Table S3 and Table S4, respectively.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones.

In a glovebox to 4 mL vial appropriate ketone (0.5 mmol) and durene as an internal standard (0.5 mmol) was added followed by *i*-PrOH (1.75 mL). Next the respective catalyst (0.25–0.5 mmol) was added as a solid followed by NaOH (0.0125 mmol) in 0.25 mL *i*-PrOH. Mixture was stirred at 90°C for 24 h. Conversion was determined by GC.

Procedure for the Cycloisomerization.

In a glovebox to 4 mL vial N,N-diallyl-4-methylbenzenesulfonamide (0.1 mmol) and durene as an internal standard (0.1 mmol) was added followed by toluene (3 mL). Next the respective catalyst (0.05 mmol) was added as a solid. Mixture was stirred at 80–90°C, and the samples in different time intervals were taken. Conversion was determined by GC.

Typical Procedure for the ROMP of endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester 1.

To the respective catalyst (0.00159 mmol) dissolved in a proper solvent (2 mL) was added a solution of (trimethylsilyl)diazomethane (0.5 M in toluene, 3 μL, 0.00159 mmol). The mixture was transferred to the monomer **1** (0.476 mmol) dissolved in proper solvent (2 mL). Reaction was carried out for 24 h. The reaction was quenched by the addition of an excess of ethyl vinyl ether. Conversion was determined by ^{1}H NMR.

Typical Procedure for Racemisation of (*S*)-1-(Naphthalen-2-yl)ethan-1-ol.

To the respective catalyst (0.005 mmol) potassium *tert*-butoxide (0.00625 mmol, 0.25 mL, 0.025M solution in toluene) was added followed by solution of (*S*)-1-(Naphthalen-2-yl)ethan-1-ol (86 mg, 0.5 mmol) in toluene (0.75 mL). The reaction was carried out at room temperature for 24 h and then was quenched by the addition of an excess of ethyl vinyl ether. Racemisation was determined by HPLC (ChiralCel®, hexane:isopropanol 95:5, 1.0 mL/min, 254 nm).

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Supplementary data

The supporting information associated with this article can be found at

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References

[1] C. Wang, C. Li, X. Wu, A. Pettman, J. Xiao, Angew. Chem. Int. Ed., 48 (2009) 6524-6528.
[2] F. Alonso, P. Riente, M. Yus, Acc. Chem. Res., 44 (2011) 379-391.
[3] R.H. Grubbs, A.G. Wenzel, D.J. O'Leary, E. Khosravi, Handbook of Metathesis, Wiley-VCH, Weinheim, 2014.
[4] K. Grela Olefin Metathesis: Theory and Practice, John Wiley & Sons, Inc., Hoboken, 2014.
[5] https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/.
[6] R. Gawin, A. Kozakiewicz, P.A. Guńka, P. Dąbrowski, K. Skowerski, Angew. Chem. Int. Ed., 56 (2017) 981-986.
[7] D.R. Anderson, T. Ung, G. Mkrtumyan, G. Bertrand, R.H. Grubbs, Y. Schrodi, Organometallics, 27 (2008) 563-566.
[8] P. Małecki, K. Gajda, O. Ablialimov, M. Malińska, R. Gajda, K. Woźniak, A. Kajetanowicz, K. Grela, Organometallics, 36 (2017) 2153-2166.
[9] M. Rouen, P. Queval, E. Borré, L. Falivene, A. Poater, M. Berthod, F. Hugues, L. Cavallo, O. Baslé, H. Olivier-Bourbigou, M. Mauduit, ACS Catal., 6 (2016) 7970-7976.
[10] T.T. Nguyen, M.J. Koh, X. Shen, F. Romiti, R.R. Schrock, A.H. Hoveyda, Science, 352 (2016) 569-575.
[11] X. Shen, T.T. Nguyen, M.J. Koh, D. Xu, A.W.H. Speed, R.R. Schrock, A.H. Hoveyda, Nature, 541 (2017) 380-385.
[12] G. Occhipinti, F.R. Hansen, K.W. Törnroos, V.R. Jensen, J. Am. Chem. Soc., 135 (2013) 3331-3334.
[13] S.M. Bronner, M.B. Herbert, P.R. Patel, V.M. Marx, R.H. Grubbs, Chem. Sci., 5 (2014) 4091-4098.
[14] A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, J. Am. Chem. Soc., 126 (2004) 9318-9325.
[15] K. Grela, S. Harutyunyan, A. Michrowska, Angew. Chem. Int. Ed., 41 (2002) 4038-4040.
[16] O.M. Demchuk, K.M. Pietrusiewicz, A. Michrowska, K. Grela, Org. Lett., 5 (2003) 3217-3220.
[17] A. Michrowska, M. Bieniek, M. Kim, R. Klajn, K. Grela, Tetrahedron, 59 (2003) 4525-4531.
[18] A.K. Chatterjee, T.-L. Choi, D.P. Sanders, R.H. Grubbs, J. Am. Chem. Soc., 125 (2003) 11360-11370.
[19] A. Jana, K. Grela, Org. Lett., 19 (2017) 520-523.
[20] T.K. Olszewski, M. Bieniek, K. Skowerski, K. Grela, Synlett, 24 (2013) 903-919.
[21] Maarten B. Dinger, Johannes C. Mol, Eur. J. Inorg. Chem., 2003 (2003) 2827-2833.
[22] N.J. Beach, J.A.M. Lummiss, J.M. Bates, D.E. Fogg, Organometallics, 31 (2012) 2349-2356.
[23] N.J. Beach, K.D. Camm, D.E. Fogg, Organometallics, 29 (2010) 5450-5455.
[24] S. Manzini, C.A. Urbina-Blanco, A. Poater, A.M.Z. Slawin, L. Cavallo, S.P. Nolan, Angew. Chem. Int. Ed., 51 (2012) 1042-1045.
[25] S. Manzini, D.J. Nelson, T. Lebl, A. Poater, L. Cavallo, A.M.Z. Slawin, S.P. Nolan, Chem. Commun., 50 (2014) 2205-2207.
[26] S. Manzini, C.A.U. Blanco, S.P. Nolan, Adv. Synth. Catal., 354 (2012) 3036-3044.
[27] M.-O. Simon, C.-J. Li, Chem. Soc. Rev., 41 (2012) 1415-1427.
[28] R. Malacea, R. Poli, E. Manoury, Coord. Chem. Rev., 254 (2010) 729-752.
[29] M. Bartók, Chem. Rev., 110 (2010) 1663-1705.
[30] R.H. Morris, Chem. Soc. Rev., 38 (2009) 2282-2291.
[31] C. Wang, X. Wu, J. Xiao, Broader, Chem. Asian J., 3 (2008) 1750-1770.

