Supplementary Material (ESI) for Chemical Communications

Highly Recoverable Pyridinium-Tagged Hoveyda-Grubbs Pre-catalyst for Olefin Metathesis. Design of the Boomerang Ligand Toward the Optimal Compromise Between Activity and Reusability.

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General. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{31}P (162 MHz) and ^{19}F (376.5 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, ^{1}H: δ 7.27 ppm, ^{13}C: δ 77.0 ppm and CD_2Cl_2, ^{1}H: δ 5.31 ppm, ^{13}C: δ 53.7 ppm). Data are reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, sept = septuplet, hept = heptuplet, bd = broad, m = multiplet), coupling constants (Hz), integration and attribution. High-resolution mass spectra (HRMS) were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1 on a Micromass ZABSpecTOF instrument. Melting points were measured on a heating microscope Reichert and were uncorrected. Optical rotations were recorded using a polarimeter Perkin-Elmer 341.

Materials:

All reactions were performed under an argon atmosphere using oven-dried glassware. Toluene was distilled from sodium metal under nitrogen. Dienes **6a-g** were synthesized and purified according to literature procedures. All chemical reagents and solvents were obtained from commercial sources and used without further purification. Analytical TLC were performed on Merck silica gel $60F_{254}$ plates, and visualised under UV-light. Chromatographic purifications were performed on a column with 230-400 mesh silica gel (Merck 9385) using the indicated solvent system.

Synthesis 3-vinyl-4-isopropoxybenzylamine 3:

To a solution of 3-bromo-4-hydroxybenzonitrile **2** (3.35 g, 16.9 mmol) and isopropyl iodide (3.38 mL, 33.8 mmol) in acetone (55 mL) were added potassium carbonate (4.66 g, 33.8 mmol). The resulting mixture was stirred at reflux for 48h. After cooling a saturated solution of sodium hydrogenocarbonate (60 mL) was added, then 3-bromo-4-isopropoxybenzonitrile was extracted with ethyl acetate (3x30 mL). The combined organics layers were washed with brine, dried over magnesium sulfate, filtered and concentrated.

^{1}**H NMR** (400 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 1.43 (d, J = 6.0 Hz, 6H, 2 CH_3), 4.72-4.63 (m, 1H, CH), 6.94 (d, J = 8.6 Hz, CH_{ar}), 7.57 (dd, J = 2.1 Hz and J = 8.6 Hz, 1H, CH_{ar}), 7.80 (d, J = 2.1 Hz, 1H).

^{13}**C NMR** (100 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 22.2, 72.8, 105.0, 113.9, 114.3, 118.3, 133.3, 137.3, 158.6.

A schlenk flask was charged with dry toluene (50 mL) and tetrakis(triphenylphosphine)palladium (1.155 g, 1 mmol) and 3-bromo-4-isopropoxybenzonitrile (2.4 g, 10 mmol). The mixture was degassed and stirred 15 min before adding tributylvinylstannane (3.51 mL, 12 mmol). The solution was warmed to 110°C overnight under argon. After cooling to room temperature the mixture was concentrated then the yellow solid was dissolved in petroleum ether and the insoluble materials were filtered on celite and wash with petroleum ether. The solvent was evaporated and a purification by silica gel chromatography using petroleum ether/ethyl acetate (9/1) afforded 3-vinyl-4-isopropoxybenzonitrile (1.73 g, 92%) as colorless oil.

^{1}**H NMR** (400 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 1.38 (d, J = 6.0 Hz, 6H, 2 CH_3), 4.69-4.60 (m, 1H, CH), 5.34 (dd, J = 0.6 Hz and J = 11.2 Hz, 1H, CH_{vinyl}), 5.76 (dd, J = 0.6 Hz and J = 17.8 Hz, 1H, CH_{vinyl}), 6.89 (d, J = 8.6 Hz, CH_{ar}), 6.96 (dd, J = 11.2 Hz and J = 17.8 Hz, 1H, CH_{vinyl}), 7.49 (dd, J = 2.1 Hz and J = 8.6 Hz, 1H, CH_{ar}), 7.73 (d, J = 2.1 Hz, 1H).

^{13}**C NMR** (100 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 21.9 (2C), 71.0, 103.4, 113.1, 116.3, 119.3, 128.6, 130.2, 130.6, 132.7, 133.6.

