



Synthesis and Application of Robust Spiro [Fluorene-9] CAAC Ruthenium Alkylidene Complexes for the “One-Pot” Conversion of Allyl Acetate to Butane-1,4-diol

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A series of a novel CAAC ligands featuring a spiro-fluorene group have been synthesized and complexed with ruthenium alkylidenes, yielding the corresponding Hoveyda-type derivatives as a new family of olefin metathesis catalysts. The novel complexes have been characterized by XRD, HRMS and NMR measurements. The synthesised complexes were tested in catalysis and showed good activity in olefin metathesis, as demonstrated on diethyl diallylmalonate and allyl acetate

substrates. The unique backbone in the ligand with the large, yet inflexible condensed system renders interesting properties to the catalyst, exemplified by the good catalytic performance and improved Z-selectivity. In addition, the complex can also serve as a hydrogenation catalyst in a consecutive (one-pot) reaction. The latter reaction can convert allyl acetate to butane-1,4-diol, a valuable chemical intermediate for biodegradable polybutylene succinate (PBS).

Introduction

The effect of structural design of transition metal carbene ligands on the catalytic activity of organometallic complexes has been intensively studied in the past decades.^[1] The common *N*-heterocyclic carbene (NHC) ligand group can be modified in several ways, while the variability of more nucleophilic cyclic (alkyl)(amino) carbene (CAAC)^[2–5] and related ligands (six-membered CAAC,^[6] CAArC,^[7,8] BICAAC^[9]) remained challenging. The fine-tuning of CAACs can be done by two different synthetic strategies: (1) the *N*-substituent can be easily

varied using different primary amines at the beginning of the synthesis, (2) the variability of the aldehyde-derived alkyl part near the carbene, which depends on the availability of aldehyde synthetic equivalents. The first representatives of the CAACs were predominantly tuned by their (amine-derived) *N*-substituent, showing significant influence on the coordinated transition metal's catalytic activity.^[10–12] Regarding the aldehyde part of the CAACs, the alpha carbon atom next to the carbene center can have various alkyl, aryl and spiro-cycloalkyl derivatives. Popular choices for such aldehydes are isobutyraldehyde, 2-phenylpropionaldehyde, or derivatives of cycloalkyl ketones, menthone and indanone. Interesting representatives incorporating an ibuprofen intermediate^[13] and a cholesterol moiety were also reported quite recently.^[14] Functional groups can be introduced by alpha-functionalization of the aldehyde or ring closure followed by alkylation of a cyclic enamine.^[15,16] The latter method was used for the synthesis of (CH₂)₃-linked bisCAAC ligands and the corresponding monometallic complexes.^[17]

Amongst numerous different applications,^[18–20] CAAC ligands became a crucial part of the ruthenium alkylidene complex-catalyzed olefin metathesis reactions.^[21] These CAAC–Ru catalysts showed superior performance in several metathesis reactions including ethenolysis involving highly sensitive ruthenium-methylidene intermediates in the catalytic cycle.^[10,22,23] Later, ruthenium complexes containing CAAC ligand derived from indanone showed exceptional efficiency, resulting in more than one million turnover numbers (TON).^[24] Consequently, it can be assumed that CAAC ligands play a major role in the stabilization of ruthenium intermediates in the catalytic cycle.^[25–27] From the perspective of green chemistry, high catalyst performance is of paramount importance, as high catalyst performance at low loading and under mild reaction conditions are key elements for sustainable industrial applications.^[25–27]

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Two phenyl ring-containing CAAC (i.e. $\text{Ph}_2\text{C}-\text{C}_{\text{carbene}}$) have been published a few years ago^[12,28] and recently by our research group.^[29] It has been demonstrated that changing the substituents on the CAAC ring from methyl ($\text{Me}_2\text{C}-\text{C}_{\text{carbene}}$) to phenyl groups ($\text{Ph}_2\text{C}-\text{C}_{\text{carbene}}$) significantly improved the catalytic olefin metathesis activity.^[27] Fluorene-containing CAAC systems are not known yet. On the other hand, NHCs, representatives such as *N*-substituted, carbene-half sandwich-like bidentate complexes are known (Scheme 1).^[30–35]

