

## Supplementary data

### **Sterically driven synthesis of ruthenium and ruthenium-silver *N*-heterocyclic carbene complexes**

C. Cesari,<sup>a</sup> S. Conti,<sup>a</sup> S. Zacchini,<sup>a</sup> V. Zanotti,<sup>a</sup> M. C. Cassani<sup>a</sup> and R. Mazzoni<sup>a\*</sup>

<sup>a</sup>Dipartimento di Chimica Industriale “Toso Montanari”, viale Risorgimento 4, 40136 Bologna, Italy.

#### **Materials and procedures**

Solvents: dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), petroleum ether referring to a fraction of bp 60-80 °C, acetonitrile (CH<sub>3</sub>CN) were dried and distilled prior to use. Acetone has been degassed and stored under inert atmosphere on molecular sieves. Other solvents such as ethylacetate (EtOAc), chloroform, ethanol (EtOH), methanol (MeOH), heptane, toluene, CDCl<sub>3</sub>, D<sub>2</sub>O, CD<sub>3</sub>CN (Sigma Aldrich) have been employed without further purification. Reagents: triruthenium-dodecacarbonyl (Ru<sub>3</sub>(CO)<sub>12</sub>) (Strem), methyl iodide, methyl bromide, bromidric and chloridric acid, silver oxide, 1-methylimidazole, 1,3 diphenylacetone, benzyl bromide, benzyl chloride, paraformaldehyde, *tert*-butylamine, 2,6-dimethylaniline, 2,6-diisopropylaniline, glyoxal, acetic acid, 2,4,6-trimethylaniline (Sigma Aldrich), 4,4'-dimethoxybenzil (Alfa Aesar) have been employed as purchased.

1,3-dimethylimidazolium iodide (**1a[I]**),<sup>1</sup> 1,3-dimethylimidazolium trifluoromethanesulfonate(**1a[OTf]**), 1,3-dimethylimidazolium hexafluorophosphate (**1a[PF<sub>6</sub>]**), 1,3-dibenzylimidazolium bromide (**1b[Br]**), 1,3-dibenzylimidazolium chloride(**1b[Cl]**),<sup>2</sup> 1-methyl-3-butyl-imidazolium chloride (**1c**), 1-methyl-3-(2-hydroxyethyl)imidazolium chloride (**1d**),<sup>3</sup> 1-methyl-3-*tert*-butylimidazolium iodide (**1e**), *N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene,1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1f[Cl]**), 1,3-bis(2,6-diisopropylphenyl)imidazolium bromide (**1f[Br]**),<sup>4</sup> 1,3-di-*tert*-butylimidazolium chloride (**1g**),<sup>5</sup> 1-methyl-3-(2,6-diisopropylphenyl)imidazolium iodide (**1h**),<sup>6</sup> 1-isopropyl-3-*tert*-butylimidazolium

iodide (**1i**),<sup>2</sup> 1,4-bis(2,4,6-trimethylphenyl)-1,4-diaza-1,3-butadiene, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (**1l**), 1,3-dimethylimidazol-2-ylidene silver iodide (**2a[I]**),<sup>7</sup> 1,3-dimethylimidazol-2-ylidene silver trifluoromethanesulfonate (**2a[OTf]**), 1,3-dimethylimidazol-2-ylidene silver hexafluorophosphate (**2a[PF<sub>6</sub>]**), 1,3-dibenzylimidazol-2-ylidene silver chloride (**2b[Cl]**),<sup>8</sup> 1,3-dibenzylimidazol-2-ylidene silver bromide (**2b[Br]**),<sup>9</sup> 1-methyl-3-butylimidazol-2-ylidene silver chloride (**2c**), 1-methyl-3-(2-hydroxyethyl)imidazol-2-ylidene silver chloride (**2d**),<sup>10</sup> 1-methyl-3-*tert*-butylimidazol-2-ylidene silver iodide (**2e**), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride (**2f[Cl]**),<sup>11</sup> 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver bromide (**2f[Br]**),<sup>12</sup> 1,3-di-*tert*-butylimidazol-2-ylidene silver chloride (**2g**), 1-methyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride (**2h**), 1-isopropyl-3-*tert*-butylimidazol-2-ylidene silver iodide (**2i**), 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene silver chloride (**2j**), 1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidene copper chloride,<sup>13</sup> 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone,<sup>14</sup> have been prepared following procedures reported in the literature.

The prepared derivatives were characterized by spectroscopic methods. The NMR spectra were recorded using Varian Inova 300 (<sup>1</sup>H, 300.1; <sup>13</sup>C, 75.5 MHz), Varian Mercury Plus VX 400 (<sup>1</sup>H, 399.9; <sup>13</sup>C, 100.6 MHz), Varian Inova 600 (<sup>1</sup>H, 599.7; <sup>13</sup>C, 150.8 MHz) spectrometers at 298 K; chemical shifts were referenced internally to residual solvent peaks. Full <sup>1</sup>H- and <sup>13</sup>C-NMR assignments were done, when necessary, by gHSQC and gHMBC NMR experiments using standard Varian pulse sequences. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer. ESI-MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in MeOH or CH<sub>3</sub>CN. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument.

### General procedure for the synthesis of silver NHC complexes (**2**)

Imidazolium salts (**1**), were reacted with Ag<sub>2</sub>O (1.2 eq.) in the appropriate solvent under inert atmosphere and with protection from light. After stirring the reaction for the time and at the temperature required in order to reach complete conversion to silver complexes (**2**), the solvent was then removed under vacuum and the silver complexes characterized by NMR spectroscopy observing the disappearance of the NC(H)N signal of imidazolium salts **1a-l** (around 8-9 ppm: <sup>1</sup>H-NMR)<sup>1-6</sup> and the concomitant arising of the NMR signals of the silver complexes **2a-l** which are consistent with literature data.<sup>7-12</sup>

1,3-dimethylimidazol-2-ylidene silver iodide (**2a[I]**): 1,3-dimethylimidazolium iodide 0.149 g (0.665 mmol), Ag<sub>2</sub>O 0.185 g (0.798 mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 6.97 (s, 2H, CH<sub>NHC</sub>), 3.84 (s, 6H, NCH<sub>3</sub>).

1,3-dimethylimidazol-2-ylidene silver trifluoromethanesulfonate (**2a[OTf]**): 1,3-dimethylimidazolium trifluoromethanesulfonate 0.075g (0.35mmol), Ag<sub>2</sub>O 0.093g (0.40mmol) room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 6.96 (s, 2H, CH<sub>NHC</sub>), 3.90 (s, 6H, NCH<sub>3</sub>). <sup>19</sup>F-NMR (282.4 MHz, CDCl<sub>3</sub>): δ -78.38 (s, 3F).

1,3-dimethylimidazol-2-ylidene silver hexafluorophosphate (**2a[PF<sub>6</sub>]**): 1,3-dimethylimidazolium hexafluorophosphate 0.075g (0.35mmol), Ag<sub>2</sub>O 0.093g (0.40mmol), 40 °C, CH<sub>2</sub>Cl<sub>2</sub>, 16h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.00 (s, 2H, CH<sub>NHC</sub>), 3.84 (s, 6H, NCH<sub>3</sub>). <sup>19</sup>F-NMR (282.4 MHz, CDCl<sub>3</sub>): δ -72.91 (d, 6F, *J*<sub>P-F</sub> = 757 Hz).

1,3-dibenzylimidazol-2-ylidene silver chloride (**2b[Cl]**): 1,3-dibenzylimidazolium chloride 0.024g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 80 °C reflux, CH<sub>3</sub>CN, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.34-7.24 (m, 10H, CH<sub>Ph</sub>), 7.05 (s, 2H, CH<sub>NHC</sub>), 5.23 (s, 4H, CH<sub>2</sub>). Suitable crystals of **2b[Cl]** has been obtained by CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether double layer (*vide infra for crystal data*).

1,3-dibenzylimidazol-2-ylidene silver bromide (**2b[Br]**): 1,3-dibenzylimidazolium bromide 0.027g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 80 °C reflux, CH<sub>3</sub>CN, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.29-7.18 (m, 10H, CH<sub>Ph</sub>), 6.99 (s, 2H, CH<sub>NHC</sub>), 5.21 (s, 4H, CH<sub>2</sub>).

1-methyl-3-butylimidazol-2-ylidene silver chloride (**2c**): 1-methyl-3-butyl-imidazolium bromide 0.018g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 80 °C reflux, CH<sub>3</sub>CN, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 6.96 (m, 1H, CH<sub>NHC</sub>), 6.93 (m, 1H, CH<sub>NHC</sub>), 4.46 (t, 2H, *J* = 7.5 Hz, NCH<sub>2</sub>), 4.06 (s, 3H, NCH<sub>3</sub>), 1.92 (m, 2H, CH<sub>2</sub>), 1.37 (m, 2H, CH<sub>2</sub>), 1.07 (t, 3H, *J* = 7.2 Hz, CH<sub>3</sub>).

