Specialized Olefin Metathesis Catalysts Featuring Unsymmetrical N-Heterocyclic Carbene Ligands Bearing N-(Fluoren-9-yl) Arm

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Received: 4 May 2020; Accepted: 24 May 2020; Published: 27 May 2020

Abstract: Beneficial structural motifs from two known state-of-the-art olefin metathesis catalysts types, bearing unsymmetrical N-heterocyclic carbene (uNHCs), were combined into a new hybridized design thereby translating the complementary beneficial reactivity demonstrated by their ‘parent’ complexes to the new N-fluorene derived olefin metathesis catalysts. Two chelating 2-iso-propoxy-benzylidene (Hoveyda-type) and two 3-phenyl-1H-inden-1-ylidene (indenylidene-type) complexes were successfully prepared by in situ generation of either the N′-mesityl (Mes) or N′-diisopropylphenyl (Dipp) derived uNHCs taking advantage of the thermal decomposition of the corresponding 2-(penta-fluorophenyl)-imidazolidines (NHC adducts). The new fluorene-derived catalysts mediate challenging olefin metathesis processes, such as α-olefin self-metathesis, with high selectivity and conversion.

Keywords: homogeneous catalysis; olefin metathesis; ruthenium; N-heterocyclic carbenes; selectivity; ethenolysis

1. Introduction

Formation of a carbon–carbon double bond can be accomplished by various chemical reactions, and catalytic olefin metathesis [1,2] is not only one of the most recent, but also goes well in line with the principles of so-called “green chemistry” [3]. The main driving force behind its development was the introduction of well-defined, active, and water stable Ru catalysts [4,5]. The development of second generation complexes [6–8] by replacement of one of the phosphine ligands with N-heterocyclic carbene (NHC) ligands represents a significant landmark in catalyst design, affording both enhanced activity and stability (Figure 1a) [7]. While these “general-purpose” catalysts dominate olefin metathesis, for some niche applications more specialized catalysts bearing unsymmetrical NHC ligands (uNHC) have been introduced. These catalysts were recently reviewed [9,10]; thus, only a few historically representative chemical structures are presented in Figures 1b and 2.
The first representatives of this new class of complexes were Grubbs-type uNHC catalysts obtained by Fürstner [11], before the Hoveyda-type complexes were synthesized by Blechert [12] and soon after by Verpoort and Ledoux [13]. Since then, the development of ruthenium catalysts bearing uNHC ligands has continued, however at a significantly slower pace as compared with a fast growing family of symmetrical NHC–Ru complexes [14,15]. This situation can be seen as disadvantageous, as uNHC-catalysts have shown enhanced application profiles in some specialized, but challenging, metathesis applications such as industrially important ethenolysis [16–20], self-metathesis of α-olefins [21,22], and other challenging transformations [23]. Indeed, the replacement of symmetrical NHC ligands with their unsymmetrical counterparts, in particular those with sterically differentiated substituents on nitrogen atoms, significantly increases the stability of resulting complexes in ethylene atmosphere and at higher temperatures [16,21,22,24–27]. This inhibits the formation of catalyst decomposition products which are known to promote the undesirable double bond migrations, and thus increases the yield and selectivity of the process [28–30]. Enhanced stability, especially under harsh conditions, has proven to be beneficial for macrocyclization reactions performed at high concentration [27]. Based on the successful design by Mauduit (Ru7) [21] and on the catalyst obtained previously by us (Ru8) [22,25,31], we decided to combine the selected structural characteristics of these complexes into a new system bearing an N-(fluoren-9-yl) side-arm (Figure 2). We speculated that formal addition of two benzene rings fused into a cyclopentene
ring of Mauduit’s Ru7 [21,32] will increase the steric bulk and produce substantial stiffness around this portion of the complex. Similarly, the fluorenyl substituent can be seen as the enlarged version of the NHC ligand present in Ru8 [25,31,33].

Lavigne and César previously studied aromatic 1-mesityl-3-(fluoren-9-yl)-imidazolium salt 1 (Scheme 1) [34]. Interestingly, deprotonation of 1 with strong base did not lead to a corresponding free N-(fluoren-9-yl)-imidazol-2-ylidene NHC 4 but to the mesomeric N-ylide betaine 2, consisting of a fluorenyl anion directly attached to an imidazolium ring. This product does not exist in equilibrium with a free NHC tautomer, and upon the reaction with gold and rhodium salts the fluorenyl position is metallated exclusively, not the apparently non-existent carbenic center. Moreover, the pronounced ylidic character of betaine 2 was proven by its reaction with electrophiles, such as methyl iodide, leading to fully selective methylation at the fluorenyl position to yield cleanly the imidazolium iodide 3 (Scheme 1).

![Scheme 1. Formation of mesomeric betaine 2 instead of free carbene 4 in deprotonation reaction of 1-mesityl-3-(fluoren-9-yl) imidazolium bromide (1), as reported by Lavigne and César [34].](image)

2. Results and Discussion

The results reported by Lavigne and César [34] (Scheme 1) were not surprising for us, as we expected that the reactivity of a fluorene-substituted NHC can be very different than the one exhibited by standard SIMes or SIPr (see Scheme 2 for definitions) carbenes. Indeed, in our preliminary work [35], we observed that corresponding (saturated) imidazolium salt 7 treated with base and ruthenium complex Ru1 did not lead to even traces of the expected Ru–NHC complex Ru9 (Scheme 2). Eventually, a solution to that problem was proposed [35], but because in our previous work we focused on studying the ylidic character of the deprotonated 7 and products of its further reactions (such as dimer 8, Scheme 1), the use of 7 for preparation of Ru metathesis catalysts was signaled only but not explored in detail [35]. Thus, applications of Ru9 in catalytic olefin metathesis remained generally unknown. In the present work, we describe the synthesis, characterization, and a detailed catalytic activity screening of this complex along with three new derivatives.
Scheme 2. Synthesis of Ru indenylidene complexes bearing N-(fluoren-9-yl) substituted NHC ligands with N′-mesityl (Mes) or N′-diisopropylphenyl (Dipp) (this work) N-aryl wings, versus the previously reported azolinium 7 and deprotonation product 8 [35].

