Ruthenium Indenylidene Complexes Bearing $N$-Alkyl/$N$-Mesityl Substituted $N$-Heterocyclic Carbenes Ligands

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Supporting information

**Fig. S1** NOESY spectrum of 8a, chemical shift of $^1H$-NMR range from 1.0 to 5.0 ppm (horizontal) and $^1H$-NMR range from 5.0 to 8.5 ppm (vertical).

**Fig. S2** ORTEP representation of the structure of complex 1c (thermal ellipsoids are drawn at the 30% probability level), showing the atom labeling scheme of the heteroatoms. The hydrogen atoms are omitted for clarity.
Crystals of complex 1c were obtained by evaporation of the complex solution in hexane/EtOAc/CH₂Cl₂ and analyzed by single crystal X-ray analysis. 1c crystallized in the triclinic centro-symmetric space group P-1 with one RuCl₂(benzylidene)(1-mesityl-3-methyl-4,5-dihydroimidazol-2-ylidene)(PCy₃) molecule (Fig. S2) in the asymmetric unit. The bond length between the ruthenium and C_benzylidene is 1.840(3) Å. The Ru-Cl bond lengths are 2.3793(8) Å and 2.4061(8) Å as well as the Ru-P bond length is 2.4243(9) Å. The C₃NH₃-Ru-P and C₃NH₃-Ru=C_benzylidene angles are 160.61(1) and 100.7(1)°, respectively. The Cl-Ru-Cl angle is equal to 164.29(3)°.

Initiation studies of complexes 1c, 2 and 8a-c

It is known that a reaction of ruthenium alkylidene complexes with vinyl ether could generate Fischer-carbene complexes, which are inert to metathesis reaction. This method is often used for catalysts initiation studies and the quenching of metathetic reactions. Here, initiation studies were carried out by using the ruthenium complexes (10 mmol) to react with 30 eq. of ethyl vinyl ether in Toluene-d₈ at 20 °C (Scheme S1). The kinetic plots of conversion of the initial complexes to the formed relative ruthenium ethoxymethylene complexes are shown in Fig. S3. In the figure, it is shown that the benzylidene complex 1c exhibits the fastest initiation rate, followed by complex 8a, then the complexes 8b and 8c. However, for the reference complex 2, after 5 hours no detectable amount of desired ruthenium ethoxymethylene complex was observed from the reaction mixture. Actually, only 18% of complex 2 was found to convert after 24 hours.

Experimental Section

Unless otherwise stated, all the reactions were carried out under an argon atmosphere by using Schlenk technique and all solvents which involved in reactions were dried and freshly distilled prior to use: dichloromethane (CaH₂), toluene (sodium). Pentane, methanol, dichloromethane and toluene were purchased from Fiers. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Acros Organics. Diethyl 2,2-diallylmalonate, cis,cis-cycloocta-1,5-diene, potassium bis(trimethylsilyl)amide (KHMD), allylbenzene were purchased from Sigma Aldrich. cis-1,4-diacetoxy-2-butene was obtained from ABCR. RuCl₂(3-phenyl-1-indenylidene)(PCy₃)₂ was obtained from Umicore. 1-mesityl-3-methyl-4,5-dihydro-imidazolium chloride, 1-...
Gas chromatography (GC) was conducted using a Finning Trace GC ultra from Thermo Electron Corporation equipped with a 10 m length, 0.10 mm internal diameter 5% diphenyl/95% polydimethylsiloxane capillary column and a flame ionization detector (FID). For IR, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were recorded on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a N2 cooled MCT-A (mercury-cadmium-tellurium) detector and a KBr beam splitter.

Elemental analyses were performed on a CHNS-0 analyzer from Interscience. HPLC-MS (ESI) was done by Agilent NOD series HPLC with G1946CMSD. Single crystal X-ray diffraction data were collected using an Agilent Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using CuKα radiation (λ = 1.54178 Å) or MoKα radiation (λ = 0.71073 Å) and α scans. All images were interpreted and integrated with the program CrysalisPro (Agilent Technologies).8 The structures were solved by direct methods using the ShelXS structure solution program10 and refined by full-matrix least-squares on F² using the ShelXL program11. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups).

