

## Supplementary information

### Materials

All experiments with free phosphines or with ruthenium catalysts were carried out in a glove-box or using Schlenk techniques connected to an argon line. Solvents were dried over  $\text{CaH}_2$ , distilled, and degassed before use when necessary. Dicyclohexylphosphine-borane and  $\text{RuCl}_2(=\text{CHPh})(\text{PPh}_3)_2$  were prepared by previously reported methods<sup>1</sup>.

DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) (20 mg/mL in  $\text{CHCl}_3$ ,) (Fluka) and sodium tetraborate 20 mM buffer solution at pH=8, tris(hydroxymethyl)-methylamine (Tris) powder, calcium chloride, Coomassie brilliant Blue and 5-norbornene-2-carboxylic acid (endo/exo mixture) (all from Aldrich) were used as received. Powders were dried under vacuum before their introduction in the glove box containing less than 1 ppm of  $\text{O}_2$ . Solutions were degassed with argon for 30 minutes before their introduction in the glove box. Samples were observed by optical microscopy using an inverted microscope (IX70, Olympus).

### Characterizations

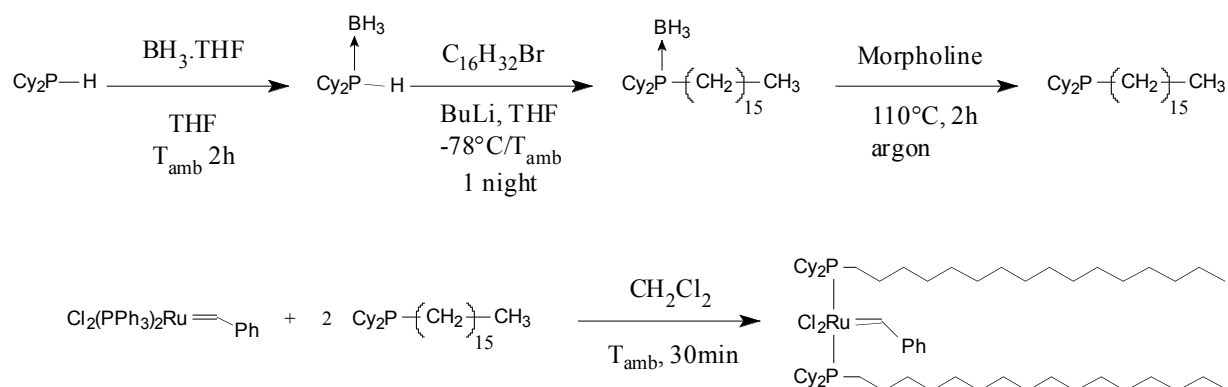
$^1\text{H}$  NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.13 MHz.  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}$  NMR spectra were recorded on a multinucleus Bruker DPX400 spectrometer respectively at 100.61, 161.98 and 64.21 MHz. IR spectra were carried out on a Perkin Elmer FTIR 1760X spectrometer. The average molecular weight of the formed polymers was determined after termination by ethylvinylether by size exclusion chromatography (SEC) analysis in aqueous solution of 0.1M NaCl, 50mM  $\text{NaH}_2\text{PO}_4$  and 200 ppm  $\text{NaN}_3$  (flow rate 0.3 mL/min) on an apparatus equipped with a PL RI-800 interferometric refractometer (Polymer Laboratories). Separation was performed on Shodex OHpak columns SB-G, SB 805-HQ, SB-803 HQ, and SB-802 HQ connected in series. The molecular

weights **polydispersities** of the polymers are reported relative to monodisperse poly(ethyleneoxide) standards (800000; 160000; 10000  $\text{g.mol}^{-1}$ ).