To a suspension of lithium aluminium hydride (476 mg, 12.5 mmol) in dry tetrahydrofuran (10 mL) was added slowly at 0°C a solution of 3-vinyl-4-isopropoxybenzonitrile (400 mg, 2.09 mmol) in dry tetrahydrofuran (30 mL). The resulting mixture was stirred 5h at room temperature. After cooling at 0°C water (0.5 mL) then a solution of sodium hydroxide (0.5 mL, 15%) was added. The mixture was stirred vigorously for 10 min, the solid was filtered off on celite and wash by dichloromethane then hot THF. The filtrate was concentrated to afford 3-vinyl-4-isopropoxybenzylamine **3** (245 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 1.34 (d, J = 6.0 Hz, 6H, 2 CH_3), 4.54 (sept, J = 6.0 Hz, 1H, CH), 3.79 (s, 2H, CH_2), 5.24 (dd, J = 1.5 Hz and J = 11.2 Hz, 1H, CH_{vinyl}), 5.75 (dd, J = 1.5 Hz and J = 17.8 Hz, 1H, CH_{vinyl}), 6.85 (d, J = 8.4 Hz, CH_{ar}), 7.03 (dd, J = 11.2 Hz and J = 17.8 Hz, 1H, CH_{vinyl}), 7.14 (dd, J = 2.3 Hz and J = 8.4 Hz, 1H, CH_{ar}), 7.42 (d, J = 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 22.1 (2C), 46.0, 71.0, 114.0, 114.5, 125.2, 127.4, 127.8, 131.8, 135.3, 154.0.

Synthesis of ligand 1-(4-isopropoxy-3-vinylbenzyl)pyridinium hexafluorophophate 5.

A 25mL round bottom flask equipped with a condenser was charged with 4-isopropoxy-3-vinylbenzylamine **3** (100mg, 0.52mmol) the Zincke salt **4** (162mg, 0.57mmol, 1.1eq.) and n-butanol (6.5mL). The mixture was stirred over night at 120°C then the solvant was removed under vacuum. The residue was dissolved in distilled water (15mL) and filtered through celite to remove the unsoluble salt. The resulting aqueous phase was washed with a mixture of petroleum ether and ethyl acetate (1:1, v:v) (4x4mL). The resulting aqueous solution of chlorinated salt was then treated with potassium hexafluorophosphate (96mg, 0.52mmol, 1eq.). After 1 hour stirring at room temperature, the salt was extracted with dichloromethane (3x5mL). The organic phase was washed with brine (2x4mL), dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography using dichloromethane/acetone (4:1) as eluent to afford the pyridinium hexafluorophosphate salt **5** as a yellowish solid (157mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ (ppm):: 1.30 (d, J = 6.1 Hz, 6H, $(CH_3)_2$), 4.52 (sept, J = 6.1 Hz, 1H, CH), 5.23 (dd, J = 11.3 Hz and J = 1.1 Hz, 1H, CH_{vinyl}), 5.58 (s, 2H, CH_2), 5.80 (dd, J = 17.9 Hz and J = 1.1 Hz, 1H, CH_{vinyl}), 6.86 (d, J = 8.7 Hz, 1H, CH_{Ar}), 6.93 (dd, J = 17.9 Hz and J = 11.3 Hz, 1H, CH_{vinyl}), 7.29 (dd, J = 8.7 Hz and J = 2.3 Hz, 1H,

CH_{Ar}), 7.54 (d, *J* = 2.3 Hz, 1H, CH_{Ar}), 7.89 (dd, *J* = 7.8 Hz and *J* = 6.8 Hz, 2H, CH_{pyr}), 8.35 (tt, *J* = 7.8 Hz and *J* = 1.2 Hz, 1H, CH_{pyr}), 8.69 (dd, *J* = 6.8 Hz and *J* = 1.2 Hz, 2H, CH_{pyr}).

^{19}F NMR (376 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): -72.2 (d, *J* = 713 Hz, 6F, F_6).

^{31}P NMR (162 MHz, $CDCl_3$, 25°C, TMS) δ (ppm):: -143.08 (sept., *J* = 712.5 Hz, 1P, P).

^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS) δ (ppm):: 22.0 (2C), 64.8, 70.8, 114.4, 115.8, 123.4, 128.4, 128.4, 128.6, 130.2, 130.6, 143.7, 145.7, 156.4.