1-methyl-3-(2-hydroxyethyl)imidazol-2-ylidene silver chloride (**2d**): 1-methyl-3-(2-hydroxyethyl)imidazolium chloride 0.014g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), room temperature, CH<sub>3</sub>CN, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.17 (s, 1H, CH<sub>NHC</sub>), 6.99 (s, 1H, CH<sub>NHC</sub>), 4.24 (t, *J* = 5.2 Hz, 2H, CH<sub>2</sub>), 3.86 (t, *J* = 5.2 Hz, 2H, CH<sub>2</sub>), 3.68 (s, 3H, CH<sub>3</sub>).

1-methyl-3-*tert*-butylimidazol-2-ylidene silver iodide (**2e**): 1-methyl-3-*tert*-butylimidazolium iodide 0.026g (0.098mmol), Ag<sub>2</sub>O 0.027g (0.117 mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 4h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.14 (s, 1H, CH<sub>NHC</sub>), 6.93 (s, 1H, CH<sub>NHC</sub>), 3.77 (s, 3H, NCH<sub>3</sub>), 1.72 (s, 9H, CH<sub>3tBu</sub>).

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride (**2f[Cl]**): 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride 0.070g (0.17mmol), Ag<sub>2</sub>O 0.047g (0.20mmol), 40 °C, CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.49 (d, *J* = 7.8 Hz, 2H, CH<sub>Ph</sub>), 7.29 (d, *J* = 7.8 Hz, 4H, CH<sub>Ph</sub>), 7.21 (s, 2H, CH<sub>NHC</sub>), 2.54 (sept, *J* = 6.8 Hz, 4H, CH<sub>iPr</sub>), 1.23 (d, *J* = 6.8 Hz, 12 H, CH<sub>3iPr</sub>), 1.18 (d, *J* = 6.8 Hz, 12 H, CH<sub>3iPr</sub>).

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver bromide (**2f[Br]**): 1,3-bis(2,6-diisopropylphenyl)imidazolium bromide 0.038g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 40 °C,

CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.49 (m, 2H, CH<sub>Ph</sub>), 7.30 (m, 4H, CH<sub>Ph</sub>), 7.21 (s, 2H, CH<sub>NHC</sub>), 2.54 (sept, *J* = 6.8 Hz, 2H, CH<sub>iPr</sub>), 1.28 (d, *J* = 6.8 Hz, 12 H, CH<sub>3iPr</sub>), 1.20 (d, *J* = 6.8 Hz, 12 H, CH<sub>3iPr</sub>).

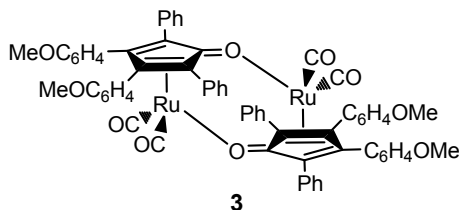
1,3-di-*tert*-butylimidazol-2-ylidene silver chloride (**2g**): 1,3-di-*tert*-butylimidazolium chloride 0.018g (0.083mmol), Ag<sub>2</sub>O 0.023 g (0.099mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.11 (s, 2H, CH<sub>NHC</sub>), 1.76 (s, 18H, CH<sub>3tBu</sub>).

1-methyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride (**2h**): 1-methyl-3-(2,6-diisopropylphenyl)imidazolium iodide 0.038g (0.10mmol), Ag<sub>2</sub>O 0.028 g (0.12 mmol) room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 3h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.46 (t, *J* = 7.8 Hz, 1H, CH<sub>Ph</sub>), 7.23 (m, 2H, CH<sub>Ph</sub>), 7.17 (m, 1H, CH<sub>NHC</sub>), 6.98 (m, 1H, CH<sub>NHC</sub>), 3.98 (s, 3H, NCH<sub>3</sub>), 2.35 (sept, *J* = 6.8 Hz, 2H, CH<sub>iPr</sub>), 1.22 (d, *J* = 6.8 Hz, 6 H, CH<sub>3iPr</sub>), 1.10 (d, *J* = 6.8 Hz, 6 H, CH<sub>3iPr</sub>).

1-isopropyl-3-*tert*-butylimidazol-2-ylidene silver iodide (**2i**): 1-isopropyl-3-*tert*-butylimidazolium iodide 0.031g (0.11mmol), Ag<sub>2</sub>O 0.029g (0.13mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 24h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.16 (s, 1H, CH<sub>NHC</sub>), 6.97 (s, 1H, CH<sub>NHC</sub>), 4.83 (sept, *J* = 6.8 Hz, 1H, CH<sub>iPr</sub>), 1.72 (s, 9H, CH<sub>3tBu</sub>), 1.46 (d, *J* = 6.8 Hz, 6H, CH<sub>3iPr</sub>).

1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene silver chloride (**2l**): 1,3-bis(2,4,6-trimethylphenyl)imidazoliumchloride 0.028g (0,083mmol), Ag<sub>2</sub>O 0.023g (0,099mmol), 40 °C, CH<sub>2</sub>Cl<sub>2</sub>, 4h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): 7.13 (s, 2H, CH<sub>NHC</sub>), 6.99 (s, 4H, CH<sub>Ph</sub>), 2.35 (s, 6H, *p*-CH<sub>3Ph</sub>), 2.07 (s, 12H, *o*-CH<sub>3Ph</sub>).

**Synthesis of dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer(**3**).**

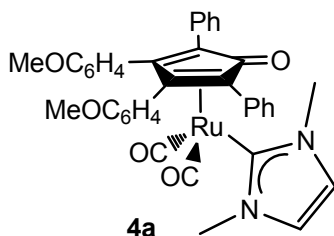


Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**3**) has been prepared following a procedure reported in the literature for a similar complex,<sup>15</sup> by reacting 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone 1.04g (2.35mmol) and  $\text{Ru}_3(\text{CO})_{12}$  0.50g (0.78mmol) in heptane (130°C for 5 days, inert atmosphere). **3** was purified by filtration as a yellow solid and obtained with an yield of 80%.  $^1\text{H-NMR}$  (399.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.10-6.40 (m, 36H,  $\text{CH}_{\text{aryl}}$ ), 3.60 (s, 12H,  $-\text{OCH}_3$ );  $^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.91 (CO), 169.65 (C=O), 158.53 ( $-\text{COCH}_3$ ), 132.70 ( $\text{CH}_{\text{aryl}}$ ), 130.96 ( $\text{C}_{\text{qaryl}}$ ), 130.58 ( $\text{CH}_{\text{aryl}}$ ), 126.27 ( $\text{CH}_{\text{aryl}}$ ), 122.67 ( $\text{C}_{\text{qaryl}}$ ), 113.32 ( $-\text{CH}_{\text{aryl}}$ ), 112.54 ( $\text{CH}_{\text{aryl}}$ ), 97.78 ( $\text{C}_{2,5}\text{Cp}$ ), 87.76 ( $\text{C}_{3,4}\text{Cp}$ ), 54.90 ( $-\text{OCH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2018, 1967 ( $\nu_{\text{CO}}$ ); 1610, 1519 ( $\nu_{\text{C=C}}$ ).

## General procedure for the synthesis of dicarbonyl- $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(NHC)ruthenium complexes (**4**)

I step: imidazolium salts (**1**), were reacted with  $\text{Ag}_2\text{O}$  (1.2 eq.) in the appropriate solvent under inert atmosphere and with protection from light. After stirring the reaction for the time and at the temperature required in order to reach complete conversion to silver complexes (**2**), the solvent, if different from  $\text{CH}_2\text{Cl}_2$ , was removed under vacuo and the solid obtained dissolved in  $\text{CH}_2\text{Cl}_2$ . II step: then dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**3**) (0.5 eq. vs. imidazolium salts) was straightforwardly added to the *in situ* prepared silver complexes solution. The reaction mixture was stirred until the end of the reaction at room temperature. Upon filtration on a celite pad and removal of the solvent the quantitative formation of the dicarbonyl- $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(NHC)ruthenium complexes (**4**) was verified by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , ESI-MS and X-Ray crystal structure when suitable crystals were available.

## Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethylimidazol-2-ylidene)ruthenium (**4a**)



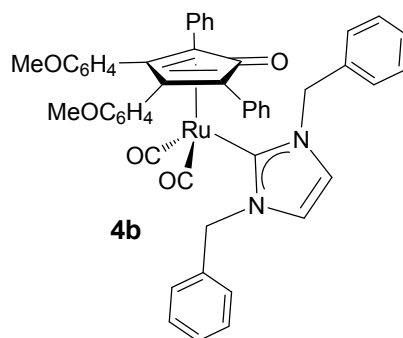
I step: 1,3-dimethylimidazolium iodide 0.149g (0.665mmol),  $\text{Ag}_2\text{O}$  0.185g (0.798mmol), room temperature,  $\text{CH}_2\text{Cl}_2$ , 3h. II step: **3** 0.400g (0.332mmol), 10 min. The beige solid obtained was identified as **4a** (0.208 g, 90% yield). Suitable crystals of **4a** for X-Ray diffraction were obtained by slow diffusion ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ).

