

## Supplementary information for the manuscript:

# Si-C bond activation in the reaction of first generation Grubbs' catalyst with alkynylsilanes - formation of $[\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Ru}(\text{=CHCH=CHPh})]$ and disiloxanes

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### Materials and methods

All manipulations were carried out under dry argon using standard Schlenk techniques.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Gemini 300 at 300 and 75 MHz, respectively.  $^{31}\text{P}$  NMR spectra were recorded on INOVA 400 at 161 MHz. GC-MS analyses were made on Varian Saturn 2100T (DB-1, 30 m capillary column) equipped with an ITD. FAB MS was recorded on modified Finnigan MAT 312. All the chemicals were purchased from Aldrich. All liquid reagents were dried with molecular sieves and degassed by repeated freeze-pump-thaw cycles. Methylene chloride and benzene were dried and distilled over  $\text{CaH}_2$  under dry argon atmosphere prior to use. Benzene- $\text{d}_6$  was dried by distilling from  $\text{CaH}_2$  and storing over molecular sieves,  $\text{CD}_2\text{Cl}_2$  was dried with molecular sieves and degassed by repeated freeze-pump-thaw cycles. Elemental analysis was performed by the analytical laboratory of the Institute of Organic Chemistry PAS in Warsaw.

### Stoichiometric reactions

The stoichiometric reactions were performed in NMR tubes and controlled by  $^1\text{H}$  NMR spectroscopy. In a typical procedure  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (0.01g,  $1.21\times 10^{-5}$  mol) and anthracene (0.001g) (internal standard) were dissolved in 0.65 mL of  $\text{C}_6\text{D}_6$ . Then  $1.21\times 10^{-5}$  mol of the corresponding silylalkyne was added. Progress of the reaction was controlled by  $^1\text{H}$  NMR spectroscopy. Conversions and selectivities were calculated using the internal standard method.

### Synthesis of 3 (optimised procedure)

Schlenk flask (20mL) equipped with condenser and side arm closed with septa was charged under argon with  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (0.1g,  $1.21\times 10^{-4}$  mol), 3mL of methylene chloride, 86  $\mu\text{L}$  ( $6.05\times 10^{-4}$  mol) of ethynyltrimethylsilane and 8.7  $\mu\text{L}$  ( $4.85\times 10^{-4}$  mol) of deoxygenated water. The mixture was heated and stirred at reflux for 0.5h. Then solvent was evaporated and 2mL of cold acetone ( $-30^\circ\text{C}$ ) was added. Precipitate was filtrated off, washed ( $2 \times 1$  mL) with acetone ( $-30^\circ\text{C}$ ), ( $2 \times 1$  mL) with pentane ( $-50^\circ\text{C}$ ) and dried in vacuum. Orange microcrystalline solid was obtained 82.5mg (80% yield).

### Analytical data:

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm)  $\delta$ : 19.06 (d,  $J=10.5$ , 1H)  $\text{Ru}=\text{CH}$ ; 8.55 (dd,  $J=15.6$ , 10.5, 1H)  $=\text{CH}$ ; 7.42 (d,  $J=15.6$ , 1H)  $\text{CHPh}$ ; 7.70 (psd, 2H) Ph; 7.48 (pst, 1H) Ph; 7.32 (pst, 2H) Ph; 1.20-1.31, 1.38-1.55, 1.62-1.92, 2.55-2.67 (m, 66H) Cy;  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm)  $\delta$ : 36.9;  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm)  $\delta$ : 290.4, 146.2, 138.7, 130.9, 130.1, 129.5, 129.1, 128.7, 32.6-26.6; MS (FAB) M (rel. int.): 850 (60), 848 (62), 813 (12), 787 (15), 495 (15), 410 (18), 396 (100), 375 (47), Anal. calcd. for:  $\text{C}_{46}\text{H}_{77}\text{Cl}_2\text{P}_2\text{Ru}$  (%): C 63.66, H 8.79; found: C 63.87, H 8.70;

### Labeling studies

Typical procedure:  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (0.005g,  $6.08\times 10^{-6}$  mol) was dissolved in 0.65 mL of  $\text{C}_6\text{D}_6$ . Then ethynyltrimethylsilane- $\text{d}_1$  (0.85  $\mu\text{L}$ ,  $6.01\times 10^{-6}$  mol) and water (0.54  $\mu\text{L}$ ,  $3.04\times 10^{-5}$  mol) were added by syringe. The reactions were carried out at  $40^\circ\text{C}$  in an NMR tube and monitored by  $^1\text{H}$  NMR spectroscopy.