Supporting Information

Activation of olefin metathesis complexes containing unsymmetrical unsaturated N-heterocyclic carbenes by copper and gold transmetalation

Fadwa Kamal, Sophie Colombel-Rouen, Adrien Dumas, Jean-Paul Guégan, Thierry Roisnel, Vincent Dorcet, Olivier Baslé, Mathieu Rouen and Marc Mauduit*

a Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France.
b DEMETA SAS, 6 rue Pierre-Joseph Colin, 35000 Rennes, France

* marc.mauduit@ensc-rennes.fr

† Present address: LCC-CNRS, Université de Toulouse, CNRS, UPS, Toulouse, France

1. General Information .......................................................... 2
2. GC method ........................................................................ 3
3. Synthesis of Imidazolium Salts ............................................ 4
  3.1. Synthesis of 2-benzhydryl-6-fluoro-4-methylaniline (3a) ........ 4
  3.2. General procedure for synthesis of imidazolium salts: ........ 5
4. Synthesis of bis-NHC complexes .......................................... 6
  4.1. General procedure for synthesis of bis-NHC complexes: ......... 6
  4.2. General procedure for transmetalsation ................................ 11
    4.2.1. Transmetalation process using Copper(I) chloride ........... 11
    4.2.2. Transmetalation process using Gold(I) chloride .............. 14
5. General procedure for kinetic studies .................................... 16
6. Scope of Metathesis Transformations .................................... 22
  6.1. Ring Closing Metathesis (RCM) ...................................... 22
  6.2. Self-Metathesis (SM) ...................................................... 51
7. NMR Spectra ....................................................................... 64
  7.1. NHC Precursors ............................................................. 64
  7.2. Ruthenium Complexes .................................................... 70
8. X-Ray crystallographic data ................................................ 86
1. General Information

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques unless otherwise noticed. Toluene, diethyl ether, dichloromethane and tetrahydrofuran were purified using MBraun Solvent Purification Systems. Toluene was also degased for kinetic studies. All commercial chemicals were used as received unless otherwise noted. Diethyl diallylmalonate (DEDAM) was used as received. Mesitylene was distilled over calcium hydride. 1-dodecene and 11-bromoundecene were distilled over sodium and filtrated over basic alumina prior to used. All scope substrats were dried over basic alumina. Imidazolium salt 3-cyclooctyl-1-mesitylimidazolium tetrafluoroborate\(^1\) and catalyst bis(1-cyclooctyl-3-mesityl-imidazol-2-ylidene)(3-phenyl-1H-inden-1-ylidene)ruthenium dichloride (Ru-\textbf{1a})\(^2\) were synthesized according to the literature. The 0.5 M solution of potassium bis(trimethylsilyl)amid in toluene was purchased from Acros Organics with AcroSeal packaging. Flash chromatography was performed on silica gel 60 (230-400 mesh). NMR spectra were recorded on a Bruker ARX400 spectrometer (\(^1\)H (400 MHz), \(^{13}\)C (101 MHz), \(^{19}\)F (376 MHz) and \(^{11}\)B (128 MHz)) with complete proton decoupling for nucleus other than \(^1\)H. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl\(_3\), \(^1\)H: δ 7.26 ppm, \(^{13}\)C: δ 77.16 ppm; CD\(_2\)Cl\(_2\), \(^1\)H: δ 5.32 ppm, \(^{13}\)C: δ 53.84 ppm; C\(_6\)D\(_6\), \(^1\)H: 7.16 ppm, \(^{13}\)C: 128.06 ppm; Toluene-\(d_8\), \(^1\)H: δ 2.08 ppm, \(^{13}\)C: δ 20.43 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tt = triplet of triplets, q = quartet, sept = septuplet, m = multiplet, br = broad, bs = broad signal, Cq = quaternary carbon. High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QTof-I spectrometer using electrospay ionization at the Centre Régional de Mesures Physiques de l’Ouest (CRMPO), Université de Rennes 1. Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected.


2. GC method

Instrument: Shimadzu GC-2014
Column: TR5, 25 m x 0.25 mm x 0.25 µm.

GC and column conditions: Injector temperature: 250°C, FID: 250°C.
Oven temperature:
- Starting temperature: 60°C, hold time: 5 minutes.
- Ramp rate 2°C/min to 120°C, hold time: 0 minute.
- Ramp rate 5°C/min to 180°C, hold time: 0 minute.
- Ramp rate 10°C/min to 280°C, hold time: 0 minute.
- Ramp rate 15°C/min to 340°C, hold time: 9 minutes.

Carrier gas: Helium, u = 40 cm/sec.
Injection volume: 1 µl.
Split ratio: 20:1.
Run time: 70 minutes.

Calibration curves:

A GC method was developed to separate Docosene P12 and tetradecane as the internal standard (see Figure S1).
Determination of GC yield:

\[
Yield = \frac{0.7499 \times \left[ \frac{A_{\text{Docosene}}}{A_{\text{Tetradecane}}} - 0.6522 \right] \times \frac{m_{\text{Aliquot}} \times m_{\text{Tetradecane}}}{m_{\text{overall mass}}} \times \frac{m_{\text{Dodecene}}}{m_{\text{Aliquot}}} \times 100}{M_{\text{Docosene}}} \\
\]

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>tetradecane</td>
<td>32.30</td>
</tr>
<tr>
<td>1-dodecene</td>
<td>18.66</td>
</tr>
<tr>
<td>docosene</td>
<td>52.53</td>
</tr>
</tbody>
</table>

3. Synthesis of Imidazolium Salts

3.1. Synthesis of 2-benzhydryl-6-fluoro-4-methylaniline (3a)

A mixture of ZnCl₂ (735 mg, 5.37 mmol, 0.5 equiv.) and concentrated aqueous HCl (35% w/w, 0.98 mL, 32.4 mmol, 3.0 equiv.) was added at 100 °C to 2-fluoro-4-methylaniline (1.22 mL, 10.7 mmol, 1.0 equiv.) and benzhydrol (1.98 g, 10.7 mmol, 1.0 equiv.). The resulting mixture was stirred and heated to 160 °C for 30 minutes. DCM (25 mL) and saturated NaHCO₃ solution (25 mL) were added to create a biphasic mixture which was stirred overnight. Organic layer was extracted and washed with water (2 x 40 mL) and dried over magnesium sulfate then the solvents were evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (Pentane/AcOEt : 80/20) to yield the aniline as a white solid (2.79 g, 89% yield).

\(^1\)H NMR (400 MHz, CDCl₃) δ (ppm) 7.34-7.30 (m, 4H), 7.28-7.23 (m, 2H), 7.14-7.11 (m, 4H), 6.76 (dd, J = 11.4 and 1.9 Hz, 1H), 6.27 (s, 1H), 5.50 (s, 1H), 3.26 (br, 2H), 2.14 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ (ppm) 153.4, 151.0, 142.1, 136.8, 131.6, 131.6, 129.8, 129.7, 129.5, 128.6, 127.7, 127.6, 126.8, 125.6, 125.5, 113.7, 52.1, 20.8. \(^{19}\)F NMR (376 MHz, CDCl₃) δ (ppm) -135.8.
3.2. General procedure for synthesis of imidazolium salts:

The reaction was performed in open vessel under air atmosphere. In a round-bottomed flask were placed alkylamine (1.0 mmol, 1.0 equiv.), cyclooctylamine (1.0 mmol, 1.0 equiv.) and acetic acid (4.5 or 9.0 mmol, 4.5 or 9.0 equiv.) then the mixture was heated at 60 °C for 20 minutes (mixture A). In another round-bottomed flask were placed ZnCl$_2$ (1.5 or 1.2 mmol, 1.5 or 1.2 equiv.), glyoxal (40% w/w, 1.0 mmol, 1.0 equiv.), formaldehyde (37% w/w, 1.0 mmol, 1.0 equiv.) and acetic acid (4.5 or 9.0 mmol, 4.5 or 9.0 equiv.) then the mixture was heated at 60 °C for 20 minutes (mixture B). At the same temperature, mixture B was added to mixture A and the resulting mixture was stirred at 60 °C for 30 minutes then cooled down to room temperature. An aliquot of the crude reaction mixture was taken and a $^1$H NMR was recorded to determine the selectivity of the reaction, which was calculated by integration of characteristic signals of the different compounds. Dichloromethane (50 mL) was added and the organic layer was successively washed with water (100 mL) then brine (2 x 50 mL). The combined aqueous layers were extracted with dichloromethane (50 mL). Water (20 mL) and KBF$_4$ (1.0 mmol, 1.0 equiv.) was added and the resulting mixture was stirred at room temperature for 1 hour. The organic layer was separated, dried over magnesium sulfate, filtered and the solvents were evaporated under reduced pressure. The desired imidazolium salt was isolated by recrystallization in AcOEt.

