Supporting Information

Anion Metathesis in Facile Preparation of Olefin Metathesis Catalysts Bearing a Quaternary Ammonium Chloride Tag

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**General information**

Analytical thin-layer chromatography (TLC) was performed using aluminium oxide 60 F\textsubscript{254} neutral precoated plates (0.25 mm thickness, Merck) with a fluorescent indicator.

The flash column chromatography was performed using Sigma Aldrich aluminium oxide neutral gel 60 (0.05 - 0.15 particle size).

NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm and referred to residual solvent peaks 5.32 and 53.84 ppm for \textsuperscript{1}H and \textsuperscript{13}C in CD\textsubscript{2}Cl\textsubscript{2}. The following abbreviations were used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), sep (septet), m (multiplet), br (broad). \textsuperscript{1}H NMR signals were given followed by multiplicity, coupling constants \textit{J} in Hertz and integration in parentheses.

MS analyses were performed by means of Synapt G2-S HDMS (Waters Inc) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. The instrument was controlled and recorded data were processed using MassLynx V4.1 software package (Waters Inc).

IR was performed on FTIR Jasco 6200 spectrometer.

Ratio of Cl/I at the ruthenium coordination centre was established based on integration of benzylidene signals in \textsuperscript{1}H NMR.

Ratio of Cl/I in the quaternary ammonium tag was established by thin-layer chromatography and in selected cases confirm by elemental analysis.

Deuterated dichloromethane was purchased from Sigma-Aldrich, stored over molecular sieves and used without further purification.

\textit{n}-Hexane, ethyl acetate, and dichloromethane were purchased from Avantor Performance Materials Poland S.A. and distilled prior to use.

Dichloromethane and tetrahydrofuran used for reactions were purified using mBraun’s SPS (solvent purification system), water content was measured with Karl-Fisher apparatus (Titroline® 7500 KF trace) and did not exceeded 2 ppm in each case. Acetonitrile (anhydrous), dimethyl carbonate (anhydrous) and methanol (anhydrous) were purchased from Sigma Aldrich and used as received. Isopropanol was purchased from Sigma Aldrich dry over molecular sieves over month and freeze pump thaw degassed.

Dried and oxygen-free CuCl\textsubscript{2} and CuCl were purchased from Sigma Aldrich and kept in a glove box. NaCl was purchased from Avantor Performance Materials Poland S.A. and used as received.

Lead(II) chloride was prepared by precipitation lead(II) nitrate water solution with concentrated hydrochloric acid. Colourless precipitate was collected, washed with water and dried under vacuum (10\textsuperscript{-4} Torr) overnight. Afterwards it was dried in an oven (150 °C) overnight.

Silver chloride was prepared by precipitation silver nitrate water solution with concentrated hydrochloric acid. Colourless precipitate was collected and solubilised in ammonia, filtrated, and precipitated once more with concentrated hydrochloric acid. The resulted precipitate was then washed with water followed by acetone and ethyl ether and dried under vacuum (10\textsuperscript{-4} Torr) at 80°C overnight. Silver chloride was then stored in a dark glass bottle.
Scrambled Ru10 batches were obtained from Apeiron company.

![Diagram of complexes with different content of Cl⁻ and I⁻ ions at ruthenium centre and at quaternary ammonium tag.]

- EA calculated for: $C_{35}H_{48}Cl_3N_3$ORu (Ru4) Cl 14.48, I 0.00.
- EA calculated for: $C_{35}H_{48}Cl_2I_2N_3$ORu (Ru9) Cl 8.59, I 15.37.
- EA calculated for: $C_{35}H_{48}ClI_2N_3$ORu (Ru13) Cl 3.87, I 27.67.
- EA calculated for: $C_{35}H_{48}I_3N_3$ORu (Ru14) Cl 0.00, I 37.75.
- EA found for sample of Ru10: Cl 8.07, I 13.36.

The ratio of Cl/I at the ruthenium coordination centre was established by $^1$H NMR as 91:9 and with additional data from EA the ratio of Cl/I in the quaternary ammonium tag was calculated as 10:90.