The same reaction performed in a J-Young valve equipped NMR tube in  $\text{CDCl}_3$  (0.7 mL) led to the *in situ* formation of the silver complex **2a** by sonication of the sample containing 1,3-dimethylimidazolium iodide 0.011g (0.050mmol) and  $\text{Ag}_2\text{O}$  0.014g (0.060mmol) for 2h. Afterwards **3** 0.030g (0.025mmol) was added and  $^1\text{H-NMR}$  analysis showed the quantitative and immediate formation of the complex **4a**. Complex **4a** is stable to air, moisture, in solution of organic solvents and in the presence of water. **4a** has been analyzed by IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , ESI-MS and X-Ray diffraction.  $^1\text{H-NMR}$  (599.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (m, 4H,  $\text{CH}_{\text{aryl}}$ ), 7.17-7.04

(m, 10H, CH<sub>aryl</sub>), 6.76 (s, 2H, CH<sub>NHC</sub>), 6.65 (m, 4H, CH<sub>aryl</sub>), 3.71 (s, 6H, -OCH<sub>3</sub>), 3.09 (s, 6H, -NCH<sub>3</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>, g-HSQC, g-HMBC): δ 202.47 (CO), 172.72 (C<sub>carbene</sub>), 169.33 (C=O, Cp), 158.54 (-COCH<sub>3</sub>), 135.43 (C<sub>q</sub>aryl), 133.62 (CH<sub>aryl</sub>), 129.16 (CH<sub>aryl</sub>), 127.43 (CH<sub>aryl</sub>), 125.27 (C<sub>q</sub>aryl), 124.90 (CH<sub>aryl</sub>), 123.62 (CH<sub>NHC</sub>), 112.93 (CH<sub>aryl</sub>), 103.85 (C<sub>2,5</sub>, Cp), 78.46 (C<sub>3,4</sub>, Cp), 55.00 (-OCH<sub>3</sub>), 38.23 (-NCH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2004, 1945 (ν<sub>CO</sub>); 1586 cm<sup>-1</sup>(ν<sub>C=O</sub>); 1601, 1518 (ν<sub>C=C</sub>). ESI-MS (m/z) (+): 699 [M+H]<sup>+</sup>; 721 [M + Na]<sup>+</sup>. Anal. Calcd (%) for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub>Ru: C, 65.41; H, 4.62. Found: C, 65.33; H, 4.58.

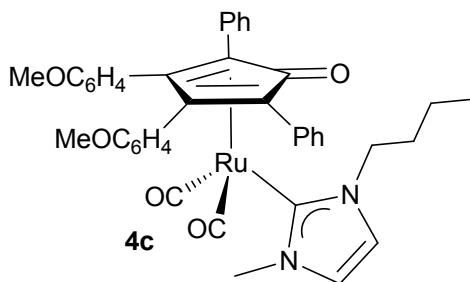
By using imidazolium salts with non-coordinating anions such as 1,3-dimethylimidazolium trifluoromethanesulfonate or 1,3-dimethylimidazolium hexafluorophosphate the formation of the corresponding silver complexes **2a**[OTf] and **2a**[PF<sub>6</sub>] occurs. The latter undergo a transmetallation reaction with **3** leading to the formation of complex **4a**.

#### Dicarbonyl(η<sup>4</sup>-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dibenzylimidazol-ylidene)ruthenium (**4b**)



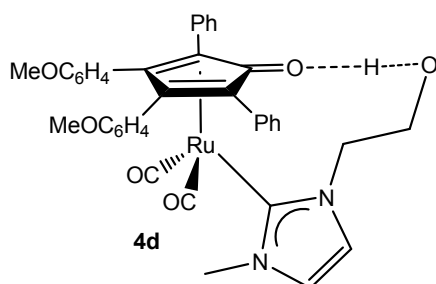
I step: 1,3-dibenzylimidazolium bromide 0.027g (0,083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 80 °C reflux, CH<sub>3</sub>CN, 3h. II step: **3** 0.050g (0.042mmol), 2h. The beige solid obtained was identified as **4b** (0.081g, 97% yield). Suitable crystals of **4b** for X-Ray diffraction were obtained by slow diffusion (toluene/hexane). The same result is obtained employing 1,3-dibenzylimidazolium chloride as imidazolium salt. **4b** has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS and X-Ray diffraction. <sup>1</sup>H-NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.85-6.60 (m, 28H, CH<sub>aryl</sub>), 6.57 (s, 2H, CH<sub>NHC</sub>), 4.67 (s, 4H, -CH<sub>2</sub>Ph), 3.69 (s, 6H, -OCH<sub>3</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>): δ 201.69 (CO), 174.73 (C<sub>carbene</sub>), 169.90 (C=O, Cp), 158.54 (-COCH<sub>3</sub>), 136.13-112.90 (C<sub>aryl</sub>), 122.71 (CH<sub>NHC</sub>), 104.03 (C<sub>2,5</sub>, Cp), 78.87 (C<sub>3,4</sub>, Cp), 54.99, 54.27 (CH<sub>2</sub>Ph, -OCH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2006, 1947 (ν<sub>CO</sub>); 1586 (ν<sub>C=O</sub>); 1603, 1518 (ν<sub>C=C</sub>). ESI-MS (m/z) (+): 851 [M+H]<sup>+</sup>. Anal. Calcd (%) for C<sub>50</sub>H<sub>40</sub>N<sub>2</sub>O<sub>5</sub>Ru: C, 70.66; H, 4.74. Found: C, 70.58; H, 4.71.

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-butyl-imidazol-ylidene)ruthenium (**4c**)**



I step: 1-methyl-3-butyl-imidazolium bromide 0.018g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), 80 °C reflux, CH<sub>3</sub>CN, 3h. II step: **3** 0.050g (0.042mmol), 1h. The beige solid obtained was identified as **4c** (0.059g, 96% yield). **4c** has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS. <sup>1</sup>H-NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.67-6.63 (m, 18H, CH<sub>aryl</sub>), 7.82 (s, 1H, CH<sub>NHC</sub>), 6.77 (s, 1H, CH<sub>NHC</sub>), 3.69 (s, 6H, -OCH<sub>3</sub>), 3.31 (m, 2H, -NCH<sub>2</sub>), 3.05 (s, 3H, -NCH<sub>3</sub>), 1.39, 0.89 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>), 0.72 (-CH<sub>3</sub>). <sup>13</sup>C-NMR (150.8MHz, CDCl<sub>3</sub>): δ 202.44 (CO), 172.23 (C<sub>carbene</sub>), 169.50 (C=O, Cp), 158.50 (-COCH<sub>3</sub>), 135.41-112.90 (C<sub>aryl</sub>), 124.04 (CH<sub>NHC</sub>), 121.41 (CH<sub>NHC</sub>), 103.88 (C<sub>2,5</sub>, Cp), 78.35 (C<sub>3,4</sub>, Cp), 54.97(-OCH<sub>3</sub>), 50.22(-NCH<sub>2</sub>), 38.12 (-NCH<sub>3</sub>), 33.24, 19.38 (-CH<sub>2</sub>CH<sub>2</sub>-), 13.72 (-CH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2003, 1943 (ν<sub>CO</sub>); 1586 (ν<sub>C=O</sub>); 1600, 1517 (ν<sub>C=C</sub>). ESI-MS (m/z) (+): 741 [M+H]<sup>+</sup>. Anal. Calcd (%) for C<sub>41</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>Ru: C, 66.56; H, 5.18. Found: C, 66.51; H, 5.17.

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-(2-hydroxyethyl)imidazol-ylidene)ruthenium (**4d**)**

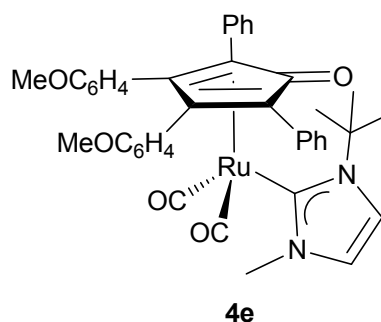


I step: 1-methyl-3-(2-hydroxyethyl)imidazolium chloride 0.014g (0.083mmol), Ag<sub>2</sub>O 0.023g (0.099mmol), room temperature, CH<sub>3</sub>CN, 3h. II step: **3** 0.050g (0.042mmol), 1h. The beige solid obtained, was identified as **4d**, (0.060g, 98% yield). Suitable crystals of **4d** for X-Ray diffraction were obtained by slow diffusion (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether). **4d** has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS and X-Ray diffraction. <sup>1</sup>H-NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.67-6.65 (m, 18H, CH<sub>aryl</sub>), 7.01 (s, 1H, CH<sub>NHC</sub>), 6.86 (s, 1H, CH<sub>NHC</sub>), 3.86 (m, 2H, -NCH<sub>2</sub>), 3.72 (s, 6H, -OCH<sub>3</sub>), 3.22 (s, 3H, -NCH<sub>3</sub>), 3.15 (m, 2H, -CH<sub>2</sub>OH). <sup>13</sup>C-NMR (150.8MHz, CDCl<sub>3</sub>): δ 201.82 (CO), 172.88



(C<sub>carbene</sub>), 166.15 (C=O,Cp), 158.67 (-COCH<sub>3</sub>), 134.07-112.95 (C<sub>aryl</sub>), 124.23(CH<sub>NHC</sub>), 121.03 (CH<sub>NHC</sub>), 104.98 (C<sub>2,5</sub>, Cp), 80.68 (C<sub>3,4</sub>, Cp), 58.94 (-NCH<sub>2</sub>), 55.04 (-OCH<sub>3</sub>), 52.47 (-CH<sub>2</sub>OH), 38.29 (-NCH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2011, 1952 (ν<sub>CO</sub>); 1558 (ν<sub>C=O</sub>); 1609, 1518 (ν<sub>C=C</sub>). ESI-MS (m/z) (+): 729 [M+H]<sup>+</sup>, 751 [M+Na]<sup>+</sup>. Anal. Calcd (%) for C<sub>39</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>Ru: C, 64.36; H, 4.71. Found: C, 64.29; H, 4.69.