3-(2-chloro-4,6-dimethylphenyl)-1-cyclooctyl-1H-imidazol-3-ium tetrafluoroborate (4a)

Following the general procedure for the synthesis of imidazolium salts, with 2-chloro-4,6-dimethylaniline (1.00 g, 6.43 mmol), cyclooctylamine (880 µL, 6.43 mmol), ZnCl$_2$ (1.05 g, 7.70 mmol), glyoxal (740 µL, 6.43 mmol), formaldehyde (480 µL, 6.43 mmol), acetic acid (3.30 mL, 57.8 mmol, 9 equiv.) (selectivity imidazolium salt-OAc/bisC$_8$-OAc/bisaniline-OAc = 97/03/00) and KBF$_4$ (809 mg, 6.43 mmol) the desired product was isolated as a white solid (1.64 g, 63% yield, mp = 158 °C) after recrystallization in AcOEt.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.04 (s, 1H), 7.58 (s, 1H), 7.23 (s, 1H), 7.12 (s, 1H), 4.96-4.89 (m, 1H), 2.38 (s, 3H), 2.17-2.05 (m, 7H), 1.84-1.59 (m, 11H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 142.9, 137.1, 136.4, 130.9, 130.7, 128.5, 123.9, 120.8, 122.9, 62.3, 33.9, 33.4, 26.3, 25.4, 23.8, 21.2, 17.7. $^1$B NMR (128 MHz, CDCl$_3$) δ (ppm) -0.9. $^{19}$F NMR (376 MHz,
CDCl₃ δ (ppm) -151.7, -151.8. HRMS (ESI) calcd. for C₁₉H₂₆N₂⁺Cl: m/z 317.1779, found: 317.1781 (1 ppm).

3-(2-benzhydryl-6-fluoro-4-methylphenyl-1-cycloctyl-1H-imidazol-3-ium tetrafluoroborate (4b)

Following the general procedure for the synthesis of imidazolium salts, 2-benzhydryl-6-fluoro-4-methylaniline (1.00 g, 3.43 mmol), cyclooctylamine (470 µL, 3.43 mmol), ZnCl₂ (701 mg, 5.14 mmol), glyoxal (400 µL, 3.43 mmol), formaldehyde (260 µL, 3.43 mmol), acetic acid (7.00 mL, 61.7 mmol, 18.0 equiv.) (selectivity imidazolium salt-OAc/bisC₈OAc/bisaniline-OAc = 97/03/00) and KBF₄ (432 mg, 3.43 mmol) the desired product was isolated as a white solid (1.14 g, 62% yield, mp = 185 °C) after recrystallization in AcOEt.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.77 (t, J = 1.7 Hz, 1H), 7.28-7.19 (m, 7H), 7.04-6.99 (m, 5H), 6.72 (t, J = 1.7 Hz, 1H), 6.57 (s, 1H), 5.54 (s, 1H), 4.75-4.67 (sept, 1H), 2.31 (s, 3H), 2.04-1.87 (m, 4H), 1.75-1.58 (m, 10H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 158.4, 155.9, 143.7, 142.9, 140.9, 136.4, 129.5, 129.2, 128.2, 127.3, 127.2, 126.3, 124.5, 119.6, 119.0, 115.7, 115.6, 62.0, 51.6, 33.6, 26.2, 25.4, 23.8, 21.9. ¹¹B NMR (128 MHz, CDCl₃) δ (ppm) -0.8. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -123.4, -129.8, -151.2, -151.2. HRMS (ESI) calcd. for C₃₁H₃₄N₂F: m/z 453.27005, found: 453.2704 (1 ppm).

Single-crystals of 4b were obtained by slow diffusion between dichloromethane and pentane. CCDC 19378686

4. Synthesis of bis-NHC complexes

4.1 General procedure for synthesis of bis-NHC complexes:

To a suspension of imidazolium salt (1.5 or 2.5 equiv.) in dry toluene (0.1 M) stored in a schlenk was added a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (1.4 or 2.5 equiv.). The mixture was stirred 30 minutes at room temperature. Commercial Dichloro(3-phenyl-1H-inden-1-ylidene)bis(triphenylphosphine)ruthenium(II) M10 or [1,3-Bis(2,4,6-trimethylphenyl)
-2-imidazolidinylidene)dichloro(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine) ruthenium(II) M2 ruthenium complexes (1.0 equiv.) was then added in one portion to the schlenk and the resulting mixture was stirred at 40 °C or 100 °C under argon atmosphere until TLC analysis showed complete conversion. After evaporation of the solvents, the crude material was purified by flash chromatography on silica gel using a mixture of Pentane/Et₂O (9/1 to 7/3). The desired complex was collected as a red solid.

(Cyclooctyl-IMes)(SIMes)RuCl₂(3-phenylindenylid-1-ene) (Ru-1b)

Following the general procedure for the synthesis of bis-carbene complexes with 3-cyclooctyl-1-mesitylimidazolium tétrafluoroborate (308 mg, 0.80 mmol, 1.5 equiv.), 0.5 M KHMDS solution in toluene (1.60 mL, 0.80 mmol, 1.5 equiv.) and commercial M2 (505 mg, 0.53 mmol, 1.0 equiv.) in toluene (4.40 mL, c = 0.1 M) at 100 °C, the desired product was obtained as a red solid (281 mg, 55% yield).

\[ \text{Ru-1b} \]

\[ \text{C}_{16} \text{H}_{27} \text{Cl}_{14} \text{N}_{16} \text{Ru} \]

\[ 965.13 \text{ g/mol} \]

\[ ^1H \text{ NMR (400 MHz, CD}_2\text{Cl}_2) \delta (ppm) 8.31 \text{ (dd, } J = 7.4, 1.3 \text{ Hz, } 1\text{H, H}_29), 7.76 \text{ (dd, } J = 8.3, 1.2 \text{ Hz, } 2\text{H, H}_32), 7.57 \text{ (tt, } J = 7.4, 1.2 \text{ Hz, } 1\text{H, H}_34), 7.46 \text{ (tt, } J = 7.5, 1.4 \text{ Hz, } 2\text{H, H}_33), 7.18 \text{ (d, } J = 1.8 \text{ Hz, } 1\text{H, H}_46), 7.17 \text{ (s, } 1\text{H, H}_3), 7.16 \text{ (s, } 1\text{H, H}_3), 7.15 \text{ (td, } J = 7.4, 1.3 \text{ Hz, } 1\text{H, H}_27), 7.05 \text{ (s, } 1\text{H, H}_23), 7.08 \text{ (td, } J = 7.4, 1.4 \text{ Hz, } 1\text{H, H}_26), 6.51 \text{ (d, } J = 1.8 \text{ Hz, } 1\text{H, H}_45), 6.25 \text{ (s, } 1\text{H, H}_14), 6.21 \text{ (s, } 1\text{H, H}_38), 5.83 \text{ (s, } 1\text{H, H}_16), 5.81 \text{ (s, } 1\text{H, H}_40), 4.94-4.87 \text{ (m, } 1\text{H, H}_47), 3.91-3.82 \text{ (m, } 2\text{H, H}_11), 3.72 \text{ (t, } J = 9.5 \text{ Hz, } 1\text{H, H}_10), 3.62 \text{ (t, } J = 9.5 \text{ Hz, } 1\text{H, H}_11), 2.72 \text{ (s, } 3\text{H, H}_8), 2.71 \text{ (s, } 3\text{H, H}_7), 2.48 \text{ (s, } 3\text{H, H}_6), 2.17-1.97 \text{ [m, } 4\text{H: 2.09 (s, } 3\text{H, H}_19) \text{ and } 1\text{H, CH}_2 \text{ of cyclooctyl}], 1.89-1.74 \text{ [m, } 18\text{H: 1.89 (s, } 3\text{H, H}_18), 1.77 \text{ (s, } 3\text{H, H}_44), 1.76 \text{ (s, } 3\text{H, H}_26), 1.74 \text{ (s, } 3\text{H, H}_43), \text{ and } 6\text{H, CH}_2 \text{ of cyclooctyl}], 1.59-1.45 \text{ [m, } 9\text{H: 1.53 (s, } 3\text{H, H}_42) \text{ and } 6\text{H, CH}_2 \text{ of cyclooctyl}], 1.33-1.18 \text{ (m, } 1\text{H, CH}_2 \text{ of cyclooctyl}). \]

\[ ^{13}C \text{ NMR (101 MHz, CD}_2\text{Cl}_2) \delta (ppm) 292.2 \text{ (Cq, C}_22\text{), 220.0 (Cq, C}_21\text{), 183.2 (Cq, C}_35\text{), 143.9 (Cq, C}_30\text{), 140.0 (Cq, C}_25\text{), 139.0 (Cq, C}_2\text{, C}_6\text{), 138.2 (Cq, C}_4\text{), 137.6 (Cq, C}_31\text{), 137.3 (Cq, Mesityl), 137.1 (Cq, C}_39\text{), 137.0 (Cq, Mesityl), 136.4 (Cq, Mesityl), 136.3 (Cq, Mesityl), 136.2} \]

S7
Both Methyl 7 and 8 of Mesityl A as well as Methyl 18 and 19 of Mesityl B show dipolar coupling with proton H\textsubscript{23} by ROESY. This can be explained by a rotation around the Ru-C\textsubscript{21} axis. This hypothesis is confirmed by the existing exchange cross peak between the Methyl 7 and 8 of Mesityl A and Methyl 18 and 19 of Mesityl B (see Figure S42 and S43).