In this project, we focused on the self-metathesis of allyl acetate to 2-butene-1,4-diol diacetate.^[37] Nowadays, allyl acetate is mainly used as a precursor of allyl alcohol and its related derivatives.^[38] The 2-butene-1,4-diol diacetate can be considered as a precursor of butane-1,4-diol (**13**). **13** is the raw material of a wide range of commercial chemicals including tetrahydrofuran (THF), γ -butyrolactone (GBL) and polyurethane foams,^[39] as well as biodegradable polymers such as polybutylene succinate (PBS).^[40,41] Recently, our group has developed a ruthenium-catalyzed tandem isomerization metathesis reaction (ISOMET),^[42] which is able to convert the pyrolysis oils of polyethylene (PE) to propylene. This process models the value-added reuse of PE waste to generate a versatile chemical intermediate, propylene.^[43,44] Upon oxidative esterification with acetic acid, the propylene could be easily converted to allyl acetate. In addition to all this, the catalytic conversion of allyl acetate into 1,4-butanediol enables the synthesis of the environmentally benign polymers such as PBS from persistent plastics such as polyethylene.^[45]

Results and Discussion

Synthesis of Ligands and Complexes

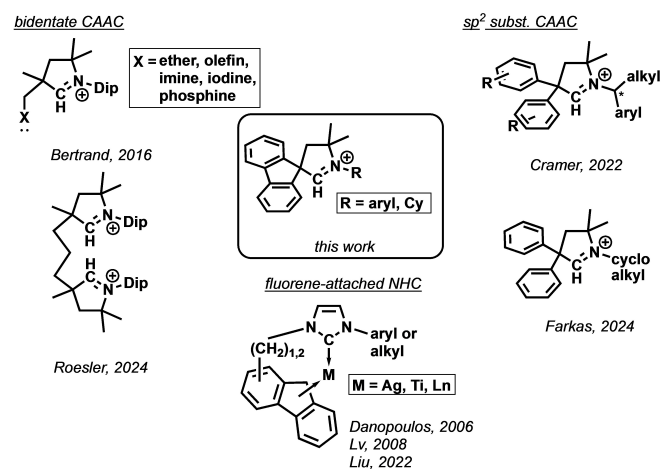
The key intermediate for the synthesis is the 9*H*-fluorene-9-carbaldehyde (**2**) was synthesized from fluorene (**1**) by deprotonation with potassium *tert*-butoxide, followed by reaction with methyl formate (**i**).^[46] The subsequent synthesis steps are based

on literature procedures: the aldehyde forms an imine with a bulky amine (cycloalkyl or 2,6-dialkyl substituted aniline, **ii**). Notably, the enamine is the preferred tautomeric form of the compounds **3a–d**. The enamines were deprotonated by *in situ* generated lithium diisopropylamide (LDA), then they were alkylated by 3-chloro-2-methylprop-1-ene (**iii**), followed by an intramolecular hydroiminium reaction, upon heating the hydrochloric acid protonated alkylated imine in dry dioxane and toluene solvent (**iv**). The iminium precursors of the new CAAC ligands could be obtained in reasonable yields (**5a–c**, 52–78%), except the *N*-cyclohexyl compound (**5d**), which was synthesized in low yield (7%).

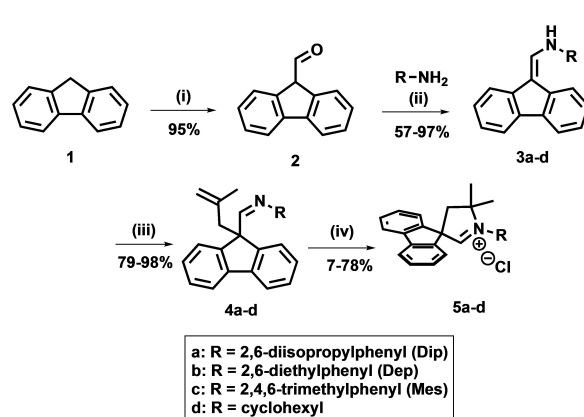
The formed chlorides appeared as white or bright powders after purification (ether washing or recrystallization), and no anion exchange was performed due to the water sensitivity of the ligand. Furthermore, the chloride anion did not interfere with the performed complexation reactions (Scheme 2; for additional synthetic details, see SI).