**Dicarbonyl(η<sup>4</sup>-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-*tert*-butyl-imidazol-ylidene)ruthenium (4e)**

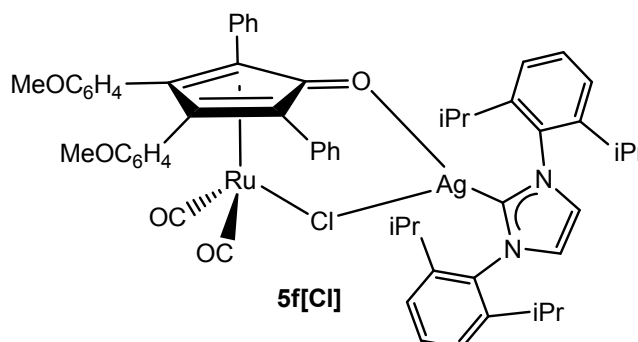


I step: 1-methyl-3-(*tert*-butyl)imidazolium iodide 0.026g (0.097mmol), Ag<sub>2</sub>O 0.027g (0.17mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 4h. II step: **3** 0.059g (0.049mmol), 2h. The beige solid obtained, was identified as **4e**, (0.070 g, 98% yield). **4e** has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS. <sup>1</sup>H-NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.73 (s, 1H, CH<sub>NHC</sub>), 7.71-6.62 (m, 18H, CH<sub>aryl</sub>), 6.08 (s, 1H, CH<sub>NHC</sub>), 3.71 (s, 6H, -OCH<sub>3</sub>), 3.24 (s, 3H, -NCH<sub>3</sub>), 1.31 (s, 9H, CH<sub>3tBu</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>): 203.75 (CO), 182.15 (C<sub>carbene</sub>), 168.31 (C=O, Cp), 158.29 (-COCH<sub>3</sub>), 149.03 (CH<sub>NHC</sub>), 135.86-112.73 (C<sub>aryl</sub>, CH<sub>NHC</sub>), 103.18 (C<sub>2,5</sub>, Cp), 79.42 (C<sub>3,4</sub>, Cp), 56.62 (C<sub>qtBu</sub>), 55.00 (-OCH<sub>3</sub>), 37.63 (-NCH<sub>3</sub>), 29.69 (CH<sub>3tBu</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1996, 1933 (ν<sub>CO</sub>); 1590 (ν<sub>C=O</sub>); 1604, 1518 (ν<sub>C=C</sub>). ESI-MS (m/z) (+): 741 [M+H]<sup>+</sup>. Anal. Calcd (%) for C<sub>41</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>Ru: C, 66.56; H, 5.18. Found: C, 66.53; H, 5.19.

### General procedure for the synthesis of ruthenium-silver complexes (5)

I step: imidazolium salts (**1**), were reacted with Ag<sub>2</sub>O in the appropriate solvent under inert atmosphere and with protection from light. After stirring the reaction for the time and at the temperature requested in order to reach complete conversion, the solvent, if different from CH<sub>2</sub>Cl<sub>2</sub>, was removed and the solid obtained dissolved in CH<sub>2</sub>Cl<sub>2</sub>. II step: successively dicarbonyl(η<sup>4</sup>-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**3**) (0.5 eq. vs. imidazolium salts) was straightforwardly added to the *in situ* prepared silver complexes solution. The reaction mixture was stirred until the end of the reaction at room temperature. Upon filtration on a celite pad and removal of the solvent the quantitative formation of the dicarbonyl-η<sup>4</sup>-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(NHC)silverhalogenide)ruthenium complexes (**5**) was verified by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS and X-Ray crystal structure when suitable crystals were available.

### Dicarbonyl(η<sup>4</sup>-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride)ruthenium(**5f**[Cl])

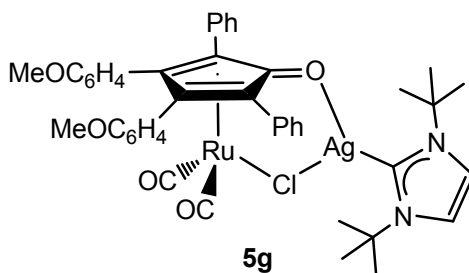


I step: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride 0.070g (0.17mmol), Ag<sub>2</sub>O 0.047g (0.20mmol), 40 °C, CH<sub>2</sub>Cl<sub>2</sub>, 3h. II step: **3** 0.100g (0.083mmol), 1h. The beige solid obtained, was identified as **5f**[Cl], (0.187g, 96% yield). Suitable crystals of **5f**[Cl] for X-Ray diffraction were obtained by slow diffusion (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether). **5f**[Cl] has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS and X-Ray diffraction. **5f**[Cl] is stable in the solid state; it decomposes in solution of CH<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>, Tol-d<sub>8</sub> in more than 24h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>): δ 7.57-6.51 (m, 24H, CH<sub>aryl</sub>), 7.24 (s, 2H, CH<sub>NHC</sub>), 3.68 (s, 6H, -OCH<sub>3</sub>), 2.53 (sept, *J* = 6.8 Hz, 4H, CH<sub>iPr</sub>), 1.16 (d, *J* = 6.8 Hz, 12H, CH<sub>3iPr</sub>), 1.13 (d, *J* = 6.8 Hz, 12H, CH<sub>3iPr</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>): δ 200.54 (CO), 188.6 (dd, *J* (<sup>109</sup>Ag-<sup>13</sup>C) = 271 Hz; *J* (<sup>108</sup>Ag-<sup>13</sup>C) = 235 Hz), 165.38 (C=O, Cp), 158.47 (-COCH<sub>3</sub>), 145.53-112.55 (C<sub>aryl</sub>), 123.04, 122.96 (CH<sub>NHC</sub>), 99.61 (C<sub>2,5</sub>, Cp), 83.12 (C<sub>3,4</sub>, Cp), 55.03 (-OCH<sub>3</sub>), 28.60 (CH<sub>iPr</sub>), 24.34, 24.05 (CH<sub>3iPr</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2013, 1953 (ν<sub>CO</sub>); 1608,

1518 ( $\nu_{C=C}$ ). ESI-MS ( $m/z$ ) (-): 1169  $[M+Cl]^-$ . Anal. Calcd (%) for  $C_{60}H_{60}AgClN_2O_5Ru$ : C, 63.58; H, 5.34. Found: C, 63.49; H, 5.29.

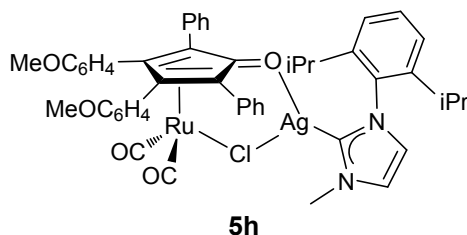
The same reaction was performed on 1,3-bis(2,6-diisopropylphenyl)imidazolium bromide as starting material leading to the formation of the equivalent dicarbonyl- $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone(1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidene silver bromide)]ruthenium(**5f[Br]**) which show a  $^1H$ -NMR and IR characterization superimposable to the one of **5f[Cl]**.  $^1H$ -NMR (399.9 MHz,  $CDCl_3$ ):  $\delta$  7.57-6.51 (m, 24H,  $CH_{aryl}$ ), 7.24 (s, 2H,  $CH_{NHC}$ ), 3.68 (s, 6H,  $-OCH_3$ ), 2.53 (sept,  $J = 6.8$  Hz, 4H,  $CH_{iPr}$ ), 1.16 (d,  $J = 6.8$  Hz, 12H,  $CH_{3iPr}$ ), 1.14 (d,  $J = 6.8$  Hz, 12H,  $CH_{3iPr}$ ). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 2013, 1953 ( $\nu_{CO}$ ); 1608, 1518 ( $\nu_{C=C}$ ).