(Cyclooctyl-chloromesityl)\textsubscript{2}RuCl\textsubscript{2}(3-phenylindenylid-1-ene) (Ru-1c)

Following the general procedure for the synthesis of bis-carbene complexes with imidazolium salt 4a (567 mg, 1.40 mmol, 2.5 equiv.), 0.5 M KHMDS solution in toluene (2.80 mL, 1.40 mmol, 2.5 equiv.) and commercial M10 (503 mg, 0.57 mmol, 1.0 equiv) in toluene (5.60 mL, c = 0.1 M) at 40 °C, the desired product was obtained as a red solid (320 mg, 57% yield).
$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 250 K) δ (ppm) 294.8-294.1 (4Cq, C$_{13}$, 2 major forms: 294.6, 294.1 and 2 minor forms: 294.8 and 294.5), 177.6-174.5 (8Cq, C$_{11}$, C$_{26}$, 2 major: 177.3, 176.6, 175.7, 175.3 and 2 minor forms: 177.6, 177.5, 174.6, 174.5), 144.6-144.3 (4Cq, C$_{15}$, 2 major forms: 144.6, 144.5 and 2 minor forms: 144.4, 144.3), 141.6-140.7 (8Cq, C$_{16}$, 2 major forms: 141.1, 141.08, 140.9, 140.7 and 2 minor forms: 141.6, 141.5, 141.2, 141.06), 139.6-136.37 (28CH, Ar, 2 major and 2 minor forms: 139.6, 139.4, 139.39, 139.38, 139.2, 139.1, 138.8, 138.4, 138.38, 138.2, 138.0, 137.98 (C$_{14}$), 137.88 (C$_{14}$), 137.83 (C$_{14}$), 137.7 (C$_{14}$), 137.6, 137.33, 137.30, 137.27, 137.01, 136.99, 136.84, 136.82, 136.7, 136.58, 136.57, 136.45, 136.37), 134.6-133.8 (4Cq, C$_{21}$, 2 major and minor forms: 134.6, 134.4, 134.3, 133.8), 133.06-126.12 (56CH, Ar, 2 major and 2 minor forms: 133.06, 133.03, 132.91, 132.87, 132.2, 132.08, 132.06, 132.05, 131.97, 131.9, 131.8, 131.72, 130.70, 130.4, 130.0, 129.91, 129.86, 129.8, 129.54, 129.48, 129.45, 129.37, 129.35, 129.32, 129.29, 129.23, 129.21, 129.04, 129.03, 128.97, 128.7, 128.6, 128.5, 128.41, 128.37, 128.29, 128.28, 128.2, 127.9, 127.8, 127.7, 127.53, 127.47, 127.45, 127.21, 127.19, 127.15, 127.07, 126.3, 126.22, 126.18, 126.12), 123.0-122.5 (8CH, C$_9$, C$_{36}$, 2 major and 2 minor: 123.0, 122.9, 122.89, 122.85, 122.84, 122.83, 122.7, 122.5), 118.1-117.5 (8CH, C$_{16}$, C$_{35}$, 2 major and 2 minor: 118.1, 118.0, 117.9, 117.8, 117.77, 117.7, 117.6, 117.5), 58.5 (bs, C$_{12}$), 58.2 (bs, C$_{17}$), 37.0-36.3 (bs, CH$_2$ of cyclooctyl), 33.25 (bs, CH$_2$ of cyclooctyl), 27.3-22.9 (bs, CH$_2$ of cyclooctyl), 21.1-21.0 (CH$_3$ of Mesityl), 20.1-19.9 (CH$_3$ of Mesityl).

HRMS (ESI) calcd. for C$_{53}$H$_{60}$N$_4$Cl$_4$Ru$^{[M]^+}$: m/z 994.26101, found : 994.2614 (0 ppm).
Following the general procedure for the synthesis of bis-carbene complexes with imidazolium salt 4b (764 mg, 1.41 mmol, 2.5 equiv.), 0.5 M KHMDS solution in toluene (2.82 mL, 1.41 mmol, 2.5 equiv.) and commercial M10 (500 mg, 0.56 mmol, 1.0 equiv.) in toluene (5.60 mL, c = 0.1 M) at 40 °C, the desired product was obtained as a red solid (350 mg, 52% yield).

\[ \text{Ru-1d} \]

\[
\begin{align*}
\text{C}_7\text{H}_{77}\text{Cl}_2\text{F}_2\text{N}_4\text{Ru} \\
1267.45 \text{ g mol}^{-1}
\end{align*}
\]

\( ^1H \text{ NMR (500 MHz, C}_2\text{D}_6, 300 K) \) δ (ppm) 9.14-8.84 [1H, H₃₂, 1 major form: 9.14 (d, J = 7.2 Hz) and 1 minor form: 8.84 (d, J = 7.3 Hz)], 8.18-5.50 [39H, Ar, insaturated protons: H₂₁, H₂₂, H₆₁, H₆₂ and H₂₆, H₃₀, H₃₁, H₈₈, H₄₈, H₂₃ or 6₃], 3.75-3.64 (m, 1H, CH, H₂₃, H₆₃), [3.30-3.15 (CH₂), 2.56-2.47 (m, CH₂ of cyclooctyl and CH₃)].

\( ^{13}C \text{ NMR (126 MHz, C}_6\text{D}_6, 300 K) \) δ (ppm) 293.2 (Cq, C₂₅, major form), 286.4 (Cq, C₂₅, minor form), [180.1, 177.7 (Cq, C₂₄, C₄₀, major form)], [178.1, 176.4 (Cq, C₂₄, C₄₀, minor form)], 160.1, 160.0, 159.8, 158.1, 158.0, 157.7, 156.2, 156.1, 145.5, 144.6, 144.5, 144.2, 144.1, 144.0, 143.8, 143.7, 143.6, 143.1, 142.8, 142.6, 141.8, 140.7, 141.6, 141.2, 139.2, 139.1, 139.0, 138.9, 137.9, 137.7, 137.6, 137.5, 132.1, 132.0, 131.7, 131.2, 130.9, 130.8, 130.7, 130.4, 130.1, 130.0, 129.9, 129.8, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 128.1, 127.3, 127.1, 126.6, 126.5, 126.4, 125.8, 125.4, 125.3, 125.1, 125.0, 123.9, 123.8, 118.1, 117.8, 117.2, 116.4, 116.0, 115.0, 114.8, 114.7, [61.3, 59.0, 58.1, 57.9, 58.9 (CH, C₂₃, C₆₃)], [52.5, 52.4, 52.4, 48.5 (CH, C₈, C₄₈)], [38.6, 36.7, 36.5, 36.1, 36.0, 35.4, 33.2, 31.3, 31.1, 29.8, 28.8, 28.7, 27.2, 27.7, 27.6, 26.4, 26.3, 26.1, 25.9, 25.4, 25.3, 25.1, 24.8, 24.6, 24.4, 24.0, 23.8, 23.6, 23.5, 23.3 (CH₂ of cyclooctyl)], 21.0 (CH₃), 20.9 (CH₃). Many carbons under C₆D₆ can be observed and many others are overlaps.

\( ^{19}F \text{ NMR (471 MHz, C}_6\text{D}_6, 300 K) \) δ (ppm), -119.8 (s, major form), -121.5 (s, major form), -121.8 (d, J = 13.3, minor form), -121.9 (d, J = 13.3, minor form).
HRMS (ESI) calcd. for C$_{77}$H$_{76}$N$_4$F$_2$Cl$_2$Ru$^{^{102}}$: m/z 1266.44531, found : 1266.4462 (1 ppm).

