

## Supporting Information

### A. Experimental section

#### General remarks

All manipulations were carried out under argon unless otherwise stated, using glassware which was flame-dried prior to use. The solvents were freshly distilled before use according to the literature procedure. 4-Isobutylstyrene<sup>S-1</sup>, 2-vinyl-6-methoxynaphthalene<sup>S-2</sup>, and N,N,N',N'-tetrabenzylethylenediamine(TBzEDA)<sup>S-3</sup> were prepared according to known procedures. Other chemicals were purchased from commercial sources.

#### *Synthesis of [(TMEDA)Rh(COD)][(COD)RhCl<sub>2</sub>], 2*

A solution of **1** (300 mg, 0.61 mmol) in toluene (15 mL) was stirred with a solution of N,N,N',N'-tetramethylethylenediamine (TMEDA) (100 g, 0.64 mmol) in toluene(10 mL) at room temperature for 16 hr. The orange colored crystalline solid product was isolated by filtration. Yield 90 %, <sup>1</sup>H NMR (CDCl<sub>3</sub> solvent, 300 MHz, 298 K) δ: 4.2 (m, 8H), 2.4(m, 24H), 1.7(m, 8H). Anal. Calc. For C<sub>22</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>2</sub>Rh<sub>2</sub>: C, 43.37; H, 6.62; N, 4.60. Found: C, 43.30; H, 6.62; N, 4.64.

#### *Synthesis of [(TEEDA)Rh(CO)<sub>2</sub>][Cl<sub>2</sub>Rh(CO)<sub>2</sub>], 3a.*

A solution of **1** (300 mg, 0.61 mmol) and N,N,N',N'-tetraethylethylenediamine (TEEDA) (115 mg, 0.67 mmol) in toluene(30 mL) was injected in a 150-mL high pressure glass reactor, and the reactor was pressurized with CO(80 psig). After reaction for 4-5 h at room temperature, a yellow colored solid was obtained by filtration. Yield 87 %. <sup>1</sup>H NMR

(CDCl<sub>3</sub> solvent, 300 MHz, 298 K)  $\delta$  3.2(*m*, 12H) 1.5(*m*, 12H). <sup>13</sup>C NMR(CDCl<sub>3</sub> solvent, 300 MHz, 298 K)  $\delta$  12.90, 54.84, 55.58, 181.11, 182.07, 182.40, 183.31. IR (powder, cm<sup>-1</sup>):  $\nu$ (CO) 1989, 2011, 2065, 2079. Anal. Calc. For C<sub>14</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Rh<sub>2</sub>: C, 29.97; H, 4.31; N, 4.99. Found: C, 29.96; H, 4.13; N, 3.19.

*Synthesis of [(TBzEDA)Rh(CO)<sub>2</sub>][Cl<sub>2</sub>Rh(CO)<sub>2</sub>], **3b**.*

Complex **3b** was prepared in a manner analogous to that described above for complex **3a** by simply replacing TEEDA with N,N,N',N'-tetrabenzylethylenediamine (TBzEDA). Yield 83 %, <sup>1</sup>H NMR (CDCl<sub>3</sub> solvent, 300 MHz, 298 K)  $\delta$  7.44 (*m*, 20H), 4.0 (*m*, 4H), 3.8 (*m*, 4H), 3.5(*s*, 4H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub> solvent, 300 MHz, 298 K)  $\delta$  54.62, 65.25, 129.37, 130.43, 132.79, 133.32, 180.62, 181.45, 181.56, 182.40. IR (powder, cm<sup>-1</sup>):  $\nu$ (CO) 1973, 2014, 2059, 2073. Anal. Calc. For C<sub>34</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Rh<sub>2</sub>: C, 50.46; H, 3.99; N, 3.46. Found: C, 50.48; H, 3.89; N, 3.46.

**General Procedure for the Hydroformylation reactions:** All the hydroformylation reactions were conducted in a 45 mL stainless steel autoclave equipped with a magnetic stirring bar. The reactor was charged with an appropriate amount of the substrate, catalyst, and solvent. After flushing 3 times with carbon monoxide, the reactor was pressurized with 1000 psig of syn-gas (CO: 500 psig, H<sub>2</sub>: 500 psig). The reactor was stirred at room temperature, or heated to the specified temperature. After the reaction, the autoclave was cooled to room temperature (if heated) and the reaction mixtures - orange colored solution with small amount of orange colored precipitate - were analyzed by <sup>1</sup>H-NMR and gas

chromatography.

*Example* – A glass liner containing styrene (860 mg, 8.21 mmol), catalyst – complex **2** (10 mg, 0.0164 mmol), toluene (10 mL), and magnetic stirrer was placed in a 45 mL autoclave. The autoclave was flushed 3 times with carbon monoxide and pressurized to 500 psig. The hydrogen line was then attached to the autoclave and purged. The autoclave was pressurized up to 1000 psig with hydrogen and placed in an oil bath preset to the desired temperature on a stirring hot plate. After the appropriate reaction time, the autoclave was removed from the oil bath and cooled (if heated) to room temperature prior to the release of excess carbon monoxide and hydrogen. The reaction mixture was analyzed by <sup>1</sup>H NMR and gas chromatography.

## References

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(S-3) A. R. Katritzky, W. Fan, C. Fu, *J. Org. Chem.* 1990, **55**, 3209.