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-di-*tert*-butylimidazol-2-ylidene silver chloride)ruthenium (**5g**)**



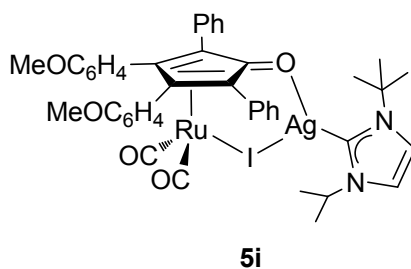
I step: 1,3-di-*tert*-butylimidazolium chloride 0.018g (0.083mmol),  $Ag_2O$  0.023g (0.10mmol), room temperature,  $CH_2Cl_2$ , 3h. II step: **3** 0.050g (0.042mmol), 2h. The beige solid obtained was identified as **5g** (0.088g, 95% yield). **5g** has been analyzed by IR,  $^1H$ -NMR,  $^{13}C$ -NMR, ESI-MS. **5g** is stable in the solid state; it decomposes in solution in more than 24h.  $^1H$ -NMR (300.1 MHz,  $CDCl_3$ ):  $\delta$  7.50-6.55 (m, 18H,  $CH_{aryl}$ ), 7.01 (s, 2H,  $CH_{NHC}$ ), 3.70 (s, 6H,  $-OCH_3$ ), 1.60 (s, 18H,  $CH_{3tBu}$ ).  $^{13}C$ -NMR (150.8 MHz,  $CDCl_3$ ):  $\delta$  200.46 (CO), 177.51 (s,  $C_{carbene}$ ), 165.20 (C=O, Cp), 158.60 ( $-COCH_3$ ), 133.14-112.75 ( $CH_{aryl}$ ), 116.16 ( $CH_{NHC}$ ), 99.71 ( $C_{2,5}$ , Cp), 84.00 ( $C_{3,4}$ , Cp), 55.00 ( $-OCH_3$ ), 57.45 ( $C_{qtBu}$ ), 31.60 ( $CH_{3tBu}$ ). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 2014, 1955 ( $\nu_{CO}$ ); 1608, 1518 ( $\nu_{C=C}$ ). ESI-MS ( $m/z$ ) (-): 961  $[M+Cl]^-$ . Anal. Calcd (%) for  $C_{44}H_{44}AgClN_2O_5Ru$ : C, 57.12; H, 4.79. Found: C, 57.02; H, 4.75.

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene silver chloride)ruthenium (**5h**)**



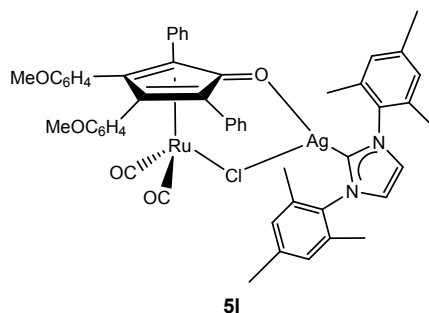
I step: 1-methyl-3-(2,6-diisopropylphenyl)imidazolium iodide 0.038g (0.10mmol), Ag<sub>2</sub>O 0.028g (0.12mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 3h. II step: **3** 0.061g (0.051mmol), 2h. The beige solid obtained was identified as **5h** (0.096g, 97% yield). **5h** has been analyzed by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS. **5h** is stable in the solid state; it decomposes in solution in more than 24h. <sup>1</sup>H-NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  7.53-6.54 (m, 21H, CH<sub>aryl</sub>), 7.07, 7.09 (m, 2H, CH<sub>NHC</sub>) 3.73 (3H, -NCH<sub>3</sub>), 3.72 (s, 6H, -OCH<sub>3</sub>), 2.33 (sept,  $J = 6.8$  Hz, 2H, CH<sub>iPr</sub>), 1.20 (d,  $J = 6.8$  Hz, 6H, CH<sub>3iPr</sub>), 1.09 (d,  $J = 6.8$  Hz, 6H, CH<sub>3iPr</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta$  200.27 (CO), 176.85 (C<sub>carbene</sub>), 168.36 (C=O, Cp), 158.59 (-COCH<sub>3</sub>), 145.68-112.71 (C<sub>aryl</sub>), 123.33, 121.23 (CH<sub>NHC</sub>), 100.39 (C<sub>2,5</sub>, Cp), 83.60 (C<sub>3,4</sub>, Cp), 55.00 (-OCH<sub>3</sub>), 38.55 (-NCH<sub>3</sub>), 28.06 (CH<sub>iPr</sub>), 24.40, 24.35 (CH<sub>3iPr</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2014, 1955 ( $\nu_{CO}$ ); 1609, 1518 ( $\nu_{C=C}$ ). ESI-MS ( $m/z$ ) (-): 1023 [M+Cl]<sup>-</sup>. Anal. Calcd (%) for C<sub>49</sub>H<sub>46</sub>AgClN<sub>2</sub>O<sub>5</sub>Ru: C, 59.61; H, 4.70. Found: C, 59.54; H, 4.67.

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-isopropyl-3-*tert*-butyl)imidazol-2-ylidene silver iodide)ruthenium (**5i**)**



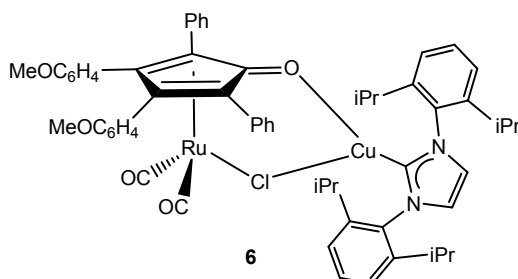
I step: 1-isopropyl-3-*tert*-butylimidazolium iodide 0.062g (0.22mmol), Ag<sub>2</sub>O 0.058g (0.26mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 24h. II step: **3** 0.128g (0.106mmol), 2h. The beige solid obtained, was identified as **5i** by IR and <sup>1</sup>H-NMR. **5i** decomposed in solution preventing <sup>13</sup>C-NMR analysis. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>):  $\delta$  7.54-6.56 (m, 20H, CH<sub>aryl</sub>, CH<sub>NHC</sub>), 3.71 (s, 6H, -OCH<sub>3</sub>), 4.52 (m, 1H, CH<sub>iPr</sub>), 1.56 (s, 9H, CH<sub>3tBu</sub>), 1.31 (d, 6H,  $J = 6.8$  Hz, CH<sub>3iPr</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2016, 1958 ( $\nu_{CO}$ ); 1609, 1518 ( $\nu_{C=C}$ ).

**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene silver chloride)ruthenium (**5I**)**



I step: 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride 0.056g (0.17mmol), Ag<sub>2</sub>O 0.046g (0.20mmol), room temperature, CH<sub>2</sub>Cl<sub>2</sub>, 2h. II step: **3** 0.100g (0.083mmol), 1h. The beige solid obtained, was identified as **5I** by IR and <sup>1</sup>H-NMR. **5I** decomposed in solution preventing <sup>13</sup>C-NMR analysis. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>):  $\delta$  7.25-6.41 (m, 22H, CH<sub>aryl</sub>, CH<sub>NHC</sub>), 3.59 (s, 6H, -OCH<sub>3</sub>), 2.35 (s, 6H, *p*-CH<sub>3Ph</sub>), 1.91 (s, 12H, *o*-CH<sub>3Ph</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2013, 1954 ( $\nu_{CO}$ ); 1608, 1517 ( $\nu_{C=C}$ ).

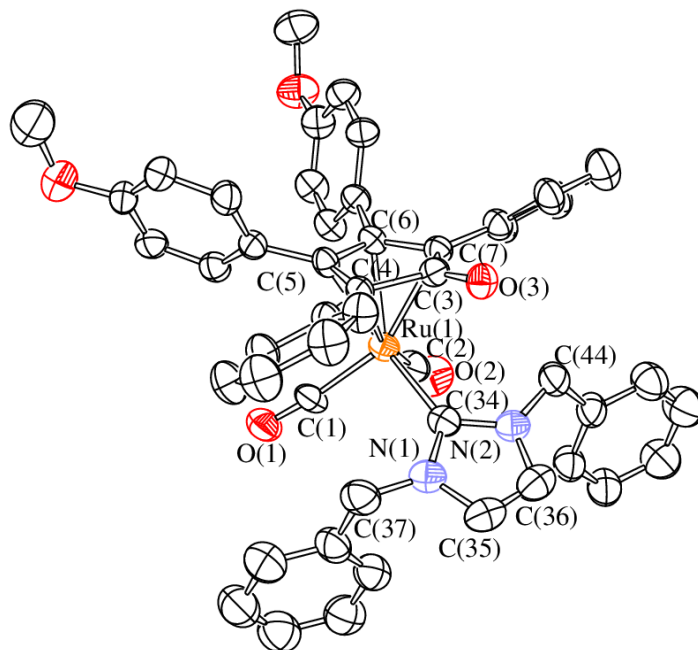
**Dicarbonyl( $\eta^4$ -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidene copper chloride)ruthenium (**6**)**