4.2. General procedure for transmetalation

To a Schlenk apparatus was introduced 1-isopropoxy-2-vinylbenzene (0.07 mmol), activator (0.07 mmol), trimethoxybenzene (0.002 mmol) and dichloromethane (0.7 mL, c = 0.1M) under argon. The complex (0.06 mmol) was added and the mixture was heated at 50 °C. The reaction was monitored by $^1$H NMR (CD$_2$Cl$_2$) until complete conversion. After evaporations of the solvents, the crude material was purified on SiO$_2$ using the gradient of eluent : Pentane/Acetone = 90/10 to 70/10.

4.2.1. Transmetalation process using Copper(I) chloride.

4.2.1.1. Transmetalation process between Cu(I)Cl and Ru-1a

Following the general procedure at 50 °C for transmetalation reactions with the Ru-1a complex (57.8 mg, 0.06 mmol, 1 equiv.), 1-isopropoxy-2-vinylbenzene (12.3 mg, 0.07 mmol, 1.2 equiv.), CuCl (6.9 mg, 0.07 mg, 1.2 equiv.) in dichloromethane, conversion was determined by $^1$H-NMR (>95% after 5h of reaction). Ru-2a was isolated as a brown solid (33.8 mg, 91% yield) and Cu-1a was isolated as a white solid (20.6 mg, 86% yield).
Figure S2: \(^1\)H-NMR monitoring of Ru-1a Copper (I) transmetalation

(1-cyclooctyl-3-mesityl-2,3-dihydro-1H-imidazol-2-ylidene)(2-isoproxybenzylidene) ruthenium(V) chloride (Ru-2a)

\(^1\)H NMR (400 MHz, \(\text{CD}_2\text{Cl}_2\)): \(\delta\) (ppm) 16.35 (s, 1H), 7.58 (ddd, \(J = 8.5, 7.0, 2.0\) Hz, 1H), 7.27 (d, \(J = 2.1\) Hz, 1H), 7.13 (br. s, 2H), 7.04-6.96 (m, 3H), 6.91-6.89 (m, 1H), 5.68 (tt, \(J = 10.1, 3.3\) Hz, 1H), 5.18 (sep., \(J = 6.1\) Hz, 1H), 2.51 (s, 3H), 2.49-2.40 (m, 2H), 2.10-2.03 (m, 2H), 1.97 (s, 6H), 1.94-1.82 (m, 6H), 1.78 (d, \(J = 6.1\) Hz, 6H), 1.75-1.68 (m, 4H).

\(^{13}\)C NMR (101 MHz, \(\text{CD}_2\text{Cl}_2\)): \(\delta\) (ppm) 287.4, 170.0, 152.8, 144.8, 140.2, 138.0, 129.6, 129.3, 125.5, 123.2, 122.2, 119.5, 113.5, 75.6, 62.9, 36.0, 27.5, 26.6, 25.3, 22.5, 21.6, 18.2.

HRMS (ESI) : m/z : M\(^+\) (\(\text{C}_{30}\text{H}_{40}\text{N}_2\text{OCl}_2\text{Ru}\)) calc.: 616.15557; found: 616.1557 (1 ppm).
Single-crystals of Ru-2a were obtained by slow diffusion between dichloromethane and pentane. CCDC 1937863

(1-cyclooctyl-3-mesityl-2,3-dihydro-1H-imidazol-2-ylidene)copper(II) chloride (Cu-1a)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) 7.15 (s, 1H), 7.00 (s, 2H), 6.88 (s, 1H), 4.68 (sep., $J = 4.1$ Hz, 1H), 2.34 (s, 3H), 2.17-2.03 (m, 4H), 1.99 (s, 6H), 1.90-1.79 (m, 2H), 1.76-1.52 (m, 8H).

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): δ (ppm) 139.9, 136.3, 135.4, 129.7, 122.5, 118.8, 63.0, 35.5, 27.2, 26.4, 25.0, 21.4, 18.1.

4.2.1.2. Transmetalation process between Cu(I)Cl and Ru-1b

Following the general procedure at 50 °C for transmetalation reactions with the Ru-1b complex (59.4 mg, 0.06 mmol 1 equiv.), 1-isoproxy-2-vinylbenzene (12.9 mg, 0.07 mmol, 1.2 equiv.), CuCl (7.4 mg, 0.07 mg, 1.2 equiv.) in dichloromethane, conversion was determined by $^1$H-NMR (>95% after 1h of reaction). Ru-2b was isolated as a green solid (37.0 mg, 95% yield) and Cu-1a was isolated as a white solid (18.4 mg, 75% yield).
(1,3-Bismesityl-2-imidazolidin-2-yl)(2-isopropoxybenzylidene)ruthenium dichloride (Ru-2b)

\[
{^{1}H\text{ NMR (400 MHz, } CD_{2}Cl_{2}) : \delta (ppm) 16.51 (s, 1H), 7.55 (ddd, } J = 7.2, 1.8, 0.8 \text{ Hz, } 1H), 7.07 (s, 4H), 6.96 (dd, } J = 7.6, 1.8 \text{ Hz, } 1H), 6.93-6.88 (m, 1H), 6.84 (d, } J = 8.3 \text{ Hz, } 1H), 4.88 (sep., } J = 6.2 \text{ Hz, } 1H),
4.16 (s, 4H), 2.55-2.30 (m, 18H), 1.23 (d, } J = 6.1 \text{ Hz, } 6H).
\]

\[
{^{13}C\text{ NMR (101 MHz, } CD_{2}Cl_{2}) : \delta (ppm) 296.2, 211.3, 152.5, 145.7, 139.4, 130.0, 129.8, 122.9, 122.7, 113.5, 75.7, 52.1, 21.4, 21.3, 19.7.}
\]

Analytical data for this compound are consistent with the previously reported data\(^3\)

4.2.2. Transmetalation process using Gold(I) chloride.

Following the general procedure at 50 °C for transmetalation reactions with the Ru-1a complex (56.7 mg, 0.06 mmol 1 equiv.), 1-isopropoxy-2-vinylbenzene (11.4 mg, 0.07 mmol, 1.2 equiv.), AuCl (17.2 mg, 0.07 mg, 1.2 equiv.) in dichloromethane, conversion was determined by \(^1\)H-NMR (>69% after 24h of reaction). Ru-2a was isolated as a brown solid (16.2 mg, \textbf{45% yield}) and Au-1a was isolated as a white solid (12.2 mg, \textbf{39% yield}).

---

**Figure S3:** $^1$H-NMR monitoring of Ru-1b Gold (I) transmetalation

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) 7.21 (d, $J = 2.0$ Hz, 1H), 7.02 (br. s, 2H), 6.90 (d, $J = 2.0$ Hz, 1H), 4.68 (sep., $J = 4.8$ Hz, 1H), 2.36 (s, 3H), 2.12-2.05 (m, 4H), 2.01 (s, 6H), 1.90-1.79 (m, 2H), 1.79-1.56 (m, 8H).

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) 171.1, 140.3, 135.8, 135.6, 129.8, 122.7, 118.4, 62.7, 34.7, 27.2, 26.4, 24.9, 22.9, 21.5, 18.1, 14.4.

HRMS (ESI): m/z: [M+Na$^+$] (C$_{20}$H$_{28}$N$_2$ClNaAu) calc.: 551.14988; found: 551.1502 (1 ppm).

Single-crystals of Au-1a were obtained by slow evaporation of a saturated solution in dichloromethane/Pentane. CCDC 1937862
5. General procedure for kinetic studies

Diethylallylmalonate (DEDAM) S1 (48.5 µL, 0.2 mmol), trimethoxybenzene (5.6 mg, 0.033 mmol) as the internal standard and toluene (1.8 mL) were added in a Schlenk tube under argon. The solution was equilibrated at 30 or 80 °C before the activator addition (0.1 mL of a 0.1 M solution of activator, 5 mol%) and catalyst addition (0.1 mL of a 0.02 M solution of catalyst, 1 mol%). Aliquots were taken and the conversion was calculated from $^1$H NMR spectra by comparing the characteristic signal for allylic proton to the internal standard.

Example of $^1$H-NMR spectra at 100 % conversion :

![Figure S4: $^1$H-NMR monitoring of DEDAM S1 RCM](image)
Figure S5: Catalytic activity profiles of complexes Ru-1a (1 mol%) for RCM of DEDAM S1 at 30 °C in toluene (1.8 mL). Conversions were monitored by 1H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).

Figure S6: Catalytic activity profiles of complexes Ru-1a (0.1 mol%) for RCM of DEDAM S1 at 30 °C in toluene (1.8 mL). Conversions were monitored by 1H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 0.5 mol% (orange); AuCl – 0.5 mol% (blue).
**Figure S7**: Catalytic activity profiles of complexes Ru-1a (1mol%) for RCM of DEDAM S1 at 80 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).
**Figure S8:** Catalytic activity profiles of complexes Ru-1b (1 mol%) for RCM of DEDAM S1 at 30 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).