As no desired complex formation was observed via direct deprotonation of azolium salt and reaction with Ru1, the catalysts were prepared in good yields by generating the base sensitive fluorene derived uNHCs via thermal disproportionation of 2-(pentafluorophenyl)imidazolidines (9) and 10 in the presence of Ru1 (Scheme 2). To do so, pentafluorophenyl adducts of NHC precursors were prepared in a three-step procedure (for use of pentafluorophenyl adducts in olefin metathesis catalyst synthesis see [25,36,37]). First, condensation of the corresponding N-arylethane-1, 2-diamine, and fluorenone was performed, followed by reduction with sodium borohydride. A further condensation of diamines 5 and 6 with pentafluorobenzaldehyde afforded the desired products 9 and 10 with moderate to good yield. Next, the corresponding second-generation indenyldiene-type complexes Ru9 and Ru10 were obtained in 66% and 35% yield via the in situ generation of free NHC carbenes in the presence of indenyldiene first-generation catalyst.

In a similar way, two fluorenyl-NHC Hoveyda-type complexes were obtained (Scheme 3). The preparation was even more efficient, allowing the synthesis of compounds Ru11 and Ru12 in improved yields of 67% and 74%, respectively.
Scheme 3. Synthesis of Hoveyda-type complexes bearing N-(fluoren-9-yl) substituted NHC ligands.

The identity of Ru9–Ru12 was unambiguously characterized by single-crystal X-ray diffraction analysis (Figure 3). The investigated compounds crystallized in the orthorhombic $P_{2_1}2_12_1$ (Ru9 and Ru10) or $Pbc_1$ (Ru11) and monoclinic $P2_1/c$ space groups (Ru12) with one (Ru9, Ru10, and Ru12) and two molecules (Ru11) of a given compound in the asymmetric part of the unit cell (Figure S1 in Supplementary Materials). The asymmetric parts of Ru10 and Ru12 also contain molecules of solvents (Figure S1). The values of selected parameters describing the geometry of molecules of Ru9–Ru12 are given in Table 1, while the details of crystallographic data and refinement parameters as well as a full list of bond lengths and values of valence and torsion angles are summarized in Tables S7–S18.

Figure 3. Molecular structures of the Ru9–Ru12 complexes. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms, except those attached to the C4/C4A and C32A/C35 atoms, as well as the second independent molecule B of Ru11 and the solvent molecules were omitted for clarity.
Table 1. Selected geometrical parameters of Ru9–Ru12.

| Geometrical Parameters (Å, °) | Ru9         | Ru10        | Ru11 (Molecule A/Molecule B) | Ru12        |
|-----------------------------|-------------|-------------|------------------------------|-------------|
| Bond lengths (Å)            |             |             |                              |             |
| Cl1–N1                      | 1.324(12)   | 1.345(6)    | 1.337(8)/1.364(9)            | 1.349(3)    |
| Cl1–N2                      | 1.333(13)   | 1.343(6)    | 1.372(7)/1.361(8)            | 1.352(3)    |
| Ru–C                        | 2.076(9)    | 2.082(4)    | 1.974(7)/1.958(7)            | 1.975(2)    |
| Ru–Cl1                      | 2.378(2)    | 2.397(2)    | 2.325(2)/2.320(2)            | 2.317(2)    |
| Ru–Cl2                      | 2.384(2)    | 2.412(2)    | 2.331(2)/2.336(2)            | 2.329(2)    |
| Ru–O                        | −           | −           | 2.274(5)/2.277(5)            | 2.294(2)    |
| Ru–P                        | 2.440(2)    | 2.423(2)    | −                            | −           |
| Ru=C                        | 1.922(11)   | 1.872(5)    | 1.850(7)/1.819(7)            | 1.828(2)    |
| Angles (°)                  |             |             |                              |             |
| Cl–Ru–Cl                   | 162.80(10)  | 163.55(4)   | 151.01(6)/149.64(6)          | 151.33(2)   |
| N–C–N                      | 110.0(8)    | 107.8(4)    | 106.5(6)/105.9(6)            | 106.85(18)  |
| C–Ru–O                     | −           | −           | 176.5(2)/178.8(2)            | 176.42(7)   |
| C–Ru–P                     | 156.3(3)    | 157.63(13)  | −                            | −           |
| A                           | 81.5(5)     | 81.42(16)   | 84.49(19)/92.1(2)            | 97.44(8)    |
| B                           | 93.0(5)     | 100.75(19)  | 90.4(2)/89.3(3)              | 86.18(9)    |
| C                           | 8.5(3)      | 14.11(14)   | 19.8(2)/18.8(3)              | 11.45(10)   |
| D                           | −           | −           | 0.11/0.10                    | 0.42/0.49   |
| τ5                         | 0.11        | 0.10        | 0.42/0.49                    | 0.42        |

Notes: A: dihedral angle between the mean-planes defined by the non-hydrogen atoms of the fluorene and the NHC moiety; B: dihedral angle between the mean-planes defined by the non-hydrogen atoms of the phenyl ring of the Mes/Dipp substituent and the NHC moiety; C: dihedral angle between the phenyl ring of the Mes/Dipp substituent and the indenylidene moiety; D: dihedral angle between the mean-planes defined by the non-hydrogen atoms of the NHC moiety and the phenyl ring of the o-isopropoxy-benzyl-methylene unit; τ5: geometry index [38].