The Electrospray Ionization Mass Spectra (ESI-MS) of **5a–d** showed the presence of ions formed by elimination of chloride ion from the neutral compounds to form positively charged $[\text{M}-\text{Cl}]^+$ ions. Both the isotopic pattern and the accurate masses determined agree well with those calculated for the corresponding elementary compositions. The differences between the measured and the calculated *m/z* values for the mono-isotopic peaks are within 1 ppm accuracy. For example, $[\text{5a}-\text{Cl}]^+$ ions, corresponding to the composition of $\text{C}_{30}\text{H}_{34}\text{N}^+$, appeared at *m/z* 408.2686, for which a value of *m/z* 408.2687 has been calculated. (Further information for the mass spectra and *m/z* values, see SI.)

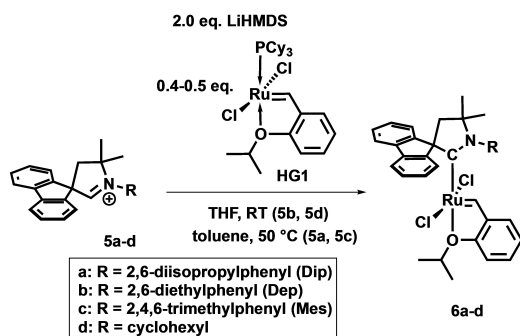
The ruthenium-alkylidene complexes of the novel CAAC ligands were prepared similarly according to reported procedures. The cyclic iminium precursors (**5a–d**) were deprotonated by LiHMDS in dry THF or toluene, then the solution of the formed free carbene was added to the solution of the commercially available Hoveyda-Grubbs 1st generation complex (**HG1**, Scheme 3). The free carbenes were relatively unstable. For example, only undefined decomposition product formation was observed within one hour reaction time using **5b** precursor



Scheme 1. Some recent representative cyclic alkyl amino carbene (CAAC) precursor salts and fluorene-NHC complexes.



Scheme 2. Synthesis of CAAC ligand precursors (**5a–d**). Conditions: (i) THF, room temperature, *t*BuOK and methyl formate; (ii) 1 eq. amine, dry toluene, molecular sieves (3 Å), 50–110 °C, (iii) 1.2 eq. LDA, THF, 0 °C, 1.1 Equation (3)-chloro-2-but-1-ene, (iv) 3 eq. HCl in dry dioxane (3 M), toluene, 110 °C.

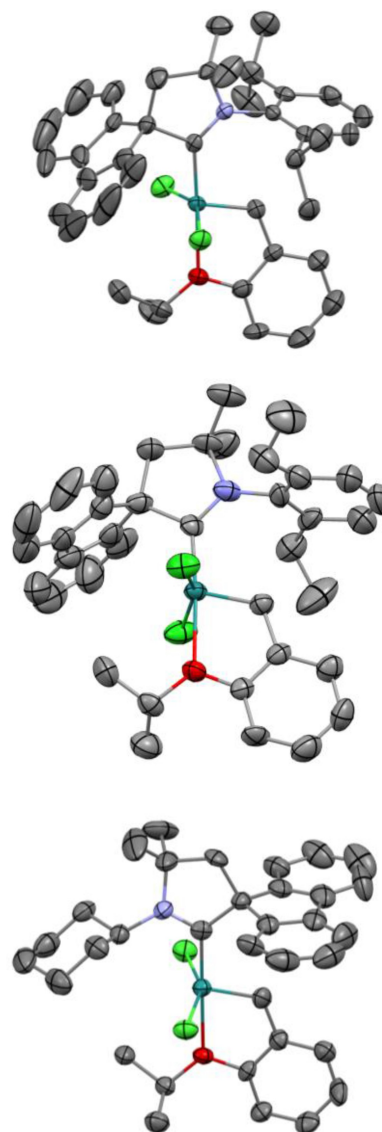
Scheme 3. Synthesis of the complexes **6a-d**.

salt. Free carbene was not detectable in the reaction mixture. Similarly to other CAAC Ru-alkylidene species, the novel complexes are relatively stable on air, can be purified by column chromatography on alumina, and can be stored as stock solution in glovebox for several days.