**Figure S9:** Catalytic activity profiles of complexes Ru-1b (1 mol%) for RCM of DEDAM S1 at 80 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).
Figure S10: Catalytic activity profiles of complexes Ru-1c (1 mol%) for RCM of DEDAM S1 at 30 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).

Figure S11: Catalytic activity profiles of complexes Ru-1c (1 mol%) for RCM of DEDAM S1 at 80 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).
Figure S12: Catalytic activity profiles of complexes Ru-1d (1 mol%) for RCM of DEDAM S1 at 30 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).

Figure S13: Catalytic activity profiles of complexes Ru-1d (1 mol%) for RCM of DEDAM S1 at 80 °C in toluene (1.8 mL). Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl – 5 mol% (orange); AuCl – 5 mol% (blue); without activators (black).
6. Scope of Metathesis Transformations

Figure S14: Scope of metathesis transformations catalyzed by Ru-1b, 1c et 1d/ CuCl or AuCl

6.1. Ring Closing Metathesis (RCM)

General Procedure for RCM Reactions:

To a Schlenk apparatus was introduced substrate (0.2 mmol, 1.0 equiv.), 1,3,5-trimethoxybenzene (0.066 mmol, 0.33 equiv.), CuCl (0.01 mmol, 0.05 equiv.) and toluene (2 mL, c = 0.1M) under argon. Precatalyst (0.002 mmol, 0.01 equiv.) was added and the mixture was heated at 30 or 80 °C. Aliquots were taken, quenched with Ethylvinylether and concentrated. The reaction was monitored by 1H NMR (CDCl3) until complete conversion or catalyst death.

S22
Diethyl cyclohex-3-ene-1,1-dicarboxylate (P2)

With Ru-1c - Freshly made solutions in toluene were prepared:

- 60.3 mg of Diethyl 2-allyl-2-(but-3-en-1-yl)malonate in 0.12 mL of toluene.
- 33.1 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 5.3 mg of CuCl in 0.53 mL of toluene.
- 4.8 mg of Ru-1c in 0.24 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(but-3-en-1-yl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by \(^1\)H-NMR. 99% conversion and 99% yield with Ru-1c after 10 min of reaction.

\(^1\)H-NMR spectra with Ru-1c at T0:

[Image of H-NMR spectra]

Internal Standard

[Further details or analysis related to the spectra]
$^1$H-NMR spectra with Ru-1c at 99% conversion and 99% NMR yield [(1.35/1.36) x 100 = 99%] after 10 min of reaction:

With Ru-1d - A freshly made solutions in toluene were prepared:

- 70.3 mg of Diethyl 2-allyl-2-(but-3-en-1-yl)malonate in 0.14 mL of toluene.
- 6.8 mg of CuCl in 0.68 mL of toluene.
- 6.0 mg of Ru-1d in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(but-3-en-1-yl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.063 mmol, 10.6 mg) in Toluene (1.7 mL), conversion was determined by $^1$H-NMR comparing standard peak with internal olefin peak on the starting material. 95% conversion and 92% yield with Ru-1d after 30 min of reaction.

$^1$H-NMR spectra with Ru-1d at T0:
\(^1\)H-NMR spectra with Ru-1d at 95% conversion \([100 - (0.19/4.21) \times 100) = 95\%\) and 92% NMR yield \([(1.82/1.98) \times 100) = 92\%\) after 30 min of reaction:
Diethyl cyclohept-3-ene-1,1-dicarboxylate (P3)

With Ru-1c - Freshly made solutions in toluene were prepared:

- 61.0 mg of Diethyl 2-allyl-2-(pent-4-enyl)malonate in 0.11 mL of toluene.
- 33.1 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 5.3 mg of CuCl in 0.53 mL of toluene.
- 4.8 mg of Ru-1c in 0.24 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(pent-4-enyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR comparing standard peak with internal olefin peak on the starting material. 92% conversion and 83% yield with Ru-1c after 20 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:
$^1$H-NMR spectra with Ru-1c at 92% conversion \([100 - (0.18/2.14) \times 100] = 92\%\) and 83% NMR yield \([(1.75/2.11) \times 100] = 83\%\) after 20 min of reaction:

With Ru-1d - Freshly made solutions in toluene were prepared:

- 62.8 mg of Diethyl 2-allyl-2-(pent-4-enyl)malonate in 0.12 mL of toluene.
- 6.8 mg of CuCl in 0.68 mL of toluene.
- 6.0 mg of Ru-1d in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(pent-4-enyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.071 mmol, 12.0 mg) in Toluene (1.7 mL), conversion was determined by $^1$H-NMR comparing standard peak with internal olefin peak on the starting material. 88% conversion and 78% yield with Ru-1d after 20 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

Internal Standard

$^1$H-NMR spectra with Ru-1d at 88% conversion \[100 - \left(\frac{0.45}{3.72}\right) \times 100 = 88\%\] and 78% NMR yield \[\left(\frac{2.80}{3.60}\right) \times 100 = 78\%\] after 20 min of reaction:

Internal Standard
1-tosyl-2,3,4,7-tetrahydro-1H-azepine (P4)

With Ru-1c - Freshly made solutions in toluene were prepared:

- 67.9 mg of N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide in 0.12 mL of toluene.
- 5.1 mg of CuCl in 0.51 mL of toluene.
- 5.4 mg of Ru-1c in 0.27 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 11.0 mg) in Toluene (1.7 mL), conversion was determined by $^1$H-NMR comparing standard peak with internal olefin peak on the starting material. 91% conversion and 84% yield with Ru-1c after 10 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:

![Internal Standard]
\(^1\)H-NMR spectra with Ru-Ic at 91% conversion \([100 - (0.39/4.14 \times 100) = 91\%]\) and 84% NMR yield \([(1.76/2.10) \times 100) = 84\%\] after 10 min of reaction:

With Ru-I\(d\) - Freshly made solutions in toluene were prepared:

- 67.1 mg of N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide in 0.12 mL of toluene.
- 8.0 mg of CuCl in 0.80 mL of toluene.
- 6.1 mg of Ru-I\(d\) in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-(pent-4-enyl)-4-methylbenzonesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 11.1 mg) in Toluene (1.7 mL), conversion was determined by \(^1\)H-NMR comparing standard peak with internal olefin peak on the starting material. 89% conversion and 89% yield with Ru-I\(d\) after 20 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

$^1$H-NMR spectra with Ru-1d at 89% conversion [100 - (0.45/4.20) x 100] = 89%] and 89% NMR yield [(1.89/2.11) x 100] = 89%] after 20 min of reaction:
1-benzyl-1,3,4,7-tetrahydro-2H-azepin-2-one (P5)

With Ru-1c - Freshly made solutions in toluene were prepared:
- 100.9 mg of N-allyl-N-benzylpent-4-enamide in 0.22 mL of toluene.
- 66.1 mg of 1,3,5-trimethoxybenzene in 0.60 mL of toluene.
- 9.1 mg of CuCl in 0.91 mL of toluene.
- 9.9 mg of Ru-1c in 0.50 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-benzylpent-4-enamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 98% conversion and 90% yield with Ru-1c after 10 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:
\(^1\)H-NMR spectra with Ru-1c at 98% conversion \([100 - (0.06/2.96) \times 100) = 98\%\) and % NMR yield \([(1.30/1.44) \times 100) = 90\%\) after 10 min of reaction:

With Ru-1d - Freshly made solutions in toluene were prepared:

- 67.8 mg of N-allyl-N-benzylpent-4-enamide in 0.15 mL of toluene.
- 9.5 mg of CuCl in 0.95 mL of toluene.
- 7.2 mg of Ru-1d in 0.30 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-N-benzylpent-4-enamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.069 mmol, 11.6 mg) in Toluene (1.7 mL), conversion was determined by \(^1\)H-NMR. 70% conversion and 69% yield with Ru-1d after 20 min of reaction.
^1^H-NMR spectra with Ru-1d at T0:

Internal Standard

^1^H-NMR spectra with Ru-1d at 70% conversion [(100 - (1.16/3.90) x 100) = 70%] and 69% NMR yield [(1.35/1.95) x 100) = 69%] after 20 min of reaction:

Internal Standard
2,5-dihydrobenzo[b]oxepine (P6)

With Ru-1c - Freshly made solutions in toluene were prepared:

- 80.7 mg of 1-allyl-2-(allyloxy)benzene in 0.21 mL of toluene.
- 55.5 mg of 1,3,5-trimethoxybenzene in 0.50 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 5.6 mg of Ru-1c in 0.28 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), 1-allyl-2-(allyloxy)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 99% conversion and 90% yield with Ru-1c after 10 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:

Internal Standard
$^1$H-NMR spectra with Ru-1c at 99% conversion and 90% NMR yield [(1.07/1.19) x 100] = 90%] after 10 min of reaction:

Internal Standard

With Ru-1d - Freshly made solutions in toluene were prepared:
- 80.7 mg of 1-allyl-2-(allyloxy)benzene in 0.21 mL of toluene.
- 55.5 mg of 1,3,5-Trimethoxybenzene in 0.50 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 5.8 mg of Ru-1d in 0.24 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), 1-allyl-2-(allyloxy)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 97% conversion and 89% yield with Ru-1d after 10 min of reaction.

