Supporting Information
for
Latent ruthenium–indenylidene catalysts bearing a $N$-heterocyclic carbene and a bidentate picolinate ligand.

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**General**

All the reactions were carried out under inert atmosphere (argon). Dichloromethane was distilled over calcium hydride prior to use. Tetrahydrofuran was distilled over sodium/benzophenone prior to use. All commercial chemicals were used as received unless otherwise noted. $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer with complete proton decoupling for $^{13}$C. $^1$H and $^{13}$C chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl$_3$, $^1$H: $\delta$ 7.26 ppm, $^{13}$C: $\delta$ 77.16 ppm; CD$_2$Cl$_2$, $^1$H: $\delta$ 5.31, $^{13}$C: $\delta$ 53.8 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, sep = septet, m = multiplet, br = broad. High-resolution mass spectrometry (HMRS) analyses were performed at the Centre Régional de Mesures Physiques de l’Ouest (CRMPO), Université de Rennes 1.

**Synthesis and analytical data of chloro-(2-pyridinecarboxylato)(1,3-dimesitylimidazolidin-2-ylidene))(3-phenyl-$^1$H-inden-1-ylidene) ruthenium(II) (2).**

![Chemical structure](image)

In a flame-dried Schlenk tube equipped with a stirring bar, complex 1 (500.0 mg, 0.53 mmol), 2-picolinic acid (71.4 mg, 0.58 mmol) and copper(I) chloride (97%, 80.7 mg, 0.79 mmol) were added. The Schlenk tube was then submitted to 3 argon–vacuum cycles after which 12 mL of CH$_2$Cl$_2$ were added. The reaction mixture was stirred for 2 h at 35 °C after what it was evaporated to dryness. The solid was dissolved in acetone and filtrated on a short plug of celite to remove the copper salts. The filtrate was concentrated under reduced pressure and the crude material was then purified by flash chromatography on silica gel (pentane/acetone, 9:1 to 8:2), affording compound 2 as a red powder in 62% yield (272.0 mg, 0.36 mmol).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.83 (br s, 3H, Ar-CH$_3$), 1.98 (br s, 3H, Ar-CH$_3$), 2.06-2.16 (m, 3H, Ar-CH$_3$), 2.23-2.34 (m, 3H, Ar-CH$_3$), 2.51 (br s, 3H, Ar-CH$_3$), 2.65 (br s, 3H, Ar-CH$_3$), 4.12-4.59 (m, 4H, C$_4$-H, C$_5$-H), 6.04-6.13 (m, 1H, Ar-H), 6.43-6.53 (m, 1H, Ar-H), 6.71-6.83 (m, 2H, Ar-H), 6.95-6.99 (m, 1H, Ar-H), 7.17-7.18 (m, 2H, Ar-H), 7.29-7.39 (m, 3H, Ar-H), 7.48-7.50 (m, 2H, Ar-H), 7.65 (d, $^3$J$_{H-H} = 7.2$ Hz, 2H, Ar-H), 7.78-7.80 (m, 1H, Ar-H), 7.90 (br s, 1H, Ar-H), 8.21-8.52 (m, 1H, Ar-H), 8.69-8.83 (m, 1H, Ar-H).

Due to the instability of compound 2 in solution, a $^{13}$C NMR spectra of sufficient quality could not be recorded.

HRMS (ESI): m/z: [M]$^+$ (C$_{42}$H$_{40}$N$_3$O$_2$Cl$_{102}$Ru) calc. 755.1847; found 755.1833 (2 ppm)

Synthesis and analytical data of chloro-(2-pyridincarboxylato)(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene))(3-phenyl-1H-inden-1-ylidene) ruthenium(II) (4a).

In a flame-dried Schlenk tube equipped with a stirring bar, complex 5 (100.0 mg, 0.12 mmol) and 2-picolinic acid (22.2 mg, 0.18 mmol) were added. The Schlenk tube was then submitted to 3 argon–vacuum cycles after which 2 mL of CH$_2$Cl$_2$ were added. The reaction mixture was stirred for 3 hours after which it was evaporated to dryness.