**General procedure for the preparation of complexes 8a-c**

In an oven dried Schlenk vessel, HKMDS (2 eq., 3.2 mL, 1.6 mmol) (0.5 M toluene solution) was added to a suspension of imidazolium salt (1.5 eq., 1.2 mmol) in dry toluene (24 mL) at room temperature. The resulting solution was vigorously stirred for 30 minutes then was added in a solution of RuCl₃(3-phenyl-1-indenylidene)(PCy₃)(1 eq., 0.74 g, 0.8 mmol) in toluene (16 mL) in the reactor. The mixture was further stirred overnight. Purification using silica-gel chromatography (hexane:EtOAc, from 60:1 to 20:1) afforded a red-brown colored sludge. Further, methanol was added to the resulting sludge. The solid suspension was filtered and was washed several times with methanol and pentane.

![Image of complex 8a-c](image)

Red-brown powder (0.37 g, Yield: 55%). Red crystals, suitable for X-ray diffraction analysis of 8a were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH₂Cl₂. The complex consists two rotamers in a ratio of 100:5 and the NMR data for this major rotamer is presented in following.

**RuCl₃(3-phenyl-1-indenylidene)(1-mesityl-3-octyl-4,5-dihydroimidazol-2-ylidene)(PCy₃)(8a)**

Red-brown powder (0.37 g, Yield: 55%). Red crystals, suitable for X-ray diffraction analysis of 8a were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH₂Cl₂. The complex consists two rotamers in a ratio of 100:5 and the NMR data for this major rotamer is presented in following.

**RuCl₃(3-phenyl-1-indenylidene)(1-mesityl-3-methyl-4,5-dihydroimidazol-2-ylidene)(PCy₃)(8b)**

![Image of complex 8b](image)
Red-brown powder (0.44 g, Yield: 58%). Red crystals, suitable for X-ray diffraction analysis of 8b were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH₂Cl₂. The complex consists two rotamers in a ratio of 100:2.5 and the NMR data for this major rotamer is presented in following: ¹H-NMR (500 MHz, CDCl₃, TMS, 20 °C): δ 8.39 (d, 1 H, J_H-H = 7.3 Hz, H-7), 7.70 (d, 2 H, J_H-H = 7.3 Hz, H-11, H-15), 7.49 (t, 1 H, J_H-H = 7.3 Hz, H-13), 7.39 (t, 2 H, J_H-H = 7.6 Hz, H-12, H-14), 7.20 (t, 1 H, J_H-H = 7.3 Hz, H-5), 7.14 (t, 1 H, J_H-H = 7.3 Hz, H-6), 7.11 (s, 1 H, H-2), 7.02 (d, 1 H, J_H-H = 7.3 Hz, H-4), 6.38 (s, 1 H, H-21), 5.98 (s, 1 H, H-23), 4.45-4.59 (m, 2 H, H-28), 3.85-3.95 (m, 2 H, H-17), 3.64-3.77 (m, 2 H, H-18), 2.27-2.37 (m, 3 H, H-36), 2.10 (s, 3 H, H-26), 1.96-2.02 (m, 5 H, H-25, H-29), 1.85-1.87 (m, 6 H, H-27, H-37), 1.71-1.74 (m, 3 H, H-38), 1.64-1.67 (m, 3 H, H-38), 1.57-1.59 (m, 8 H, H-38, H-39), 1.25-1.45 (m, 14 H, H-31, H-32, H-33, H-34, H-39, H-40), 1.05-1.16 (m, 9 H, Hax-38, Hax-39), 0.89-0.92 (t, 3 H, J_H-H = 6.7 Hz, H-35); ¹³C[¹H] NMR (126 MHz, CDCl₃, 20 °C): δ 292.3 (d, 2_P,C = 6.1 Hz, C-1), 215.4 (d, 2_P,C = 70.2 Hz, C-16), 144.0 (C-8), 140.7 (C-9), 137.6 (C-3), 137.2 (C-2), 137.1 (C-17), 137.0 (C-20), 136.9 (C-22), 136.8 (C-10), 136.1 (C-19), 128.9 (C-12, C-14), 128.7 (C-21), 128.6 (C-7), 128.4 (C-23), 128.1 (C-6), 127.6 (C-13), 127.1 (C-5), 126.4 (C-11, C-15), 116.0 (C-4), 51.2 (C-18), 51.6 (C-18), 49.4 (C-7); 31P[¹H] NMR (202 MHz, CDCl₃, 20 °C): δ 75.2 (major), 78.0 (minor). IR (Neat): ν = 2931, 2852, 1538, 1446, 1377, 1325, 1267, 1248, 1175, 1130, 1074, 1049, 1027, 1006, 977, 889, 845, 775, 753, 735, 700, 651; Anal. Calcd. for C₃₆H₃ₐCl₃N₃P₄Ru (942.41): C 67.50, H 0.82, N 2.97; Found: C 67.27, H 7.94, N 2.99; ESI-MS: [M-CI]⁺ Calcd: for C₃₆H₃ₐCl₃N₃P₄Ru, 907.4400; Found: 907.4428.