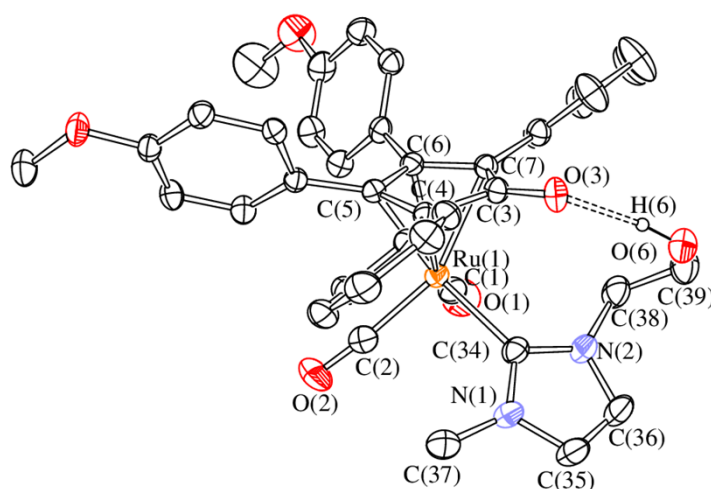
To a CH<sub>2</sub>Cl<sub>2</sub> solution of 1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidene copper chloride 0.081g (0.16mmol), **3** 0.100g (0.083mmol) was added. The reaction mixture was stirred for 1h at room temperature. Upon filtration on a celite pad and removal of the solvent the quantitative formation of **6** as a beige solid (0.164g, 94% yield) was verified by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ESI-MS. Suitable crystals of **6** for X-Ray diffraction were obtained by slow diffusion (toluene/hexane). **6** is stable in the solid state. It decomposes in solution in more than 24h. <sup>1</sup>H-NMR (399.9 MHz, CDCl<sub>3</sub>):  $\delta$  7.57-6.52 (m, 24H, CH<sub>aryl</sub>), 7.05 (s, 2H, CH<sub>NHC</sub>), 3.69 (s, 6H, -OCH<sub>3</sub>), 2.68 (sept, *J* = 6.6 Hz, 4H, CH<sub>iPr</sub>), 1.17 (d, *J* = 6.6 Hz, 12H, CH<sub>3iPr</sub>). <sup>13</sup>C-NMR (150.8 MHz, CDCl<sub>3</sub>):  $\delta$  200.43 (CO), 183.45 (C<sub>carbene</sub>), 165.56 (C=O, Cp), 158.47 (-COCH<sub>3</sub>), 145.66-112.70 (C<sub>aryl</sub>), 130.76 (CH<sub>NHC</sub>), 99.17 (C<sub>2,5</sub>, Cp),

84.94 (C<sub>3,4</sub>, Cp), 54.91 (-OCH<sub>3</sub>), 28.44 (CH<sub>1Pr</sub>), 24.23, 23.84 (CH<sub>31Pr</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2014, 1956 (ν<sub>CO</sub>); 1609, 1520 (ν<sub>C=C</sub>). ESI-MS (m/z) (-): 1125 [M+Cl]<sup>-</sup>. Anal. Calcd (%) for C<sub>60</sub>H<sub>60</sub>CuClN<sub>2</sub>O<sub>5</sub>Ru: C, 66.16; H, 5.55. Found: C, 66.10; H, 5.51.

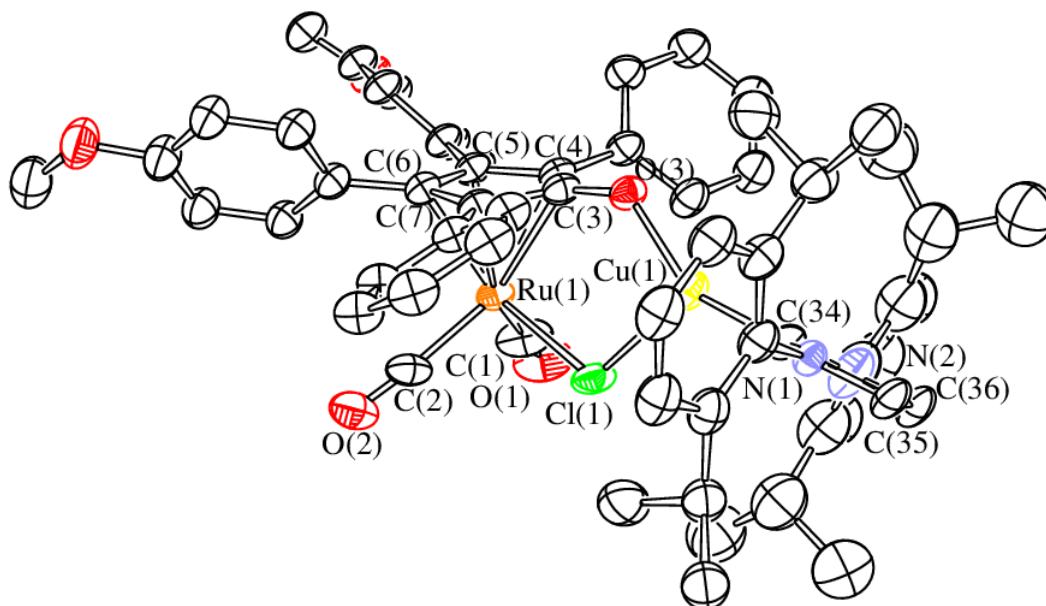
### X-Ray diffraction studies



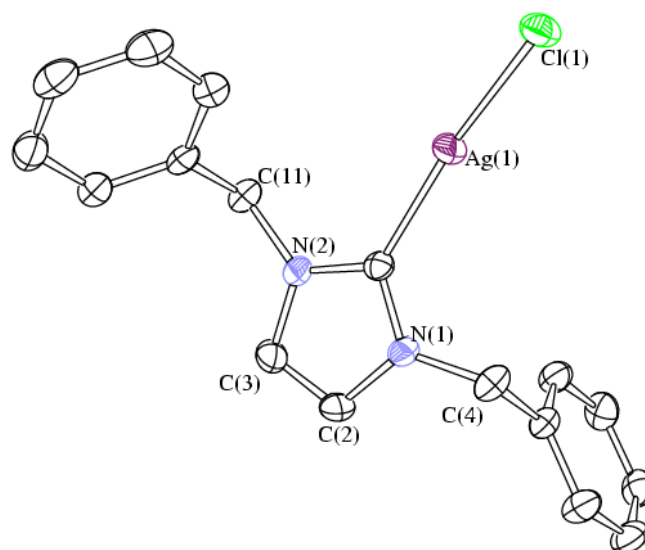
**Figure S1** ORTEP drawing of **4b**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity.



**Figure S2** ORTEP drawing of **4d**. Displacement ellipsoids are at the 30% probability level. H-atoms, except H(6), have been omitted for clarity. The H-bond between O(6)H(6) and O(3) is represented as a dashed line.



**Figure S3** ORTEP drawing of **6**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity.



**Figure S4** ORTEP drawing of **2b[Cl]**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity.

**Table S1**Main bond lengths (Å) and angles (deg) of **4a**, **4b** and **4d**.

|                | <b>4a</b> | <b>4b</b> | <b>4d</b> |
|----------------|-----------|-----------|-----------|
| Ru(1)-C(1)     | 1.892(5)  | 1.868(10) | 1.884(3)  |
| Ru(1)-C(2)     | 1.881(5)  | 1.840(11) | 1.879(4)  |
| Ru(1)-C(3)     | 2.471(3)  | 2.503(10) | 2.474(3)  |
| Ru(1)-C(4)     | 2.263(3)  | 2.242(8)  | 2.269(3)  |
| Ru(1)-C(5)     | 2.206(3)  | 2.203(8)  | 2.217(3)  |
| Ru(1)-C(6)     | 2.211(3)  | 2.181(8)  | 2.197(3)  |
| Ru(1)-C(7)     | 2.274(3)  | 2.269(8)  | 2.291(3)  |
| Ru(1)-C(34)    | 2.118(4)  | 2.103(10) | 2.128(3)  |
| C(1)-O(1)      | 1.128(5)  | 1.144(9)  | 1.139(4)  |
| C(2)-O(2)      | 1.145(5)  | 1.170(10) | 1.145(4)  |
| C(3)-O(3)      | 1.247(4)  | 1.235(9)  | 1.259(3)  |
| C(3)-C(4)      | 1.467(5)  | 1.510(11) | 1.472(4)  |
| C(4)-C(5)      | 1.455(5)  | 1.418(11) | 1.445(4)  |
| C(5)-C(6)      | 1.431(5)  | 1.412(11) | 1.426(4)  |
| C(6)-C(7)      | 1.448(5)  | 1.439(11) | 1.453(4)  |
| C(7)-C(3)      | 1.473(5)  | 1.481(11) | 1.463(4)  |
| C(34)-N(1)     | 1.353(5)  | 1.361(11) | 1.357(4)  |
| C(34)-N(2)     | 1.356(5)  | 1.369(11) | 1.357(4)  |
| N(1)-C(35)     | 1.366(5)  | 1.392(12) | 1.384(4)  |
| N(1)-C(37)     | 1.451(7)  | 1.409(11) | 1.454(5)  |
| N(2)-C(36)     | 1.375(6)  | 1.378(12) | 1.387(4)  |
| N(2)-C(38)     | 1.430(6)  | 1.439(12) | 1.460(5)  |
| C(35)-C(36)    | 1.321(7)  | 1.284(13) | 1.322(6)  |
| C(3)-C(4)-C(5) | 108.4(3)  | 108.0(7)  | 107.9(2)  |
| C(4)-C(5)-C(6) | 108.2(3)  | 109.3(7)  | 108.7(2)  |
| C(5)-C(6)-C(7) | 108.1(3)  | 108.7(8)  | 108.0(2)  |
| C(6)-C(7)-C(3) | 108.6(3)  | 108.5(8)  | 108.4(2)  |
| C(7)-C(3)-C(4) | 105.2(3)  | 103.2(8)  | 105.7(2)  |
| C(7)-C(3)-O(3) | 127.2(3)  | 128.7(8)  | 126.5(2)  |
| C(4)-C(3)-O(3) | 127.3(3)  | 127.7(8)  | 127.6(3)  |