In all four investigated complexes, the Ru(II) center is pentacoordinated (Figure 3). The indenyl derived Ru9 and Ru10 moieties display distorted square pyramidal coordination, while in latter Hoveyda-type complexes Ru11 and Ru12, the geometry of the metallic center is intermediary between the square pyramid and trigonal bipyramid. The above statement is confirmed by the values of τ5, which is a structural parameter characterizing the geometry of the coordination center for five coordinated compounds [38]. In case of investigated complexes these values are 0.11, 0.10, 0.43/0.49, and 0.42 for Ru9, Ru10, Ru11 (molecule A/molecule B), and Ru12, respectively. The Ru–C and Ru=C bond lengths are in the ranges from 1.958(7) up to 2.082(4) and from 1.819(7) to 1.922(11) Å, respectively, and these bonds are slightly longer in the case of both phosphine complexes. The lengths of the Ru–P bond in the Ru9 and Ru10 are comparable (2.440(2) and 2.423(2) Å, respectively). In turn, the Ru–O bond is slightly longer for Ru12 (2.294(2) Å) than for Ru11 (2.274(5)/2.277(5) Å). The distance between the Ru and O atoms within Ru11 and Ru12 is a bit longer than in other similar ruthenium o-isopropoxybenzylidene NHC complexes bearing mesityl, cyclohexyl or cyclopentyl instead of the fluorenyl [32,39–41]. The exception is an unsymmetrical Ru complex, where the NHC unit is substituted by the N′-diisopropylphenyl (Dipp) and cyclohexyl moieties [40]. In this case, the length of the Ru–O bond is comparable to the corresponding bond in Ru12.

A closer look at Figure 4 reveals that the N-fluorenyl group in all investigated catalysts is placed on the side opposed to alkylidene. The analysis of the angle between the mean-planes of the fluorene and the NHC ring fragments shows that for the fluorene moiety in the o-isopropoxy-benzylidene derivatives, the angle between the above fragments is higher than in Ru9 and Ru10. In both phosphine complexes, the fluorene fragment is situated above the one of the cyclohexyl units of the PCy3 ligand. Moreover, a specific mutual arrangement of the above-mentioned moieties in the molecule of Ru10 results in the appearance of a weak intramolecular C–H···π interaction involving the H59 atom of cyclohexane and the five-membered ring of the fluorene (d(D···A) = 3.773(6) Å; <(D–H···A) = 166°). In the above PCy3 complexes, the presence of the mentioned substituents in a near neighborhood of
the chlorine atoms results in the increase of the Cl–Ru–Cl angle by more than 10° compared to values observed in Ru11 and Ru12.

![Diagram](image)

**Figure 4.** Superimposed molecules of Ru9–Ru12. The hydrogen atoms were omitted for clarity.

The aromatic rings of the mesityl and the diisopropylphenyl substituents in both phosphonium Ru complexes are positioned towards the indenylidene aromatic ring system. In the case of Ru9, the above moieties are inclined to each other by the angle of 8.5(3)° and the intramolecular π–π contacts were identified (d(CgI···CgI) = 3.389(6)–3.761(6) Å) involving the phenyl ring of N'-mesityl (Mes) with the five-membered and six-membered ring of the indenylidene. In turn, in a complex bearing the more bulky diisopropylphenyl, the phenyl ring of Dipp and the indenylidene ring system are inclined towards one other by a greater degree (14.11(14)°). Here, the intramolecular π–π contact is also present, however, it involves only the phenyl ring of Dipp and the five-membered ring of indenylidene. The distance between the geometrical ring centroids of the above-mentioned rings is found to be 3.509(3) Å. It is worth mentioning that the existence of such intramolecular π–π stacking can also be observed for other Ru-PCy₃ systems containing aromatic ring fragments [13,42–46]. A comparison of the spatial orientation of the whole 3-phenyl-1H-inden-1-ylidene substituent shows that this moiety in Ru9 and Ru10 is rotated to the opposite side. In the case of Ru11 and Ru12, the orientation of the
Mes and Dipp is typical for the Hoveyda-type catalysts [32,39–41,47]. Namely, the phenyl rings of the above substituents are directed towards the benzylidene fragment in a way that the benzylidene hydrogen is located directly under the Mes/Dipp aromatic ring. In both cases, these H-atoms and the aromatic rings adjacent to them are engaged in weak intramolecular C−H···π interactions. The distance between the donor and acceptor of the H-atom in these interactions is shortest in the case of Ru12 (3.371(2) Å). A replacement of Mes by the bulkier Dipp substituent (see Ru12 and Ru11) manifests itself in a noticeable change of the angle between the mean-planes of the NHC and phenyl ring of the benzylidene moiety. The value of this angle is almost two times higher in the case of Ru11 in comparison to Ru12.

Typically, complexes containing unsymmetrical NHC ligands display increased stability in a solution, also at elevated temperatures [22,32,48]. We were curious if fluorene moiety, combining structural elements introduced by Mauduit [32] and us [22], would also have a positive influence on catalysts’ resistance towards decomposition. To explore their robustness in solvent, we prepared toluene solutions (0.02 M) of four fluorene-based catalysts and 1,3,5-trimethoxybenzene (for details see Materials and Methods section), that were heated to 50 °C and stored over 9 (for indenylidene-type complexes) and up to 40 days (for Hoveyda–Grubbs-type complexes), respectively. The degree of decomposition was determined by means of 1H NMR (1,3,5-trimethoxybenzene was used as the internal standard). Catalysts with the o-isoproxy-benzylidene ligand, regardless of the type of uNHC, showed superior stability in comparison to their indenylidene counterparts, and the most stable complex was Dipp-bearing Ru12 which after 10 days at 50 °C remained unchanged in 85%, and even after 40 days 70% remained intact. A little worse, but still very resilient, was its SIMes-based analogue Ru11 (75% and 45%, respectively over the same period). Among indenylidene-type complexes, the SIMes-based uNHC Ru9 was the least prone to decomposition (46% after 9 days), followed by its SIPr analogue Ru10 (25% left unchanged after 9 days).