**General procedure for complexes quaternisation and subsequent anion metathesis**

A 4 mL oven-dried vial was charged with complex prior quaternisation. The vial was evacuated, three times flushed with argon, and dry CH$_2$Cl$_2$ (2 mL) was added followed by MeI or EtI (40 equiv.). The resulting solution was heated at 60 °C until full conversion of starting material was reached. The mixture was filtered through Celite® pad, washed with CH$_2$Cl$_2$, and solvent was evaporated. The residue was dissolved in minimal amount of CH$_2$Cl$_2$ and precipitated with pentane. Precipitate was washed with ethyl ether and heptane and dried under vacuum overnight to provide pure product.

An oven-dried vial was charged with AgCl (1.1 equiv. per iodide) and Ru-complex (50 mg). The vial was evacuated and three times flushed with argon, dry CH$_2$Cl$_2$ (1 mL) of was added, and the resulting mixture was stirred for 30 minutes at room temperature. The resulting solution was centrifuged, filtered through Celite® pad and washed with MeOH (20 mL). Solvents were evaporated and the residue was dissolved in minimal amount of CH$_2$Cl$_2$ and precipitated with heptane. Precipitate was washed with ethyl ether and heptane and dried under vacuum overnight to provide pure product.

Ru4 was obtained according to general procedure: Complex prior quaternisation (80 mg, 0.12 mmol, obtained according to literature procedure$^1$), and MeI (564 mg, 0.25 mL, 4 mmol, 40 equiv.) were stirred at 60 °C for 1 h to provide complex bearing a quaternary ammonium tag (98 mg, 0.11 mmol, 91%, RuCl$_2$:Ru(Cl):RuI$_2$ = 39:41:20, only NR$_4$I$^–$). This complex (50 mg, 0.056 mmol) was reacted with AgCl (16 mg, 0.112 mmol, 1.1 equiv. per each iodide) to afford Ru 4 as a green solid (39 mg, 0.053 mmol, 95%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 16.33 (s, 1H), 7.57 (dt, J = 8.7, 4.6 Hz, 1H), 6.98 (ddd, J = 70.8, 29.9, 7.9 Hz, 8H), 5.21 (d, J = 9.6 Hz, 1H), 4.89 (p, J = 6.1 Hz, 1H), 4.75 (d, J = 10.3 H...
Ru 6 was obtained according to general procedure: Complex prior quaternisation (80 mg, 0.095 mmol, obtained according to literature procedure\(^3\)), and Mel (564 mg, 0.25 mL, 4 mmol, 40 equiv.) were stirred at 60 °C for 1 h to provide complex bearing a quaternary ammonium tag (93.8 mg, 0.095 mmol, 95%, RuCl\(_2\):Ru(ClI):RuI\(_2\) = 90:10:0, only NR\(_4\)^+I\(^-\)). This complex (50 mg, 0.051 mmol) was reacted with AgCl (8.75 mg, 0.061 mmol, 1.1 equiv. per each iodide) to afford Ru 6 as a green solid (44 mg, 0.05 mmol, 98%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 16.34 (s, 1H), 7.58 (dt, \(J = 8.8, 4.3\) Hz, 1H), 6.98 (dd, \(J = 66.5, 31.5, 8.3\) Hz, 7H), 5.16 (s, 1H), 5.03 - 4.67 (m, 2H), 4.52 (s, 1H), 4.41 - 4.17 (m, 1H), 3.55 (s, 2H), 3.20 (s, 8H), 2.45 (d, \(J = 22.9\) Hz, 19H), 1.22 (t, \(J = 5.1\) Hz, 7H), 0.91 (s, 3H).\(^3\)