In line with our expectation, the ESI-MS spectra of **6a-d** revealed the formation of $[M-Cl]^+$ ions by elimination of Cl^- ion from the complexes similarly to those observed in the case of ligands **5a-d**. Both the observed isotopic pattern and the m/z values with lower than 1 ppm accuracy support also the corresponding elementary compositions of complexes **6a-d**. For example, the $[6c-Cl]^+$ ions (the composition is $C_{37}H_{39}NORu^+$) occurred at m/z 650.1766 and the calculated m/z values for this composition is 650.1765. (Further information for the mass spectra and m/z values, see SI).

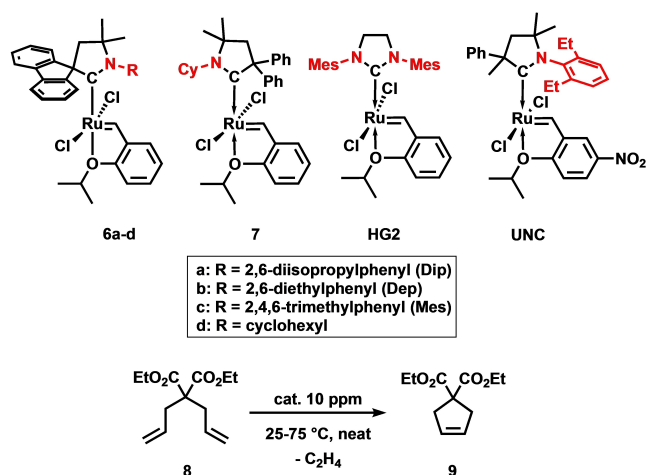
Single crystals of complexes **6a**, **6b** and **6d** could be obtained by the slow evaporation of dichloromethane solutions or cooling the toluene solution to $-20^\circ C$ for several days. The observed carbene(CAAC)-Ru bond lengths: 1.941(6) Å for **6a**, 1.921(9) Å for **6b** and 1.924(15) Å for **6d** and C(spiro)-C(carbene)-N angles: 106.5° for **6a**, 107.5° for **6b** and 109.2° for **6d** are similar to the previously known complexes, e.g. to the **HG2** or non-spiro CAAC complexes. Further crystallographic data can be found in the deposited structures. Unlike in the case of other complexes, the orientation of the CAAC ligand in the **6d** complex is "inverted", i.e. the *N*-cyclohexyl substituent is situated at the opposite site of the alkylidene moiety (Figure 1).

An important aspect of the ruthenium alkylidene CAAC complexes is the rotation of the CAAC ligand over the Cl_2Ru -alkylidene plane.^[47-49] As indicated by the 1H and nOe NMR measurements, no dynamic behavior was observed in case of complexes **6a** and **6d** at room temperature, while the CAAC ligands of complexes **6b** and **6c** appear to rotate along the $Ru-C_{CAAC}$ bond at similar condition. This behavior is attributed to the bulky 2,6-diisopropylphenyl (Dip) substituent and the cyclohexyl group, which can be both hindered by the steric repulsion of the chloride ligands. In the solution state, the rigid **6a** complex exists in the classical rotamer configuration, with the *N*-aryl group positioned over the benzylidene proton. Conversely, the non-fluxional **6d** exhibits nOe correlations consistent with the "inverted" structure, where the *N*-alkyl group is located opposite to the benzylidene side. These observations are consistent with our previous experience.^[29]

Figure 1. ORTEP view of **6a** (top), **6b** (middle) and **6d** (bottom) at 30% probability level, hydrogen atoms are omitted for better visibility.