$^1$H-NMR spectra with Ru-1d at T0 :
$^1$H-NMR spectra with Ru-1d at 97% conversion [100 - (0.09/3.24) x 100) = 97%] and 89% NMR yield [(1.56/1.76) x 100) = 89%] after 10 min of reaction:
2-phenyl-3,6-dihydro-2H-pyran (P7)

With Ru-1c - Freshly made solutions in toluene were prepared:
  - 49.3 mg of (1-allyloxy)but-3-en-1yl benzene in 0.13 mL of toluene.
  - 5.1 mg of CuCl in 0.51 mL of toluene.
  - 4.5 mg of Ru-1c in 0.23 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), (1-allyloxy)but-3-en-1yl benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.134 mmol, 22.6 mg) in Toluene (1.7 mL), conversion was determined by $^1$H-NMR. 99% conversion and 99% yield with Ru-1c after 10 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:

Internal Standard
$^1$H-NMR spectra with Ru-Ic at 99% conversion and 99% NMR yield \[\left(\frac{0.47}{0.47} \times 100\right) = 99\%\] after 10 min of reaction:

Internal Standard

With Ru-Id - Freshly made solutions in toluene were prepared:
- 48.1 mg of (1-allyloxy)but-3-en-1-yl)benzene in 0.13 mL of toluene.
- 8.0 mg of CuCl in 0.80 mL of toluene.
- 6.1 mg of Ru-Id in 0.25 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), (1-allyloxy)but-3-en-1-yl)benzene (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.074 mmol, 12.5 mg) in Toluene (1.7 mL), conversion was determined by $^1$H-NMR. 98% conversion and 93% yield with Ru-Id after 30 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

Internal Standard

$^1$H-NMR spectra with Ru-1d at 98% conversion [100 - (0.06/3.26) x 100) = 98%] and 93% NMR yield [(0.75/0.81) x 100) = 93%] after 30 min of reaction:

Internal Standard
Diethyl 3-methylocyclopent-3-ene-1,1-dicarboxylate (P8)

With Ru-1c - Freshly made solutions in toluene were prepared:
- 314.2 mg of diethyl 2-allyl-2-(2-methylallyl)malonate in 0.62 mL of toluene.
- 61.4 mg of 1,3,5-trimethoxybenzene in 0.55 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 6.4 mg of Ru-1c in 0.32 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 99% conversion and 99% yield with Ru-1c after 10 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:

Internal Standard
$^1$H-NMR spectra with Ru-Ic at 99% conversion and 99% NMR yield [(0.75/0.75) x 100) = 99%] after 10 min of reaction:

Internal Standard

With Ru-Id - Freshly made solutions in toluene were prepared:

- 314.2 mg of diethyl 2-allyl-2-(2-methylallyl)malonate in 0.62 mL of toluene.
- 61.4 mg of 1,3,5-trimethoxybenzene in 0.55 mL of toluene.
- 8.4 mg of CuCl in 0.84 mL of toluene.
- 7.3 mg of Ru-Id in 0.30 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2-allyl-2-(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 99% conversion and 93% yield with Ru-Id after 10 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

Internal Standard

$^1$H-NMR spectra with Ru-1d at 99% conversion and 93% NMR yield [(0.77/0.82) x 100] = 94%] after 10 min of reaction:

Internal Standard

S43
With Ru-1c - Freshly made solutions in toluene were prepared:

- 233.4 mg of N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide in 0.44 mL of toluene.
- 69.8 mg of 1,3,5-trimethoxybenzene in 0.63 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 6.3 mg of Ru-1c in 0.32 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 99% conversion and 96% yield with Ru-1c after 20 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:

Internal Standard
\(^1\)H-NMR spectra with Ru-1c at 99% conversion and 96% NMR yield \([(0.64/0.67) \times 100) = 96\%]\) after 20 min of reaction:

Internal Standard

With Ru-1d - Freshly made solutions in toluene were prepared:

- 233.4 mg of N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide in 0.44 mL of toluene.
- 69.8 mg of 1,3,5-trimethoxybenzene in 0.63 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 5.5 mg of Ru-1d in 0.23 mL of toluene.

Following the general procedure at 30 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by \(^1\)H-NMR. 99% conversion and 92% yield with Ru-1d after 10 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

Internal Standard

$^1$H-NMR spectra with Ru-1d at 99% conversion and 92% NMR yield [(0.67/0.73) x 100) = 92%] after 10 min of reaction:

Internal Standard
3,4-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrole (P10)

With Ru-1c - Freshly made solutions in toluene were prepared:

- 78.5 mg of 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide in 0.14 mL of toluene.
- 20.7 mg of 1,3,5-trimethoxybenzene in 0.19 mL of toluene.
- 5.5 mg of CuCl in 0.55 mL of toluene.
- 3.3 mg of Ru-1c in 0.17 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 42% conversion and 38% yield with Ru-1c after 30 min of reaction.

$^1$H-NMR spectra with Ru-1c at T0:
\(^1\)H-NMR spectra with Ru-1c at 42% conversion \([100 - (1.88/3.24) \times 100) = 42\%\) and 38% NMR yield \([(1.22/3.24) \times 100) = 38\%\) after 30 min of reaction:

![Internal Standard](image)

With Ru-1d - Freshly made solutions in toluene were prepared:
- 66.4 mg of 4-methyl-N,N-bis(2-methylallyl)benzenesulfonamide in 0.12 mL of toluene.
- 9.6 mg of CuCl in 0.96 mL of toluene.
- 4.4 mg of Ru-1d in 0.18 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), N-allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.077 mmol, 12.9 mg) in Toluene (1.7 mL), conversion was determined by \(^1\)H-NMR. 62% conversion and 61% yield with Ru-1d after 30 min of reaction.
$^1$H-NMR spectra with Ru-1d at T0:

$^1$H-NMR spectra with Ru-1d at 62% conversion [(100 - (1.48/3.93) x 100) = 62%] and 61% NMR yield [(2.41/3.93) x 100) = 61%] after 30 min of reaction:
Diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (P11)

With Ru-1c - Freshly made solutions in toluene were prepared:
- 127.1 mg of diethyl 2,2-bis(2-methylallyl)malonate in 0.24 mL of toluene.
- 33.3 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 7.3 mg of CuCl in 0.73 mL of toluene.
- 4.1 mg of Ru-1c in 0.21 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2,2-bis(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-Trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 0% conversion and 0% yield with Ru-1c after 30 min of reaction.

With Ru-1d - Freshly made solutions in toluene were prepared:
- 127.1 mg of diethyl 2,2-bis(2-methylallyl)malonate in 0.24 mL of toluene.
- 33.3 mg of 1,3,5-Trimethoxybenzene in 0.30 mL of toluene.
- 7.3 mg of CuCl in 0.73 mL of toluene.
- 3.8 mg of Ru-1d in 0.16 mL of toluene.