**RuCl₃(3-phenyl-1-indenylidene)(1-mesityl-3-cyclohexyl-4,5-dihydroimidazol-2-ylidene)(PCy₃)(8c)**

Red-brown powder (0.46 g, Yield: 63%). Red crystals, suitable for X-ray diffraction analysis of 8e were obtained by slow evaporation of a complex solution in hexane/EtOAc/CH₂Cl₂. The complex consists two rotamers in a ratio of 100:2.5 and the NMR data for this major rotamer is presented in following: ¹H-NMR (500 MHz, CDCl₃, TMS, 20 °C): δ 8.43 (d, 1 H, J_H-H = 7.3 Hz, H-7), 7.70 (d, 2 H, J_H-H = 7.3 Hz, H-11, H-15), 7.50 (t, 1 H, J_H-H = 7.3 Hz, H-13), 7.39 (t, 2 H, J_H-H = 7.6 Hz, H-12, H-14), 7.21 (t, 1 H, J_H-H = 7.0 Hz, H-5), 7.15 (t, 1 H, J_H-H = 7.3 Hz, H-6), 7.13 (s, 1 H, H-2), 7.02 (d, 1 H, J_H-H = 6.7 Hz, H-4), 6.38 (s, 1 H, H-21), 5.96 (s, 1 H, H-23), 5.19 (s, 1 H, H-28), 3.88-3.91 (m, 2 H, H-27, H-29), 3.59-3.72 (m, 2 H, H-28, H-30), 2.52-2.56 (m, 2 H, H-27), 2.20-2.24 (m, 3 H, H-33), 2.10 (s, 3 H, H-26), 1.91-1.95 (m, 8 H, H-25, H-29, H-33), 1.83 (s, 3 H, H-27), 1.77 (s, 4 H, Hax-37, H-37), 1.57-1.63 (m, 13 H, H-29, H-30, H-31, H-34, H-35), 1.39-1.47 (m, 6 H, H-33, H-34), 1.25-1.27 (m, 1 H, Hax-31), 1.09 (br, 9 H, Hax-34, Hax-35); ¹³C[¹H] NMR (126 MHz, CDCl₃, 20 °C): δ 294.0 (C-1), 212.4 (d, J_C=C = 73.2 Hz, C-2), 144.2 (C-8), 140.9 (C-9), 137.49 (C-2), 137.46 (C-3), 137.3 (C-10), 137.2 (C-12), 136.9 (C-24), 136.9 (C-19), 136.8 (C-17, C-22), 136.8 (C-18, C-20), 136.5 (C-13), 136.3 (C-15), 116.0 (C-4), 58.1 (C-28), 51.1 (C-18), 43.6 (C-17), 33.6 (C-32), 30.5 (30.1, C-29, 29.5, 29.3 (C-33), 27.6, 27.5 (C-34), 26.3 (C-35), 25.4 (C-31), 24.8, 24.7 (C-30), 21.0 (C-27), 18.53 (C-25), 18.47 (C-26); 31P[¹H] NMR (202 MHz, CDCl₃, 20 °C): δ 22.7 (major), 16.0 (minor). IR (Neat): ν = 2933, 2850, 1551, 1484, 1479, 1376, 1352; Found: C 67.09, H 7.62, N 3.07; Found: C 66.78, H 7.74, N 3.15; ESI-MS: [M-CI]⁺ Calcd: for C₃₆H₃ₐCl₃N₃P₄Ru, 877.3930; Found: 877.3954.