Despite some individual differences between the catalysts, one can state that the N-fluorenyl uNHC-based catalysts demonstrated in general improved stability in solution at elevated temperature. With this result, we opted to test their catalytic activity: first in standard model olefin metathesis reactions [49], then in some more demanding industrially-important processes, such as ethenolysis or self-metathesis of α-olefins.

First, we studied the activity profiles in ring-closing metathesis (RCM) of a relatively “easy” model substrate [49] 2,2-diallyl-tosylate (11) in the presence of 0.1 mol % of catalyst, in 0.1 M toluene at 50 °C (Figure 5). As expected [24], catalysts containing symmetric NHC ligands Ru2 and Ru5 exhibited the highest activity, reaching full conversion of 11 after only 20 and 5 min, respectively. Indenylidine based Ru9 (Ar = Mes) and Ru10 (Ar = Dipp) led to incomplete but high conversions but were still propagating the reaction after 90 min (no visible plateau). Interestingly, at the beginning of the reaction, complex Ru10 initiated visibly faster than SIMes bearing Ru2 before beginning to plateau, meaning the initially less active Ru9 reached a similar high conversion after 90 min (Figure 5). Hoveyda–Grubbs-type complexes bearing fluorene moiety acted in a slower pace than their symmetrical NHC analogue Ru5, but after approximately 1 h also achieved very high conversion. Interestingly, in this case the SIMes-bearing Ru11 acted slightly faster than its SIPr-containing analogue Ru12 (for indenylidene-type catalysts the trend was opposite).
Next, RCM of a more sterically hindered substrate, 2-allyl-2-(2-methylallyl)tosylate (13) [49] was performed (Figure 6) in toluene at 50 °C in the presence of 1 mol % of catalyst. In addition, general purpose complexes with symmetrical NHC ligands (Ru2 and Ru5) turned out to be more efficient. Fluorene-based complexes proceeded slower, but extension of reaction time allowed complete or almost complete conversions in these cases. Similar to the RCM reaction of 11, catalyst Ru9 initiated a little bit faster than Umicore M2 catalyst Ru2, however the latter was able to outperform it quickly.

**Figure 5.** Time-conversion curves for ring-closing metathesis (RCM) of 11. Flu = fluoren-9-yl. Lines are as a visual aid only.
In the Hoveyda–Grubbs series the activity of catalysts with fluorene-substituted uNHC was more than satisfactory, with both leading to almost complete conversions in just over an hour.

With the basic profiling of new uNHC complexes completed, we examined them in a more diverse set of RCM reactions (Table 2). We attempted these tests not because we believed the fluorenyl uNHC catalysts will find applications in natural products synthesis or in medicinal chemistry—the fields of applications where catalysts bearing symmetrical NHC are traditionally much more suitable [50,51]—but to be consistent with our previous studies using similar sets of more advanced substrates [26,48,52]. All reactions were performed in 0.1 M solution in toluene at 60 °C in the presence of 1000 ppm (0.1 mol %)
of catalysts to compare the new system with well-established general purpose Umicore M2 (Ru2) and Hoveyda–Grubbs (Ru5) catalysts.

Table 2. Application of fluorene-based catalysts Ru9–Ru12 in RCM reactions.

| Entry | Substrate | Product | Catalyst | Conv. (%) |
|-------|-----------|---------|----------|-----------|
| 1 a   | ![Substrate 1](image1) | ![Product 1](image2) | Ru2 | 100 |
|       |           |         | Ru9     | 93 |
|       |           |         | Ru10    | 92 |
|       |           |         | Ru5     | 100 |
|       |           |         | Ru11    | 98 |
|       |           |         | Ru12    | 98 |
| 2     | ![Substrate 2](image3) | ![Product 2](image4) | Ru2 | 100 |
|       |           |         | Ru9     | 99 |
|       |           |         | Ru10    | 96 |
|       |           |         | Ru5     | 100 |
|       |           |         | Ru11    | 87 |
|       |           |         | Ru12    | 96 |
| 3     | ![Substrate 3](image5) | ![Product 3](image6) | Ru2 | 100 |
|       |           |         | Ru9     | 87 |
|       |           |         | Ru10    | 98 |
|       |           |         | Ru5     | 98 |
|       |           |         | Ru11    | 92 |
|       |           |         | Ru12    | 100 |
| 4     | ![Substrate 4](image7) | ![Product 4](image8) | Ru2 | 100 |
|       |           |         | Ru9     | 100 |
|       |           |         | Ru10    | 75 |
|       |           |         | Ru5     | 100 |
|       |           |         | Ru11    | 100 |
|       |           |         | Ru12    | 98 |
| 5     | ![Substrate 5](image9) | ![Product 5](image10) | Ru2 | 99 |
|       |           |         | Ru9     | 80 |
|       |           |         | Ru10    | 100 |
|       |           |         | Ru5     | 98 |
|       |           |         | Ru11    | 86 |
|       |           |         | Ru12    | 86 |
| 6     | ![Substrate 6](image11) | ![Product 6](image12) | Ru2 | 100 |
|       |           |         | Ru9     | 67 |
|       |           |         | Ru10    | 84 |
|       |           |         | Ru5     | 100 |
|       |           |         | Ru11    | 62 |
|       |           |         | Ru12    | 98 |

Conditions: 0.1 mol % of catalyst, toluene (0.1 M), 60 °C, 4 h. a Reaction time 1.5 h.