The crude mixture was then purified by flash chromatography on silica gel (pentane/acetone, 8/2), affording compound 4a as a red powder in 62% yield (62 mg, 0.073 mmol). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane in a solution of 4a in CH$_2$Cl$_2$ (ca. 5 mg in 0.5 mL CH$_2$Cl$_2$, 2 mL pentane).

For the NMR analysis, 8.4 mg (0.01 mmol) of the complex was dissolved in 0.6 mL CD$_2$Cl$_2$. A stock solution of mesitylene (40.0 mg) in CD$_2$Cl$_2$ (1 mL) was prepared and 10 $\mu$L (0.0033 mmol) of this solution was added to the NMR tube through a septum under argon. This procedure resulted in an
improvement of the resolution, the $^1H$ NMR is therefore reported in the presence of mesitylene.

$^1H$ NMR (400 MHz, CD$_2$Cl$_2$ in the presence of mesitylene): $\delta$ (ppm) 1.08 (br d, $^3J_{HH} = 5.6$ Hz, 6H, CH-CH$_3$), 1.15 (d, $^3J_{HH} = 7.2$ Hz, 6H, CH-CH$_3$), 1.18 (d, $^3J_{HH} = 6.8$ Hz, 6H, CH-CH$_3$), 1.37 (br d, $^3J_{HH} = 3.6$ Hz, 6H, CH-CH$_3$), 3.33-3.73 (m, 4H, C$_2$H$_4$H, C$_2$H$_5$), 4.23-4.37 (m, 4H, C$_4$H$_7$H, C$_5$H$_7$), 6.20 (s, 1H, Ind-H), 6.84 (d, $^3J_{HH} = 7.6$ Hz, 2H, Ar-H), 6.95-7.09 (m, 6H, Ar-H), 7.16 (td, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, 1H, Ar-H), 7.31-7.35 (m, 3H, Ar-H), 7.47-7.52 (m, 1H, Ar-H), 7.53-7.55 (m, 2H, Ar-H), 7.69 (d, $^3J_{HH} = 7.2$ Hz, 1H, Ar-H), 7.75 (td, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.6$ Hz, 1H, Ar-H), 8.11 (br d, $^3J_{HH} = 1.6$ Hz, 1H, Ar-H), 8.72 (br s, 1H, Ar-H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) 22.7 (s), 22.9 (s), 27.1 (s), 29.0 (s), 29.1 (s), 54.6 (s), 117.6 (s), 123.9 (s), 124.7 (s), 125.1 (s), 126.3 (s), 126.9 (s), 127.3 (s), 128.2 (s), 129.0 (s), 129.7 (s), 130.2 (s), 134.7 (br s), 136.5 (s), 138.0 (br s), 139.5 (br s), 140.3 (s), 141.5 (s), 143.1 (s), 148.3 (br s), 148.8 (s), 149.4 (br s), 151.1 (s), 172.8 (s), 217.2 (s, C$_2$), 298.6 (s, C$_1$).

HRMS (ESI): m/z: [M+H]$^+$ (C$_{48}$H$_{53}$N$_3$O$_2$$_{35}$Cl$^{102}$Ru) calc.: 840.28698; found: 840.2880 (1 ppm).

**Synthesis and analytical data of chloro-(5-bromo-2-pyridincarboxylato)(1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene))(3-phenyl-1H-inden-1-ylidene) ruthenium (II) 4b.**