**Applied procedure for stability test**

An NMR tube was charged with ruthenium catalyst (15 μmol) and internal standard bis(3,5-dimethoxyphenyl)methanone (2.3 mg, 7.5 μmol) together with non-pretreated CDCl₃ (0.6 mL), the result solution was kept at 20 °C. The ruthenium complex stability was monitored as a function of time by integrating the ¹H NMR signals every day of the decomposing complex.

**Applied procedure for the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate/diethyl 2,2-diallylmalonate**

A substrate stock solution (0.1 M) was prepared by dissolving the substrate (4 mmol) and the internal standard dodecanol (0.68 g, 4 mmol) in CH₂Cl₂ (40 mL). The substrate solution (5 mL) and the ruthenium complex (0.125-1
mol%) were added in a Schlenk tube under argon at 30 °C. The reaction progress was monitored aliquot sampling of the reaction solution and further quenched by ethoxyethene before inject to GC for determination the conversion.

**Applied procedure for the ROMP of cis,cis-cycloocta-1,5-diene**

A ruthenium complex solution was made by dissolving the complex (4.07 µmol) in CDCl3 (1 mL). An NMR tube was filled with cis,cis-cycloocta-1,5-diene (0.81 mmol, 0.1 mL), CDCl3 (0.5 mL) and complex solution (0.1 mL), then the results solution was subjected into 1H-NMR measurement for determination of the conversion at 40 °C. The conversion was determined by integration of the olefinic 1H-NMR signals of the formed polymer and the consumed monomer.

**Applied procedure for the RCEYM of (1-allyloxy)prop-2-yne-1,1-diyldibenzene**

The substrate (1-(allyloxy)prop-2-yne-1,1-diyldibenzene (0.99 g, 4 mmol) and the internal standard dodecane (0.184 g, 1 mmol) and dry CH2Cl2 (10 mL). The flask was further charged with ruthenium complex (50 µmol) and cis-1,4-diacetoxy-2-butene (0.69 g, 4 mmol). The reaction mixture was stirred at 35 °C. A sampling of reaction solution (1 mmol) and dry CH2Cl2 and ethoxyethene before GC analysis.

**Applied procedure for the CM between allylbenzene and cis-1,4-diacetoxy-2-butene**

An oven dried flask was added with allylbenzene (0.236 g, 2 mmol) and internal standard α-tridecane (0.184 g, 1 mmol) and dry CH2Cl2 (10 mL). The flask was filled with ruthenium complex (50 µmol) and cis-1,4-diacetoxy-2-butene (0.69 g, 4 mmol). The reaction mixture was stirred at 35 °C. A sampling of reaction solution (1 mL) and quenched with an ethyl vinyl ether solution (1 mL) as well as further analysed by GC and 1H-NMR.

**Applied procedure for initiation test**

An NMR tube was charged with ruthenium catalysts (10 µmol) and toluene-d8 (0.3 mL). Thereafter, ethyl vinyl ether (30 eq., 0.022 g, 0.3 mmol) in toluene-d8 (0.3 mL) was added and the resulting solution was kept at 20 °C. The reaction progress was monitored by 1H-NMR signals as a function of time of the intact complex and the new formed complex.

**Single crystal X-ray diffraction**

Crystal data for compound 1c. CCDC 1049433, C38H32Cl2N2PRu, M = 744.80, triclinic, space group P-1 (No. 2), a = 11.9873(5) Å, b = 12.0758(4) Å, c = 13.9907(6) Å, α = 67.575(4)°, β = 84.7813(3)°, γ = 74.448(3)°, V = 1803.40(14) Å³, Z = 2, T = 100 K, ρcalc = 1.372 g cm⁻³, μ(Cu-Kα) = 5.507 mm⁻¹, F(000) = 784, 20352 reflections measured, 7221 unique (Rint = 0.0415) which were used in all calculations. The final R1 was 0.0360 (I >2σ(I)) and wR2 was 0.0933 (all data).