As expected, well established catalysts Ru2 and Ru5 bearing symmetrical NHC gave the best results in virtually all reactions, although the newly obtained uNHC complexes also showed high activity. In the first three examples (Table 2, entries 1–3), no significant differences between these two classes of complexes were observed as the yield of the desired products was usually around 90–100%. More significant differences appeared when synthesis of a more challenging three substituted C–C double bond was attempted (entry 4), showing some advances of sterically reduced catalysts Ru9 and Ru11. Substrates forming spiro-compounds were next examined. In the case of 2,2-diallyl-2,3-dihydro-1H-inden-1-one (23) (Table 2, entry 5) the drop-in conversion was not too pronounced; all catalysts achieved at least 80% conversion, with uNHC Ru10 giving 100%. With barbituric acid derivative 25 (Table 2, entry 6), most fluorene-substituted catalysts showed limited
reactivity in comparison to general purpose symmetrical NHC complexes. Of the uNHC complexes Ru12 gave some of the best results.

Given their high stability, complexes containing unsymmetrical NHC ligands are particularly useful in industrially relevant reactions of \( \alpha \)-olefins—substrates particularly susceptible to migration of double bond—as well as in ethenolysis [21,24,26]. As shown before, benzyl derived indenylidene-type complex Ru8 is more robust than standard Umicore M2 [25,31], while the \( N \)-cycloalkyl substituted complex Ru7 investigated by Mauduit et al. proved to be a truly excellent catalyst for self-metathesis of \( \alpha \)-olefin at low catalysts loading (TON, turnover number 11,680 at 50 ppm) [21]. We were curious whether the new catalysts combining structural features of the \( N \)-cyclopentyl and \( N \)-benzyl moiety into one substituent, the \( N \)-fluorenyl group, would outperform their parental complexes in these challenging reactions. Based on our previous results [24,35], for these tests we selected a Mes bearing, indenylidene-type complex Ru9, as the most optimal candidate.

Firstly, the self-metathesis reaction of 1-octene 26, being a good representative of Fischer–Tropsch \( \alpha \)-olefins [21], conducted neat at 80 and 50 °C with different loadings of Ru9 was investigated. The progress of reaction was monitored by means of gas chromatography (GC). When the reaction was carried out at 80 °C in the presence of 100 ppm catalyst (Figure 7a), the fastest increase and the highest yield of the desired primary metathesis product 27 was observed, although also about 10% of unwanted byproducts, containing longer or shorter carbon chains were created (the unwanted isomerization/secondary metathesis process is a well-known and serious limitation of Ru-catalyzed self-cross metathesis (self-CM) of \( \alpha \)-olefins) [21,53,54].

Decreasing the temperature to 50 °C (Figure 7b) slightly reduced the reaction rate—after 3 h 79% of the substrate was consumed—but at the same time significantly improved selectivity (from 87% for reaction at 80 °C, to 97% for the one performed at 50 °C). For academic research, 100 ppm of catalyst seems to be a low loading, but in industrial production it is still too high. Thus, we investigated self-CM of 1-octene at reduced catalyst loadings of 50, 10, and 1 ppm of Ru (Figure 7c–e). With decreased catalyst loadings an increase of the reaction time was necessary to achieve satisfactory substrate conversion but still maintain low levels of undesired byproducts [55]. As a result, even at 1 ppm loading of the new fluorene-containing Ru9, 52% conversion of 27 was reported that translates to TON of 260,000 and TOF (turn-over frequency) of 12,381 over 21 h (selectivity 89%). Self-metathesis of 1-octene was investigated at 50 ppm with other \( N \)-fluorenyl uNHC catalysts, and the Mes substituted Hoveyda (Ru11) was found to give highest selectivity (92%) but did not outperform Ru9 (see Supplementary Materials for more details). These results indicate the superiority of the Mes substitution in \( N \)-fluorenyl uNHC complexes when applied to self-metathesis of 1-octene.

Finally, it shall be stressed that in the above self-CM reaction the general purpose catalysts, such as Ru2 and Ru5, were reported to give very low selectivity, sometimes as low as 20% [24], probably due to extensive catalysts decomposition forming Ru-hydride species [56,57], dimers [29], and possibly other yet undefined species.

Ethenolysis is another industrially relevant process enabling valorization of biomass [58–60]. This process is usually carried out in the presence of specialized cyclic alkyl amino carbene (CAAC) or uNHC-bearing complexes, as the general-purpose SIMes and SIPr Ru catalysts give suboptimal results in this case [16,18,19,61–64].
of double bond—as well as in ethenolysis \[21,24,26\]. As shown before, benzyl derived indenylidene-type complex Ru8 is more robust than standard Umicore M2 \[25,31\], while the N-cycloalkyl substituted complex Ru7 investigated by Mauduit et al. proved to be a truly excellent catalyst for self-metathesis of α-olefin at low catalysts loading (TON 11,680 at 50 ppm) \[21\].

We were curious whether the new catalysts combining structural features of the N-cyclopentyl and N-benzyl moiety into one substituent, the N-fluorenyl group, would outperform their parental complexes in these challenging reactions. Based on our previous results \[24,35\], for these tests we selected a Mes bearing, indenylidene-type complex Ru9, as the most optimal candidate.