[32] T. Ikariya, A.J. Blacker, Acc. Chem. Res., 40 (2007) 1300-1308.
[33] X. Wu, J. Xiao, Chem. Commun., (2007) 2449-2466.
[34] C.M. Moore, N.K. Szymczak, Chem. Commun., 49 (2013) 400-402.
[35] J. Li, Y. Tang, Q. Wang, X. Li, L. Cun, X. Zhang, J. Zhu, L. Li, J. Deng, J. Am. Chem. Soc., 134 (2012) 18522-18525.
[36] I. Sorribes, G. Wienhöfer, C. Vicent, K. Junge, R. Llusar, M. Beller, Angew. Chem. Int. Ed., 51 (2012) 7794-7798.
[37] M.A. Ariger, E.M. Carreira, Org. Lett., 14 (2012) 4522-4524.
[38] K.M. Steward, E.C. Gentry, J.S. Johnson, J. Am. Chem. Soc., 134 (2012) 7329-7332.
[39] H. Vázquez-Villa, S. Reber, M.A. Ariger, E.M. Carreira, Angew. Chem. Int. Ed., 50 (2011) 8979-8981.
[40] L.T. Ghoochany, S. Farsadpour, Y. Sun, W.R. Thiel, Eur. J. Inorg. Chem., 2011 (2011) 3431-3437.
[41] Y. Shvo, D. Czarkie, Y. Rahamim, D.F. Chodosh, J. Am. Chem. Soc., 108 (1986) 7400-7402.
[42] S.U. Sonavane, R.V. Jayaram, Synth. Commun., 33 (2003) 843-849.
[43] X. Gstrein, D. Burtscher, A. Szadkowska, M. Barbasiewicz, F. Stelzer, K. Grela, C. Slugovc, J. Polym. Sci. A, 45 (2007) 3494-3500.
[44] J. Broggi, C.A. Urbina-Blanco, H. Clavier, A. Leitgeb, C. Slugovc, A.M.Z. Slawin, S.P. Nolan, Chem. Eur. J., 16 (2010) 9215-9225.
[45] C.A. Urbina-Blanco, A. Leitgeb, C. Slugovc, X. Bantreil, H. Clavier, A.M.Z. Slawin, S.P. Nolan, Chem. Eur. J., 17 (2011) 5045-5053.
[46] A. Leitgeb, A. Szadkowska, M. Michalak, M. Barbasiewicz, K. Grela, C. Slugovc, J. Polym. Sci. A, 49 (2011) 3448-3454.
[47] C.A. Urbina-Blanco, X. Bantreil, J. Wappel, T.E. Schmid, A.M.Z. Slawin, C. Slugovc, C.S.J. Cazin, Organometallics, 32 (2013) 6240-6247.
[48] A. Kozłowska, M. Dranka, J. Zachara, E. Pump, C. Slugovc, K. Skowerski, K. Grela, Chem. Eur. J., 20 (2014) 14120-14125.
[49] C.S.s. Xcalibur/SuperNova CCD system, Version 1.171.36.32; Agilent Technologies UK Ltd.: Oxford, UK,. in, 2012.
[50] G. Sheldrick, Acta Crystallogr. A, 71 (2015) 3-8.
[51] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr., 42 (2009) 339-341.

Highlights:

- Nitroso- chelated acylruthenium complexes were prepared and fully characterized
- The unique structure of the complexes has been confirmed by X-ray structural analysis
- Ru-complex exhibit good activity in transfer hydrogenations of aromatic ketones
- Nitroso- chelated acylruthenium complexes catalyze ring opening metathesis polymerization in the presence of (trimethylsilyl)diazomethane