In a flame-dried Schlenk tube equipped with a stirring bar, complex 5 (100.0 mg, 0.12 mmol) and 5-bromopyridine-2-carboxylic acid (36.4 mg, 0.18 mmol) were added. The Schlenk tube was then submitted to 3 argon–vacuum cycles after what 2 mL of CH$_2$Cl$_2$ were added. The reaction was stirred for 2 hours after what it was evaporated to dryness. The crude mixture was then purified by flash chromatography on silica gel (pentane/acetone, 8/2), affording compound 4b as a brownish powder in 43% yield (47 mg, 0.051 mmol).
For the NMR analysis, 9.6 mg (0.01 mmol) of the complex was dissolved in 0.6 mL CD$_2$Cl$_2$. A stock solution of mesitylene (40.4 mg) in CD$_2$Cl$_2$ (1 mL) was prepared and 10 µL (0.0033 mmol) of this solution was added to the NMR tube through a septum under argon. This procedure resulted in an improvement of the resolution, the $^1$H NMR is therefore reported in the presence of mesitylene.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$ in the presence of mesitylene) : δ (ppm) 1.08 (br d, $^3$J$_{H-H}$ = 5.6 Hz, 6H, CH-CH$_3$), 1.15 (d, 6H, $^3$J$_{H-H}$ = 6.8 Hz, CH-CH$_3$), 1.18 (d, $^3$J$_{H-H}$ = 6.8 Hz, 6H, CH-CH$_3$), 1.37 (br d, $^3$J$_{H-H}$ = 5.2 Hz, 6H, CH-CH$_3$), 3.33-3.70 (m, 4H, CH-CH$_3$), 4.24-4.35 (m, 4H, C$^4$-H, C$^5$-H), 6.15 (s, 1H, Ind-H), 6.60 (d, $^3$J$_{H-H}$ = 7.2 Hz, 2H, Ar-H), 6.95-7.03 (m, 5H, Ar-H), 7.09 (td, $^3$J$_{H-H}$ = 7.2 Hz, $^4$J$_{H-H}$ = 0.8 Hz, 1H, Ar-H), 7.17 (td, $^3$J$_{H-H}$ = 7.4 Hz, $^4$J$_{H-H}$ = 0.8 Hz, 1H, Ar-H), 7.31-7.35 (m, 2H, Ar-H), 7.48-7.59 (m, 4H, Ar-H), 7.87 (dd, $^3$J$_{H-H}$ = 8.4 Hz, $^4$J$_{H-H}$ = 2.0 Hz, 1H, Ar-H), 8.05 (br d, $^3$J$_{H-H}$ = 7.2 Hz, 1H, Ar-H), 8.77 (br s, 1H, Ar-H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) : δ (ppm) 22.6 (s), 22.8 (s), 27.1 (s), 29.0 (s), 29.1 (s), 54.5 (s), 117.7 (s), 123.1 (s), 124.0 (s), 124.7 (s), 126.2 (s), 126.9 (s), 127.3 (s), 128.3 (s), 129.0 (s), 129.2 (s), 129.9 (s), 130.3 (s), 134.5 (br s), 136.3 (s), 138.3 (s), 141.4 (s), 142.9 (s), 143.1 (s), 148.3 (s), 149.5 (s), 149.8 (s), 150.0 (s), 172.1 (s), 216.1 (s, C$^2$), 300.1 (s, C$^1$).

HRMS (ESI) : m/z : [M$^+$] (C$_{48}$H$_{51}$N$_3$O$_2$$_{35}$Cl$_{79}$Br$_{102}$Ru) calc. 917.18966 ; found 917.1915 (2 ppm) ; [M-Cl]$^+$ (C$_{48}$H$_{51}$N$_3$O$_2$$_{79}$Br$_{102}$Ru) calc. 882.22081 ; found 882.2254 (5 ppm).
NMR Spectra of new complexes

$^{1}$H NMR of complex 2 (CDCl$_3$, 400 MHz)

$^{1}$H NMR of complex 4a in the presence of mesitylene (CD$_2$Cl$_2$, 400 MHz)
$^{13}$C NMR of complex 4a (CD$_2$Cl$_2$, 400 MHz)

$^1$H NMR of complex 4b in the presence of mesitylene (CD$_2$Cl$_2$, 400 MHz)
$^{13}$C NMR of complex 4b (CD$_2$Cl$_2$, 400 MHz)
Determination of the acid quantity influence in the RCM of DEDAM with 4a

In a flame-dried NMR tube under Argon, DEDAM (19 μL, 0.08 mmol), mesitylene (11 μL, 0.08 mmol) and CD₂Cl₂ (800 μL) were added. A solution of catalyst 4a in CD₂Cl₂ was prepared in a separate flask under Argon and the catalyst was injected in the NMR tube (0.0008 mmol). After 30 minutes, an NMR spectrum was recorded after what the tube was ejected and TFA (between 1 and 12 μL) was added. NMR spectra were then taken at regular intervals and the reaction conversion was determined with the integral ratio of the reaction product with mesitylene.