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![Figure 7. Self-cross metathesis (self-CM) of 1-octene.](image)

(\text{a}) Ru9 100 ppm, 80 °C.
(\text{b}) Ru9 100 ppm, 50 °C.
(\text{c}) Ru9 50 ppm, 50 °C.
(\text{d}) Ru9 10 ppm, 50 °C.
(\text{e}) Ru9 1 ppm, 50 °C. Lines are as a visual aid only.

Decreasing the temperature to 50 °C (Figure 7b) slightly reduced the reaction rate—after 3 h 79% of the substrate was consumed—but at the same time significantly improved selectivity (from 87% to 91%).

Therefore, we opted to check how the new uNHC complexes work in this case. To do so, we selected ethyl oleate as a model substrate (oleic acid esters are commonly used for such purpose) under industrially-friendly conditions \[19,48\] (i.e., in an ordinary steel autoclave outside a glovebox using ethylene grade 3). Some preliminary studies have shown that the lowest Ru loading where our catalysts are still giving practically useful conversions is equivalent to 100 ppm. Under such conditions, the bulkier Dipp-bearing fluorenyl catalysts (Ru10, Ru12) gave good results, both in terms of conversion and selectivity (Figure 8). Interestingly, the Mes-derived fluorenyl catalysts (Ru9, Ru11) performed with lower conversion, however, exhibiting only slightly reduced selectivity. These results (TON up to 7140) obtained for Ru10 and Ru12 outperform not only earlier Ru uNHC complexes \[16\] but also more recent complexes bearing uNHC with a thiophene wing, as well the recently disclosed Ru complex bearing highly engineered bulky phenanthrene-based uNHC, which under the same conditions provided TON of 4550 \[19\] and 1370, respectively \[48\]. It shall be at the same time noted, however, that our fluorenyl uNHC catalysts that need 100 ppm to maintain acceptable conversion are less powerful than CAAC complexes, such as Ru13, which was reported to work in ethenolysis with grade 3 ethylene under similar conditions at 25 ppm resulting in TONs up to 28,000 \[63\].
3. Materials and Methods

3.1. General

All reagents were purchased from Sigma-Aldrich, Apeiron, Strem, TCI, and Alfa Aesar and used without further purification unless stated otherwise. Reactions which required use of moisture and oxygen-free conditions were performed using the Schlenk technique or in a glovebox, under an atmosphere of argon with use of dry and degassed solvents from SPS (Solvent Purification System). The stock solutions of catalyst were prepared in the glovebox under moisture and oxygen-free conditions. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light or by KMnO₄ water solution. Flash chromatography was performed using silica gel 60 (230–400 mesh). GC analysis was done using Clarus 580 chromatograph using tetradecane as an internal standard. ¹H and ¹³C NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. Chemical shifts (δ) are given in ppm with coupling constants (J) in Hz; they are reported relative to reference solvent peaks in deuterated solvent: 7.26 and 77.16 ppm for ¹H and ¹³C NMR, respectively in CDCl₃; 5.32 and 53.84 ppm for ¹H and ¹³C NMR, respectively in CD₂Cl₂. The following abbreviations are used to denote multiplicity: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublets, dt-doublet of triplets, ddd-doublet of doublets of doublets. IR spectra were recorded on JASCO FT/IR-6200 spectrometer. Wavenumbers are given in cm⁻¹. High resolution electrospray mass spectroscopy (ESI-HRMS) was obtained on AutoSpec Premier spectrometer. Melting points were recorded on an OptiMelt SRS apparatus with a heating rate of 10 °C/min.

3.2. Synthesis of New Complexes

Synthesis of complex Ru10. The pentafluorobenzene adduct (338 mg, 0.600 mmol, 1.1 equiv.) was weighed into an oven-dried Schlenk flask under argon and dissolved in dry toluene (3 mL). Umicore M1 (504 mg, 0.545 mmol, 1.0 equiv.) was added and the resulting red/brown reaction mixture was stirred at 90 °C (in preheat oil bath). The reaction mixture was monitored by TLC over a period of 5 h as

![Image of reaction scheme](image)
significant amounts of start material appeared to be present. Phosphine scavenger copper (I) chloride (27 mg, 0.273 mmol, 0.5 equiv.) was added and the mixture was reacted for another hour. After cooling, the reaction mixture was diluted with n-hexane (10 mL) and placed onto a short column packed in neat hexane. The column was eluted with neat hexane to remove toluene before eluting with 1% ethyl acetate/n-hexane until all start material was removed, then the polarity was gradually increased to 5% (in 1% increments) to elute the product. After evaporation the product was recrystallized from n-hexane affording the product as a red crystalline solid (200 mg, 193 mmol, 35%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.77 (dd, $J = 7.4, 1.3$ Hz, 1H), 8.69–8.55 (m, 1H), 8.34 (dd, $J = 7.4, 1.0$ Hz, 1H), 7.83–7.75 (m, 2H), 7.65–7.57 (m, 3H), 7.56–7.35 (m, 7H), 7.29–7.15 (m, 2H), 7.14–7.04 (m, 1H), 6.90 (s, 1H), 6.85 (t, $J = 7.7$ Hz, 1H), 6.59 (dd, $J = 26.4, 7.8$ Hz, 2H), 4.09–3.87 (m, 1H), 3.83–3.66 (m, 1H), 3.55–3.40 (m, 1H), 3.36–3.17 (m, 2H), 3.02 (hept, $J = 6.6$ Hz, 1H), 2.45–2.19 (m, 3H), 1.76 (d, $J = 13.9$ Hz, 6H), 1.55–1.35 (m, 5H), 1.28 (dt, $J = 12.3, 3.1$ Hz, 8H), 1.21 (d, $J = 6.6$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 0.85 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) δ 216.9 (d, $J = 71.2$ Hz), 147.7, 147.1, 144.6, 142.1, 141.8, 141.7, 141.7, 141.6, 139.0, 137.5, 137.4, 137.2, 130.7, 129.8, 129.1, 128.9, 128.3, 128.2, 128.1, 128.1, 127.9, 127.3, 124.3, 123.8, 120.3, 116.9, 65.0, 55.6, 44.0, 43.9, 32.9, 32.7, 30.2, 29.7, 28.5, 28.3, 28.2, 28.2, 28.1, 28.1, 27.5, 27.4, 27.1, 26.7, 26.0, 23.3, 22.5. $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) δ 31.62. IR (neat): v = 3052, 2926, 1587, 1436, 1358, 1338, 1322, 1295, 1257, 1200, 1173, 1130, 1107, 1048, 1027, 1005, 977, 949, 916, 886, 848, 819, 801, 774, 747, 697, 681, 647, 621, 583, 555, 505, 490, 420 cm$^{-1}$. HRMS (ESI): m/z calculated for C$_3$H$_7$Cl$_2$N$_2$Ru [M]+ 1036.3932, found 1036.3932.