|                  |          |           |          |
|------------------|----------|-----------|----------|
| Ru(1)-C(34)-N(1) | 127.7(3) | 130.2(8)  | 128.2(2) |
| Ru(1)-C(34)-N(2) | 128.5(3) | 127.6(8)  | 127.2(2) |
| N(1)-C(34)-N(2)  | 103.8(3) | 102.2(9)  | 104.5(3) |
| C(34)-N(1)-C(35) | 111.2(4) | 111.7(9)  | 110.6(3) |
| N(1)-C(35)-C(36) | 107.2(4) | 106.5(11) | 107.1(3) |
| C(35)-C(36)-N(2) | 107.2(4) | 108.8(11) | 107.5(3) |
| C(36)-N(2)-C(34) | 110.6(4) | 110.7(9)  | 110.3(3) |
| Ru(1)-C(1)-O(1)  | 178.8(4) | 174.1(9)  | 178.3(3) |
| Ru(1)-C(2)-O(2)  | 177.7(4) | 177.0(9)  | 174.8(3) |

**Table S2**

Main bond lengths (Å) and angles (deg) of **5f[Cl]** and **6**.

|             | <b>5f[Cl]</b> | <b>6</b>  |
|-------------|---------------|-----------|
| Ru(1)-C(1)  | 1.877(8)      | 1.884(12) |
| Ru(1)-C(2)  | 1.864(8)      | 1.897(14) |
| Ru(1)-C(3)  | 2.425(6)      | 2.388(11) |
| Ru(1)-C(4)  | 2.251(6)      | 2.259(11) |
| Ru(1)-C(5)  | 2.199(6)      | 2.201(10) |
| Ru(1)-C(6)  | 2.193(6)      | 2.211(10) |
| Ru(1)-C(7)  | 2.243(6)      | 2.255(10) |
| Ru(1)-Cl(1) | 2.4379(17)    | 2.411(3)  |
| C(1)-O(1)   | 1.145(8)      | 1.112(14) |
| C(2)-O(2)   | 1.146(9)      | 1.112(15) |
| C(3)-O(3)   | 1.248(7)      | 1.252(12) |
| C(3)-C(4)   | 1.458(9)      | 1.440(14) |
| C(4)-C(5)   | 1.449(9)      | 1.446(15) |
| C(5)-C(6)   | 1.451(9)      | 1.451(14) |
| C(6)-C(7)   | 1.442(8)      | 1.431(14) |
| C(7)-C(3)   | 1.468(9)      | 1.470(16) |
| O(3)-M(1)   | 2.222(4)      | 1.923(7)  |
| Cl(1)-M(1)  | 2.6277(18)    | 2.449(3)  |
| M(1)-C(34)  | 2.090(6)      | 1.868(11) |
| N(1)-C(34)  | 1.355(8)      | 1.353(13) |

|                  |           |            |
|------------------|-----------|------------|
| N(2)-C(34)       | 1.344(7)  | 1.362(15)  |
| N(1)-C(35)       | 1.386(8)  | 1.376(13)  |
| N(2)-C(36)       | 1.389(8)  | 1.376(13)  |
| C(35)-C(36)      | 1.327(9)  | 1.307(16)  |
| C(3)-C(4)-C(5)   | 108.7(5)  | 107.9(9)   |
| C(4)-C(5)-C(6)   | 107.6(5)  | 108.6(8)   |
| C(5)-C(6)-C(7)   | 108.2(5)  | 107.4(9)   |
| C(6)-C(7)-C(3)   | 108.3(5)  | 108.4(9)   |
| C(7)-C(3)-C(4)   | 106.1(5)  | 107.1(9)   |
| C(7)-C(3)-O(3)   | 127.9(6)  | 127.3(9)   |
| C(4)-C(3)-O(3)   | 125.8(6)  | 125.4(10)  |
| Ru(1)-Cl(1)-M(1) | 112.32(7) | 110.07(11) |
| C(3)-O(3)-M(1)   | 127.7(4)  | 129.3(7)   |
| M(1)-C(34)-N(1)  | 123.9(4)  | 131.8(8)   |
| M(1)-C(34)-N(2)  | 131.9(5)  | 125.3(9)   |
| N(1)-C(34)-N(2)  | 104.2(5)  | 102.9(10)  |
| C(34)-N(1)-C(35) | 111.7(5)  | 111.3(9)   |
| N(1)-C(35)-C(36) | 106.1(6)  | 107.6(10)  |
| C(35)-C(36)-N(2) | 107.4(6)  | 106.9(10)  |
| C(36)-N(2)-C(34) | 110.7(5)  | 111.4(11)  |
| Ru(1)-C(1)-O(1)  | 175.1(7)  | 178.0(17)  |
| Ru(1)-C(2)-O(2)  | 179.1(10) | 174.1(11)  |

### X-ray Crystallography

Crystal data and collection details for **4a·0.5Et<sub>2</sub>O·0.5H<sub>2</sub>O**, **4b**, **4d·0.5CH<sub>2</sub>Cl<sub>2</sub>**, **5f[Cl]·0.75C<sub>5</sub>H<sub>12</sub>**, **6·0.75C<sub>5</sub>H<sub>12</sub>** and **2b[Cl]** (CCDC 1016378-1016383) are reported in Table S3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–K $\alpha$  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).<sup>16</sup> Structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ .<sup>17</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise stated. All hydrogen atoms were fixed at calculated positions and refined by a riding model.

**4a·0.5Et<sub>2</sub>O·0.5H<sub>2</sub>O:** The asymmetric unit of the unit cell contains one Ru-complex (located on a general position), one Et<sub>2</sub>O molecule disordered over two symmetry related (by 2) positions (occupancy factor 0.5) and half of a H<sub>2</sub>O molecule (located on 2). The Et<sub>2</sub>O and H<sub>2</sub>O molecules have been refined isotropically. Similar *U* restraints [SIMU line in SHELXL, *s.u.* 0.005] were applied to the Et<sub>2</sub>O molecule and its C-C and C-O distances restrained to 1.53 and 1.43 Å [*s.u.* 0.01]. The independent H-atom bonded to O(50) in the H<sub>2</sub>O molecule has been located in the Fourier Map and refined isotropically using the 1.5 fold *U*<sub>iso</sub> value of the parent O(50); the O(50)-H(50) distance was restrained to 0.87 Å [*s.u.* 0.01].

**4b:** The asymmetric unit of the unit cell contains one Ru-complex located on a general position. **4b** crystallizes in very small and low-quality plate-like crystals. Therefore, the data have been cut at  $2\theta = 47.06^\circ$  and several restraints have been applied during the refinement. Similar *U* restraints [SIMU line in SHELXL, *s.u.* 0.01] have applied to all the C-atoms. Some of the C and O atoms have been restrained to as isotropic like behavior [ISOR line in SHELXL, *s.u.* 0.01]. The aromatic rings have been constrained to fit regular hexagons [AFIX 66 line in SHELXL].

**4d·0.5CH<sub>2</sub>Cl<sub>2</sub>:** The asymmetric unit of the unit cell contains one Ru-complex (located on a general position) and half of a CH<sub>2</sub>Cl<sub>2</sub> molecule located on a 2-fold axis. Similar *U* restraints [SIMU line in SHELXL, *s.u.* 0.01] have applied to all the C-atoms. H(6) bonded to O(6) has been located in the Fourier Map and refined isotropically using the 1.5 fold *U*<sub>iso</sub> value of the parent O(6); the O(6)-H(6) distance was restrained to 0.89 Å [*s.u.* 0.02].

**5f[Cl]·0.75C<sub>5</sub>H<sub>12</sub>:** The asymmetric unit of the unit cell contains two Ru-complexes (located on general positions), one C<sub>5</sub>H<sub>12</sub> molecule (on a general position) and half of a C<sub>5</sub>H<sub>12</sub> molecule disordered over two symmetry related (by an inversion center) positions. Similar *U* restraints [SIMU line in SHELXL, *s.u.* 0.005] have applied to all the C, O and N-atoms. Some of the C and O atoms have been restrained to as isotropic like behavior [ISOR line in SHELXL, *s.u.* 0.005]. The aromatic rings have been constrained to fit regular hexagons [AFIX 66 line in SHELXL]. The C<sub>5</sub>H<sub>12</sub> molecules have been restrained to have similar geometries [SAME line in SHELXL, *s.u.* 0.02]. Restraints to bond distances have been applied as follows [*s.u.* 0.01]: 1.53 Å to C-C in C<sub>5</sub>H<sub>12</sub>.