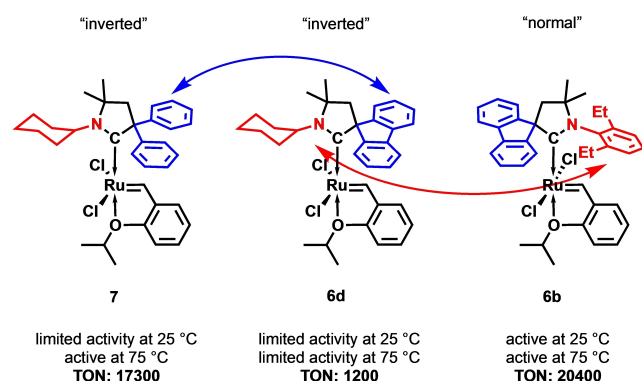
Catalytic Tests

The catalytic activity of the new complexes **6a-d** has been tested in the ring-closing metathesis (RCM) reaction of diethyl diallylmalonate (**8**) in solvent-free conditions. For comparison, known olefin metathesis catalysts (Hoveyda-Grubbs 2nd generation complex: **HG2**, UltraNitroCat: **UNC**, **7**, Scheme 4) were also tested. To achieve a comparable conversion, only 0.001 mol% (i.e. 10 ppm) catalyst load was applied. The new, spiro-fluorene CAAC complexes showed good catalytic activity, a comparable performance to the commercially available **HG2** and **UNC** complexes. The 2,6-diethylphenyl group containing complex (**6b**) presented the best activity at $25^\circ C$, slightly better than the **HG2** and **UNC** complexes, which showed approximately the same performance as the mesityl derivative (**6c**). The Dip complex (**6a**) was almost inactive at this temperature, while it became active at $75^\circ C$, showing some latent (temperature-



Scheme 4. Test reaction for the comparison of the different complexes: RCM of diethyl diallylmalonate.

activated) property – similarly to the Ph_2 complex **7**^[29] and previously published BICAAC complexes.^[43] Interestingly, the *N*-cyclohexyl derivative (**6d**) showed limited activity. Considering the structural similarity of **6d** and **7**, it was found that the connection of the phenyl ring to each other has a significant impact on the RCM catalytic performance. However, when the cyclohexyl group has been replaced by a Mes or Dep group, the



Scheme 5. Structural differences and their effect on the catalytic RCM activity of **8** of the examined complexes **7**, **6d** and **6b**. For conditions see Table 1.

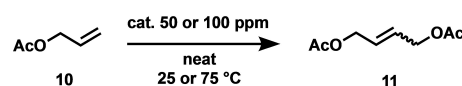
Table 1. Comparison of different Ru-alkylidene complexes in the RCM of **8**. Values refer to the TONs of **9**, based on ¹H NMR. No side reaction was observed.

Catalyst	25 °C, 3 h	25 °C, 24 h	75 °C, 3 h	75 °C, 24 h
6a	500	800	6000	6000
6b	15000	15000	20300	20400
6c	8600	9100	15200	16800
6d	200	200	1200	1200
7	2400	2400	13200	17300
HG2	8000	8000	20000	20000
UNC	13900	13900	14000	14600

geometry of the complex completely changed and the RCM catalytic activity was regained (Scheme 5, Table 1).

In another experiment series, the self-metathesis (SM) of allyl acetate (**10**) was tested with **6a–d**, **7**, **HG2** and **UNC** complexes (Schemes 4, 6 and Table 2). The observed catalytic activity of the novel complexes was found to be similar to **8**'s RCM reaction, the **6b** complex showed the best performance at room temperature. The longer reaction time only slightly improved the product yield, however, raising the reaction temperature to 75 °C significantly improved the catalytic activity. Catalyst **HG2** produced less SM products, while the **UNC** complex showed slightly better performance than **6b** at 75 °C or prolonged reaction time. Interestingly, the new fluorene-functionalized CAAC complexes render slightly higher *Z*-selectivity than the **HG2** or **UNC** complexes. Although these values are still far from the expected selectivity, it clearly indicates that the bulky fluorene ring or aromatic phenyl rings can play a decisive role in the *Z/E* selectivity.