Synthesis of complex Ru11. Hoveyda–Grubbs I (210 mg, 0.35 mmol, 1 equiv.) and the corresponding pentafluorobenzene adduct (200 mg, 0.385 mmol, 1.1 equiv.) were weighed into an oven-dried Schlenk tube under argon and sealed with a septum. Toluene (3 mL) was added and the reaction mixture was heated to 90 °C (in preheated oil bath) for 30 min, monitoring progress by TLC. Copper (I) chloride (38.5 mg, 0.385 mmol, 1.1 equiv.) was added and the reaction mixture was heated for a further 10 min. The cooled reaction mixture was poured onto a column of silica packed in neat hexane and flushed with neat hexane until the toluene was removed. The column was then eluted with a silica’s length of 5% ethyl acetate/n-hexane affording the product as a red crystalline solid (200 mg, 193 mmol, 35%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 16.25 (s, 1H), 8.37 (d, $J = 7.5$ Hz, 2H), 7.81 (dd, $J = 7.5, 1.0$ Hz, 2H), 7.59 (ddddd, $J = 8.5, 5.2, 3.8, 0.9$ Hz, 1H), 7.49 (td, $J = 7.5, 0.9$ Hz, 2H), 7.41 (tt, $J = 7.6, 1.1$ Hz, 2H), 7.29 (s, 1H), 7.13 (s, 2H), 7.01 (d, $J = 0.9$ Hz, 2H), 7.00–6.98 (m, 1H), 5.14 (dq, $J = 12.4, 6.2$ Hz, 1H), 3.89–3.78 (m, 2H), 3.32–3.22 (m, 2H), 2.49 (s, 3H), 2.29 (s, 6H), 1.62 (dd, $J = 6.2, 0.9$ Hz, 6H), 1.53 (d, $J = 0.9$ Hz, 2H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) δ 209.1, 152.8, 144.6, 142.4, 141.6, 139.6, 138.6, 138.5, 130.1, 129.7, 128.3, 127.1, 123.7, 122.9, 120.4, 113.5, 76.0, 75.9, 65.3, 65.3, 43.9, 22.3, 21.5, 18.4, 18.4. IR (neat): v = 2975, 1473, 1436, 1411, 1327, 1260, 1217, 1156, 1109, 1096, 933, 842, 747, 680 cm$^{-1}$. HRMS (ESI): m/z calculated for C$_{35}$H$_{30}$Cl$_2$N$_2$ORuNa [M + Na]+ 695.1146, found 695.1123.

Synthesis of complex Ru12. Hoveyda–Grubbs I catalyst (485 mg, 0.81 mmol, 1 equiv.) and the corresponding pentafluorobenzene adduct (500 mg, 0.89 mmol, 1.1 equiv.) were added to a Schlenk flask and argonated. Dry toluene (6 mL) was added and the resulting dark brown mixture was stirred for about 30 min at 80 °C. The reaction was monitored by TLC. When the reaction was complete, phosphine scavenger copper (I) chloride (121 mg, 1.21 mmol, 1.5 equiv.) was added and the mixture was stirred for a further 10 min and checked by TLC. After cooling the mixture was put onto a column packed in neat hexane and then eluted with n-hexane to remove the toluene. The column was eluted with the silica’s length of 5% ethyl acetate/n-hexane followed by 10% ethyl acetate/n-hexane until the red/brown fraction was collected. The product was then eluted with 20% ethyl acetate/n-hexane. Product fractions were checked by TLC, collected into one flask, concentrated to dryness, and recrystallized from DCMMeOH on the rotary evaporator. The product was obtained.
as lustrous dark green crystals (389 mg, 0.54 mmol, 67%). $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 16.23 (d, $J$ = 0.9 Hz, 1H), 8.41–8.37 (m, 2H), 7.82 (ddd, $J$ = 7.5, 1.2, 0.7 Hz, 2H), 7.69–7.61 (m, 1H), 7.56 (ddd, $J$ = 8.3, 6.1, 3.0 Hz, 1H), 7.50 (td, $J$ = 7.5, 1.2, 0.6 Hz, 2H), 7.47–7.39 (m, 4H), 7.34 (s, 1H), 7.00 (dt, $J$ = 8.3, 0.7 Hz, 1H), 6.96–6.92 (m, 2H), 5.19–5.08 (m, 1H), 3.94–3.72 (m, 2H), 3.35–3.15 (m, 4H), 1.65 (d, $J$ = 6.1 Hz, 6H), 1.22 (d, $J$ = 7.0 Hz, 6H), 0.95 (d, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 149.0, 142.4, 141.6, 130.2, 130.0, 129.7, 128.3, 127.7, 125.4, 123.0, 122.6, 120.3, 113.5, 76.0, 65.5, 55.6, 43.6, 28.6, 25.9, 24.2, 22.5. IR (neat): $v$ 3063, 3049, 2923, 2892, 2866, 1958, 1918, 1823, 1720, 1604, 1588, 1575, 1477, 1449, 1429, 1419, 1384, 1337, 1316, 1294, 1249, 1217, 1177, 1158, 1142, 1111, 1098, 1049, 1037, 1021, 1003, 981, 951, 879, 842, 810, 794, 756, 745, 680, 657, 640, 620, 582, 492, 438, 418 cm$^{-1}$. HRMS (ESI): m/z calculated for C$_{38}$H$_{42}$Cl$_2$N$_2$ORuNa [M + Na]$^+$ 737.1615, found 695.1608.