Following the general procedure at 80 °C for metathesis reactions with the desired precatalyst (0.002 mmol, 0.1 mL), diethyl 2,2-bis(2-methylallyl)malonate (0.2 mmol, 0.1 mL), CuCl (0.01 mmol, 0.1 mL) and 1,3,5-trimethoxybenzene (0.066 mmol, 0.1 mL) in Toluene (1.6 mL), conversion was determined by $^1$H-NMR. 0% conversion and 0% yield with Ru-1d after 30 min of reaction.
6.2. Self-Metathesis (SM)

General procedure for Self-Metathesis

\[
\text{Ru-Cat (X mol\%)} \quad \text{AuCl (X mol\%)} \quad \text{neat - 20 min} \quad \text{60°C}
\]

Alcene (1.0 equiv.) was added under Ar to a dry schlenk containing solid complex (0.001 equiv.) and internal standard (0.00002 equiv.). The reaction was initiating upon addition of activator (0.001 equiv.). The resulting mixture was allowed to stir at 60°C for 20 minutes. Aliquots of reactions (approximately 45 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

Self Metathesis of 1-dodecene with Ru-1c

1-dodecene (2 mL, 9.0 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-1c (22.5 mg, 0.023 mmol, 0.0025 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.028 equiv.). The reaction was initiating upon addition of CuCl (2.8 mg, 0.009 mmol, 0.003 equiv.). Aliquots of reactions (43.4 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.
GC trace of P12 with Ru-1c

Figure S15: GC Chromatogram of P12 with Ru-1c and CuCl: Selectivity 69%

Self Metathesis of 1-dodecene with Ru-1d

1-dodecene (2 mL, 9.0 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-1d (11.4 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of CuCl (2.3 mg, 0.023 mmol, 0.0025 equiv.). Aliquots of reactions (42.5 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.
GC trace P12 Ru-1d

Figure S16: GC Chromatogram of P12 with Ru-1d and CuCl: Selectivity 24%

Self Metathesis of 1-dodecene with Ru-1c

1-dodecene (2 mL, 9.0 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-1c (9.2 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of AuCl (2.3 mg, 0.009 mmol, 0.001 equiv.). Aliquots of reactions (46.4 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.
**GC trace of P12 with Ru-1c**

![Chromatogram of P12 with Ru-1c](image)

**Peak Table**

<table>
<thead>
<tr>
<th>SFID1</th>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Area%</th>
<th>Height</th>
<th>Height%</th>
<th>Resolution(JP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>17.81</td>
<td>26557</td>
<td>1658</td>
<td>0.3</td>
<td>0.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18.66</td>
<td>136374</td>
<td>20508</td>
<td>1.7</td>
<td>2.0</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>19.71</td>
<td>13032</td>
<td>1625</td>
<td>0.2</td>
<td>0.2</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>50.46</td>
<td>8826</td>
<td>613</td>
<td>0.1</td>
<td>0.1</td>
<td>109.18</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>51.45</td>
<td>33412</td>
<td>2802</td>
<td>0.4</td>
<td>0.3</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>52.53</td>
<td>7758212</td>
<td>1008804</td>
<td>97.3</td>
<td>97.4</td>
<td>5.34</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>7976414</td>
<td>1036009</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

**Figure S17: GC Chromatogram of P12 with Ru-1c**

Calculation detail:

\[
\text{Yield of 1-Docosene} = \frac{[(0.7499*(7758212/280611)-0.6522) \times \left(\frac{46.4*19}{1565.6}\right) \times \left(\frac{1516/46.4}{308.6}\right)}{\left(\frac{758/168.32}{2}\right)} \times 100 = 67 \%
\]

**Figure S18: GC Chromatogram of P12 with Ru-1c: Selectivity >97%**
Self Metathesis of 1-dodecene with Ru-1d

1-dodecene (2 mL, 9.0 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-1d (11.3 mg, 0.009 mmol, 0.001 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00002 equiv.). The reaction was initiating upon addition of AuCl (2.4 mg, 0.009 mmol, 0.001 equiv.). Aliquots of reactions (47.7 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.

GC trace of P12 Ru-1d

Calculation detail:

Yield of 1-Docosene = [((0.7499*(11454487/322470)-0.6522) * ((47.7*19)/1570.3) * (1516/47.7)/308.6] / [(758/168.32)/2]]* 100 = 69 %
Figure S20: GC Chromatogram of P12 with Ru-1d: Selectivity >97%

Self Metathesis of 1-dodecene with Ru-1b

1-dodecene (1 mL, 4.50 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing solid complex Ru-1b (21.8 mg, 0.022 mmol, 0.005 equiv.) and internal standard tetradecane (25 µL, 0.0002 mmol, 0.00004 equiv.). The reaction was initiating upon addition of AuCl (27.7 mg, 0.119 mmol, 0.026 equiv.). Aliquots of reactions (49.5 mg) were taken, filtered through syringe filter (0.2 µm, 25 mm) and rinsed with 1.5 mL of ether. The resulting solution was analyzed by GC.
GC trace of P12 with Ru-1b

**Figure S21: GC Chromatogram of P12 with Ru-1b**

Calculation detail:

Yield of 1-Docosene = \[\frac{[(0.7499 \times \frac{1655045}{271217}) - 0.6522] \times \frac{(49.5 \times 19)}{826.5} \times \frac{(758/49.5)}{308.6}}{[(758/168.32)/2]} \times 100 = 10\% \]
Self Metathesis of 11-bromoundecene with Ru-1c

A stock solution of Ru-1c complex (5 mg) in toluene (300 µL) was prepared under argon. A stock solution of AuCl (2.7 mg) in toluene (500 µL) was prepared in toluene.

11-bromoundecene (94.7 mg, 0.41 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing internal standard 1,2,3-trimethoxybenzene (23.1 mg, 0.137 mmol, 0.33 equiv.). 24 µL of the freshly stock solution of complex Ru-1c was added. The reaction was initiating upon addition of 17 µL of the freshly stock solution of AuCl). First aliquot of reactions was taken and filtered through syringe filter (0.2 µm, 25 mm), rinsed with CDCl₃ (0.5mL) and then analyzed by ¹H NMR. After evaporation of solvent, the aliquot was diluted with Et₂O (1.5 mL) and analyzed by GC.
$^1$H-NMR spectra with Ru-1c at T0:

*Figure S23: $^1$H-NMR of P13: T0*

$^1$H-NMR spectra with Ru-1c at T20min:

*Figure S24: $^1$H-NMR of P13 with Ru-1c at T20min*
Yield of 1,20-dibromoicos-10-ene = (0.50/0.92) X 100= 54%

GC trace of P13 with Ru-1c

![Chromatogram]

### Peak Table

<table>
<thead>
<tr>
<th>Peak#</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
<th>Height%</th>
<th>Resolution(JP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56.25</td>
<td>2777</td>
<td>386</td>
<td>0.3</td>
<td>0.2</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>56.89</td>
<td>51247</td>
<td>6729</td>
<td>4.6</td>
<td>3.1</td>
<td>3.52</td>
</tr>
<tr>
<td>3</td>
<td>57.63</td>
<td>1050817</td>
<td>211837</td>
<td>95.1</td>
<td>96.8</td>
<td>5.50</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1104841</td>
<td>218952</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

**Figure S25:** GC Chromatogram of P13 with Ru-1c: Selectivity >95%

**Self Metathesis of 11-bromoundecene with Ru-1d**

A stock solution of Ru-1c complex (5 mg) in toluene (300 µL) was prepared under argon. A stock solution of AuCl (2.7 mg) in toluene (500 µL) was prepared in toluene.

11-bromoundecene (95.9 mg, 0.41 mmol, 1.0 equiv.) was added under Ar to a dry schlenk containing internal standard 1,2,3-trimethoxybenzene (22 mg, 0.131 mmol, 0.33 equiv.). 31 µL
of the freshly stock solution of complex Ru-1d was added. The reaction was initiating upon addition of 17 µL of the freshly stock solution of AuCl. First aliquot of reactions was taken and filtered through syringe filter (0.2 µm, 25 mm), rinsed with CDCl₃ (0.5mL) and then analyzed by ¹H NMR. After evaporation of solvent, the aliquot was diluted with Et₂O (1.5 mL) and analyzed by GC.

¹H-NMR spectra with Ru-1d at T0:

Figure S26: ¹H-NMR of P13: T0
$^1$H-NMR spectra with Ru-1c at T20min:

![NMR Spectra](image)

Figure S2: $^1$H-NMR of P13 with Ru-1d at T20min

Yield of **1,20-dibromoicos-10-ene** = (0.71/0.99) × 100 = 72%
GC trace of P13 with Ru-1d

Figure S28: GC Chromatogram of P13 with Ru-1d: Selectivity >95%
7. NMR Spectra

7.1. NHC Precursors

Figure S29: $^1$H NMR (400 MHz, CDCl$_3$) of 3a
Figure S30: $^{13}$C NMR (101 MHz, CDCl$_3$) of 3a

Figure S31: $^{19}$F NMR (376 MHz, CDCl$_3$) of 3a
Figure S32: $^1$H NMR (400 MHz, CDCl$_3$) of 4a

Figure S33: $^{13}$C NMR (101 MHz, CDCl$_3$) of 4a
Figure S34: $^{11}$B NMR (128 MHz, CDCl$_3$) of 4a

Figure S35: $^{19}$F NMR (376 MHz, CDCl$_3$) of 4a
Figure S36: $^1$H NMR (400 MHz, CDCl$_3$) of 4b

Figure S37: $^{13}$C NMR (101 MHz, CDCl$_3$) of 4b
Figure S38: $^{11}$B NMR (128 MHz, CDCl$_3$) of 4b

Figure S39: $^{19}$F NMR (376 MHz, CDCl$_3$) of 4b
7.2. Ruthenium Complexes

Figure S40: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of Ru-1b

Figure S41: $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) of Ru-1b
Figure S42: ROESY NMR of Ru-1b