**6·0.75C<sub>5</sub>H<sub>12</sub>:** The asymmetric unit of the unit cell contains two Ru-complexes, one C<sub>5</sub>H<sub>12</sub> molecule (on a general position) and half of a C<sub>5</sub>H<sub>12</sub> molecule disordered over two symmetry related (by an inversion center) positions. The crystals appears to be pseudo-merohedrally twinned with twin matrix 1 0 0 0 -1 0 0 0 -1 and refined batch factor 0.2530(14). Similar *U* restraints [SIMU line in SHELXL, *s.u.* 0.005] have applied to all the C and O-atoms. Some of the C and O atoms have been restrained to as isotropic like behavior [ISOR line in SHELXL, *s.u.* 0.01]. The aromatic rings have been constrained to fit regular hexagons [AFIX 66 line in SHELXL]. The C<sub>5</sub>H<sub>12</sub> molecules have

been restrained to have similar geometries [SAME line in SHELXL, *s.u.* 0.02]. Restraints to bond distances have been applied as follows [*s.u.* 0.01]: 1.53 Å to C-C in C<sub>5</sub>H<sub>12</sub>.

**2b[Cl]**: The asymmetric unit of the unit cell contains one Ag complex located on a general position.

**Table S3**

Crystal data and experimental details for **4a·0.5Et<sub>2</sub>O·0.5H<sub>2</sub>O**, **4b**, **4d·0.5CH<sub>2</sub>Cl<sub>2</sub>**, **5f[Cl]·0.75C<sub>5</sub>H<sub>12</sub>**, **6·0.75C<sub>5</sub>H<sub>12</sub>** and **2b[Cl]**.

|   | <b>4a·0.5Et<sub>2</sub>O·0.5H<sub>2</sub>O</b>                  | <b>4b</b>  | <b>4d·0.5CH<sub>2</sub>Cl<sub>2</sub></b>                            |
|---|---|--|--|
| Formula   | <b>C<sub>40</sub>H<sub>38</sub>N<sub>2</sub>O<sub>6</sub>Ru</b> | C <sub>50</sub> H <sub>40</sub> N <sub>2</sub> O <sub>5</sub> Ru | C <sub>39.5</sub> H <sub>35</sub> ClN <sub>2</sub> O <sub>6</sub> Ru |
| <i>F</i> w  | <b>743.79</b>   | 849.91   | 770.22   |
| T, K  | <b>295(2)</b>   | 293(2)   | 294(2)   |
| $\lambda$ , Å   | <b>0.71073</b>  | 0.71073  | 0.71073  |
| Crystal system  | <b>Monoclinic</b>   | Monoclinic   | Monoclinic   |
| Space group   | <b><i>P</i>2/<i>c</i></b>                                       | <i>P</i> 2 <sub>1</sub> / <i>n</i>                               | <i>C</i> 2/ <i>c</i>   |
| <i>a</i> , Å  | <b>16.2736(16)</b>  | 14.602(4)  | 24.188(4)  |
| <i>b</i> , Å  | <b>13.5024(13)</b>  | 15.790(4)  | 14.213(3)  |
| <i>c</i> , Å  | <b>17.6132(17)</b>  | 17.850(5)  | 24.171(4)  |
| $\beta$ , °   | <b>113.2960(10)</b>   | 101.118(3)   | 117.822(2)   |
| Cell Volume, Å <sup>3</sup>                                 | <b>3554.7(6)</b>  | 4038.4(19)   | 7349(2)  |
| <i>Z</i>  | <b>4</b>  | 4  | 8  |
| <i>D</i> <sub>c</sub> , g cm <sup>-3</sup>                  | <b>1.390</b>  | 1.398  | 1.392  |
| $\mu$ , mm <sup>-1</sup>                                    | <b>0.490</b>  | 0.440  | 0.547  |
| F(000)  | <b>1536</b>   | 1752   | 3160   |
| Crystal size, mm  | <b>0.18×0.16×0.12</b>   | 0.15×0.13×0.10   | 0.24×0.21×0.18   |
| $\theta$ limits, °  | <b>1.36–25.66</b>   | 1.65–23.53   | 1.72–25.02   |
| Reflections collected                                       | <b>34962</b>  | 31532  | 30056  |
| Independent reflections                                     | <b>6723 [<i>R</i><sub>int</sub> = 0.0387]</b>                   | 6003 [ <i>R</i> <sub>int</sub> = 0.1717]                         | 6287 [ <i>R</i> <sub>int</sub> = 0.0324]                             |
| Data / restraints<br>/parameters                            | <b>6723 / 15 / 440</b>  | 6003 / 378 / 451   | 6287 / 211 / 450   |
| Goodness on fit on F <sup>2</sup>                           | <b>1.035</b>  | 0.966  | 1.051  |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | <b>0.0417</b>   | 0.0675   | 0.0327   |
| <i>wR</i> <sub>2</sub> (all data)                           | <b>0.1284</b>   | 0.1946   | 0.1060   |

|  |                |                |                |
|--|----------------|----------------|----------------|
| Largest diff. peak and hole, e Å <sup>-3</sup> | 0.785 / -0.610 | 0.638 / -0.600 | 0.496 / -0.490 |
|--|----------------|----------------|----------------|

|  | <b>5f[Cl]·0.75C<sub>5</sub>H<sub>12</sub></b>                          | <b>6·0.75C<sub>5</sub>H<sub>12</sub></b>                               | <b>2b[Cl]</b>                                      |
|--|--|--|--|
| Formula  | <b>C<sub>63.75</sub>H<sub>69</sub>AgClN<sub>2</sub>O<sub>5</sub>Ru</b> | <b>C<sub>63.75</sub>H<sub>69</sub>ClCuN<sub>2</sub>O<sub>5</sub>Ru</b> | C <sub>17</sub> H <sub>16</sub> AgClN <sub>2</sub> |
| <i>F</i> <sub>w</sub>                              | <b>1187.60</b>   | <b>1143.27</b>   | 391.64   |
| T, K   | <b>295(2)</b>  | <b>291(2)</b>  | 293(2)   |
| λ, Å   | <b>0.71073</b>   | <b>0.71073</b>   | 0.71073  |
| Crystal system                                     | <b>Monoclinic</b>  | <b>Monoclinic</b>  | Triclinic  |
| Space group  | <b><i>P</i><sub>2</sub><sub>1</sub>/<i>c</i></b>                       | <b><i>P</i><sub>2</sub><sub>1</sub>/<i>c</i></b>                       | <i>P</i> $\bar{1}$                                 |
| <i>a</i> , Å                                       | <b>15.6360(14)</b>   | <b>15.469(3)</b>   | 8.1352(9)  |
| <i>b</i> , Å                                       | <b>20.8474(19)</b>   | <b>20.983(5)</b>   | 10.0028(11)  |
| <i>c</i> , Å                                       | <b>38.030(4)</b>   | <b>37.639(8)</b>   | 10.5175(11)  |
| α, °   | <b>90</b>  | <b>90</b>  | 88.1710(10)  |
| β, °   | <b>90.6730(10)</b>   | <b>90.260(3)</b>   | 68.1080(10)  |
| γ, °   | <b>90</b>  | <b>90</b>  | 85.0180(10)  |
| Cell Volume, Å <sup>3</sup>                        | <b>12396(2)</b>  | <b>12217(5)</b>  | 791.14(15)   |
| <i>Z</i>   | <b>8</b>   | <b>8</b>   | 2  |
| <i>D</i> <sub>c</sub> , g cm <sup>-3</sup>         | <b>1.273</b>   | <b>1.243</b>   | 1.644  |
| μ, mm <sup>-1</sup>                                | <b>0.649</b>   | <b>0.686</b>   | 1.437  |
| F(000)   | <b>4908</b>  | <b>4764</b>  | 392  |
| Crystal size, mm                                   | <b>0.19×0.16×0.13</b>  | <b>0.19×0.16×0.14</b>  | 0.21×0.19×0.12                                     |
| θlimits, °   | <b>1.07–25.03</b>  | <b>0.97–25.03</b>  | 2.04–26.00   |
| Reflections collected                              | <b>116143</b>  | <b>114909</b>  | 8194   |
| Independent reflections                            | <b>21866 [R<sub>int</sub>= 0.0524]</b>                                 | <b>21528 [R<sub>int</sub>= 0.0838]</b>                                 | 3092 [R <sub>int</sub> = 0.0176]                   |
| Data / restraints /parameters                      | <b>21858 / 1014 / 1153</b>   | <b>21528 / 918 / 1159</b>  | 3092 / 0 / 190                                     |
| Goodness on fit on F <sup>2</sup>                  | <b>1.029</b>   | <b>1.019</b>   | 1.064  |
| <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) | <b>0.0619</b>  | <b>0.0878</b>  | 0.0270   |
| <i>wR</i> <sub>2</sub> (all data)                  | <b>0.2014</b>  | <b>0.22824</b>   | 0.0667   |
| Largest diff. peak and hole, e Å <sup>-3</sup>     | <b>1.038/ -0.795</b>   | <b>1.845 / -1.085</b>  | 0.643 / -0.268                                     |

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