HRMS ESI+, [M^+] ion, m/z 254: $C_{17}H_{20}NO^+$, m/z calcd. 254.1539, m/z found 254.1545

Synthesis of ionic catalyst 1l:

The 1-(4-isopropoxy-3-vinylbenzyl)pyridinium hexafluorophophate **5** (10mg, 0.025mmol), the Grubbs II precatalyst **1a** (21mg, 0.025mmol, 1eq.) and the copper (I) chloride (2,5mg, 0.025mmol, 1eq.) was introduced in a schlenk flask under argon. Then dichloromethane (3mL) was introduced and the solution was degased three times (vacuum/argon). The reaction mixture was stirred for 2h at 30°C under argon and the dichloromethane was removed under vacuum. The residue was dissolved with acetone (5mL) and the unsoluble salt was filtered off through a Celite plug. The filtrate was concentrated to dryness and the residue was purified by silica gel chromatography using dichloromethane/acetone (4:1) as eluent to afford the desired complex **1l** as a green solid (18mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): 1.24 (d, *J* = 6.1 Hz, 6H, $(CH_3)_2$), 2.38 (s, 6H, $2CH_3$), 2.44 (s,18H, $6CH_3$), 5.00 (sept, *J* = 6.1 Hz, 1H, CH), 6.09 (s, 2H, CH_2), 7.01 (d, *J* = 2.1 Hz, 1H, CH_{Ar}), 7.04 (s, 4H, $2CH_2$), 7.16 (d, *J* = 8.6 Hz, 1H, CH_{Ar}), 7.81 (dd, *J* = 8.5 Hz and *J* = 2.1 Hz, 1H, CH_{Ar}), 8,33 (t, *J* = 7.2 Hz, 2H, CH_{pyr}), 8.81 (t, *J* = 7.8 Hz,1H, CH_{pyr}), 9.23 (d, *J* = 5.9 Hz, 2H, CH_{pyr}), 16.50 (s, 1H, CH_{Ru}).

^{19}F NMR (376 MHz, $CDCl_3$, 25°C, TMS) δ (ppm):: -73.0 (d, *J* = 707Hz, 6F, F_6).

^{31}P NMR (162 MHz, $CDCl_3$, 25°C, TMS) δ (ppm): -143.0 (sept., *J* = 708Hz, 1P, P).

HRMS ESI+, [M^+] ion, m/z 718: $C_{37}H_{44}N_3O^{35}Cl_2{}^{102}Ru^+$, m/z calcd. 718.1909, m/z found 718.1890.

Procedure for RCM reactions in BMI.PF6/toluene (25/75):

BMI.PF_6 (1.25 mL) was introduced into a Schlenk flask and dried for 2 hours under vacuum at 70°C. The ionic liquid-catalyst **1l** (22 mg, 0.025 mmol, 0.025 equiv) was added and the mixture was stirred for 1h at room temperature under vacuum to afford a complete dissolution of the catalyst. The diene (1 mmol, c = 0.2 M) was then introduced followed by dry toluene

(3.75 mL) and the reaction mixture was stirred at the indicated temperature. The reaction mixture was then allowed to separate and the toluene layer was removed. The BMI.PF_6 layer was successively washed with dry toluene (4 x 10 mL). The combined toluene extracts layers were evaporated to afford the crude product, which was examinated by 400 MHz ^{1}H NMR spectroscopy to reveal complete conversion of diene and clean formation of the corresponding cyclised product. The BMI.PF_6 phase containing the IL-catalyst **1l** was dried under vacuum before its reuse with a new addition of diene and toluene.

Procedure for recover the BMI.PF_6:

The ionic liquid BMI.PF_6 containing the decomposed IL-catalyst (5mL) was dissolved in 10 mL of dichloroethane. Black carbon (500 mg) was added and the resulting mixture was refluxed for 12 h. The mixture was cooled to room temperature and then filtered onto a plug of celite. The solvent was removed to afford the pure BMI.PF_6 as colorless oil which was finally dried for 4h at 70°C under vacuum. This recovered BMI.PF_6 was used in a RCM reaction with a new loading of IL-catalyst **1l** and substrate without lost of performance compared to the fresh one.

Procedure for ICP-MS measurement:

All samples were prepared by weighing 5 mg of the crude compound (that was previously filtered through a slim bed of silica gel in order to remove BMI.PF_6 traces) and then adding 10 mL of 0.12 M hydrochloric acid in glacial acetic acid. The analyses were performed on a PE Instrument Elan 6000 Inductive Coupled Plasma Mass Spectrometer (ICP-MS) using ^{99}Ru and ^{101}Ru isotopes, which are not interfered by molybdenum oxide. All samples were diluted 10 times in ultra pure water. The Ru level was determined by comparison with a standard Ru sample (10µg/mL). The analyses have been realised by UT2A Company, France (http://www.univ-pau.fr/ut2a).