Crystal data for compound 8a. CCDC 1049431, C36H41N3PCl3Ru, M = 844.91, triclinic, space group P-1 (No. 2), a = 9.8957(5) Å, b = 12.6238(6) Å, c = 17.6587(6) Å, α = 92.1103(4)°, β = 100.9644(3)°, γ = 102.5384(4)°, V = 2107.00(17) Å³, Z = 2, T = 100 K, ρcalc = 1.332 g cm⁻³, μ(Cu-Kα) = 4.782 mm⁻¹, F(000) = 888, 24516 reflections measured, 8618 unique (Rint = 0.0630) which were used in all calculations. The final R1 was 0.0533 (I >2σ(I)) and wR2 was 0.1531 (all data). The 3-phenyl-1-indenylidene moiety was found disordered over two positions, rotated about 175° with respect to each other and refined with occupancy factors of 0.819(3) and 0.181(3), respectively.

Crystal data for compound 8b. CCDC 1049430, C33H25N3PCl3Ru, M = 943.09, triclinic, space group P-1 (No. 2), a = 13.8813(6) Å, b = 16.8687(7) Å, c = 24.0954(7) Å, α = 70.0903(3)°, β = 76.9103(3)°, γ = 70.6254(4)°, V = 4961.14(4) Å³, Z = 4, T = 100 K, ρcalc = 1.263 g cm⁻³, μ(Mo-Kα) = 4.114 mm⁻¹, F(000) = 2000, 33426 reflections measured, 17300 unique (Rint = 0.0766) which were used in all calculations. The final R1 was 0.0625 (I >2σ(I)) and wR2 was 0.1674 (all data). The asymmetric unit contains two RuCl3(3-phenyl-1-indenylidene)(1-mesityl-3-octyl-4,5-dihydroimidazol-2-ylidine)(PCy3) molecules. The octyl group on one of the two ruthenium complexes was found disordered over two positions and was refined with occupancy factors of 0.677(13) and 0.323(13), respectively.

Crystal data for compound 8c. CCDC 1049495, C100H110N4P5Cl4Ru2, M = 1910.97, monoclinic, space group C2/c (No. 15), a = 33.7446(6) Å, b = 14.6670(3) Å, c = 19.0468(3) Å, β = 94.2889(14)°, V = 9400.0(3) Å³, Z = 4, T = 100 K, ρcalc = 1.350 g cm⁻³, μ(Mo-Kα) = 0.575 mm⁻¹, F(000) = 4024, 55212 reflections measured, 11830 unique (Rint = 0.0783) which were used in all calculations. The final R1 was 0.0576 (I >2σ(I)) and wR2 was 0.1252 (all data). The asymmetric unit contains one ruthenium complex and one half of dichlorometane molecule on a special position (two-fold rotation axis).

1H, 31P, 13C NMR spectra
Fig. S4 $^{31}$P($^1$H)NMR spectrum of 8a in CDCl$_3$.

Fig. S5 $^1$H-NMR spectrum of 8a in CDCl$_3$.
Fig. S6 $^{13}$C{H}NMR spectrum of 8a in CDCl$_3$.

Fig. S7 $^{31}$P{H}NMR spectrum of 8b in CDCl$_3$. 
Fig. S8 H-NMR spectrum of 8b in CDCl$_3$.

Fig. S9 $^{13}$C{H}NMR spectrum of 8b in CDCl$_3$. 

Fig. 58 H-NMR spectrum of 8b in CDCl$_3$.

Fig. 59 $^{13}$C{H}NMR spectrum of 8b in CDCl$_3$. 
Fig. S10 $^{31}$P-$^1$H NMR spectrum of $8c$ in CDCl$_3$.

Fig. S11 $^1$H NMR spectrum of $8c$ in CDCl$_3$. 
Fig. S12 $^{13}$C{[H]}NMR spectrum of 8c in CDCl$_3$.

References