The SM of **10** has been upscaled to 5 mL using 500 ppm catalyst **6b** at 75 °C reaction temperature in a Schlenk tube. The reaction time was 12 hours (¹H NMR yield of **11**: 85%). Then, the reaction mixture was placed under oil pump vacuum to remove the volatiles including the unreacted starting material. In the next step, the remaining mixture containing ruthenium was transferred to an autoclave pressurized to 50 bars of hydrogen. The mixture was heated to 100 °C in the presence of potassium *tert*-butoxide for 24 h giving butane-1,4-diol diacetate in 99% yield based on ¹H NMR (**12**). Following the complete hydrogenation of the reaction mixture, sodium hydroxide was added and then the target butane-1,4-diol (**13**) was isolated by distillation (overall yield 45%). To the best of our knowledge, such consecutive olefin metathesis/olefin hydrogenation process is rare. The hydrogenation activity of the ruthenium species generated from **6b** is not surprising, since the hydride



Scheme 6. Self-metathesis of allyl acetate catalyzed by the different complexes.

Table 2. Comparison of different Ru-alkylidene complexes in the self-metathesis (SM) of **10**. Values refer to the TONs of **11**, based on ¹H NMR. No side reaction was observed [a]: *Z/E* ratio values refer to reactions carried out at 75 °C with 50 ppm catalyst load and 24 h reaction time.

Catalyst	25 °C, 3 h, 100 ppm	25 °C, 24 h, 100 ppm	75 °C, 3 h, 50 ppm	<i>Z/E</i> ratio ^[a]
6a	200	720	1400	0.42
6b	2900	3500	11200	0.32
6c	1500	2300	1500	0.35
6d	0	600	200	0.35
7	0	0	5400	0.40
HG2	830	1180	3700	0.17
UNC	2800	4600	14900	0.29

formation affinity of the ruthenium-alkylidene complexes is well documented.^[50,51]

From atom economy point of view, it should be mentioned that the formed ethylene can be recycled to the ISOMET reaction, while the acetic acid can be reused in the oxidative esterification step of propylene (Scheme 7).

Conclusions

In this communication, a novel series of spiro-fluorene functionalized CAAC-ruthenium-alkylidene complexes are reported and tested in olefin metathesis reactions. The complexes showed good catalytic activity compared to the commercially available NHC-containing HG2 and CAAC-derived UNC complexes. Using the most active catalyst, **6b**, butane-1,4-diol was synthesized in reasonable yield via consecutive metathesis and hydrogenation reaction steps using **6b** catalyst. This process represents a green approach in which waste PE can be converted into a propylene platform molecule that serves as a starting material for the production of high-value butane-1,4-diol (**13**), a precursor to biodegradable polymers such as PBS.

Experimental Section

General Information

All metathesis reactions were conducted under inert (nitrogen or argon) atmosphere using Schlenk technique or under argon using a glovebox. The reagents and solvents (Aldrich) including deuterated solvents (Eurisotop) were used as received. Allyl acetate (Aldrich) was filtered through a short pad of activated alumina in the glovebox. 9H-fluorene-9-carbaldehyde was synthesized according to literature process (see SI). NMR experiments were carried out on a 500, 400 and 300 MHz Varian NMR System spectrometers equipped with inverse detection probes. ¹H and ¹³C assignment of ruthenium complexes was obtained using the combination of two-dimensional ¹H-¹H COSY, ¹H-¹H TOCSY, ¹H-¹H ROESY, ¹H-¹³C HSQC and ¹H-¹³C HMBC measurements. In case of complexes where the inefficient proton decoupling hampered the detection of the benzylidene carbons' ¹³C peaks, ¹H-¹³C HMBC extensions are presented for clarity. The mass spectrometric measurements were carried out by a MicroTOF-Q type Electrospray Ionization-Time of Flight (ESI-TOF) mass spectrometer (Bruker, Daltoniks, Bremen,

Germany) equipped with an electrospray ion-source (spray voltage: 4.0 kV, drying and nebulizer gas: 200 °C, 4 L/min and 0.5 bar, respectively). The mass spectra were recorded by means of a digitizer at a sampling rate of 2 GHz. The mass spectra were recorded and evaluated by the DataAnalysis 3.4 software from Bruker. The samples were dissolved in a mixture of dichloromethane and acetone (50/50 V/V) at a concentration of 0.01 mg/mL, and the solutions were injected into the ESI ion-source at a rate of 1 μL/min.