3.3. Catalysis

General procedure for thermal stability studies. In a Young NMR tube, the corresponding catalyst (12.8 µmol) was dissolved in 0.65 mL of toluene-$d_8$ followed by addition of 0.13 M solution of 1,3,5-trimethoxybenzene in toluene-$d_8$ (internal standard, 50 µL, 6.4 µmol) in a glove box. An NMR tube was removed from the glove box and placed in a preheated (50°C) water batch. $^1$H NMR spectra were recorded in frequent time intervals. Degradation of catalyst was calculated by comparing the integration of benzylidene and indenylidene signal in complexes and 9 protons from methoxy groups in internal standard.

General procedure for model RCM reactions. The substrate was accurately weighed into a Radley carousel under inert atmosphere and dissolved in dry toluene (3.8 mL) with stirring. In the glovebox the catalyst (0.01 mmol) was dissolved in dry toluene (2 mL), then 0.2 mL of this stock solution were transferred to the reaction mixture and heated at 80°C overnight under a flow of argon. The reaction was cooled, quenched with SnatchCat and concentrated in vacuo before being dispersed on 70–230 Silica and purifying on the Combi-flash. Concentration of fractions afforded the pure products. $^1$H NMR analysis was done to determine the structure of each product.

General procedure for $\alpha$-olefin metathesis. In the glovebox a stock solution of catalyst was made up in a 1 mL volumetric flask. A solution of 1-octene (1.5 mL, 9.37 mmol) in tetradecane (0.5 mL, 1.9 mmol) as internal standard was stirred at a certain temperature before a sample without catalyst was taken. The appropriate volume of stock solution was added via micro syringe to the reaction mixture before reaction samples (0.1 mL) for GC analysis were taken at relevant time intervals. Samples were quenched with SnatchCat solution (35 µmol, 1 mL). Conversion and selectivity were determined by GC measurement according to the calculations below.

General procedure for ethenolysis reaction. Into a dry autoclave tube charged with ethyl oleate (28) (purified by passing through an Al$_2$O$_3$ pad, 4.66 g, 15 mmol) and tetradecane (internal standard, 0.61 g, 3 mmol), the stock solution of catalyst (100 ppm, dissolved in 0.1 mL of HPLC grade DCM) was added. The autoclave was closed, purged with ethylene (3 times), and stirred at 50°C for 3 h with 10 bar continuous ethylene pressure. On completion the reaction was quenched by ethyl-vinyl ether addition. Conversion and selectivity were determined by GC measurement.

4. Conclusions

New indenylidene- and Hoveyda–Grubbs-type complexes with fluorene-based NHC ligands were obtained via direct reaction between pentafluorophenyl-adducts 9 and 10 and corresponding Ru complexes Ru1 and Ru4. The introduction of fluorene moiety in conjunction with either the Mes or Dipp group was found to have a profound influence on stability and activity of the resulting catalysts, especially in reactions of demanding substrates, such as cross-metathesis of oleic substrate with ethylene and self-CM of $\alpha$-olefins. For ethenolysis, the Dipp substituted N-fluorenyl uNHC complexes (independent of their initiating alkylidene) gave results better than some other recently disclosed uNHC systems [48], but worse than modern engineered CAAC and bis(CAAC) systems [52,63]. Importantly, in the self-CM of $\alpha$-olefins, the Mes substituted N-fluorenyl uNHC complexes performed very well,
making it possible to decrease catalysts loading of Ru9 to 1 ppm and obtain the desired primary metathesis product 27 with high efficiency (TON = 260,000) and selectivity. Therefore, despite catalysts Ru9–Ru12 not being universal as the general-purpose Umicore M2 or Hoveyda–Grubbs systems (Ru2, Ru5), we believe that their superior performance in self-metathesis can find a number of important applications, especially in the industrial context.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/599/s1 Data concerning crystallography data for this paper (CCDC 1979853–1979856) can be obtained freely via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting directly the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033).

Author Contributions: Conceptualization, K.G.; investigation, P.I.J., A.M., P.M. and D.T.; writing—original draft preparation, A.K. and K.G.; writing—review and editing, D.T., K.W., A.K. and K.G.; visualization, K.G., P.M. and A.K.; supervision, P.I.J., K.W., A.K. and K.G.; funding acquisition, P.I.J. All authors have read and agreed to the published version of the manuscript.

Funding: P.I.J. is grateful to the POLONEZ project financed from the National Science Centre, Poland on the basis of decision DEC-2016/21/P/ST5/04016. This project received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 665778. The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by the European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007–2013. The X-ray diffraction data collection was collected at the Core Facility for crystallographic and biophysical research to support the development of medicinal products established within the TEAM-TECH Core Facility programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

Conflicts of Interest: The authors declare no conflicts of interest.

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