Figure S43: ROESY NMR of Ru-1b
Figure S44: COSY NMR of Ru-1b

Figure S45: HMBC NMR of Ru-1b
Figure S46: HSQCed NMR of Ru-1b

Figure S47: $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 250 K) of Ru-1c
Figure S48: $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 250 K) of Ru-1c

Figure S49: COSY NMR of Ru-1c
Figure S50: HMBC NMR of Ru-1c

Figure S51: HSQCed NMR of Ru-1c
**Figure S52:** ROESY NMR of Ru-1c

**Figure S53:** $^1$H NMR (500 MHz, C$_6$D$_6$, 300 K) of Ru-1d
Figure S54: $^{13}$C NMR (500 MHz, C$_6$D$_6$, 300 K) of Ru-1d

Figure S55: $^{19}$F NMR (471 MHz, C$_6$D$_6$, 300 K) of Ru-1d
Figure S56: COSY NMR of Ru-1d

Figure S57: HMBC NMR of Ru-1d
Figure S58: HSQCed NMR of Ru-1d

Figure S59: ROEY NMR of Ru-1d
Figure S60: COSY $^1H$-$^{19}F$ NMR of Ru-Id

Figure S61: NOESY $^{19}F$-$^{19}F$ NMR of Ru-Id
Figure S62: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of Ru-2a

Figure S63: $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) of Ru-2a
Figure S64: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of Cu-1a

Figure S65: $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) of Cu-1a
Figure S66: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of Ru-2b

Figure S67: $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) of Ru-2b
Figure S68: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of Au-1a

Figure S69: $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) of Au-1a
Figure S70: Catalytic activity profiles of complex M71 SIPr (1 mol%) for RCM of DEDAM S1 at 30 °C. Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl 5 mol% (orange); without activator (black).

Figure S71: Catalytic activity profiles of complex Grela SIPr (1 mol%) for RCM of DEDAM S1 at 30 °C. Conversions were monitored by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. CuCl 5 mol% (orange); without activator (black).
# 8. X-Ray crystallographic data

## X-Ray structure of 4b

![Diagram of 4b](image)

<table>
<thead>
<tr>
<th><strong>Table S1: Crystal data and structure refinement for 4b</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>$\alpha$</td>
</tr>
<tr>
<td>$\beta$</td>
</tr>
<tr>
<td>$\gamma$</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
</tr>
<tr>
<td><strong>Z, Calculated density</strong></td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
</tr>
<tr>
<td><strong>Crystal color</strong></td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
</tr>
<tr>
<td>h$<em>{\text{min}}$, h$</em>{\text{max}}$</td>
</tr>
<tr>
<td>k$<em>{\text{min}}$, k$</em>{\text{max}}$</td>
</tr>
<tr>
<td>l$<em>{\text{min}}$, l$</em>{\text{max}}$</td>
</tr>
<tr>
<td><strong>Reflections collected / unique</strong></td>
</tr>
<tr>
<td><strong>Reflections [I&gt;2\sigma]</strong></td>
</tr>
<tr>
<td><strong>Completeness to theta_max</strong></td>
</tr>
<tr>
<td><strong>Absorption correction type</strong></td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
</tr>
<tr>
<td><strong>R$^1$ (Goodness-of-fit)</strong></td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2\sigma]</strong></td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
</tr>
</tbody>
</table>
X-Ray structure of Ru-1b

Table S2: Crystal data and structure refinement for Ru-1b

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{58}H_{64}Cl_{2}N_{4}Ru</td>
</tr>
<tr>
<td>Formula weight</td>
<td>965.08 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>150 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>monoclinic, P 2_1/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 19.709(2) Å, b = 35.361(4) Å, c = 16.4229(17) Å, α = 90 °, β = 104.021(4) °</td>
</tr>
<tr>
<td>Volume</td>
<td>11105(2) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.155 g.cm⁻³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.415 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>4048</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.320 x 0.210 x 0.160 mm</td>
</tr>
<tr>
<td>Crystal color</td>
<td>red</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.149 to 27.510 °</td>
</tr>
<tr>
<td>h_min, h_max</td>
<td>-25, 25</td>
</tr>
<tr>
<td>k_min, k_max</td>
<td>-45, 45</td>
</tr>
<tr>
<td>l_min, l_max</td>
<td>-21, 21</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>97591 / 25363 [R(int)²=0.0372]</td>
</tr>
<tr>
<td>Reflections [I&gt;2σ]</td>
<td>21968</td>
</tr>
<tr>
<td>Completeness to theta_max</td>
<td>0.993</td>
</tr>
<tr>
<td>Absorption correction type</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.936, 0.791</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>25363 / 2 / 1016</td>
</tr>
<tr>
<td>bS (Goodness-of-fit)</td>
<td>1.036</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ]</td>
<td>R1c = 0.0745, wR2d = 0.1900</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1c = 0.0843, wR2d = 0.1981</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.850 and -1.597 e⁻.Å⁻³</td>
</tr>
</tbody>
</table>
X-Ray structure of complexe Ru-2a

Table S3: Crystal data and structure refinement for Ru-2a

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{30}$H$</em>{40}$Cl$_2$N$_2$ORu</td>
</tr>
<tr>
<td>Formula weight</td>
<td>616.61 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>orthorhombic, $Pbcn$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 11.861(19) Å, b = 14.803(2) Å, c = 33.715(4) Å, α = 90 °, β = 90 °, γ = 90 °</td>
</tr>
<tr>
<td>Volume</td>
<td>5919.6(14) Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>8, 1.384 g.cm$^{-3}$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.735 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>2560</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.460 x 0.260 x 0.090 mm</td>
</tr>
<tr>
<td>Crystal color</td>
<td>black</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.965 to 27.481 °</td>
</tr>
<tr>
<td>h_min, h_max</td>
<td>-15, 13</td>
</tr>
<tr>
<td>k_min, k_max</td>
<td>-19, 18</td>
</tr>
<tr>
<td>l_min, l_max</td>
<td>-41, 43</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>51163 / 6766 [R(int)$^a$ = 0.0352]</td>
</tr>
<tr>
<td>Reflections [I&gt;2σ]</td>
<td>6113</td>
</tr>
<tr>
<td>Completeness to theta_max</td>
<td>0.996</td>
</tr>
<tr>
<td>Absorption correction type</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.936, 0.773</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6766 / 0 / 330</td>
</tr>
<tr>
<td>$b$S (Goodness-of-fit)</td>
<td>1.143</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ]</td>
<td>R1$^c$ = 0.0373, wR2$^d$ = 0.0879</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1$^c$ = 0.0429, wR2$^d$ = 0.0903</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.889 and -0.818 e$^-$.Å$^{-3}$</td>
</tr>
</tbody>
</table>
X-Ray structure of complexe Au-1a

![X-Ray structure of complexe Au-1a](image)

**Table S4: Crystal data and structure refinement for Au-1a**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{20}H_{28}AuClN_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>528.86 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>monoclinic, P 2_1/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.5726(16) Å</td>
</tr>
<tr>
<td></td>
<td>b = 10.5813(19) Å</td>
</tr>
<tr>
<td></td>
<td>c = 20.181(3) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90 °</td>
</tr>
<tr>
<td></td>
<td>β = 97.631(6) °</td>
</tr>
<tr>
<td></td>
<td>γ = 90 °</td>
</tr>
<tr>
<td>Volume</td>
<td>2026.1(6) Å^3</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.734 g.cm^−3</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>7.397 mm^−1</td>
</tr>
<tr>
<td>F(000)</td>
<td>1032</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.500 x 0.290 x 0.170 mm</td>
</tr>
<tr>
<td>Crystal color</td>
<td>grey</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.962 to 27.485 °</td>
</tr>
<tr>
<td>h_min, h_max</td>
<td>-12, 12</td>
</tr>
<tr>
<td>k_min, k_max</td>
<td>-13, 12</td>
</tr>
<tr>
<td>l_min, l_max</td>
<td>-24, 26</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>16293 / 4623 [R(int)^a = 0.0502]</td>
</tr>
<tr>
<td>Reflections [I&gt;2σ]</td>
<td>4182</td>
</tr>
<tr>
<td>Completeness to theta_max</td>
<td>0.991</td>
</tr>
<tr>
<td>Absorption correction type</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.284, 0.108</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4623 / 0 / 220</td>
</tr>
<tr>
<td>^bS (Goodness-of-fit)</td>
<td>1.130</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ]</td>
<td>R1^c = 0.0306, wR2^d = 0.0677</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1^c = 0.0358, wR2^d = 0.0695</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.116 and -2.205 e^−.Å^3</td>
</tr>
</tbody>
</table>