Deposition Numbers 2353760 for **6a**, 2353761 for **6b** and 2353762 for **6d** contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

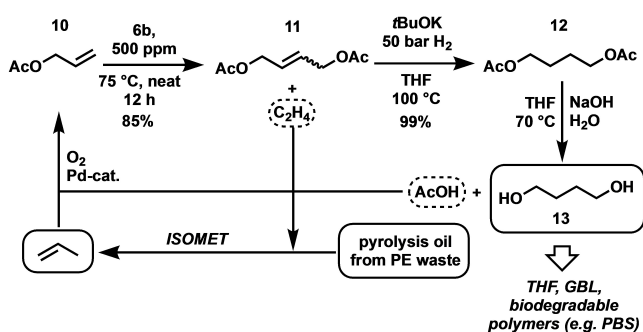
Representative example of enamine synthesis (3b). A Schlenk tube was charged with 3 Å molecular sieves (4 g), toluene (10 mL), **2** (9.19 mmol) and 2,6-diethylaniline (7.35 mmol). The mixture was heated for reflux overnight. Reaction was carried out without stirring. The molecular sieves were filtered out, washed with excess dichloromethane (DCM) and the solvent was evaporated. Product was used in the next step without further purification. Orange oil, yield: 68%.

Representative example of alkylation of enamines (4b). In a Schlenk tube, diisopropylamine (8.15 mmol, 1.2 eq.) was dissolved in dry THF (10 mL) and was cooled down to -78 °C. *n*-BuLi solution (2.5 M in hexane, 8.15 mmol, 1.2 eq.) was added dropwise. The mixture was allowed to reach room temperature. **3b** (6.79 mmol, 1.0 eq.) was dissolved in dry THF (5 mL) and the LDA solution was added dropwise at 0 °C. The ice bath was removed, and the solution was stirred for three hours at room temperature. After that the mixture was cooled down to 0 °C and 3-chloro-2-methyl-1-propene (7.47 mmol, 1.1 eq.) was added, followed by stirring overnight. Solvent was then evaporated, water and DCM was added to the crude reaction mixture and stirred for 10 minutes. Phases were separated and the aqueous layer was extracted with DCM two times, the combined organic phase was washed with water three times and dried on anhydrous sodium sulfate, filtered and evaporated to yield **4b** as an orange solid. Yield: 79%.

Representative example of cyclic iminium salt synthesis (5b). **4b** (6.06 mmol, 1 eq.) was dissolved in dry toluene (9 mL) and HCl in dioxane (4 M in 1,4-dioxane, 4.54 mL, 3 eq.) solution was added. The mixture was stirred at 110 °C for 3 days. After cooling to room temperature, the crude **5b** precipitated. The mixture was filtered and washed with diethyl ether and boiling hexane to remove impurities. Off-white solid. Yield: 54%.

Representative example of HG-type Ru complex synthesis (6b). In a glovebox, a Schlenk flask was charged with **5b** (0.50 mmol, 1 eq.) and anhydrous toluene (5 mL). The flask was heated to 50 °C and KHMDS solution (0.5 M in toluene, 1.99 mL, 1.00 mmol, 2 eq.) was added dropwise. The mixture was stirred for 10 min at 50 °C, followed by the addition of first-generation Hoveyda-Grubbs complex (149 mg, 0.25 mmol, 0.5 eq. in 5 mL toluene). The mixture was stirred at 50 °C for 1 h then filtered through alumina and the solvent was evaporated. The crude product was purified by column chromatography using alumina as stationary phase with gradient elution (pure hexane to hexane:THF 1:1). The solvent was evaporated yielding the pure product **6b** as a green solid. Yield: 34%. Single crystals for XRD analysis were obtained by dissolving the product in a minimal amount of toluene and placing it into the freezer (-20 °C).