Catalyst comparison in the RCM of DEDAM with TFA

In a flame-dried NMR tube under Argon, DEDAM (19 μL, 0.08 mmol), mesitylene (11 μL, 0.08 mmol) and CD₂Cl₂ (800 μL) were added. A solution of catalyst in CD₂Cl₂ was prepared in a separate flask under Argon and the catalyst was injected in the NMR tube (0.0008 mmol). After 30 minutes, an NMR spectrum was recorded after what the tube was ejected and TFA (9 μL, 0.12 mmol) was added. NMR spectra were then taken at regular intervals and the reaction conversion was determined with the integral ratio of the reaction product with mesitylene.

Acid comparison in the RCM of DEDAM with 4a

In a flame-dried NMR tube under Argon, DEDAM (19 μL, 0.08 mmol), mesitylene (11 μL, 0.08 mmol) and CD₂Cl₂ (800 μL) were added. A solution of catalyst 4a in CD₂Cl₂ was prepared in a separate flask under Argon and the catalyst was injected in the NMR tube (0.0008 mmol). After 30 minutes, an NMR spectrum was recorded after what the tube was ejected and the acid (0.12 mmol) was added. NMR spectra were then taken at regular intervals and the reaction conversion was determined with the integral ratio of the reaction product with mesitylene.
General procedure for metathesis reactions

In a flame-dried round bottomed flask, catalyst 4a (2 mg, 0.00238 mmol) was added and the flask was submitted to 3 cycles of vacuum–argon. CH₂Cl₂ (2.4 mL) was added and the substrate (0.238 mmol) was injected. A 2 M solution of HCl in Et₂O (180 µL, 0.357 mmol) was added and the mixture was stirred at room temperature for 2 h. The conversion was controlled by TLC (Pentane/Et₂O 95/5). After complete conversion, the solvent was removed under vacuum and the crude mixture was purified on silica gel (pentane/Et₂O, 95:5), affording the pure product. The ¹H NMR spectra of the obtained products for entries 1,¹ 2,² 3,³ 4,² 5,⁴ and 6⁵ were found to be in accordance with the literature.

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X-ray data for 4a

CCDC 1405734

Identification code: shelx
Empirical formula: C50.50 H58 Cl N3 O2 Ru
Formula weight: 875.52
Temperature: 100(2) K
Wavelength: 1.54184 Å
Crystal system, space group: Monoclinic, P 21/c
Unit cell dimensions:
- a = 13.3934(6) Å, alpha = 90 deg.
- b = 20.0867(4) Å, beta = 99.927(3) deg.
- c = 17.5572(4) Å, gamma = 90 deg.
Volume: 4652.7(3) Å³
Z, Calculated density: 4, 1.250 Mg/m³
Absorption coefficient: 3.563 mm⁻¹
F(000): 1836
Crystal size                      0.172 x 0.130 x 0.054 mm
Theta range for data collection  3.350 to 70.951 deg.
Limiting indices                 -16<=h<=16, -24<=k<=24, -20<=l<=21
Reflections collected / unique   61346 / 8924 [R(int) = 0.0909]
Completeness to theta = 67.684    100.0 %
Absorption correction            Semi-empirical from equivalents
Max. and min. transmission       1.00000 and 0.71311
Refinement method                Full-matrix least-squares on F^2
Data / restraints / parameters   8924 / 4 / 579
Goodness-of-fit on F^2           1.015
Final R indices [I>2sigma(I)]    R1 = 0.0665, wR2 = 0.1812
R indices (all data)             R1 = 0.0823, wR2 = 0.1929
Extinction coefficient           0.00011(4)
Largest diff. peak and hole      2.784 and -0.870 e.A^-3