Supporting Information

Supramolecularly Controlled Surface Activity of an Amphiphilic Ligand. Application to Aqueous Biphasic Hydroformylation of Higher Olefins

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$$r = [1]/([1] + [\beta-CD])$$
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Phosphane selenides were synthesized by stirring overnight at room temperature excess selenium (10 equiv.) with 1 (250 mg) in absolute ethanol (15 mL) under nitrogen. The resulting mixture was directly analyzed by $^{31}$P{$^1$H} NMR without any purification. NMR spectra exhibit the presence of phosphane selenides characterized by a singlet with two satellites due to only 7.6% of active selenium isotope ($^{77}$Se) in NMR spectroscopy. The upfield phosphorus signal (-83.09 ppm) was characteristic of the PTA phosphorus atom. The first order phosphorus-selenium coupling constants ($^1J_{P-Se}$) of the Se=1 selenide allowed for the estimation of the basicity of 1. The higher the $^1J_{P-Se}$ value, the lower the basicity. Ligand 1 ($^1J_{P-Se} = 814.6$ Hz) was thus more basic than the previously synthesized CD non-interacting phosphane N-Bz-PTA (Scheme 1) for which a $^1J_{P-Se} = 817.7$ Hz constant was determined.
S14. Reaction profiles of entries 5, 6, 8 and 9.

Experimental conditions: Rh(acac)(CO)₂ (4.07 × 10⁻² mmol), water-soluble ligand (0.21 mmol), cyclodextrin (0.48 mmol), H₂O (11.5 mL), 1-alkene (20.35 mmol), 1500 rpm, CO/H₂ (1/1): 50 bar, 6 h. Entry 5: 80 °C without CD; Entry 6: 80 °C with RAME-β-CD; Entry 8: 100 °C without CD; Entry 9: 100 °C with RAME-β-CD.

The reaction profiles of these four relevant experiments highlight the poisoning effect of RAME-β-CD at 80 °C (red arrow) and the increase in activity observed at 100 °C (blue arrow).