Ru 11 was obtained according to general procedure: Complex prior quaternisation (80 mg, 0.10 mmol, obtained according to literature procedure\(^4\)), and Mel (564 mg, 0.25 mL, 4 mmol, 40 equiv.) were stirred at 60 °C for 4 h to provide complex bearing a quaternary ammonium tag (84.6 mg, 0.08 mmol, 80%, RuCl\(_2\):Ru(ClI):RuI\(_2\) = 6:27:67, only NR\(_4\)^+I\(^-\)). This complex (50 mg, 0.047 mmol) was reacted with AgCl (19.5 mg, 0.14 mmol, 1.1 equiv. per each iodide) to afford Ru 11 as a green solid (38 mg, 0.046 mmol, 98%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 16.16 (s, 1H), 7.76 - 7.23 (m, 8H), 6.86 (p, \(J = 7.0\) Hz, 3H), 4.91 (h, \(J = 6.1\) Hz, 1H), 4.38 (p, \(J = 9.5\) Hz, 2H), 4.14 (t, \(J = 8.7\) Hz, 1H), 3.86 (q, \(J = 6.7\) Hz, 2H), 3.78 (d, \(J = 15.9\) Hz, 2H), 3.67 (d, \(J = 13.5\) Hz, 1H), 3.60 (d, \(J = 7.0\) Hz, 1H), 3.52 (d, \(J = 9.9\) Hz, 1H), 3.43 (t, \(J = 10.7\) Hz, 2H), 3.33 (s, 3H), 3.26 (q, \(J = 6.8\) Hz, 1H), 2.95 - 2.53 (m, 7H), 1.56 - 1.16 (m, 30H), 1.08 (s, 4H), 0.94 - 0.73 (m, 3H). MS (TOF): m/z calculated for C\(_{68}\)H\(_{69}\)Cl\(_3\)N\(_4\)ORu: [M-Cl\(^-\)]\(^+\) 786.24, found: 785.23. IR (KBr): \(\nu\) = 3334, 2917, 2855, 1928, 1607, 1588, 1574, 1528, 1475, 1451, 1416, 1381, 1314, 1257, 1155, 1138, 1112, 1096, 1034, 934, 876, 841, 802, 746, 707, 673, 653, 576, 493, 432 cm\(^{-1}\).

Ru 12 was obtained according to general procedure: Complex prior quaternisation (80 mg, 0.12 mmol, obtained according to literature procedure\(^5\)), and Mel (624 mg, 0.32 mL, 4 mmol, 40 equiv.) were stirred at 60 °C for 6 h to provide complex bearing a quaternary ammonium tag (96.3 mg, 0.096 mmol, 88%, RuCl\(_2\):Ru(ClI):RuI\(_2\) = 0:21:79, only NR\(_4\)^+I\(^-\)). This complex (50 mg, 0.049 mmol) was reacted with AgCl (mg, 0.15 mmol, 1.1 equiv. per each iodide) to afford Ru 12 as a green solid (22.1 mg, 0.097%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 16.37 (s, 1H), 7.76 - 7.53 (m, 4H), 7.24 (t, \(J = 11.0\) Hz, 3H), 7.08 (d, \(J = 12.8\) Hz, 2H), 7.00 - 6.84 (m, 4H), 5.17 - 5.05 (m, 0H), 4.94 (p, \(J = 6.2\) Hz, 1H), 4.80 (t, \(J = 12.4\) Hz, 1H), 4.62 (d, \(J = 12.8\) Hz, 2H), 4.14 (s, 1H), 4.06 (s, 3H), 2.88 (s, 3H), 2.79 - 2.27 (m, 21H), 1.59 (s, 14H), 1.27 (d, \(J = 6.4\) Hz, 12H), 0.95 - 0.84 (m, 2H). MS (TOF): m/z calculated for C\(_{55}\)H\(_{56}\)Cl\(_3\)N\(_4\)ORu: [M-Cl\(^-\)]\(^+\) 713.24, found: 712.24. IR (KBr): \(\nu\) = 3359, 3009, 2976, 2918, 2857, 1942, 1606, 1589, 1575, 1475, 1453, 1421, 1383, 1313, 1258, 1218, 1155, 1140, 1113, 1096, 1035, 1015, 982, 934, 877, 852, 840, 804, 787, 773, 748, 654, 653, 573, 493, 439 cm\(^{-1}\).
$^1$H NMR spectra

Sample of Ru10 from Apeiron Synthesis (RuCl$_2$:Ru(Cl)I = 63:37, NR$_4^+$Cl$^-$:NR$_4$I$^-$ = 50:50)

Sample of Ru10 from Apeiron Synthesis – other batch (RuCl$_2$:Ru(Cl)I = 91:9, NR$_4^+$Cl$^-$:NR$_4$I$^-$ = 20:80)
Ru4 after quaternisation (Table 3)

Ru4 after anion metathesis (Table 3)
Ru11 after quaternisation (Table 3)

Ru11 after anion metathesis (Table 3)
Ru12 after quaternisation (Table 3)

Ru12 after anion metathesis (Table 3)
References