Representative example of RCM reaction. In a glovebox, a small vial with a septa cap was charged with 120 μL (0.50 mmol) diethyl diallylmalonate. The sample temperature was equilibrated (at RT or



Scheme 7. Proposed production of butane-1,4-diol from allylic acetate. This reaction is presented as a module of the waste PE-based, propylene-mediated industrial material feed flowchart.

75 °C) and the solution of the catalyst (**6b**, 0.001 mol%, 0.005 μmol, 3.5 μg in 35 μL benzene solution) was added. The septum was pierced with a small needle to vent the forming ethylene gas. Samples were taken at the appropriate intervals over a period of 24 h. The conversion was determined by ¹H NMR in CDCl₃ comparing the integral areas of the starting material (d, 2.65 ppm) and the cyclic product (s, 3.02 ppm).

Representative example of self-metathesis of allyl acetate. In a glovebox, a small vial with a septa cap was charged with 110 μL (1.0 mmol) allyl acetate. The sample temperature was equilibrated (at RT or 75 °C) and the solution of the catalyst (**6b**, 0.01 mol%, 0.1 μmol, 70 μg in 70 μL benzene solution) was added. The septum was poked through with a small needle to vent the forming ethylene gas. At 24 h reaction time, the reaction mixture was dissolved in CDCl₃, the NMR yield was determined by ¹H NMR using 1,3,5-trimethylbenzene as internal standard by comparing the integral areas of the starting material (ddt, 5.92 ppm) and both *E* and *Z* products (t, 5.86 ppm for *E* isomer and m, 5.74 ppm for *Z* isomer).

Representative example of the one-pot conversion of allyl acetate to butane-1,4-diol. In a glovebox, a Schlenk flask was charged with 5 mL (46.4 mmol) allyl acetate and 16.3 mg (0.023 mmol, 0.05 mol%) **6b** catalyst. The mixture was stirred at 75 °C for 12 h, then evaporated gently to yield the crude but-2-ene-1,4-diyl diacetate, which was transferred to an autoclave, where THF (5 mL) and *t*BuOK (2.6 mg, 0.023 mmol, 1.0 eq. to **6b** catalyst) was added. The autoclave was purged with hydrogen gas 8 times, pressurized to 50 bar and stirred at 100 °C for 24 h. The reactor was depressurized and aqueous solution of NaOH (2 M, 120 mL, 5 eq.) was added and refluxed for 3 h while intense stirring. The pH was set to 7 by adding 2 M aqueous HCl, and product was obtained by vacuum distillation. Overall yield: 45 %.

Author Contributions

Ádám Erdélyi: concept (ligand and complex synthesis, catalytic investigation), Vajk Farkas: concept (ligand and complex synthesis), Gábor Turczel: NMR measurements and studies, Márton Nagyházi: writing and editing, Attila Bényei and Merell Lystra Ledesma Recta: XRD measurements and studies, Tibor Nagy and Sándor Kéki: HRMS investigations, Ole Osterthun: writing and editing, Jürgen Klankermayer: conceptualization, Róbert Tuba: conceptualization, visualization, editing.

Acknowledgements

R. Tuba is grateful for the Alexander von Humboldt Research Linkage Alumni program. This research has been supported by the National Research, Development and Innovation Office (NKFIH) through the project nr. 2022–1.1.1-KK-2022-00002, titled “Establishment of a waste management competence center at the University of Pannonia”. R. Tuba thanks the NKFIH under the Grant TKP2021-EGA-31. The project [2021-1.2.4-TÉT-2021-00021] has been implemented with the support provided from the NKFIH, financed under the [2021-1.2.4-TÉT] funding scheme. Financial support from NKFIH grant OTKA K-147142 is gratefully acknowledged (R. Tuba). The research was also supported by the EU and co-financed by the European Regional

Development Fund under the project GINOP-2.3.3-15-2016-00004 for purchasing the X-ray diffractometer and the HR-MS instrument.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Fluorene · CAAC · Olefin metathesis · Allyl acetate · Butane-1,4-diol

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Manuscript received: May 16, 2024

Accepted manuscript online: June 12, 2024

Version of record online: August 2, 2024