-  **$\text{Cy}_2\text{P}(\text{BH}_3)-(\text{CH}_2)_{15}-\text{CH}_3$** : 3.1 g of dicyclohexylphosphine borane (14.6 mmol) were dissolved in THF (40mL) and the solution was cooled to  $-78^\circ\text{C}$ . BuLi (9.5 mL, 1.5 M in hexane) was added dropwise. The solution was stirred during 2 h while slowly warming to room temperature, after which it was cooled again to  $-78^\circ\text{C}$ . 5.28 g of hexadecylbromide (17.3 mmol) in solution in THF (20 mL) was added dropwise and the solution was stirred during 2 hours while slowly warming to room temperature. The stirring was continued at room temperature overnight. Diethylether (50 mL) was added and the solution was washed with HCl 10% and brine until neutral pH. It was dried over  $\text{MgSO}_4$  and the solvent evaporated. The resulting product was purified by column chromatography over silica (eluent cyclohexane/ethylacetate 98/2 v/v). Yield: 5.0g (80%).  $^1\text{H}$  NMR: 1.6-1.9 (m, 12H,  $-\text{CH}_2-$ ), 1.3-1.55 (2m, 40H,  $-\text{CH}_2-$ ), 0.87 (t  $^3J=7\text{Hz}$ , 3H, Me), -0.7-0.7 (broad q,  $\text{BH}_3$ ).  $^{13}\text{C}$  NMR: 31.8 (d  $J_{\text{C-P}}=32.3\text{Hz}$ , CH-P), 19.6 (d  $J_{\text{C-P}}=31.8\text{Hz}$ ,  $\text{CH}_2\text{-P}$ ), 32.1 32.0 31.8 29.9 29.8 29.7 29.6 29.3 27.2 27.1 27.0 26.9 26.2 23.9 22.9 ( $-\text{CH}_2-$ ), 14.3 (Me).  $^{31}\text{P}$  NMR: 24.9 (m).  $^{11}\text{B}$  NMR: -53.9 (broad). IR (KBr pellet)  $\bar{\nu}$  ( $\text{cm}^{-1}$ ) : 2921, 2848 str (CH stretching), 2385, 2367 str (BH stretching), 1463, 1445 m ( $\text{CH}_2$  bending, P-CH stretching), 1065 m, 1004, 893, 854, 754, 723, 589 w. EI mass spectrum (relative intensity): 433 (6.8), 422 (100)  $\text{M}^+ - \text{BH}_3$ , 340 (29.2)  $\text{M}^+ - \text{BH}_3 - \text{cylohexane}$ , 198 (23.0)  $\text{M}^+ - \text{BH}_3 - \text{hexadecane}$ , 117 (15.8), 84 (35.1), 57 (19.9), 49 (79.2). Ammoniac CI mass spectrum (relative intensity): 454 (100)  $\text{M} + \text{NH}_4^+$ , 433 (50.2), 423 (11.1), 341 (4.9), 214 (17.5), 199 (10.6).

-  **$\text{Cl}_2\text{Ru}(\text{CHPh})(\text{Cy}_2\text{P}-(\text{CH}_2)_{15}-\text{CH}_3)_2$** : 0.25 g of the free phosphine (0.57 mmol) was heated at  $110^\circ\text{C}$  in 5 mL morpholine under argon. The solvent was then removed under vacuum leaving a gummy white residue which was used immediately. This was redissolved in

3 mL methylenechloride and added to a solution of 200 mg of  $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PPh}_3)_2$  in 2 mL of methylenechloride under argon. The solution changed from green to dark red and was stirred during 30 min, after which time the solvent was removed under vacuum. The resulting product was washed with methanol then dried. Owing to the small quantity of product, crystallization was found to be difficult. The product was therefore used without further purification. This crude product contains 64% in mass of initiator **1**, as determined by  $^1\text{H}$  NMR. Considering the  $^1\text{H}$  NMR spectrum and the synthesis, the other products are supposed to be triphenylphosphine and an analogue of **1** without any carbene. The only carbene present in the spectrum is that of **1**, no signal corresponding to  $\text{Cl}_2(\text{PPh}_3)\text{Ru}(=\text{CH-Ph})$  is observed.  $^1\text{H}$  NMR: 19.8 (s,  $\text{Ru}=\text{CH-}$ ), 8.58 (d  $J=7.4\text{Hz}$ , *o* aromatics), 6.9-7.6 (m, aromatics), 0.7-2.4 (m,  $-\text{CH}_2-$  and  $-\text{CH-}$ ).



## Liposome preparation

Liposomes were prepared by first drying under vacuum in a rotaflo flask connected to a fast rotating evaporator, 20  $\mu\text{l}$  of the DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) solution in  $\text{CHCl}_3$  (20 mg/mL). The flask was then introduced in the glove box and 40  $\mu\text{l}$  of the initiator **1** solution in dichloromethane (about  $10^{-3}\text{mol.L}^{-1}$ ) were added to allow for an active

initiator/phospholipid ratio of ca 1/20 in all experiments. After drying again under vacuum, a buffer solution at pH=8 (sodium tetraborate solution or a 20mM of CaCl<sub>2</sub> solution in a Tris buffer) was then added and the mixture was vortexed to give 2 mL of liposomes solution with typical diameters in the 1 to 4 µm range. Under this pH condition, monomer **2** was soluble in water. In some experiments, coomassie brilliant blue (1 mg in the 2 mL buffer solution) was added as a dye.

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<sup>1</sup> Mohr, B.; Lynn, D.M.; Grubbs, R.H.; *Organometallics* **1996**, *15*, 4317-4325 ; Mingotaud, A.F.; Reculosa, S.; Mingotaud, C.; Keller, P.; Sykes, C.; Duguet, E.; Ravaine, S.; *J. Mater. Chem.* **2003**, *13*, 1920-1925.